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Experimental investigation and thermodynamic assessment of the Al-Co-Ni system

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ABSTRACT

The Al-Co-Ni system is essential to both Co- and Ni-based superalloys. In this study phase relationships among A1, $L1_2$ and B2 at 800 °C have been investigated by using equilibrated alloys. Four samples were prepared and annealed at 800 °C for 14 days. SEM-EDXS and XRD were used to analyze the annealed samples. The results indicated that two-phase $L1_2$ + B2 and three-phase A1 + $L1_2$ + B2 regions exit.

A thermodynamic reassessment of the entire Al-Co-Ni system has been made according to the CALPHAD method. Compared to the previous assessments, more recent experimental results have been considered. In the Al-Co binary system, the phase named Y-Co_4Al_{13} has been added on the basis of the available literature. The order-disorder model has been adopted to describe the A1/$L1_2$ and A2/B2 phase relations, respectively. Three ternary compounds in the Al-rich region have been introduced. Three-sublattice model has been selected to describe the τ_1 phase with a considerable solubility extension. Thermodynamic interaction parameters have been optimized, considering the available experimental data. In this work several diagrams were calculated, which can fit experimental results in the whole composition range. A satisfactory agreement was obtained. As a result phase equilibria in the interested ferromagnetic shape memory alloys are calculated.

1. Introduction

The Al-Co-Ni system is of interest for both cobalt and nickel based alloys and for the formation of quasicrystalline phases. Nickel base superalloys are often used for applications that require high strength at high temperature such as turbine blades or nuclear reactors. Due to the higher melting point, Co-based alloys are preferred to Ni-base ones for applications at higher temperature, such as first stage stator blades in gas turbines. In both cases metallic coatings (typically AlCoCrNiY) are applied to the bulk alloy. A detailed thermodynamic description of both base alloys and coating are then crucial in view of the next generation turbines which are supposed to work at higher temperatures.

On the other hand a reliable calculation of phase equilibria and thermodynamic properties is fundamental in the materials design process, in order to simulate materials behavior during synthesis and application. For this reason a multi-component thermodynamic database including Co, Cr, Ni, Ta, W and C has been implemented by the present authors [1] in order to simulate the Co superalloy constitution and equilibria as a function of composition, temperature and other state variables.

The Al-Co-Ni phase equilibria have long been the object of experimental investigations resulting in quite complete knowledge of phase relations. Due to the industrial applications, the earlier experimental investigations mainly focused on the phase relationships among A1, $L1_2$ and B2 phases in the Co-Ni side. Phase equilibria in the Al-rich corner, however have been determined only after 2000.

The Al-Co-Ni system has been assessed by Dupin [2], Liu et al. [3] and Wang et al.[4]. Among these thermodynamic descriptions, the first two versions focused on the phase equilibria in the Co-Ni rich side and the experimental data in the Al-rich region were neglected. Wang et al. [4] produced a thermodynamic description of the whole system, where the large homogeneity range of the ternary phase τ_1 was simplified as a line compound at constant Al. Moreover the Ni_3Al_4 phase was missing in the selected binary subsystem and the solubility of Co in this phase was less accurately reproduced. Finally the Gibbs energy contribution due to the thermal vacancy in the bcc ordered and disordered structure, not directly mentioned in the work by Wang et al., was likely set to 0, which is not acceptable.

As part of the construction of a thermodynamic database for the Co-based alloys, the Al-Co-Ni system has been reassessed by taking into account the latest experimental results and relevant literature data. The available thermodynamic descriptions for the binary sub-systems Al-Co, Al-Ni and Co-Ni have been critically reviewed and then some modifications have been developed to ensure the quality of the

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Table 1
Al-Co-Ni solid phases: summary of crystal structures and sublattice models.

