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Phase equilibria in the Ni–Al–Ga system at 700 °C

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ABSTRACT

Phase relations in the ternary Ni–Al–Ga system at 700 °C have been established by the X-ray powder diffraction methods. In addition to already known $Ni_3(Al,Ga)$ continuous solid solution, Ni(Al,Ga) continuous solid solution as well as $Ni_2(Al,Ga)_3$ and $Ni_5(Al,Ga)_3$ extended solid solutions were found to exist in this system. It was shown that the ternary $Ni_2(Al,Ga)_3$ and $Ni_5(Al,Ga)_3$ compounds do not belong to the continuous solid solutions because of two-phase gaps on the Ni_2Al_3–Ni_2Ga_3 (~30–50 at.% Ga) and Ni_5Al_3–Ni_5Ga_3 (~12–25 at.% Ga) isolines at 700 °C. Some crystal structure peculiarities such as atomic ordering–disordering and presence of structural vacancies have been revealed for all solid solutions existing in the Ni–Al–Ga system. It was found that the compressive strength of the $Ni_3(Al,Ga)$ solid solution increases with small additions of gallium (about 2.5 at.%).

The isothermal section (700 °C) of the ternary Ni–Al–Ga system including four extended solid solutions ($Ni_3(Al,Ga)$, $Ni_5(Al,Ga)_3$, Ni(Al,Ga) and $Ni_2(Al,Ga)_3$) has been constructed and plotted.

1. Introduction

The growing interest for the intermetallic compounds as functional materials is caused by a wide range of their technological application. So, utilization of binary aluminides of transition metals (including nickel) stems from their attractive properties, such as corrosion resistance and relatively low densities combined with their ability to retain strength and stiffness at elevated temperatures.

Several intermetallic compounds have been formed during interaction of nickel and aluminum (Table 1). Two of them (Ni_3Al and NiAl) have been applied for material creation. Investigations being done on these alloys revealed that Ni_3Al behaves as a strengthening phase in the most superalloys [1,2] as well as NiAl is a perspective compound for high temperature structural materials [2].

It is known that mechanical properties of the Ni_3Al based materials could be improved not only by varying the technological modes of their preparation but also through adding of *p*-element (B) or some *d*-metal additives (Ti, Zr, Hf, V, Nb, Ta, Mo, W) [3–5]. As far as we know, the influence of gallium additive on the properties of the Ni_3Al compound has not been studied yet. However, it was shown that NiAl intermetallic alloyed with about 0.25 at.% Ga has significantly improved the ductility at room temperature as compared to binary NiAl intermetallic or NiAl alloyed with higher percentages of gallium [6].

The Ni-rich ternary alloys have been studied except the mentioned above Ni(Al,Ga) ones and a part of the isothermal section of Ni–Al–Ga system at 1000 °C ($Ni_{65}Al_{35}$–$Ni_{65}Ga_{35}$–Ni region) has been constructed in Ref. [7]. This concentration range was shown to be characterized not only by the $Ni_3(Al,Ga)$ continuous solid solution but also by large solubility of aluminum and gallium in nickel (~12 at.% Al and ~16 at.% Ga). Some ternary alloys near the γ-phase (Ni_2Al_3) were examined in Ref. [8], too.

Here, we introduce a novel study of the phase equilibria in the ternary Ni–Al–Ga system in the whole concentration range by the X-ray powder diffraction method.

2. Experimental details

More than 100 ternary alloys (Fig. 1) were prepared by the arc melting of gallium (99.999 wt.%) with electrolytic aluminum (99.99) and nickel (99.99) under purified argon atmosphere. The ingots were remelted several times to achieve perfect homogeneity. In order to prevent possible formation of the metastable martensite Ni–Al phases [9] the alloyed ingots were slightly heated directly in an arc furnace for their slow cooling. After arc melting the specimens were wrapped into molybdenum foil, sealed in the argon filled quartz tubes and annealed at 700 °C for 250 h with the subsequent quenching in cold water.

The X-ray powder diffraction data were collected with a DRON-3 automatic diffractometer (Cu $K\alpha$ radiation) [10]. The samples for the X-ray study have been prepared either by grounding ingots into powders (for the alloys containing less than 65 at.% Ni and including ductile alloys from NiAl–NiGa and Ni_5Al_3–Ni_5Ga_3 sections) or by polishing surface of the nickel-rich alloys. The diffraction patterns of the samples were obtained in a discrete mode under the following scanning parameters: observation range 2θ (10–120)°, step scan (0.02–0.05)°, counting time per step (3–5) s. The peak positions and integral intensities of the observed reflections were determined using a full profile analysis. After removal of the Cu $K\alpha_2$ components the diffraction profiles were fitted by the Lorentz function. The peak positions and integral intensities have been calculated with accuracy not less than ±(0.001–0.005)° and ±(5–10)%, respectively.

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Table 1
Crystal structure data for binary compounds.

