SUPPRESSION OF THE MARTENSITIC PHASE TRANSITION IN NI-RICH NI-AL THIN FILMS

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We have prepared thin Ni$_x$Al$_{1-x}$ alloy films in the concentration range $0.56 \leq x \leq 0.70$ by co-sputtering from element targets. Structural investigations utilizing TEM and XRD reveal that the films consist of ultra-fine grains with $d_{\text{grain}} \approx 10$ nm. Similar to bulk material the nano-grained Ni-Al samples undergo a structural phase change from (ordered) bcc to (ordered) fcc with increasing Ni content, which is, however, shifted towards higher Ni concentrations. From measurements of the electrical resistivity we find no indication for a martensitic phase transition for $x = 0.635$ and $x = 0.65$.

1 Introduction

The nucleation mechanism of martensitic phase transformations is an intensively debated problem.\(^1\) In thin films and small particles, due to the reduced crystallite size, the energetic balance between chemical, elastic, and surface free energies is shifted with respect to those in bulk materials, and as a consequence, the martensitic phase transition occurs at reduced temperatures or is even completely suppressed.\(^2,3,4,5\) Most investigations on micro- and nano-crystalline materials have been carried out in the Fe-Ni system, or have dealt with Fe or Co alloys. In the Ni-Al alloy system stoichiometric NiAl thin films play an important role in the field of magnetic recording, since they offer the possibility of providing a particular texture, which is advantageous for growing high coercivity magnetic material.\(^6\) However, little is known on the structural properties of Ni-rich Ni-Al thin films, although in bulk form these alloys undergo a thermoelastic martensitic transformation.\(^7,8,9\) Thus, the question arises as to whether the martensitic transformation is suppressed in Ni-rich Ni-Al films. In the present paper we report on the preparation of such Ni-rich Ni-Al alloy thin films by sputter deposition. We present results of investigations on the occurrence and the temperature range of stability of parent phase $\beta$-NiAl.
2 Experimental

The samples are prepared in a UHV preparation chamber by co-sputtering from two independently controlled sputter guns in Ar at room temperature (RT). The base pressure of the UHV chamber is $10^{-7}$Pa and during deposition at a continuous gas flow of 0.6sccm/min it rises to $2.5\times10^{-1}$Pa. We use 99.995% Ni and 99.999% Al as primary target materials. 99.999% Ar is passed through a gas purifying system capable to reduce both, O$_2$ and water contaminations to below 50ppb before being fed to the sputter guns immediately at the targets. The target to substrate distance is 130nm. We use glass, sapphire, and NaCl substrates, which are mounted on a substrate holder that rotates with a typical frequency of 1Hz. Deposition rate and layer thickness are monitored by quartz crystal oscillators, which are calibrated utilizing an optical interference method. The Ni concentration is varied between 56at% and 70at% (0.56 $\leq$ x $\leq$ 0.70). Accordingly, the deposition rate of RF-sputtered Ni is kept constant at $r_{Ni} \approx 0.4$nm/s (RF power: $P_{RF}$ $\approx$ 270W), while the deposition rate of DC-sputtered Al is varied in the range 0.26nm/s $\leq r_{Al} \leq$ 0.42nm/s (DC power: 100W $\leq P_{DC} \leq$ 170W).

Structural investigations are carried out utilizing X-ray diffraction (XRD) and transmission electron microscopy (TEM). In order to prepare TEM samples, the films grown on NaCl substrates are exposed to deionized water. After dissolution of the NaCl, the free NiAl films are placed onto Cu grids, which are then examined in a Philips CM12 scanning transmission electron microscope (STEM) (LaB$_6$ cathode, acceleration voltage = 120kV). The concentration of the alloy films is determined utilizing energy dispersive X-ray analysis (EDX) by means of an EDAX PW9900 system attached to the STEM.

The electrical resistivity is measured in 4-terminal geometry in the temperature range 4.2K $\leq$ T $\leq$ 800K. The low-temperature (4.2K $\leq$ T $\leq$ 300K) experiments are carried out in a He$^4$ gas flow cryostat at normal pressure, whereas the high-temperature measurements (300K $\leq$ T $\leq$ 800K) are conducted in a tube oven in Ar atmosphere ($p_{Ar}$ $\approx$ 5-$\times$10$^3$Pa). Measuring currents are in the range 0.1mA $\leq I \leq$ 1mA.

