THE EFFECT OF COOLING RATE DURING RAPID SOLIDIFICATION ON THE STRUCTURE AND TEXTURE OF NiTi

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ABSTRACT

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A study has been conducted on the effects of increasing cooling rate during rapid solidification of NiTi upon the phases that are produced. The hammer and anvil rapid solidification technique and laser melting with a nanosecond excimer laser were used, which allow the cooling rate to be varied by three to four orders of magnitude. Although 1/3 {110} superlattice reflections are seen in the selected area diffraction (SAD) patterns of the splat quenched (SQ) specimens, x-ray diffraction analyses show the presence of only B2 phase and martensite. On the other hand, laser treatment (LT) of the specimens produces a layer that has a Ll_0 structure with a slight monoclinic distortion. This phase can be envisaged as a small distortion of a B2 unit cell with a volume per atom $\sim 3.3\%$ lower than the equilibrium B2 phase. Also martensite is present in the layer. SQ alloys exhibit a marked {200} texture due to columnar growth opposite to the direction of heat extraction, while LT produces epitaxial regrowth of the melted layer. No substantial disordering is obtained in NiTi rapidly solidified alloys.

INTRODUCTION

Intermetallic Ni-Ti alloys of near equiatomic composition have a high temperature B2 (CsCl) ordered structure up to the melting point. These compounds exhibit a martensitic transformation into an orthorhombic phase, B19', with a small monoclinic distortion [1] and intermediate transitions between the austenitic and the martensitic phases. Those transitions together with accompanying changes in various physical properties are widely known as premartensitic phenomena. Great effort has been devoted to the study of these phenomena [1-6]. However, there is still considerable controversy regarding the nature of the transitions and the crystalline structure of the phases that NiTi alloys of near equiatomic composition exhibit [6,7]. Among the factors that may play a role in the transition phenomena, the cooling rate appears to be an important one, as indicated for instance by the experiments of Shabalovskaya [8]. Buschow studied the thermal stability of amorphous alloys of the Ni_xTi_{1-x} system in the range $0.24 < x < 0.64$, produced by melt spinning [9]. For $x < 0.40$ and $x > 0.58$, the alloys were produced in the fully amorphous state. Glass forming tendency, however, decreased in the range 40-58 at. pct. Ni.

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EXPERIMENTAL PROCEDURE

Commercially available NiTi (50.5 at. pct. Ni) was used for the experiments. Two sets of specimens were selected for laser treatment, one in the as-received (AR) condition and the other processed by rapid solidification using a hammer and anvil apparatus.

Laser irradiations were conducted by scanning the selected surface area with a XeCl (308 nm) excimer laser having a FWHM pulse duration of 41 ns. Laser energy densities up to a maximum of 3 J/cm² were employed.

X-ray diffraction measurements were performed with a Rigaku diffractometer, system Geigerflex D/Max, equipped with a copper target and a monochromator. Most of the measurements were done in the para-focusing geometry. A few diffraction patterns were taken at grazing angles with the purpose of probing a thinner near-surface region.

Specimens for analytical electron microscopy (AEM) were prepared by ion milling in a Gatan dual ion miller. Splat quenched (SQ) specimens were milled from both sides, whereas laser treated (LT) samples were milled from the backside. AEM was performed using either a Philips EM400/FEG or EM/430, both equipped with energy dispersive x-ray spectroscopy (EDXS) capability.

EXPERIMENTAL RESULTS

The x-ray diffraction pattern of the AR specimens revealed the presence of the high temperature B2-phase and of martensite. The lattice parameter of the B2 phase was determined, using least squares fitting, as 0.3014 ± 0.0001 nm, in good agreement with reported data [10].

SQ and LT specimens were prepared from the AR material. The chemical composition of the AR and the SQ samples was found to be the same by EDXS. As characterized by x-ray diffraction, the SQ samples (cooling rate $\sim 10^6$ K/s) contained B2 and martensite (see Table I). In some samples, however, a slight splitting ($\sim 0.7^\circ$) of the $\{110\}$ line was apparent. No other diffraction lines were observed. Although the very small splitting of the $\{110\}$ peak was only occasionally detected, $1/3$ $\{110\}$ superlattice spots were observed by SAD, as shown in Figure 1a. This result suggests some kind of long-range ordering with no accompanying change of structure. As presented in Table I, another interesting effect was produced, viz., a decrease of the lattice parameter of the B2-phase. Although the decrease is small, it was consistently detected by shifts of all the main B2 reflections toward higher Bragg angles.

The B2 $\{200\}$ line of the SQ material was much stronger, while the $\{110\}$ line was weaker than the corresponding lines of the AR material, indicating a difference of texture of the two specimen types. The texture of the SQ specimens is related to the pattern of heat extraction during the quenching process, which is mostly bi-directional from the external surfaces inwards. The diffraction patterns taken at grazing angles confirmed the pronounced $\{200\}$ texture of the SQ samples. Scanning electron microscopy (SEM) does indeed show a fully columnar structure, with grains a few microns thick, extending from both external surfaces to the middle of the samples. No

S.Q.	B2	1.366×10^{-2}	$a_0 : 0.3012$
S.Q. & L.T. (Sample 1)	Monoclinic	1.326×10^{-2}	$a:0.2966;b:0.4215$ $c:0.4242;\beta:90.30^\circ$
S.Q. & L.T. (Sample 2)	Monoclinic (near $L1_0$)	1.322×10^{-2}	$a:0.2960;b:0.4221$ $c:0.4232;\beta:90.0^\circ$

*Martensite is detected in all the specimens, in decreasing proportion with increasing cooling rate.