Phase name	*Pearson symbol* *Prototype* *Space group*	*Sublattice model*	*Reference*
Liquid	– – – – – –	(Al, Co, Ni)$_1$	
A1, fcc	*c*F4 - Cu $Fm\bar{3}m$	(Al, Co, Ni)$_1$	[5]
A2, bcc	*c*I2 - W $Im\bar{3}m$	(Al, Co, Ni, Va)$_1$	[6]
A3, hcp (εCo)	hP2 - Mg *P63/mmc*	(Al, Co, Ni)$_1$	[6]
L1$_2$, Ni$_3$Al	*c*P4 - Cu$_3$Au $Pm\bar{3}m$	(Al, Co, Ni)$_{.75}$(Al, Co, Ni)$_{.25}$ Disordered contribution from A1	[7]
B2, (Co, Ni)Al	*c*P2- CsCl $Pm\bar{3}m$	(Al, Co, Ni, Va)$_{.5}$(Al, Co, Ni, Va)$_{.5}$ Disordered contribution from A2	[8]
NiAl$_3$	*o*P16 - CFe$_3$ *Pnma*	(Co, Ni)$_1$(Al)$_3$	[9]
Ni$_2$Al$_3$	*h*P5 –Ni$_2$Al$_3$ $P\bar{3}m1$	(Al, Co, Ni)$_2$(Al)$_3$ (Co, Ni, Va)$_1$	[8]
Ni$_3$Al$_4$	*c*I112 – Ni$_3$Ga$_4$ Ia $\bar{3}$ d	(Co, Ni)$_3$(Al)$_4$	[10]
Ni$_5$Al$_3$	*o*C16 - Pt$_5$Ga$_3$ *Cmmm*	(Ni)$_5$(Al)$_3$	[11]
Co$_2$Al$_9$	mP22 - Co$_2$Al$_9$ *P21/a*	(Co, Ni)$_2$(Al)$_9$	[12]
Co$_2$Al$_5$	hP28 - Co$_2$Al$_5$ *P63/mmc*	(Co, Ni)$_2$(Al)$_5$	[13]
CoAl$_3$	mC34 – Os$_4$Al$_{13}$ P2/m	(Co, Ni)$_1$(Al)$_3$	[14]
M-Co$_4$Al$_{13}$	C2/m	–	Modeled as Y-Co$_4$Al$_{13}$[15]
O-Co$_4$Al$_{13}$	oP102 – O-Co$_4$Al$_{13}$ Pmn2$_1$	–	Modeled as Co$_4$Al$_{13}$[13]
O’-Co$_4$Al$_{13}$	*Pnma*	–	Modeled as Co$_4$Al$_{13}$[16]
Y$_1$-Co$_4$Al$_{13}$	monoclinic	–	Modeled as Y-Co$_4$Al$_{13}$[17]
Co$_4$Al$_{13}$	–	(Co, Ni)$_4$(Al)$_{13}$	
Y-Co$_4$Al$_{13}$	–	(Co, Ni)$_{4.9}$ (Al)$_{15.1}$	
τ_1	*P10/mmm*	(Co,Ni)$_5$(Al,Co,Ni)$_1$Al$_{14}$	[18]
τ_2	oI96 *Immm*	(Co,Ni)$_1$Al$_3$	[19]
τ_3	mS26 C2/m	Co$_2$(Co,Ni)$_2$Al$_9$	[20]

thermodynamic description of the ternary system. Thermodynamic phase models have been carefully selected with attention to the consistency with the available crystal structure data, the experimentally determined homogeneity ranges and the models already adopted in the Co superalloy database mentioned above. For this reason, in particular, a two-sublattice model has been taken to describe the order/disorder relation between A2 and B2 as well as A1 and L1$_2$ phases.

Moreover, equilibrated alloys were experimentally investigated to better identify the detailed position of the A1 + B2 + L1$_2$ field at 800 °C.

2. Literature review

Constitution and phase equilibria of the three binary Al-Co-Ni subsystems are briefly reviewed in the following. All the binary and ternary phases involved in this ternary system are listed in Table 1.

