THE ROLE OF THE BASE ELEMENT IN γ' STRENGTHENED COBALT/NICKEL-BASE SUPERALLOYS

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Abstract

Two series of polycrystalline model superalloys – one without and one containing Cr – with varying Ni/Co ratios and otherwise constant element contents were produced and are characterized by a variety of methods. All alloys form a γ/γ' microstructure after a standard aging treatment at 900 °C for 100 h. Upon long term aging for 1100 h, the Cr containing Co-base alloy forms undesired intermetallic phases. Liquidus and solidus temperatures are hardly influenced by the Ni/Co content, but the γ' solvus temperature is strongly decreasing with increasing Co content. Addition of Cr to the alloy series lowers liquidus and solidus, but does not influence the solvus temperature substantially. Neutron diffraction experiments conducted on the Cr containing alloys show that the misfit is negative for alloys rich in Ni, but linearly increases to positive values with increasing Co content. 3D atom probe tomography shows that W preferentially partitions to the γ phase for the Ni-base alloys, whereas it is enriched in γ' for the Co-base alloys. The partitioning of Co (γ), Cr (γ) and Al (γ') to their respective phases is much more pronounced in Ni rich alloys, i.e. all elements distribute more equally in the Co-base alloys. Nanoindentation on the Cr free alloy variants reveals that the hardness of the Co-base alloy is higher than the one for the Ni-base alloy. However when Cr is present in the alloy, the hardness of the Ni-base alloy is superior. The same behavior is observed in compressive creep experiments at 900 °C. The addition of Cr strongly improves the creep resistance of the Ni-base alloy, whereas it slightly worsens the performance of the Co-base alloy.

Introduction

Since the discovery of a ternary $L1_2$ phase in the Co-Al-W system in 2006 [1] γ' strengthened Co-base superalloys have increasingly gained worldwide scientific interest [2–7]. Co- and Ni-base superalloys possess a very similar microstructure consisting of a high volume fraction of cuboidal intermetallic $L1_2$ precipitates (γ'), which are coherently embedded within an fcc solid solution (γ). Co-base alloys and intermediate Co/Ni-base alloys have already shown creep

properties, that are similar to or even better than those of first generation Ni-base superalloys [3,8–11].

Despite the similarities, there are also many differences: The liquidus and solidus temperatures of Co-base alloys are generally higher than those of typical Ni-base alloys, whereas the γ' solvus temperature is lower [3,6].

The γ'/γ partitioning behaviour of certain elements in Co- and Ni-base alloys can also differ. Especially W, which is typically slightly enriched in γ in Ni-base alloys and is a strong γ' forming element for the Co-base alloys [12,13].

This is also the main reason why Co-base alloys have a positive lattice misfit δ , i.e. the lattice parameter of the precipitate phase is larger than the one for the matrix phase. This effect prevails also at high temperatures, which is generally not the case for the majority of Ni-base superalloys [6]. Mughrabi [14] argues, that a positive misfit at operating temperatures might be beneficial for creep strength.

Another aspect that has been reported in literature is that deformation mechanisms in Ni-base, intermediate Co/Ni-base and Co-base alloys are different. In intermediate alloys with similar contents of Co and Ni, anti phase boundaries (APBs) have been observed, which extend completely through the precipitates over few hundred of nanometres, suggesting that the APB energy may be much lower than in typical Ni-base alloys [15]. In pure Co-base alloys deformation by super lattice intrinsic stacking fault formation in the γ' precipitates has been observed, which suggests that planar fault energies are different yet again.

Another dissimilarity between Ni- and Co-base alloys is their tolerance for alloying elements without destabilizing the γ/γ' microstructure. In Ni-base superalloys rather large amounts of alloying elements can be added without forming undesired intermetallic phases. Compared to that, the compositional range, in which γ' strengthened Co-base superalloys can exist is very narrow. Especially Cr, which is essential for oxidation & corrosion resistance has been shown to be very critical, as adding more than 4 at.% Cr to a Co-9 at.%Al-9 at.%W alloy causes the formation of other inter-

