Texture Development and Anisotropic Behaviour in a Ti-45Ni-5Cu (at.%) Shape Memory Alloy

Lie ZHAO
This research was performed in the Materials Science and Engineering Group of the Mechanical Engineering Faculty of the University Twente, Enschede, the Netherlands, and was financially supported by the Technology Foundation (STW) under project no. TWT 22.2699 MK-STW.

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TEXTURE DEVELOPMENT AND ANISOTROPIC BEHAVIOUR IN A TI-45NI-5CU (AT.%)
SHAPE MEMORY ALLOY

PROEFSCHRIFT

Ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. F.A. van Vught,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 17 oktober 1997 te 13.15 uur

door
Lie ZHAO
geboren op 19 mei, 1963
te Hangzhou, P.R. China
Dit proefschrift is goedgekeurd door de promotor:
Prof.dr. W. Wei
en de assistent-promotor:
Dr.ir. J. Beyer
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• My uncle Yongshen Chen and his family in Zevenbergen of the Netherlands for their continuous help on my life, especially in the first year after I came to the Netherlands.
Summary

The objective of this work was to determine the relationship between texture development and anisotropy of shape memory properties. A commercial Ti-45Ni-5Cu (at.%) shape memory alloy was selected. Textures were developed by controlling rolling parameters, such as rolling temperature, intermediate annealing temperature, thickness reduction and annealing temperature. The anisotropy of shape memory properties, in particular the transformation strain, was measured by tensile and thermal cyclic testing under constant load. Texture measurements were made after rolling, tensile testing and after thermal cyclic testing. The anisotropy of shape memory alloys was then related to the textures obtained based on the experimental results as well as theoretical modelling.

Two main types of austenite texture components, (110)[1\bar{1}0]_p or (111)[1\bar{1}0]_p, were qualitatively and quantitatively determined in the rolled and annealed materials. The (111)[1\bar{1}0]_p texture component becomes pronounced when rolling temperature increases up to 300°C. Martensite textures were measured, which are in agreement with the existing orientation relationship between austenite and martensite phase. Texture development after loading was found to be dependent on the loading direction.

The anisotropy of shape memory properties, mainly the transformation strain, was experimentally determined. The transformation strain in cold-rolled and annealed sheets with a (110)[1\bar{1}0]_p major texture component is more anisotropic (anisotropy parameter A=1.83) than in warm-rolled and annealed sheets with a (111)[1\bar{1}0]_p texture (A=1.24). The transformation strain has an almost constant value from the rolling direction (RD) to an angle 60° from the RD, and a minimum value along the transverse direction. The permanent strain produced during thermal cyclic testing has a minimum value along the transverse direction, independent of the rolling parameters.

The strains were the result of a combination of 12 martensite variants developed during rolling process and thermal cyclic testing. The anisotropic behaviour of the transformation strain could be predicted based on the texture analysis. Four methods were used to predict the transformation strain. One of the methods was a calculation combining a modified Taylor model for polycrystalline shape memory alloys with inverse pole figures calculated from the orientation distribution function. Among the four methods, the calculated results from this method were found to be closest to the experimentally measured strains.
Samenvatting

Het doel van dit onderzoek was om de relatie vast te leggen tussen de textuur ontwikkeling bij walsen en de anisotrope eigenschappen van vormgeheugen materialen. Hiervoor is gebruik gemaakt van een commercieel verkrijgbare Ti-45Ni-5Cu (at.%). Variatie van de walsparameters zoals walstemperatuur, tussentijdse warmtebehandeling, walsgraad eind warmtebehandeling, resulteerde in verschillende texturen. De anisotropie in de vormgeheugen eigenschappen, in het bijzonder de transformate rek, werd bepaald door middel van trekproeven en thermisch cycleren onder konstante belasting. Textuurmetingen werden uitgevoerd zowel na het walsen en de trekproeven als na het thermisch cycleren. Het anisotroop gedrag van de vormgeheugen legeringen werd vervolgens gerelateerd aan zowel de experimenteel gemeten texturen als aan beschikbare theoretische modellen.

In de gewalste en gegloeide materialen werden in hoofdzaak twee austeniet textuur componenten, (110)[110]_p en/of (111)[110]_p, zowel kwalitatief als kwantitatief als kwantitatief bepaald. De (111)[110]_p textuur component werd overwegend waargenomen als de walstemperatuur toename tot 300°C. De gemeten martensiet texturen waren in overeenstemming met de bekende orientatie relatie tussen de austeniet en martensiet fasen. De ontstane texturen na de trekproef en het thermisch cycleren waren afhankelijk van de belastingsrichting.

De anisotropie in de vormgeheugen eigenschappen, met name de transformatie rek, werd experimenteel bepaald. De transformatie rek in koud gewalst en gegloeid plaamateriaal met hoofdzakelijk een (110)[110]_p textuur component is meer anisotroop (met anisotropie parameter A=1.83) dan in warmgewalst en gegloeid plaamateriaal met een (111)[110]_p textuur (A=1.24). De transformatie rek varieerde vrijwel niet gemeten tussen de walsrichting (WR) en 60° van de WR, maar vertoonde een minimum waarde gemeten in de dwars richting. De permanente rek onstaan tijdens het thermisch cycleren vertoonde een minimum waarde in de dwarsrichting, onafhankelijk van de walsparameters.

De waargenomen rekken waren het resultaat van de vorming van een combinatie van 12 martensiet varianten tijdens het walsen en het thermisch cycleren. Het anisotroop gedrag van de transformatie rek kon ook voorspeld worden uit de resultaten van de textuur analyse. Vier methoden werden gebruikt om de transformatie rek te voorspellen. Een van de methoden was een berekening waarbij een gemodificeerd Taylor model voor polykristallijne vormgeheugen legeringen gekombineerd werd met de inverse poligraaf, berekend uit de orientatie distributie functie (ODF). Van de vier methoden benaderden de berekende waarden van deze laatste methode het dichtst de experimenteel gemeten rekken.
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<tr>
<td>a,b,c</td>
<td>nm</td>
<td>Monoclinic lattice parameters</td>
</tr>
<tr>
<td>a_o</td>
<td>nm</td>
<td>Cubic lattice parameter</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>Anisotropy factor</td>
</tr>
<tr>
<td>A_f</td>
<td>°C</td>
<td>Austenite finish temperature</td>
</tr>
<tr>
<td>A_p</td>
<td>°C</td>
<td>Austenite peak temperature</td>
</tr>
<tr>
<td>A'_p</td>
<td>°C</td>
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<tr>
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<td>C_{av}</td>
<td></td>
<td>C-coefficient</td>
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<tr>
<td>d</td>
<td>nm</td>
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<tr>
<td>E</td>
<td>KJ/mol</td>
<td>Activation energy</td>
</tr>
<tr>
<td>E_{ch}</td>
<td>KJ/mol</td>
<td>Chemical energy</td>
</tr>
<tr>
<td>E_{el}</td>
<td>KJ/mol</td>
<td>Elastic stored energy</td>
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<tr>
<td>E_{fr}</td>
<td>KJ/mol</td>
<td>Frictional energy</td>
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<tr>
<td>f</td>
<td>%</td>
<td>Transformed volume fraction</td>
</tr>
<tr>
<td>f(g)</td>
<td></td>
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</tr>
<tr>
<td>(hkl), {hkl}</td>
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<td>(hkl)_m, {hkl}_m</td>
<td></td>
<td>Miller's indices of plane(s) in the martensite phase</td>
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<tr>
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<td>k_o</td>
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<td>Pre-exponential index</td>
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<tr>
<td>M_d</td>
<td>°C</td>
<td>Maximum temperature to induce martensite by stress</td>
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<td>°C</td>
<td>Martensite finish temperature</td>
</tr>
<tr>
<td>M_p</td>
<td>°C</td>
<td>Martensite peak temperature</td>
</tr>
<tr>
<td>M'_p</td>
<td>°C</td>
<td>Martensite transformation temperature under stress</td>
</tr>
<tr>
<td>M_s</td>
<td>°C</td>
<td>Martensite start temperature</td>
</tr>
<tr>
<td>M'_s</td>
<td>°C</td>
<td>Martensite start temperature under stress</td>
</tr>
<tr>
<td>Q_{A}</td>
<td>mJ/mg</td>
<td>Reverse transformation heat</td>
</tr>
<tr>
<td>Q_{M}</td>
<td>mJ/mg</td>
<td>Martensite transformation heat</td>
</tr>
<tr>
<td>R</td>
<td>J/(mol·K)</td>
<td>Gas constant</td>
</tr>
<tr>
<td>s</td>
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<td>Standard deviation</td>
</tr>
<tr>
<td>t_o</td>
<td>mm</td>
<td>Initial thickness before rolling</td>
</tr>
<tr>
<td>t_f</td>
<td>mm</td>
<td>Final thickness after rolling</td>
</tr>
<tr>
<td>T_i</td>
<td>°C</td>
<td>Intermediate annealing temperature</td>
</tr>
<tr>
<td>T_o</td>
<td>°C</td>
<td>Equilibrium temperature</td>
</tr>
<tr>
<td>T_r</td>
<td>°C</td>
<td>Rolling temperature</td>
</tr>
<tr>
<td>T_R</td>
<td>°C</td>
<td>R-phase transformation temperature</td>
</tr>
<tr>
<td>tr.</td>
<td>%</td>
<td>Thickness reduction</td>
</tr>
<tr>
<td>[uvw], &lt;uvw&gt;</td>
<td></td>
<td>Miller's indices for crystallographic direction(s)</td>
</tr>
<tr>
<td>V</td>
<td>°C/min.</td>
<td>Heating or cooling rate</td>
</tr>
<tr>
<td>β</td>
<td>°</td>
<td>Monoclinic lattice angle</td>
</tr>
<tr>
<td>2θ</td>
<td>°</td>
<td>Bragg angle</td>
</tr>
<tr>
<td>Δg_c</td>
<td>KJ/mol</td>
<td>Change in chemical free energy</td>
</tr>
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Symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$\Delta g_s$</td>
<td>KJ/mol Resistance energy</td>
</tr>
<tr>
<td>$\Delta g_{nc}$</td>
<td>KJ/mol Increase in the non-chemical free energy</td>
</tr>
<tr>
<td>$\varepsilon_{\text{M}\rightarrow\text{P}}$</td>
<td>% Reverse transformation strain</td>
</tr>
<tr>
<td>$\varepsilon_{\text{P}\rightarrow\text{M}}$</td>
<td>% Martensite transformation strain</td>
</tr>
<tr>
<td>$\varepsilon_f$</td>
<td>% Fracture strain</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>% Calculated strain for single crystal</td>
</tr>
<tr>
<td>$\varepsilon_u$</td>
<td>% Unload strain</td>
</tr>
<tr>
<td>$\rho$</td>
<td>kg/m³ Material density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>MPa Stress</td>
</tr>
<tr>
<td>$\sigma_f$</td>
<td>MPa Fracture stress</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>MPa Plateau stress</td>
</tr>
<tr>
<td>$\phi$</td>
<td>° Rotation angle</td>
</tr>
<tr>
<td>$\Phi, \phi_1, \phi_2$</td>
<td>° Euler angles</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>° Tilt angle</td>
</tr>
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</table>

Abbreviation | Definition
---|---
at.% | Atomic Percentage
A | Austenite
bcc | Body-Centred Cubic
bct | Body-Centred Tetragonal
B2 | Crystallographic Notation for Parent Austenite Phase
B19 | Crystallographic Notation for Orthorhombic Martensite
B19’ | Crystallographic Notation for Monoclinic Martensite
DSC | Differential Scanning Calorimetry
fcc | Face-Centered Cubic
FWHM | Full Width at Half Maximum
HTXRD | High Temperature X-Ray Diffraction
HV | Vicker’s Hardness
hys. | Hysteresis
IPS | Invariant Plane Strain
LIS | Lattice Invariant Shear
M | Martensite
ND | Normal Direction
ODF | Orientation Distribution Function
P | Parent (Austenite)
PE | Pseudoelasticity
RD | Rolling Direction
R-phase | Rhombohedral Phase
rpm | Revolutions per minute
RT | Room Temperature
SF | Schmid Factor
SIM | Stress-Induced Martensite
SMA | Shape Memory Alloy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>SME</td>
<td>Shape Memory Effect</td>
</tr>
<tr>
<td>TD</td>
<td>Transverse Direction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TWME</td>
<td>Two-Way Memory Effect</td>
</tr>
<tr>
<td>vol.%</td>
<td>Volume Percentage</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight Percentage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
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</table>
Chapter 1

Introduction

The development of new materials will play an increasingly important role in future technological advances in the world. Such developments, however, will aim not only at materials alone (structural materials), but also new functions and capabilities obtained from the materials themselves (functional materials). Structural materials are those materials that are principally characterized by their mechanical strength and are generally employed in load-bearing situations. Functional materials are those materials whose principal functional characteristics are exploited rather than the structural properties of the material\(^1\). The functional characteristics may include piezoelectricity, photoconductivity, photoelectricity, viscoelasticity, pyroelectricity, and shape-memory properties. For example, the rapid evolution of hardware in computers has been made possible by integrated circuits featuring silicon chips. This progress has not come from the mechanical strength of the materials, but instead, from the exploitation of the functional properties of silicon, i.e. its electrical and physical properties.

The progress in the areas of functional materials makes it possible to use the functions of the materials themselves, for instance, as mechanical elements to realize substantially more advanced mechanical systems. Shape memory alloys (SMAs) are such a class of functional materials. The term shape memory alloys is applied to that group of metallic materials that demonstrate the ability to return to a previously defined shape or size when subjected to appropriate thermal processes\(^2\). This kind of behaviour is known as the shape memory effect (SME), as shown in Fig. 1.1. A spring made of a SMA can be plastically deformed at a relatively low temperature. Upon exposure to a higher temperature the spring will return to the shape prior to the deformation. The material "remembers" its previous shape before deformation and thus has a "shape memory" function. This thermomechanical shape memory property furnishes design engineers with the opportunity to design on the basis of an entirely new principle. By exploitation of these unique properties, it is possible to construct mechanical systems that are

![Diagram of shape memory effect](image-url)

*Fig. 1.1 A schematic illustration of the shape memory effect (one-way SME).*
simple in design, more compact, self-regulating and that possess previously unthinkable capabilities.

The underlying mechanism of shape memory alloys is based on a thermoelastic martensitic transformation. The first recorded observation of a thermoelastic martensitic transformation in which martensite plates grow and shrink as the temperature changes was in 1932 by Olander\(^3\) in a AuCd alloy. In 1951, Chang and Read\(^4\) observed the reversibility of the transformation in a bent bar of the AuCd alloy which they termed a "rubber-like" behaviour. Later, the behaviour was also observed in an In-Ti alloy\(^5\). However, it was not until 1962, when the shape memory effect was discovered in equiatomic Ni-Ti alloys by Buehler, Gilfich and Wiley of the U.S. Naval Ordnance Laboratory\(^6\), that research into both the metallurgy and potential practical application began actively. These Ni-Ti alloys, called Nitinol (NIckel Tiتانium Navy Ordnance Laboratory), are based on the intermetallic compound NiTi and have chemical compositions in the range from 53 to 57 (wt.%) nickel. Useful properties were measured for Nitinol, and one of the most important aspects is its ability to experience large, reproducible shape recovery\(^7\). Since then, the study of shape memory alloys has continued at an increasing pace, and understanding of the effect has advanced considerably.

A number of SMAs have been developed and a large number of commercial products using these materials have appeared on the market. Applications of SMAs are seen at present mainly in several areas as reviewed by van Humbeeck\(^8\): (1) mechanical engineering, (2) electronic engineering, (3) safety technology, (4) sensors, actuators, heating and ventilating engineering, (5) domestic appliance industry, (6) aircraft and space exploration, (7) automobile industry, (8) arts, toys and gadgets, (9) composite materials and (10) medical applications. For example, SMAs are used as fasteners\(^9\) and couplings\(^10\), robots\(^11,12\) and actuators\(^13,14\), heat engines\(^15\), SMA reinforced composites\(^16,17\), air conditioners\(^18\), orthopaedic devices\(^19\) and scoliosis correction systems\(^20,21\). Damping characteristics of SMAs are applied in tennis rackets\(^22\). With a better understanding of its behaviour and properties, SMAs are expected to be more widely applied in the near future.

On a microscopic scale, the reversible movement of martensite variant and twin boundaries are responsible for the shape memory effect. The mechanism of the movement of the intervariant boundaries in single crystal SMAs has been clarified up to date\(^23,24,25\). The anisotropic shape memory properties in single crystal SMAs were thus established. However, SMAs are mostly applied in the polycrystalline state. They are usually produced by vacuum induction melting, followed by deformation and subsequent heat treatment of the ingot. The deformation generally results in a preferred orientation (texture) of the crystallites. The presence of such texture leads to anisotropic behaviour of the polycrystalline SMAs. The pronounced anisotropy in single crystal SMAs can be used to its full extent in polycrystalline materials by careful control of texture. For instance, the recoverable strain of NiTi single crystals along a [111] direction is 4 times higher than the one along a [100] direction. To profit from this pronounced anisotropy in a specific application, a sharp texture in polycrystalline materials should be produced.
At present, although the importance of the texture in polycrystalline SMAs is well recognised, only a few papers account for the contribution of the texture to the anisotropic behaviour in SMAs. In some cases, the effect of texture was not even taken into account. For instance, Nam et al\(^\text{26}\) measured transformation strain by thermal cyclic testing under constant load and concluded that the maximum transformation strain associated with a B2 \(\rightarrow\) B19\(^\prime\) transformation in a hot-rolled Ti-45Ni-5Cu (at.\%) alloy is 3.3\%. The maximum recoverable strain associated with a B2 \(\rightarrow\) B19 transformation decreases from 3.2 to 2.7\% with increasing Cu content (from 10\% to 20\%). It is shown in this thesis that the strain can range from 2.8\% to 5.2\% in an alloy close to Ti-45Ni-5Cu (at.\%) alloy after considering the effect of texture. On the other hand, the shape memory effect is associated with the martensite transformation from a cubic phase with high symmetry to a martensite phase with lower symmetry. Despite the available knowledge of textures in high symmetry materials, the full interpretation of texture in the materials with less symmetry, such as the monoclinic martensite phase in NiTi alloys, is still under development.

In this thesis, the evolution of texture and related anisotropic behaviour were systematically investigated. The investigation was concentrated on a widely used commercial Ti-45Ni-5Cu(at.\%) shape memory alloy. Two main advantages of this material are\(^{27,28}\) the low sensitivity of transformation temperatures on the composition and its good workability. The work in this thesis is presented as follows:

Chapter 2 gives a survey of the fundamental aspects and recent progress in shape memory alloys, texture development, mechanical properties, and anisotropic behaviour. Based on these, the objectives and tasks of this thesis will be introduced and explained.

Chapter 3 discusses the experimental procedures, including the rolling of the materials, texture measurements, mechanical testing and transformation analysis.

Chapters 4 to 6 present the results of texture development and anisotropic behaviour of the rolled materials, as well as thermal transformation characteristics.

In Chapter 7 the anisotropy of transformation strain will be calculated based on texture analysis using different models. The texture development and anisotropic behaviour will be discussed in Chapter 8. Conclusions drawn from the present work are given in Chapter 9.
Chapter 2

Literature

2.1 Shape Memory Effects and the Martensite Transformation

2.1.1 Shape memory effects

a. Shape memory alloys: The basis of shape memory behaviour is now accepted to be a thermoelastic martensitic transformation. Compared with other metallic materials showing a martensitic transformation, the hysteresis between the forward and reverse martensitic transformation temperature in SMAs is rather small. For instance, the martensitic transformation temperature hysteresis in a AuCd SMA is around 15°C, whereas the hysteresis in an FeNi alloy is 420°C\(^{(29)}\), and in normal steels around 200°C. Many alloys have been found to show this small temperature hysteresis and thus show SME. A selection of those alloys is compiled in Table 2-1\(^{(30)}\).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>(M_s) (°C)</th>
<th>Hysteresis</th>
<th>Type of Transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCd</td>
<td>44 - 49at.%Cd</td>
<td>-190 to -50</td>
<td>15°C</td>
<td>B2 - M2H</td>
</tr>
<tr>
<td>AuCd</td>
<td>46.5 - 50at.%Cd</td>
<td>30 to 100</td>
<td>15°C</td>
<td>B2 - M2H</td>
</tr>
<tr>
<td>CuAlNi</td>
<td>14 - 14.5wt.%Al 3 - 4.5wt.%Ni</td>
<td>-140 to 100</td>
<td>35°C</td>
<td>DO(_3) - 2H</td>
</tr>
<tr>
<td>TiNi</td>
<td>49 - 51at.%</td>
<td>-50 to 100</td>
<td>30°C</td>
<td>B2 - B19</td>
</tr>
<tr>
<td>CuZnX (X=Al, Si, Ga, Sn)</td>
<td>38.5 - 41.5wt.%Zn few wt.%X</td>
<td>-180 to 100</td>
<td>10°C</td>
<td>B2 - 9R or M9R DO(_3) -18R OR M18R</td>
</tr>
<tr>
<td>NiAl</td>
<td>36 - 38at.%Al</td>
<td>-50 to 100</td>
<td>10°C</td>
<td>B2 - M3R</td>
</tr>
<tr>
<td>FePt</td>
<td>~25at.%Pt</td>
<td>~ -130</td>
<td>4°C</td>
<td>L1(_2) - BCT</td>
</tr>
</tbody>
</table>

Although a relatively wide variety of alloys are known to exhibit the shape memory effect, only those that can recover substantial amounts of strain or that generate significant force upon changing shape have been exploited for commercial purposes. In particular, nickel-titanium alloys and copper-based alloys have these characteristics. NiTi alloys have higher recovery strains and stresses, longer cyclic life, tend to be more thermally stable, have
excellent corrosion resistance and have much better ductility\textsuperscript{(31)} than Cu-based alloys\textsuperscript{(32,33,34)}. Therefore, the performance characteristics of NiTi SMAs are superior to those of Cu-based alloys. However, NiTi alloys cost about ten times more than Cu-based alloys. If high performance is not required and cost considerations are important, for instance, in safety devices, temperatures fuses and fire alarms, the use of Cu-based SMAs can be recommended.

In NiTi alloys, the addition of a third element is effective in improving transformation behaviour, shape memory characteristics and mechanical properties. For instance, when Ni is partially replaced by Co or Fe\textsuperscript{(35)} or Ti is replaced by V, Cr or Mn\textsuperscript{(36)}, the transformation temperatures are shifted significantly to lower temperatures. The addition of Zr, Hf\textsuperscript{(37,38,39)}, Pd, Pt or Au\textsuperscript{(40,41,42)} can raise transformation temperatures. Substitution of Cu has the unique effect of reducing the composition sensitivity of the martensitic transformation start temperature\textsuperscript{(43,44)}, to narrow the hysteresis, to reduce the flow stress level in the martensite state, to suppress the R-phase transformation and to prevent X-phase (Ti\textsubscript{3}Ni\textsubscript{4}) precipitation\textsuperscript{(7)}.

\textbf{b. Shape memory effects:} If a shape memory alloy is mechanically deformed in the martensitic state, it will return to its original form when the temperature is raised above the reverse transformation temperature A\textsubscript{f}. The process is known as the \textit{one-way shape memory effect} because the shape change occurs only upon heating, see Fig. 2.1 (a). Subsequent cooling of the material will not reverse the shape change. Further research on SMAs has found more useful effects, mainly the \textit{two-way memory effect} (TWME), \textit{all-round SME} and \textit{pseudoelasticity}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{stress_strain_curves.png}
\caption{Schematic illustration of three types of stress-strain curves for SMAs. \(T_1\): Austenite. \(T_2\): Pseudoelastic. \(T_3\): Martensite. \(M_d > T_2 > A_f > M_s > T_3\). (a) One-way shape memory effect: Deformation of martensite, heating above \(A_f\). (b) Pseudoelasticity: Loading and unloading at \(M_d < T < A_f\). (c) No shape memory effect: Deformation at temperatures above \(M_s\).}
\end{figure}
SMAs can be trained to memorize two configurations in both the martensitic state and austenitic state. This phenomenon is known as the two-way memory effect to emphasize that the shape changes both upon heating and upon cooling. The alloy is trained by appropriate stress and/or thermal cycling below a critical temperature. Recently, the TWME was explained as being caused by thermodynamic anisotropy\(^{(45,46,47)}\). The origin of the TWME is ascribed to the introduction of specific dislocation arrays during the training which produce internal stresses. Based on free energy calculations, the energy of the complex dislocation arrays generated during training depends on the martensite variants formed. Therefore, the crystallographically equivalent variants are not thermodynamically equivalent. This so-called thermodynamic anisotropy is thus to the microstructural anisotropy induced by transformation cycling. Training (thermomechanical cycling) limits the number of variants of martensite and only two configurations are memorized.

Nishida and Honma\(^{(48,49,50)}\) observed a spontaneous shape change in a Ti-51Ni (at.%) alloy solution treated at 100°C for 1 hour and aged at 400°C for 100 hours. The shape change was greater than in any of the previously described SMEs, and the shapes at high and low temperatures are exactly inverse. This type of shape change is termed "all-round" SME. This phenomenon was attributed to the effect of the Ti\(_{11}\)Ni\(_{14}\) precipitates (coherent Ti\(_{3}\)Ni\(_{4}\)) which introduce internal stress fields that make the transformations of R-phase and martensite proceed in certain ways\(^{(51,52)}\).

At temperatures above the finish temperature of the reverse martensitic transformation, \(A_f\), and below \(M_d\), the maximum temperature to induce martensite by a stress, plastic deformation apparently occurs after linear deformation of the matrix. This strain is, however, recovered almost completely upon unloading. This phenomenon is called pseudoelasticity and is characterized by the presence of a closed stress-strain loop\(^{(53)}\), see Fig. 2.1 (b). In applications of shape memory alloys, both the shape memory effect and pseudoelasticity are often used. Pseudoelasticity is attributed to a stress-induced transformation. Applied stress changes the thermodynamic equilibrium between the austenite phase and martensite phase and transformation temperatures are shifted to higher values. Once the temperature is higher than \(M_d\), the SMAs behave as normal steels, see curve (c).

c. Crystallographic characteristics of Ti-Ni alloys: The crystal structures of the parent phase and the product phase associated with the martensite transformation in NiTi alloys are shown in Fig. 2.2. All reports agree that the parent phase of NiTi alloys has a B2 structure (CsCl type) with \(a_0 = 0.3010\) to \(0.3020\) nm. The first determination of the crystal structure of the martensitic phase was in a polycrystalline Ti-49.75 at.%Ni alloy by Otsuka \textit{et al.}\(^{(54)}\). Their results, obtained from both X-ray diffraction measurements (XRD) and transmission electron microscopy (TEM), show that the unit cell of the martensite phase is monoclinic. The crystal structure was also further confirmed in a single crystal Ti-49.2 at.%Ni by Kudoh \textit{et al.}\(^{(55)}\) using a 4-circle diffractometer, in a polycrystalline equiatomic NiTi alloy by Michal \textit{et al.}\(^{(56)}\) using TEM techniques, by Bührer \textit{et al.}\(^{(57)}\) using neutron diffraction measurements and by Knowles\(^{(58)}\) using high resolution electron microscopy. The lattice parameters and atomic positions in the monoclinic martensitic crystal structure determined by the different authors are shown in Table 2-2. Although slight differences exist, the lattice parameters reported by Otsuka \textit{et al.} have been widely recognized as the standard structure.
Chapter 2 Literature

Fig. 2.2 The crystal structures of TiNi alloys: (a) cubic B2 parent structure with $a_0 = 0.3015$ nm; (b) monoclinic B19' martensite structure with $a = 0.2889$ nm, $b = 0.4120$ nm, $c = 0.4622$ nm and $\beta = 96.8^\circ$.

Bricknell et al. (59) investigated the influence of Cu additions (up to 25 at.%Cu) on the lattice parameters in NiTi alloys by XRD and TEM. The morphology as well as the crystal structures of both the austenitic and martensitic phases of all of the alloys are remarkably similar in these alloys, although there are slight changes in lattice parameters. For the alloy with 5 at.%Cu, the lattice parameters are $a_0 = 0.3025$ nm for the austenitic phase, and $a = 0.293$ nm, $b = 0.421$ nm, $c = 0.458$ nm and $\beta = 97.3^\circ$ for the martensite phase, as determined by the present author from the figures in the published paper.

Fig. 2.3 schematically shows one of the lattice transformations from B2 to B19' via the orthorhombic B19 base ($X_{B19}$, $Y_{B19}$ and $Z_{B19}$). Since the martensitic transformation is diffusionless, a given vector in the parent phase transforms into a specific vector in martensite through so called lattice correspondence. From the difference of symmetry between the B2 and B19' crystal structures in NiTi alloys (60), there are, in total, twelve martensite lattices which can be formed from the B2 lattice, that is, the $a$, $b$, $c$ axes in the B19 lattice can originate from twelve different crystal directions in the B2 lattice. Each correspondence is called a correspondence variant. Table 2-3 lists the notation of these twelve correspondences according to S. Miyazaki et al. (23). Correspondences with the same number but without and with prime symbols (e.g. 1 and 1') represent correspondence variants with an opposite monoclinic shear.

During the martensitic transformation, an intermediate phase characterized by a rhombohedral distortion of the B2 structure along $<111>_p$ directions can also form (61,62). This phase, called the R-phase, has a rhombohedral structure and occurs by a displacive first-order transformation that precedes the martensitic transformation (63,64,65). A great deal of
Table 2-2  Monoclinic martensite lattice parameters a, b, c, β and atomic positions in the crystal structure measured by different authors.

<table>
<thead>
<tr>
<th></th>
<th>Ostuka et al(^{(51)})</th>
<th>Kudoh et al(^{(52)})</th>
<th>Michal and Sinclair(^{(53)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.2889 nm</td>
<td>0.2898 nm</td>
<td>0.2885 nm</td>
</tr>
<tr>
<td>b</td>
<td>0.4120 nm</td>
<td>0.4108 nm</td>
<td>0.4622 nm</td>
</tr>
<tr>
<td>c</td>
<td>0.4662 nm</td>
<td>0.4646 nm</td>
<td>0.4120 nm</td>
</tr>
<tr>
<td>β</td>
<td>96.8°</td>
<td>97.78°</td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td></td>
<td></td>
<td>96.8°</td>
</tr>
<tr>
<td>Ti</td>
<td>0, 0, 0</td>
<td>0, 0, 0</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td></td>
<td>0, 1/3, 1/2</td>
<td>0.1648, 0.5672, 1/2</td>
<td>0.055, 1/2, 0.558</td>
</tr>
<tr>
<td>Ni</td>
<td>1/2, 1/2, 0</td>
<td>0.6196, 0, 0.4588</td>
<td>0.580, 0, 0.472</td>
</tr>
<tr>
<td></td>
<td>1/2, 5/6, 1/2</td>
<td>0.5452, 0.1084, 1/2</td>
<td>0.475, 1/2, 0.086</td>
</tr>
</tbody>
</table>

Fig. 2.3  Schematic representation of the correspondence of the lattices B2 and B19' via the B19 base X\(_{B19}\), Y\(_{B19}\) and Z\(_{B19}\) in which [100]\(_{B19}\)//[001]\(_{B2}\) and [010]\(_{B19}\)//[110]\(_{B2}\), but [001]\(_{B19}\)//[110]\(_{B2}\) rather than [001]\(_{B19}\)//[110]\(_{B2}\).
attention has been paid to the R-phase in connection with the practical application of SMAs, because the R-phase can transform reversibly without hysteresis and has proven very promising for use in cyclic operations\(^{(66)}\). The lattice parameters of the R-phase are well accepted as \(a = 0.3015 \text{ nm} \) and \(\alpha = 89.46^\circ\) at the R-phase transformation temperature \(T_R = 35^\circ\text{C}\) for NiTi alloys\(^{(67)}\). It was found that thermal cycling could lead to a clear R-phase transformation\(^{(68)}\).

d. Transformation sequences for TiNi(Cu) alloys: In NiTi alloys, three types of transformation sequence have been reported:

<table>
<thead>
<tr>
<th>Variant</th>
<th>([100]_m)</th>
<th>([010]_m)</th>
<th>([001]_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([100]_p)</td>
<td>([011]_p)</td>
<td>([0\bar{1}1]_p)</td>
</tr>
<tr>
<td>1'</td>
<td>([\bar{1}00]_p)</td>
<td>([0\bar{1}1]_p)</td>
<td>([0\bar{1}1]_p)</td>
</tr>
<tr>
<td>2</td>
<td>([100]_p)</td>
<td>([0\bar{1}1]_p)</td>
<td>([0\bar{1}1]_p)</td>
</tr>
<tr>
<td>2'</td>
<td>([\bar{1}00]_p)</td>
<td>([01\bar{1}]_p)</td>
<td>([0\bar{1}1]_p)</td>
</tr>
<tr>
<td>3</td>
<td>([010]_p)</td>
<td>([101]_p)</td>
<td>([10\bar{1}]_p)</td>
</tr>
<tr>
<td>3'</td>
<td>([0\bar{1}0]_p)</td>
<td>([\bar{1}0\bar{1}]_p)</td>
<td>([10\bar{1}]_p)</td>
</tr>
<tr>
<td>4</td>
<td>([010]_p)</td>
<td>([10\bar{1}]_p)</td>
<td>([\bar{1}0\bar{1}]_p)</td>
</tr>
<tr>
<td>4'</td>
<td>([0\bar{1}0]_p)</td>
<td>([\bar{1}01]_p)</td>
<td>([\bar{1}0\bar{1}]_p)</td>
</tr>
<tr>
<td>5</td>
<td>([001]_p)</td>
<td>([110]_p)</td>
<td>([\bar{1}10]_p)</td>
</tr>
<tr>
<td>5'</td>
<td>([0\bar{1}1]_p)</td>
<td>([\bar{1}10]_p)</td>
<td>([\bar{1}10]_p)</td>
</tr>
<tr>
<td>6</td>
<td>([001]_p)</td>
<td>([\bar{1}10]_p)</td>
<td>([\bar{1}10]_p)</td>
</tr>
<tr>
<td>6'</td>
<td>([0\bar{1}1]_p)</td>
<td>([\bar{1}10]_p)</td>
<td>([\bar{1}10]_p)</td>
</tr>
</tbody>
</table>

where B2 stands for the parent phase, M for the B19' and/or B19 martensite phase and R for the R-phase. The occurrence of the transformation depends on the conditions of the sample. For instance, Todoroki et al\(^{(69)}\) showed that the transformation sequence depends on annealing temperature. The transformation type (I) occurs in samples annealed at high temperatures; for samples heat-treated at intermediate temperatures, transformation type (II) occurs; for samples heat-treated at low temperatures, transformation type (III) occurs. Morawiec et al\(^{(70)}\) reported that the sequence of transformation during cooling in a cold rolled and then low-temperature annealed Ti-50.6Ni (at.\%) alloy is B2 \(\rightarrow\) R \(\rightarrow\) B19'. They observed two peaks on differential thermal analysis (DTA) and differential scanning calorimetry (DSC) cooling curves in the martensite range, and explained this to be caused by an inhomogeneity in the stress field which results from changes in the dislocation configuration during the recovery process.