3 Results and discussion

In order to characterize the as-deposited samples, we firstly focus on the structural investigations on a series of Ni$_x$Al$_{1-x}$ thin films in the range 0.56 $\leq$ x $\leq$ 0.70. All samples are prepared at RT and have a nominal thickness of t = 100nm. From TEM and XRD investigations the mean crystallite size is determined to be $d_{cryst}$ $\leq$ 10nm.
Figure 1. (a) Radial line scans through electron diffraction patterns of 8 Ni\(_{x}\)Al\(_{1-x}\) thin films. Background subtracted intensity is plotted vs. the radius of the diffraction patterns. The positions of diffraction fringes are labelled \(\bullet\), \(\circ\), and \(\triangle\) for \(\beta\)-NiAl, Ni\(_5\)Al\(_3\), and Ni\(_3\)Al, respectively. Figures (b),(c), and (d) show diffraction patterns of the samples with \(x = 0.7\), \(x = 0.635\), and \(x = 0.56\). The individual fringes are marked with their phase symbol and the according Miller indices.

In Fig. 1 we present the results of electron diffraction (ELD) experiments on 8 samples. Fig. 1(a) shows line scans taken radially from the center (radius, \(R = 0\)) to the periphery of the patterns. The positions of diffraction fringes are labelled according to the crystal structure they are associated with. In the concentration range under investigation we observe the occurrence of the following phases: \(\beta\)-NiAl (\(\bullet\)) has an ordered CsCl-type crystal structure [space group (SG): Pm\(\overline{3}\)m], Ni\(_5\)Al\(_3\) (\(\circ\)) has an orthorhombic unit cell (SG: Cm\(\overline{m}\m\)), and Ni\(_3\)Al (\(\triangle\)) exhibits an ordered L1\(_2\) structure (SG: Pm\(\overline{3}\)m). To illustrate
Table 1. Summary of the various structural phases present in our as-deposited sputtered Ni$_x$Al$_{1-x}$ thin films at RT as determined from the analysis of electron diffraction patterns. For samples containing $\beta$-NiAl phase contributions the approximate martensite start temperatures, $M_{S}^{\text{bulk}}(\beta\text{-NiAl})$, of the according bulk alloys are also given (see Text for details).

<table>
<thead>
<tr>
<th>$x$</th>
<th>Phase (T = 300K)</th>
<th>$M_{S}^{\text{bulk}}(\beta\text{-NiAl})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
<td>$\beta$-NiAl</td>
<td>0</td>
</tr>
<tr>
<td>0.58</td>
<td>$\beta$-NiAl</td>
<td>0</td>
</tr>
<tr>
<td>0.62</td>
<td>$\beta$-NiAl + Ni$_5$Al$_3$</td>
<td>250K</td>
</tr>
<tr>
<td>0.635</td>
<td>$\beta$-NiAl + Ni$_5$Al$_3$</td>
<td>450K</td>
</tr>
<tr>
<td>0.65</td>
<td>$\beta$-NiAl + Ni$_5$Al$_3$</td>
<td>660K</td>
</tr>
<tr>
<td>0.673</td>
<td>Ni$_5$Al$_3$ + Ni$_3$Al</td>
<td>-</td>
</tr>
<tr>
<td>0.68</td>
<td>Ni$_5$Al$_3$ + Ni$_3$Al</td>
<td>-</td>
</tr>
<tr>
<td>0.70</td>
<td>Ni$_3$Al</td>
<td>-</td>
</tr>
</tbody>
</table>

The essential modifications in the ELD patterns with varying Ni concentration we show in Figs. 1(b)-(d) exemplarily the patterns obtained from samples with $x = 0.70, 0.635, 0.56$. The individual diffraction fringes are marked with the according Miller indices.

ELD patterns of samples with the lowest Ni contents ($x = 56, 58$) show a clear signature of the $\beta$-NiAl phase (●). No evidence for the occurrence of significant amounts of any other phase is found. In the range $0.62 \leq x \leq 0.65$, the films consist of both, $\beta$-NiAl and Ni$_5$Al$_3$ (○) phases, whereas for $x \geq 0.673$, the Ni$_3$Al phase (○) evolves and becomes dominant for $x = 0.70$. These findings are summarized in Tab. 1. They are in principal agreement with the structural phase diagram of bulk Ni-Al.\textsuperscript{9,10} However, the existence of significant $\beta$-NiAl phase contributions up to a Ni concentration of $x = 0.65$ is in contrast to the findings in bulk Ni-Al, where for $x \geq 0.62$, $\beta$-NiAl is known to undergo a thermoelastic martensitic phase transition from the CsCl-type B2 to a face-centered tetragonal (fct) L1$_0$ structure at temperatures above RT.\textsuperscript{9,10,11} According to the bulk phase diagram the martensite start temperatures, $M_{S}^{\text{bulk}}$, for alloys with $x = 0.62, 0.635, 0.65$ are $M_{S}^{\text{bulk}} = 250K, 450K, 660K$, respectively.\textsuperscript{10} As a consequence, the occurrence of $\beta$-NiAl at RT is not expected at Ni concentrations $x > 0.62$.