Table I. Nominal and Actual Alloy Compositions as Measured by EDS (in Brackets)*

Designation	$f_B(\text{Co})$ / %	$c(\text{Co})$ / at.%	$c(\text{Ni})$ / at.%	$c(\text{Al})$ / at.%	$c(\text{W})$ / at.%	$c(\text{Cr})$ / at.%
ERBO-NC0 _{0Cr}	0	0 (0)	83 (84.3±0.2)	9 (9.2±0.2)	8 (6.41±0.1)	-
ERBO-NC25 _{0Cr}	25	20.75 (22.0±0.2)	62.25 (61.8±0.3)	9 (8.9±0.2)	8 (7.39±0.1)	-
ERBO-NC50 _{0Cr}	50	41.5 (42.5±0.2)	41.5 (40.5±0.3)	9 (9.6±0.2)	8 (7.38±0.1)	-
ERBO-NC75 _{0Cr}	75	62.25 (62.7±0.3)	20.75 (20.7±0.2)	9 (9.2±0.2)	8 (7.41±0.1)	-
ERBO-NC100 _{0Cr}	100	83 (83.4±0.2)	0 (0)	9 (9.4±0.2)	8 (7.53±0.1)	-
ERBO-NC0 _{8Cr}	0	0 (0)	75 (75.8±0.2)	9 (8.7±0.2)	8 (7.2±0.1)	8 (8.2±0.1)
ERBO-NC25 _{8Cr}	25	18.75 (19.3±0.2)	56.25 (55.9±0.3)	9 (9.0±0.2)	8 (7.5±0.1)	8 (8.2±0.1)
ERBO-NC50 _{8Cr}	50	37.5 (39±0.2)	37.5 (36.6±0.3)	9 (9.0±0.2)	8 (7.3±0.1)	8 (8.0±0.1)
ERBO-NC75 _{8Cr}	75	56.25 (57±0.3)	18.75 (18.1±0.2)	9 (9.2±0.2)	8 (7.6±0.1)	8 (8.0±0.1)
ERBO-NC100 _{8Cr}	100	75 (75.5±0.2)	0 (0)	9 (8.7±0.2)	8 (7.9±0.1)	8 (8.0±0.1)

* All alloys also contain 400 ppm B, which is not listed here. f_B : Co-fraction of the base materials Co and Ni (in %), $c(i)$: nominal (measured±measurement error) content of element i (in at.%) in the alloy.

metallic phases at the expense of the γ/γ' microstructure [16]. Shinagawa *et al.* [17] found that the addition of Ni widens the γ/γ' two phase field in quaternary Co-Ni-Al-W alloys, and so enables alloying by other elements. However no mechanical properties of these alloy variants are available. Also there was no Cr present, which has a dramatic influence on the various alloy properties, e.g. it reduces the lattice misfit and causes a deterioration of the creep strength [18]. To systematically address the change in alloy properties, when the base element changes, two sets of model superalloys – one without and one containing Cr – were designed, where Ni was successively substituted by Co. Each series consists of 5 alloys, where the Ni:Co ratio is 0:100, 25:75, 50:50, 75:25 and 100:0. Several alloy properties have been studied by a variety of methods including scanning electron microscopy (SEM), neutron diffraction (ND), differential scanning calorimetry (DSC), thermodynamic phase diagram calculations (CALPHAD), 3D atom probe tomography (APT) and creep tests. Some preliminary results on creep, lattice misfit and oxidation of the Cr containing alloys can also be found in [19].

Experimental Procedures

The compositions of all the alloys investigated in this study are listed in Table I along with their respective designations, which are used throughout this paper without the prefix *ERBO*. The number used in the acronym is the Co percentage of the base elements Co and Ni, i.e.

$$f_B = c(\text{Co}) / (c(\text{Co}) + c(\text{Ni})) \quad (1)$$

The two alloy series differ only in their Cr content, which is indicated as an index on the acronym. All alloys also contain 400 ppm B, which is not listed in the table. The B was added at the expense of Co in order to increase the grain boundary strength [16, 20].

The alloys were arc-melted using raw elements of at least 99.9% purity. The melting was performed under an Ar

back-filled atmosphere and the samples were flipped and re-melted at least 3 times to improve their homogeneity. The samples were subjected to a solution and homogenisation heat treatment at 1250 °C for 24 h before a precipitate ageing step for 100 h at 900 °C was performed. A long term heat treatment for an additional 1000 h has been performed to investigate the microstructural stability. After both heat treatment steps, the samples were quenched in water.

The microstructures of all alloys were examined by SEM using a *Zeiss Crossbeam 1540 EsB*, after standard sample preparation consisting of grinding by SiC paper up to 2500 grit followed by polishing using diamond suspension and finally a silica suspension (*Struers OPS*). Using the same device, energy dispersive X-ray spectroscopy (EDS) was conducted to determine the actual alloy compositions.

The γ' area fraction was determined from the micrographs of the standard annealed state using the image analysis software *ImageJ*.