The transformation mechanism in TiNiCu alloys has been measured by Nam et al\(^{(26)}\) using electrical resistivity measurements, DSC and thermal cyclic testing under constant load and Tsuji et al\(^{(71,72)}\) using DSC and XRD analysis. Fig. 2.4 shows a diagram with the dependence of transformation temperatures on Cu-content for solution-treated alloys measured by Nam et al (solid line) and Tsuji et al (broken line). When the Cu content is around 5\%, the direct B2 \(\rightarrow\) B19' transformation occurs. Upon increasing the Cu content, the B2 \(\rightarrow\) B19 transformation temperature \(M'_s\) increases slightly and the B2 \(\rightarrow\) B19' transformation temperature \(M_s\) decreases significantly.
Chernov et al.\textsuperscript{(73)} measured the transformation kinetics in ternary Ti-Ni-Cu alloys with up to 4 at.\%Cu by XRD. The direct B2 $\rightarrow$ B19’ transformation was found when Cu substitutes for nickel, and the two-stage B2 $\rightarrow$ R $\rightarrow$ B19’ transformation was measured when Cu substitutes for both nickel and titanium. Fukuda et al.\textsuperscript{(74,75)} investigated the transformation mechanism in Ti-44.5Ni-5.0Cu alloys and Ti-44.0Ni-5.0Cu-1.0Al (at.\%) alloys by means of \textit{in situ} TEM observation, electrical resistivity measurements and X-ray diffraction analysis. A two-stage transformation B2 $\rightarrow$ B19 $\rightarrow$ B19’ upon cooling was observed by TEM, but not by the electric resistivity measurement. It was explained that upon cooling, B19’ starts to replace B19 before the B2 $\rightarrow$ B19 transformation finishes. Only a small amount of B19 exists throughout the transformation. Therefore, the B2 $\rightarrow$ B19 transformation can not be differentiated from the B19 $\rightarrow$ B19’ transformation in the XRD analysis and the electrical resistivity measurements.

Goubaa et al.\textsuperscript{(76)} compared several techniques for detecting the R-phase in Ti-Ni (based) alloys. For the 49.6Ti-46.2Ni-4.2Cu (at.\%) alloy, the R-phase was found by TEM observations ($\alpha=89.3^\circ$). The R-phase was also observed during internal friction measurements and could be detected with more sensitivity if higher heating or cooling rates are adopted. From DSC measurements, overlapping peaks were detected. Thermal treatment at 500°C for 160 hours allows a separation of these peaks by increasing the difference between the nucleation temperatures of the R-phase and martensite.
2.1.2 Phenomenological theory of the crystallography of martensitic transformations

The phenomenological theory of the crystallography of martensitic transformations is based on the experimental observation that the interface plane between austenite and martensite, the habit plane, is macroscopically undistorted. This is called the invariant plane strain (IPS) condition. The theory was developed independently by Wechsler, Lieberman and Read (W-L-R)⁷⁷,⁷⁸, and Bowles and Mackenzie (B-M)⁷⁹,⁸⁰. In their theory, the transformation consists of three operational processes, 1) a pure strain B which creates the martensite structure from the parent; 2) a lattice invariant shear (LIS) P₂; and 3) a lattice rotation R. Thus, the total strain associated with the transformation, the shape strain P₁, is written in matrix form as

\[ P₁ = RP₂B \]  

(2.1)

This is the so-called W-L-R theory. The theory requires that the interface be macroscopically invariant, i.e. a plane of no distortion and rotation. This is equivalent to saying that P₁ is an invariant plane strain consisting of a shear strain parallel to the habit plane and a uniform expansion or contraction normal to it. In matrix form, an invariant plane strain (IPS), P₁, is written as

\[ P₁ = I + m₁d₁p₁' \]  

(2.2)

where I is the 3×3 identity matrix, m₁ is the magnitude of the shape strain, d₁ is a unit vector in the direction of the shape strain, and p₁’ is a unit vector in the direction normal to the invariant plane, see Fig. 2.5. The prime is used to indicate that p₁’ is a row vector in contrast to d₁ which is a column vector.

Let P₂ be equal to the reciprocal of matrix P₁, i.e. P₂=P₁⁻¹. Eqn. 2.1 becomes

**Fig. 2.5 Schematic illustration of the martensitic transformation, where m₁ is the magnitude of the shape strain, d₁ is a unit vector in the direction of the shape strain, and p₁’ is a unit vector in the direction normal to the habit plane.**
\[ P_1 P_2 = RB \] (2.4)

This is the B-M theory. Since \( P_1 \) and \( P_2 \) are all invariant planes, RB is an invariant linear strain. Although the formulations from the B-M theory and the W-L-R theory are different, both lead to the same results\(^{85}\). The phenomenological theory can predict quantitatively the crystallographic parameters such as the habit plane and the shape strain. The treatment of this theory is presented in Wayman’s textbook\(^{86}\) and a program to calculate these crystallographic parameters was introduced\(^{87}\). The theory has been successfully applied to many alloy systems, for instance, in a Au-47.5Cd (at.\%) alloy with a cubic to orthorhombic transformation\(^{61}\), in an In-20.7Tl (at.\%) with a cubic to tetragonal transformation\(^{88}\), and in Cu-Al-Ni alloys with cubic to monoclinic transformations\(^{89,90}\).

According to this theory, only the following three input parameters are required to calculate these crystallographic parameters: 1) lattice parameters of the parent and martensite phase; 2) lattice correspondence and 3) lattice invariant shear (LIS). The lattice parameters and lattice correspondence for NiTi alloys were discussed in the previous section. A lattice invariant shear may, in general, either be twinning, slip or faulting. In most cases it is, in fact, twinning. Twinning is said to be any region of a parent which has undergone a homogeneous shear to give a reoriented region with the same crystal structure. A description of twins is characterized by five crystallographic elements\(^{91}\): \( K_1 \)=twinning plane; \( \eta_1 \)=twinning shear direction; \( K_2 \)=another undistorted plane; \( \eta_2 \)=intersection of \( K_2 \) and the plane of shear; and \( s \)=magnitude of twinning shear. With a knowledge of two of these elements, the other three elements are determined, according to Bilby-Crocker’s theory of deformation twinning\(^{92}\). In NiTi alloys, three types of twinning have been found by electron microscopy in the work of Knowles et al\(^{93}\) for \( <011>\)\(_m\) type II twins, Otsuka et al\(^{94}\) and Gupta et al\(^{95}\) for \( \{111\}\)\(_m\) type I twins and/or \( \{001\}\)\(_m\) compounds. The crystallographic data of twins in NiTi alloys are compiled in Table 2-4. Calculations using phenomenological theory give solutions for the crystallographic parameters, such as the habit plane and the shape strain, for \( \{111\}\)\(_m\) type I and \( <011>\)\(_m\) type II twinning, but no solution exists for \( \{001\}\)\(_m\) compound twinning.

Based on the phenomenological theory, there are 24 solutions for habit planes for NiTi alloys. These solutions are called habit plane variants. The habit plane variant is the combination

<table>
<thead>
<tr>
<th>Twin</th>
<th>( K_1 )</th>
<th>( \eta_1 )</th>
<th>( K_2 )</th>
<th>( \eta_2 )</th>
<th>( s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}</td>
<td>(-1 -1 1)</td>
<td>[0.54 0.46 1]</td>
<td>(0.25 0.51 1)</td>
<td>[-2 1 1]</td>
<td>0.31</td>
</tr>
<tr>
<td>Type I</td>
<td>(1 1 1)</td>
<td>[-1.51 0.51 1]</td>
<td>(-0.67 0.34 1)</td>
<td>[2 1 1]</td>
<td>0.14</td>
</tr>
<tr>
<td>(&lt;011&gt;)</td>
<td>(-0.72 1 1)</td>
<td>[0 1 -1]</td>
<td>(0 1 -1)</td>
<td>[-1.57 1 1]</td>
<td>0.28</td>
</tr>
<tr>
<td>Type II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>(0 0 1)</td>
<td>[1 0 0]</td>
<td>(1 0 0)</td>
<td>[0 0 1]</td>
<td>0.24</td>
</tr>
</tbody>
</table>
of two correspondence variants. For example, the habit plane variant 1(+) consists of the correspondence variants of 1-2. The first number of the correspondence variant combination which has the same number of correspondence variants indicates the dominant correspondence variant, i.e. the major volume fraction of twins. The plus or minus signs in the parentheses of the habit plane variant correspond to the second number (without or with prime). In Ti-Ni alloys, using <011> type II twinning, the lattice parameters of Otsuka et al., and the correspondence variants in Table 2-3, the calculated habit plane as well as the magnitude and direction of the shape strain are as follows (taking variant 1(+) as an example):

habit plane: (-0.89, -0.22, 0.40), $d_1 = [0.43, -0.76, 0.49]$, $m_1 = 0.13$

The crystallographic data concerning habit plane, orientation relationship and shape strain were experimentally determined in single crystal TiNi alloys by Ostuka et al (96, 97) and Saburi et al (98). Compared with the above results from the calculation using <011> $m$ type II twinning, the solution agrees well with the experimental data. For instance, the observed orientation relation agreed with the predicted one within 1.2°, where the measured habit plane for variant 1(+) is (-0.78, -0.39, 0.48) (90). The agreement is, however, not as good as for other alloys such as Cu-Al-Ni alloys (90, 91).

The phenomenological theory of martensitic transformation crystallography gives the microscopic description of the transformation. In NiTi SMAs, this knowledge was applied to calculate the transformation strain, to explain the self-accommodation phenomenon and set up models for polycrystalline SMAs. These applications will be introduced in the following sections.

2.1.3 Thermodynamics and the kinetics of martensitic transformations

a. Thermodynamics: The difference in Gibbs free energy between two phases gives the driving force for the transformation from one phase to the other, as shown in Fig. 2.6. For a thermoelastic transformation, a local equilibrium between competing forces is reached for all of the transforming interfaces at each temperature. In the forward martensite transformation, the driving force resulting from the lower energy of the martensite phase is balanced by the increase in elastic strain energy and interfacial energy, and by resistive forces against interfacial motion. In the reverse transformation, the elastic energy previously stored promotes the reversion into the parent phase together with the driving force for the reverse transformation. This is balanced by resistive forces. The change of the total free energy in the transformation can be written as $^{99, 100}$

$$-\Delta G(T)^{P-M} = \Delta g_c^{P-M}(T) + \Delta g_{nc}^{P-M} + \Delta g_s^{P-M} \tag{2.5}$$

For the reverse transformation, the change is

$$\Delta G(T)^{M-P} = -\Delta g_c^{M-P}(T) + \Delta g_{nc}^{M-P} + \Delta g_s^{M-P} \tag{2.6}$$

where the superscripts "M" and "P" indicate martensite phase and parent austenitic phase, $\Delta g_c$ is the change in chemical free energy and $\Delta g_{nc}$ is the increase in the non-chemical free energy.
The energy term, $\Delta g_s$, corresponds to forces resisting either the growth and shrinkage of existing martensite crystals, or the creation and annihilation of new martensite crystals. Some authors\textsuperscript{(101)} omitted the energy term, $\Delta g_s$, and assumed that it belongs to the change in the non-chemical free energy $\Delta g_{nc}$. In both transformations, a change in temperature modifies the driving force and displaces the equilibrium, whereby the martensite plate grows or shrinks.

Based on this concept, efforts have been made to develop expressions to explain the changes of the values measured experimentally. The effects of both externally applied stress as well as temperature are taken into account. Results to date include the following:

1) Heat of transformation: According to the thermodynamic analysis of a thermally induced martensitic transformation by Ortin and Planes\textsuperscript{(102)}, the absolute values of the exothermic heat, $Q_M$, and endothermic heat, $Q_A$, in DSC curves are expressed as

$$-Q_M = -\Delta H_{ch}^{P-M} + \Delta H_{el}^{P-M} + E_{fr}^{P-M}$$  \hspace{1cm} (2.7)$$

$$Q_A = \Delta H_{ch}^{M-P} - \Delta H_{el}^{M-P} + E_{fr}^{M-P}$$  \hspace{1cm} (2.8)$$

where $\Delta H_{ch}^{P-M}$ is the chemical enthalpy change resulting from a structure contribution; $\Delta H_{el}^{M-P}$ is the elastic strain enthalpy change stored in the sample to accommodate the transformational shape and volume change; and $E_{fr}$ is the work done to overcome frictional barriers opposing interfacial motion. Lin and Wu\textsuperscript{(103)} recently measured a large change in the heat of transformation.
transformation, $Q_A$, between the first and second runs in DSC curves in a TiNi alloy. They proposed a modified equation for the heat of the reverse martensitic transformation

$$Q_A = \Delta H_{ch} - \Delta H_{el} + E_{fr} - \Delta H_{cr}$$

(2.9)

The extra term, $\Delta H_{cr}$, for cold-rolled samples is contributed by defect recovery. They explained that a part of the martensite reversibly transformed to a so-called stress-induced parent by mechanical stresses during cold rolling. The effect of the occurrence of stress-induced parent and accumulated elastic energy, $\Delta H_{el}$, play a major part in the first 10% of cold rolling. When the degree of cold rolling is larger than 10%, defects, such as dislocations and vacancies, are a major contribution to the heat.

With the help of these equations, the change of the heat of transformation can be explained. For NiTi based alloys, the heats of transformation were found to be influenced by the amount of third element additions(26,104), work hardening (105,106,107), rolling temperatures and thickness reduction as well as subsequent heat treatment methods or temperatures (108,109).

2) Transformation temperatures and hysteresis: From the thermodynamics of the martensite transformation, Hornbogen et al(110,111) established an approximate expression for the start temperature, $M_s$,

$$M_s = T_0 - K\sigma_y$$

(2.10)

where $K$ is a constant, $T_0$ is the equilibrium temperature, and the yield stress, $\sigma_y$, can be regarded to be proportional to the hardness. This equation can connect the transformation temperature and hardness through the retained dislocation density caused by work hardening. From this equation, any strengthening mechanism that can impede the transformation can lower the transformation temperature. For instance, Lin et al(112) reported that the martensite transformation temperature is found to decrease with decreasing rolling temperature and increasing thickness reduction. Kwarciak et al(113) reported that thermal cycling causes a decrease in the characteristic temperatures and heats of transformation in NiTi alloys. It was explained that the decrease is associated with an increase in the number of defects in the matrix.

Models to simulate the transformation hysteresis have also been developed based on the concepts of thermodynamic analysis. Lu et al(114) explained that differences between $M_s$ and $A_f$ and between $M_f$ and $A_s$ (the width of the hysteresis loop) are caused by a frictional stress. The differences between $M_s$ and $M_f$ and between $A_s$ and $A_f$ are characterized both by the stored elastic strain energy and the dissipated energy. Segui et al(115) came to the similar conclusion that irreversible energies play a major role for the hysteresis.

3) Effect of applied stress: The effect of applied stress on shape memory behaviour at a temperature above $M_s$ but below $M_d$ can be derived from a thermodynamic approach. The stress-temperature relationship can be expressed with a Clausius-Clapeyron type equation(116,117,118,119)

$$\frac{d\sigma}{dT}$$

where $d\sigma/dT$ is the temperature coefficient of the critical stress for the transformation, $\Delta\varepsilon$ is
the amount of strain due to the stress-induced martensite transformation, $\rho$ is the density of the alloy, and $\Delta H$ is the heat of transformation. $T_0$ is usually represented as $(M_s + A_f)/2$ although there is some dispute over this definition (for instance, some authors use $T_0 = (A_s + M_s)/2$). Equation 2.10 indicates that there is a rapid change of tensile properties in the vicinity of the temperature of the phase transformation. Upon increasing the test temperature above $M_s$ but below $M_d$, the critical stress, $\sigma$, increases until no plateau is observed because the higher the temperature, the greater the stress required to induce martensite. For the Ti-45Ni-5Cu (at.%) alloy, the temperature coefficient of the critical stress was reported to be 4.6 MPa/K.

b. The kinetics of thermoelastic martensitic transformations: For non-thermoelastic transformations such as in Fe-Ni alloys, new martensite crystals are nucleated in the remaining parent phase and then grow almost instantaneously to their final size and do not grow further as the temperature decreases. In thermoelastic transformations, once martensite crystals are nucleated, they further grow at a velocity proportional to the cooling rate. For thermoelastic martensitic transformations, it was confirmed that the martensite plates which first formed at $M_s$ are the last to undergo the reverse transformation at $A_f$. Similarly, the crystals shrink when heat is applied. It is thus easy to regard thermoelastic transformation as a non-isothermal transformation. Several empirical formulas have been suggested to quantitatively describe the course of the transformation in SMAs. Strotzki gives

$$f = 1 - \left(\frac{T - M_f}{M_s - M_f}\right)^n$$

where $f$ is the volume fraction of transformed martensite and the exponent $n$ is an empirical exponent. In Ti-Ni alloys, $n=3$ based on the results of DSC measurements.

Kwarciak et al. measured the transformation temperatures for various heating or cooling rates in a Ni-45Ti (wt.%) SMA. The activation energy, $E$, of the transformations was calculated by using a Kissinger-type equation

$$\frac{d(\ln(V/T_p^2))}{d(1/T_p)} = -\frac{E}{R}$$

where $T_p$ is the peak temperature at maximum transformation rate, $V=\text{dT/dt}$ is the heating rate, and $R$ the gas constant. The activation energy can be determined by the linear relationship of the $\ln(V/T_p^2)$ versus $1/T_p$ curve. However, the physical meaning of the thermally supplied activation energy in SMAs was not clear because the growth of martensite crystals can not be regarded as a combination of transport processes (atomic diffusion) with a chemical reaction (formation of a new phase). A thermally supplied activation energy could not account for such a process.
2.2 Texture Development

2.2.1 General introduction to texture and its analysis

a. Texture: In a polycrystalline material each grain normally has a crystallographic orientation different from that of its neighbours. If the orientations of all grains tend to cluster about some particular orientations, the material is said to have a texture\textsuperscript{(123)}. The texture produced by a deformation process, such as wire drawing or sheet rolling, is called a deformation texture. When the material with a deformation texture is recrystallized, the new grain structure may have a texture different from the deformation texture. This texture is called a recrystallization texture. In describing a macrotexture, the grains in a polycrystal are regarded as constituting a single statistical population without regard to the spatial location of any particular grain or its relation to its neighbours. By contrast, a microtextural description involves determining the orientation of each grain of a population and determining the nature and degree of its misorientation with respect to its immediate neighbours. Therefore, a microtextural description is more complete than a macrotextural description\textsuperscript{(124)}.

A texture could be a fibre texture or a sheet texture, depending on the deformation process. A fibre texture is to be expected in any material deformed by forces which have rotational symmetry about an axis, for example, in wire or rod formed by drawing, swaging or extrusion. Every grain in the wire has almost the same crystallographic orientation parallel to the wire axis. Therefore a fibre texture is described by the crystallographic orientation [uvw] in Miller’s indices. For a sheet texture, most of the grains are oriented with a certain crystallographic plane (hkl) roughly parallel to the sheet surface, and a certain direction [uvw] in that plane roughly parallel to the direction in which the sheet is rolled, as shown in Fig. 2.7. Such a texture is described by the shorthand notation (hkl)[uvw]. A texture is conventionally described in two dimensions by means of pole figures. A pole figure is a stereographic projection with a specific orientation relative to the specimen, which shows the variation of pole density with pole orientation for a selected set of crystal planes\textsuperscript{(125)}. Texture can also be presented in the form of inverse pole figures, which show the distribution of a selected direction in the specimen relative to the crystal axes.

Texture is the result of the rotation of slip systems in grains during plastic deformation. Such rotations are along particular directions. For instance, in the case of tension, the slip vector rotates gradually towards the tensile direction and the slip plane rotates towards an orientation parallel to the tensile axis. The individual grains in a polycrystal behave in an analogous way. Each grain is, however, constrained by its neighbours. To analyze this problem, Taylor\textsuperscript{(126)} introduced a criterion which states that the deformation performed by at least five independent slip systems will minimize a so-called Taylor factor

\[
M = \sum \frac{\tau_j}{\varepsilon}
\]  

(2.13)

where M is the Taylor factor, \(\tau_j\) is the shear stress in the jth slip system and \(\varepsilon\) is the macroscopic tensile or compressive strain. One can see that the Taylor factor can be
compared with the reciprocal of the Schmid factor. On this basis, Taylor was able to show how grains of different initial orientations become reoriented in different ways under stress. He was the first to show how a preferred orientation can come into existence. According to this theory, each crystallite undergoes homogeneous deformation by the operation of at least five slip systems. This assumption is called Taylor’s model or the upper-band model. Based on Taylor’s original work, many revised theories have been developed. In the so-called full constraints Taylor-type approach, the imposed strain is entirely transferred into each grain where it results in crystallographic slip or twinning. Consequently, incompatibilities between neighbouring grains are avoided. In the variants of the so-called relaxed constraints Taylor-type approach, some of the external shear components are not transferred into the grain, i.e. the relaxed constraints Taylor theory assumes that shear strains also occur microscopically.

There are many types of textures to be found depending on material and processing. An analysis of slip systems in bcc metals, for example, shows that four rolling textures are possible, \{001\}<110>, \{112\}<110>, \{111\}<112> and \{111\}<01\bar{1}>. The intensity of the texture components increases with cold deformation. For a carbon steel, the \{112\}<110> and \{111\}<112> textures were found, and the \{112\}<110> component increases with the amount of cold rolling. Annealing above the recrystallization temperature can change the type of texture. The textures found for cold rolled bcc metals after recrystallization include \{111\}<1\bar{1}0>, \{111\}<1\bar{1}2>, and \{110\}<001>. Annealing of a textured material below the recrystallization temperature does not change the type of texture.

The texture may lead to anisotropic behaviour of many physical, chemical and mechanical properties. Some important examples are elastic modulus and Poisson’s ratio, strength,
ductility, toughness, magnetic permeability and the energy of magnetisation. On the one hand, this anisotropy is an advantage for many applications. For instance, silicon steel in a transformer is required to have a strong $<100>$ texture in order to increase its magnetism. For the manufacture of tubes, rolled steel plates are required to be somewhat stronger in the transverse direction than in the rolling direction. On the other hand, anisotropy is harmful in other applications of materials and should be avoided. An example is the "earing" effect (planar anisotropy) in deep drawing. In ball bearing components, the pronounced localized textures in the surface layer result in cracking and spalling fatigue\(^{(137)}\).

\(b. \ Orientation \ distribution \ function:\) In work on an extremely anisotropic uranium material whose properties are exceptionally sensitive to texture, Strucken and Croach\(^{(138)}\) showed that it is not possible to derive accurate relationships between materials properties and information obtained from pole figures or inverse pole figures. To overcome this, they proposed determining a continuous orientation distribution function (ODF), synthesized by a least-squares procedure from a discrete set of diffracted intensities. The ODF is obtained from the combination of many pole figures by the process shown in Fig. 2.8. From experimentally measured pole figures, $P(hkl)_{\text{exp}}$, the values of the experimental F-functions, $F^{v}_{i}(hkl)_{\text{exp}}$, can be calculated. C-coefficients are then calculated by the least square method. Finally, calculated pole figures, $P(hkl)_{\text{cal}}$, ODF $f(\phi_{1},\Phi_{2})$, and calculated inverse pole figures, $R(y)_{\text{cal}}$, are obtained. The calculation results will be used in the prediction of strain in this thesis. Bunge\(^{(139)}\) has developed a computer program for calculating the ODF for the cubic lattice. The ODF calculation for the monoclinic lattice is under development.

![Fig. 2.8 Procedure for the calculation of the orientation distribution function: input of experimentally determined pole figures $P(hkl)_{\text{exp}}$, use of C-coefficient and experimental functions $F^{v}_{i}(hkl)_{\text{exp}}$ to obtain 1) calculated pole figures $P(hkl)_{\text{cal}}$, 2) calculated inverse pole figures $R(y)_{\text{cal}}$ and 3) the orientation distribution function $f(g)$.](image-url)
The ODF can be described in Euler space. The orientation \( \mathbf{g} \) in Euler space is
\[
\mathbf{g} = \{ \phi_1, \Phi, \phi_2 \} \tag{2.14}
\]

The definition of the Euler angles \( \{ \phi_1, \Phi, \phi_2 \} \) is shown in Fig. 2.9, describing the plane rotation from XYZ to X'Y'Z'. The Euler angles are obtained by setting a variable cartesian coordinate initially parallel to RD, TD and ND, and then rotating it successively to a coordinate X'Y'Z'. The relationship between the Euler angles and the conventional expression of a texture (hkl)[uvw] can be derived, as presented by Bunge as\(^{140}\)

\[
\begin{align*}
\phi &= \arccos \frac{1}{\sqrt{h^2 + k^2 + l^2}} \\
\varphi_2 &= \arccos \frac{k}{\sqrt{h^2 + k^2}} \\
\varphi_1 &= \arcsin \left( \frac{w}{\sqrt{u^2 + v^2 + w^2}} \sqrt{\frac{h^2 + k^2 + l^2}{h^2 + k^2}} \right) \tag{2.15}
\end{align*}
\]

This defines the orientation space which is in this particular case the Euler space. Each orientation is represented by a point in this space and vice-versa, each point represents an orientation. The totality of all orientations is called the texture, which may then be described by a continuous distribution function. The ODF, \( f(\mathbf{g}) \), of the crystallites is given by the volume fraction, \( dV/V \), of crystallites having the orientation \( \mathbf{g} \) and is defined as:
\[
\frac{dV}{V} = f(\mathbf{g}) \, dg \tag{2.16}
\]

![Fig. 2.9 Definition of the Euler angles \( \{ \phi_1, \Phi, \phi_2 \} \) which describe a rotation of the XYZ plane to the X'Y'Z' plane.](image)
The f(g) can be represented in the form of a series of generalized spherical functions

\[ f(g) = \sum_{\lambda=0}^{\infty} \sum_{\mu=1}^{M(\lambda)} \sum_{\nu=1}^{N(\lambda)} C_{\mu \nu}^{\lambda} T_{\lambda}^{\mu \nu}(g) \]

(2.17)

where \( T_{\lambda}^{\mu \nu} \) are invariant with respect to the crystal symmetry of rotation as well as to sample symmetry rotation. \( M(\lambda) \) is the number of independent harmonic functions of crystal symmetry and \( N(\lambda) \) is that of sample symmetry. These numbers are given as a function of the degree \( \lambda \).

The ODF gives more complete information about the nature of the texture than pole figures can. The information from an ODF can only be depicted in the form of a three-dimensional diagram. Generally, the ODF is shown in terms of a number of parallel plane sections, i.e. showing the relationship of two of the Euler angles \( \phi_1 \), \( \Phi \), or \( \phi_2 \) with the other Euler angles.

2.2.2 Textures in NiTi shape memory alloys

a. Textures: In 1968, de Lange et al.(141) measured pole figures for 6 martensite diffraction positions in 55.1Ni44.9Ti (wt.%) sheets hot-rolled at 750°C and annealed at 750°C with a thickness of 3 mm. The sheets were bent and then straightened. They found a remarkable difference between the texture on the tension side and compression side. The texture was not analyzed because the lattice parameters of martensite were unknown at that time. The present author compared published pole figures with stereographic projections of the martensite. It was found that the texture was (120)\[1\bar{1}0\] on the compression side and the crystallographic direction in most grains was rotated about 75° on the tension side, i.e. the texture on the tension side was (120)\[\bar{2}13\]on the compression side and the crystallographic direction in most grains along the rolling direction rotated 11°. Compared to the effect of the texture on the all-around SME, it was found that the (111)\[\bar{1}12\]p texture reduced the degree of preferred precipitation of Ti_{11}Ni_{14}
which resulted in a decrease of the all-around SME.

Eucken and Hirsch\(^{144,145,146}\) investigated the texture of NiTi and Cu-based SMAs. The processed NiTi alloys were hot-rolled to a thickness of 0.5 mm and recrystallized. (The hot-rolling and recrystallization temperatures were not given). The alloys were induction-melted and subsequently meltspun to produce ribbons of variable thickness between 5 and 150 µm by controlling cooling rates. An equiaxed grain structure was observed in the ribbons produced at slower cooling rates and a columnar grain structure at high cooling rates. In the latter, only one grain grows through the thickness direction. In the hot-rolled and recrystallized NiTi sheets, a less pronounced \(<110>_{p}\) texture was measured. This texture, the so-called Eucken’s texture, is not exactly the typical recrystallization texture. A very strong \(<100>_{p}\) fibre texture was observed in the meltspun NiTi (and Cu-based) ribbons having the columnar grain structure. A nearly random distribution of orientations (no texture) was observed in Cu-based alloys produced by melting at low cooling rates. The \(<100>_{p}\) texture is a typical recrystallization texture for the bcc alloys. The martensite texture of the ribbons with the \(<100>_{p}\) austenite fibre texture is very weak, which was attributed to a randomization which occurred during a stress free martensitic transformation by self-accommodation. The measurements of recoverable strain in the rolled samples and meltspun samples indicated that optimum shape memory properties can be obtained by optimization of the texture.

Mulder et al\(^{147}\) found a \((110)[1\bar{1}0]_{p}\) parent phase texture and corresponding \((111)[(1\bar{1}1)]_{m}, \,(111)[(1\bar{1}1)]_{m}\) martensite textures in a Ti-49.2Ni (at.%) alloy. The development of these textures in fatigued specimens is dependent on the direction of external stress. When the external stress is along the rolling direction, the \((111)[(1\bar{1}1)]_{m}\) component develops. When the stress is along the transverse direction, a \((1\bar{1}1)[(1\bar{1}1)]_{m}\) component develops. An \((0\bar{1}1)[011]\) texture was determined from a \((110)\) pole figure in a cold rolled Ti-50.8Ni (at.%) alloy with a thickness reduction of 20%\(^{148}\). The texture in the Ti-50.0Ni (at.%) was regarded to have the same texture as that in a Ti-50.8Ni (at.%) alloy. The determination of the texture was corrected by further measurements of inverse pole figures\(^{149}\). Strong \((111)\) orientations in the ND and \((110)\) in the RD were found, and the texture could not be expressed in the form of a particular \{hkl\}\(<uvw>\) system.

Willemse et al\(^{150}\) measured fibre texture in a Ti-44Ni-5Cu (at.%) alloy which was cold-drawn with an intermediate annealing treatment at 650°C, followed by annealing at 550°C for 3 min under a tensile stress of ~ 200 MPa. A \([111]_{p}\) parent phase fibre texture was estimated. Four martensite fibre texture components, \([\bar{1}01]_{m}, [101]_{m}, [110]_{m}\) and \([1\bar{1}0]_{m}\), were determined and the \([\bar{1}01]_{m}\) fibre texture component was more pronounced than the others. The fibre textures of both the parent phase and the martensite phase in the wire with 67.2% deformation were more pronounced than that with 20.9% deformation. The preference for the \([\bar{1}01]_{m}\) component disappeared after heating the wire above A\(_{t}\) and cooling down to room temperature. However, subsequent thermomechanical cycling restrengthened the preference for the \([101]_{m}\). The preference for the \([\bar{1}01]_{m}\) was explained by a larger d-spacing which gives the best accommodation to the tensile deformation during wire drawing and thermomechanical cycling.
Monasevich et al\cite{151} measured the texture in a Ti-50Ni (at.\%) alloy in which the ingot was forged and hot-rolled to a sheet with a thickness of 1 mm. The (112)[\overline{1}10]_p texture was determined from a \{110\}_p pole figure.

**b. Texture component selection:** During martensite transformations of SMAs free of stresses, the martensite variants form in groups of more than two variants. The variants which are selected are those which minimize the strain components of the average shape strain matrix, and form crystallographically junction planes between variants. This effect is called self-accommodation. For Ti-Ni alloys, a triangular morphology consisting of three martensite variants is formed. Textures of both the parent phase and product phase can be analyzed from pole figures. The crystallographic correspondence between parent phase and product phase can be calculated. For example, the correspondence of the (110)[\overline{1}10]_p texture and (111)[110]_p based on the notation of Miyazaki shown in Table 2-3 is listed in Table 2-5. Some of the variants would have the same contribution to the pole figures according to the symmetry of the monoclinic lattice and the symmetry of the sheet sample, for example, the variant 5 and 5' from the (110)[\overline{1}10]_p texture. These variants belong to the same texture component.