(a)

(b)

Figure 1. (a) 111 SAD pattern of SQ material. Note the presence of $1/3 \{110\}$ superlattice reflections. (b) 111 SAD pattern of near-surface region of SQ and LT specimen. Note absence of $1/3 \{110\}$ superlattice reflections and presence of TiO rings.

substantial disordering effect was observed, since the (200) line intensity increase was accompanied by a corresponding intensity increase of the (100) line.

Laser treatment (cooling rate $\sim 10^9 - 10^{10}$ K/s) affects only a thin near surface layer $1.2 \mu\text{m}$ thick, as measured by SEM. The thickness, as well as changes that may be induced by the quenching treatment, can be measured using a surface sensitive x-ray technique [11]. Laser melting is generally associated with epitaxial regrowth from the substrate. In order to study

monoclinic distortion observed in some specimens and not in others. Best fitting was obtained by assuming the atomic positions as derived from distorting a B2 structure. Table II shows the measured Bragg angles of samples 1 and 2 listed in Table I, and the calculated angles for the best lattice parameter fits. The structure factors also are presented for the case of a randomly oriented specimen.

Figure 2 shows the (100), (110), (200) and (211) diffraction lines before and after laser processing of sample 2. The "after processing" lines have been deconvoluted, the peaks' locations being shown in the figure. The deconvolution allowed us to separate the lines coming from the substrate and those originating in the LT layer by comparison with the pattern obtained before the treatment. By comparing the two integrated intensities of the substrate line we were also able to evaluate the layer thickness [11]. Again, no other diffraction peaks but those of the B2 and tetragonal phases, coming respectively from substrate and layer (and of martensite, present in the substrate and in a lower proportion in the layer), were observed. A comparison of the intensities seen in the figure and the structure factors given in Table II further emphasizes the strong preferential {200} grain orientation parallel to the external surface.

Table II. Observed and calculated Bragg angles, and structure factors of the main reflections

hk ^l	Structure Factor*, %	SAMPLE 1		SAMPLE 2	
		Meas. Bragg angle, 2 θ	Calc. Bragg angle, 2 θ	Meas. Bragg angle 2 θ	Calc. Bragg angle, 2 θ
001	0.00	Not obs.	20.92	Not obs.	20.97
011	2.06	29.25	29.86	29.92	29.87
100	2.00	30.45	30.11	30.15	30.17
002	24.19	42.60	42.59	42.60	42.70
020	23.94	42.85	42.88	42.65	42.81
111	23.61	43.15	43.00	43.30	42.97
022	5.49	62.05	62.03	62.17	62.06
200	5.26	62.65	62.59	62.70	62.73
113	2.19	78.35	78.36	78.30	78.37
131	2.18		78.64		78.53

*The structure factors are very similar for both cases. Multiplicity and temperature factors are not included.

(a)

(b)

(c)

(d)

Figure 2. Diffraction patterns of sample 2 around the B2 lines (a) {110}; (b) {200}; (c) {211}; (d) {100}. Light lines correspond to pattern before LT. Bold lines correspond to pattern after LT. M denotes martensite lines.

TEM studies revealed the formation of a thin (~30 nm) TiO layer at the sample surface, most probably formed during the laser processing. This explains the decrease by approximately 3% of the titanium content in the nickel-rich matrix, as measured by EDXS. Changes in the first 100 - 200 nm adjacent to the surface cannot be detected by x-rays which probe a much larger thickness. In this first region, the SAD patterns only show B2 spots, in addition to the oxide spots, and no superlattice reflections similar to those observed in the SQ specimen, as can be seen in Figure 1b.

AR plus LT samples exhibited similar changes in their diffraction patterns to those observed in the SQ plus LT specimens. Namely, a well-

accompanying shifts of all the split lines towards higher angles. There is, however, a difference in the relative intensities of the related peaks that are obtained in this case, in comparison with the SQ plus LT samples. This difference is due to the different orientation of the substrate grains, from which epitaxial regrowth of the melted layer occurs.

CONCLUSIONS

In near equiatomic NiTi alloys significant effects of changes in the cooling rate have been observed, using two different rapid solidification procedures:

- 1) SAD patterns of SQ specimens exhibit superlattice reflections. However, x-ray diffraction patterns demonstrate that the crystalline structure of those specimens is the same as that of AR ones, viz., B2, while the volume fraction of martensite is less. These results suggest the possibility of an incommensurate phase, as observed for instance in NiTiFe by Hwang et al.[5a]. However, further experiments are necessary to confirm this hypothesis and rule out any possible thin film artifacts.
- 2) Laser treatment of NiTi specimens produces a tetragonal ($L1_0$) phase with a slight monoclinic distortion in the melted and re-solidified layer.
- 3) Laser irradiation results demonstrate that very high quenching rates from the liquid state produce a crystalline phase which has a lower volume per atom than the B2 structure obtained with conventional cooling rates.
- 4) No substantial decrease of long range order is induced by rapid solidification.
- 5) Splat quenched specimens exhibit a marked {200} texture due to columnar growth parallel to the direction of heat extraction. Epitaxial regrowth occurs by laser treatment.

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