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SPINODAL DECOMPOSITION OF Ni-Ti

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Abstract - An Ni-12 at% Ti-alloy was investigated using field ion microscopy (FIM) and atom probe (AP) analysis. A study of the homogeneous state and of annealed specimen (24 to 512 h, 550°C) has been carried out. The decomposition is of spinodal type. An increase with time in concentration amplitude and wavelength has been found. The experiments have been compared with computer simulations of a spinodally decomposing alloy. In the later stages of decomposition the FIM showed a contrast. Additionally spinodal ordering (L1_2-Type) was found for the Ti enriched regions.

I - INTRODUCTION

Yoshida et al. recently have investigated the decomposition of supersaturated Ni-Ti alloys by means of high resolution electron microscopy /1/. Lattice images show the existence of ordered regions even in the as-quenched state of alloys containing less than 10 at% Ti. These regions correspond to higher Ti concentrations as derived from lattice spacings. The Ni-14.7 at% Ti alloy could not be homogenized but shows ordering of the Ti enriched regions in an even more pronounced manner. The suggestion is that some modulation in composition and degree of order appear within the ordered regions. Ni-14 at% Ti was also investigated by Sinclair et al. /2/ using FIM but the alloy was not homogeneos either. An Ni-12 at% Ti alloy studied by Watts and Ralph /3/ with FIM and TEM show a slight decomposition not explained by statistical fluctuations even in the as-quenched state. Further ageing lead first to ordering and then to phase separation.

To investigate the stages of decomposition it is necessary to start from a really homogeneous alloy. Otherwise the quenched-in fluctuations give an unknown starting point for the decomposition. Cahn and Hilliard /4/ implicitly demonstrated the way a metallurgist should prove the spinodal character in a decomposing alloy: the concentration amplitude of the fluctuations should increase with ageing time, as the concentration gradient gets steeper. To investigate sinusoidal fluctuations by the AP and to distinguish them from nucleation and growth of small particles with sharp interfaces, computer simulations of the decomposed alloy are necessary. They also help to estimate the error due to the finite lateral resolution of the AP.

II - EXPERIMENTAL

A Ni-12 at% Ti alloy was levitation-melted and quenched into water; then wire drawing was performed (Ø=0.2mm). The material was homogenized at 1200°C for 90 min and finally quenched into iced brine. Subsequently the wire was encapsulated in an argon atmosphere and aged at 550°C for various times up to 256 h. FIM-tips were prepared by electropolishing between 15 and 2 V DC in a solution of 10% perchloric acid in acetic acid.

The FIM and atom probe investigations were performed on the Göttingen instrument described by Piller /5/ and Wagner /6/.
The measurement conditions of the FIM-p were a pressure of $10^{-9}$ mbar in the UHV-chamber, a specimen temperature of about 80 K and a neon pressure of $5 \times 10^{-6}$ mbar. The AP-studies were carried out with an aperture radius $r_{ap}$ in the range of 1.0 to 1.6 nm depending on the voltage between tip and channelplates.

### III - RESULTS AND DISCUSSION

The quenching rate of the solution treated wire was found to be sufficient to avoid any concentration fluctuations greater than the statistical noise. Fig.1a shows a concentration profile over a depth of 68 nm. The autocorrelation of this profile (fig.1b) indicates that no long range fluctuations exist and that the noise on the profile derives from the limited number of detected atoms per atomic layer, here: on an average of 50 atoms per (002) plane /7/. The field ion image did not reveal any contrast, neither between two phases of the alloy, nor between subsequent (002) planes indicating ordering.

Annealing the supersaturated alloy at 550 °C leads to an ordering on the \{002\} planes. Subsequent micrographs of the permanent field evaporating tip, aged for 64 h, first show the disappearance of a bright Ti rich plane (fig.2a). Then a smaller Ni rich, dark plane turns up (c), is removed fast, and leads again to a conspicuous bright plane (d). Figs. 2e,f show the disappearance of the next dark plane. A concentration profile and a ladder diagram (figs. 3a and b) of a specimen aged for 256 h at 550 °C recorded close to a \{002\} pole in a Ti enriched region, show the alternating composition of these crystallographic planes: a nearly pure Ni plane changes to a Ti enriched plane. If the ordering of the expected L12-structure (\{111\}/\{-112\}) would be complete in the Ti enriched regions, a layer containing 50 at% Ti would alternate with a 0 at% Ti layer. Up to 256 h at 550 °C these concentrations are still not achieved. This seems to be a good indication for spinodal ordering.

Furthermore ageing for 256 h yields a clear contrast in the field ion micrographs between the Ti enriched bright and the Ti depleted dark regions. An example of a specimen aged for 256 h at 550 °C (fig.4) shows no strict alignment of the bright areas. The micrograph 4a was taken at a slightly higher voltage than the following 4b. Here the alignment is more evident but only two parts of the picture show contrast. Remarkable is the lack of strict periodicity contrary to the observations of Sinclair et al. /2/.

