Martensitic transformations studied on nano- and microscopic length scales

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Summary: This contribution will focus on recent results of transmission electron microscopy studies on alloys such as Ni-Al, Ni-Ti-Cu and Cu-Zn-Al undergoing a martensitic transformation. The emphasis will be on details at different length scales between the atomic and microscopic level. In Ni-Al local lattice deformations at the vicinity of macrotwin planes between two martensite plates as observed by high resolution transmission electron microscopy will be described and discussed in view of the dynamics of the transformation and its relation with symmetry changing elements. The effects of nanoscale composition fluctuations on the microstructure in Ni-Al melt-spun ribbons will be discussed using structural and analytical electron microscopy tools. The microstructure of melt-spun Ni-Ti-Cu films will also be discussed in view of its relation with the martensitic transformation. The atomic ordering in the austenite phase in Cu-Zn-Al is investigated using a new indirect retrieval method based on electron diffraction data.

1 Introduction

Martensitic transformations involve structural features at different length scales. Flat polished surfaces often reveal a clear surface relief after the transformation. Microstructures between the micron and millimeter scales can thus be observed by optical microscopy. Often similar shapes and configurations exist at a much smaller scale, where they have to be investigated by more powerful tools, such as transmission electron microscopy (TEM). Examples of both situations are presented in Fig. 1. The variety of different instrumental modes in a TEM make this an extremely valuable tool for the investigation of these features. Parent and product structures can be observed after well defined thermal or mechanical
treatments, while also in-situ experiments can be performed. These days high or atomic resolution (HRTEM) can be achieved by which detailed information on the atomic structures of the lattices, interfaces and defects involved can be obtained below the nanometer scale. Also ultrafine scale electronic data is becoming available by applying electron energy loss spectroscopy (EELS) in TEM instruments equipped with nanoprobe imaging systems.

In the present contribution an overview of some recent results obtained with advanced TEM tools will be given. The focus will be on Ni- and Cu-based alloy systems, all having an ordered austenite phase with cubic symmetry. Depending on the actual alloy, the martensite structure has a tetragonal (Ni-Al), orthorhombic (Ni-Ti-Cu) or monoclinic (Cu-Zn-Al) structure. The actual change in symmetry dictates that observed atomic and microstructures. The Ni-Al martensitic transformation and accompanying atomic and microstructure have been investigated in great detail over the past 3 decades [1] [2] [3]. The austenite structure is based on a body centered cubic (bcc) lattice and has the B2 (CsCl type) ordering. The martensitic transformation occurs in Ni-rich alloys, in which the excess Ni is randomly accommodated on the Al sublattice. This implies the existence of numerous point or cluster defects which can play an important role in the nucleation of the martensite. The martensite structure is formed by elongating one of the cubic axis while equally shortening the other two, resulting in a body centered tetragonal lattice. The lowering in symmetry implies the existence of several variants which can be arranged in energy minimizing configurations. In Ni-Al the lattice invariant shear is twinning on close packed planes, which leads to the formation of multiply twinned martensite plates. The atomic configurations at the interfaces between two such plates will be described based on HRTEM images [4]. Also the structural effects of small composition inhomogeneities at the nanoscale will be described. The latter were found in melt-spun samples of
Ni-Al [5]. Ni-Ti thin films are currently attracting a lot of attention for use in micro shape memory devices [6]. One possibility to optimize the characteristics of such film (e.g. transformation temperature, hysteresis, ...) is by adding a third alloying element, such as Hf or Cu. Here some results on Ni-Ti-Cu films, with Cu replacing Ni, will be presented. The as-received films are amorphous and can be crystallised in the austenite structure by annealing up to 500°C. Subsequent cooling then produces the martensitic structure. In Cu-Zn-Al the emphasis is on finding special compositions which correlate with special conditions for non-generic twins. The existence of such twin systems could improve certain shape memory parameters [7]. A first step is to apply a new indirect structure retrieval method to obtain new insight into the exact nature of the L2₁ type ordering of the austenite phase. The conclusions of this procedure applied to Cu-Zn-Al material will be presented.

