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773 K isothermal section of Gd-Ni-Ti ternary system①

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[Abstract] The 773 K isothermal section of the Gd-Ni-Ti system was investigated by X-ray diffractometry, optical microanalysis and electron probe microanalysis techniques. The results show that it consists of 13 single-phase regions, 23 two-phase regions and 11 three-phase regions. The maximum solid solubility of Ti in Ni, Gd_2Ni_{17}, $GdNi_5$ and Gd_2Ni_7 are 6.0%, 3.0%, 3.0%, and 2.5% (mole fraction), respectively.

[Key words] phase diagram; isothermal section; Gd-Ni-Ti system
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1 INTRODUCTION

For decades, the researchers in the fields of materials science have shown more and more interest in shape memory alloys. Among them, NiTi alloys are most attractive from both fundamental and applied aspects due to their thermoelastic martensite transformation. Recently the researchers try to improve the shape memory effect and the processing properties of NiTi alloys by adding the third element, where the rare earth elements are good candidates.

The Ni-Ti phase diagram was first calculated by Kaufman et al[1], and later was confirmed by experimental results[2]. There are three compounds, namely $NiTi_2$, NiTi and Ni_3Ti in the Ni-Ti systems. The Gd-Ni binary system has been studied by many researchers[3~5] with different results. Novy et al[4] and Pan et al[5] reported the existence of nine intermetallic compounds: Gd_3Ni, Gd_3Ni_2, GdNi, $GdNi_2$, $GdNi_3$, Gd_2Ni_7, $GdNi_4$, $GdNi_5$ and Gd_2Ni_{17}. While Copeland and Kato[3] did not observe the existence of Gd_3Ni_2 and GdNi4, and regarded the Gd_2Ni_{17} compound as Gd_2Ni_{15}. The Gd-Ti binary phase diagram was reported in Ref.[6] and summarized in Ref.[7], and no binary compounds exist in the Gd-Ti system. Structural data for the intermetallic compounds in the three binary systems are given in Table 1.

In this work, the authors try to study the phase relations in the Gd-Ni-Ti ternary system.

2 EXPERIMENTAL

Purities of gadolinium, nickel and titanium used in this work are 99.9%, 99.99% and 99.95% respectively. 168 samples with mass of 3 g each were prepared in an arc furnace under an atmosphere of purified argon. The samples were sealed in evacuated quartz tubes for homogenization. The homogenization temperatures were chosen on the basis of the binary phase diagrams of the Gd-Ni, Ni-Ti and Gd-Ti systems. The Ni-rich alloys were homogenized at 1 173 K for 750 h, the Ti-rich alloys at 1 073 K for 750 h and the Gd-rich alloys at 873 K for 960 h. The alloys with the composition near the NiTi phase were homogenized at 1 173 K for 1 200 h, then kept at 883 K for 1 200 h. After that, all samples were cooled down at a rate of 8 K/h to 773 K, and kept at 773 K for 240 h, then quenched into ice water. The samples for X-ray diffraction (XRD) analysis were powdered and annealed at 773 K for 4 d in vacuum glass tubes and quenched into liquid nitrogen. The X-ray diffraction analysis was performed using a Rigaku 3015 diffractometer with molybdenum target and zirconium filter operated at 47 kV and 15 MA. The metallographic analyses were carried out by optical microscopy and electron probe microanalysis (EPMA) techniques. Metallographic samples were etched by etchant (4 mL nitric acid+ 96 mL ethanol) for 1 min.

3 RESULTS AND DISCUSSION

3.1 Phase analysis

3.1.1 Gd-Ni binary system

In view of the different results of Ref.[3] and Ref.[4, 5] about the phases Gd_3Ni_2 and $GdNi_4$. The authors prepared a series of alloy samples in the Gd-Ni binary line with the composition between the two phases of Gd_3Ni, GdNi and the two phases of Gd_2Ni_7, $GdNi_5$. XRD analysis showed that the XRD patterns of the samples near the composition of Gd_3Ni_2 were obviously composed of the patterns of Gd_3Ni and GdNi, and the XRD patterns of the samples near the composition of $GdNi_4$ were obviously composed of the patterns of Gd_2Ni_7 and $GdNi_5$. No evidence was found to support the existence of Gd_3Ni_2 and $GdNi_4$ under our experimental condition.