2.1. Al-Co

A detailed critical evaluation of the Al-Co system was presented by Grushko and Cacciamani [21] based on the available literature data. The thermodynamic modeling was reported by McAlister [22], Dupin and Ansara [23], Stein et al.[24]. In order to investigate melting behavior and homogeneity range of the B2 phase, Stein et al. [24] prepared a series of Al-Co alloys in the composition range 30–60 at% Co and then analyzed them by differential thermal analysis (DTA), scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA). As a result the melting temperature of the B2 phase was found to be 1673 °C, significantly higher than the value mentioned by Dupin and Ansara. Moreover the Al-Co system was reassessed by taking into account this new result and keeping the same phase models used by Dupin and Ansara. After that, Priputen et al. [17] reinvestigated experimentally phase relationships in the vicinity of Co$_4$Al$_{13}$ family of phases. Several alloys between 20 and 23 at% Co were prepared and annealed for 330 h at various temperatures between 1070 and 1150 °C. XRD, DSC and SEM with EDXS were utilized. As a result six phases belonging to the Co$_4$Al$_{13}$ family were found: CoAl$_3$, Y$_1$-Co$_4$Al$_{13}$, Y$_2$-Co$_4$Al$_{13}$, M-Co$_4$Al$_{13}$, O-Co$_4$Al$_{13}$ and O’-Co$_4$Al$_{13}$. Small homogeneity ranges were found for O’-Co$_4$Al$_{13}$, Y$_1$-Co$_4$Al$_{13}$, M-Co$_4$Al$_{13}$ and Co$_4$Al$_{13}$ above 1000 °C. Y$_1$-Co$_4$Al$_{13}$ was found to become stable at higher temperature and to transform into M-Al$_{13}$Co$_4$ by a quasipolytypic reaction. The temperature was proposed to be around 1077 °C. Y$_2$-Co$_4$Al$_{13}$ resulted to be metastable. Maybe a transition reaction between O-Co$_4$Al$_{13}$ and O’-Co$_4$Al$_{13}$ take place below 1000 °C. At last revised Al-Co phase diagram in the composition range 20–29 at% Co above 1000 °C was established. For the sake of simplification, Dupin and Ansara treated the stable phases of the Co$_4$Al$_{13}$ family as a single stoichiometric phase named Co$_4$Al$_{13}$ (at 23.53 at% Co). In the current work, the parameters from Stein et al. [24] are considered and adjusted to fit the experimental data by Priputen et al.[17]. Moreover, in this work, a new phase named Y-Co$_4$Al$_{13}$ is added at 24.5 at% Co to describe Y$_1$-Co$_4$Al$_{13}$ and M-Co$_4$Al$_{13}$. It is formed by a peritectic reaction at 1129 °C. The quasi-polytypic transformation between the Y-Co$_4$Al$_{13}$ and M-Co$_4$Al$_{13}$ was omitted due to the uncertain temperature. The Al-Co phase diagram according to the present calculation is presented in Fig. 1. The details about the modification are discussed in Section 5.

2.2. Al-Ni and Co-Ni

The Al-Ni system was recently discussed by Wang and Cacciamani [25], and their conclusions are here accepted. As for the

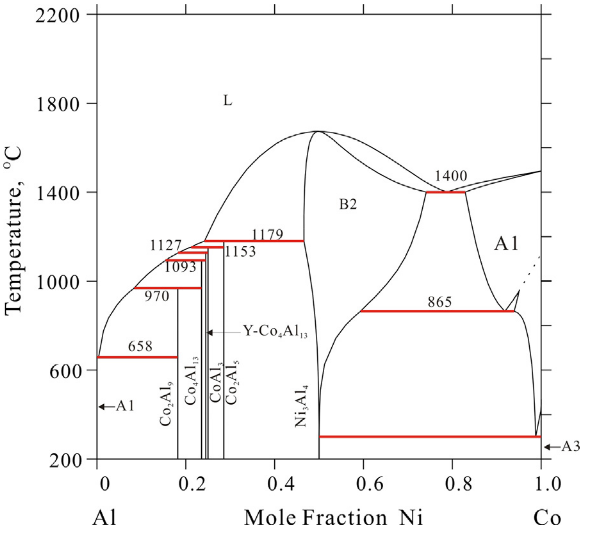

Fig. 1. Al-Co phase diagram calculated in this work.