2 Results

2.1 Fine structure of martensite-martensite interfaces in Ni-Al

The martensitic transformation in Ni-Al usually nucleates inside well developed B2 grains. The sizes of the latter depend on the production method of the material, especially the solidification rate. Bulk material slowly cooled typically consists of millimeter sized grains, whereas in splat-cooled material grain sizes below 1 micron are found [8]. Splat-cooled discs and melt-spun ribbons also reveal some texture as a result of the temperature gradient during solidification. In order to accommodate the shape change and minimize elastic strains the martensite plates in Ni-Al are microtwinned on close packed planes of the product phase. These planes originate from one of the six possible prior {110} families of the austenite B2 lattice. Also the interface between austenite and martensite, the so-called habit plane, is close to parallel with a {110} plane, be it one at 60° from the family chosen to become the microtwin plane. Combining all possible configurations, a total of 24 different orientations for the habit plane, and thus also for the microtwin planes, are possible [1]. During growth, plates originating from different nucleation sites within a given B2 grain can coalesce and form complex interfaces. The structure of the latter can be of importance in view of the reversible character of the transformation. According to symmetry considerations, such martensite-martensite interfaces can be parallel to prior {100}ₐ or {110}ₐ planes. In the first case, the two families of microtwin planes stem from {110}ₐ families at right angles, whereas in the second case these original families form an angle of 120°. According to theoretical calculations, only the latter situation can also arise within an energy minimising
configuration, nucleated and grown as a wedge or spear inside the austenite matrix (see also §2.3) [9]. Thus, whenever a martensite-martensite interface with microtwin planes at approximately 90° is observed, it has to originate from the coalescence of two separately nucleated plates. Still, as the relative orientations of the plates involved will depend on the actual case, i.e. the particular choice of habit plane for each plate, different microstructures can be expected to exist. In all of these 90° cases, however, only two of the three possible deformation variants will be involved. As seen from the drawing in Fig. 2, some configurations can be distinguished by the final angle between the involved microtwin planes.
Due to the compensation by rotation of the net shearing in a given plate, the interface formed on the (100) plane will be characterised by an angle $\alpha > 90^\circ$, whereas a (010) interface will yield an angle $\alpha < 90^\circ$. Examples of both configurations have indeed been observed as well as cases in which the interface changes its average orientation thereby also changing the indicated angle [4]. Figure 3a presents an example of the $\alpha < 90^\circ$ case in bulk Ni$_{55}$Al$_{35}$ whereas Fig. 3b shows an interface with a changing direction and angle.

From the HRTEM enlargement of $\alpha > 90^\circ$ case in Fig. 4a and the corresponding power spectra, the local lattice deformations can be studied. From the observed rectangular patterns on both sides of the interface the local deformation variants $U_i$ can be recognized. The orientation of these rectangles also indicates that the widest variants on either side consist of the same deformation variant, be it rotated in opposite sense. At the interface the rectangularity of the dot pattern remains the same, but its orientation is intermediate between the two extremes on either side. On average, the interface has a width of 5 nm. In the present example, the lattice deformations at the interface appear equally shared between the two plates. Alternatively, several interfaces with less symmetric configurations have been observed, as in Fig. 4b. Here, the microtwin plane of one plate is used as local interface between both plates. As a result, the microtwins ending perpendicular to this interface accommodate most of the local
Figure 4  HRTEM lattice images of (a) a symmetric martensite-martensite interface with $\alpha > 90^\circ$ revealing local deformations at the 5 nm wide interface shared between both plates and (b) non-symmetric case accommodating all lattice deformations on one side.

deformations. Such configurations are usually observed when local differences in microtwin widths exist between the plates [4].

2.2 Nanoscale inhomogeneities in Ni-Al melt-spun material

The martensitic transformation in Ni-Al melt-spun ribbons was also investigated. Again the rapid quench and special solidification conditions are expected to yield new insight into the relevant processes that govern the microstructure formation in these alloys. Typical compositions such as 62.5Ni and 65Ni were used. Differential scanning calorimetry (DSC) indicates that the sharp transformation of well-homogenized bulk material no longer exists. Instead, weaker exo- and endothermic peaks are measured, pointing towards an incomplete transformation spread out over a large temperature region. Several origins for this behaviour were investigated, including the existence of macroscopic strains, the appearance of many lattice defects such as dislocations and vacancies and composition inhomogeneities. Based on the exclusion of the former two by quantitative X-ray measurements and the observation of local composition differences of more than 2 at.% by energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) measurements, the latter suggestion was retained as the primary cause for the spread in transformation temperatures [5]. In Ni-Al, the Ms temperature is indeed extremely dependent on composition ($160^\circ$ change for 1 at.%).

