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Phase equilibria in Ti−Ni−Pt ternary system

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Abstract: Phase equilibria in Ti−Ni−Pt ternary system have been experimentally determined through diffusion triple technique combined with alloy samples approach. Assisted with electron probe microanalysis (EPMA) and X-ray diffraction (XRD) techniques, isothermal sections at 1073 and 1173 K of this system were constructed and existence of ternary phase $Ti_2(Ni,Pt)_3$ was confirmed. In addition, binary compounds Ti_3Pt_5 and $TiPt_{3-}$ were found to be stable at 1073 and 1173 K, and remarkable ternary solubility in some binary compounds was detected, e.g., solubility of Pt in TiNi can be up to about 36% (molar fraction) at 1073 K and 40% (molar fraction) at 1173 K. Furthermore, a ternary invariant transition reaction $TiNi_3+Ti_3Pt_5\rightarrow Ti_2(Ni,Pt)_3+TiPt_{3+}$ at a temperature between 1073 and 1173 K was deduced.

Key words: Ti−Ni−Pt ternary system; phase equilibrium; diffusion triple; solubility

1 Introduction

Titanium−nickel shape memory alloys (SMAs) are widely used in medical and industrial fields because of their superior shape memory effect and superelasticity [1−3]. However, high-temperature applications of TiNi alloys are limited because their martensite transformation temperatures (M_s) are commonly lower than 373 K [4]. Variety of studies have been performed to raise M_s of TiNi with addition of Pt [5,6], focusing on introducing precipitates which are helpful to minimize residual strain and obtain better dimensional stability [7] and oxidative stability [8]. Several types of precipitations can be introduced in several TiNiPt alloys [9], e.g. a fine coherent *P*-phase precipitate after aging at 873 K for 100 h [10] or $Ti_2(Ni,Pt)_3$ phase precipitates after aging at 873 K [11,12]. In order to provide reference in developing high-temperature shape memory alloys (HTSMAs) and well comprehending precipitations in TiNiPt alloys, knowledge concerning phase relationships of Ti−Ni−Pt system is of fundamental importance.

So far, boundary binary phase equilibria in Ti−Ni−Pt system have been widely studied. The Ni−Pt phase diagram appears simple, showing mainly the isomorphous feature between liquid and disordered FCC-solid solution at high temperature besides the order-disorder transitions at low temperature. NASH and SINGLETON [13] performed a thermodynamic assessment of liquid and FCC phase. Later, LU et al [14] re-assessed the Ni−Pt system by considering ordered phases Ni_3Pt-*L*12, NiPt-*L*10 and $NiPt_3$-*L*12 at lower temperature.

The Ti−Ni system was firstly calculated by KAUFMAN and NESOR [15]. The most recent critical assessment of the system has been carried out by MURRAY [16] who considered literature data up to 1985. Later, this system has been thoroughly investigated by several authors [17−22]. Recently, POVODEN-KARADENIZ et al [23] re-optimized this system by taking account of new thermodynamic data for *D*024-ordered $TiNi_3$ phase along with two metastable phases Ti_3Ni_4 and Ti_2Ni_3. It is accepted that the Ti−Ni system contains four stable intermetallics, i.e. $TiNi_3$, Ti_2Ni, TiNi(h) and TiNi(r).

Dissimilar to the Ti−Ni system, only a few equilibrium studies about the Ti−Pt binary system were reported. Phase diagram of Ti−Pt system was firstly constructed by NISHIMURA and HIRAMATSU [24]. MURRAY [25] evaluated and assessed this system in detail. Later, BIGGS et al [26] detected a phase Ti_4Pt_3 in compositional range of 30%−60%Pt (molar fraction).

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Recently, LI et al [27] have re-assessed the Ti−Pt system thermodynamically, considering homogeneity ranges of Ti_3Pt, TiPt(h), TiPt(r) and $TiPt_{3+}$ phases, while neglecting Ti_3Pt_5 and $TiPt_{3-}$ phase. The Ti_4Pt_3 and $TiPt_8$ phases were treated as stoichiometric compounds, for having an unnoticeable and uncertain solubility range. It is worth noting that $TiPt_{3-}$ and $TiPt_{3+}$ are different phases, respectively denoting the Pt-lean and the Pt-rich $TiPt_3$ phase.

