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# Phase relations in the Nd–Al–Si system at 500°C

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**Abstract**

The partial isothermal section of the phase diagram of the Nd–Al–Si ternary system at 500°C (50 at.% Nd or less) has been investigated by X-ray diffraction analysis, differential thermal analysis, scanning electron microscopy and electron micro-probe analysis. The existence of six binary compounds, $\alpha Nd_2Si_3$, $\beta NdSi_x$ ($x \leqslant 1.8 \leqslant 2.0$), NdAl, $NdAl_2$, $NdAl_3$ and $\alpha Nd_3Al_{11}$, and three ternary compounds, $NdAl_2Si_2$ ($\gamma$), $NdAl_{1.75}Si_{0.25}$ ($\delta$), $NdAl_{1.25}Si_{0.25}$ ($\eta$), was confirmed. The ternary compound $NdAl_{1.5}Si_{0.5}$ was not found in this section. This isothermal section consists of 11 single-phase regions, 21 two-phase regions and 11 three-phase regions. The compound $NdAl_{1.25}Si_{0.25}$ has a large homogeneity range, while the other ternary compounds are non-solubility compounds. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Rare earth alloys; X-ray diffraction; Isothermal analysis; Phase diagram

## 1. Introduction

Al–Si alloys have light weight, low thermal expansion and good resistance to wear. They are important alloys and widely used in industries. The improvement of the properties of these alloys by modifying their microstructure is a topic for the scientists. The addition of rare elements to these alloys plays an important role for this purpose and has been extensively studied by many researchers [1–5]. A phase diagram can provide useful information to study the mechanism of the modification of rare earths on Al–Si alloys. The phase diagrams of the Al–Si–Y [6], Al–Si–Gd [7] and Al–Si–Ho [8] ternary systems have been reported. However, the phase diagram of the Nd–Al–Si ternary system has not been reported. The purpose of the present investigation is to determine the partial isothermal section of the phase diagram of the termary system Nd–Al–Si at 500°C (50 at.% Nd or less).

Al–Si is a simple eutectic system [9–12]. No binary compound exists in this system. The solubility of Si in Al is 0.8 wt.% (or 0.77 at.%). For the solubility of Al in Si, Hansen [9] reported that no solubility was found at 500°C, while Elliott [10] reported that it should be 0.4 at.% at 577°C (eutectic).

The Nd–Al binary system has been studied by several researchers [13–15]. There are six intermetallic compounds, $Nd_3Al$, $Nd_2Al$, NdAl, $NdAl_2$, $NdAl_3$ and $NdAl_4$, in this system. According to Buschow et al. [15], the Al-rich compound $NdAl_4$ has been revised as $Nd_3Al_{11}$, which forms peritectically at 1235°C from the melt and $NdAl_2$ and exists in two allotropic modifications, $\alpha Nd_3Al_{11}$ and $\beta Nd_3Al_{11}$. $\alpha Nd_3Al_{11}$ has an orthorhomic structure, whereas $\beta Nd_3Al_{11}$ has the tetragonal Al-deficient $Al_4Ba$-type structure. The allotropic transformation occurs at about 950°C ($\alpha Nd_3Al_{11} \leftrightarrow \beta Nd_3Al_{11}$). Crystal structures and lattice constants of all Nd–Al phases can be found in Ref. [16].

The phase diagram and the compounds of the binary Nd–Si system were reported in Ref. [17]. Six compounds, $Nd_5Si_3$, $Nd_5Si_4$, NdSi, $Nd_3Si_4$, $Nd_2Si_3$ and $NdSi_x$ exist in this system. For the Nd–Al–Si ternary system, the ternary compounds, $NdAl_{1.25}Si_{0.75}$, $NdAl_{1.5}Si_{0.5}$, $NdAl_{1.75}Si_{0.25}$ and $NdAl_2Si_2$, in ternary Nd–Al–Si system have been given by Gschneidner et al. [18].