Under stress, some variants are preferred and grow at the expense of the others during the transformation. The following theories have been developed to interpret the effect of stress on variant development or texture component selection:

(1) In single crystal SMAs, it has been experimentally shown that the variants with maximum transformation strain will be developed upon the application of stress\cite{23,24}. The results are in good agreement with calculated results using the phenomenological theory of martensite transformations\cite{25}. This criterion was applied to polycrystalline SMAs. According to Mulder et al\cite{147}, the martensite variant selection during thermal fatigue of a 50.8Ti-49.2Ni (at.\%) alloy has also been shown to be governed by the maximization of the transformation strain.

(2) Miyaji and Furubayashi\cite{152,153,154,155} studied the inherited texture in Fe-Ni alloys which show a martensitic transformation from fcc to body-centred tetragonal (bct). This theory is based on the assumption that preferential variant selection reflects the presence of the stress. In light of the Bain strain model for the transformation, the work done by the applied stress, $\sigma_a$ (both internal stress or external stress) in the loading direction during

<table>
<thead>
<tr>
<th>Variant</th>
<th>(110)[\overline{1}10]_p</th>
<th>(111)[110]_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(11\bar{1})[2\bar{1}1]</td>
<td>(\bar{1}\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>1'</td>
<td>(\bar{1}\bar{1}\bar{1})[\bar{2}\bar{1}1]</td>
<td>(\bar{1}\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>2</td>
<td>(1\bar{1}\bar{1})[2\bar{1}1]</td>
<td>(1\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>2'</td>
<td>(\bar{1}\bar{1}\bar{1})[\bar{2}\bar{1}1]</td>
<td>(\bar{1}\bar{2}0)[\bar{2}\bar{1}1]</td>
</tr>
<tr>
<td>3</td>
<td>(1\bar{1}1)[2\bar{1}1]</td>
<td>(1\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>3'</td>
<td>(\bar{1}\bar{1}1)[2\bar{1}1]</td>
<td>(\bar{1}\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>4</td>
<td>(1\bar{1}1)[2\bar{1}1]</td>
<td>(1\bar{2}0)[2\bar{1}1]</td>
</tr>
<tr>
<td>4'</td>
<td>(\bar{1}\bar{1}1)[\bar{2}\bar{1}1]</td>
<td>(\bar{1}\bar{2}0)[\bar{2}\bar{1}1]</td>
</tr>
<tr>
<td>5</td>
<td>(\bar{2}00)[00\bar{2}]</td>
<td>(1\bar{2}0)[00\bar{2}]</td>
</tr>
<tr>
<td>5'</td>
<td>(\bar{2}00)[00\bar{2}]</td>
<td>(\bar{1}\bar{2}0)[00\bar{2}]</td>
</tr>
<tr>
<td>6</td>
<td>(00\bar{2})[\bar{2}\bar{2}0]</td>
<td>(1\bar{2}0)[\bar{2}\bar{2}0]</td>
</tr>
<tr>
<td>6'</td>
<td>(00\bar{2})[\bar{2}\bar{2}0]</td>
<td>(1\bar{2}0)[\bar{2}\bar{2}0]</td>
</tr>
</tbody>
</table>
If the sample is heated through the reversion temperature range, $A_s$ to $A'_f$, while constraining the sample (for instance, at $\varepsilon_x$ in Fig. 2.10), an internal reversion stress, $\sigma_R$, will develop. The reversion stress increases in sigmoidal fashion as the temperature increases over the transformation range\(^\text{[157]}\). It should be noted that the $A'_f$ temperature is the austenite finish temperature under stress, i.e. $A'_f > A_f$. Reversion strain is a direct function of the initial induced strain, $\varepsilon_x$, which can be increased by increasing the induced strain to a limit near $\varepsilon_L$. If an initial strain greater than $\varepsilon_x$ is introduced, the potential to develop reversion stress decreases. If a part of the initial strain is allowed to reverse freely prior to the constraint of the remaining strain, the sample has a correspondingly lower value of $\sigma_R$. The influence of the amount of deformation and subsequent heat treatment of the sample on the reversion strain has been widely investigated. In general, high thickness reduction and low heat treatment temperature reduce the reversion strain\(^\text{[158,159,160,161]}\).

The elastic moduli $E_1$ and $E_2$ for two linear elastic stages can be determined. In the second linear stage, it has been observed that some dislocations are already active\(^\text{[162]}\). Beyond the strain limit $\varepsilon_L$, true plastic deformation will occur and $\varepsilon_R$ and $\sigma_R$ will decrease. For NiTi alloys, the yield stress for slip can be raised by introducing dislocations\(^\text{[163]}\) or fine precipitates\(^\text{[164,165]}\) (only in the case of Ni-rich alloys).

NiTi alloys are ductile in the polycrystalline state based on fracture strains, $\varepsilon_f$, on the order of 20 to 30%. Miyazaki et al\(^\text{[166]}\) found that annealing can be effective for increasing the ductility of cold worked samples, and that the martensite phase is more ductile than the parent phase.
2.3.2 Thermal cyclic testing under constant load

The behaviour of SMAs is associated with three variables, temperature, strain and stress, and can be described by the thermomechanical constitutive equation\(^{(167)}\):

\[
\dot{\sigma} = D\dot{\varepsilon} + \Theta \dot{T} + \Omega \dot{f}
\]

where \(\sigma, \varepsilon, T\) and \(f\) represent the stress, strain, temperature and volume fraction, respectively. The superimposed dot denotes the time derivative. The coefficients \(D, \Theta\) and \(\Omega\) represent the elastic constant, thermoelastic constant and the transformation expansion constant, respectively. These coefficients are generally functions of the state variables \((\varepsilon, \sigma, T, f)\). For simplicity they can be assumed to be time-independent constants.

Thermal cyclic testing gives the strain-temperature relationship under constant stress, i.e. \(d\sigma/dT = 0\). Fig. 2.11 schematically illustrates the strain-temperature curve under constant load, in which the loop ABCD is the curve in the \(n\)th cycle and the loop EFGH in the \((n+1)\)th cycle. When the transformations occur, the strain increases or decreases considerably, see line segments BC, DA, FG and HE. The transformation strains, the permanent strain and the hysteresis can be obtained by thermal cyclic testing.

It was shown that the axial transformation strain increases with increasing applied tensile stress during the thermal cyclic testing in a NiTi alloy\(^{(168)}\). Similar results were also present in Ti-Ni-Cu alloys\(^{(26)}\). Internal friction measurements and neutron diffraction measurements indicated that this behaviour was due to preferential selection of the variants.

\[\text{Fig. 2.11 Schematic illustration of strain-temperature curve during thermal cyclic testing under a constant load. Loop ABCD stands for the curve in nth cycle and the loop EFGH in (n+1)th cycle.}\]
which give a large axial extension\(^{(169)}\).

Strnadel et al\(^{(170)}\) found that the hysteresis decreases as the number of cycles grows during thermal cyclic testing. The reason for this depends on the type of cycling. In hard cycling (under a high constant stress), the increasing residual strain leads to the lessening of the transformation strain. In soft cycling (under a low stress), the reason is the rising resistance of the dislocation structure to any displacement of the interphase boundary.

Nam et al\(^{(26)}\) measured permanent strain and transformation hysteresis during thermal cyclic testing under constant load in Ti\(_{50-}\)Ni\(_{50-x}\)-Cu\(_x\) (at.\%) alloys (x=5 to 20). The permanent strain ranged from 0.1\% to 1.2\% and decreased with increasing Cu content. The transformation hysteresis associated with the B\(_2\) \(\rightarrow\) B\(_{19}'\) transformation in 5 at.\%Cu alloy is 17°C, and that associated with the B\(_2\) \(\rightarrow\) B\(_{19}\) transformation decreases from 12°C to 4°C with increasing Cu contents from 7.5 to 20 at.\%. The presence of permanent strain produced by thermal cyclic testing was due to irreversible microstructural change during transformation. It was suggested that the permanent strain is related to the transformation hysteresis. The increase of the irreversible microstructural changes may hinder the motion of the interface between the parent and martensite phases, and thus result in the increase of the transformation hysteresis.

### 2.4 Anisotropic Behaviour

#### 2.4.1 Origin of anisotropic behaviour

Material properties may be anisotropic, i.e. they may depend on the direction in which they are measured. The directional dependence of the structure and properties of natural materials, for instance, wood or bone, has been known for many thousands of years. The anisotropic behaviour originates from arrangements of the atoms which build up the materials. The simplest structures are single crystals, which can show anisotropy of physical properties on an atomic level. These are completely described by giving the position of the atoms in the unit cell.

The anisotropic behaviour of polycrystalline materials may depend on the size, shape, crystallographic orientation, and arrangement of the crystallites. Normally, anisotropy has been investigated by measuring the angular dependence of the properties. However, in some cases, it may be convenient to consider a simple anisotropy parameter rather than the total directional dependence of a physical property\(^{(171)}\). The anisotropy parameter, A, may be defined by the ratio of the maximum and minimum values of the physical property, S, as

\[
A = \frac{S_{\text{max}}}{S_{\text{min}}} \tag{2.21}
\]

By this definition, A = 1 for a fully isotropic material, and increasing values of A indicate more anisotropy.
2.4.2 Calculation of the anisotropy of the transformation strain in single crystal SMAs

The knowledge of the directional dependence of the transformation strain of each variant in single crystals is essential for calculating the amount of the strain in polycrystalline SMAs. The anisotropy of the transformation strain in single crystals can be calculated either from the lattice deformation matrix (25) or the invariant plane strain matrix (172) (eqn 2.2). The calculation using the lattice deformation matrix gives the directional dependence of the strain due to changes in the lattice parameters during the transformation. The invariant strain matrix gives the strain of each habit plane variant, which is closely related to the transformation crystallography.

If the lattice correspondence relationship and lattice parameters of the parent phase and the martensite phase are known, the transformation strain in any direction \([uvw]\) can be calculated based on the deformation matrix. The process will be discussed using the NiTi SMA as an example. The lattice correspondence used follows the notation of Miyazaki (23) in Table 2-3 and the lattice parameters are taken from Otsuka et al in Table 2-2.

The lattice deformation matrix, \(M\), is derived from the analysis of the change of the lattice structure of both phases (25, 171). The matrix, \(M\), consists of an orthonormal Bain strain required for producing the lattice parameters of martensite and a simple shear \(t = -\tan(\beta - 90^\circ)\) ensuring the required monoclinic distortion, see Figs. 2.2 and 2.3. It can be expressed as follows:

\[
M = \frac{1}{\sqrt{2a_o}} \begin{bmatrix} \sqrt{2a} & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix} \begin{bmatrix} 0.958209 & 0 & -0.128349 \\ 0 & 0.966262 & 0 \\ 0 & 0 & 1.076371 \end{bmatrix}
\]  

(2.22)

The deformation matrix \(M\) is based on a linear operation of the martensitic transformation. It is worth noting that the matrix is also related to the type of the notation of lattice correspondence. In Miyazaki et al’s (23) notation, the principal strain \(a/a_o = 2.889/3.015\) is in the \([100]_m\) direction. Saburi et al (25) defined this principal strain in the \([010]_m\) direction and Cizek (171) in the \([001]_m\) direction. Different notations would lead to different expressions of the deformation matrix. However, the same amount of strain would be obtained, except that the correspondence of the variants would be different.

The transformation operation of a vector \(x\) in base B19 to a vector \(y\) in base B19’ of the monoclinic lattice can be described by a linear operation \(y = Mx\). The lengths \(l_x\) and \(l_y\) of the vectors of \(x\) and \(y\) and the transformation strain \(\varepsilon\) are thus calculated as

\[
l_x = \sqrt{x'x} - 1 \quad l_y = \sqrt{y'y} - \sqrt{x'M'Mx} \\
\varepsilon = (\sqrt{x'M'Mx} - 1) \times 100\%
\]  

(2.23)

where the prime indicates the transposition of a matrix or a vector. In order to describe the characteristics of the transformation, the eigen-operation is analyzed, i.e. converting the
normal quadratic forms of the matrix $M'M$ to the diagonal form after applying the orthogonal transformation. Thus the eigenvalues, $\lambda_i$, and eigenvectors, $v_i$, of the matrix, $M'M$, are obtained. The eigenvectors are the three main axes in the reciprocal strain ellipsoid, and the reciprocal values of the square root of the eigenvalues are the length of these main axes. For the case of NiTi alloys, they are as follows:

$$
\begin{align*}
\varepsilon_1 &= -6.79\%, \quad \lambda_1 = 0.87, \quad v_1 = [0.927972, 0, 0.372650]_{B19} \\
\varepsilon_2 &= -3.37\%, \quad \lambda_2 = 0.93, \quad v_2 = [0, 1, 0]_{B19} \\
\varepsilon_3 &= 10.65\%, \quad \lambda_3 = 1.22, \quad v_3 = [0.372650, 0, -0.927972]_{B19}
\end{align*}
$$

Therefore, the maximum possible transformation strain during elongation or contraction is the strain along one of the main axes, i.e. $\varepsilon_{\text{max}}$ (elongation) = $\varepsilon_3 = 10.65\%$ and $\varepsilon_{\text{max}}$ (contraction) = $\varepsilon_1 = 6.79\%$. Fig. 2.12 shows the calculated transformation strain of a correspondence variant 5 in the (110)$_p$ stereographic projection.

The eigenvectors can be transformed into the cubic B2 base by applying the lattice correspondence in Table 2-3. The projection (defined by three directional cosines $\cos\alpha$, $\cos\beta$, $\cos\gamma$) of an arbitrary vector, $x_{B2}$, onto these eigenvectors can be mathematically found. The transformation strain, $\varepsilon$, would then be:

$$
\varepsilon = \sqrt{\cos^2\alpha \lambda_1 + \cos^2\beta \lambda_2 + \cos^2\gamma \lambda_3 - 1} \times 100\% 
$$

(2.24)

The method described above, i.e. first to find the eigenvectors in the orthonormal B19 base and then to transform it into the B2 base, is simpler compared to the direct calculation of the

Fig. 2.12 The calculated transformation strain for correspondence variant 1 in the (110)$_p$ stereographic projection. The lattice parameters used for the calculation are $a_o = 0.3015$ nm, $a = 0.2889$ nm, $b = 0.4120$ nm, $c = 0.4622$ nm and $\beta = 96.8^\circ$. 
Chapter 2 Literature

The eigenvectors in the B2 base in the present author’s opinion. It simplifies the development of calculation programs, while producing the same results.

The calculation of the transformation strain based on the deformation matrix can be further checked in several ways. The easiest way is to simply use the definition of the strain, i.e. to calculate the strain from the change of the distance of the crystal directions along [uvw]_{B2} and [u’v’w’]_{B19} (see Appendix I),

\[ \varepsilon = \left( \frac{I_{B19}}{I_{B2}} - 1 \right) \times 100\% \]  \hspace{1cm} (2.25)

The calculation of the transformation strain based on habit plane variants follows the same procedure mentioned above, except that the lattice deformation matrix is replaced by the invariant plane strain matrix, \( P_1 \). The transformation strain based on either the correspondence variants or the habit plane variants describe the strain in different ways. The calculated maximum transformation strains of the habit plane variant are smaller than the ones from the correspondence variant because a habit plane variant consists of two correspondence variants.

| Table 2-7. Orientation dependence of the calculated maximum transformation strains in various shape memory alloys. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Alloy           | Elongation (%)  | Contraction (%) |
|                | <001> | <011> | <\bar{1}11> | <001> | <011> | <\bar{1}11> |
| NiAl            | 13.0  | 3.9   | 0.7          | 6.1   | 6.1   | -0.7         |
| CuAlNi          | 4.3   | 6.2   | 1.6          | 8.2   | 8.2   | 1.1          |
| AgCd            | 2.9   | 4.3   | 0.8          | 6.6   | 6.6   | 1.1          |
| CuZnGa          | 8.9   | 6.2   | 1.4          | 9.0   | 9.0   | 1.0          |
| NiTi            | 2.7   | 8.4   | 9.8          | 4.2   | 4.2   | 3.6          |

The anisotropy of the transformation strains are quite different in various single crystal SMAs. Table 2-7 lists the calculated maximum transformation strains for three important directions in a variety of alloys. For a Ti-Ni single crystal, it has been calculated that the minimum value of the maximum transformation strain is around <001>_{\rho} and the maximum around <\bar{1}11>_{\rho}, which was also shown experimentally. The strain in <111>_{\rho} is around 4 times higher than the one in <001>_{\rho}. For NiAl alloys, the difference between the maximum and the minimum is a factor of 18.6. NiAl alloys are therefore much more anisotropic than NiTi alloys.

Measurements of elastic anisotropy in an equiatomic Ti-55Ni (wt.%) single crystal were made in 1980. The elastic anisotropy \( A = C_{44}/C' \) varies around 2, in which \( C' = (C_{11} - C_{12})/2 \) is the transverse elastic constant. Compared with other \( \beta \) alloys (\( A = 10 \) to 30), \( A \) is very low. The temperature dependence of the elastic anisotropy of single crystal Ni_{50.5}Ti_{49.5} (at.%) alloy exhibits a step-like behaviour during transformation by ultrasonic velocity measurements.
2.4.3 Calculation of anisotropy in polycrystalline materials

a. Use of ODF analysis: The anisotropic behaviour of a material can be calculated based on texture studies and with the help of the results of single crystal SMAs. The anisotropy of experimentally determined transformation strains in polycrystalline materials can be explained by comparison with the anisotropy of the calculated strain in the (hkl)[uvw] orientation in single crystals, in which (hkl)[uvw] is the texture measured in polycrystalline materials. This method is still being used to explain the anisotropy of the transformation strain in polycrystalline SMAs. The experimentally determined strain was found to be consistent but smaller than the calculated strain\textsuperscript{147,148}.

However, the quantitative analysis of texture by the orientation distribution function (ODF) makes it possible to directly predict the relationship between texture and anisotropy of properties. A general expression for the orientation dependent macroscopic property $\bar{E}(g')$ in the orientation $g'$ is\textsuperscript{177}

$$\bar{E}(g') = \int E(g)f(g)dg$$

(2.26)

where $E(g)$ is the orientation dependent property of a crystallite. This equation has been successfully used to predict plastic, elastic and magnetic anisotropy. For example, the magnetic torque curves measured in an Fe-Si transformer steel were consistent with the curves calculated from the ODF\textsuperscript{178}.

By obtaining inverse pole figures, $R(y)_{\text{cal}}$ from ODF calculations, and assuming that the information from the inverse pole figures is conveniently related to physical properties, it has been suggested that the transformation strain in polycrystalline shape memory alloys is a linear summation of the related intensities times the strain in a single crystal in three typical directions [100], [110] and [111]. The following equation can be used as a first approximation for eqn. 2.26\textsuperscript{179}:

$$\bar{\varepsilon}_y = \frac{R_y(100) \cdot \varepsilon(100) + R_y(110) \cdot \varepsilon(110) + R_y(111) \cdot \varepsilon(111)}{R_y(100) + R_y(110) + R_y(111)}$$

(2.27)

where $\bar{\varepsilon}_y$ is the mean strain of the polycrystalline material in the $y$ direction
\varepsilon(uvw) is the calculated strain in a single crystal in the direction $<uvw>$
$R_y(uvw)$ is the intensity of the inverse pole figure in the direction $<uvw>$

This equation has been successfully used for the prediction of pseudoelastic elongation in Cu-Zn-Al SMAs\textsuperscript{180}. The anisotropy of pseudoelasticity is closely related to $f(g)$ of the (001)[100]$_p$ texture component in a Cu-Zn-Al SMA sheet. The stronger the (001)[100]$_p$ texture, the higher the amount of the pseudoelasticity.

b. Use of Taylor model: An essential difference between the deformation of polycrystalline materials and that of single crystals is that the polycrystal grains are subject to mutual constraint in strain. To evaluate the effect of the intergranular constraint in the plastic
deformation of polycrystalline materials, various models\(^\text{(181,182,183,183,184)}\) have been proposed following the classical Taylor model in which the strain in individual grains is taken to be homogeneous. Among these models, Ono et al\(^\text{(184,185)}\) proposed a model particularly suitable for the properties of polycrystalline shape memory alloys. In this model, the effect of the mutual strain constraint was regarded to be similar to the one which deformation is governed by slip systems, and the habit plane normal and shape strain direction are used instead of the slip systems. From this model, the modified Taylor factor, \(M'\), can be calculated and the maximum reversible strain of a grain was suggested to be:

\[
e' = \frac{m_1}{M'}
\]

where \(m_1\) is the magnitude of shape strain, see eqn. 2.2, which can be completely determined by the crystallography of the alloy.

Bhattacharya et al\(^\text{(186,187)}\) analyzed the deformation of polycrystalline SMAs. They showed that the set of recoverable strains depends not only on the texture and the transformation strain of the underlying martensitic transformation, but also critically on the change of symmetry during the underlying transformation. To obtain the homogeneous strain according to Taylor model, each grain may simply adjust its own microstructure by accommodation. This theory can be used to qualitative analyze the anisotropic behaviour in polycrystalline SMAs.

### 2.4.4 Anisotropic behaviour in polycrystalline shape memory alloys

For polycrystalline TiNi shape memory alloys, the anisotropic nature of mechanical properties such as transformation strain, fatigue, torsion and all-round SME has been reported. In a 50.8Ti-49.2Ni (at.\%) sheet with a (110)[1¯10]p texture\(^\text{(147)}\), the transformation strain under a constant load of 250 MPa and unloading strain showed a maximum at the angle 20° to the RD and a minimum in the TD. A similar angular dependence of the transformation strain under different constant loads was also demonstrated. The dependence was found to have the same tendency with the calculated transformation strain in single crystals. The permanent strain in the TD is smaller than the one in other directions.

All-round SME can be evaluated by measuring the change of the radii of curvature of strip material. In rolled plate of Ti-51.5at\%Ni alloy with a (111)[112]p texture, all-round SME in the specimen cut along the TD is almost 2 times higher than the one along RD, see Fig. 1 in the paper\(^\text{(143)}\). In a Ti-50at.\%Ni sheet with (112)[110]p texture, the maximum cumulative deformation (transformation strain) during torsion under a constant stress test was observed near the rolling direction (0° to 45° to RD)\(^\text{(151)}\). This result is consistent with the prediction that [110]p is one of the favourable orientations for recoverable elongation (8.4\%)\(^\text{(188)}\). The measurements of tensile stress-strain curves along the RD and the TD indicated that the alloy is isotropic in the as-cast condition and that anisotropy develops as rolling proceeds\(^\text{(189)}\).

The anisotropy of thermal fatigue properties was studied in a 50.8Ti-49.2Ni (at.\%) alloy\(^\text{(147)}\).
Favourable thermal fatigue behaviour was shown near the TD of the cold rolled sheet, with relatively low creep and small memory loss. However, the development of two-way memory was also slower in the TD than in the RD.

Recently, anisotropy of the shape memory behaviour of hot-rolled Ti-50.0Ni (at.%) thin plates with a thickness of 100 µm was reported by Kitamura et al.\textsuperscript{(148)} The shape memory behaviour was associated with the two-stage R-phase and martensitic transformations when the applied stress was below 50 MPa, while it was associated only with the martensitic transformation under a stress above 100 MPa. The transformation strain measured upon heating showed a directional dependence with a maximum of 5.2% at the angle 15° to the RD, while a minimum of 4.1% was measured in the TD. To present author’s understanding, the behaviour of this material is close to isotropic because the anisotropy parameter A is 1.27.

2.5 Objectives

From the literature survey it can be seen that the problem of anisotropic behaviour in NiTi shape memory single crystals has been solved experimentally and theoretically. For polycrystalline NiTi alloys, a description of the influence of the texture on the anisotropic behaviour in the SMAs presents several problems:

1) The effect of processing on texture development has not been systematically investigated. In Ni-Ti based alloys, sheet textures such as \{110\}<110>\textsubscript{p}, \{111\}<\overline{1}12>\textsubscript{p}, and \{112\}<110>\textsubscript{p}, and fibre textures such as <111>\textsubscript{p} and <100>\textsubscript{p} were reported separately by different authors. However, the influence of the processing conditions on texture was not discussed by these authors.

2) The measured mechanical properties in textured NiTi alloys was explained qualitatively using the single crystal data. The tendency of the variation of the mechanical properties on the direction was consistent with these data. However, considerable differences between the measured data and single crystal data exist. In some cases, the effect of texture on the mechanical properties was neglected in the investigation, for instance in Nam \textit{et al}’s paper\textsuperscript{(26)}.

3) For the practical application of the SMAs, substantial information is required about the effect of the texture on shape memory behaviour in order to improve shape memory properties through processing or to avoid the problems produced by texture.

To obtain a better understanding of the behaviour of SMAs, texture development and anisotropic behaviour in a Ti-Ni-Cu shape memory alloy was systematically investigated in this work. An overview of the technical programme is shown in Fig. 2.13. The following objectives are discussed in this thesis:

1. Characterization of martensitic structure, transformation and shape memory effect. The investigation was concentrated on a commercially available Ti-45Ni-5Cu (at.%) shape memory alloy. The basic material properties, e.g. transformation temperatures, heats of transformation, and transformation hysteresis which are essential for the analysis of the
martensite and austenite textures and mechanical properties produced during the transformation were determined.

2. **Rolling of the sheet:** An understanding of the texture development as a result of plastic deformation is important for the explanation of mechanical properties. The texture was varied by changing the rolling parameters, e.g. thickness reduction, rolling temperature, intermediate annealing temperature and post-rolling heat treatment temperature.

3. **Determination of texture during processing of this material; development, description and explanation of this texture.** The texture was measured in both the austenite state and martensite state, and then qualitatively analyzed by stereographic projections and quantitatively analyzed by the ODF.

4. **Determination of the relationship between the texture and anisotropic nature of mechanical properties.** The anisotropic nature of mechanical properties was first measured. The results were then compared with predicted results based on texture analysis, including quantitative analysis of texture by the orientation distribution function (ODF).

The investigations in this thesis aim at answering two questions: how to develop a particular texture in the TiNiCu alloy and how to use this texture. If a proper texture can be developed, the memory capacity in a certain direction can be improved. Knowledge about the relationship between texture and properties is also helpful for controlling mechanical properties by deformation processing and heat-treatment. The potential of this shape memory alloy for practical applications can thus be significantly improved.
Texture Development and Anisotropic Behaviour of Intermetallic Compounds

Fig. 2.13 Overview of the technical program for this thesis.
Chapter 3

Experimental Procedures

3.1 Materials and Rolling Process

3.1.1 As-received materials

A commercially available shape memory alloy was obtained from Krupp GST mbH in Germany and AMT n.v. (Advanced Materials and Technologies) in Belgium. The chemical composition of the material as given by the manufacturers was Ni 44.2, Ti 50.2, Cu 4.9, Fe 0.07, C 0.27 and O 0.30 (at.%). In this work, the material is denoted as Ti-45Ni-5Cu (at.%).

All as-received material was in the form of sheet with almost the same width of 48 mm but with various thicknesses. Table 3-1 shows the processing history of the as-received material according to the information provided by the suppliers. Material was obtained from Krupp in two conditions: one of them, abbreviated KR, was a hot-rolled sheet with a thickness of 3.6 mm; another, abbreviated KR50, was cold-rolled sheet from KR sheet with a thickness of 0.9 mm. Only one type of sheet from AMT was used which had a thickness of 3.6 mm. The difference between the materials supplied by these two manufacturers was very small except that there was more of the precipitate Ti$_2$Ni in the material from AMT than from Krupp.

<table>
<thead>
<tr>
<th>Code</th>
<th>Thickness</th>
<th>Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>KR</td>
<td>3.6 mm</td>
<td>hot-rolling at 900°C in 6 passes from a thickness of 10 mm to 3.6 mm</td>
</tr>
<tr>
<td>KR50</td>
<td>0.9 mm</td>
<td>KR + cold-rolling in 8 steps from a thickness of 3.6 mm to 0.9 mm with intermediate anneal at 600°C for 10 min. between each step</td>
</tr>
<tr>
<td>AMT</td>
<td>4.3 mm</td>
<td>hot-rolling at 900°C in 8 passes from a thickness of 17 mm to 4.3 mm</td>
</tr>
</tbody>
</table>

3.1.2 Rolling of as-received sheets

a. Terminology: For the description of the rolling of the as-received sheet, the following terminology is used:

(1) Step and pass: one "pass" here means one rolling operation. In the case of intermediate annealing, the concept of a "step" means the period between two intermediate anneals, thus
one step consists of several passes (see for example, Fig. 3.2). For instance, the KR50 sheets in Table 3-1 were rolled in 8 steps. The intermediate annealing was conducted after 3 or 4 passes. These 3 or 4 passes constitute a single step.

(2) The thickness reduction $t_r(\%)$ during rolling can be described as:

$$t_r (\%) = \frac{t_o - t_n}{t_o} \cdot 100 \quad (3.1)$$

where $t_o$ is the thickness before rolling and $t_n$ is the final thickness after rolling, regardless of the number of rolling steps during the rolling process.

**b. Rolling procedures:** The as-received sheets were rolled in order to investigate the effect of a number of rolling parameters on texture development. The rolling conditions are summarized in Table 3-2. The following parameters were investigated:


Table 3-2  A summary of rolling parameters, where $T_r$ stands for the rolling temperature, $T_i$ for the intermediate annealing temperature, $t_o$ for the initial thickness before rolling, $t_n$ for the final thickness after rolling and $t_r$ is the thickness reduction.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Pre-rolling anneal</th>
<th>$t_o$ (mm)</th>
<th>$t_n$ (mm)</th>
<th>$T_r$ (°C)</th>
<th>$T_i$ (°C)</th>
<th>$t_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KR51</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.8</td>
<td>RT</td>
<td>-</td>
<td>11%</td>
</tr>
<tr>
<td>KR52*</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.67</td>
<td>RT</td>
<td>-</td>
<td>26%</td>
</tr>
<tr>
<td>KR52L*</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.67</td>
<td>RT</td>
<td>-</td>
<td>26%</td>
</tr>
<tr>
<td>KR5A</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.65</td>
<td>0°C</td>
<td>-</td>
<td>28%</td>
</tr>
<tr>
<td>KR5B</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.65</td>
<td>45°C</td>
<td>-</td>
<td>28%</td>
</tr>
<tr>
<td>KR5C</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.57</td>
<td>100°C</td>
<td>-</td>
<td>37%</td>
</tr>
<tr>
<td>KR5D</td>
<td>650°C/60 min</td>
<td>0.9</td>
<td>0.44</td>
<td>200°C</td>
<td>-</td>
<td>51%</td>
</tr>
<tr>
<td>KRE</td>
<td>650°C/60 min</td>
<td>3.6</td>
<td>0.83</td>
<td>200°C</td>
<td>-</td>
<td>77%</td>
</tr>
<tr>
<td>3AMT**</td>
<td>800°C/60 min</td>
<td>4.3</td>
<td>1.1</td>
<td>300°C</td>
<td>-</td>
<td>74%</td>
</tr>
<tr>
<td>5AMT</td>
<td>800°C/60 min</td>
<td>4.3</td>
<td>0.8</td>
<td>RT</td>
<td>500°C</td>
<td>19%***</td>
</tr>
<tr>
<td>6AMT</td>
<td>800°C/60 min</td>
<td>4.3</td>
<td>0.9</td>
<td>RT</td>
<td>650°C</td>
<td>32%***</td>
</tr>
</tbody>
</table>

* The rolling of the KR52 and KR52L samples was conducted in 6 and 12 passes, respectively.
** Rolled at AMT n.v.
*** Only for last step.
Chapter 3 Experimental procedures

Fig. 3.1 A schematic diagram of the temperature variation in the KR5D sheets warm-rolled at 200°C.

Fig. 3.2 A schematic diagram of the temperature variation in the cold rolled 5AMT sheets with intermediate annealing at 500°C for 10 min. (A = Annealing, and R = Rolling).
Chapter 3 Experimental procedures

KRE and 3AMT): Fig. 3.1 shows an example of the warm rolling process. After the initial anneal, the sheet was put into a furnace with a temperature of 200°C and then rolled immediately. At the end of each warm rolling pass, the temperature of the sheet was observed to have dropped several degrees, which is consistent with the temperature drop during warm or hot rolling observed by other authors\(^{(189)}\).

(2) The effect of intermediate annealing: The intermediate annealing temperature was selected to be below or above the recrystallization temperature, i.e. 500°C (5AMT) or 650°C (6AMT). Fig. 3.2 shows an example of cold rolling with intermediate annealing at 500°C. Intermediate annealing was conducted, in principle, in order to avoid cracking due to hardening during rolling.

(3) The effect of thickness reduction: Various thickness reductions were obtained after rolling. In addition, an investigation was also undertaken concerning the thickness reduction per pass. The KR52 and KR52L sheets were rolled to the same final thickness in 6 or 12 passes. The thickness reduction per pass for the KR52L sheets is thus 2 times that for one for the KR52 sheets.

All sheets except the 3AMT sheets were rolled in a Bühler EW200×160A1 rolling mill where the diameter of the rollers is 160 mm. Before rolling, the following two procedures were performed:

(1) The surface of the sheet was checked for oxidation. If the oxide layer was too thick, the surface was mechanically ground.

(2) The sheets were annealed in a box-type furnace at 650°C or in a vacuum furnace at 800°C for 60 min in order to obtain a recrystallized material. During annealing, the sheet was tightly fixed between two steel plates in order to straighten bent as-received sheets or maintain the flatness of the as-received sheets. After annealing, the sheets were furnace cooled.