To determine the critical phase transition temperatures, i.e. γ' -solvus, solidus and liquidus temperatures, differential scanning calorimetry was performed on samples of the alloys in the standard heat treated state using a *Netzsch STA 409*. For these measurements, heating and cooling rates of 5 K/min were used. The characteristic phase transition temperatures, i.e. γ' -solvus, solidus and liquidus temperature were determined by peak analysis of the DSC curves. The transition temperatures determined from the peak onsets in both heating and cooling segments were averaged to approximate the actual transformation temperature which would correspond to a infinitely slow cooling/heating rate.

Calculations were performed using the *Thermo-Calc* software [21, 22] in conjunction with the TCNI8 database to compare thermophysical properties and evaluate the applicability of the database. The data on transformation temperatures is taken from metastable calculations, i.e. only liquid, γ and γ' were entered in the calculation. This was

Figure 1. SEM micrographs (backscattered electron detector) of $\text{NCX}_{0\text{Cr}}$ (top) and $\text{NCX}_{8\text{Cr}}$ (bottom) alloys after 100 h at 1173 K (900 °C).

Figure 2. Area fraction of γ' in both alloy series as determined by image analysis and mole fraction of γ' as calculated from APT results.

carried out, because other phases (e.g. μ -, β -, R-Phase) appeared in equilibrium conditions, which were not observed in the standard heat treated state.

Neutron diffraction experiments were carried out at room temperature on the Cr-containing alloys using the high resolution powder diffractometer *SPODI* (Structure Powder Diffractometer) at the research reactor Heinz Maier-Leibnitz (*FRM II*) in Garching, Germany [23]. The wavelength was 1.548 27(2) Å obtained from a vertically focused composite Ge (551) monochromator. The monochromator and zero-shift are in the range of $2\theta \approx 0.1^\circ$. The evaluation of the diffraction patterns was done by fitting all individual reflec-

tions with Voigt profiles using the technical graphing and data analysis software IGOR Pro from *WaveMetrics, Inc.* The position of the γ' sub peaks in the fundamental reflections was identified by fitting and analysing all the superlattice reflections, which correspond only to this phase. Details on the evaluation can be found elsewhere [18, 19].

Atom probe tomography analyses were performed using a reflectron equipped local electrode atom probe (*LEAP 3000XHR*, *Cameca Instruments*) in pulsed laser mode. Laser pulses of 532 nm wavelength, 12 ps pulse length, 0.4 nJ pulse energy and 100 kHz frequency were applied, while the specimen base temperature was kept at 40 K. Data reconstruction and analysis was performed using the *Cameca IVAS 3.6.8* software package. The first one million ions were not considered for data analysis due to residual Ga ions implanted during FIB milling. The γ and γ' compositions were determined from concentration profiles that were built across the isoconcentration surfaces in subvolumes at least 5 nm distant from the phase boundaries. When the phase compositions are known, the mole fraction f_N of the γ' can be calculated using the lever rule based on the mass balance equation.

To investigate the γ/γ' compound's local mechanical properties in the two Ni-Co series, nanoindentation was performed using a Nanoindenter XP (*Agilent Technologies*) with a Berkovich diamond tip. The diamond indenter tip was calibrated using amorphous fused silica with known mechanical properties (Young's modulus $E = 72$ GPa, Poisson's ratio $\nu = 0.18$). The continuous stiffness method was used, which continuously determines the contact stiffness by superimposing the load signal with an oscillation of 45 Hz. The final indentation depth of 2000 nm was chosen to minimize the indentation size effect, which is described elsewhere [24]. Hardness and Young's modulus were analyzed according to the Oliver-Pharr method [25].

Figure 3. Microstructure (backscattered electron detector) of $\text{NCX}_{0\text{Cr}}$ (top) and $\text{NCX}_{8\text{Cr}}$ (bottom) alloys after long term annealing for 1100 h at 1173 K (900 °C).

The high temperature mechanical properties were characterized in terms of compressive creep tests at 900 °C and 250 MPa on cylindrical samples of 7.5 mm length and a diameter of 5 mm. The tests were interrupted after 4 to 6 % plastic strain.

Results & Discussion

The compositions of all alloys as measured by EDS are given in Table I. The results are in good agreement with the nominal element content. However, apparently the W content is lower than intended in most alloys with the largest deviation of $\Delta c(\text{W}) \approx 1.6 \text{ at.}\%$ in alloy $\text{NC0}_{0\text{Cr}}$.