Phase and its nickel content (at.%) at 700 °C	Temperature (°C) and mode of formation	Structure type	Lattice parameters, nm			Refs.
			a	*b*	*c*	
Ni–Al system						
Ni_3Al, 72–77	1385, *P*[a]	Cu_3Au	0.3570 0.3571(2)	–	–	[11]*[b]
Ni_2Al	Metastable	Geks./Monocl.	?	?	?	[12]
Ni_5Al_3	~700, *S*	Pt_5Ga_3	0.7475 0.7554(5)	0.6727 0.6522(5)	0.3732 0.3789(6)	[11,12]*
NiAl, 45–60	1338, *L*	CsCl	0.2887 0.2885(1)	–	–	[11]*
Ni_3Al_4	580, *S*	Ni_3Ga_4	1.1408	–	–	[14]
Ni_2Al_3, 36–40	1133, *P*	Ni_2Al_3	0.4036 0.4036(3)	–	0.4900 0.4896(3)	[11]*
$NiAl_3$, 25	854, *P*	Fe_3C	0.6611 0.6623(3)	0.7366 0.7353(2)	0.4812 0.4798(1)	[11]*
Ni–Ga system						
Ni_3Ga, 71–76	1220, *P*	Cu_3Au	0.3585 0.3581(2)	–	–	[15–17]*
Ni_2Ga	940–790, *Pd*	Ni_2In/NiAs Ni_2In	0.400 0.3991(7)	–	0.498 0.4975(4)	[15–17]*
Ni_5Ga_3, 62–65	740, *S*	Pt_5Ga_3	0.751 0.7277(2)	0.671 0.7030(3)	0.375 0.37352(7)	[15–17]*
$Ni_{13}Ga_9$, 59	790, *Pd*	$Ni_{13}Ga_9$	1.3822 $\angle\gamma = 35.88$ 1.3899(8) $\angle\gamma = 35.80(6)$	0.8478 0.8520(4)	0.7894 0.7908(7)	[15,17]*
NiGa, 45–55	1220, *L.*	CsCl	0.2887 0.2888(1)	–	–	[15–17]*
Ni_3Ga_4	547, *S*	Ni_3Ga_4	1.141	–	–	[15–17]
Ni_2Ga_3, 40	950, *P*	Ni_2Al_3	0.4054 0.4053(1)	–	0.4882 0.4889(3)	[15–17]*
Ni_3Ga_7	369, *P*	Ir_3Ge_7	0.843	–	–	[18,19]
$NiGa_4$	363, *P*	$NiGa_4$	0.8424	–	–	[15]
$NiGa_5$	<100, *P*	$PdGa_5$	0.631–	–	0.633	[19]

[a] Phases are formed from liquid (*L*) as well as a result of peritectic (*P*) or peritectoid (*Pd*) reactions, transformation in solid state (*S*).
[b] This study.

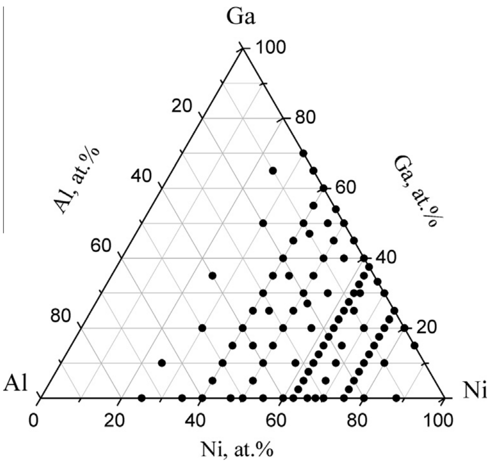

Fig. 1. Compositions of the prepared alloys.

The original software program package was used in order to determine the phase compositions of the alloys and to refine the structural parameters of compounds (including refinements on the position filling and texture). This software was elaborated for the automated DRON-3 equipment [10] and includes both full complex of the Rietveld refinement procedure and special banks (for X-ray diffraction data and crystal structures of intermetallic compounds).

Compressive strengths of alloys of the $Ni_3(Al,Ga)$ solid solutions were measured with ИП-1000M testing machine at room temperature. The cubic samples (5 × 5 × 5 mm) were uniaxially compressed with a rate of $10^{-3}\ s^{-1}$ during tests. Surfaces of samples were previously mechanically polished with 600-grit SiC abrasive. For those samples the liquidus temperatures were studied by differential scanning calorimetry (20 K/m heating rate) using Netzsch DSC 404F1 Pegasus calorimeter.

3. Results and discussion

The isothermal section of the Ni–Al–Ga phase diagram for alloys annealed at 700 °C was studied by the X-ray diffraction analysis. Due to existence of some closely related compounds in the binary Ni–Al and Ni–Ga systems (Table 1) the alloys have been mostly prepared at compositions corresponding to the definite sections of the ternary Ni–Al–Ga system, namely, Ni_2Al_3–Ni_2Ga_3, NiAl–NiGa, Ni_5Al_3–Ni_5Ga_3 and Ni_3Al–Ni_3Ga (Fig. 1).

3.1. Binary boundary systems

The binary phase diagram of the Ni–Al system was presented by Singleton [11] and includes five intermetallic compounds, namely, Ni_3Al, Ni_5Al_3, NiAl, Ni_2Al_3 and $NiAl_3$ (Table 1). According to Ref. [11] most of these compounds (excluding $NiAl_3$) are formed at temperatures higher than 700 °C and possess homogeneity regions (up to 15 at.% for NiAl and lower). It was shown that more stoichiometric Ni_3Al_4 compound exist below 580 °C [14]. Metastable ~Ni_2Al phase with unknown crystal structure has been described in Ref. [12].

The boundary Ni–Ga phase diagram has been described in Refs. [15–17] and its Ga-rich part has been supplemented in Ref. [18]. In total, the Ni–Ga system contains ten intermetallic compounds (Table 1) ($NiGa_4$ compound was identified as Ni_3Ga_7 later). The crystal structures for most of these compounds have been determined.

To verify the published crystal structure data for Ni–Al and Ni–Ga compounds (Table 1) 25 alloys have been prepared at the concentrations generally corresponding to compositions of binary compounds (Fig. 1). As a result of X-ray diffraction study nine binary compounds were found to exist at 700 °C, namely, Ni_3Al, NiAl,