Fig. 3.3 shows a schematic diagram of the rolling process. During the rolling process, the following operations were undertaken:

(1) The surfaces of the sheet and the rollers were coated with a lubricant composed of 50% (vol.%) Shell Boiling Point gasoline and 50% (vol.%) commercial OKS 320 lubricant as a measure to avoid cracking by reducing the frictional force between the rollers and the sheet. The dilution of commercial OKS 320 lubricant with the gasoline was shown experimentally to be effective in decreasing the possibility of cracking in Ti-Ni-Cu sheet.

(2) The rotational speed of the rollers was set at 50 rpm.

(3) The sheets were inserted in the roller using two guide plates to keep the sheet straight and perpendicular to the roller axis.
For each subsequent pass, the sheet was fed in alternating one end with the other in order to obtain a symmetric texture.

(5) For warm rolling ($T_r \geq RT$), two electric blowers were used to heat the surface of the rollers during rolling. A Raytek infrared non-contact temperature measurement system was used to observe the change in temperature of the sheet during rolling.

(6) The Vicker’s hardness was measured after every rolling pass or intermediate annealing with a load of 3 kg or 5 kg, using a Wolpert hardness tester. The average hardness was obtained from at least five test readings at different positions on the sheet.

(7) Intermediate annealing was conducted whenever the Vicker’s hardness reached about 340 to 400 kgf/mm² in order to avoid cracking by further rolling.

Three pieces of as-received AMT sheet were rolled at AMT n.v. in a Schmitz rolling mill with a roller diameter of 198 mm and a motor power of 60 KW to investigate the influence of rolling speed and rolling temperature on the deformation during rolling processing. The rotation speed of the rollers was 1500 - 1900 rpm, which is significantly higher than the speed of the Bühler. A Ratak WO 221 lubricant was used. The sheets were rolled from 4.2 mm to 1.1 mm at 300°C by heating the sheets in a box-type furnace after each pass.

After the rolling experiments, the sheets were cut into various shapes (described later) as required for further investigation. Subsequently, the samples were heat-treated, in which the temperature of heat treatment varied from 100°C to 700°C and the holding times varied from 15 min to 1 hour. Air cooling was usually used after the heat treatment. For heat treatments above 400°C, the samples were packaged in a thin stainless steel bag filled with argon to minimise oxidation.
3.2 Texture Measurement and Analysis

3.2.1 Texture measurements

Texture measurements were carried out using a texture goniometer in a Phillips X’pert system, operating at 40KV/30mA, using CoKα radiation. Prior to the texture measurements, the Bragg diffraction angles, θ, were determined by θ-2θ scans. Because of the effect of texture, the samples were tilted and rotated until significant clear diffraction peaks were found. The reflection mode was applied, in which the rotation angle (φ) has a pitch of 5° and the tilt angle (ψ) is up to 85° with a pitch of 5°. The definitions of rotation angle Phi (φ) and tilt angle Psi (ψ) in pole figure are shown schematically in Fig. 3.4. The counting time was taken to be 1 s/5°(φ). Corrections for background intensity were performed separately for each sample by off-Bragg angle measurements at 2θ values of 40° and 60°. Defocussing effects were corrected for by the Gale & Griffiths calibration function(190).

A heating device was developed in order to measure pole figures at temperatures above A_c. Fig. 3.5 shows a schematic illustration of the heating device. The sample was glued onto a holder using a Dow Corning 340 Heat Sink Compound. Various sample thicknesses could be used. An aluminum block beneath the sample was heated by direct current from a power supply. During the measurements, the heating device was rotated and the power was supplied via a brass contact which was held by springs. The temperature of the sample was controlled by changing the voltage of the power supply using an experimentally determined relationship between the temperature and the voltage.

For the textures measured at RT in which the material is mostly monoclinic martensite, five pole figures for {002}_m, {111}_m, {020}_m, {111}_m and {022}_m were generally measured. For the texture measurements at 120°C in which the material is in the b.c.c. austenite state, three pole figures for {110}_p, {200}_p and {211}_p were measured.

One of the texture measurements of the KR52 sample annealed at 500°C was also carried out on a Siemens X-ray diffractometer at the Technical University (TU) Clausthal, equipped with a position sensitive detector, using Cukα radiation. The purpose of using another diffractometer to measure the texture was to determine the reproducibility of the measurement and to measure the texture using a different technique, in which the influence of overlapping peaks can be separated by a fitting program(191).

3.2.2 Qualitative and quantitative analysis of texture

The textures were qualitatively analyzed by comparing the measured pole figures with standard stereographic projections. The stereographic projections of the cubic lattice and monoclinic lattice were calculated using a software program written by Mulder(192). The stereographic projections of each martensite variant originating from the (110)[110]_p and (111)[110]_p are presented in Appendix 2. These were calculated by using the lattice parameters of monoclinic martensite a=0.2889 nm, b=0.4120 nm, c=0.4622 nm, and β=96.8°. Fig. 3.6 shows an example of the stereographic projections which is one of the projections of martensite variants originating from the texture (110)[110]_p.
Fig. 3.4 Schematic illustration of the definitions of the rotation angle \( \Phi (\phi) \) and the tilt angle \( \Psi (\psi) \) in a pole figure.

Fig. 3.5 A schematic drawing of the heating device for texture measurements at high temperature.
Chapter 3 Experimental procedures

Fig. 3.6 A standard stereographic projection of the monoclinic martensite variant 4 originating from a (110)[110]p parent phase texture. Lattice parameters of the monoclinic are $a = 0.2889$ nm, $b = 0.4120$ nm, $c = 0.4622$ and $\beta = 96.8^\circ$. The variant notation is from S. Miyazaki et al.\(^{(23)}\).

To quantitatively analyze the texture, the orientation distribution function (ODF) of the measured texture was calculated. As discussed in section 2.2.1, the calculated pole figures and the calculated inverse pole figures can be obtained from the ODF. Moreover, the orientation related mechanical properties can be predicted through the ODF.

For the ODF calculation of the texture with cubic symmetry, commercial programs were available. A Philips PC Texture ODF program version 3.10 was used for the calculation, based on the measured results from three pole figures of the $\{110\}_p$, $\{200\}_p$ and $\{211\}_p$ diffraction planes. The C-coefficients, the ODF sections and the calculated pole figures were obtained from the calculation.

Due to the lack of calculated inverse pole figures from the Philips PC program version 3.10, the ODFs of three samples were calculated by a PC Program version 2.31 at the TU Clausthal. For the ODF calculation of the texture with monoclinic symmetry, another program at the TU Clausthal was used.
3.3 Mechanical Testing

3.3.1 Tensile testing

Tensile testing was conducted to the end of the plateau (see Fig. 2.10) to measure the plateau stress and plateau strain, or until fracture to measure the toughness. The plateau stress was used to determine the constant load for thermal cyclic testing, see the following section 3.3.2.

Tensile specimens were spark-cut from as-rolled sheet to sizes depending on the type of test. In order to investigate the anisotropy of mechanical shape memory properties, the sheets were cut along five different angles to the RD, i.e. 0°, 30°, 45°, 60° and 90°, respectively, as shown in Fig. 3.7. After cutting, the samples were annealed and the oxide layer was removed by chemical etching in a solution consisting of 95% H₂O₂ + 5% HF (vol.%).

The width of the samples were usually 5.0 mm, close to the size of the tensile samples used by other authors(158). Another type of sample with a width of 15 mm was also used for texture measurements after tensile testing and thermal cyclic testing. It has known that test sample size and geometry can affect the mechanical properties in a tension test(193). For instance, in a test on a cylindrical test sample, the elongation to fracture normally increases upon decreasing gauge length. This effect is due to the localization of strain during necking which occurs after maximum load(194). For the present investigation, the change of the sample width might influence the measurement results due to the inhomogeneity of the material produced during processing. To clarify this influence, the martensite transformation strain in samples with a width of 5 and 15 mm were measured and compared. The results indicated that the difference of the strain is less than 0.1%, which is within experimental error.

![Fig. 3.7 Drawing showing sample orientation in a rolled sheet for tensile measurements.](image-url)
Tensile testing was conducted with a Zwick 1445 material tester. Testing was controlled by a Zwick program version 3.5. The tensile test set-up is shown in Fig. 3.8. A MFS mini strain gauge with a gauge length of 10 mm was applied to measure the strain. The conversion constant (approximately 2.0 V/mm) of the strain gauge was regularly calibrated. Two scratches with a separation of 10 mm (gauge length) were cut on one side of the samples to fix the wheels of the strain gauge during the tensile test. The cross head speed was 2.5 mm/min. In order to react to the rapid increase of the strain during detwinning and preferred variant growth, a spring was mounted below the cross head. An analog-to-digital converter Datataker was used to record the data, including temperature, strain, stress and time. The time interval for each record ranged from less than 1 second to 4 seconds. The temperature was measured using a NiCr-Ni thermocouple which was spot-welded on the surface of the sample. The temperature of the thermocouple was calibrated using ice-water (0°C) and boiling water (100°C).

Two types of stress-strain curves were obtained for tensile testing depending on the shape of the plateau during detwinning, as shown in Fig. 3.9. The stress-strain curve (I) has a clear plateau which occurs in the case of well annealed SMAs and a loading direction along the RD. The plateau stress, $\sigma_p$, and plateau strain, $\varepsilon_p$, are determined from the plateau. The constant load for thermal cyclic testing (see section 3.3.2), $1.1\sigma_p$, was taken at the point A in Fig. 3.9.

In the as-rolled samples or in the annealed samples with the loading direction along the TD, the stress-strain curve does not show a plateau, see curve (II) in Fig. 3.9. The stress-strain curve during detwinning is almost a straight line from point B to point C. The plateau strain, $\varepsilon_p$, was defined to be the length from the intersection of the extension of line BC and the extension of the elastic line before detwinning to point C. The plateau stress, $\sigma_p$, in this type of curve was taken as the stress at point C. The constant load for thermal cyclic testing as $1.1\sigma_p$ is thus at point D. However, note that the plateau stress, $\sigma_p$, in a type (II) stress-strain curve as defined here is only the end stress of detwinning (point C in Fig. 3.9) and is not related to the start of the detwinning (point B).
3.3.2 Thermal cyclic testing

The shape memory properties, mainly transformation strain, permanent strain, transformation temperatures under loading, and transformation hysteresis, were determined from thermal cyclic testing. Thermal cyclic testing was performed under a constant load of 1.1 times the plateau stress, a load slightly higher than the plateau stress for the sake of experimental determination of the end of the plateau (points A or D in Fig. 3.9). At the end of the plateau of the stress-strain curve, the volume fraction of the favoured martensite variants is maximized. This is thus the point for the measurement of the transformation strain resulting from the variant growth, and for the measurement of the texture development after thermal cyclic testing. The sample and strain gauge were placed inside a chamber, see Fig. 3.8. The testing temperature was controlled by a software program "Cryosoft PPC graphic V2.10" using resistance heating. Cooling was conducted by pumping liquid nitrogen into the chamber, while the pressure of the liquid nitrogen was carefully controlled in order to keep a constant cooling rate. The heating and cooling rates were approximately 10°C/min.

A schematic strain-temperature curve for thermal cyclic testing under constant load is illustrated in Fig. 3.10. The testing goes from A to H in alphabetical order. From point A to point B, the specimen is loaded to the required stress level. At point B, the stress is kept constant and thermal cycling started. After two cycles, the load is released and the test ended at point H. The strains resulting from the transformation were defined to be $\varepsilon_1^{M\rightarrow P}$, $\varepsilon_1^{P\rightarrow M}$, $\varepsilon_2^{M\rightarrow P}$ and $\varepsilon_2^{P\rightarrow M}$, respectively. In these strain symbols, the numbers 1 and 2 represent the cycle number and the superscripts "P\rightarrow M" and "M\rightarrow P" indicate the martensite transformation on cooling and the reverse transformation on heating. For instance, the symbol $\varepsilon_1^{P\rightarrow M}$ stands for the strain due to the first martensite transformation. Except for $\varepsilon_1^{M\rightarrow P}$, the
transformation strain is defined here as the difference of the strain at two fixed temperatures 30°C and 100°C, in order to determine the measured transformation strain consistently. The reason for this is due to the change of the strain after the parent phase rapidly transforms to the martensite phase upon cooling from point D to point E. A continual but much slower increase of the strain on cooling was measured from point E to point F in Fig. 3.10. This change of the strain between EF is reversible. This phenomenon might be due to the movement of twin boundaries which is reversible as the temperature changes. The transformation strain, $\varepsilon_{1M\rightarrow P}$, was determined from the maximum difference of the strains before and after the first reverse transformation at a specific temperature between the transformation temperatures of the martensite and reverse transformation.

The difference of the strain in the austenitic state (at 100°C) after a full thermal cycle is called permanent strain. This is the difference of the strains at point G and point C in Fig. 3.10, i.e. the permanent strain is ($\varepsilon_{1P\rightarrow M} - \varepsilon_{2M\rightarrow P}$). The permanent strain indicates the elongation of the sample after each cycle.

The transformation temperatures under loading are characterized by $M'_p$ for the martensite transformation temperature and $A'_p$ for the reverse transformation temperature. The $M'_p$ and $A'_p$ temperatures were those where the maximum transformation rate occurred in the strain-temperature curve, see Fig. 3.10. The transformation hysteresis during thermal cyclic testing under a constant load was defined as the difference between the $A'_p$ and $M'_p$ temperatures.
3.3.3 The influence of oxide layers

A thick oxide layer of Ni$_2$Ti$_4$O was sometimes formed on the surface of the sheet hot rolled at 900°C and/or annealed at a temperature above 400°C. Oxide layers with a thickness of about 30 to 60 µm on the surface of the sample were observed. The thickness was determined by measuring the difference of the thickness of the specimen before and after the removal of the oxide layer. The oxide layer thus comprised about 5% of the whole thickness.

Thermal cyclic testing was performed to determine the effect of the oxide layers on the shape memory properties in a warm rolled 3AMT sample annealed at 500°C cut along the RD. Fig. 3.11 shows the influence of oxide layer on the thermal cyclic test. The transformation hysteresis becomes larger due to the oxide layer, increasing from 28°C to 48°C. This indicates that the growth of the martensite variants in the sample with an oxide layer is slower than the one without oxide layer. The increment of the hysteresis arises from the additional energy required for the transformation to overcome the resistance resulting from the oxide layer. The shape memory properties, such as the plateau stress and plateau strain as well as transformation strain, are also affected to some extent by the existence of the oxide layer. There is a slight increase of the plateau stress and a slight decrease of the plateau strain. The transformation temperatures are dependent on the existence of the oxide layer, whereas the slopes of the strain-temperature curve during the transformation are almost independent of the existence of the oxide layer. The existence of the oxide layer was thus thought to affect the measurement results of DSC, texture and tensile tests as well. Therefore, measures were taken to avoid the formation of the oxide layer, or to remove the oxide layer whenever it was formed.

![Graph showing the influence of oxide layer on thermal cyclic test](image)

*Fig. 3.11 The influence of oxide layer on the second thermal cycle for warm rolled 3AMT samples annealed at 500°C loading along the RD.*
Chapter 3  Experimental procedures

3.4 Transformation Analysis

3.4.1 Differential scanning calorimetry

Phase transformations in the shape memory alloy in the unstressed condition were investigated using differential scanning calorimetry (DSC). DSC is a technique in which the difference in heat flow into or out of a substance and a reference material is measured as a function of temperature\(^{(195)}\). DSC is in widespread use for phase transformation studies because the quantity of heat flow at a particular temperature directly corresponds to the quantity of transformed matter at that temperature. The thermal transformation characteristics of the material measured by DSC are as follows:

- \(M_s\): martensite start temperature;
- \(A_s\): austenite start temperature;
- \(M_p\): martensite peak temperature;
- \(A_p\): austenite peak temperature;
- \(M_f\): martensite finish temperature;
- \(A_f\): austenite finish temperature;
- \(Q_m\): heat of martensitic transformation;
- \(Q_a\): heat of austenitic transformation.

Fig. 3.12 shows schematically the method used to determine the temperatures and the heats. The transformation temperature, for instance, the \(A_s\) temperature, is extrapolated from the intersection between the slope of the curve (line a in Fig. 3.12) and the baseline. The transformation heats are calculated from the integral of the area of the peak under the DSC curves in the temperature range \(M_s\) to \(M_f\) or \(A_s\) to \(A_f\). The temperatures determined by the extrapolation method are not the exact transformation temperatures according to standard definition. For example, \(M_s\) is the temperature at which the first martensitic plate is formed, and \(M_f\) is the temperature at which the last part of the parent phase transforms into martensite. However, the extrapolation method is convenient for practical applications and is therefore widely accepted and used.

![Fig. 3.12 A schematic description of the method for determination of the transformation temperatures and the transformation heats in a DSC profile.](image-url)
The DSC profiles were measured by a Stanton Redcroft DSC-PL calorimeter or a PL Thermal Sciences calorimeter. The samples for the DSC measurements were cut by a low-speed diamond saw into a nearly cubic or rectangular shape, followed by chemical etching in a solution consisting of 95% H₂O₂ + 5% HF (vol.%) in order to remove the oxide layer. The weight of the samples varied from 8 mg to 25 mg. The transformation characteristics of samples for every rolling condition listed in Table 3-2 were measured. The samples were placed in aluminum pans. The temperature range was from -20°C to 120°C. Two cycles were run and the results were usually obtained from the second cycle. The heating or cooling rate was usually taken to be ±10°C/min, a conventional rate which is widely used for the investigation of the transformation of SMAs. The kinetics of the transformations were obtained by measuring the DSC curves at various rates. From the measured DSC profile, the transformation temperatures and the transformation heats were calculated by the equipment software packages.

The shape of the DSC profiles was described by the Kissinger shape indices\(^{(121)}\), Kₐ and Kₘ, where Kₐ stands for the index for the reverse transformation and Kₘ for the martensitic transformation. The definitions of Kₐ and Kₘ are

\[
K_m = \frac{M_p - M_s}{M_f - M_p}, \quad K_a = \frac{A_p - A_s}{A_f - A_p}
\]  

(3.2)

From this definition, one can see that the larger the index, the later the transformation reaches its maximum transformation rate. The transformation hysteresis was defined by the difference of the peak temperatures, Aₚ - Mₚ.

### 3.4.2 Transmission electron microscopy

Transmission electron microscopy (TEM) was used to investigate the crystal structure, the internal defect structure, and the phase morphology, in order to study the effect of rolling parameters and post-rolling annealing on microstructure and the phase transformation. The severely deformed KRE samples rolled at 200°C and cold rolled KR52 samples were selected for TEM observation.

A JEOL JEM 200CX microscope equipped with a rotation-tilt specimen stage was used, operating at 200 KV. A heating stage was applied for \textit{in situ} observation of the change of the microstructure and crystal structure during the transformation. Specimens for TEM were mechanically ground to a thin foil with a thickness of 50-200 µm. Disks with a diameter of 3 mm were punched from the thin foil, and then were usually jet-polished in an electrolyte mixture of 8% perchloric acid and 92% acetic acid at RT. Occasionally, the disks were jet-polished in a methanol solution at a temperature of -20°C in order to complete the martensite transformation.

To some extent, the TEM can be regarded as an auxiliary measure for the transformation analysis in this work when DSC and X-ray techniques are not effective. For instance, in a severely rolled sample, there would be an almost straight line on the DSC profile, or a
broadened diffraction peak in X-ray diffractograms due to high internal stress. The present phases can, however, be distinguished by TEM observation with the help of the knowledge of the crystal structure of the possible phases.

3.4.3 X-ray diffraction

X-ray diffraction (XRD) techniques were used to supplement the DSC and TEM work for the samples annealed at low temperature. For DSC, there was not enough information to analyze the transformation because of peak overlap, and by the TEM, only phases in specific local areas could be analyzed. For the XRD work, the sample was mounted on a platinum strip which was also used as a resistance heater. A NiCr-Ni thermocouple was spot-welded onto the platinum strip underneath the sample. The sample was mounted in a chamber which was evacuated to a level of about 5×10⁻⁵ Torr before heating. The temperature was controlled by changing the current through the heater which was in turn, controlled by a variable voltage power supply.

X-ray diffraction patterns of the sample with a size of 20×18 mm² were recorded on a Philips X’pert system with a PW 3020 x-ray generator at 40KV/30mA, using CoKα radiation and 0.2 mm slit. The transformation process was measured step by step in the temperature range from RT to 250°C with 5 second counting time for every 0.05° 2θ value.
Chapter 4

Texture Development

4.1 Introduction

For this investigation, various textures in the Ti-45Ni-5Cu alloy were developed by controlling the processing conditions for rolling, including rolling temperature, thickness reduction, intermediate annealing temperature and post-rolling heat treatment. The martensite texture was further developed during tensile loading as a result of the growth of favoured martensite variants.

Textures were measured and presented in pole figures for particular sets of diffraction planes. The first step for the measurement of pole figures was therefore to determine and index the Bragg angles for the material and thus determine the diffraction planes of interest.

The diffraction peaks were obtained by rotation and tilt of the sample until the peak with the maximum intensity was found in order to determine the Bragg angles as accurately as possible. Rotation angle ($\phi$) and tilting angle ($\psi$) for the visible diffraction peaks depend on the type of texture. Fig. 4.1 shows an example of a high temperature X-ray diffraction (HTXRD) pattern of the cubic austenite phase in the as-received KR50 material, measured at a temperature of about 120°C by $\theta$-2$\theta$ scans. In this sample, the peak indexed {110}$_p$ was obtained without rotation and tilting, whereas a peak indexed {200}$_p$ was found by a rotation of 90° and a tilt of 45°, and a peak indexed {211}$_p$ by a rotation of 90° and a tilt of 20°. The relative intensity of these peaks, described by the ratio $I_{hkl}/I_{110}$, is 20% for both the {200}$_p$ and {211}$_p$ peaks.

According to the lattice correspondence relationship between the parent austenite phase and the monoclinic martensite phase, as shown in Table 2-5, the {110}$_p$ peak would be split into four martensite peaks, {002}$_m$, {111}$_m$, {020}$_m$ and {111}$_m$. Fig. 4.2 shows an example of the XRD pattern of the monoclinic martensite phase in the as-received KR50 material, measured at room temperature. The diffraction peaks were identified with the help of the published lattice parameters for monoclinic martensite. Among the four mentioned martensite peaks, the {111}$_m$ and {002}$_m$ peaks are the most suitable for texture measurement because these two peaks have relatively high intensities and are only slightly influenced by neighbouring peaks. However, to determine a martensite texture, more reflections are required. In most cases, five pole figures of the {002}$_m$, {111}$_m$, {020}$_m$, {111}$_m$ and {022}$_m$ diffraction planes were measured.
Fig. 4.1 HTXRD pattern for the cubic austenite phase in the as-received KR50 sample, measured at about 120°C using CoKα radiation. \( \phi \) is the rotation angle and \( \psi \) is the tilt angle in the pole figure.

Fig. 4.2 XRD pattern for the monoclinic martensite phase in the as-received KR50 sample, using CoKα radiation.
4.2 Texture Development of Material Pre-annealed at 800°C (AMT)

4.2.1 Cold rolled material with intermediate annealing at 500°C (5AMT)

5AMT material was cold-rolled with intermediate annealing at 500°C, see Fig. 3.2 and Table 3.2. The pole figures of the \(\{110\}_p, \{200\}_p\) and \(\{211\}_p\) austenite diffraction planes were measured at a temperature of about 120°C (above \(A_f\)) for each sample after each intermediate anneal. The \(\{110\}_p\) pole figures of the recrystallization texture before rolling and the deformation texture after completion of rolling and annealing at 500°C are shown in Fig. 4.3. These represent the initial state and final state of texture development. After recrystallization at 800°C, the pole figures show a very weak <331> fibre texture. The maximum relative intensities in the \(\{110\}_p\) pole figures are 3.64 (at \(\psi=10° \text{ and } \phi=87.5°\)), 3.61 (at \(\psi=35° \text{ and } \phi=267.5°\)) and 2.98 (at \(\psi=35° \text{ and } \phi=47.5°\)), respectively. These maximum relative intensities are very low for a fibre texture, where a maximum intensity of 5.0 is considered to be a "random" (weak) texture, and a fibre texture with a maximum intensity of more than 20 is considered to be strong\(^{144-146}\). Therefore, the recrystallization texture of the 5AMT sample was regarded as being close to a random texture.

Cold-rolling with intermediate annealing results in a dominant deformation texture, as shown in Fig. 4.3b. The texture was qualitatively analyzed by comparison of measured pole figures with the standard stereographic projections of the cubic lattice. The maximum relative intensity of the \(\{110\}_p\) pole figure is 7.72 at \(\psi=5.0° \text{ and } \phi=154.5°\), near the centre of the \(\{110\}_p\) pole figure. This indicates the presence of a strong \(\{110\}[110]_p\) texture component. An elliptically shaped contour was found near the centre, indicating that the crystallographic planes in the rolling plane are a result of rotation around the rolling direction, e.g. from \(\{320\}_p\) to \(\{110\}_p\) to \(\{230\}_p\). The intensity in the "eyes" between \(\psi=30° \text{ and } \psi=60°\) is from the combined contribution of the neighbouring components \(\{110\}[1\overline{1}0]_p\) (■) and \(\{111\}[1\overline{1}0]_p\) (•). The texture was thus determined to be a mixture of two major components of \(\{110\}[1\overline{1}0]_p\) and \(\{111\}[1\overline{1}0]_p\). The intensity at \(\psi=90°\) is very weak. This is probably due to the defocussing effect.

Based on the mathematical methods mentioned in section 2.2.1, the orientation density, \(f(g)\), was calculated from the measured austenite pole figures using the Philips ODF program. Fig. 4.4a shows the ODF sections at constant \(\phi_2\) values for the 5AMT sample after rolling and annealing at 500°C. From these sections, the texture component can be quantitatively analyzed from the relative intensities of orientation density by means of the relationship between the coordinate of Euler angles \(\{\phi_1, \Phi, \phi_2\}\) and a texture expression \((hkl)[uvw]\) using eqn 2.15. For instance:

<table>
<thead>
<tr>
<th>in the ODF section</th>
<th>corresponds to</th>
<th>orientation density</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi_1=90°, \Phi=45°, \phi_2=0°)</td>
<td>(011)[0\overline{1}1]_p</td>
<td>more than 12.91 (contour 6)</td>
</tr>
<tr>
<td>(\phi_1=0°, \Phi=90°, \phi_2=45°)</td>
<td>(110)[1\overline{1}0]_p</td>
<td>more than 12.91 (contour 6)</td>
</tr>
<tr>
<td>(\phi_1=0°, \Phi=55°, \phi_2=45°)</td>
<td>(111)[1\overline{1}0]_p</td>
<td>around 10.29 (contour 5)</td>
</tr>
</tbody>
</table>
Fig. 4.3 The pole figures of {110}_p in the 5AMT samples: (a) after recrystallization before rolling; (b) after completion of rolling and annealing at 500°C for 30 min. "•" contribution of the {110}<110>_p texture component to the pole figures, "■" contribution of the {111}<110>_p texture.
Fig. 4.4-a ODF sections calculated from the measured austenite pole figures for the cold rolled 5AMT sample with intermediate annealing at 500°C. The number at the top left corner of each section indicates the constant $\phi_2$ value.
φ₁ = 60°, Φ = 55°, φ₂ = 45° (111) p around 10.29 (contour 5)

Fig. 4.4-b ODF sections at φ₂ = 45° for the cold rolled 5AMT sample with intermediate annealing at 500°C.

The ODF section at φ₂ = 45° is enlarged in Fig. 4.4b. Three orientations {hkl}<uvw> mentioned above are marked in the enlarged ODF section. From eqn 2.15, the angles φ₂ and Φ are independent of [uvw]. Thus in the ODF section at φ₂ = 45°, the line at Φ = 55° represents the {111} plane. From the figure, the orientation density in the {111}<uvw>_p in which <uvw>_p ranges from [110] at φ₁ = 0° to [112] at φ₁ = 90° via [011] at φ₁ = 60° are very close. This means that the relative intensity in the circle of ψ = 35° of the {110}_p pole figure should be the same if the contribution is only from the (111)[110] p component. The component (111)[110] p in this case is the (111)[uvw] p component. In contrast to the (111)[110] p component, the (110)[110] p component is closely related to [uvw]. The orientation density decreases considerably away from the point of (110)[110] p at Φ = 90°, φ₁ = 0° and φ₂ = 45° or the point of (011)[011] p at Φ = 45°, φ₁ = 90° and φ₂ = 0°. The orientation density of the component (110)[110] p is higher than that of the component (111)[110] p. The {110}<110>_p texture component is thus stronger than the {111}<110>_p component.

The ODF was also calculated by the program at the TU Clausthal. The C-coefficients and the ODF sections calculated with the Clausthal program were consistent with the ones from the Philips program, although there were minor differences. An example of the inverse pole figure is shown in Fig. 4.5 for the rolling direction. There is a strong (110) density in the RD, which belongs to both texture components of (110)[110] p and (111)[110] p. The relative density at three important positions (100), (110) and (111) is compiled in Table 4-1. The maximum density of the (100)_p plane (2.03) was found in the TD. The maximum density of the (111)_p plane (2.89) is at an angle 40° to the RD. The density of (110)_p decreases as the angle to the RD increases from 0° to 50° and slightly increases as the angle to the RD
increases from 50° to 90°. This is consistent with the qualitative analysis which indicated that the (110)[110]p texture component is dominant, in which the plane with the maximum density for the RD is (110)p, for the TD (100)p, and for an angle around 35° to the RD (111)p.

The (110)[1¯10]p and (111)[1¯10]p major texture components were also measured after each step of rolling and intermediate annealing at 500°C. The orientation density, f(g), was calculated from the measured austenite pole figures using the Philips ODF program. Fig. 4.6 shows the change of the orientation density of the components (110)[1¯10]p and (111)[1¯10]p during the rolling process. Before rolling, the recrystallization texture of the hot-deformed material is weak and the density is low. The (111)[110]p texture component is slightly higher than the (110)[110]p component. The orientation density of these two components increases during rolling because intermediate annealing at 500°C does not change the type of texture components. Further cold-rolling after intermediate annealing produces a more pronounced texture. The increase of the orientation density of the (111)[110]p component proceeds slowly except for the fourth step where the density clearly increases. The increase of the orientation

Table 4-1 The relative density of (100)p, (110)p, and (111)p in the calculated inverse pole figures as a function of the angle to the rolling direction for the cold rolled 5AMT sample with intermediate annealing at 500°C and post-rolling annealing at 500°C.

<table>
<thead>
<tr>
<th>Angle to RD</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.10</td>
<td>0.00</td>
<td>0.10</td>
<td>0.00</td>
<td>1.38</td>
<td>2.03</td>
</tr>
<tr>
<td>(110)</td>
<td>6.46</td>
<td>4.66</td>
<td>2.40</td>
<td>1.47</td>
<td>1.13</td>
<td>0.99</td>
<td>1.02</td>
<td>1.05</td>
<td>1.18</td>
<td>1.25</td>
</tr>
<tr>
<td>(111)</td>
<td>0.59</td>
<td>0.98</td>
<td>1.52</td>
<td>2.70</td>
<td>2.89</td>
<td>1.70</td>
<td>0.67</td>
<td>0.03</td>
<td>0.00</td>
<td>0.09</td>
</tr>
</tbody>
</table>
density of the (110)[1\overline{1}0]_P component is almost linear, except for the second to last step. This is, probably, due to the higher thickness reduction (34\%) produced during the second to last step, which leads to a lower recrystallization temperature, closer to the intermediate annealing temperature\(^{(104)}\). Partial recrystallization occurred, and both the creation of a random texture and retention of the deformation texture resulted in the decrease of the orientation density.

The relative thickness reduction per step was controlled by measuring the hardness. The hardness increases as the thickness reduction increases until a value of HV 350 kgf/mm² is reached, as shown in Fig. 4.6. After intermediate annealing at 500°C, the hardness decreases to about HV 220 kgf/mm² and the thickness slightly increases due to the shape memory effect.

### 4.2.2 Cold rolled material with intermediate annealing at 650°C (6AMT)

6AMT material was cold-rolled with intermediate annealing at 650°C and post-rolling annealing at 500°C, see Table 3.2. The \{110\}_P, \{200\}_P and \{211\}_P pole figures were measured at a temperature of about 120°C (above A_\text{f}). The orientation density in the ODF sections was calculated using the Philips ODF program. The major texture components (110)[1\overline{1}0]_P and (111)[1\overline{1}0]_P after each intermediate anneal were determined and the dependence of the orientation density on the number of rolling steps is shown in Fig. 4.7. The X-axis in this figure is the step number instead of the total reduction which is used in
The major texture components (110)[1\bar{1}0]_p (\Delta) and (111)[1\bar{1}0]_p (\bullet) during cold rolling of 6AMT samples with intermediate annealing at 650°C for 10 min. The numbers in the figure indicate the relative thickness reduction.

The major texture components (110)[1\bar{1}0]_p and (111)[1\bar{1}0]_p after each intermediate anneal were determined and the dependence of the orientation density on the number of rolling steps is shown in Fig. 4.7. The X-axis in this figure is the step number instead of the total reduction which is used in Fig. 4.6 because intermediate annealing at a temperature above the recrystallization temperature could completely change the texture. It is, therefore, not clear that there is a relationship of the texture with the different steps.

The major texture components (110)[1\bar{1}0]_p and (111)[1\bar{1}0]_p become more pronounced as compared to the texture before rolling. After rolling steps 1 and 2, the orientation density increases and the texture becomes stronger. However, the texture becomes weaker after steps 3 and 4. After the last rolling step, the texture again becomes stronger. The orientation density of the (111)[1\bar{1}0]_p texture component is comparable to the (110)[1\bar{1}0]_p component. A comparison of the 5AMT samples (intermediate anneal at 500°C) and the 6AMT samples (intermediate anneal at 650°C) shows that the texture of the 6AMT samples after rolling is weaker because the orientation density is smaller than that of the 5AMT sample.