In TEM, these inhomogeneities show up as nanoscale martensite plates in the austenite matrix of the 62.5Ni ribbon and austenite regions within large martensite plates in the 65Ni ribbon. Examples of those are given in Fig. 5a
Figure 5 TEM images of (a) a nanoscale martensite plate in the austenite matrix in melt-spun Ni_{82.5}Al_{17.5} and (b) a nanoscale austenite region inside a martensite plate in melt-spun Ni_{65}Al_{35}.

and 5b. A typical EELS spectrum revealing the composition difference by the relative heights of the Ni L\textsubscript{3} sup-peaks is presented in Fig. 6 [5]. The latter is due to hybridisation between Ni d and Al s shells, which is strongly affected by the composition.

From the image in Fig. 5b it is clear that the twig density in the martensite plate increases when approaching the remaining B2 region. Whether or not this should only be attributed to a gradual change in composition, is still unclear. Indeed, around 63 at.% Ni, the martensite appears as a long period finely (5-2) twinned structure, referred to as 14M in the Otsuka scheme. On the other hand, local stress fields are also known to affect the twinning sequence, as observed e.g. at the vicinity of a microcrack.

2.3 Nucleation and growth of a self-accommodating martensite plate

The small hysteresis and the extreme composition dependency of the martensitic transformation in Ni-Al are usually hindering factors in the investigation of the nucleation and dynamics of the transformation. However, as shown above, melt-spun ribbons of 62.5 and 65 at.% Ni exhibit composition fluctuations of about 2 to 3 at.% on a lateral scale of a few hundred nanometers. As a result, strong fluctuations in the Ms temperature exist in a given sample. For the 62.5Ni material this yields austenite regions, which are, at room temperature, extremely close to Ms. In-situ cooling transforms, in some cases, such regions into the martensitic structure. In Fig. 7 a wedge shaped structure is shown inside an austenite matrix, revealing the formation of an energy-minimising configuration consisting of all three transformation variants occurring in the present cubic-to-tetragonal deformation [10].
The surrounding austenite is viewed along a $<111>$ zone axis with three families of $\{110\}$ type planes observed edge-on. Two of those families, $(01\overline{1})$ and $(1\overline{1}0)$, become close packed microtwin planes, one on either side of the midrib, the latter being parallel with the third $(\overline{1}01)$ family. As a result the angle between the different microtwin planes is close to $120^\circ$, instead of the $90^\circ$ cases described in §2.1.

2.4 Martensite in Ni-Ti-Cu melt spun ribbons

Binary NiTi alloys transform martensitically from the austenite B2 structure to a monoclinic structure [11], currently referred to as B19'. Depending on the thermal or mechanical history of the sample, this transformation can occur directly or pass over the so-called R-phase [12]. When Ni is replaced by Cu, the orthorhombic B19 structure can appear as an intermediate between B2 and B19' [13]. As-received melt spun films of Ni$_{40}$Ti$_{50}$Cu$_{10}$ are amorphous and can be crystallised in the B2 phase by annealing for several minutes at $500^\circ$C. This produces B2 grains of micron size. Cooling such films transforms these grains
Figure 7. Self-accommodating martensite wedge involving all three deformation variants of the transformation and observed during in-situ cooling of a melt-spun Ni$_{62.5}$Al$_{37.5}$ sample.

