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Phase Equilibria in the Ni–Al–W System at 900°C

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Summary. Multicomponent Ni-base alloys exhibit good mechanical properties even at elevated temperatures and they are widely used for industrial production of exertion-resistive parts of engines. These properties are mainly determined by the coexistence of a disordered γ matrix with a face centred cubic lattice and cuboidal domains of its ordered γ' structure. Therefore it is useful to study phase equilibria in Ni-base systems, namely in the regions involving both mentioned phases. One of the conclusions of our recent work on Ni–Al–Cr–W system was a necessity of modification of selected thermodynamic parameters of the ternary Ni–Al–W subsystem in order to achieve a better agreement of our experimental observations with theoretical modelling. This involves new measurements of the microstructure of selected samples of the Ni–Al–W system at 900°C and the comparison of the results with existing literature data in order to confirm our conclusions on higher order system investigated before. It is a first step on the way to an assessment of the Ni–Al–W system, which has not been done before.

Keywords. Thermodynamics; Alloys; Electron microscopy; Phase diagrams.

Introduction

Further improvement of advanced Ni-based superalloys calls for better understanding of phase transformations at service temperatures and better knowledge of equilibrium phase diagrams. For real systems containing typically over seven alloying components it is difficult to achieve the complete thermodynamic description. Therefore, it is convenient to start from lower order model systems that are relatively simple, yet sufficiently representative for commercial Ni-based superalloys. In some cases the adequate thermodynamic description for higher order model systems suffers from the insufficiency of suitable experimental data for lower order subsystems. Namely in the case of Ni–Al–W system, the limited extent of

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available experimental data led to a thermodynamic description which is not able to describe correctly higher order systems (as shown, *e.g.*, in our previous study on Ni–Al–Cr–W system [1]). For this reason, this work is focused on the ternary Ni–Al–W system at 900°C with the aim to clarify the phase constitution in the Ni-rich composition range. The main attention is focused on γ (disordered, type A1) and γ' (ordered, type $L1_2$) phase coexistence, *i.e.* to the composition range important for practical use.

Thermodynamic description of the Ni–Al–W system can be found in Ref. [2] as a part of the commercial database TCNI for Ni-base superalloys. Unfortunately, no thermodynamic analysis leading to an assessment of this ternary system could be found in literature. On the other hand a sufficient amount of phase data exists. This system was extensively analysed by *Udovskii et al*. [3] and *Jia et al*. [4] in the field of γ, γ', α, and β phase existence at temperatures covering the range 800–1500°C. The data by *Jia et al*. [4] were already used in our recent study on higher order system Ni–Al–Cr–W [1] for a better understanding of the region at lower concentrations of chromium. For detailed analysis of the ternary system in this work the data at 900°C were taken mainly from *Udovskii et al*. [3].

Software package Thermo-Calc [5] was used for all calculations in our study. In the program, the thermodynamic model based on the CALPHAD approach is implemented with the description of ordering according to *Ansara et al*. [6]. Thermodynamic parameters for phase equilibria calculations in the Ni–Al–W system were taken from the above-mentioned database TCNI [2] as well as from our previous study [1].

Results and Discussion

Overall compositions of studied specimens as well as phases experimentally identified using selected area diffraction by transmission electron microscopy (TEM) and calculated by means of Thermo-Calc software are reported in Table 1. Detailed data on individual phase compositions are not present here, though they were obtained.

A comparison of experimental and calculated data indicates different phase structures in samples RW2 and RW4. Figure 1 shows characteristic microstructure identified in selected alloys. Sample RW1 has three-phase structure of fine $\gamma+\gamma'$ matrix with large particles of W-rich α surrounded by γ envelopes. RW3 reveals particles of α embedded in γ' matrix. RW4 is solely formed by $\gamma+\gamma'$.

Table 1. Chemical compositions of experimental alloys (at.%) together with phase constitution after long-term annealing at 900°C

Alloy	Ni	Al	W	Equilibrium phases	
				Experiment	Calculation
RW1	75.0	14.6	10.4	$\gamma+\gamma'+\alpha$	$\gamma+\gamma'+\alpha$
RW2	79.9	6.6	13.5	$\gamma+\gamma'/Ni_4W+\alpha/NiW$[a]	$\gamma+\alpha$
RW3	72.1	21.2	6.7	$\gamma'+\alpha$	$\gamma'+\alpha$
RW4	85.9	13.5	0.6	$\gamma+\gamma'$	γ