About the relationship between the phases Gd_2Ni_7 and Gd_2Ni_{15}, Ref.[8] indicated the existence

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of the intermetallic compounds RE_2Ni_{17} (RE—Er, Dy, Gd, Nd, Y, etc.) with space group of $P6_3/mmc$ and structure type of Th_2Ni_{17}. The authors carried out the program LAZY[9] with crystallographic data of Gd_2Ni_{17}[10], and found that this calculated diffraction data were very close to the data of Gd_2Ni_{15} offered by JCPDS PDF card[11]. XRD patterns of the samples near the composition of Gd_2Ni_{17} and Gd_2Ni_{15} are in agreement with the calculated diffraction data of Gd_2Ni_{17}. Thus it can be drawn the conclusion that Gd_2Ni_{15} provided by the PDF card[11] is actually Gd_2Ni_{17}.

3.1.2 NiTi phase

The phase stability of the NiTi compound below 903 K is the most controversial issue. Ref. [2] reported the experimental evidence of a possible eutectoid decomposition of NiTi into $NiTi_2$ and Ni_3Ti, but Ref. [12~14] argued that the NiTi compound exists as a stable phase from the thermodynamics. Under the experimental conditions, it is found that the NiTi phase partially decomposes into $NiTi_2$ and Ni_3Ti. EPMA results for two alloy samples are summarized in Table 2. According to the phase law, it is impossible for the third phase to exist in the two-phase region. The NiTi phase decomposes at 773 K although the decomposition is incomplete. This process in NiTi is very slow, whether it can help to achieve the full decomposition at 773 K by extending the annealing time remains uncertain. Therefore in Fig. 1, GdNi and NiTi were linked by the dotted line.

Table 1 Crystal structure data in Gd-Ni-Ti ternary system

Compound	Space group	Structure type	Lattice parameter/ Å			Reference
			a	*b*	*c*	
Gd_3Ni	Pnma(62)	Fe_3C	6.950	9.680	6.360	[11]
Gd_3Ni_2			7.280		8.061	[4]
GdNi	Cmcm(63)	CrB	3.776	10.381	4.244	[11]
$GdNi_2$	Fd3m9(227)	$MgCu_2$	7.244			[11]
$GdNi_3$	R-3m(166)	$PuNi_3$	4.990		24.540	[11]
Gd_2Ni_7	$P6_3$/mmc(194)	Ce_2Ni_7	4.960		24.090	[11]
Gd_2Ni_7	R-3m	Gd_2Co_7	4.960		36.140	[11]
$GdNi_4$			5.350		3.830	[4]
$GdNi_5$	P6/mmm(191)	$CaIn_5$	4.902		3.964	[11]
Gd_2Ni_{17}	$P6_3$/mmc(194)	Th_2Ni_{17}	8.430		8.040	[10]
Gd_2Ni_{15}	$P6_3$/mmc(194)		8.336		8.054	[11]
Ni_3Ti	$P6_3$/mmc(194)	Ni_3Ti	5.093		8.320	[11]
NiTi	Pm3m(221)	CsCl	2.972			[11]
$NiTi_2$	Fd3m(227)	$NiTi_2$	11.27			[11]

Table 2 EMPA results for ternary Gd-Ni-Ti alloys

No	Nominal composition			Phase	Results of EPMA		
	x(Gd)/%	*x*(Ni)/%	*x*(Ti)/%		*x*(Gd)/%	*x*(Ni)/%	*x*(Ti)/%
1	0	50	50	Ni_3Ti	0	74.388	25.612
				$NiTi_2$	0	30.075	69.925
				NiTi	0	47.053	52.946
2	15	45	40	GdNi	48.934	51.066	0
				NiTi	0	49.613	50.347
				$NiTi_2$	0	32.376	67.624