Phase relations in the Ti−Ni−Pt ternary system are far from being accomplished. Only the ternary phase $Ti_2(Ni,Pt)_3$ reported by YANG et al [12] is available. It is obvious that the phase diagram is the map of material design. In order to assist the design and fabrication of Ti−Ni based alloys, extensive investigation of phase equilibria in the Ti−Ni−Pt ternary system is necessary. Crystal structure data for solid phases in Ti−Ni−Pt system are summarized in Table 1. This work aims at measuring phase equilibria in the Ti−Ni−Pt ternary system at 1073 and 1173 K.

2 Experimental

Pure titanium (99.999% Ti), nickel (99.99% Ni), and platinum (99.99% Pt) were used as starting materials for diffusion triple and alloys. To fabricate diffusion couples, titanium block and nickel block were machined into proper shapes (cuboid with size of 3 mm × 5 mm × 10 mm). The platinum wire with diameter of 0.5 mm was nipped between titanium and nickel blocks, and then was heated to and kept at 1173 K for 10 h for diffusion-bonding in a chamber filled with Ar of 10^{-2} Pa. Subsequently, the so-obtained triples were sealed in evacuated quartz capsules and then annealed at 1073 K for 1000 h and 1173 K for 500 h. After annealing, diffusion triples were taken out of the diffusion furnace and quenched into water.

In order to confirm the relations determined with diffusion triple, a set of button alloys in different compositions were prepared by arc-melting on a water-cooled copper plate under purified argon atmosphere with titanium as getter material placed in the arc chamber. To ensure a good homogenization, all samples were turned over before each melting and re-melted at least three times. The mass losses of the so-obtained as-cast button shaped alloys did not exceed 1%. Subsequently, majority of samples were sealed in evacuated quartz capsules and then heat-treated at 1073 K for 2000 h and at 1173 K for 1000 h. After annealing, those annealed diffusion triples and button-alloys were taken out of the diffusion furnace and quenched into water. And they were ground on abrasive paper, polished with diamond paste and cleaned with alcohol in a standard method.

Constituent phases of samples were investigated by electron probe microanalysis (EPMA) (JXA−8800R, JEOL, Japan) equipped with OXFORD INCA 500 wavelength dispersive X-ray spectrometer (WDS). The

Table 1 Crystallographic data of solid phases in Ti−Ni−Pt system from references

System	Phase	Prototype	Pearson's symbol	Lattice parameter			Ref.
				a/nm	*b*/nm	*c*/nm	
Ti	HCP-A3, α(Ti)	Mg	*hp*2	0.2950	0.2950	0.4681	[28]
	BCC-A2, β(Ti)	W	*cI*2	0.3307	0.3307	0.3307	[28]
Ni	FCC-A1, (Ni)	Cu	*cF*4	0.35236	0.35236	0.35236	[29]
Pt	FCC-A1, (Pt)	Cu	*cF*4	0.39234	0.39234	0.39234	[30]
Ti−Ni	Ti_2Ni	Ti_2Ni	*cF*96	1.13193	1.13193	1.13193	[31]
	TiNi(h) (>353 K)	ClCs	*cP*2	0.3007	0.3007	0.3007	[31]
	TiNi(r) (<353 K)	TiNi	*mP*4	0.2898	0.4108	0.4646	[31]
	$TiNi_3$	$TiNi_3$	*hP*16	0.51088	0.51088	0.83187	[29]
Ti−Pt	Ti_3Pt	Cr_3Si	*cP*8	0.50327	0.50327	0.50327	[32]
	Ti_4Pt_3	–	–	–	–	–	[26]
	TiPt(h) (>1307 K)	CsCl	*cP*2	0.3129	0.3129	0.3129	[33]
	TiPt(r) (<1313 K)	AuCd	*oP*4	0.459	0.276	0.482	[34]
	Ti_3Pt_5	$GaZn_2Au_5$	*oI*32	1.0953	0.5441	0.8169	[35]
	$TiPt_{3-}$	$TiNi_3$	*hP*16	0.552	0.552	0.9019	[36]
	$TiPt_{3+}$	$AuCu_3$	*cP*4	0.3923	0.3923	0.3923	[37]
	$TiPt_8$	$TiPt_8$	*tI*18	0.8312	0.8312	0.3897	[38]
Ti−Ni−Pt	$Ti_2(Ni,Pt)_3$	Ti_2Pd_3	*oC*20	1.359	0.457	0.444	[39]