## 2. Experimental details

All alloy samples (260 in total) with a mass of 3 g for each sample were prepared by high frequency induction melting or arc melting the appropriate amounts of starting materials in alumina crucibles under an atmosphere of ultrapure argon gas. The starting materials for the synthesis

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of the alloys were from commercially available metals of high purity (neodymium, 99.9%; alumium, 99.99%; silicon, 99.999%). Excesses of 2% Nd were added to compensate for mass loss due to the evaporation of the rare earth elements during melting. To ensure homogeneity, the sample was remelted three times. The weight losses during melting were less than 2 wt.% for a total 260 specimens.

The samples were sealed in quartz capsules in vacuum and homogenized. The temperature for homogenization was chosen on the basis of the three binary phase diagrams and the results of differential thermal analysis (DTA) of some typical ternary alloy samples. The alloy samples containing more than 20 at.% Nd were annealed at 750°C for 90 days, those containing 20–10 at.% Nd at 600°C for 110 days and those containing less than 10 at.% Nd at 520°C for 140 days. After homogenization treatment, all samples were cooled down to 500°C at a rate of about 3°C/h and kept there for 7 days, then quenched into ice–water. The samples for X-ray diffraction analysis were powdered by hammering the brittle ingots or chiseling the ductile ingots. The powder was annealed at 500°C±5°C for 10 days and subsequently quenched into liquid nitrogen.

The phase identification of the samples was carried out by X-ray power diffraction, using a Rigaku 3015 diffractometer, Cu-radiation and Ni-filters. High-purity Si powder was used as an internal standard for measurements of the lattice parameter. By comparing and analyzing the X-ray diffraction patterns of the samples annealed for different periods of time, it was shown that the equilibrium state of the sample at 500°C was retained by the above treatment. The diffraction lines were coherent and sharp. Second phases were easily detected when the compositions of the alloys deviated from the phase boundary by 1 at.%. Thus the phase diagram can be determined by X-ray diffraction.

The phase boundaries were determined by X-ray diffraction analysis and were checked by electron probe microanalysis and scanning electron microscopy. Metallographic samples were etched by using solution of $HNO_3+HCl+H_3PO_4+HAc$ mixture. These are given in the figure captions.

## 3. Result and discussion

### *3.1. Phase analysis*

The results obtained from S.E.M. examination of the samples in the two-phase and three-phase regions agree with those obtained by X-ray diffraction analysis. The microstructure of some samples are shown in Figs. 1 and 2.

The existence of six binary compounds, $Nd_2Si_3$, $NdSi_x$ ($x\leqslant 1.8\leqslant 2.0$), NdAl, $NdAl_2$, $NdAl_3$ and $Nd_3Al_{11}$, and three ternary compounds, $NdAl_2Si_2$, $NdAl_{1.75}Si_{0.25}$, $NdAl_{1.25}Si_{0.75}$, were confirmed in this isothermal section at 500°C by XRD analysis. The single-phase samples were obtained at the respective nominal composition. XRD also shows that the compound $Nd_2Si_3$ exists with its low temperature form ($\alpha Nd_2Si_3$) while $NdSi_x$ is in its high temperature phase ($\beta NdSi_x$). The existence of $NdAl_{1.5}Si_{0.5}$ reported in Ref. [18] could not be confirmed in this work. In our experiment, the XRD pattern for the sample with