The texture development in the 6AMT samples could be explained as follows. In steps 1 and 2, the deformation texture is retained and sharpened, as compared to the weak texture in the pre-annealed sheet. In steps 3 and 4 in which the thickness reduction is higher than the reduction in the other steps, both the development of a random texture and retention of the deformation texture occurred which resulted in a decrease of the orientation density. In the last step, the texture is sharpened again. The random textures formed in steps 3 and 4 might be, possibly, associated with the higher relative thickness reduction. A higher reduction would result in less time required to complete recrystallization. After the completion of
recrystallization, the grains would grow further which would lead to the formation of a partial random texture.

### 4.2.3 Warm-rolled material (3AMT)

3AMT material was warm-rolled at 300°C, see Table 3-2. The pole figures of \{110\}_p, \{200\}_p and \{211\}_p for three samples post-rolling annealed at 500°C were measured at a temperature of about 120°C (above \(A_t\)). The pole figures from each sample are the same. Fig. 4.8 shows the \{110\}_p pole figure. The maximum intensity areas are in the circle of \(\psi=35^\circ\) which come from the contribution of the \{111\}[1\bar{1}0]_p texture component, whereas the intensity in the centre of the \{110\}_p pole figure is relatively weak. The major texture component is thus \{111\}[1\bar{1}0]_p and the minor component \{110\}[1\bar{1}0]_p. Therefore warm-rolled 3AMT samples have a texture significantly different from the cold-rolled 5AMT and 6AMT materials.

The ODF was calculated using the pole figures of \{110\}_p, \{200\}_p and \{211\}_p by the Philips ODF program. Fig. 4.9 shows the ODF section at \(\varphi_2=45^\circ\). A high orientation density (higher than contour 6) was calculated at the Euler angles for the \{111\}[1\bar{1}0]_p component and a low density (lower than contour 1) at the Euler angles for the \{110\}[1\bar{1}0]_p component. At the line at \(\Phi=55^\circ\) and \(\phi_2=45^\circ\) which corresponds to the \{111\} plane, the orientation density along the [1\bar{1}0]_p direction (higher than contour 6) is somewhat higher than the ones in the other directions, for instance, the one along [1\bar{2}0]_p direction (higher than contour 5). This can be understood by the fact that the texture is \{111\}[uvw]_p, and the intensity of the corresponding circle in pole figure should be almost the same because the texture can rotate to any angle in the rolling plane. For instance, almost the same intensity should be present in the circle of \(\psi=35^\circ\) of the \{110\}_p pole figure (Fig. 4.8). However, this property was not exactly measured in the pole figures. The measured intensities in the \{110\}_p pole figure at \(\psi=35^\circ\) show more differences than one would expect from the analysis using the ODF section. The minimum intensity in the circle of \(\psi=35^\circ\) is less than the intensity of contour 4. In the \{200\}_p pole figure, the difference is even more in the circle of \(\psi=55^\circ\). In the circle of \(\psi=20^\circ\) in the \{211\}_p pole figure, the difference is almost the same with the one in the \{110\}_p pole figure. This discrepancy might arise from calculation errors using the ODF program. Nevertheless, the results from the ODF sections are generally in agreement with the qualitative analysis using pole figures.

The ODF was also calculated by the program at TU Clausthal. The inverse pole figures from the RD to the TD were calculated at intervals of 10° and the relative density at three important positions \{100\}_p, \{110\}_p and \{111\}_p are compiled in Table 4-2. There is a strong \{110\}_p density in the RD. Upon increasing the angle away from the RD, the density of \{110\}_p decreases and the density of \{100\}_p and \{111\}_p increases. The density of \{111\}_p has a maximum value at an angle 50° to the RD. The maximum density of the \{110\}_p is about 2.6 times higher than the maximum for the \{111\}_p and 7.9 times higher than that for \{100\}_p, which reflects the strength of the texture in the RD.

The pole figures of the \{002\}_m, \{11\bar{1}\}_m, \{020\}_m, \{111\}_m and \{022\}_m diffraction planes were measured in the warm-rolled 3AMT sample annealed at 500°C. Fig. 4.10 shows the \{11\bar{1}\}
Chapter 4 Texture development

Fig. 4.8 Austenite pole figure of the \{110\}_p diffraction plane in a 3AMT sample warm-rolled at 300°C and annealed at 500°C. 

"■" contribution of the \{110\)<110>_p texture component to the pole figures, 

"●" contribution of the \{111\)<110>_p texture.

Fig. 4.9 ODF section at $\phi_2 = 45^\circ$ for the 3AMT sample warm-rolled at 300°C and annealed at 500°C.
Table 4.2 The relative density of three important positions (100)\(_p\), (110)\(_p\), and (111)\(_p\) in the calculated inverse pole figures as a function of the angle to the rolling direction for the sample warm-rolled at 300°C and annealed at 500°C.

<table>
<thead>
<tr>
<th>angle to RD</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)(_p)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.06</td>
<td>0.12</td>
<td>0.16</td>
<td>0.28</td>
<td>0.41</td>
<td>0.44</td>
</tr>
<tr>
<td>(110)(_p)</td>
<td>3.46</td>
<td>3.05</td>
<td>2.13</td>
<td>1.51</td>
<td>1.38</td>
<td>1.43</td>
<td>1.44</td>
<td>1.32</td>
<td>1.22</td>
<td>1.15</td>
</tr>
<tr>
<td>(111)(_p)</td>
<td>0.34</td>
<td>0.64</td>
<td>0.80</td>
<td>0.94</td>
<td>1.20</td>
<td>1.33</td>
<td>1.21</td>
<td>0.98</td>
<td>0.95</td>
<td>0.92</td>
</tr>
</tbody>
</table>

pole figure. From the maximum intensity contours near the circle of \(\psi = 30°\), the (120)[2\(\bar{1}\)1]\(_m\), (120)[2\(\bar{1}\)1]\(_m\), (120)[001]\(_m\), (102)[2\(\bar{1}\)1]\(_m\), and (102)[010]\(_m\) components can be calculated because the interplanar angle between (120)\(_m\) and (11\(\bar{1}\))\(_m\) is 32.7° and the interplanar angle between (102)\(_m\) and (11\(\bar{1}\))\(_m\) is 38.0°. Similarly, the (102)[2\(\bar{1}\)1]\(_m\) and (102)[010]\(_m\) components can be calculated from the {111}\(_m\) or {002}\(_m\) pole figures. The corresponding intensity of these variants was also found in the {020}\(_m\) or {022}\(_m\) pole figures. From the pole figures, a relatively high intensity was found in the centre of the pole figures, indicating minor components originating from the (110)[1\(\bar{1}\)0]\(_p\) were present. Seven main martensite texture components were determined: (120)[2\(\bar{1}\)1]\(_m\), (120)[2\(\bar{1}\)1]\(_m\), (120)[001]\(_m\), (102)[2\(\bar{1}\)1]\(_m\), (102)[010]\(_m\), (102)[2\(\bar{1}\)1]\(_m\) and (102)[010]\(_m\). These variants all originated from the (111)[1\(\bar{1}\)0]\(_p\) austenite texture. Among these components, the (120)[2\(\bar{1}\)1]\(_m\), (120)[2\(\bar{1}\)1]\(_m\) and (120)[001]\(_m\) components have the same plane, but the angles between the directions are around 60° to each other. A similar property can be found in (102)[2\(\bar{1}\)1]\(_m\) and (102)[010]\(_m\) and (102)[2\(\bar{1}\)1]\(_m\) and (102)[010]\(_m\).

Fig. 4.10 The \{11\(\bar{1}\)\}_\(m\) pole figure for the 3AMT sample warm-rolled at 300°C and annealed at 500°C, see Fig. AII.3 for contribution of each variant to the pole figure.
4.3 Texture Development of Material Pre-annealed at 650°C (KR)

4.3.1 Texture development during the rolling process

The pole figures of the {110}p, {200}p and {211}p diffraction planes of the materials pre-annealed at 650°C were measured at a temperature of 120°C (above Ar). The ODF were calculated from the measured pole figures using the Philips program. Fig. 4.11 shows the {110}p pole figures for the as-received KR50 sample recrystallized at 650°C for 60 min, the KR51 sample cold-rolled to a thickness reduction of 11% and the KR52 sample cold-rolled to a reduction of 26%. The cold rolled KR51 and KR52 samples were subjected to a post-roll anneal at 500°C for 30 min.

For the recrystallized KR50 sample, Fig. 11a, the maximum intensity is at ψ=25° and φ=342.5° which comes from the contribution of the texture close to (111)[1 ¯21]p. However, from the ODF section, both the (110)[1 ¯10]p and (111)[1 ¯10]p components are present with almost equal orientation density (10.5). One obvious characteristic of this pole figure is the asymmetry around the axis φ=0° and the symmetry around the axis φ=90°. The asymmetry of the texture was probably produced by the manufacturer of this as-received sheet. For instance, the sheet was not fed in alternating one end with the other for each subsequent pass.

The KR51 and KR52 samples have a combined (110)[1 ¯10]p + (111)[1 ¯10]p texture, which is similar to the austenite texture measured in the cold-rolled 5AMT sample in Fig.4.3b. The intensity in the "eyes" between ψ=30° and ψ=60° for the KR52 sample (contour 5 in Fig. 4.11c) is stronger than the one for the KR51 sample (contour 4 in Fig. 4.11b), indicating that the texture component (110)[1 ¯10]p of the KR52 sample is stronger than the KR51 sample.

The orientation density of these three sample was calculated using the Philips ODF program. It was found that the orientation density increases as thickness reduction increases. The density increases from 12.5 for the (110)[110]p component and 8.0 for the (111)[110]p component in the KR51 sample to 13 for the (110)[110]p component and 9.0 the (111)[110]p component for the KR52 sample. The ODF sections are similar to the one for the cold-rolled 5AMT sample shown in Fig. 4.4.

4.3.2 Texture development as a function of annealing temperature

The effect of annealing temperature on texture development at constant ψ and φ values was investigated, using θ-2θ XRD pattern taken at RT. Fig. 4.12 shows, as an example, the XRD patterns for KR52 samples. For the as-rolled sample, one broad peak was observed due to the presence of microstresses resulting from the plastic deformation. The co-existence of martensite and austenite is indicated by the shoulders on both sides of the peak. The presence of both phases is due to the depression of the Ms temperature by the deformation, i.e. Ms < RT < Mf. When the annealing temperature increases up to 300°C, the intensity from the {110}p diffraction plane increases and the peak sharpens due to stress relief. The martensite {111}m intensity does not vary noticeably, verifying that the change of the Ms is very small. For annealing temperatures higher than 400°C, the martensite peaks become more pronounced.
Fig. 4.11 The \{110\}_p pole figures of samples annealed at 500°C: a) as-received KR50 sample; b) KR51 sample cold-rolled to 11% reduction.

"•" contribution of the \{111\}<1\bar{1}0>_p texture component to the pole figures.

"●" contribution of the \{110\}<1\bar{1}0>_p texture.

Relative intensity:

a) KR50

1---0.98
2---1.97
3---2.95
4---3.94
5---4.92
6---5.91

Max: 6.89
Psi: 25.0
Phi: 342.5

b) KR51

1---0.70
2---1.39
3---2.09
4---2.79
5---3.48
6---4.18

Max: 4.88
Psi: 0.0
Phi: 32.5
because the $M_s$ and $M_f$ temperatures are shifted above RT. This is due to the considerable decrease of dislocation density when the annealing temperature is higher than 400°C. The intensity of the $\{11\bar{1}\}_m$ peak is maximum among the four main peaks $\{002\}_m$, $\{11\bar{1}\}_m$, $\{020\}_m$ and $\{111\}_m$.

The XRD profiles of the other samples, such as KR50, KR51 and KRE, were also measured. A similar dependence of the diffraction peaks on annealing temperature was found for KRE samples. For the KR50 and KR51 samples, there are only separated martensite diffraction peaks for the as-rolled sample and the annealed samples. The austenite peak did not appear, indicating a higher $M_s$ temperature. The $M_s$ is not depressed as much as for KR52 samples because the amount of deformation is less in the KR50 and KR51 samples. Therefore, broadened and overlapping peaks were not observed in these samples.

The martensite texture development as a function of annealing temperature was investigated. For the as-rolled sample and all the samples annealed at a temperature less than 300°C, only the pole figures of $\{002\}_m$ and $\{11\bar{1}\}_m$ were measured because the other two martensite peaks were completely overlapped by the $\{110\}_p$ peak. For the KR52 samples annealed at a temperature exceeding 400°C, the pole figures of the $\{002\}_m$, $\{11\bar{1}\}_m$, $\{020\}_m$, $\{111\}_m$ and $\{022\}_m$ diffraction planes could be measured since the martensite peaks were separated. The pole figures of the $\{002\}_m$ plane for the as-rolled sample and the samples annealed at 200°C, 400°C and 500°C are shown in Fig. 4.13. When the annealing temperature is less than

---

**Fig. 4.11 (cont’d) The $\{110\}_p$ pole figures of samples annealed at 500°C: c) KR52 sample cold-rolled to 26% reduction.**

<table>
<thead>
<tr>
<th>Relative intensity:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1---0.68</td>
</tr>
<tr>
<td>2---1.36</td>
</tr>
<tr>
<td>3---2.03</td>
</tr>
<tr>
<td>4---2.71</td>
</tr>
<tr>
<td>5---3.39</td>
</tr>
<tr>
<td>6---4.07</td>
</tr>
</tbody>
</table>

Max: 4.75
Psi: 5.0
Phi: 297.5
Chapter 5

Anisotropic Behaviour

5.1 Selection of constant load for the thermal cyclic tests

The anisotropic mechanical behaviour of three series of the textured materials, the warm rolled 3AMT samples, the cold rolled 5AMT and KR52 samples, were measured in order to relate the anisotropic behaviour to the texture development. The texture of the materials was also measured after testing. The difference between the KR52 and 5AMT samples was the pre-rolling annealing temperature, 650°C for the KR52 materials and 800°C for the AMT materials. While the KR and AMT materials have nominally the same composition, the as-delivered AMT materials were thicker (4.3 mm) than the KR materials (0.9 mm). Experience with 3.6 mm thick sheet indicates that a pre-rolling annealing temperature of 650°C is not high enough for a thick material to avoid cracking after severe deformation. It was expected that the difference of pre-rolling annealing temperature would not result in different texture, but may influence mechanical and shape memory properties to some extent. This was based on the premise that the pre-rolling annealing may influence the grain size, but not considerably affect the rotation of the slip planes during the rolling process.

Due to the anisotropy of the plateau stress in the textured materials, the selection of 1.1 times this stress for thermal cyclic testing resulted in different loads for the samples cut at various angles to the RD. It is well known that the transformation strain increases as the applied load increases\(^{(26,167,168)}\). This would mean that the transformation strain of the samples cut at various angles to the RD would be compared under different absolute load values. The reason for the selection of a variable load in this work was that the measurements of the transformation strain and texture development require all variants to be fully developed. If the load is lower than the plateau stress, the variants are not fully developed. If the load is higher than the plateau stress and far from the end of the plateau, the deformation behaviour is elastic, see stage III in Fig. 2.10. At the end of the plateau a more pronounced texture would be developed, which would result in strong anisotropy of elastic deformation and influence the measurement of the transformation strain. Microstructural features such as dislocation density would change if the constant load was higher than the plateau stress\(^{(161)}\). This would influence the values of permanent strain and transformation temperatures.

Fig. 5.1 shows the influence of applied load on the anisotropy of the martensite transformation strain in the cold rolled 5AMT samples annealed at 500°C. The broken line is the strain during thermal cyclic testing as a function of angle to the rolling direction. The solid line is the anisotropy of the transformation strain measured under a fixed constant load of 140 MPa which is the maximum value of the 1.1 plateau stress among these five samples. For higher constant loads, higher transformation strains were measured. The maximum difference of the strain is around 0.7% at an angle of 45° to the RD. From these results, the rate of increase of strain as a function of applied load was roughly estimated to be 1% per 100 MPa. From
5.1 Anisotropic behaviour of warm-rolled materials

The anisotropic behaviour of warm-rolled materials was investigated for the 3AMT material annealed at 500°C for 30 min prior to testing. All tests were conducted in triplicate in order to demonstrate the reproducibility of the results.

Tensile testing was conducted to the end of plateau of the stress-strain curves for each direction in order to determine the anisotropy of the plateau stress. The maximum plateau stress of around 85 MPa (average value) was found in the transverse direction (TD), while a minimum of 76 MPa was found at the angles 30° or 45° to the RD. The minimum plateau strain was in the TD while the maximum was at the angles 0° to 45°. The anisotropy factor of the plateau stress averaged over three samples was $A = 85/76 = 1.21$, close to isotropic.

Typical stress-strain curves for the thermal cyclic testing samples are shown in Fig. 5.2. The
curves are all type I curves (see Fig. 3.9), which is typical for shape memory alloys in the martensitic condition. At the end of the plateau, the stress was set constant and the temperature was cycled at a constant rate of ±10°C/min. After two thermal cycles, the constant stress was released and an unloading stress was observed.

The average loads of approximately 1.1 times the plateau stress for the samples cut along 0°, 30°, 45°, 60° and 90° to the RD are 92 MPa, 86 MPa, 87 MPa, 93 MPa and 97 MPa, respectively. The transformation strain was determined using the method shown in Fig. 3.10. The anisotropy of the average value of the transformation strains \( \varepsilon_{1}^{M\rightarrow P} \), \( \varepsilon_{1}^{P\rightarrow M} \), \( \varepsilon_{2}^{M\rightarrow P} \) and \( \varepsilon_{2}^{P\rightarrow M} \) is shown in Fig. 5.3. The error bars, \( \Delta \), are based on three measurements, using the following equation:

\[
\Delta = \frac{ts}{\sqrt{n}}, \quad \text{where} \quad s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}
\]

is the standard deviation, \( x_i \) the measurement data, \( n \) is the number of the measurements, and \( \bar{x} \) is the average value of the measurements. \( t = t_2 = 4.303 \) for two degrees of freedom at a confidence level of 95%\(^{(197)}\). The calculated deviation of the measured strains from the average values varies from ±0.01% to ±0.12%, which is not particularly large.

At an angle 0° to 60° to the RD, there is little variation in transformation strains. In the RD, the strain is always maximum while in the transverse direction, the strain is about 0.5% - 0.7% lower. The anisotropy factor A of the strain is:

- For \( \varepsilon_{1}^{M\rightarrow P} \): \( A = 3.94/3.26 = 1.21 \)
- For \( \varepsilon_{1}^{P\rightarrow M} \): \( A = 5.01/4.04 = 1.24 \)
- For \( \varepsilon_{2}^{M\rightarrow P} \): \( A = 4.56/3.85 = 1.18 \)
- For \( \varepsilon_{2}^{P\rightarrow M} \): \( A = 5.26/4.24 = 1.24 \)

The anisotropy of transformation strain in the 3AMT material is thus weak compared with the other series of samples to be presented in the following sections.

The curves in Fig. 5.3 also show that \( \varepsilon_{1}^{M\rightarrow P} < \varepsilon_{2}^{M\rightarrow P} < \varepsilon_{1}^{P\rightarrow M} < \varepsilon_{2}^{P\rightarrow M} \). The first reverse transformation strain \( \varepsilon_{1}^{M\rightarrow P} \) is always smaller than the following ones, regardless of the angle to the RD. This phenomenon was observed not only in the 3AMT samples, but also in the other series of samples including the cold-rolled 5AMT samples and the KR52 samples, see also Fig. 3.10. This is most likely due to the effect of the restriction of the variants on the growth of the favoured variants during the first tensile loading. At the beginning of the tensile test (point A in Fig. 3.10), the variants in the annealed samples are present predominantly in a self-accommodated manner. During the tensile test from point A to point B in Fig. 3.10, the favoured martensite variants grow at the expense of the other martensite variants, but will also be restricted by their interfaces. The growth of the favoured variants results in the plateau strain. Subsequently, the transformation strain, \( \varepsilon_{1}^{M\rightarrow P} \), during the first reverse transformation under constant stress is produced by the reversion of the strain resulting from this restricted growth. During following transformations, the transformation strains are a result of preferred variant growth by free movement of the austenite-martensite
Fig. 5.2  Stress-strain curve for thermal cyclic testing under constant load of a 3AMT sample warm-rolled at 300°C and annealed at 500°C. The numbers in the figure indicates the angle to the RD.

Fig. 5.3  The dependence of the average transformation strain on angle to the RD for the 3AMT samples warm-rolled at 300°C and annealed at 500°C. Error bars were calculated using the student-t test.
interface under the influence of stress. The free movement of the austenite-martensite interface thus results in a larger strain, as compared to the reversion of the restricted growth during the first reverse transformation.

The permanent strain \( (\varepsilon_{1-\text{P}} - \varepsilon_{2-\text{M}}) \) in the TD has a minimum value of 0.19%. The permanent strains at angles less than 60° varied from 0.35% to 0.47% which are about 2 times higher than that in the TD. The presence of the permanent strain is due to the resistance of the irreversible dislocation microstructure to the movement of the interphase boundary, as introduced in § 2.3.2(26,169). When the loading direction is along the TD, fewer dislocations are produced by the resistance to the movement of the austenite-martensite boundary. Therefore, the permanent strain in the TD is less than the strain in the other directions.

Table 5-1 The dependence of transformation temperatures (\( M'_p \) and \( A'_p \)) under loading and the transformation hysteresis (hys.) on the loading direction (LD) in the warm-rolled 3AMT sample annealed at 500°C.

<table>
<thead>
<tr>
<th>LD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M'_p )</td>
<td>61.0°C</td>
<td>58.5°C</td>
<td>60.0°C</td>
<td>58.4°C</td>
<td>60.1°C</td>
</tr>
<tr>
<td>( A'_p )</td>
<td>84.0°C</td>
<td>82.1°C</td>
<td>82.5°C</td>
<td>81.9°C</td>
<td>81.7°C</td>
</tr>
<tr>
<td>hys.</td>
<td>21.0°C</td>
<td>23.4°C</td>
<td>22.5°C</td>
<td>23.5°C</td>
<td>21.6°C</td>
</tr>
</tbody>
</table>

The characteristic transformation temperatures \( A'_p \) and \( M'_p \) and the transformation hysteresis under loading were determined and are compiled in Table 5-1. The transformation temperatures and hysteresis were found to be independent of the loading direction within experimental error. The martensite transformation temperature \( M'_p \) is 60±2°C and the reverse transformation temperature \( A'_p \) is 82±2°C. The transformation hysteresis (\( A'_p \) - \( M'_p \)) is about 22±1°C. This value is comparable to values experimentally measured by other authors for a Ti-Ni-5%Cu alloy(43,44).

5.3 Anisotropic behaviour of cold-rolled material pre-annealed at 800°C

The anisotropic behaviour of cold-rolled material with intermediate annealing at 500°C (5AMT) was investigated after a final anneal at 500°C for 30 min. The anisotropic behaviour of the stress-strain curve of the tensile tests to the end of the plateau is shown in Fig. 5.4. The stress-strain curves in the cold-rolled 5AMT samples are similar to the ones in the warm-rolled 3AMT samples except for the curve in the TD. At angles of 30° and 45° to the RD, the plateau strain is a maximum and the plateau stress is a minimum, whereas in the TD the plateau stress is a maximum and the plateau strain is a minimum. At angles of 30° and 45° to the RD, the interfacial resistance against the growth of the favoured variant(s) is small upon loading. Detwinning occurs at a low stress level. In the TD, the stress-strain curve does not show a clear plateau, indicating that further reorientation of the martensite variants requires an increase of the applied stress. Therefore, the mobility of the martensite
Chapter 5 Anisotropic behaviour

Fig. 5.4 The anisotropic behaviour of stress-strain curves from tensile tests to the end of the plateau in the 5AMT samples cold rolled at 500°C and annealed at 500°C. The numbers in the figure indicate the angle to the RD.

The anisotropy factor of the plateau stress is $A = 150/80 = 1.6$, higher than the one in the warm-rolled 3AMT samples.

The anisotropy of the transformation strain as measured by thermal cyclic testing is shown in Fig. 5.5. The constant loads were shown in Fig. 5.1. For the first martensite transformation strain, $\varepsilon_1^{P\rightarrow M}$, the maximum values (5.04% - 5.13%) at the angles 0° - 45° to the RD are approximately 1.81 times that of the minimum one in the TD (2.80%). The anisotropy factor $A$ of the transformation strains are:

- For $\varepsilon_1^{M\rightarrow P}$: $A = 4.49/2.26 = 1.99$
- For $\varepsilon_2^{M\rightarrow P}$: $A = 4.99/2.76 = 1.81$
- For $\varepsilon_1^{P\rightarrow M}$: $A = 5.07/2.80 = 1.81$
- For $\varepsilon_2^{P\rightarrow M}$: $A = 5.10/2.82 = 1.81$

This measured anisotropy factor, is very close to the one measured by other authors in Ti-Ni alloys. For instance, Monasevich et al.\textsuperscript{(151)} measured $A=1.75$ for the transformation strain with a constant stress of 50 MPa in a forged and hot-rolled Ti-50Ni (at.%) alloy. Mulder et al.\textsuperscript{(147)} measured the anisotropy of the transformation strain as ranging from 1.7 to 2.5 in a binary Ti-49.2Ni (at.%) alloy under constant loads of 100 MPa to 260 MPa.

The behaviour of the transformation strains $\varepsilon_2^{P\rightarrow M}$ and $\varepsilon_2^{M\rightarrow P}$ is very close to that of $\varepsilon_1^{P\rightarrow M}$. Thus, $\varepsilon_1^{M\rightarrow P} < \varepsilon_2^{M\rightarrow P} = \varepsilon_1^{P\rightarrow M} = \varepsilon_2^{P\rightarrow M}$. The permanent strain has a minimum of 0.04% (in the TD at 60°) through 0.05% (45°) and 0.07% (30°) to a maximum of 0.08% (in the RD). Compared with the warm-rolled 3AMT samples, the permanent strain ($\varepsilon_1^{P\rightarrow M} - \varepsilon_2^{M\rightarrow P}$) in the
cold rolled 5AMT samples is about 10 times smaller. As explained in previous section, the permanent strain depends on the resistance to the interphase boundary movement. In the 5AMT material, the amount of dislocations produced during the interphase boundary movement is much less than in the 3AMT material. This is most likely due to the lower resistance to the interphase boundary movement presented in the 5AMT material.

Table 5-2 The dependence of transformation temperatures ($M'_p$ and $A'_p$) under loading and the transformation hysteresis (hys.) on the loading direction (LD) in the cold-rolled 5AMT sample annealed at 500°C.

<table>
<thead>
<tr>
<th>LD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M'_p$</td>
<td>54.0°C</td>
<td>52.1°C</td>
<td>52.4°C</td>
<td>53.9°C</td>
<td>55.0°C</td>
</tr>
<tr>
<td>$A'_p$</td>
<td>76.7°C</td>
<td>77.9°C</td>
<td>75.8°C</td>
<td>74.2°C</td>
<td>71.8°C</td>
</tr>
<tr>
<td>hys.</td>
<td>22.7°C</td>
<td>25.8°C</td>
<td>23.4°C</td>
<td>20.3°C</td>
<td>16.4°C</td>
</tr>
</tbody>
</table>

From the thermal cyclic tests, the characteristic transformation temperatures, $A'_p$ and $M'_p$, and the transformation hysteresis under loading tests were determined and compiled in Table 5-2. The transformation temperatures and hysteresis are slightly dependent on the loading direction (a few degree difference) except in the TD, where the transformation hysteresis was considerably depressed to 16.4°C.
References
5.4 Anisotropic behaviour of cold-rolled material pre-annealed at 650°C (KR)

5.4.1 Anisotropic behaviour of material with post-rolling anneal

The cold-rolled Krupp material with a thickness reduction of 26% (KR52) was used. After rolling, the sheets were annealed at 500°C for 30 min. The anisotropy of the plateau stress, $\sigma_p$, plateau strain, $\varepsilon_p$, fracture stress, $\sigma_f$, and fracture strain, $\varepsilon_f$, was measured by tensile testing to fracture and is shown in Fig. 5.6. Both plateau strain and fracture strain have a maximum value at 30° to the RD, and a minimum value in the TD. The plateau stress and the fracture stress have a minimum value at 30° to the RD, and a maximum value in the TD. The fracture strain is generally regarded as a measure of the ductility for shape memory alloys\(^{(165)}\). For these KR52 samples, the fracture strain at 30° to the RD is 6 times higher than the strain in the TD, indicating a high anisotropy of ductility. The stress-strain curves are similar to the ones for the cold-rolled 5AMT sample shown in Fig. 5.4.

Thermal cyclic testing was performed where the constant loads for the samples 0°, 30°, 45°, 60° and 90° to the RD were 100 MPa, 88 MPa, 90 MPa, 102 MPa and 160 MPa, respectively. The maximum transformation strain was found at an angle of 30° to the RD, and the minimum strain was in the TD. The anisotropy factor of the transformation strains were

\[
\begin{align*}
\text{For } \varepsilon_{1}^{M \rightarrow P} & : A = 3.85/2.18 = 1.77; & \quad \text{For } \varepsilon_{1}^{P \rightarrow M} & : A = 5.20/2.84 = 1.83 \\
\text{For } \varepsilon_{2}^{M \rightarrow P} & : A = 4.81/2.68 = 1.79; & \quad \text{For } \varepsilon_{2}^{P \rightarrow M} & : A = 5.18/2.78 = 1.86
\end{align*}
\]

The anisotropy factor of the KR52 materials is thus close to that of the 5AMT samples.

![Fig. 5.6 Anisotropic behaviour of plateau stress, plateau strain, fracture stress and fracture strain in the cold rolled KR52 samples.](image_url)
The behaviour of the transformation strains $\varepsilon_{1}^{P\rightarrow M}$ and $\varepsilon_{2}^{P\rightarrow M}$ are similar to each other. A comparison of the four transformation strains shows that $\varepsilon_{1}^{M\rightarrow P} < \varepsilon_{2}^{M\rightarrow P} < \varepsilon_{1}^{P\rightarrow M} \approx \varepsilon_{2}^{M\rightarrow P}$. The permanent strain ($\varepsilon_{1}^{P\rightarrow M} - \varepsilon_{2}^{M\rightarrow P}$) varied from a minimum of 0.10% (in the TD) through 0.28% (at 60°) and 0.31% (at 45° and the RD) to a maximum of 0.37% (at 30°). The permanent strains are smaller than for the 3AMT samples and larger than for the 5AMT samples.

Table 5-3 The dependence of transformation temperatures ($M'_{p}$ and $A'_{p}$) under loading and the transformation hysteresis (hys.) on the loading direction (LD) in the cold-rolled KR52 sample annealed at 500°C.

<table>
<thead>
<tr>
<th>LD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M'_{p}$</td>
<td>65.0°C</td>
<td>65.4°C</td>
<td>65.1°C</td>
<td>66.0°C</td>
<td>67.4°C</td>
</tr>
<tr>
<td>$A'_{p}$</td>
<td>88.4°C</td>
<td>89.1°C</td>
<td>89.5°C</td>
<td>88.6°C</td>
<td>87.5°C</td>
</tr>
<tr>
<td>hys.</td>
<td>23.4°C</td>
<td>23.7°C</td>
<td>24.4°C</td>
<td>22.6°C</td>
<td>20.1°C</td>
</tr>
</tbody>
</table>

The characteristic transformation temperatures $A'_{p}$ and $M'_{p}$ and the transformation hysteresis under loading were determined and compiled in Table 5-3. The transformation temperatures are slightly dependent on the loading direction. For the loading direction along the TD, the hysteresis is 2° to 4° lower than in the other directions.

5.4.2 Anisotropic behaviour of the samples produced by a larger reduction per pass

KR52L sheets were produced by the same rolling process as the KR52 samples except that a larger thickness reduction per step was obtained and rolling was thus conducted in fewer steps. After rolling, the KR52L sheets were annealed at 500°C for 30 min. An approximately 50 µm thick surface layer with co-existing martensite and austenite phases was found at room temperature in the sheet rolled in 6 steps, while a fully martensitic structure was observed in the KR52 sheets rolled in 12 steps.

The difference between the KR52 and KR52L sheets in terms of unloading strain and transformation strain $\varepsilon_{1}^{P\rightarrow M}$ during thermal cyclic tests are negligible as can be seen in Fig. 5.7. Thus, the thickness of the two phase surface layer is apparently too small (less than 10% of the total thickness) to produce a significant difference.

5.5 Texture development due to tensile loading

The texture development in the martensite due to tensile loading along different angles to the RD was investigated for samples in three conditions: (1) before tensile testing; (2) unloading from the end of the stress-strain plateau; and (3) after completion of the first thermal cycle under constant load. The purpose for these measurements was to determine if the martensite texture is modified as a result of mechanical testing. It was found that the texture development in the cold rolled KR52 samples is very similar to that in the cold rolled 5AMT samples, compare Fig. 4.3b and 4.11c. Therefore, the texture development in two series of
the samples, the 5AMT samples and the 3AMT samples are presented here.

5.5.1 Cold rolled material

The pole figures of the martensite diffraction planes \{002\}_m, \{1\bar{1}1\}_m, \{020\}_m, \{111\}_m and \{022\}_m in the cold-rolled 5AMT samples with intermediate annealing at 500°C and post-rolling annealing at 500°C were measured. The martensite variants under the three conditions were qualitatively analyzed by comparing the pole figures with the stereographic projections for the monoclinic martensite NiTi phase. The residual strain upon unloading of the tensile test and thermal cyclic test is shown in Table 5-4, indicating the strain level during the texture measurement. The strain is a minimum in the TD and the difference in strain between tensile testing and thermal cyclic testing is higher in the RD and TD (ca. 1%) than in the other directions (ca. 0.5%).