The decomposition of this alloy can be investigated using the atom probe. To be able to distinguish between a homogeneous alloy, a spinodally decomposing alloy or an alloy that decomposes by nucleation and growth of particles, the wavelength of fluctuations or the particle sizes have to be greater than the region covered by the smallest possible aperture of the atom probe; i.e. greater than 1.4 nm in diameter. The problem in analysing such a small lateral region is that the noise on the concentration profiles is large because the number of collected atoms per field evaporated layer is small. As the wavelengths are greater than 2 nm in the analysed alloy, in our case an aperture radius of more than 1 nm is sufficient. The concentration profile in the \{111\} direction of an alloy aged for 90 h at 550 °C (fig.5a) shows two Ti enrichments of 4 and one of 5 nm in diameter and in the related autocorrelogram (fig.5b) one sees an interparticle distance $k_z$ of 8 nm. A second maximum in the autocorrelation diagram indicates a periodic alignment /7/. As there is no strict periodicity visible in the profile, the second maximum $k_z$ in the autocorrelogram is broader. The lack of strict periodicity is seen as well in the field ion micrograph (fig.4). Furthermore the concentration profiles show that the mean concentration is lower than the nominal one. In other recorded profiles a lower mean concentration could be observed even better, computer simulations of concentration profiles can explain this effect.

With the help of a computer a three-dimensional sinusoidal concentration variation was produced. Hereby a structure of decomposition aligned in \{001\} directions is assumed. The spatial concentration distribution is described by

$$ c(x,y,z) = \frac{\Delta c}{3} \cdot \left( \sin(k_x x) + \sin(k_y y) + \sin(k_z z) + c_0 \right), $$

where $\Delta c$ denotes the concentration amplitude of the sinusoidal wave, $k=2\pi/\lambda$ the wave-
vector \( x, y, z \) the three \([100]\) directions of the crystal, \( 4x, 4y, 4z \) the initial phase of the sinus wave, and \( c_0 \) the nominal concentration. Within this structure of decomposition a cylinder is placed. The cylinder represents in its dimension and location the volume analysed with the AP. In fig. 6 the analysed cylinder lies parallel to the \( <002> \) direction and its cross section of \( \pi_{\text{Ap}}^2 \) contains 45 atoms per \( (002) \) plane. This limited number of collectable atoms in the cross section leads to a statistical noise on top of the "ideal" concentration profile: a lattice site for an atom can only be occupied by a Ni or a Ti atom. To show the critical effect of the "right" location of the analysed cylinder and to enhance the effect in concentration amplitude a computer simulated concentration profile was produced with the parameters presented in fig. 6. The decrease of the mean concentration with respect to the nominal one is caused by the location of the cylinder: the cylinder is situated in such a way that the lowest possible concentration amplitude within the crystal was recorded. In the related autocorrelagram the wavelength and periodicity are still obtained.

The following table shows the AP-results obtained up to now. The wavelength of the 90 h aged specimen in \( <111> \) direction is converted into a \( <002> \) wavelength. The amplitudes were taken from the concentration profiles comparing them with simulated profiles.

<table>
<thead>
<tr>
<th></th>
<th>64 h</th>
<th>90 h</th>
<th>256 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>2.5 nm</td>
<td>4.5 nm</td>
<td>4.9 nm</td>
</tr>
<tr>
<td>Amplitude</td>
<td>6 at% Ti</td>
<td>7.5 at% Ti</td>
<td>9.5 at% Ti</td>
</tr>
</tbody>
</table>

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REFERENCES

Fig. 1 - Concentration profile along a ⟨002⟩ axis into the depth of a Ni-12 at% Ti alloy and the related autocorrelation analysis. The alloy was homogenized at 1200 °C for 90 min.

Fig. 2 - Field ion micrographs of step by step field evaporation with the ⟨002⟩ pole in a bright area of an aged specimen (64 h, 550 °C) showing the L1₂-ordering in a Ti enriched region.
Fig. 3 - Concentration profile and ladder diagram along a<002> axis of a specimen aged for 256 h at 550°C.

Fig. 4 - Field ion micrographs of a Ni-12 at% Ti specimen aged for 256 h at 550°C (Vdc=15 kV, imaging gas: Neon) showing brightly imaging Ti enriched regions.
Fig. 5 - Concentration profile along a (111) axis into the depth of a Ni-12 at% Ti specimen aged for 90 h at 550°C and the related autocorrelation analysis.

Fig. 6 - Computer simulated concentration profile of a Ni-Ti alloy with three-dimensional sinusoidal concentration variation and related autocorrelation analysis. Assumed parameters: nominal Ti concentration $c_0 = 12$ at%, wavelength $\lambda = 10.56$ nm, aperture radius $r_{ap} = 1.00$ nm, concentration amplitude $\Delta c = 11$ at%, shift of analysed cylinder which is situated along z-axis relative to the concentration variation $\Delta x = \lambda / 4, \Delta y = \lambda / 4$. 