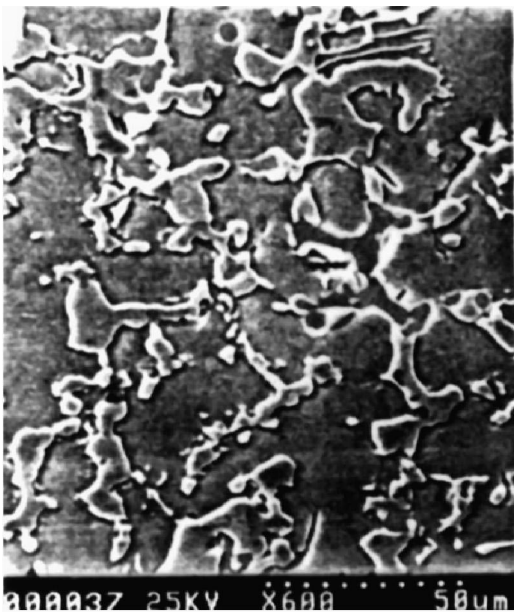


Fig. 1. The microstructure of the Nd-33.3 at.% Si-16.7% Al alloy located in the two-phase region ($\delta+\eta$). Magnification 600×. $\eta$ (lip), $\delta$ (substrate).

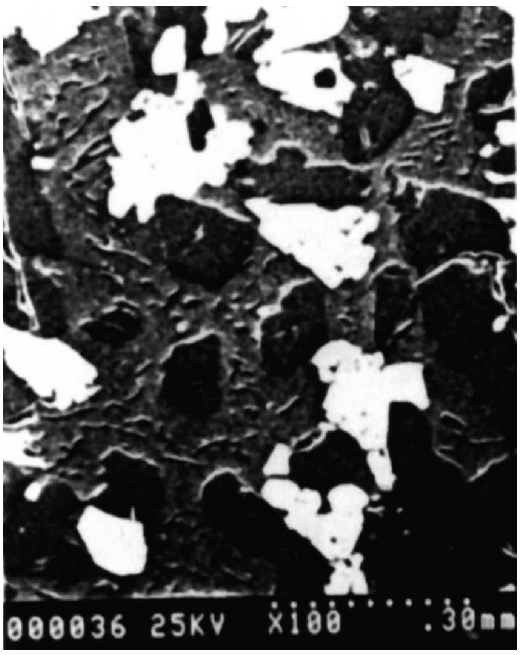


Fig. 2. The microstructure of the Nd-6 at.% Si-50 at.% Al alloy located in the three region (Al+Si+$\gamma$). Magnification 100×. Si (black, lip), $\gamma$ (white), Al+Si (substrate).

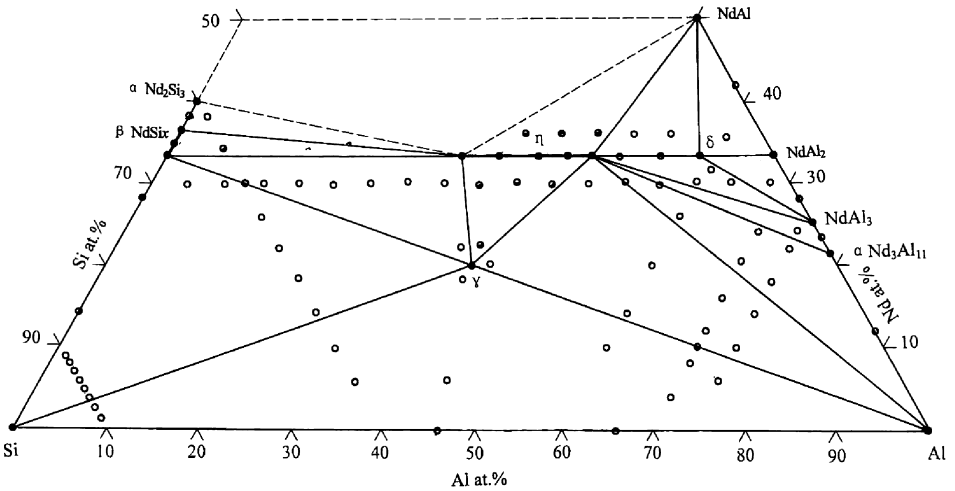


Fig. 3. The partial isothermal section (500°C) of the phase diagram of the Nd–Al–Si (50 at.% Nd or less) ternary system: ●, single-phase region; ○, two-phase region; ○, three-phase region; $\delta(\mathrm{Nd\ Al_{1.75}Si_{0.25}})$, $\gamma(\mathrm{NdAl_2Si_2})$, $\eta(\mathrm{NdAl_{1+y}Si_{1-y}}\ 0 \leqslant y \leqslant 0.4)$.