The microstructure of all alloys after standard aging for 100 h is shown in Figure 1. All alloys show the typical γ/γ' microstructure. The γ' morphology is mostly cuboidal, although the precipitates in the Cr containing alloys appear more rounded. Cr was already shown to decrease the γ/γ' lattice misfit [18], which is the likely reason for the change of the precipitate shape. This will be discussed later. The contrast of the backscattered electron images changes from dark γ' to bright γ' in both alloy series. This is caused by a reversion of the partitioning behavior of W and will be discussed later on. All alloys show rather low γ' volume fractions. The results on the γ' fraction as obtained by image analysis of the standard annealed state is shown in Figure 2. For cubic precipitates the γ' volume fraction f_V is lower than the γ' area fraction f_A in a (001) section micrograph. In the present case however, the precipitates are partially rounded or at least show rounded corners, which suggests that $f_V = f_A$.

The results from the lever rule approach using the APT data on the Cr containing alloys are also included in Figure 2. As the atomic density of γ and γ' are nearly equal, the γ' mole fraction $f_N = f_V$. The data obtained by APT and image

analysis are in good agreement and show that f_V increases with increasing Co content and reaches a maximum in alloy $\text{NC75}_{8\text{Cr}}$. The deviation of image analysis and APT in alloy $\text{NC100}_{8\text{Cr}}$ is probably caused by secondary γ' precipitates, which were found in the APT reconstruction of this alloy.

The Cr free alloy variants also show the maximum f_V in the intermediate composition range, but it is more distinct and situated in the alloy with a Ni/Co ratio of 50:50.

The long term annealed state (1100 h at 900 °C) is shown in Figure 3. The precipitates are only slightly coarsened and have changed their morphology towards more cubic shapes with the exception of alloy $\text{NC50}_{8\text{Cr}}$. This already indicates that this alloy exhibits an especially low γ/γ' lattice misfit.

The γ/γ' microstructure starts to decompose in the Cr containing alloy without Ni. Consistently with the findings of [16] it was confirmed that a critical Ni content is necessary in this alloy system to stabilize the γ/γ' microstructure and avoid the formation of undesired intermetallic phases.

The transformation temperatures of all alloys as measured by DSC and as calculated by CALPHAD are plotted in Figure 4. The DSC measurements on both series show that the γ' solvus temperature decreases with increasing Co-content, whereas the solidus and liquidus temperatures are not significantly affected. The addition of 8 at.% chromium decreases solidus and liquidus temperatures over the whole compositional range by about 40 K. The Cr has no effect on the solvus temperature for those alloys which are rich in Co, but it increases the solvus temperature of $\text{NC25}_{0\text{Cr}}$ by about 30 K. In alloy $\text{NC0}_{0\text{Cr}}$ there was no distinct onset of a γ' solvus peak, which is why it is missing in the Figure 4. The trends are described correctly by the CALPHAD cal-

Figure 4. Transformation temperatures as obtained by DSC measurements and calculated from ThermoCalc (TCNI8) for the alloys a) without Cr and b) including Cr.

culations (TCNI8 database), although deviations from the transformation temperatures of up to 50 K are observed. Additionally, other intermetallic phases (e.g. $\mu/D8_5$, $\beta/B2$) are calculated to be in equilibrium with γ' at 900 °C for the Co-rich alloys, which have not been observed experimentally after standard annealing at this temperature.

The neutron diffraction patterns of the Cr containing alloy series are shown in Figure 5. They are not scaled with respect to each other. It can be seen that no reflections other than those of the γ and γ' are present. The intensity of all reflections decreases as the Co content is increased. This is due to a lower neutron scattering length of Co as compared to Ni. The intensity of the superlattice reflections declines even more with the Co content and disappear almost completely in $NC75_{8Cr}$ and $NC100_{8Cr}$. Two other explanations are possible: i) The degree of order in the $L1_2$ phase is decreasing or ii) the average neutron scattering length of the B atoms in the A_3B lattice equals the one of those on the A sublattice. The reason for the disappearing superlattice reflections can be understood by diffraction experiments using a different kind of radiation. After determination of the individual lattice parameters $a_{0,\gamma}$ and $a_{0,\gamma'}$ the γ/γ' lattice misfit δ was calculated by equation 2:

$$\delta = 2 \cdot \frac{a_0(\gamma') - a_0(\gamma)}{a_0(\gamma') + a_0(\gamma)} \quad (2)$$

Figure 6 shows δ of alloy series NCX_{8Cr} . It is revealed that it is negative in the pure Ni-base alloy (−0.11 %) and linearly increases with the Co-content towards +0.19 %. Although the measurements were performed at room temperature, the precipitate shapes (round in the middle of the composition range) indicates that this trend is sustained also at the aging temperature. That δ increases with higher Co-content

was already observed by Shinagawa *et al.* [17], whose data are also included in Figure 6. However in their Co-xNi-10Al-7.5W alloy series, δ is higher by approximately 0.26 % over the full compositional range, i.e. the misfit was positive for all alloys. The difference in composition between these alloys and the present alloys NCX_{0Cr} is quite small. As mentioned before, the actual W content in the present alloys is lower than intended and indeed very close to the 7.5 at.%. The difference in the Al content of approximately 1 at.% is believed to be too small to cause a negative lattice misfit in $NC0_{0Cr}$ or $NC25_{0Cr}$. It is therefore deduced, that all alloys without Cr exhibit a positive lattice misfit. The crossover in the lattice misfit, observed in the present alloy series NCX_{8Cr} therefore indicates that Cr has a large – direct or indirect – influence on the lattice misfit.