Fig. 5.8 shows the \{1\bar{1}1\}_m pole figures of the samples before tensile testing (a) and after

<table>
<thead>
<tr>
<th>angle to RD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>after tensile test</td>
<td>4.02%</td>
<td>4.42%</td>
<td>4.49%</td>
<td>3.45%</td>
<td>1.60%</td>
</tr>
<tr>
<td>after thermal cyclic test</td>
<td>5.06%</td>
<td>4.90%</td>
<td>4.86%</td>
<td>4.09%</td>
<td>2.57%</td>
</tr>
</tbody>
</table>
Fig. 5.8 Martensite pole figures of the \{11\bar{1}\}_m diffraction plane in the 5AMT samples cold rolled and annealed at 500°C: (a) before testing; after thermal cyclic testing (b) 0°, (c) 45°, and (d) 90° to the RD. The Roman numerals (I, II, III, IV) in (c) indicate the quarters.
tensile testing with loading directions $0^\circ$ (b), $45^\circ$ (c), and $90^\circ$ (d) to the RD. The intensity contours in the pole figures differ considerably each other. For the sample before straining, 4 martensite texture components of $\langle 002 \rangle_{\langle 020 \rangle_m}$, $\langle 11\overline{1} \rangle_{\langle 2\overline{1}1 \rangle_m}$, $\langle 020 \rangle_{\langle 001 \rangle_m}$, $\langle 111 \rangle_{\langle 211 \rangle_m}$ were determined. Among them, the $\langle 111 \rangle_{\langle 211 \rangle_m}$ component is relatively weak. These four components include all 12 variants originating from the $\langle 110 \rangle_{\langle 1\overline{1}0 \rangle_p}$ austenite texture. The minor texture components originating from the $\langle 111 \rangle_{\langle 110 \rangle_p}$ can be seen from the direction in which the intensity contours spread. However, it is difficult to determine them because they are overlapped by the major texture components.

The results of the variants after loading are summarized in Table 5-5, which shows that the formation of the martensite variants after tensile testing thus depend on the loading direction. In the RD, the intensity in the centre of the $\langle 11\overline{1} \rangle_m$ becomes very weak, compared with the one before straining, which means that the variants 1, 2, 3’, 4 have disappeared. Similarly, the variants 6 and 6’ were found to be very weak by the analysis of the $\{002\}_m$ pole figure. In general, it can be concluded that the 6 variants (variant 1’, 2’, 3, 4’, 5 and 5’) remain after straining along the RD by considering the change of the intensity of all 5 pole figures.

<table>
<thead>
<tr>
<th>angle to RD</th>
<th>$0^\circ$</th>
<th>$30^\circ$, $45^\circ$ and $60^\circ$</th>
<th>$90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>after tensile test</td>
<td>1’,2’,3,4’,5,5’</td>
<td>1’,4’,5</td>
<td>ca. 12 variants</td>
</tr>
<tr>
<td>after thermal cycling test</td>
<td>1’,2’,3,4’,5,5’</td>
<td>1’,4’,5</td>
<td>ca. 12 variants</td>
</tr>
</tbody>
</table>

The pole figures after thermal cyclic testing along $30^\circ$ and $60^\circ$ are similar to the pole figure of $45^\circ$ in Fig. 5.10c and different from the pole figure in Fig. 5.10b. The intensities in the second and fourth quarter become very weak while the intensities in the first and third quarter are still high. The intensity is thus not symmetric along the horizontal and vertical lines of the pole figure, making it possible to distinguish the variants with the same texture component. For instance the texture component $\langle 111 \rangle_{\langle 211 \rangle_m}$ consists of four variants (1’, 2’, 3 and 4’), where each variant has a different contribution to a pole figure (see appendix II). In the pole figures of the samples with loading directions of $30^\circ$ or $45^\circ$, the remaining variants are 1’, 4’ and 5.

The variants 1’, 4’ and 5 are also present in the pole figure for the sample with the loading direction $60^\circ$ to the RD. However the intensities in the centre, the second and fourth quarter, and the top or bottom areas are higher than the ones in the samples with the loading direction at $30^\circ$ or $45^\circ$. This comes from the contribution of the other 9 variants. However, the intensities from these 9 variants are relatively low, considering all 5 pole figures. Therefore the major variants are 1’, 4’ and 5 and the amount of the other 9 variants originating from the $\langle 110 \rangle_{\langle 110 \rangle_p}$ increase.

For the pole figures with loading along the TD, the intensities become symmetric along the horizontal and vertical lines of the pole figure. All 12 variants originating from the $\langle 110 \rangle_{\langle 110 \rangle_p}$ texture seem to be present. Among them, the $\langle 002 \rangle_{\langle 010 \rangle_p}$ and $\langle 11\overline{1} \rangle_{\langle 2\overline{1}1 \rangle_m}$
components are stronger than the (020)[001]_m and (111)[211]_m components.

After completion of thermal cyclic testing the martensite texture was found to have, qualitatively, the same types of variants with the ones after the tensile testing. This conclusion was obtained by comparison of the pole figures measured after the tensile test with those measured after the thermal cyclic testing. Nevertheless, the textures after the thermal cyclic test are, however, more pronounced than those after tensile testing. This difference arises from the different conditions for variant growth in relation to the transformation strains $\varepsilon^{M\rightarrow P}_1$ and $\varepsilon^{P\rightarrow M}_1$, as explained in section 5.2. It can also be seen from the fact that the residual strain after thermal cyclic testing is larger than after tensile testing (Table 5-4). The variants after thermal cyclic testing grow to a higher extent than after tensile testing. Therefore, the textures are stronger and residual strain are larger after thermal cyclic testing.

### 5.5.2 Warm rolled sample

The pole figures of the martensite diffraction planes {002} _m, {111} _m, {020} _m, (111) _m and {022} _m in the warm-rolled 3AMT samples annealed at 500°C were measured. The residual strain upon unloading after tensile and thermal cyclic testing is shown in Table 5-6, indicating the strain level during the texture measurements. The minimum strain was found in the TD. The difference in strain between tensile testing and thermal cyclic testing is almost independent of the angle to the RD (ca. 1.3%).

**Table 5-6 The unloading strain after tensile and thermal cyclic testing in the warm rolled 3AMT samples with intermediate annealing at 500°C.**

<table>
<thead>
<tr>
<th>angle to RD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>after tensile test</td>
<td>4.02%</td>
<td>4.20%</td>
<td>4.02%</td>
<td>3.85%</td>
<td>3.02%</td>
</tr>
<tr>
<td>after thermal cyclic test</td>
<td>5.30%</td>
<td>5.58%</td>
<td>5.32%</td>
<td>5.08%</td>
<td>4.30%</td>
</tr>
</tbody>
</table>

Fig. 5.9 shows the (111) _m pole figures of the samples before tensile testing (a) and after thermal cyclic testing with loading directions 0° (b), 30° (c), and 60° (d) to the RD. The pole figures of the samples after loading along 45° and 90° to the RD are similar to the pole figures along 30° and 0°, respectively. In contrast to the pole figures of the cold-rolled 5AMT samples, the intensity in the centre of every pole figure of the warm-rolled 3AMT samples is considerably low, indicating that the texture components originating from the (110)[110]_p texture are very weak.

The martensite texture before straining, as discussed in section 4.2.3, consists of 7 main martensite texture components: (120)[211]_m, (120)[211]_m, (120)[001]_m, (102)[211]_m, (102)[010]_m, (102)[211]_m and (102)[010]_m. These components originate from the (111)[110]_p texture, as shown in Table 2-5. The variant development after loading is given in Table 5-7. After thermal cyclic testing, the texture depends on the loading direction. When the loading direction is along the RD, the intensity contours in the {111}_m pole figure in Fig. 5.9b were...
Fig. 5.9 Martensite pole figures of the \{11\bar{1}\}_m diffraction plane in the warm rolled 3AMT samples annealed at 500°C: (a) before testing; after thermal cyclic testing (b) 0°, (c) 30°, and (d) 60° to the RD. The Roman numerals (I, II, III, IV) in (c) indicate the quarters, and the numbers with or without prime indicate the variants.
attributed to the contribution of variants 1’, 3, 4’, 5, 5’ and 6. A comparison of the pole figures with the stereographic projections in Appendix II shows that this also fits the intensity distribution in other pole figures, i.e. the \{002\}_m, \{020\}_m, \{111\}_m and \{022\}_m pole figures. Among these variants, the variants 1’ and 6 are slightly stronger than the other variants because the maximum intensity is very close to the circle of \(\Psi=30^\circ\).

When the loading direction is 30° or 45° to the RD, the intensity is neither symmetrical along the horizontal nor the vertical line of the pole figure. The contours with high intensity are present in the first (I) and third (III) quarter, in which the number of quarter is defined in Fig. 5.9c. The variants were determined to be 1’, 3’ and 5. When the loading direction is 60° to the RD, the contours with high intensity of the \((11\bar{1})_m\) pole figure are present at \(\Phi = 0^\circ\) or 180°. The direction of spread of the intensity contours is along the rolling direction. The variants were determined to be 1, 1’, 3’, 4, 5 and 5’. Among these variants, the variants 1, 3’ and 4 are stronger than the variant 1’, 5 and 5’ because the intensity contours are closer to the axis \(\Phi = 0^\circ\) or 180°.

<table>
<thead>
<tr>
<th>angle to RD</th>
<th>0°</th>
<th>30°, 45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>after thermal cycling test</td>
<td>1’,3,4’,5,5’,6</td>
<td>1’,3’,5</td>
<td>1’,3’,4,5,5’</td>
<td>1’,3,4’,5,5’,6</td>
</tr>
</tbody>
</table>

A comparison of the pole figures measured after tensile testing with those after the thermal cyclic testing for the 3AMT samples shows a similar results for the 5AMT samples. Namely, the types of variants after thermal cyclic testing were found but they are stronger after thermal cycling. This reflects the presence of the residual strain.

5.6 Sample temperature change during tensile and thermal cyclic testing

A variation of the sample temperature was observed during tensile testing. Fig. 5.10 shows an example of the variation of the stress and sample temperature on strain during tensile testing at the RT. An external stress was applied with a constant crosshead speed of 2.5 mm/min until it reached 1.1 times the plateau stress, followed by unloading.

A rapid temperature increase of about 3°C from point A to point B was measured, which occurred during the process of detwinning and variant growth. This period took less than 1 second. The rapid temperature increase corresponds with the growth of the martensite variants from point A’ to B’. The growth rate of the martensite variants is thus high. This would lead to the increase of the sample temperature because there is not enough time to dissipate the heat to the environment.

Comparable results were reported for alloys with a two-stage transformation, by Mulder et
Chapter 6

Transformation Analysis

6.1 Results of Differential Scanning Calorimetry (DSC)

6.1.1 Example of DSC results for a cold-rolled sample

In this section, the differential scanning calorimetry (DSC) results for one of these samples, the cold-rolled KR52 sample with a thickness reduction of 26%, will be presented in detail. In the next section, the results for other samples will be reported and the thermal transformation characteristics compared.

a. The influence of annealing temperature: During the annealing process, the mechanical properties and the thermal transformation characteristics are considerably influenced by changes in the microstructure. Dislocations can be annihilated or rearranged, and therefore the dislocation density decreases on increasing annealing temperature.

The effect of annealing temperature on thermal transformation characteristics was investigated after annealing at various temperatures from 100°C to 700°C for 30 min. The DSC profiles of the second thermal cycle are shown in Fig. 6.1, in which the fluctuation of the curve during the reverse martensite transformation of the sample annealed at 400°C is due to the instability of the evaporated liquid nitrogen pressure. The transformation temperatures $M_s$, $M_p$, $M_f$, $A_s$, $A_p$, and the heat of transformation $Q_m$, $Q_a$ were determined using the method shown in Fig. 3.12 and are shown in Figs. 6.2 and 6.3.

For the as-rolled sample and the samples annealed at temperatures less than 300°C, the phase transformation peaks are not visible since severe deformation results in a high dislocation density and a high elastic stored energy, $H_{el}$. The high elastic stored energy would offset the chemical enthalpy change, $\Delta H_{ch}$, resulting from the structure change for both the martensite transformation and the reverse transformation. According to eqns. 2.6 and 2.7, the heats of transformation, $Q_a$ and $Q_m$, are thus small due to the high dislocation density. On the other hand, the elastic stored energy is a main cause for the transformation regions "$M_s - M_f$" and "$A_f - A_s$"\textsuperscript{110,111}. The high elastic energy, $H_{el}$ leads to a broad transformation region and a small peak height of the DSC peaks. The transformation peaks are thus too broad to be visible. However, the broadened peak does not mean that there is no transformation. From the XRD profile in Fig. 4.12 or the thermal cyclic testing (see b, following), the transformation has started at a temperature above RT.

Upon increasing the temperature to above 400°C, clear transformation peaks develop. The transformation temperatures $M_s$, $M_p$, $M_f$, $A_s$, $A_p$ and $A_f$ increase upon increasing the annealing temperature, see Fig. 6.2. The increase of the transformation temperatures are attributed to a decrease in dislocation density, as predicted by eqn 2.9. For the annealing temperatures
Fig. 6.1 The DSC profiles of the cold rolled KR52 samples with a thickness reduction of 26% annealed at various temperatures.

Fig. 6.2 The dependence of transformation temperature on annealing temperature in cold-rolled KR52 samples with a thickness reduction of 26%.
above the recrystallization temperature (600°C), the increase of the transformation temperature becomes slightly smaller.

It was found that the transformation temperature hysteresis slightly decreases upon increasing the annealing temperature. The frictional stress resisting interfacial movement is the main factor causing a transformation hysteresis (110). The frictional energy, \( E_{fr} \), should decrease with the increase of annealing temperature because annealing at a higher temperature results in easier interfacial movement. However, from the experimental results, one can see that the change in frictional energy with the annealing temperature increases is small. This indicates that the annealing temperature slightly influence the frictional barriers, for instance, interfacial boundaries, opposing interfacial movement.

The heats of transformation, \( Q_m \) and \( Q_a \), increase as the annealing temperature increases from 400°C to 700°C, see Fig. 6.3. The endothermic heat \( Q_m \) is close to but always higher than the exothermic heat \( Q_a \). The difference varied from about 1.0 mJ/mg to 4.0 mJ/mg which is 3-10% of the absolute value of the heats. This difference may reflect the existence of irreversible defects such as dislocations within martensite. This means that the contribution of the frictional energy, \( E_{fr} \), in equations 2.6 and 2.7 to the heats is very small compared with the elastic stored energy, \( H_{el} \).

**b. Determination of transformation temperature by thermal cyclic testing:** When the cold rolled KR52 sample was annealed at 300°C, a relatively low temperature, high internal stresses were still present. Therefore, the transformation temperatures could not be determined using X-ray diffraction at different temperatures or calorimetry, as discussed in sections 4.3.2 and 6.1.1a. The transformation temperatures can, however, be determined from
the strain-temperature curves of thermal cyclic testing in the sample annealed at 300°C. The reason for this is that a high elastic stored energy exists in the sample annealed at 300°C raising the difference of the transformation temperatures between $M'_s$ and $M'_f$ or $A'_s$ and $A'_f$. To obtain information concerning the transformation temperatures in this sample, thermal cyclic testing was conducted under 4 different constant loads: 50 MPa, 100 MPa, 150 MPa and 200 MPa, in which the temperature ranged from -40°C to 120°C.

The experimental results of thermal cyclic testing showed that the martensite transformation is not finished upon cooling to the lowest temperature possible in the chamber, -40°C. Thus only the $M'_s$ and $A'_f$ temperatures were thus determined. Using the transformation temperatures $M'_s$ and $A'_f$ under loading and a linear extrapolation of the temperatures on loading to zero stress, the $M_s$ and $A_f$ temperatures under stress-free conditions were found to be 49°C and 66°C, as shown in Fig. 6.4. This means that for the sample annealed at a low temperature, the martensitic transformation starts at a temperature above room temperature under the free-stress condition and does not finish at -40°C. The sample at RT thus has two co-existent phases, which agrees with the XRD patterns in Fig. 4.12.

c. The volume fraction of transformed martensite calculated from DSC curves: When the martensite transformation in a SMA occurs, the volume fraction of martensite is a function of the temperature. The ratio of the growth of the peak area to the total peak area is proportional to the degree of the transformation. The volume fraction $f(T_i)$ of the transformed phase in the DSC profiles can be calculated as follows:

$$f(T_i) = \frac{\sum_{i} (y_i \Delta t_i)}{S} = \frac{\sum_{i} (y_i \Delta T_i)}{SV}$$

![Fig. 6.4 The dependence of transformation temperature on applied load in a cold-rolled KR52 sample annealed at 300°C.](image)
where \( V \) is the heating or cooling rate which was kept constant during the DSC measurements, \( y_i \) stands for the measured heat flow (mJ/mg/sec) at temperature \( T_i \), and \( S \) for the whole area of the DSC peaks. Fig. 6.5 shows the change of volume fraction, \( f(T) \), of the martensite phase for the KR52 sample annealed at 500°C. Compared with the calculated results using the empirical eqn (2.11), in which the \( M_s \) and \( M_f \) temperature are from the measured DSC curve and the power \( n \) set to be 1 and 3, the best fitting curve between \( M_s \) (52.0°C) and \( M_f \) (41.9°C) is the one with \( n=1 \) instead of \( n=3 \) as suggested by Strotzki for NiTi alloys. This means that the power \( n \) in eqn (2.11) depends not only on the type of alloy and the measurement parameters, but also on the rolling process and subsequent heat treatment. When the sample is severely deformed or subsequent heat treatment is conducted at a low temperature, it is known that high elastic stored energy would lead to a broadened peak. The curve of volume fraction versus temperature thus becomes less steep. From the DSC profile in Fig. 6.1, the DSC peaks of the samples annealed at 500°C and 600°C are steeper than the peaks of the samples annealed at lower temperatures. Therefore, the higher the elastic stored energy, the lower the power \( n \) should be.

![Fig. 6.5](image)

**Fig. 6.5** The change of volume fraction \( f(\text{vol.}) \) during the martensite transformation for the KR52 sample annealed at 500°C. The curve (+) was calculated from the DSC curve of the second cycle; the curve (o) was calculated by the empirical formula where \( n=1 \); the curve (Δ) is from the empirical formula where \( n=3 \).

### 6.1.2 DSC results in the rolled samples

**a. Comparison:** In addition to the KR52 samples, DSC profiles were measured for the other samples in Table 3-2, annealed at various temperatures. Table 6-1 shows the transformation temperatures, hysteresis and heats of transformation of part of the samples annealed at 500°C.

The KR50, KR51 and KR52 samples had thickness reductions of 0%, 11% and 26%,
respectively. From the DSC results, an increase in the thickness reduction leads to a decrease of the transformation temperatures and a decrease of heat of transformation. This is due to the increase of the stored elastic energy, \( H_{el} \), as the thickness reduction increases. From the severely deformed KRE sample rolled at 200°C with a thickness reduction of 77%, the heats of transformation and the transformation temperatures are the lowest among all the samples in Table 6-1. The 3AMT samples rolled at 300°C have a relatively high hysteresis. The cold rolled 5AMT samples with intermediate annealing at 500°C has high transformation temperatures and a small hysteresis, indicating a low stored elastic energy \( H_{el} \) and a low frictional energy. For most of these samples, the heat of the martensite transformation, \( Q_m \), is always slightly higher than the heat of the reverse transformation, as explained in the previous paragraph. All of the \( M_s \) temperatures are between 40°C to 60°C, indicating that any test at RT is in the martensitic condition.

**b. Transformation characteristics of the KR50, KR51 and KR52 samples:** The KR50 and KR51 samples have less deformation than the KR52 samples. Therefore, DSC transformation peaks could be measured for lower annealing temperatures. Clear peaks were even measured for as-rolled samples. Figs. 6.6-6.8 show the dependence of transformation temperatures and heats of transformation for these two samples. Upon increasing the annealing temperature, the transformation temperatures decrease slightly to a minimum at the annealing temperatures 300°C - 400°C and then increase at the annealing temperatures above 400°C. This is consistent with the X-ray scanning results concerning the influence of annealing temperature.

### Table 6-1 A comparison of thermal transformation characteristics of the samples annealed at 500°C for 30 min. All of the results were determined from the DSC profiles of the second thermal cycle.

<table>
<thead>
<tr>
<th>sample reduction</th>
<th>KR50</th>
<th>KR51</th>
<th>KR52</th>
<th>KRE</th>
<th>3AMT*</th>
<th>5AMT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M_s (°C)</strong></td>
<td>59.4</td>
<td>53.4</td>
<td>52.0</td>
<td>43.8</td>
<td>47.6</td>
<td>56.9</td>
</tr>
<tr>
<td><strong>M_p (°C)</strong></td>
<td>49.1</td>
<td>43.7</td>
<td>46.0</td>
<td>30.3</td>
<td>35.0</td>
<td>51.0</td>
</tr>
<tr>
<td><strong>M_f (°C)</strong></td>
<td>41.1</td>
<td>38.5</td>
<td>41.9</td>
<td>18.5</td>
<td>26.6</td>
<td>41.8</td>
</tr>
<tr>
<td><strong>A_s (°C)</strong></td>
<td>64.4</td>
<td>65.4</td>
<td>61.4</td>
<td>39.8</td>
<td>50.3</td>
<td>61.9</td>
</tr>
<tr>
<td><strong>A_p (°C)</strong></td>
<td>79.1</td>
<td>78.0</td>
<td>71.7</td>
<td>54.6</td>
<td>67.2</td>
<td>73.1</td>
</tr>
<tr>
<td><strong>A_f (°C)</strong></td>
<td>87.0</td>
<td>83.6</td>
<td>76.8</td>
<td>68.3</td>
<td>74.9</td>
<td>83.6</td>
</tr>
<tr>
<td>hys.</td>
<td>34.3</td>
<td>30.0</td>
<td>25.7</td>
<td>24.3</td>
<td>32.2</td>
<td>22.1</td>
</tr>
<tr>
<td>( Q_m (J/g) )</td>
<td>-35.1</td>
<td>-32.7</td>
<td>-34.4</td>
<td>-18.7</td>
<td>-30.9</td>
<td>-28.9</td>
</tr>
<tr>
<td>( Q_a (J/g) )</td>
<td>34.0</td>
<td>33.6</td>
<td>30.9</td>
<td>17.6</td>
<td>28.3</td>
<td>28.7</td>
</tr>
</tbody>
</table>

* average value of three measurements
** in last step
Fig. 6.6 The dependence of transformation temperatures on annealing temperature for an as-received KR50 sample.

Fig. 6.7 The dependence of the transformation temperatures on annealing temperature for a cold-rolled sample (KR51) with a thickness reduction of 11%.
Fig. 6.8 The dependence of the heat of transformation on annealing temperature in (a) an as received KR50 sample; (b) a cold-rolled KR51 sample with a thickness reduction of 11%.
Chapter 6 Transformation analysis

on the XRD profiles, for which an example for the KR52 samples was shown in Fig. 4.12. The sharpest and highest \( \{110\}_p \) austenite peak is present when the annealing temperature is 300°C.

Martensite peaks were found in the XRD patterns at RT, but appeared to be no visible austenite peak. However, using a fitting program, a small amount of residual austenite was suspected. The presence of possible residual austenite phase was confirmed by cooling the sample below room temperature. For the KR51 as-rolled sample, the change of the peak areas as a function of the minimum temperature of cycling, 20°C, -20°C and -60°C, was determined to be

\[
\begin{align*}
\text{for } Q_a: & \quad 6.55 \text{ mJ/mg (20°C)} \quad 7.34 \text{ mJ/mg (-20°C)} \quad 8.94 \text{ mJ/mg (-60°C)}; \\
\text{for } Q_m: & \quad 8.45 \text{ mJ/mg (20°C)} \quad 9.03 \text{ mJ/mg (-20°C)} \quad 9.13 \text{ mJ/mg (-60°C)};
\end{align*}
\]

At lower minimum temperatures, higher heats of transformation are measured, indicating the transformation of residual austenite.

c. Transformation characteristics during the rolling process: After each rolling step, samples were cut to measure texture development and the transformation temperatures. Fig. 6.9 shows the variation of thermal transformation temperatures during the rolling process for the cold-rolled 5AMT samples with intermediate annealing at 500°C. The variation of the hardness, thickness reduction and texture development of this sample was shown in Fig. 4.6. The transformation temperatures are not influenced by the rolling process. This is due to the fact that the same hardness was obtained after each intermediate anneal.

6.1.3 The effect of heating and cooling rate

The effect of heating and cooling rate on the transformation characteristics was investigated for the KR51 samples annealed at 500°C and 700°C. Thermal transformation characteristics were investigated by the DSC for heating and cooling rates of 1°C/min, 3°C/min, 10°C/min, 20°C/min, 40°C/min, and a temperature range from -20°C to 120°C for two cycles. Fig. 6.10 shows typical DSC profiles of the second thermal cycle for the KR51 samples annealed at 700°C.

a. Transformation temperatures: The reverse transformation temperatures increase as the heating or cooling rate increases, see Figs. 6.11 - 6.12. The start temperature, A\(_s\), increases slightly (several degrees) while the finish temperature, A\(_f\), and peak temperature, A\(_p\), increase by about 20°C, indicating that the transformation becomes slower upon increasing the rates. For the martensitic transformation, the tendency is the opposite, namely, the transformation temperatures decrease as the cooling rate increases. The transformation hystereses increased substantially upon increasing the rates, as a result of the increase of the A\(_p\) temperature and the decrease of the M\(_p\) temperature. The transformation temperatures of the recrystallized sample (700°C anneal) are always higher than those of the sample before recrystallization (500°C anneal). This is due to the decrease in hardness after recrystallization.

The transformation temperatures can be adequately determined by extrapolating the
Fig. 6.9 The variation of the transformation temperatures during the rolling process for the cold-rolled 5AMT samples with intermediate annealing at 500°C.

Fig. 6.10 DSC profiles of the KR51 sample annealed at 700°C, measured at heating and cooling rates of 1°C/min, 3°C/min, 10°C/min, 20°C/min and 40°C/min, respectively.
Fig. 6.11 The dependence of transformation temperatures and hysteresis on heating or cooling rate in the cold-rolled KR51 sample annealed at 500°C.

Fig. 6.12 The dependence of transformation temperatures and hysteresis on heating or cooling rate in the cold-rolled KR51 sample annealed at 700°C.
temperatures to "zero" rate of heating or cooling, using a linear function. A comparison of
the transformation temperatures at "0°C/min" and at a rate of 10°C/min is shown in Table 6-
2. There is only a slight change (0.4°C to 2.6°C) of the start temperatures $A_s$ and $M_s$.
However, the change of the finish temperatures, $M_f$ and $A_f$ (4.0°C to 8.0°C) with respect of
the rates is significant. Therefore, for practical applications of these SMAs the effect of the
heating and cooling rate should be taken into account.

Table 6-2 A comparison of the transformation temperatures obtained by linearly
extrapolating the temperatures to a rate of "0°C/min" with the transformation temperatures
measured at a rate 10°C/min for KR51 samples heat treated at 500°C or 700°C for 30 min.

<table>
<thead>
<tr>
<th>Heat-treatment</th>
<th>rate</th>
<th>$M_s$</th>
<th>$M_f$</th>
<th>$A_s$</th>
<th>$A_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>0°C/min</td>
<td>54.1°C</td>
<td>47.9°C</td>
<td>62.8°C</td>
<td>73.8°C</td>
</tr>
<tr>
<td></td>
<td>10°C/min</td>
<td>53.4°C</td>
<td>38.5°C</td>
<td>65.4°C</td>
<td>83.6°C</td>
</tr>
<tr>
<td></td>
<td>difference</td>
<td>0.7°C</td>
<td>9.4°C</td>
<td>2.6°C</td>
<td>9.8°C</td>
</tr>
<tr>
<td>700°C</td>
<td>0°C/min</td>
<td>61.3°C</td>
<td>53.7°C</td>
<td>69.1°C</td>
<td>81.5°C</td>
</tr>
<tr>
<td></td>
<td>10°C/min</td>
<td>61.7°C</td>
<td>47.5°C</td>
<td>70.4°C</td>
<td>87.5°C</td>
</tr>
<tr>
<td></td>
<td>difference</td>
<td>0.4°C</td>
<td>5.8°C</td>
<td>1.3°C</td>
<td>4.0°C</td>
</tr>
</tbody>
</table>

b. Heats of transformation: The heats of transformation, $Q_A$ and $Q_M$, are almost independent
of the rates, see Fig. 6.13. This independence was also observed by other authors for a NiTi
alloy\textsuperscript{(121)} as well as for other materials\textsuperscript{(122)}. The measured values of the heats for the sample annealed at 700°C (around 40 mJ/mg) is higher than (around 40 mJ/mg) for the sample annealed at 500°C. This is a result of grain growth in the recrystallized sample, which would decrease the elastic stored energy, $H_{el}$. The values of the heat of transformation are a little higher than the 25 to 35 mJ/mg which was reported by other authors for a NiTi alloy\textsuperscript{(121)}. The absolute value $Q_M$ is about 5% higher than $Q_A$. The difference may come from the dislocation density in martensite phase, as explained in section 6.1.1.

Some authors\textsuperscript{(121)} suggested that the presence of R-phase is responsible for the difference between $Q_A$ and $Q_M$ in a NiTi alloy. In order to detect the presence of R-phase, the sample was further annealed at 500°C for 150 hours. According to Goubaa \textit{et al}\textsuperscript{(76)}, long term annealing would increase the difference between the nucleation temperatures of R-phase and martensite, and a shoulder would appear on the peak upon cooling in DSC profile. However, the shoulder did not appear in this Ti-Ni-Cu alloy, indicating that the R-phase transformation does not occur.

c. The shape of DSC profiles: The Kissinger shape indices which describe the shape of the DSC profiles, $K_m$ and $K_a$, were calculated using eqn 3.2. The dependence of Kissinger shape index on the rate reaches a maximum value at 10°C/min for the KR51 sample annealed at 500°C, see Fig. 6.14 whereas the index has a tendency to increase with increasing rates for the sample heat treated at 700°C. This is quite different from the results of other authors\textsuperscript{(121)} who concluded that the Kissinger shape index decreases as the rate increases. The Kissinger index of the austenite peak is larger than that of martensite, which might be associated with the difference of the heats of transformation.

d. Calculation of the activation energy: According to eqn 2.12, the activation energy, E, for the transformation can be obtained whenever the peak temperature at various rates are known. Fig. 6.15 shows the relationship of $\ln(V/T^2)$ versus $1/T$, in which T is regarded to

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig6_14}
\caption{The dependence of heating or cooling rate on Kissinger shape index in the cold-rolled KR51 samples.}
\end{figure}
Fig. 6.15 The relationship of $\ln(V/T^2)$ versus $1/T$ in the KR51 sample annealed at 500°C (solid lines) and 700°C (broken lines). The activation energy $E$ is determined from the slope of the regressed line.

be the peak temperature, $A_p$ or $M_p$. The activation energies were determined from the slope of the linear regression line, and are compiled in Table 6-3.

The activation energy of the sample annealed at 700°C is higher than the sample annealed at 500°C. The activation energy reflects the ease of the transformation. A higher activation energy means that the transformation needs to overcome a higher energy barrier. Therefore, the transformation range, $A_s - A_f$ or $M_f - M_s$, would become larger in the sample annealed at 700°C than in the sample annealed at 500°C. This is in agreement with the experimental results.

Table 6-3 Results of the calculation of activation energy $E$ and pre-exponential index $k_0$ for the KR51 samples.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Martensitic transformation</th>
<th>Reverse transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$</td>
<td>$k_0$</td>
</tr>
<tr>
<td>500°C</td>
<td>-146.93 kJ/mol</td>
<td>$-2.0\times10^{-59}$ (1/s)</td>
</tr>
<tr>
<td>700°C</td>
<td>-371.05 kJ/mol</td>
<td>$-6.2\times10^{-25}$ (1/s)</td>
</tr>
</tbody>
</table>
6.2 Results of X-ray Diffraction (XRD)

6.2.1 XRD measurements at various temperatures

X-ray diffraction measurements were made at various temperatures in order to support the DSC work. Cold-rolled KR52 samples annealed at 300°C and 500°C were heated from RT to 250°C and then cooled. In the vicinity of the expected transformation temperatures, measurements were conducted with small temperature intervals of 10°C. At temperatures farther from the transformation temperature, temperature intervals of 30°C ~ 50°C were used.

The transformation temperature was determined from the appearance or disappearance of diffraction peaks of the phase of interest. The volume fraction of the phase was determined from the change of the intensity of the {110}_p diffraction peaks. The volume fraction of the austenite phase \( f_a(T) \) during phase transformation analysis was estimated as follows:

\[
f_a(T) = \frac{I(T)}{I(T_o)} \times 100\%
\]  

(6.1)

where \( I(T_o) \) is the intensity at a temperature above \( A_t \) for a fully austenite phase and \( I(T) \) is the intensity at a temperature where the austenite phase is present.

For the cold-rolled KR52 sample annealed at 500°C, use of the {110}_p austenite peak or {002}_m, {111}_m, {020}_m, {111}_m martensite peaks resulted in the following transformation temperatures: \( A_s \) about 60°C, \( A_f \) about 80°C, \( M_s \) between 50°C and 60°C, \( M_f \) about 40°C. These results are consistent with the DSC measurements in Fig. 6.1, where the temperatures are \( A_s = 61°C, \ A_f = 77°C, \ M_s = 52°C, \ M_f = 41°C \). The volume fraction \( f_a(T) \) was calculated as follows:

For heating: \( f_a(20°C)=1.5\%, \ f_a(60°C)=2.5\%, \ f_a(70°C)=86.6\%; \ f_a(80°C)=99.9\%; \)

For cooling: \( f_a(60°C)=99.9\%, \ f_a(50°C)=10.9\%, \ f_a(40°C)=1.9\% \).