composition of $NdAl_{1.5}Si_{0.5}$ shows a mixture of $NdAl_{1.75}Si_{0.25}$ and $NdAl_{1.2}5Si_{0.75}$ phases. Therefore, this sample consists of two phases rather than a single phase. This is also confirmed by S.E.M. observation (as shown in Fig. 1).

### *3.2. Solid solubility*

The range of solid solubility for each phase at 500°C has been determined by XRD, viz. from the appearance of the reflections of the adjacent phase as well as from the variation of the lattice parameters with composition, together with S.E.M. observation and electron micro-probe analysis. The solid solubility of Si in Al determined by lattice-parameter measurements is 0.82 at.%, however, there is not any detectable solid solubility of Al in Si at 500°C. The results are convincing due to the high-purity Al and Si used in the investigation and the long enough annealing time to reach phase equilibrium. The solubilities of Nd in Al and Si are not detectable by X-ray diffraction. The compound $\beta NdSi_x$ has a homogeneity range extending from about 64 to 67 at.% Si. The compound $NdAl_{1.25}Si_{0.75}$ has a rather wide composition range and its diffraction pattern shifted rather continuously as the composition is changed. It may be expressed as $NdAl_{1+y}Si_{1-y}$, with $0 \leqslant y \leqslant 0.4$.

### *3.3. Partial isothermal section at 500°C*

By comparing and analyzing the X-ray diffraction patterns of 260 samples and identifying the phase in each sample, the partial isothermal section of the phase diagram of the ternary system Nd–Al–Si(Nd⩽50 at.% or less) has been determined (as shown in Fig. 3). The isothermal section consists of 11 single-phase regions, 21 two-phase regions and 11 three-phase regions. The single-phase regions are NdAl, $NdAl_2$, $NdAl_3$, $\alpha Nd_3Al_{11}$, Al, Si, $\beta NdSi_x$ $(1.8 \leqslant x \leqslant 2.0)$. $\alpha Nd_2Si_3$, $NdAl_{1.75}Si_{0.25}$ $(\delta)$, $NdAl_2Si_2$ $(\gamma)$ and $NdAl_{1+y}Si_{1-y}$ $(\eta 0 \leqslant x \leqslant 0.4)$. The two-phase regions are $NdAl + NdAl_2$, $NdAl_2 + NdAl_3$, $NdAl_3 + \alpha Nd_3Al_{11}$, $\alpha Nd_3Al_{11} + Al$, $Al + Si$, $Si + \beta NdSi_x$, $\beta NdSi_x + \alpha Nd_2Si_3$, $\delta + NdAl$, $\delta + NdAl_2$, $\delta + NdAl_3$, $\delta + \eta$, $\gamma + Al$, $\gamma + Si$, $\gamma + \beta NdSi_x$, $\gamma + \eta$, $\eta + NdAl$, $\eta + NdAl_3$, $\eta + \alpha Nd_3Al_{11}$, $\eta + Al$, $\eta + \beta NdSi_x$ and $\eta + \alpha Nd_2Si_3$. The three-phase regions are $NdAl + NdAl_2 + \delta$, $NdAl + \delta + \eta$, $NdAl_2 + NdAl_3 + \delta$, $\delta + NdAl_3 + \eta$, $NdAl_3 + \alpha Nd_3Al_{11} + \eta$, $\eta + \alpha Nd_3Al_{11} + Al$, $Al + \gamma + \eta$, $Al + Si + \gamma$, $Si + \beta NdSi_x + \gamma$, $\beta NdSi_x + \gamma + \eta$ and $\beta NdSi_x + \alpha Nd_2Si_3 + \eta$.

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