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The Ni-rich part of the Al–Ge–Ni phase diagram

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ABSTRACT

The Ni-rich part of the ternary system Al–Ge–Ni (x_{Ni} > 50 at.%) was investigated by means of optical microscopy, powder X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM). The two isothermal sections at 550 °C and 700 °C were determined. Within these two sections a new ternary phase, designated as τ4, $Al_yGe_{9-y}Ni_{13\pm x}$ (*hP*66, $Ga_3Ge_6Ni_{13}$-type) was detected and investigated by single crystal X-ray diffraction. Another ternary low temperature phase, τ5, was found only in the isothermal section at 550 °C around the composition $AlGeNi_4$. This compound was found to crystallise in the Co_2Si type structure (*oP*12, *Pnma*). The structure was identified by Rietveld refinement of powder data. The NiAs type (B8) phase based on binary Ge_3Ni_5 revealed an extended solid solubility of Al and the two isotypic compounds $AlNi_3$ and $GeNi_3$ form a complete solid solution.

Based on DTA results, six vertical sections at 55, 60, 70, 75 and 80 at.% Ni and at a constant Al:Ni ratio of 1:3 were constructed. Furthermore, the liquidus surface projection and the reaction scheme (Scheil diagram) were completed by combining our results with previous results from the Ni-poor part of the phase diagram. Six invariant ternary reactions were identified in the Ni-rich part of the system.

1. Introduction

The manufacturing of high temperature alloy components based on Ni-aluminides requires sophisticated joining techniques. Diffusion brazing, also called transient liquid phase joining (TLP) [1], is one possible technique which already was applied successfully on Ni-based superalloys [2,3]. Possible new brazing materials should show considerable lower melting points than the substrates and thus require the presence of melting point depressant elements like e.g. Ge, which forms eutectics with Ni and Al. A systematic development of new Ge-based filler materials requires good knowledge of the corresponding phase diagrams. Therefore we started a detailed investigation of the Al–Ge–Ni phase diagram. The phase equilibria in the Ni-poor part of the system were published recently [4] while the current work presents the experimental results in the Ni-rich corner. A brief literature review of relevant binary phase equilibria is given below.

A critical assessment of the Al–Ni phase diagram was given in 1990 by Singleton et al. [5]. In addition to the solid solutions (Al) and (Ni) they reported 5 intermetallic phases: Al_3Ni, Al_3Ni_2, AlNi, Al_3Ni_5 and $AlNi_3$, where Al_3Ni_5 is considered by Robertson and Wayman [6] to be stable only at temperatures below ca. 700 °C. A further intermetallic compound, Al_4Ni_3, was found by Ellner et al. [7]. AlNi shows a significant homogeneity range and melts congruently, whereas the other compounds are formed peritectically. New findings were summarised by Okamoto [8], who reversed the peritectic formation reaction for $AlNi_3$ to L + (Ni) = $AlNi_3$, according to the results of Schramm [9] who was later supported by several other authors [10–12]. Recently Bitterlich et al. [13] found a much higher solidus temperature for stoichiometric AlNi (1681 °C).

The system Ge–Ni is quite complex with many invariant reactions, intermediate high- and low temperature phases and also superstructure formation. A first assessment was given by Nash and Nash [14], who showed a phase diagram mainly based on the works of Ruttewit and Masing [15], Ellner et al. [16] and Dayer and Feschotte [17]. The five intermetallic phases $GeNi_3$, γ$GeNi_3$, Ge_2Ni_5, Ge_3Ni_5 and GeNi are well established and reported by the mentioned authors [15–17].