On cooling to 50°C, the diffraction peaks from both monoclinic martensite and cubic austenite were observed, indicating the co-existence of two phases. The \( \{110\}_p \) peak is 'split' into four martensite peaks of \( \{002\}_m, \{111\}_m, \{020\}_m \), and \( \{111\}_m \).

For the sample annealed at 300°C, the XRD patterns show a narrow peak at the \( \{110\}_p \) position and a small peak at the \( \{111\}_m \) position, see Fig. 6.16. The DSC peaks for the sample annealed at 300°C (Fig. 6.1) are diffuse and the characteristic parameters can not be clearly discerned from the DSC profiles. These two phenomena are a consequence of the effect of work hardening which considerably lowered the heats of transformation and broadened the transformation range. From the measurement of the XRD at various temperatures, the austenite peak at the \( \{110\}_p \) position becomes sharper with increasing temperature. According to the relative change of the small \( \{111\}_m \) peak which is partially overlapped by the \( \{110\}_p \) peak, the martensite start temperature \( M_s \) was estimated to be 50°C and the austenite finish temperature \( A_f \) to be 80°C. These temperatures are roughly close to the temperatures extrapolated to be zero stress from the thermal cyclic testing under various loads, in which
Fig. 6.16 XRD patterns of the cold rolled KR52 sample annealed at 300°C, measured at various temperatures: RT, 50°C, 60°C, 70°C, 80°C, and 150°C. Each pattern was shifted up 500 counts for comparison purposes.
$M_s = 49^\circ C$ and $A_f = 68^\circ C$ as shown in Fig. 6.4. The change of volume fraction of the {110}$_p$ peak was calculated as follows:

For heating: $f_a(20^\circ C)=37.1\%$, $f_a(60^\circ C)=61.2\%$; $f_a(80^\circ C)=86.4\%$;
For cooling: $f_a(60^\circ C)=94.1\%$, $f_a(40^\circ C)=63.3\%$, $f_a(20^\circ C)=45.1\%$.

### 6.2.2 Determination of lattice parameters

The lattice parameters of the parent phase and martensite phase are of great importance for the calculation of the transformation strains. It is known that the lattice parameters for the Ti-45Ni-5Cu(at.\%) alloy are very close to the published values for NiTi alloys (section 2.1c). Nevertheless, the lattice parameters were determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) to confirm the published data. Interplanar distances were determined using Bragg’s law with $\lambda = 0.17902$ nm (CoK$\alpha$ radiation). A least squares method, i.e. minimization of the deviation from the measured results and calculated results, was used to calculate the lattice parameters.

The XRD patterns shown in Figs. 4.1 and 4.2 for the cubic austenite and monoclinic martensite phases, respectively, were used to calculate the lattice parameters. Because texture was present in the KR50 material, the diffraction peaks were found at particular positions by rotating and tilting of the sample on the texture goniometer. The Bragg angle ($2\theta$ value) measured at $120^\circ C$ was determined to be $49.56^\circ$ for (110)$_p$, $72.74^\circ$ for (200)$_p$, and $92.91^\circ$ for (211)$_p$. The cubic austenite lattice parameter was thus determined to be $a_o = 0.3021$ nm, which is very close to the published results, see Table 6-4.

For the monoclinic martensite phase in the as-received KR50 material, ten diffraction peaks were indexed with the help of the known monoclinic martensite crystal structure. Using the least squares method, the lattice parameters were calculated, as shown in Table 6-4. The lattice parameters of the other samples were calculated and they are close to those of the as-received KR50. For instance, the lattice parameters of the KR52 samples annealed at $500^\circ C$ were determined, as shown in Table 6-4.

The variation of the lattice parameters would influence the amount of calculated transformation strain. Table 6-4 lists an example for the strain deformed along [100]$_p$, [110]$_p$, and [111]$_p$ for the correspondence variant 1, in which the strain was calculated using eqns. 2.21-2.23. It was found that slight differences in lattice parameters would influence the strain.

### 6.3 Results of Transmission Electron Microscopy (TEM)

#### 6.3.1 Determination of lattice parameters and existing phases

Lattice parameters were also determined by TEM. The diffraction patterns of the parent austenite phase in the KR52 sample were measured at a temperature above $A_f$ by means of a heating attachment in the microscope. The interplanar distance $d_{hkl}$ is determined from the
Chapter 6 Transformation analysis

Table 6-4 Lattice parameters of the austenite cubic phase \((a_o)\) and the martensite monoclinic phase \((a, b, c, \beta)\) determined by XRD and TEM, and compared with published values. \(\varepsilon[111]\) represents the calculated transformation strain for the correspondence variant \(1\). The volume change is \(\Delta V/V_p = (V_m - 2V_p)/2V_p \times 100\%\), in which the volume in the martensite cell \(V_m = abc \sin(\beta)\), \(V_p = a_o^3\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>KR50</th>
<th>XRD</th>
<th></th>
<th>KR52</th>
<th>TEM</th>
<th>Published*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_o) (nm)</td>
<td>0.3021</td>
<td>0.3020</td>
<td></td>
<td>0.2991</td>
<td>0.3015</td>
<td></td>
</tr>
<tr>
<td>(a) (nm)</td>
<td>0.2925</td>
<td>0.2908</td>
<td></td>
<td>0.2886</td>
<td>0.2889</td>
<td></td>
</tr>
<tr>
<td>(b) (nm)</td>
<td>0.4144</td>
<td>0.4162</td>
<td></td>
<td>0.4079</td>
<td>0.4120</td>
<td></td>
</tr>
<tr>
<td>(c) (nm)</td>
<td>0.4635</td>
<td>0.4601</td>
<td></td>
<td>0.4579</td>
<td>0.4622</td>
<td></td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>96.3</td>
<td>96.2</td>
<td></td>
<td>96.7</td>
<td>96.8</td>
<td></td>
</tr>
<tr>
<td>(\Delta V/V_p)</td>
<td>1.27%</td>
<td>0.50%</td>
<td></td>
<td>0.04%</td>
<td>-0.341%</td>
<td></td>
</tr>
<tr>
<td>(\varepsilon[100])</td>
<td>2.90%</td>
<td>2.72%</td>
<td></td>
<td>2.51%</td>
<td>2.68%</td>
<td></td>
</tr>
<tr>
<td>(\varepsilon[110])</td>
<td>8.49%</td>
<td>7.73%</td>
<td></td>
<td>8.25%</td>
<td>8.40%</td>
<td></td>
</tr>
<tr>
<td>(\varepsilon[111])</td>
<td>9.81%</td>
<td>9.01%</td>
<td></td>
<td>9.84%</td>
<td>9.79%</td>
<td></td>
</tr>
</tbody>
</table>

* From Ostuka et al\(^{(51)}\).

camera length \(2\lambda L\)\(^{(201)}\):
\[
d_{hkl}D = 2 \lambda L = \text{constant}
\]

where \(D\) is the distance between two spots on the film, \(\lambda\) is the electron wavelength and \(L\) is the distance of the specimen from the screen or plate. A diffraction pattern of the precipitate of f.c.c. Ti\(_2\)Ni was used as an internal calibration of the camera length, in which the lattice parameter \(a_o = 1.1278\) nm\(^{(202)}\). Fig. 6.17-(a) shows a TEM pattern of the austenite phase with a [110]\(_p\) zone axis. The lattice parameter \(a_o\) of the austenite phase in KR52 specimen was thus determined to be 0.2991 nm.

The TEM patterns of the martensite phase in the cold rolled KR52 sample annealed at 500°C were measured at room temperature, while the different patterns were found by tilting the sample. The diffraction patterns are shown in Fig. 6.17-(b) and (c). One pattern (b) was determined to have a [100]\(_m\) axis after tilting of the sample 34° and another pattern (c) a [1\(\bar{1}\)0]\(_m\) axis after tilting -19°. The lattice parameters of the monoclinic martensite phase were thus determined by measuring the distance between two \{hkl\} reflections or/and the interplanar angles, which is:

\[
a = 0.2858\ \text{nm}, \ b = 0.4079\ \text{nm}, \ c = 0.4579\ \text{nm}, \ \beta = 96.7°
\]
Fig. 6.17(a,b,c): TEM photos
The angle between \([100]_m\) and \([1\bar{1}0]_m\) was calculated to be 54.96° using eqn. A1.3, which is in good agreement with the total tilt angle \(34° - (-19°) = 53°\).

During cooling of the TEM sample from high temperature to RT, a characteristic electron diffraction pattern of the R-phase with a zone axis of \([111]_p\) was observed, as shown in Fig. 6.18. The pattern resembles that of a distorted b.c.c. cell due to the rhombohedral distortion, accompanied with extra spots at the 1/3 and 2/3 positions. The lattice parameters were determined as \(a = 0.3015\) nm and \(\alpha = 89.5°\), which are very close to the published results from Ling et al\(^{[67]}\).

The lattice parameters determined by TEM are shown in Table. 6-4 along with the calculated transformation strains for variant 1 using these lattice parameters. These are compared with the published results from Otsuka et al\(^{[51]}\). The difference between the measured values and published values is relatively small. However, this small variation of lattice parameters could lead to differences in the calculated transformation strains of \(\varepsilon[111]\), \(\varepsilon[110]\) and \(\varepsilon[100]\). The lattice parameters obtained by different techniques, TEM or XRD, differ. The discrepancy might arise from the different internal stress condition in the thin foil and bulk sample and the presence of macrostresses as well as microstresses in the sample. In this thesis, Ostuka’s lattice parameters will be used for the calculation of transformation strains and stereographic projections because the measured parameters are consistent with those of Ostuka.

### 6.3.2 Microstructure

Microstructural changes such as twinning, phase morphology, and dislocation substructure can affect the shape memory properties. TEM studies were conducted in order to investigate the microstructural changes occurring during annealing of cold rolled material (KR52).

In the cold-rolled KR52 sample annealed at 500°C, pronounced martensite twinning in bright field is seen in Fig. 6.19. The twinning was determined to be a \([111]\) type I twin, which is the same type determined in NiTi alloys by other authors, e.g. Tadaki et al\(^{[203]}\) or Beyer\(^{[204]}\). An \([001]\) compound twinning was also observed in this sample.

Fig. 6.20 shows a typical diffraction pattern of martensite and its morphology in the KR52 sample annealed at 500°C. From Fig. 6.20a, a small amount of austenite phase was observed although the \(M_f\) temperature for this sample is higher than RT, indicating the presence of residual austenite. These observations are in good agreement with the XRD and DSC measurements. From Fig. 6.20b, three martensite variants were determined from the diffraction pattern together with the pattern with \([111]\) zone axis of retained B2 phase. Two of these three martensite variant have \([1\bar{1}0]_m\) axis and the third one has a \([001]_m\) axis. Such diffraction patterns with multi-variants were often observed, which is consistent with the texture measurement. Although the TEM only can reveal information from local areas, observation of many regions can give an indication of the general orientation of the observed texture.

The morphologies and diffraction patterns of specimens taken from different parts of the sheet confirmed the results from the DSC, XRD and thermal cyclic tests that both the martensite
Fig. 6.18 Diffraction pattern for R-phase with zone axis of [111] in the cold rolled KR52 sample annealed at 500°C.

Fig. 6.19 Diffraction pattern showing a \{111\} type I twinning in cold rolled KR52 sample annealed at 500°C.
Fig. 6.20a A typical martensite morphology in the cold rolled KR52 sample annealed at 500°C (×50k, bright field).

Fig. 6.20b A typical multi-variants diffraction pattern in cold rolled KR52 sample annealed at 500°C.
and austenite phases co-exist at room temperature, as shown in Fig. 6.21a and 6.21b. The dislocation density in this material is higher than in the specimen annealed at 500°C. It is clear that there is more retained austenite in the KR52 sample annealed at 300°C than the sample annealed at 500°C, as compared to Fig. 6.20a.

6.4 Phase Transformation Sequence

The martensitic transformation was followed in the Ti-45Ni-5Cu (at.%) shape memory alloy by thermal cyclic testing under constant load and DSC measurements. Ordered cubic (B2) austenite and monoclinic martensite structures were found.

From the thermal cyclic testing under constant load, see solid curves in Fig. 6.23, it appears that only the one-stage transformation B2 → B19' martensite transformation occurred. However, from the TEM observations, the R-phase was observed and determined during cooling of a thin TEM specimen, indicating the occurrence of a two-stage transformation B2 → R-phase → B19'. Similar experimental phenomena, i.e. different transformation sequences detected by using different techniques, were also reported by Fukuda et al.\(^{(74,75)}\) and Goudaa et al.\(^{(76)}\). To clarify this problem, the measurement results were further analyzed. In Fig. 6.23, there is no additional change of the strain during the martensite transformation for the material annealed at 500°C. In the case of the B2 → R-phase transformation, the strain-temperature curve would show a step shape of the curve, as the broken line in Fig. 6.23 shows. This step-like curve has been measured in various NiTi alloys\(^{(105)}\). It has been known that the external load would increase the \(M_s\) temperature. However, the R-phase transformation temperature \(T_R\) is less sensitive to the external load. The external stress would thus make the temperature difference (\(M_s - T_R\)) larger.

Another method used to reveal B2 → R-phase was to decrease the \(M_s\) temperature by decreasing the annealing temperature. A strain-temperature curve for the KR52 sample annealed at 300°C shows no additional change of strain, see Fig. 6.23. From the DSC curve, no clear B2 → R-phase transformation takes place. Therefore the B2 → R-phase transformation should not occur when an external load is applied.

According to Matsumoto\(^{(68)}\), the precise thermal analysis by differentiation of the DSC curves is helpful in detecting the transformation from B2 to intermediate R-phase if the heat of transformation is small. Taking the KR52 sample annealed at 500°C as an example, the DSC curve during cooling (solid line) and the first derivative of the curve (broken line) are shown in Fig. 6.22. From the DSC curve, there is a small shoulder right before the peak appears. It was suspected that this was due to the transformation from B2 to R-phase. However, from the differentiated curve, this shoulder does not become an overlapping peak, as expected if R-phase is present\(^{(68)}\). This shoulder may be attributed to an inhomogeneity in the stress field, which could be produced by rolling or cutting of the sample, leading to a deviation of the transformation temperatures.

However, the R-phase was observed by TEM, which seems to be contradictory with the results from the DSC measurements and the thermal cyclic tests under constant load. To
Fig. 6.21a Bright field morphology in the cold rolled KR52 sample annealed at 300°C, in which bright area indicates martensite phase. (×15k)

Fig. 6.21b Dark field morphology in the cold rolled KR52 sample annealed at 300°C. (×15k)

Fig. 6.21c Diffraction pattern of martensite phase and austenite phase in the cold rolled KR52 sample annealed at 300°C.
Chapter 6 Transformation analysis

Fig. 6.22 The DSC profile and the first derivative during cooling for the KR52 sample annealed at 500°C.

Fig. 6.23 The dependence of strain on temperature during cooling for the KR52 samples annealed at 300°C and 500°C. Loading direction is along the RD. The temperature in the figure is the annealing temperature.
explain a similar phenomena, Fukuda et al\(^{(74, 75)}\) attributed this to a small starting transformation temperature difference between the B19 phase and B19’ phase. Goudaa et al\(^{(76)}\) detected the existence of R-phase by changing techniques, the annealing temperature and time. However, the results from Goudaa et al did not show a fully separate XRD peak. Neither Fukuda et al nor Goudaa et al mentioned the effect of thin foils on the TEM observation on the investigation of phase transformation. In fact, the results from the TEM observations are generally not exactly the same as the results for the bulk samples. The difference in martensite transformation temperature in a bulk specimen and a thin foil was experimentally determined using TEM by Kuninori et al\(^{(205)}\) in a Ti-50.2Ni (at.\%) shape memory alloy. The \(M_s\) temperature of a thin foil is considerably lower than that of a specimen in the bulk state. However, Kuninori et al did not give further explanation.

There are several possible differences between the thin foil sample and the bulk which could lead to the observed discrepancies. (1) The dislocation structure changes by the thinning of the sample. On the one hand, the dislocations may be introduced by mechanical deformation during handling of the foil. On the other hand, when the sample is thinned, the dislocations may disappear or rearrange themselves due to relaxation of long range stresses\(^{(206)}\). In the latter case, the \(M_s\) temperature would be depressed and the austenite phase stabilized. The R-phase (or B19’ martensite according to Fukuda et al\(^{(74, 75)}\)) would appear. (2) The SMAs undergo a martensitic transformation produced by shear, which would produce large stresses in the surrounding matrix. These stresses are easily relaxed at the surface of a thin foil specimen and the transformation there is not necessarily typical of bulk material. This may result in the presence of the R-phase equivalent with surface martensite because the R-phase is a slight rhombohedral distortion of the B2 structure and can be easily deformed as compared with the B19’ monoclinic martensite structure.

Based on the discussion above, it does not seem likely that the R-phase would form during cooling in a normal bulk sample. Evidence from the TEM observations is not sufficient to establish the presence of the R-phase because the specimen geometry influences the results. For the shape memory properties of the Ti-45Ni-5Cu (at.\%) SMA in this thesis, the presence of the R-phase may influence the properties of thin foil applications and thus further investigation is needed.
Chapter 7

Calculation of the Anisotropic Behaviour of Transformation Strains

7.1 Introduction

The anisotropy of the transformation strain as measured by thermal cyclic testing can be calculated using the results from the texture measurements. To calculate the transformation strain based on texture analysis, four different methods were used. The information used for each method is compiled in Table 7-1. The first two methods are based on single crystal data whereas the other two use inverse pole figures.

Table 7-1 Information used for the calculation of transformation strain for each of four methods, where \( R_y \) is the intensity of the calculated inverse pole figure, \( \varepsilon_s \) is the strain calculated from single crystal alloys, \( P \) is the parent austenite phase and \( M \) is the martensite phase.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Texture</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>components (P)</td>
<td>max ( \varepsilon_s^{P\rightarrow M} )</td>
</tr>
<tr>
<td>2</td>
<td>components (M)</td>
<td>average ( \varepsilon_s^{P\rightarrow M} )</td>
</tr>
<tr>
<td>3</td>
<td>( R_y ) (P)</td>
<td>max ( \varepsilon_s^{P\rightarrow M} )</td>
</tr>
<tr>
<td>4</td>
<td>( R_y ) (P)</td>
<td>( \varepsilon' ) (modified Taylor model)</td>
</tr>
</tbody>
</table>

The martensite transformation strains measured in the first thermal cycle, \( \varepsilon_1^{P\rightarrow M} \), were used for comparison with the calculated transformation strain based on analysis of the textures measured on the sample after that transformation. The cold rolled 5AMT samples and the warm rolled 3AMT samples were used for calculations because the anisotropic behaviour and textures for these two series of samples are significantly different.

7.2 Calculation of transformation strains using single crystal data

7.2.1 Calculation based on maximum transformation strain (method 1)

As mentioned in section 2.4.4, the transformation strain in single crystals can be calculated using the phenomenological theory of the crystallography of martensite transformations, see eqns. 2.23-2.25. The anisotropy of the transformation strain in single crystal SMAs was experimentally determined and found to be in good agreement with the calculated strain.
Therefore, many authors\(^\text{(147,148,178)}\) used single crystal data to explain the anisotropic behaviour of transformation strain in polycrystalline SMAs, as a first approximation. In this work, the dependence of the calculated transformation strains on the angle to the RD in single crystal NiTi alloys is shown in Figs. 7.1 and 7.2 for all correspondence variants originating from the (110)[1\Bar{1}0]_p and (111)[1\Bar{1}0]_p texture components. For the (110)[1\Bar{1}0]_p component, the correspondence variant(s) with the maximum transformation strain are 5 at angles between 0° to 35°, and 1’ and 4’ at angles between 35° and 90°. For the (111)[1\Bar{1}0]_p component, the variant(s) with the maximum strain are 3’ at angles between 0° to 30°, 5’ at angles between 30° to 60°, and 5 at angles between 60° to 90°.

Fig. 7.3, which is based on Figs. 7.1 and 7.2, shows the dependence of the maximum calculated transformation strain on the angle to the RD for the (110)[1\Bar{1}0]_p (line 1) and (111)[1\Bar{1}0]_p texture components (line 2). As mentioned in section 4.2.1, the texture in the 5AMT sample was determined to be a mixture of the (110)[1\Bar{1}0]_p and (111)[1\Bar{1}0]_p components. The maximum transformation strain in line 3 was calculated by a rule of mixtures type sum using 55% of line 1 and 45% of line 2, where the ratio of 55% and 45% was estimated from the analysis of the orientation density of each component. The anisotropy parameter A of the maximum strain in single crystals was calculated to be

\[
\begin{align*}
\text{for the (110)[1\Bar{1}0]_p component} & \quad A = 10.64/2.68 = 3.97 \\
\text{for the (111)[1\Bar{1}0]_p component} & \quad A = 10.01/8.40 = 1.19 \\
\text{for the mixture component} & \quad A = 10.35/5.78 = 1.79
\end{align*}
\]

The calculated transformation strain was compared with the measured transformation strain, \(\varepsilon_{\text{P→M}}\), in the 3AMT samples in Fig. 5.3 and the 5AMT samples in Fig. 5.5. For both samples, the anisotropic parameter A (A=1.24 for the 3AMT samples and A=1.83 for the 5AMT samples) is close to the calculated ones (A=1.19 and 1.79). The variation of the measured transformation strain with the angle to the RD agrees systematically with the calculated strain in single crystals. However, the absolute values of the calculated transformation strain are approximately two times higher than the measured ones.

The dependence of these maximum transformation strains such as line 1 in Fig. 7.3 has often been used by other authors to describe the measured transformation strain in polycrystalline SMAs. For instance, Mulder et al\(^\text{(147)}\) and Kitamura et al\(^\text{(148)}\) used this dependence to analyze the measured strains in polycrystalline NiTi alloys with a (110)[1\Bar{1}0]_p texture. In Kitamura et al’s work, the anisotropy factor A of the measured strains is 1.27 while A is 3.97 for the calculated strains. The discrepancy most likely comes from the fact that texture was only roughly determined from pole figures. That is, only the main component was taken into account for the calculation of the maximum transformation strains. If the ODF had been calculated, the other components should have been found.
Fig. 7.1 Anisotropy of transformation strains in single crystal TiNi alloy.
(a) for variants 1, 2, 3’, 4, 6 and 6’;
(b) for variants 1’, 2’, 3, 4’, 5 and 5’.
The numbers in the figure stand for the variants originating from (110)[110]p.
Fig. 7.2 Anisotropy of transformation strains in single crystal TiNi alloy.  
(a) for variants 1, 1’, 2, 2’, 3 and 3’;  
(b) for variant of 4, 4’, 5, 5’, 6 and 6’.  
The numbers in the figure stand for the variants originating from (111)[110].
Chapter 7 Calculation of anisotropic behaviour of transformation strains

7.2.2 Calculation based on martensite texture development (method 2)

It was found experimentally that the martensite variants with the largest and second largest transformation strains determine the transformation strain in most cases. Method 1 is therefore not completely correct for polycrystalline materials. To improve the calculation in method 1, the martensite variants obtained from texture measurements were taken into account instead of only the variants with the maximum strains. Because there is no quantitative result concerning the relative percentage of each developed variant, it was assumed that an equal amount of each variant was transformed. The transformation strain is thus the average transformation strain of the variants. On the other hand, it was assumed that the variant(s) with a compressive transformation strain would be impossible to form during tensile testing. The calculated transformation strains for the 5AMT and 3AMT samples are shown in Fig. 7.4. The calculated results using method 2 are systematically lower than the results using method 1, but there is less agreement in the form of the curves with the experimental results.

7.3 Calculation of transformation strain using inverse pole figures

7.3.1 Calculation using average strain (method 3)

The quantitative analysis of the texture using the ODF facilitates the calculation of an orientation dependent property in the textured material. The anisotropy of the property is directly related to the density in the inverse pole figure, and can thus be predicted using
An approximate equation for calculating the transformation strain is

\[
\epsilon_y = \frac{R_y(100) \cdot \epsilon_y(100) + R_y(110) \cdot \epsilon_y(110) + R_y(111) \cdot \epsilon_y(111)}{R_y(100) + R_y(110) + R_y(111)}
\]

where \( y \) = the direction
\( \epsilon_y \) = the mean strain of the polycrystalline material in the \( y \) direction
\( \epsilon_y \) = the calculated strain in a single crystal in the direction \(<uvw>\)
\( R_y \) = the density of the inverse pole figure in the direction \(<uvw>\)

This formula is similar with eqn. 2.27. Eqn. 7.1 uses a weighted sum of the relative intensities, \( R_y(<uvw>) \), of an inverse pole figure in three typical positions (100), (110) and (111). The average strain of the martensite variants (as in method 2) was used for \( \epsilon(<uvw>) \).

The \( R_y(<uvw>) \) values in the inverse pole figures were compiled in Table 4-1 for the 5AMT sample and Table 4-2 for the 3AMT sample. The calculated and experimentally determined transformation strains are shown in Fig. 7.5. The calculated strains are still higher than the experimental results. Nevertheless, the calculated transformation strains are closer to the experimental results as compared to the calculated results using method 1. Discrepancies might arise from the fact that the effect of mutual strain constraint in polycrystalline materials is not taken into account.
Fig. 7.5 Comparison of the anisotropy of calculated transformation strains, $\varepsilon_p$, based on inverse pole figures and the anisotropy of measured strain, $\varepsilon_{exp}$, in the 3AMT samples and 5AMT samples.

7.3.2. Calculation using the modified Taylor model (method 4)

An essential difference between the deformation of polycrystalline material and that of single crystals is that grains are subject to mutual constraint in strain. To evaluate the effect of intergranular constraint in the plastic deformation of polycrystalline SMAs, Ono et al \cite{183,184} proposed a model in which the calculated transformation strain for single crystals can be modified by the Taylor factor $M'$, as discussed in section 2.4.3. Using the calculated results of the modified Taylor factor, $M'$, from this model for NiTi SMAs,

$$M'_{(001)} = 4.68, \quad M'_{(011)} = 3.61, \quad M'_{(111)} = 2.40$$

the maximum transformation strain $\varepsilon'$ based on eqn. 2.27 is:

$$\varepsilon'_{(100)} = 2.91\%, \quad \varepsilon'_{(110)} = 3.77\%, \quad \varepsilon'_{(111)} = 5.67\%.$$ 

Replacing the strain, $\varepsilon_{uvw}$, in eqn 7.1 with the strain $\varepsilon'$, the transformation strain was calculated, and compared with the measured strains and the strains calculated using the other three methods, see Fig. 7.6 and 7.7. The calculated strain almost fits the experimental results $\varepsilon_{lP\rightarrow M}$, except at the angles near the RD, where the calculated value is about 1.0% smaller than the $\varepsilon_{lP\rightarrow M}$. This shows that a consideration of the effect of constraint is of great importance.

During this calculation, only the orientation distribution function of the austenite phase was used. The formation of the martensite variants was not taken into account. This probably results in the discrepancy between the experimental and the calculated results.
Fig. 7.6 Comparison between the measured transformation strain and the calculated strains in the cold-rolled 5AMT samples, using different methods: method 1: maximum transformation strain; method 2: calculated from the martensite variants; method 3: three points of inverse pole figures; method 4: Taylor factor and inverse pole figures.

Fig. 7.7 Comparison between the measured strain and the calculated strains in the warm-rolled 3AMT samples, using different methods: method 1: maximum transformation strain; method 2: calculated from the martensite variants; method 3: three points of inverse pole figures; method 4: Taylor factor and inverse pole figures.
Chapter 8
Discussion

The investigations described in this work aimed at 1) determining how texture develops during the rolling process and during transformations in a TiNiCu alloy, and 2) explaining the anisotropic behaviour of the mechanical properties as a result of texture development in this shape memory alloy. The relationships among the various aspects of this program were shown in Fig. 2.13 and are given in a simplified flow diagram in Fig. 8.1.

The main results of this work as presented in chapters 4-6 are as follows:

(1) Texture development was studied as a function of rolling parameters, including thickness reduction, rolling temperature, intermediate annealing temperature and post-rolling annealing temperature (Table 3.2). It was found that the rolling temperature is the most important parameter which can considerably influence the texture formation. Rolling in the austenitic or martensitic condition results in different textures. For the sheets warm-rolled in the austenitic condition with an ordered bcc (B2) crystal structure, the \(\{111\}<1\overline{1}0>_{p}\) texture was formed. For the sheets cold-rolled in the martensitic condition with a B19' monoclinic crystal structure the texture is a mixture of the \(\{110\}<1\overline{1}0>_{p}\) and \(\{111\}<1\overline{1}0>_{p}\) texture components, where the major texture component is \(\{110\}<1\overline{1}0>_{p}\).

(2) The experimentally determined anisotropic behaviour of mechanical properties obtained by thermal cyclic testing is dependent on rolling conditions, as summarized in Table 8-1. The transformation strain is relatively isotropic in the warm-rolled sheets.
Table 8-1 A summary of the anisotropic thermal cyclic behaviour of the 3AMT, 5AMT and KR52 samples annealed at 500°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>3AMT</th>
<th>5AMT</th>
<th>KR52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolling</td>
<td>Warm-rolled</td>
<td>Cold-rolled</td>
<td>Cold-rolled</td>
</tr>
<tr>
<td>( \varepsilon_1^{P\rightarrow M} )</td>
<td>A</td>
<td>1.24</td>
<td>1.81</td>
</tr>
<tr>
<td>Max.</td>
<td>5.01% in RD</td>
<td>5.13% in 30°</td>
<td>5.20% in 30°</td>
</tr>
<tr>
<td>Min.</td>
<td>4.04% in TD</td>
<td>2.80% in TD</td>
<td>2.84% in TD</td>
</tr>
<tr>
<td>The relations of the transformation strains</td>
<td>( \varepsilon_1^{M\rightarrow P} &lt; \varepsilon_2^{M\rightarrow P} &lt; \varepsilon_1^{P\rightarrow M} &lt; \varepsilon_2^{P\rightarrow M} )</td>
<td>( \varepsilon_1^{M\rightarrow P} &lt; \varepsilon_2^{M\rightarrow P} = \varepsilon_1^{P\rightarrow M} = \varepsilon_2^{P\rightarrow M} )</td>
<td>( \varepsilon_1^{M\rightarrow P} &lt; \varepsilon_2^{M\rightarrow P} &lt; \varepsilon_1^{P\rightarrow M} = \varepsilon_2^{P\rightarrow M} )</td>
</tr>
<tr>
<td>Permanent strains</td>
<td>0°-60°</td>
<td>0.35% - 0.47%</td>
<td>0.05% - 0.08%</td>
</tr>
<tr>
<td>Min.</td>
<td>0.19% in TD</td>
<td>0.04% in TD</td>
<td>0.10% in TD</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>22±2°C</td>
<td>22±5°C</td>
<td>23±2°C</td>
</tr>
</tbody>
</table>

(anisotropic factor \( A=1.24 \)) and is anisotropic in the cold-rolled sheets (\( A=1.81 \)). The transformation strain has an almost constant value from the RD to an angle 60° to the RD, and a minimum value in the transverse direction. The maximum experimentally observed strain in the warm rolled samples and cold rolled samples is approximately 5%. The minimum transformation strain in the warm rolled sheets along the transverse direction is, however, considerably higher than the minimum transformation strain in the cold rolled sample. The permanent strain produced during thermal cyclic testing has a minimum value along the transverse direction, irrespective of the rolling parameters.

(3) Further changes in martensite texture were found after tensile testing and after completion of thermal cyclic testing. Martensite texture and variant development depended on loading direction in both the cold and warm rolled samples. The variants developed from the two types of texture as a function of loading direction were summarized in Table 5-5 for the cold rolled samples and in Table 5-7 for the warm rolled samples.

The results show that there is a complex relationship between deformation processes, texture and microstructure for this TiNiCu alloy. The initial texture development is related to the rolling conditions, the initial microstructure and post-roll annealing. The anisotropy of the tensile and thermal cyclic properties are then related not only to the rolling texture, but also to the texture developed during testing. The understanding of the anisotropic properties of the materials must therefore begin with an explanation of the formation of the \{110\}<110> \(_p\) and \{111\}<110> \(_p\) texture components produced by rolling in martensitic or austenitic conditions.

Texture results from the rotation of crystal planes of slip systems in grains during plastic deformation. For metals with a bcc structure, the slip direction is the close-packed <111> direction with the Burgers vector of the perfect slip dislocation being \( \frac{1}{2}<111> \). There are a number of slip planes, including the \{110\}, \{112\} and \{123\} planes. Three types of
deformation texture, \{100\}<011>, \{112\}<1\overline{1}0>, and \{111\}<1\overline{1}0>, theoretically predicted to form by the interaction of slip systems. This has been confirmed experimentally\(^{(205),(206)}\), for example, in ordered \(\beta\)-brass, all three types of texture were found, while in Fe-Ni alloys, only the \{100\}<011> texture was found.

For the warm rolled TiNiCu alloy in the present work, only one of the textures, i.e. a strong \{111\}<1\overline{1}0> texture, was found. The \{100\}<011> and \{112\}<1\overline{1}0> texture components were hardly present. The reason for the preferred formation of the \{111\}<1\overline{1}0> texture might be associated with the lower deformation temperature during warm rolling than during hot rolling. A lower deformation temperature favours the formation of the \{111\}<1\overline{1}0> texture, according to experimental results obtained for a mild steel rolled at room temperature or 400\(^\circ\)C\(^{(207,208)}\).

