CHARACTERIZATION OF Ni-Ti ALLOYS SYNTHESIZED BY VAPOR QUENCHING

P. Moine, A. Naudon, J. Kim, A. Marshall, D. Stevenson

To cite this version:

P. Moine, A. Naudon, J. Kim, A. Marshall, D. Stevenson. CHARACTERIZATION OF Ni-Ti ALLOYS SYNTHESIZED BY VAPOR QUENCHING. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-223-C8-227. <10.1051/jphyscol:1985832>. <jpa-00225175>

HAL Id: jpa-00225175
https://hal.archives-ouvertes.fr/jpa-00225175
Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
CHARACTERIZATION OF Ni-Ti ALLOYS SYNTHESIZED BY VAPOR QUENCHING

P. Moine, A. Naudon, J.J. Kim†, A.F. Marshall† and D.A. Stevenson†

Laboratoire de Métallurgie Physique, Faculté des Sciences, 40, avenue de Recteur Pineau, 86022 Poitiers, France
†Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, U.S.A.

Abstract

Non crystalline Ni-Ti alloys have been synthesized by vapor quenching in the composition range 25-70 at.% Ni. Atomic size versus concentration, Radial Distribution Function (RDF) and Transmission Electron Microscopy observations suggest the existence of Short Range Order (SRO) which could explain the growth of an ordered close packed Ni$_3$Ti phase at the beginning of the crystallization of a Ni$_{56}$Ti$_{44}$ amorphous film.

Synthesis of non crystalline Ni-Ti has been made by liquid quenching (quenching rate $= 10^{10}$K.S$^{-1}$ in the composition range 25-40 at.% Ni by Polk et al. (1) which corresponds to the concentration of a deep eutectic in the Ni-Ti equilibrium phase diagram. Equiatomic NiTi alloys have also been recently obtained in an amorphous state by ion implantation (2-3) and high energy electron irradiation (4). These latter techniques may be considered as a faster quenching process ($10^{14}$K.S$^{-1}$) than that of splat quenching.

Vapor deposition, with effective atomic quench rates greater than $10^{12}$K.S$^{-1}$, is a valuable synthetic technique which may extend experimental information on the glass forming ability of the Ni-Ti system. This paper reports on a study of the microstructure of Ni-Ti alloys synthesized by magnetron sputter deposition.

I. Experimental procedure

1.1 Synthesis of sample

Samples were prepared by planar magnetron sputtering using two magnetron sources with elemental Ti and Ni targets operated in a DC mode. Ar was used as a sputtering gas at a pressure of 3 mtorr.

Two modes were employed; "concentration spread" mode and "rotating substrate" mode. The "concentration spread" mode consisted of codeposition from non-coincidental Ni and Ti sources onto static substrates fixed on a 7.6x25.5 cm liquid nitrogen cooled table. This
deposition mode formed a film with a monotonic variation of composition. The thickness of the films was 10-15 μm. In the "rotating substrate" mode, substrates clamped on the rotating table was positioned 13 cm below the target surface where the center of rotation was coincident with the center of the two sources. Substrates were rotated at 300 rpm during deposition, sufficient to ensure that no more than half of a monolayer was deposited per revolution. Therefore, the film resulting from the rotating mode should be compositionally homogeneous. Films of 7-10 μm could be obtained after 2-4 hr of deposition. In both cases electronic grade glass slides were used as substrates and were thermally floating.

1.2 Structural Characterization

First of all composition of the specimens was determined using electron microprobe analysis.

X-ray Diffraction (XRD) was performed using an automated Picker powder diffractometer with CuKα radiation.

Transmission Electron Microscopy (TEM) characterization was performed on disc 3 mm in diameter, thinned to electron transparency by ion beam milling from both sides using argon at 4 KV, a gun current of 0.05 mA and an incident angle of 20°. Specimens during the ion milling process were cooled down to liquid nitrogen temperature to avoid crystallization of the amorphous film. Selected Area Diffraction Patterns (SADP) and Bright Field (BF) and Dark Field (DF) images were taken using a Philips EM400 (120KV) TEM. Intensities of SADP were measured using a microdensitometer.

