Chemistry of
Metals and Alloys

Chem. Met. Alloys 6 (2013) 196-199
Ivan Franko National University of Lviv
www.chemetal-journal.org

Crystal structure changes in the Ni_3Ta intermetallic compound

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Received December 7, 2013; accepted December 25, 2013; available on-line August 30, 2014

The crystal structure changes in Ni_3Ta were experimentally investigated by X-ray powder diffraction of alloys prepared by arc melting, ground and annealed in the temperature range 673-1173 K for 1 day. It was found that an increase of the annealing temperatures leads to a change of the product of the transformation of the high-temperature tetragonal phase from monoclinic to orthorhombic. The changes are promoted by recovery and recrystallization processes. Some oxidation at the higher annealing temperatures led to the reappearance of the phase with monoclinic structure.

Phase transformation / Binary compound / Crystal structure

Introduction

The Ni_3Ta intermetallic compound is known as a strengthening component of high-temperature structural eutectics or directionally solidified materials (superalloys, composites, *etc.*) [1,2]. It is known that it undergoes a transformation (of unknown origin) from a high- (tetragonal [3]) to a low-temperature phase (monoclinic [4]). Recently, while searching for appropriate alloying of NiTi shape memory alloys, striking similarities between the binary phase diagrams in the vicinity of the NiTi and Ni_3Ta phases were noticed [5]. Taking into account the identical space groups of the low-temperature monoclinic phases, it was shown with the help of light optical microscopy, electrical resistivity measurements *vs.* temperature and X-ray diffraction that the tetragonal↔monoclinic transformation in Ni_3Ta is of martensitic origin [5]. Later, it was also shown that the martensitic transformation in Ni_3Ta is accompanied by a shape memory effect at elevated temperatures [6]. Besides, as it can be seen from Table 1, in addition to the tetragonal austenitic and the monoclinic martensitic phase, an orthorhombic modification of Ni_3Ta has been reported. In order to clarify the phase formation in Ni_3Ta, the present study, using X-ray powder diffraction, was carried out.

Experimental

The alloys for the present investigation were prepared from Ni (99.9 wt.%) and Ta (99.9 wt.%) by arc melting under an atmosphere of purified argon. The pellets were turned over and remelted several times in order to ensure good homogeneity. Subsequently, the samples were annealed at 1173 K for one week in evacuated silica tubes to promote homogeneity and internal stress relaxation in the specimens. The weight of the ingots was typically 15 g. The composition of the produced ingots was checked by X-ray fluorescence analysis, using a VRA-30 spectrometer. The crystal structure of the samples was analyzed by X-ray powder diffraction (XRD), using a Bruker AXS D8 Advance diffractometer with θ-2θ Bragg-Brentano geometry and monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). The powders for X-ray diffraction were annealed at 673 K, 773 K, 873 K, 973 K, 1073 K or 1173 K, for 1 day in evacuated silica tubes. MAUD software [9] was used for Rietveld refinements.

Results and discussion

Structural analysis of the powders annealed at 673 K showed, contrary to the findings on as-cast samples [6], more than 50% of tetragonal austenitic phase, in addition to monoclinic martensite (Fig. 1). It should be noted that, while the lattice parameters did not differ much with respect to the results of [8], line broadening was quite significant for both phases, indicating that the low-temperature annealing had not removed the internal stresses in the cold-worked powder. An increase of the annealing temperature resulted in the appearance of narrow

Table 1 Different crystal structures reported for Ni_3Ta.

	Space group, prototype	Lattice parameters, nm	Reference
Ni_3Ta congruent T_m = 1550°C, homogeneity range 23.2-28.9 at.% Ta at 1405°C	*I*4/*mmm*, Al_3Ti	a = 0.3627 c = 0.7455	[3]
	Pmmn, Cu_3Ti	a = 0.510 b = 0.424 c = 0.452	[7]
	$P2_1/m$, $NbPt_3$	a = 0.45319 b = 0.51253 c = 0.8632 β = 100.79°	[8]