For the cold rolled alloy, texture development occurred in the martensitic condition with a monoclinic lattice. The slip systems in the monoclinic crystal structure of this TiNiCu alloy are unknown at the moment. Therefore, a lattice resistance analysis as suggested by Willemse et al\(^{(150)}\) was used to try to explain the texture formation during cold rolling. Willemse et al explained the preference for the development of a \([\overline{1}01]\) fibre texture component in a TiNiCu alloy during wire drawing and thermomechanical cycling by the fact that planes with a larger d-spacing give the best accommodation to tensile deformation. This explanation indicates that the texture formation depends on the ease of the movement of slip systems.

For a sheet texture, as in the present work, lattice resistance would be a measure of the ease of movement. During rolling, plastic deformation occurs by the movement of dislocations on a slip system for which the resolved applied stress, \(\tau\), first exceeds a critical shear stress, \(\tau_c\), as defined by the Schmid factor. The \(\tau_c\) is associated with the lattice resistance (Peierls barrier), \(\tau_{p,N}\), which is expressed by\(^{(209)}\)

\[
\tau_{p,N} = \frac{2G}{1-v} \exp\left(-\frac{2\pi w}{b}\right)
\]  

(8.1)

where

- \(G\) = shear modulus
- \(v\) = Poisson’s ratio
- \(\overline{b}\) = Burgers vector
- \(w = d/(1-v)\) (edge dislocation)
- \(= d\) (screw dislocation)
- \(d\) = interplanar spacing

This equation shows that the lattice resistance decreases with increasing ratio \(d/\overline{b}\), which indicates that planes with larger d-spacing are easily sheared in directions with small \(\overline{b}\).

The ratios, \(d/\overline{b}\), of the martensite component originating from the \((110)[\overline{1}0]\) and \((111)[\overline{1}0]\) textures were calculated and compared, where the martensite components \((hkl)<uvw>_m\) were regarded as shear systems. The calculated results are shown in Table 8-2. The martensite components originating from the \((110)[\overline{1}0]\) texture are found to have large \(d/\overline{b}\) ratios (>0.40). Two of the martensite components originating from the \((111)[\overline{1}0]\) texture,
Chapter 8  Discussion

Table 8-2  Calculation of \( d/\bar{b} \) ratio for the martensite components originating from (110)[1\( \bar{1} \)0]_p and (111)[1\( \bar{1} \)0]_p austenite texture components.

<table>
<thead>
<tr>
<th>(110)[1( \bar{1} )0]_p component</th>
<th>d/( \bar{b} )</th>
<th>(111)[1( \bar{1} )0]_p component</th>
<th>d/( \bar{b} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martensite component</td>
<td></td>
<td>Martensite component</td>
<td></td>
</tr>
<tr>
<td>(002)[010]_m</td>
<td>0.56</td>
<td>(120)[2( \bar{1} )1]_m</td>
<td>0.19</td>
</tr>
<tr>
<td>(11( \bar{1} ))[2( \bar{1} )0]_m</td>
<td>0.54</td>
<td>(120)[2( \bar{1} )1]_m</td>
<td>0.21</td>
</tr>
<tr>
<td>(020)[001]_m</td>
<td>0.45</td>
<td>(120)[001]_m</td>
<td>0.36</td>
</tr>
<tr>
<td>(111)[2( \bar{1} )1]_m</td>
<td>0.46</td>
<td>(102)[2( \bar{1} )1]_m</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(102)[2( \bar{1} )1]_m</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(102)[010]_m</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(102)[0( \bar{1} )0]_m</td>
<td>0.41</td>
</tr>
</tbody>
</table>

(102)[010]_m and (102)[0\( \bar{1} \)0]_m also have relatively large \( d/\bar{b} \) ratios. Thus, the (110)[1\( \bar{1} \)0]_p texture is predominant, while the (111)[1\( \bar{1} \)0]_p texture is present as a secondary component. The presence of this (110)[1\( \bar{1} \)0]_p texture is consistent with the results reported by other authors. For instance, it was found in a hot rolled and recrystallized sheet\(^{145-146}\) as well as in a cold rolled 50.8Ti49.2Ni (at.%) alloy\(^{147}\). Other martensite components were calculated and also had large \( d/\bar{b} \) ratios, e.g. the martensite variants originating from the (110)[\( \bar{1} \)\( \bar{1} \)0]_p. However, a texture composed of these variants was not measured in this material. This might indicate that the lattice resistance is not the only factor which is important for texture formation. Other factors, such as the rotation and interaction of slip systems, also play an important role. Nevertheless, analysis of the lattice resistance gives a clue for solving this problem, but a complete theory for texture formation in alloys with a monoclinic lattice has not yet been established.

From the experimental results, the anisotropy of the transformation and permanent strains was different for the materials with the two different textures, the {111}<1\( \bar{1} \)0>_p and mixed {110}<1\( \bar{1} \)0>_p + {111}<1\( \bar{1} \)0>_p textures. This indicates that the anisotropy is mainly due to the presence of texture. For the samples with similar texture, e.g. the KR52 samples and 5AMT samples, the anisotropic behaviour is similar, although the rolling processing of these two samples is different. The reason for the anisotropy could be found by treatment of the parent phase texture before loading as a single crystal orientation, as a first approximation. For warm rolled sheets with the {111}<1\( \bar{1} \)0>_p texture or cold rolled sheets with the {110}<1\( \bar{1} \)0>_p texture, the amount of transformation strain in the rolling direction is similar because the rolling direction for both samples was <1\( \bar{1} \)0>_p. The crystallographic directions corresponding to the transverse directions are [11\( \bar{2} \)]_p in the warm rolled sheets and [001]_p in the cold rolled sheets. The maximum transformation strain in the [11\( \bar{2} \)]_p direction is 9.50%, and in the [001]_p direction, 2.68%, see Fig. 7.3. Therefore, the transformation strain along the transverse direction in the warm rolled sheets is higher than in the cold rolled sheets.

The previous discussion only considered the texture produced during rolling process. In this
work, it was also found that the initial rolling texture could be enhanced by post-roll annealing with the optimum temperature being 500°C. This annealing also led to a significant amount of transformation strain. These effects are related to the decrease in dislocation density, which was introduced by severe plastic deformation during the rolling process. For texture measurements, a high dislocation density leads to broadening and overlap of X-ray diffraction peaks, (see Fig. 4.12), resulting in difficulties in measuring martensite texture in this condition. The introduction of dislocations also significantly broadens the transformation range, resulting in a two-phase structure at ambient temperature, as was indicated by the various measurement techniques, such as DSC, XRD, TEM and thermal cyclic testing. The existence of a two-phase structure in the as-rolled materials or the materials annealed at low temperatures (below 300°C or 400°C) lead to low transformation strains due to a partial transformation, see Fig. 6.23. Post-roll annealing at higher temperatures (above 400°C) resulted in an upward shift of the transformation temperatures to above room temperature due to the release of the stored elastic energy. This was confirmed by TEM where visible decrease of dislocation density and clear martensite twinning was seen, by XRD showing sharper XRD peaks, by thermal cyclic testing showing higher transformation strains, and by DSC showing that the transformation temperatures increased to above RT. Sharper textures would be expected. However, it has been reported that some shape memory properties, for instance, shape recovery, are reduced for annealing above the recrystallization temperature (600°C), while the transformation strain continues to increase\(^\text{(102,105)}\). Thus, 500°C was found to be an optimal annealing temperature, which agrees with industrial practice.

Texture and microstructure also affect the anisotropy of permanent strain, as can be seen from the experimental results, see Table 8-1. The permanent strain built up during thermal cycling, which is represented by \(\varepsilon_1^{\text{P} \rightarrow \text{M}} - \varepsilon_2^{\text{M} \rightarrow \text{P}}\) (see Fig. 3.10), reflects the stability of the transformation strain during thermal cycling which is important for practical applications. It is known that the presence of the permanent strain is due to the resistance of the irreversible microstructures to the movement of the interphase boundary, as introduced in section 2.3.2\(^{\text{(26,169)}}\). These irreversible microstructures include dislocation structures, precipitates or interphase boundaries which can be semicoherent or incoherent and can be described by interphase energy. It was found that the permanent strain was always a minimum for loading in the transverse direction, irrespective of the rolling parameters. Since the crystal grains are elongated along the rolling direction after rolling, it is most likely that total energy required for interphase boundary movement is lower in the transverse direction than in the rolling direction. Therefore, the resistance is lower, fewer dislocations are produced, and the permanent strain is less in the TD, as compared with the other directions. Loading in the TD thus always results in the best dimensional stability during thermal cycling through the transformation range.

The permanent strain in the warm-rolled samples was higher than for the cold-rolled samples. This can be explained by the fact that the amount of deformation in the warm rolled samples is higher than in the cold rolled samples. The deformation, governed by glide and interaction of dislocations, is easier in the cubic structure than in the less symmetric monoclinic lattice. A relatively large amount of irreversible defects produced during warm rolling, such as slip dislocations, facilitates a large permanent strain during thermal cycling by dislocation multiplication. The larger permanent strain suggests that the critical shear stress for slip
during the cycling is lower than for the cold rolled sample. The accommodation of the variants then not only occurs by twinning but also by slip of dislocations.

Given that the rolling textures and permanent strains are dependent on active slip system and dislocation structure, it would be conceivable that the measured transformation strains and the textures found after mechanical testing could also be related to these factors as well. It was found that the martensite texture after tensile testing or thermal cyclic testing depended on loading direction in both cold and warm rolled samples. This texture consisted of martensite variants which were derived from the austenite through the lattice correspondence (see Table 2-5). The martensite texture would be changed as a result of detwinning and/or variant growth during thermal cycling or tensile loading. When the material is stressed or thermally cycled, specific variants will be developed at the expense of the others. Upon loading, detwinning and variant growth are responsible for the large transformation strains, depending on the loading direction. The starting martensite texture will, as a consequence, be modified.

This scenario can be supported by analysis of the relationship between martensite variants and transformation strains of the variants originating from the (110)[1 10]_p and (111)[1 10]_p components. This was performed by calculating the transformation strain based on the variants producing the largest strain, the second largest strain, etc. As an example, using the simplest method, eqn. 2.25, the calculation of transformation strains in a [1 11]_p crystal direction for variants 1 and 1’ would begin with an analysis of the corresponding crystal directions. The [1 11]_p direction transforms into the [1 0 1]_m and [1 0 1]_m directions for variants 1 and 1’, respectively. Using the identity distance, I, of these directions (from the equations in Appendix A1.1), the transformation strain, ε, would be

\[
\text{parent phase: } I_{[1 11]_p} = 0.522 \text{ nm}, \\
\text{product phase: } I_{[1 0 1]_m} = 0.515 \text{ nm}, \quad \varepsilon = -1.34\% \quad \text{for variant 1}, \\
I_{[1 0 1]_m} = 0.573 \text{ nm}, \quad \varepsilon = 9.79\% \quad \text{for variant 1’}.
\]

It can be seen that different variants lead to different transformation strains. In Table 8-2, calculated transformation strains for variants with the three largest strains are presented. The measured martensite variants for the 5AMT samples in Table 5-5 were compared with the variants in the parentheses in Table 8-3. The variants with the largest and the second largest strain was found to be developed after tensile testing and/or thermal cyclic testing. The development of the variant(s) with the largest strain indicates that the selection of the variant under the external load follows to a great extent the criterion valid for single crystals. The calculation of transformation strains using method 1 in Chapter 7 only accounts for the presence of these variants. The development of the variants having the second largest transformation strain might arise from the constraints put on by the neighbouring grains in polycrystalline materials. For a single crystal, it is known that only the variants with maximum transformation strain form. However, in polycrystalline materials, to fulfill the compatibility condition among grains, the formation of martensite plates under stress requires the simultaneous nucleation and the growth of several variants. Consequently, in addition to the variant with maximum strain, the variant with the second largest strain would also be formed. For instance, in a [1 11]_p direction in a single crystal, only the variant 5 is developed. In the polycrystalline 5AMT samples, variants 1’ and 4’ were also found for the loading
direction is 30° to the RD, close to the [1\bar{1}1]_p direction for the observed (110)[1\bar{1}0]_p texture. This experimental result also confirms the conclusion of Christian\(^{210}\) that the maximum strain in polycrystalline shape memory alloys is much smaller than in single crystals, since the mutual constraints will cause secondary variants to form.

For the warm-rolled 3AMT samples, the measured martensite variants in Table 5-7 were compared with the variants in Table 8-3. It was found that most of measured variants have the largest and second largest transformation strains. However, exceptions were found for the variants loaded along different angles to the RD. For instance, for the variants in the RD, only 4 variants (1’, 3, 5’ and 6) show the largest strain and second largest strains among 6 experimentally determined variants (1’, 3, 4’, 5, 5’ and 6). The other two variants (4’ and 5) have a smaller transformation strain (see Fig. 7.2), while two expected variants (2’ and 3’) were not observed. These exceptions probably arise from the complicated compatibility conditions which are not clear at the moment.

It is clear that prediction of transformation strains by calculation of the maximum

---

Table 8-3 The calculated transformation strain (in %) of the correspondence variants from (110)[1\bar{1}0]_p and (111)[1\bar{1}0]_p in NiTi alloys. The numbers in parentheses are the numbers of the variant.

<table>
<thead>
<tr>
<th>Angle to RD</th>
<th>0°</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For (110)[1\bar{1}0]_p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>largest strain</td>
<td>8.40</td>
<td>10.33</td>
<td>10.03</td>
<td>8.91</td>
<td>2.68</td>
</tr>
<tr>
<td></td>
<td>(5.5’)</td>
<td>(5)</td>
<td>(1’,4’)</td>
<td>(1’,4’)</td>
<td></td>
</tr>
<tr>
<td>second largest strain</td>
<td>3.60</td>
<td>9.35</td>
<td>8.15</td>
<td>4.35</td>
<td>-4.18</td>
</tr>
<tr>
<td></td>
<td>(1’,2’,3,4’)</td>
<td>(1’,4’)</td>
<td>(5)</td>
<td>(5)</td>
<td></td>
</tr>
<tr>
<td>third largest strain</td>
<td>-3.37</td>
<td>0.22</td>
<td>0.03</td>
<td>1.80</td>
<td>-----</td>
</tr>
<tr>
<td>(5AMT)</td>
<td>4’,5,5’</td>
<td>1’,4’,5’</td>
<td>1’,4’,5’</td>
<td>1’,4’,5’</td>
<td></td>
</tr>
<tr>
<td>For (111)[1\bar{1}0]_p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>largest strain</td>
<td>8.40</td>
<td>9.50</td>
<td>9.93</td>
<td>8.40</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>(3,3’)</td>
<td>(3’,5)</td>
<td>(5)</td>
<td>(5’,5’)</td>
<td>(1’,5’)</td>
</tr>
<tr>
<td>second largest strain</td>
<td>3.60</td>
<td>5.82</td>
<td>7.22</td>
<td>3.60</td>
<td>5.82</td>
</tr>
<tr>
<td></td>
<td>(1’,2’,5’,6)</td>
<td>(2’)</td>
<td>(3’)</td>
<td>(1’,2’,3,4)</td>
<td>(4)</td>
</tr>
<tr>
<td>third largest strain</td>
<td>-3.37</td>
<td>1.25</td>
<td>5.26</td>
<td>-3.37</td>
<td>1.25</td>
</tr>
<tr>
<td>(3AMT)</td>
<td>5,5’,6</td>
<td>5,5’,6</td>
<td>4,5,5’</td>
<td>4,5,5’</td>
<td>5,5’,6</td>
</tr>
</tbody>
</table>
transformation strain in the single crystal (method 1, Chapter 7) can qualitatively explain the observed anisotropic behaviour. However, it does not fit the experimental results, i.e. the amount of the calculated results are about 2 times higher values than the experimental results. The inclusion of multiple variants and their contributions to the transformation do not bring significant improvement (method 2, Chapter 7). A possibility for improving method 2 would be to induce the relative amount of each variant. This could not be measured by techniques available to the present author. Recent theoretical work\(^{211}\) shows, however, that the volume percentage of each variant can be calculated from the compatibility criterion. Nevertheless, the calculated variants are not yet consistent with the measured variants. For instance, for the \((111)[110]_p\) texture component, at angles 30° or 45° to the RD, the calculated relative amount of variant 1 is 11.1%, of variant 1' is 48.1% and of variant 5 is 40.8%. However, variant 1 was not measured, although the other two variants, 1' and 5, were found by texture analysis, see Table 5-7. The quantitative amounts of the variants can be also obtained by the improvement of texture analysis using the ODF calculation for the monoclinic lattice. However, this method is still under development.

Another mechanism for variant selection is that the variants which are most favourably oriented to the direction of stress would be developed, see section 2.2.2. During detwinning and/or thermal cycling, the stress is constant. The work done by external stress for each variant originating from the \((110)[110]_p\) and \((111)[110]_p\) texture components was calculated using eqn. 2.18. In this calculation, the three main strain directions were regarded to be the strains along three main axes for the sake of simplicity. The complete calculated results are shown in Appendix III and an example is shown in Fig. 8.2. It was found that the results are not in agreement with the experimentally determined texture components. For instance, the variants in the warm-rolled 3AMT samples developed after loading 30° to the RD were

![Figure 8.2](image-url)

*Fig. 8.2 Work done by external stress for variants of 1, 1’, 2, 3’, 5 and 6’ originating from the \((111)[110]_p\) component.*
measured to be 1', 3' and 5, whereas the variants 1, 2, 5 and 6' would be favoured according to the calculation. This is probably due to the fact that the straining in the B2 to B19' transformation is more complicated compared with the one in the fcc to bct transformation in Fe-Ni alloys for which the work concept was developed. In Fe-Ni alloys, the three main (Bain) strains result from the expansion or contraction of the crystal axes. In NiTi alloys, shear of the lattice is also involved. It is not certain whether the strains along three main axes include all of the strains, i.e. the calculated work using eqn. 2.18 includes all the work done by the applied stress. The modification of eqn. 2.18 which was developed for the Fe-Ni alloys is still under consideration in order to apply it to the B2 to B19' transformation.

Further improvements in the understanding of the observed anisotropic behaviour might be obtained by considering the quantitative results from the ODF analysis of the austenite texture, mainly, the orientation density in the form of inverse pole figures. The previous treatment of the textures as single crystals (methods 1 and 2) was a rough approximation because it did not reflect the presence of other orientations which also contribute to the transformation strain. From the ODF calculation, see Tables 4-1 and 4-2, other orientations sometimes have a density which is significantly close to the main orientation density. Consequently, the analysis using the orientation density would provide an improvement which was confirmed by the fact that calculated results using methods 3 and 4 in Chapter 7) are closer to the experimental results, as compared to method 1.

Besides the orientation density, it should also be considered that the transformation occurred in a polycrystalline shape memory alloy. Because of the effect of the strain constraint of neighboring grains, the transformation strains are significantly lower than the single crystal data in most cases. The interphase boundaries can not move freely, since the movement is restricted by the neighbouring grains. The variant(s) thus can not grow to their full length during transformation, and the transformation strain is thus reduced. This analysis was quantitatively realized in a modified Taylor model (method 4) developed by Ono et al, in which the habit plane normal and shape strain direction were used instead of the slip systems(183,184). The results support this model as shown by the relatively good fit of the experimental results with the calculations, see Fig. 7.6 and Fig. 7.7 for both {110}<110> p and {111}<110> p textures.

Although the results of method 4 were found to be closest to experiment, there are still discrepancies between the experimental results based on the texture analysis. These discrepancies may arise from the following factors:

1) Incomplete orientation information: Only the densities of three orientations in the inverse pole figures, viz, [100] p, [110] p and [111] p, were used in eqn. 7.1. These three orientations do not provide all of the available information, because the intermediate orientations within the stereographic triangle are not taken into account. From the pole figures or the ODF sections, one can also see that the texture is spread around a certain direction. This spread can be described by the width of the "eyes" of the pole figure of around 10°, or the "tube" in the ODF section. Mathematically, it can be treated using a Gauss distribution as an approximation,
where $\omega$ describes the angular distance from the centre orientation $\omega_0$ around an arbitrary axis and $\psi$ is the standard scatter width of the Gauss distribution. A higher accuracy would be obtained if the whole inverse pole figure is integrated with the strains $\epsilon$ from single crystal data or $\epsilon'$ from the Taylor model using eqn. 2.25.

\begin{equation}
S(\omega) = S(\omega_0) \exp\left(-\frac{(\omega - \omega_0)^2}{\psi^2}\right)
\end{equation}

(2) **The strength of texture.** In all four methods, the contribution of the texture to the transformation strain was regarded to be the same as for single crystal orientation, i.e. the texture was regarded as infinitely strong. In polycrystalline materials, the strength of the texture can vary to a great extent. It is known that the strength of texture generally increases as the thickness reduction increases\(^{137}\), and it can thus be assumed that the anisotropy of mechanical properties increases as the strength of texture increases. In order to develop a texture as strong as possible, the sheets were rolled to the maximum obtainable thickness reduction. The maximum density in ODF sections of the textures developed in this thesis varied from 8 to 20, depending on rolling processing with a total thickness reduction ranged from 10% to 80%. Although the textures observed in this thesis can not be considered to be very strong as compared with other materials\(^{212-214}\), for instance

Max. = 41.06 in a cross rolled iron with 93% reduction\(^{212}\),
Max. = 28.42 in a hot rolled CuZnAl alloy with 96% reduction\(^{213}\),

the range of strengths could effect the calculated results. It is worth noting that the orientation density only provides information concerning the relative amount of the variant(s) rather than the strength of texture, as shown in eqn. 7.1 (or eqn. 2.25). This problem might be improved using the Gauss type intensity distribution function, in which the strength of the texture is described by the term $S(\omega_0)$ in eqn. 8.2.

(3) **The grain shape and size.** The shape and size of grains could influence shape memory properties. For instance, the recoverable strain of a sample with an equiaxed grain structure is higher than that with a columnar grain structure\(^{144-146}\). It was also found that the number of grain boundaries per unit length along the transverse direction is 1.4 to 2 times than along the rolling direction in cold rolled or hot rolled a TiNi alloy\(^{215}\). The pseudoelasticity was found to become pronounced as the grain size decreases, indicating that the role of the grain boundary is important in the pseudoelasticity\(^{216}\). The grain size effect may be taken into account by using a size distribution function (SDF). However, these factors were not considered in the approaches used in this thesis.
Chapter 9

Conclusions

The texture development and anisotropic behaviour of a Ti-44.2Ni-4.9Cu (at.%) shape memory alloy have been investigated. The main conclusions are as follows:

1. The texture of the cubic austenite phase after cold-rolling and annealing at 500 °C was determined to be a mixture of the (110)[1 ¯10]_p and (111)[1 ¯10]_p texture components, in which the relative amount of the texture component depends on the rolling temperature. In the case of cold-rolling, the major texture component is generally (110)[1 ¯10]_p, while warm-rolling at 300°C leads to a dominant (111)[1 ¯10]_p texture component. This is based on the transformation from B2 austenite to B19' monoclinic martensite.

2. The development of texture has a definite influence on the anisotropic behaviour of a Ti-45Ni-5Cu(at.%) shape memory alloy. The transformation strain produced during thermal cycling under a constant load is close to isotropic for the warm-rolled sheets and is anisotropic by a factor of around 1.8 for the cold-rolled sheets. The transformation strain has an almost constant value from the RD to an angle 60° from the RD, and a minimum value along the transverse direction. The permanent strain produced during thermal cyclic testing has a minimum value along the transverse direction, irrespective of the rolling parameters.

3. The martensite texture after tensile testing and after completion of thermal cyclic testing depends on loading direction in the cold-rolled and annealed samples. The measured results indicate that only those martensite variants showing the two largest transformation strains in the loading direction were developed after tensile testing and after thermal cyclic testing.

4. Four methods to calculate the anisotropy of the transformation strain were introduced based on the texture analysis. Among those four methods, the method using the modified Taylor model for polycrystalline shape memory alloys combined with the pole densities from the calculated inverse pole figures has the closest fit to the experimentally measured results. This conclusion was confirmed in the materials having two different types of texture.

The conclusions obtained in this thesis offer a possibility for controlling the shape memory properties for particular applications by controlling texture development during the rolling process. For example, for applications under multiaxial loading where the behaviour of the sheet should be isotropic, the sheet which is warm-rolled at a temperature around 300°C would be preferred to sheet which is cold rolled. Although the strain for the transverse direction is less than the other directions, the material is more stable in this direction. This
is important for many applications, including actuators and in medical science. In any case, the Taylor model calculations can assist in designing materials processing for specific applications. Further investigations would be helpful to understand this material better for the practical applications of the results in this thesis. These include studies of anisotropic behaviour of the recovery stress and the effect of anisotropy on thermal cyclic life.
References

References

30. ibid, p.7.
57. W. Bührer, R. Gotthardt, A. Kulik and O. Mercier, J.de Phys. Suppl. 43, No.12, 1982,
141 References

References

208. K. Bhattacharyya and Y-C Shu, Private communication, 1996.
Appendix I: Calculation of cubic and monoclinic lattice constants

In this appendix, formulas for calculating the various lattice constants of the cubic and monoclinic structures are given. $a_o$ stands for the lattice parameter of the cubic cell; $a$, $b$, $c$ and $\beta$ for lattice parameters of the monoclinic cell; $u^i$ for the contravariant vector and $h_i$ for the covariant vector.

AI.1 Interplanar spacing, $d$, of plane (hkl) and identity distance $I$ along a direction [uvw]:

Tensor expression:

$$d = (a^{ij}h_i h_j)^{-\frac{1}{2}}$$

$$I = (a_{ij}u^i u^j)^{\frac{1}{2}}$$

For the cubic lattice:

$$d = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}}$$

$$I = a_o \sqrt{u^2 + v^2 + w^2}$$

For the monoclinic lattice:

$$d = \left(\frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2 \sin^2 \beta} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2 hl \cos \beta}{ac \sin^2 \beta}\right)^{-\frac{1}{2}}$$

$$I = (a^2 u^2 + b^2 v^2 + c^2 w^2 + 2 abc u w \cos \beta)^{\frac{1}{2}}$$

AI.2 Angle $\psi$ between two planes $(h_1,k_1,l_1)$ and $(h_2,k_2,l_2)$

Tensor expression:

$$\psi = \text{arccos}\left(\frac{(a^{ij}h_i h_j)(a^{ij}h_i h_j)^{-\frac{1}{2}}}{(a^{ij}k_i k_j)^{-\frac{1}{2}}}(a^{ij}k_i k_j)^{-\frac{1}{2}}\right)$$

For the cubic lattice:

$$\psi = \text{arccos}\left(\frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}\right)$$

For the monoclinic lattice:

$$\psi = \text{arccos}\left[\frac{1}{d_1 d_2} \left(\frac{h_1 h_2}{a^2 \sin^2 \beta} + \frac{k_1 k_2}{b^2 \sin^2 \beta} + \frac{l_1 l_2}{c^2 \sin^2 \beta} - \frac{(h_1 l_2 + h_2 l_1) \cos \beta}{ac \sin^2 \beta}\right)\right]$$

where $d_1$ and $d_2$ are the interplanar spacings of the planes $(h_1,k_1,l_1)$ and $(h_2,k_2,l_2)$. 
AI.3 Angle $\phi$ between two directions $(u_1, v_1, w_1)$ and $(u_2, v_2, w_2)$

Tensor expression:

$$\phi = \arccos[(a_{ij}u^i v^j)(a_{ij}u^i v^j)^{-\frac{1}{2}}(a_{ij}u^i v^j)^{-\frac{1}{2}}]$$

For the cubic lattice:

$$\phi = \arccos \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{u_1^2 + v_1^2 + w_1^2} \sqrt{u_2^2 + v_2^2 + w_2^2}}$$

For the monoclinic lattice:

$$\phi = \arccos \frac{u_1 u_2 + b^2 v_1 v_2 + c^2 w_1 w_2 + \frac{1}{2}n \beta (u_1 w_2 + u_2 w_1)}{\sqrt{a^2 u_1^2 + b^2 v_1^2 + c^2 w_1^2 + 2acu_1 w_1 \cos \beta} \sqrt{a^2 u_2^2 + b^2 v_2^2 + c^2 w_2^2 + 2acu_2 w_2 \cos \beta}}$$
Appendix II: Stereographic projections of cubic and monoclinic lattice

In this appendix, stereographic projections for the cubic and monoclinic structures are given.

Fig. AII.1 Stereographic projections of the cubic lattice.

For the projections for the monoclinic lattice, the following lattice parameters are used:

\[
a=0.2889 \text{ nm}, \quad b=0.4120 \text{ nm}, \quad c=0.4662 \text{ nm}, \quad \text{and } \beta=96.8^\circ.
\]

The calculated lattice correspondence between parent phase and martensite using the notation of the correspondence variant from Miyazaki\(^{\text{23}}\) is shown in the table to the right.

<table>
<thead>
<tr>
<th>Variant</th>
<th>{110}&lt;1\bar{1}0&gt;_p</th>
<th>{111}&lt;1\bar{1}0&gt;_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(11\bar{1})[2\bar{1}1]</td>
<td>(\bar{1}20)[2\bar{1}1]</td>
</tr>
<tr>
<td>1'</td>
<td>(\bar{1}1\bar{1})[\bar{2}11]</td>
<td>(\bar{1}20)[\bar{2}11]</td>
</tr>
<tr>
<td>2</td>
<td>(\bar{1}1\bar{1})[211]</td>
<td>(10\bar{2})[211]</td>
</tr>
<tr>
<td>2'</td>
<td>(\bar{1}1\bar{1})[\bar{2}11]</td>
<td>(\bar{1}0\bar{2})[\bar{2}11]</td>
</tr>
<tr>
<td>3</td>
<td>(111)[\bar{2}11]</td>
<td>(120)[\bar{2}11]</td>
</tr>
<tr>
<td>3'</td>
<td>(\bar{1}1\bar{1})[\bar{2}11]</td>
<td>(\bar{1}20)[\bar{2}11]</td>
</tr>
<tr>
<td>4</td>
<td>(11\bar{1})[\bar{2}1\bar{1}]</td>
<td>(10\bar{2})[\bar{2}1\bar{1}]</td>
</tr>
<tr>
<td>4'</td>
<td>(\bar{1}1\bar{1})[\bar{2}1\bar{1}]</td>
<td>(\bar{1}0\bar{2})[\bar{2}1\bar{1}]</td>
</tr>
<tr>
<td>5</td>
<td>(020)[00\bar{2}]</td>
<td>(120)[00\bar{2}]</td>
</tr>
<tr>
<td>5'</td>
<td>(0\bar{2}0)[00\bar{2}]</td>
<td>(\bar{1}20)[00\bar{2}]</td>
</tr>
<tr>
<td>6</td>
<td>(00\bar{2})[020]</td>
<td>(10\bar{2})[020]</td>
</tr>
<tr>
<td>6'</td>
<td>(00\bar{2})[020]</td>
<td>(\bar{1}0\bar{2})[020]</td>
</tr>
</tbody>
</table>
Fig. AII.2  Stereographic projections of variants originating from (110)[110].
Fig. AII.2 (Cont’d) Stereographic projections of variants originating from (110)[110]_p.
Fig. AII.3 Stereographic projections of variants originating from $(111)[1\bar{1}0]$.
Fig. AII.3 (cont’d)  Stereographic projections of variants originating from (111)[110]_p.
Appendix III: Calculated results of work done by a stress

In this appendix, the work done by the applied stress, $\sigma_a$, in the loading direction during transformation is calculated using the following formula

$$W = \cos \theta_1 \cdot e_1 \cdot \sigma_a + \cos \theta_2 \cdot e_2 \cdot \sigma_a + \cos \theta_3 \cdot e_3 \cdot \sigma_a$$

where $\theta$ is the angle between the direction of the stress, $\sigma_a$, and the strain, $\varepsilon$.

*Fig. AIII.1 Work done by external stress. The numbers in the figure stand for the variants originating from $(110)[1\bar{1}0]_p$. 
Fig. AIII.2 Work done by external stress. The numbers in the figure stand for the variants originating from $(111)[1\bar{1}0]_p$. 
About the Author

Lie Zhao was born on May 19, 1963, in Hangzhou, Zhejiang Province, P.R. China. It was here that he completed his 11 years of schooling before entering university. Mr. Zhao began his studies in Metallic Materials Science and Heat Treatment, Department of Materials Science and Engineering, Zhejiang University in 1980. He was awarded a Bachelor degree of Engineering in July, 1984. The title of his undergraduate thesis was "Influence of Erosion Parameter on Morphology and Property of Various Steels".

From Aug., 1984 to Aug. 1986, Mr. Zhao was employed as an assistant engineer in the heat treatment workshop of Hangzhou Sewing Machine Co. In Sept. 1986, he returned to Zhejiang University to pursue a Master’s degree in the field of Chemical Heat Treatment. In July, 1989, he was awarded a Master’s degree. Prof.E.L.Wu was his supervisor. Title of thesis was "The Study of the Morphology and Property of Steel with Boro-Carburized and Carbo-Boronized Treatments". After his masters, Mr. Zhao worked as a lecturer and operator in the laboratory of Electron Microscopes, Laboratories Centre in Hangzhou University.

In Dec. 1991, he decided to pursue his academic career in the Netherlands. From Jan. 1992 utill the present, he has worked on his Ph.D. research. The project was "Texture Development and Anisotropic Behaviour of Intermetallic Compounds". His supervisors were Dr.ir.J.Beyer, ir.F.P.Willeme and Prof.dr.W.Wei in the Group of Materials Science and Engineering, Faculty of Mechanical Engineering, University Twente.