Annealings of amorphous specimens were performed in high vacuum (10⁻⁶ Torr) furnace.

II. Results

2.1 "Concentration Spread" Mode; Preliminary results, first deductions

An as-deposited sample made by "concentration spread" mode was investigated by XRD. The results of this investigation (peak positions, relative half height width of the first peak, atomic size...) are gathered in table I. The atomic size can be deduced from the structure of crystalline samples when it is known (first interatomic distance) or from the Ehrenfest relation when the samples are amorphous (The Ehrenfest relation: \( S x r ̂ = 7.72 \) assumes that the first maximum of the interference function is close to the first maximum of \( \frac{\sin S r}{S r} \) with \( S = 4\pi \sin \theta/\lambda \)), \( r \) nearest neighbor distance. Atomic size versus composition is plotted in figure 1.

TEM investigation confirms that the Ni concentration range for amorphous Ni-Ti forming is 25 - 70 at.%. 

2.2 Sputtered films of constant composition ("Rotating Substrate" Mode)

Three films of constant composition obtained by rotating substrate mode were investigated by X-ray with CuKα radiation and TEM. The composition of these specimens corresponds to the edges and the centre of the amorphous concentration range i.e. Ni₃⁵Ti₇₀, Ni₅₆Ti₄₄, and Ni₆₈Ti₃₂.

Although, except for a specimen with 56 at.% Ni, any atomic-scale structure has not been yet determined from X-ray scattering, raw scans
obtained with CuKα radiation reveal an amorphous state in the same composition range as that obtained with the "concentration spread mode" (Fig. 1). Further evidence for amorphous state was obtained from TEM.

Table I. Main XRD characteristics of vapor-deposited (magnetron sputtering) Ni-Ti films, using the "concentration spread" mode, versus Ni concentration. $S_1$ is the position of the first peak in $\lambda^{-1}(S=4\pi \sin \theta/\lambda)$. $\Delta_r$ is the ratio, in arbitrary units, between the half-height width of the first peak and intensity.

<table>
<thead>
<tr>
<th>Slide Number</th>
<th>At. % Ni</th>
<th>$S_1(\lambda^{-1})$</th>
<th>$\Delta_r$</th>
<th>Structure</th>
<th>Nearest Neighbor Distance in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5-8</td>
<td>2.68</td>
<td>0.35</td>
<td>BCC(Ti)</td>
<td>2.86</td>
</tr>
<tr>
<td>2</td>
<td>8-12</td>
<td>2.68</td>
<td>0.1</td>
<td>BCC(Ti)</td>
<td>2.86</td>
</tr>
<tr>
<td>3</td>
<td>14-22</td>
<td>2.64</td>
<td>0.12</td>
<td>CRYSTAL</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25-40</td>
<td>2.72-2.87</td>
<td>50</td>
<td>AMORPHOUS</td>
<td>2.83-2.69</td>
</tr>
<tr>
<td>5</td>
<td>40-60</td>
<td>2.91-2.94</td>
<td>40</td>
<td>AMORPHOUS</td>
<td>2.65-2.63</td>
</tr>
<tr>
<td>6</td>
<td>60-80</td>
<td>2.98-3.00</td>
<td>27-4</td>
<td>AMORPHOUS</td>
<td>2.58</td>
</tr>
<tr>
<td>7</td>
<td>80-90</td>
<td>3.04-3.07</td>
<td>2.0</td>
<td>CRYSTAL</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>90-94</td>
<td>3.07</td>
<td>0.14</td>
<td>FCC (Ni)</td>
<td>2.51</td>
</tr>
<tr>
<td>9</td>
<td>94-96</td>
<td>3.08</td>
<td>0.1</td>
<td>FCC (Ni)</td>
<td>2.49</td>
</tr>
<tr>
<td>10</td>
<td>96-98</td>
<td>3.10</td>
<td>0.25</td>
<td>FCC (Ni)</td>
<td>2.48</td>
</tr>
</tbody>
</table>

Figure 1
Average nearest neighbor distance calculated by Ehrenfest relation in the amorphous domain

2.3 Thermal stability and crystallization microstructure
DSC data indicate that the crystallization temperatures are 448°C, 520°C and 435°C for Ni$_{30}$Ti$_{70}$, Ni$_{56}$Ti$_{44}$, and Ni$_{68}$Ti$_{32}$, respectively. Although scans exhibit only one DSC exotherm peak, TEM and X-ray
Diffraction indicate that the crystallized microstructure is quite complicated.