The only investigations of the low temperature region of Ge–Ni were done by Ellner et al., who found the two intermetallic low temperature phases $GeNi_2$ and ε Ge_3Ni_5 [16]. They also investigated the broad homogeneity range of the NiAs type phase Ge_3Ni_5 and found this area split into three sections: Ge_3Ni_5, $Ge_{12}Ni_{19}$ and Ge_2Ni_3, separated by two-phase fields. The phase $Ge_{12}Ni_{19}$ forms an own structure type, which is a superstructure of the NiAs type, while Ge_2Ni_3 was found to be of NiAs type, similar to Ge_3Ni_5. The authors presume a congruent formation of Ge_3Ni_5, whereas $Ge_{12}Ni_{19}$ and Ge_2Ni_3 are formed in peritectic reactions at 1050 and 990 °C, respectively. However, Ellner et al. stated in their paper that

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these reaction temperatures are only tentative, as they did not find hard experimental evidence. Nevertheless, their suggestions were implemented in the assessment of Nash [14]. Later Larsson and Withers [18] reinvestigated the area of the B8-superstructures by electron diffraction. They confirmed the existence of $Ge_{12}Ni_{19}$ and stated commensurate modulation in the area of Ge_3Ni_5 and no long range superstructure ordering in Ge_2Ni_3.

Liu et al. [19] calculated the phase diagram of Ge–Ni by thermodynamic modelling according to Nash's assessment. Ma and Ardell [20] recently presented new experimental results on the phase boundaries between the (Ni) solid solution and $GeNi_3$, as well as on the compositional dependence of the ferromagnetic Curie temperature.

The ternary phase diagram Al–Ge–Ni has been investigated by Yanson et al. [21], who determined an isothermal section through the whole system at 770 K. The authors found a complete solid solution of $AlNi_3$ and $GeNi_3$ and a ternary phase Σ with the nominal composition $AlGeNi_4$. No further structural information was given for Σ and no other ternary compounds were reported. Ochiai et al. [22] investigated the solid solution $AlNi_3$–$GeNi_3$ by XRD and metallography and confirmed a continuous solid solution at 1000 °C.

In our recent investigation of the Ni-poor part of the Al–Ge–Ni phase diagram [4] we present two isothermal sections at 400 °C and 700 °C, which differ strongly from the section by Yanson et al. [21]. Three new ternary phases were detected and designated as τ1 (oC24, $CoGe_2$-type), τ2 (at approximately $Al_{67.5}Ge_{18.0}Ni_{14.5}$) and τ3 (cF12, CaF_2-type). Ternary phase reactions were studied in three vertical sections at 10, 20 and 35 at.% Ni. Eleven invariant phase reactions were derived in this part of the phase diagram and a reaction scheme and a liquidus projection were given.

A list of crystallographic data of binary and ternary phases relevant for this study is given in Table 1.

2. Experimental

As starting materials for all prepared alloys served aluminium slug (Alfa Aesar, 99.999%), germanium pieces (Alfa Aesar. 99.999%) or germanium pieces (Advent, 99.9999%) and nickel foil (Advent, 99.99%). A total number of 47 samples were prepared in the system Al–Ge–Ni.

The calculated amounts of the elements were weighed with a semi-micro balance with an accuracy of at least 0.5 mg. The proper amounts of the elements were then mixed and melted in an arc-furnace (Johanna Otto GmbH, MAM1). For homogenisation the samples were turned around and melted three times in an inert argon atmosphere. To further protect the samples from oxidation a zirconium getter was used in the arc chamber.

The sample-pills were sealed in evacuated quartz glass ampoules. To prevent samples containing aluminium from reactions with the quartz glass, these samples were put in alumina crucibles before sealing. The sealed samples were annealed for at least one month and afterwards quenched in cold water to keep the adjusted equilibrium conditions.

For further investigations parts of the samples were embedded in phenolic hot mounting resin. The surfaces of the embedded samples were then ground with different SiC abrasive papers and finally polished with corundum powder. Quantitative analysis of phase compositions was done with a scanning electron microscope (Zeiss Supra 55 VP ESEM) in combination with energy dispersive X-ray spectroscopy (EDX). An acceleration voltage of 20 kV was applied.