[a] sample not in equilibrium

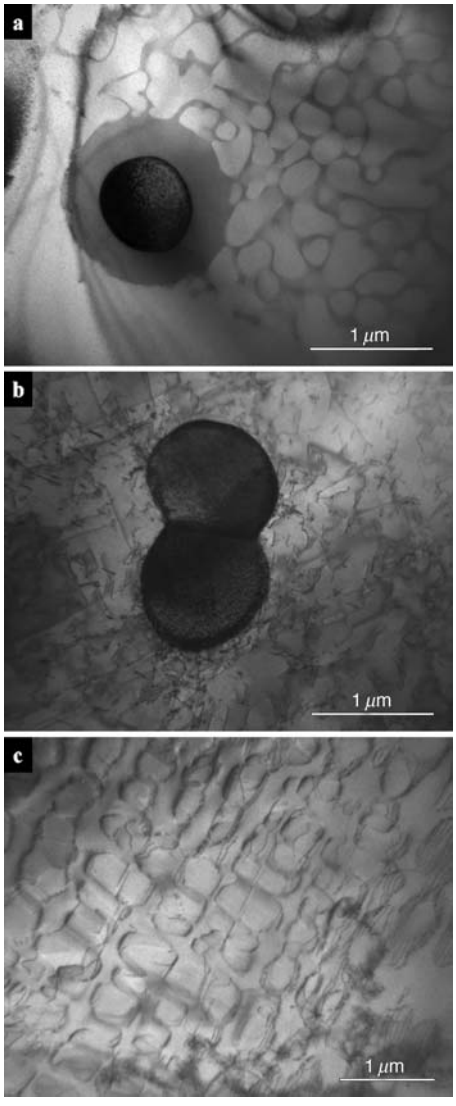

Fig. 1. TEM micrographs showing the microstructure of experimental alloys after long term annealing at 900°C: RW1 with a dark spherical particle of α with γ envelope embedded in $\gamma+\gamma'$ matrix (a), RW3 with dark particles of α in γ' matrix (b), and RW4 revealing uniform $\gamma+\gamma'$ structure (c)

The structure of RW2 sample presents a number of phases higher than allowed by *Gibbs* rule, probably due to the slow diffusion of W. Besides the matrix γ and large particles of α, substantial amount of Ni_4W phase was found in the matrix together with the remnants of γ'. Particles of α were found in coexistence with NiW. Further prolonged annealing of the same alloy and additional experiments will hopefully solve this ambiguity. However, according to our measurements the amount of Al in Ni_4W is substantial (at least 3 at.%). Consequently the description of the Ni_4W phase should be modified as, at present, no solubility has been considered.

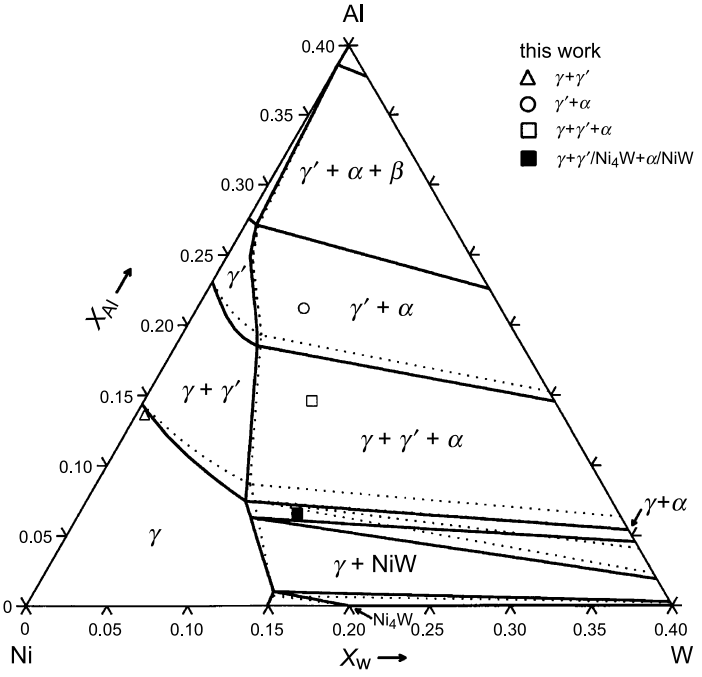

Fig. 2. Section of ternary phase diagram Ni–Al–W at 900°C with calculated phase boundaries; (- - - - - -) and (———) indicate calculated phase boundaries obtained using the database from Ref. [2] and the revised parameters from Ref. [1], respectively, (△, ○, □, ■) nominal compositions of our experimental alloys together with phase information

The results of thermodynamic modelling and their comparison with experimental data are presented in Fig. 2. This shows a comparison of our experimental results with calculated phase boundaries using the commercial database TCNI [1] and/or the revised parameters from our previous study on the Ni–Al–Cr–W system [1], respectively. Our results are further compared with those of the literature in Fig. 3.