into multiply twinned B19 martensite although some indication of B19' is observed. In Ni$_{25}$Ti$_{50}$Cu$_{25}$ films the crystallised B2 grains not always transform martensitically when returning to room temperature. Apparently, the annealing time and conditions at the crystallisation temperature play an important role in determining the final transformation path. For example, well developed B19 martensite was obtained after annealing at 500°C for 5 min, whereas retained austenite as well as martensite structures were recognized after annealing for one hour at the same temperature. When increasing the annealing temperature to 700°C, Cu-enriched precipitation occurs, leaving the matrix with a Ni enriched B2 structure. Upon cooling this matrix transforms to a periodically twinned martensitic structure around 300°C, a temperature much higher then normally observed in these alloys. Images of the crystallised B2 with some small precipitates as well as the twinned martensite with larger precipitates are shown in Fig. 8. The diffraction pattern of the martensite can be explained by a mixture of the [110] zones of the orthorhombic B19 structure and two variants of the monoclinic B19', which indicates a two-step transformation sequence B2→B19→B19'. In the latter the twinning occurs on the (001) planes, which can be related with a compound twin mode in binary NiTi [14].
2.5 Ordered structure of $L_2_1$ Cu-Zn-Al austenite

Many aspects of the cubic-to-monoclinic martensitic transformation in Cu-rich Cu-Zn-Al material have been thoroughly investigated by different researchers. New insight into the generic and non-generic appearance of twin systems in the martensite structure, based on systematic mathematical models, now indicate that for special lattice deformations, and thus lattice constants of parent and product structures, previously unexpected twin configurations could arise [7]. These could have a pronounced impact on the shape memory behaviour of such materials. As for many systems, the lattice constants in Cu-Zn-Al alloys depend on the exact composition. A systematic study of the relation between the lattice constants and the composition could thus eventually lead to the fabrication of a given composition for which the special conditions hold. However, the actual austenite structure involved in the martensitic transformation in this system depends on composition and thermal treatment [15]. Indeed, although the basic lattice is always body centered cubic (bcc), the ordering can either be of the B2 or $L_2_1$ type. In the case of B2 the Cu atoms occupy the corners of the cube while the Zn and Al atoms as well as the remaining Cu atoms are randomly distributed on the central site. The $L_2_1$ cell has a Fm$\overline{3}$m space group and consists of 2x2x2 bcc cells in which the 8c positions are fully occupied by Cu atoms. The remaining 4a and 4b positions are filled with the remaining Cu atoms as well
as with the Al and Zn atoms, as shown in Fig. 9. The actual distribution of the latter, however, cannot be concluded from symmetry arguments or conventional electron diffraction experiments.

In order to properly study the effects of composition on the lattice constants, a new indirect structure retrieval method based on electron diffraction was used to determine the actual occupation parameters for the L2₁ case of a Cu₆₆.₉Zn₂₃.₇Al₉.₄ alloy. In this method, which is referred to as multi-slice-least-squares (MSLS), dynamical electron diffraction intensities calculated by a multi-slice method and based on a starting model with several parameters are fitted to a large number of experimental electron diffraction intensities obtained in different zones and for different thicknesses and recorded on CCD [11]. In the present case, the fitting parameters used are, next to thickness, orientation and Debye-Waller factors, the occupations on the 4a and 4b sites. Two atomic models are compared. In the first the 4a positions are occupied by all the Al atoms plus Zn to fill all places, whereas the 4b positions contain the remaining Zn and Cu atoms. In the second model the Al atoms remain on the 4a positions but this set is completed with Cu atoms. The 4b positions still contain Cu and Zn atoms. The final results of the present study indicate that the first model yields the best fit for the diffraction data. In the second model the Debye-Waller factors for the atoms on the 4a positions reduce to zero, whereas the occupation on the 4b positions converges to the set value of model I, leading to a final composition of Cu₈₀.₇₅Zn₉.₅Al₉.₇₅, which strongly deviates from the nominal composition of the alloy. This confirms the results of an earlier study using neutron diffraction [17]. After further refinement, the finally obtained composition for model I is
Cu_{65.7}Zn_{26.1}Al_{8.2} with an overall R-factor of 2%. Of course, the possibility of obtaining a nanometer sized probe in the electron microscope offers the means for very local and non-averaged data and results.

3 Conclusions

Transmission electron microscopy remains an extremely valuable tool for the study of micro- and nanoscopic features of martensitic phase transformations and structures. Conventional as well as advanced methods reveal details unattainable by other methods. From this information new material with high potential for applications can be developed.

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Martensitic transformations studied on nano- and microscopic length scales 387