Crystallization studies through XRD and electron diffraction pattern analysis show that only long annealing of several days well above the crystallization temperature $T_c$ leads to the usual equilibrium phases but short annealing gives intermediate phase. Here, we will illustrate this behavior in the case of Ni$_{56}$Ti$_{44}$. A complete amorphous - crystalline transition study will be presented elsewhere. When a Ni$_{56}$Ti$_{44}$ amorphous film (fig. 2a) is heated up to 520°C for five minutes, only Ni$_3$Ti reflections are observed in SADP (fig. 2b) and BF image show highly faulted Ni$_3$Ti grains embedded in a region without contrast (fig. 2b). After annealing of 1 1/2 hr. at 650°C, B2, TiO$_2$ and possibly Ti$_2$Ni$_3$ rings appear together with some remaining Ni$_3$Ti rings (fig. 2c). XRD scan after long annealing of 6 1/2 days at 650°C show weak Ni$_3$Ti lines, B2-NiTi lines and Ni$_3$Ti$_2$ lines.

Fig. 2:
BF image and SADP of a Ni$_{56}$Ni$_{44}$ thin film:
- as deposited in a)
- annealed at 520°C for 5 minutes in b)
- annealed at 650°C for 1 1/2 hour in C)

Microdensitometer traces are taken along diameter of amorphous rings through the center of the SADP.
III. Discussion, and Conclusion

From both "concentration spread" mode and "rotating substrate" mode it has been shown that magnetron sputtering (vapor deposition) is a powerful technique to get amorphous Ni-Ti phases in a large composition range (25 to 70 at.% Ni instead of 25-40 at.% Ni by liquid quenching).

Although the microstructural characterization (at the atomic level) versus the concentration is still in progress some information of particular interest, especially for a Ni$_{56}$Ti$_{44}$ amorphous film, can be deduced from the first results.

The amorphous structure obtained by vapor deposition is characteristic of simple glassy alloys as indicated by the shoulder observed on the second peak of the RDF (Fig. 3).

Atomic size decreases continuously with Ni concentration. This behavior can be explained in terms of difference of atomic radius since Ni atoms are smaller than Ti atoms; however, the average nearest neighbor spacing is smaller than the weighted mean distance between nearest neighbors in the corresponding pure metals. This result could indicate the existence of a Short Range Order (SRO) which favors short Ti-Ni bonds with respect to long Ti-Ti bonds. This result was also mentioned by Ruppersberg et al. (6) for amorphous Ti$_{60}$Ni$_{40}$.

Ni$_{56}$Ti$_{44}$ RDF shows a broad non-symmetrical first peak (P. Moine, A. R. Pelton, R. Sinclair, to be published and (5)) (fig. 3) which can be explained by a weighted superposition of the partial distribution functions such that the weight of G$_{TiTi}$ function is weaker than that of G$_{NiTi}$ and G$_{NiNi}$ function. Indeed partial distribution functions G$_{NiTi}$ and G$_{TiTi}$ have a maximum respectively at 2.58Å and 2.92Å (7) and the maximum of the first peak of the Ni$_{56}$Ti$_{44}$ RDF is at 2.58Å. That confirms that Ti atoms are preferentially surrounded by Ni atoms as first neighbours.

Crystallization study of a Ni$_{56}$Ti$_{44}$ amorphous film also confirms this result. Indeed the first crystallized phase to appear is a Ni$_3$Ti ordered close packed structure such that each nickel atom has 4 nickel atoms and 8 titanium atoms as nearest neighbours while the titanium atoms have 12 Ni atoms as nearest neighbours and no titanium atoms (8). Longer annealing leads to the formation of equilibrium phases like B2 phase which is unlikely to be favored at the beginning of the crystallization since each atom has only 8 nearest neighbors in the B2 phase and each atom has an average of 11.5 first neighbors in the amorphous state (5).

References