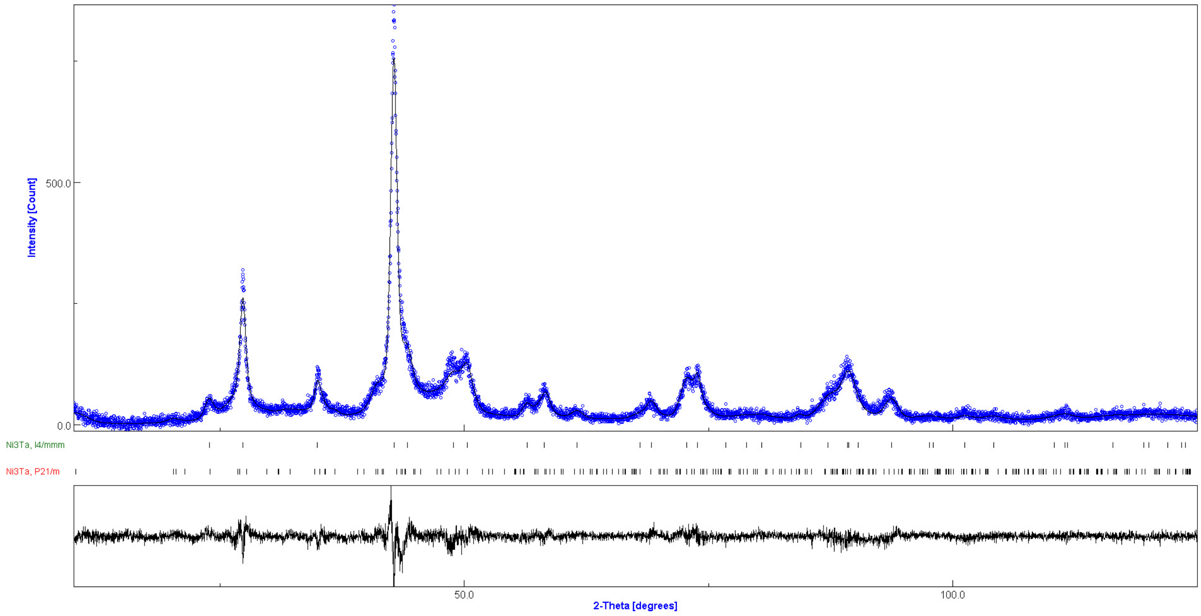

Fig. 1 Rietveld refinement of X-ray powder diffraction data collected for Ni_3Ta powder annealed at 673 K for 1 day. The volume fraction of the monoclinic martensite (space group $P2_1/m$) is 47.7%, that of the tetragonal austenite (*I*4/*mmm*) 52.3%; R_{wp} = 15.8%, R_p = 12.2%, R_{exp} = 14.01%. Dots correspond to the experimental data, the line to the calculations. Reflection positions for both phases and the difference line are also shown.

reflections belonging to the orthorhombic phase, against a background of peaks from the still stressed tetragonal and monoclinic phases (Fig. 2). In addition, some clear, but low-intensity reflections belonging to Ta_2O_5 oxide were already visible. Further increase of the annealing temperature led to an increase of the volume fraction of the unstressed orthorhombic phase and Ta_2O_5 oxide, in such a way that the tetragonal and monoclinic phases had almost disappeared after annealing at 1073 K (Fig. 3). Annealing at 1173 K, as it can be seen from Fig. 3, led to a surprising result: the monoclinic phase had reappeared, although its volume fraction was not large and could be compared with the volume fraction of Ta_2O_5 oxide. Still, most of the volume was occupied by the orthorhombic phase and the reflections of all of the phases were narrow (not shown).

Considering the possible causes of such phase formation with increasing annealing temperature as shown in Fig. 3, it can be concluded that up to 700 K only recovery processes take place in the highly stressed powders of Ni_3Ta. The stress appears during the powder preparation and suppresses the monoclinic martensite phase, in favor of tetragonal austenite. After annealing at temperatures up to 700 K, the recovery processes have already removed some stress,