To identify phase transformations and their temperature, differential thermal analysis (DTA) was performed on a Netzsch DSC 404 C Pegasus and a Setaram Setsys Evolution 2400 measurement system. The Pt/Pt10%Rh thermocouples were calibrated at the melting points of pure Al, Au and Ni. For each sample two heating and cooling circles in open alumina crucibles under a constant argon flow of 50 mL/min and a heating rate of 5 K/min were performed.

Phase identification was done by powder XRD using a Bruker D8 diffractometer (Discover Serie 2) in Bragg-Brentano pseudo-focussing geometry using Cu-Kα radiation and a silicon strip detector (Lynxeye). The measurements were done in a θ/2θ arrangement, with a variable slit aperture (12 mm illumination) for 1 h. Analysis of the obtained powder patterns was done by Rietveld refinement with the software program Topas.

The single crystal X-ray diffraction experiment was carried out at room temperature. Reflections were collected on a Nonius Kappa CCD diffractometer at a crystal-detector distance of 30 mm. In total 781 frames were measured with 2° rotation and 2 × 80 s exposure time per frame. The obtained reflections were indexed with a trigonal unit cell. Structure determination and refinement was done using the software SHELX-97 [23].

Table 1
Crystal structure data of binary and ternary phases relevant for this study.

Phase	Pearson symbol	Space group	Structure type
AlNi	*cP*2	*Pm*-3*m*	CsCl
$AlNi_3$	*cP*4	*Pm*-3*m*	$AuCu_3$
Ni	*cF*4	*Fm*-3*m*	Cu
$GeNi_3$	*cP*4	*Pm*-3*m*	$AuCu_3$
γ$GeNi_3$	/	/	/
Ge_2Ni_5	*hP*84	$P6_3/mmc$	Pd_5Sb_2
Ge_3Ni_5	*hP*4	$P6_3/mmc$	NiAs
$Ge_{12}Ni_{19}$	*mC*62	*C*2	$Ge_{12}Ni_{19}$
GeNi	*oP*8	*Pnma*	MnP
$Al_yGe_{9-y}Ni_{13\pm x}$ (τ4)	*hP*66	$P3_121$	$Ga_3Ge_6Ni_{13}$
$AlGeNi_4$ (τ5)	*oP*12	*Pnma*	Co_2Si

3. Results and discussion

3.1. Isothermal sections at 550 °C and 700 °C

The combined results of XRD and SEM measurements were used to construct isothermal sections at 550 °C and 700 °C. The detailed results for selected samples covering all relevant phase fields are given in Table 2.

The isothermal section at 550 °C is shown in Fig. 1 together with experimental data points obtained by EDX. The solid solubility of (AlNi) extends to 61 at.% Ni in the ternary, which is slightly more than in the binary at this temperature. The content of Ge rises from about 3 at.% in the Ni-richer part to 8 at.% at 51 at.% Ni. GeNi shows a solubility of 2 at.% Al. As this phase is a line compound in the binary and the lattice parameter refinement shows hardly any deviation from the binary data, no additional solubility of Ni was assumed. Therefore the phase equilibria in the figure are drawn to 50 at.% Ni although the EDX data revealed a small deviation (51 at.% Ni) in the ternary.

Based on the EDX measurements we found that the two compounds with $L1_2$ structure, $AlNi_3$ and $GeNi_3$, form a continuous solid solution, confirming previous results from Yanson et al. [21] and Ochiai et al. [22]. The two separate binary B8 phase fields Ge_3Ni_5 and Ge_2Ni_3 were found to form an extended common ternary phase field. None of the investigated samples in the area showed any sign for superstructure formation, so the binary superstructure $Ge_{12}Ni_{19}$ is presumably only present in a small region in the vicinity of the binary system. The solubility of Al in the B8 phase varies from about 13 at.% in the Ni-rich part to 4 at.% in the Ni-poor part of the phase.