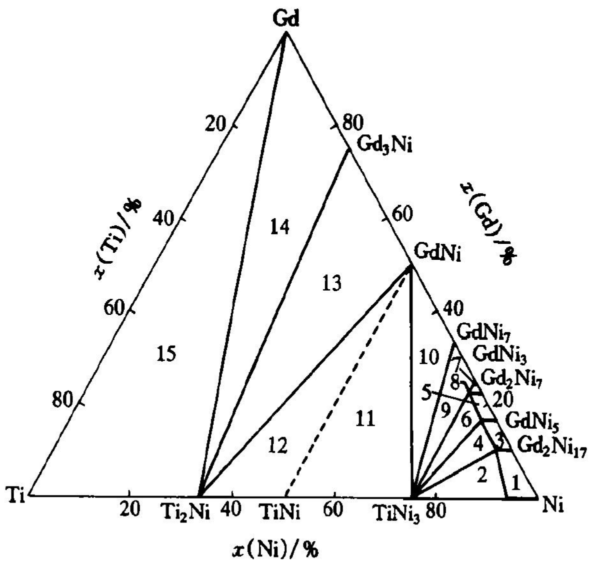

Fig. 1 773 K isothermal section of phase diagram of Gd-Ni-Ti system

3.2 Solid solubility

The single-phase ranges in the isothermal section at 773 K were determined by X-ray diffractometry and optical microanalysis. The results show that a certain amount of Ni atoms can be replaced by Ti to form single-phase regions of Gd_2Ni_{17}, $GdNi_5$ and Gd_2Ni_7 extending parallel to the Ni-Ti boundary line. At 773 K, the maximum solid solubilities of Ti in Ni, Gd_2Ni_{17}, $GdNi_5$ and Gd_2Ni_7 are about 6.0%, 3.0%, 3.0% and 2.5% (mole fraction), respectively. Solid solubilities in other phases were not observed.

3.3 Isothermal section at 773 K

By comparing and analyzing the X-ray diffraction patterns of 168 samples, combined with metallograph and EPMA, and identifying the phases presented in each sample, the existence of 10 binary compounds, namely Gd_2Ni_{17}, $GdNi_5$, Gd_2Ni_7, $GdNi_3$, $GdNi_2$, GdNi, Gd_3Ni, $NiTi_2$, NiTi, Ni_3Ti, at 773 K were confirmed, and no new ternary compound was found. The 773 K isothermal section of the phase diagram of the Gd-Ni-Ti system was determined, as shown in Fig. 1. This section consists of 13 single-phase regions, 23 two-phase regions and 11 three-phase regions. The 13 single-phase regions are α(Gd), β(Ni), γ(Ti), θ(Gd_2Ni_{17}), σ($GdNi_5$), ε(Gd_2Ni_7), μ($GdNi_3$), δ($GdNi_2$), ω(GdNi), φ(Gd_3Ni), π($NiTi_2$), ρ(NiTi), τ(Ni_3Ti). Details of the phase relations are given in Table 3.

Table 3 Phase regions and phase relations in Gd-Ni-Ti ternary system

Phase region	Phase composition
1	Ni+ Gd_2Ni_{17}
2	$TiNi_3$+ Ni+ Gd_2Ni_{17}
3	$GdNi_5$+ Gd_2Ni_{17}
4	$GdNi_5$+ Gd_2Ni_{17}+ $TiNi_3$
5	Gd_2Ni_7+ $GdNi_5$
6	$TiNi_3$+ Gd_2Ni_7+ $GdNi_5$
7	$GdNi_3$+ Gd_2Ni_7
8	$TiNi_3$+ $GdNi_3$+ Gd_2Ni_7
9	$TiNi_3$+ $GdNi_3$+ $GdNi_2$
10	GdNi+ $TiNi_3$+ $GdNi_2$
11	GdNi+ $TiNi_3$+ TiNi
12	Ti_2Ni+ TiNi+ GdNi
13	Gd_3Ni+ Ti_2Ni+ GdNi
14	Gd+ Gd_3Ni+ Ti_2Ni
15	Gd+ Ti+ Ti_2Ni

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