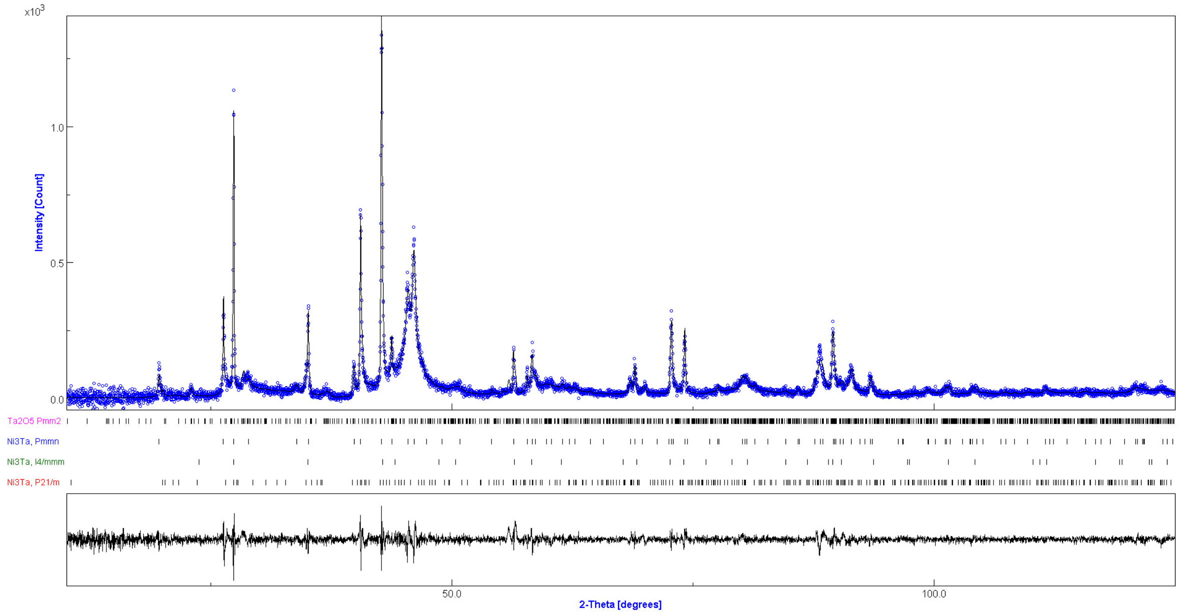

Fig. 2 Rietveld refinement of X-ray powder diffraction data collected for Ni_3Ta powder annealed at 973 K for 1 day. The volume fraction of the orthorhombic phase (space group *Pmmn*) is 45.4%, that of monoclinic martensite ($P2_1/m$) 41.2%, and that of tetragonal austenite (*I*4/*mmm*) 13.2%; small amounts of Ta_2O_5 oxide (*Pmm*2) were detected; R_{wp} = 12.5%, R_p = 9.1%, R_{exp} = 10.4%. Dots correspond to the experimental data, the line to the calculations. Reflection positions for each of the phases and the difference line are also shown.

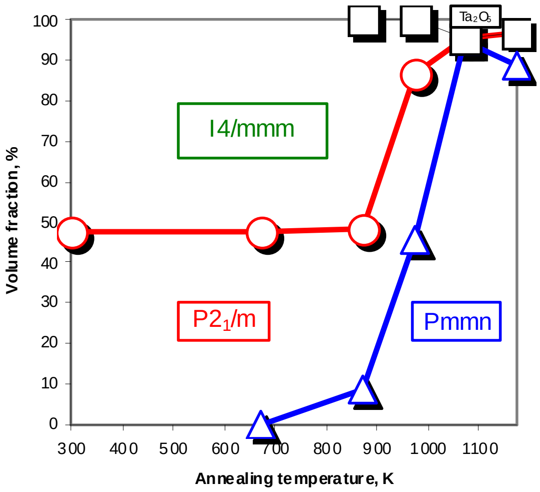

Fig. 3 Volume fractions of the phases observed in Ni_3Ta powders annealed at different temperatures for 1 day. The values were obtained from Rietveld refinements.

but, instead of the expected formation of monoclinic martensite, the orthorhombic phase starts to form, mostly at the expense of the monoclinic martensite phase. Further increase of the annealing temperature stabilizes the orthorhombic phase even more, already at the expense of both the tetragonal and monoclinic phases. It is likely that we observe a situation similar to that described in [10]. At low temperatures, when the time to reach phase equilibria may become astronomical, a diffusionless (martensitic) phase transformation mechanism takes place. But once we increase the temperature, a diffusional mechanism starts to help the stable orthorhombic phase to form. This process is slightly hindered by high-temperature oxidation, when unexpected reappearance of the monoclinic phase occurs (Fig. 3). In this case, the monoclinic phase may form with the help of diffusion. Of course, one should take into account that the observed phase formation was taking place in powders. Anyhow, it is possible to conclude that in Ni_3Ta the competition between diffusionless and diffusional mechanisms may lead to martensitic transformation of the high-temperature tetragonal phase to monoclinic martensite, or to the formation (from the same tetragonal phase) of an orthorhombic phase through diffusion.

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