According to Fig. 3, the position of the phase boundaries has to be changed in order to obtain a more realistic phase diagram of the system. As follows from both our own and the previous experimental literature data, the phase boundaries between the regions with and without γ phase as well as the phase boundaries between the regions with and without the γ' phase have to be shifted markedly to lower concentrations of aluminum. This conclusion agrees with that of our previous study on the higher order Ni–Al–Cr–W system [1], where a change of selected thermodynamic parameters leading to phase boundaries shifts had to be done to ensure the existence of the $\gamma' + \alpha$ two phase region at nickel concentrations close to 75 at.%. This trend is also evident from Fig. 2 where the application of the modified thermodynamic parameters produces the desired shift of the phase boundaries to lower concentrations of aluminum. Nevertheless, the agreement of modelling with experimental data is still far from ideal and further studies on this ternary system (also at other temperatures) would be profitable.

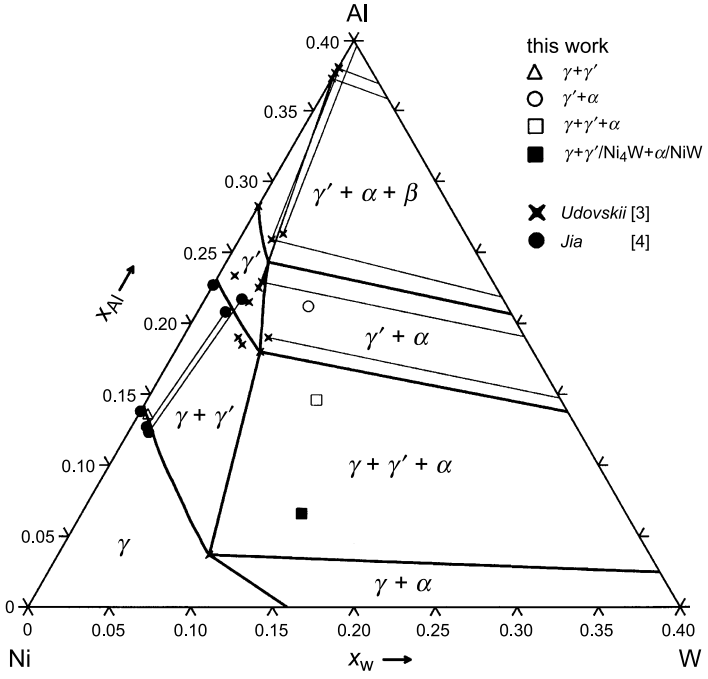

Fig. 3. Section of ternary phase diagram Ni–Al–W at 900°C with extrapolated phase boundaries based on experimental information from literature; (———) extrapolated phase boundaries, (✕, ●) phase compositions according to *Udovskii et al.* [3] and *Jia et al.* [4], (△, ○, □, ■) nominal compositions of our experimental alloys together with phase information

Experimental

Four alloys (RW1 to RW4) were prepared by melting pure metals with compositions chosen to obtain a wide range of the γ, γ', and α phase existence. Approximately 40 g ingots were prepared; 4 mm by 4 mm by 12 mm pieces were then cut from the ingots and annealed at 900°C for 650 hours in vacuum-sealed quartz capsules, followed by water quenching. The time of heat treatment was chosen on the basis of kinetic calculations with the aim to reach the thermodynamic equilibrium state.

The compositions were determined using an energy dispersive X-ray spectrometer (EDS) with an ultra thin Be window. A Philips SEM 505 scanning electron microscope and a Philips CM12 STEM transmission electron microscope both equipped with an EDAX energy dispersive X-ray analyser were used. Spectra were collected for 100 s. The standardless method using a thin foil approximation was used for spectra evaluation in scanning TEM; standard bulk specimen corrections were applied in the case of scanning electron microscopy (SEM) measurements. The specimens for SEM investigations were ground and electro-mechanically polished using an etchant OPS by Struers. Applied SEM voltage was 20 kV, spot size was about 100 nm for SEM measurements. For TEM measurements foils were prepared from 3 mm discs, 0.1 mm thick by dimpling (spherical grinding) followed by ion milling; the voltage used was 120 kV, and the spot size was 7.5 nm. The phases were identified by means of selected area diffraction.

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References

[1] Buršík J, Brož P, Picha R (2003) Intermetallics **11**: 483
[2] Dupin N, Sundman B (2001) Scan J Metal **30**: 184
[3] Udovskii AL, Oldakovskii IV, Moldavskii VG (1991) Russian Metallurgy **4**: 111
[4] Jia CC, Ishida K, Nishizawa T (1994) Metall Trans **25A**: 473
[5] Andersson JO, Helander T, Höglund L, Shi PF, Sundman B (2002) Calphad **26**: 273
[6] Ansara I, Dupin N, Lukas HL, Sundman B (1997) J Alloys and Comp **247**: 20