The temperature dependence of the electrical resistivity has proved to be a sensitive physical property, in which the occurrence of a martensitic phase
transition shows up as a distinct and hysteretic increase of the resistivity with decreasing temperature.\textsuperscript{11,12} Thus, to shed more light on the question as to whether or not the martensitic phase transition is suppressed in our sputtered Ni\textsubscript{x}Al\textsubscript{1-x} thin films, we present in Fig. 2 the results of resistivity measurements on the samples with x = 0.635 and x = 0.65. We plot the resistance normalized to its value at T = 300K, R/R\textsubscript{300}, as function of the temperature. Starting at RT, both samples are cooled to T = 4.2K, then heated to T \approx 700K, and finally cooled to T = 4.2K, again.

During the first cooling cycle, and before reaching roughly T \approx 500K when being heated, the resistance of the films hardly changes with temperature. Specifically, in the sample with x = 0.635 there is no indication of a significant drop in R/R\textsubscript{300} at T \approx 425K, i.e. where the martensitic phase transition occurs in the bulk material\textsuperscript{12} (cf. Tab. 1). We like to point out that the resistance change associated with a martensitic transformation in \beta-NiAl is a major effect and is expected to amount to some 30\%.\textsuperscript{11,12} In our Ni\textsubscript{x}Al\textsubscript{1-x} thin films with x = 0.635 and x = 0.65, however, the maximum changes in R/R\textsubscript{300}(T) below T \approx 500K are in the order of 1%. A comparably weak temperature dependence of the resistance is observed in additional low-temperature measurements on a sample with x = 0.62 (not shown here),

Figure 2. Temperature dependence of the electrical resistance, R, normalized to its value at T = 300K, R\textsubscript{300}, for two sputtered Ni\textsubscript{x}Al\textsubscript{1-x} thin films with x = 0.635 and x = 0.65. Arrows indicate the chronological sequence of the measurements (see text for details).
though the martensite start temperature of the according bulk alloy is known to be $M_S^{\text{bulk}} \approx 250\text{K}$.

As can be seen from Fig. 2, $R/R_{300}$ increases strongly when the samples with $x = 0.635$ and $x = 0.65$ are heated to temperatures $500\text{K} \leq T \leq 700\text{K}$.

From measurements on bulk Ni-Al alloys this resistivity increase is known to originate from the formation of Ni$_5$Al$_3$.\textsuperscript{11} It sets in at lower temperatures in the sample with $x = 0.65$, and the effect is larger as compared to the film with the lower Ni concentration ($x = 0.635$), which is in good agreement with the findings in bulk Ni-Al.

A striking feature in $R/R_{300}(T)$ on finally cooling the samples down to $T = 4.2\text{K}$ is the anomalous increase of the resistance with decreasing temperature. We observe the occurrence of a weak maximum at temperatures below roughly $T \approx 100\text{K}$. A similar, though significantly smaller effect with its maximum lying at a somewhat larger temperatures is already observed in the initial cooling cycle. No hysteresis is found, and $R/R_{300}(T)$ is perfectly reversible below RT. The reason for this behavior is not yet understood. However, it is known that the occurrence and growth of small precipitates leads to additional contribution in the electrical resistivity that increase with decreasing temperature.\textsuperscript{13}

4 Conclusions

We have explored the structural properties of nano-grained Ni$_x$Al$_{1-x}$ thin films in the concentration range $0.56 \leq x \leq 0.70$. Electron diffraction experiments on as-deposited samples at RT show the occurrence of $\beta$-NiAl phase contributions in films with Ni contents as high as $x = 0.65$. These findings differ from the results on bulk Ni-Al alloys, which are known to undergo a martensitic phase transition from the B2 structure of $\beta$-NiAl to an fct $L1_0$ phase at temperatures above RT when $x > 0.62$. The ELD experiments thus indicate a suppression of the martensitic transformation in thin films. These results of our structural investigations are confirmed by measurements of the electrical resistivity. $\beta$-NiAl containing Ni$_x$Al$_{1-x}$ films in the concentration range $0.62 \leq x \leq 0.65$ do not exhibit any features in the temperature dependence of the resistivity that indicate a martensitic transformation.

In order to understand the microphysical origin of the suppression of the martensitic transformation in Ni-rich Ni-Al thin films, furthergoing experiments including a systematic variation of the crystallite sizes and film thicknesses will be necessary in the future.
5 Acknowledgements

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References

1. For a review see: C. M. Wayman, Mat. Sci. Forum 56-58, 1 (1990); and references therein.
11. J. Lašek, T. Chráska, P. Krček, and P. Bartuška, Scr. Mater. 37, no. 6, 897 (1997); and references therein.