To analyze compositional changes of both phases, which might be responsible for the change in the lattice misfit, 3D atom probe tomography (APT) was performed. The reconstruction of the APT samples is visualized in elemental maps showing the Al and Cr atoms (Figure 7). The γ/γ' interface is highlighted by an 8 at.% Cr isoconcentration surface. It can already be seen qualitatively, that both elements distribute more evenly in the Co-rich sample $NC75_{8Cr}$.

The elemental partitioning behavior is quantitatively described by the partitioning coefficient $k_i^{\gamma'/\gamma} = c_i^{\gamma'}/c_i^{\gamma}$. The individual $k_i^{\gamma'/\gamma}$ are shown in Figure 8. Al is strongly enriched in γ' in the Ni-rich alloys ($k_{Al}^{\gamma'/\gamma} > 4$) and is distributed almost equally between γ and γ' in the pure Co-base alloy $k_{Al}^{\gamma'/\gamma} \approx 1$. Chromium shows a very strong partitioning to the γ matrix in the Ni-rich alloys $k_{Cr}^{\gamma'/\gamma} < 0.2$ and tends to distribute more evenly in the Co-base alloy ($k_{Cr}^{\gamma'/\gamma} \approx 0.6$). W shows the strongest change in partitioning behavior, as

Figure 5. Neutron diffraction patterns of the Cr-containing alloys $\text{NCX}_{8\text{Cr}}$. The Co content is increasing from the top to bottom.

it is enriched in γ for the Ni-base alloys ($k_W^{\gamma'/\gamma} \approx 0.7$) and in γ' for the Co-base alloys ($k_W^{\gamma'/\gamma} \approx 1.7$), whereas it is distributed quite evenly in the intermediate composition range. The reverse partitioning of W is probably the main reason for the increase of the misfit with increasing Co content, as it has the highest Vegard coefficient in both phases among all the elements included [26].

Figure 6. γ/γ' lattice misfit of the Cr containing alloys $\text{NCX}_{8\text{Cr}}$ as a function of Co content in comparison to the Cr free Co-xNi-10Al-7.5W alloys from reference [17].

In Figure 8, the partitioning behavior of the Cr containing alloy series $\text{NCX}_{8\text{Cr}}$ is plotted versus the fraction of Co in the base material and compared to the data from [17]. The trends of all common elements are in good agreement, however their partitioning to the respective preferred phase seems to be more pronounced, when Cr is present in the alloys. In agreement with [18], W is the exception, as it is less enriched in γ' when Cr is added to the Co-base alloys. The very pronounced enrichment of Cr in the γ phase is believed to be the reason for the negative misfit of alloys $\text{NC0}_{8\text{Cr}}$ and $\text{NC25}_{8\text{Cr}}$ as opposed by the positive values of δ for the respective Ni-rich alloys investigated in [17].

Nanoindentation was performed to measure the local mechanical properties. The Young's modulus did not show a clear dependence on the Co content and was in the range of 220 to 270 GPa. The derived hardness (H) values for all alloys are shown in Figure 9. The error bars denote their standard deviation.

Comparing H of pure Ni base alloys with the pure Co-base alloys, it can be seen that in the alloy series without Cr, the Co-base alloy is superior, whereas it is the Ni-base alloy that is superior in the Cr containing alloys. That the Cr free Co-base alloy shows a higher hardness than the Ni-base alloy can probably be partly explained by higher coherency stresses due to the higher lattice misfit. Contrary to that, the coherency stress levels in the Cr containing pure Ni- and Co-base alloys should be similar, but have a inverted sign. Nevertheless both alloy series qualitatively show the same evolution of the hardness as a function of the Co content: Starting from the alloys without Co, the hardness firstly in-

Figure 7. Atom probe tomography elemental maps of alloys a) ERBO-NC25_{8Cr} and b) ERBO-NC75_{8Cr}.

creases with the Co content, whereupon it decreases again between $f_B(\text{Co}) = 25$ to 75 %. Then again, the pure Co-base alloys are slightly harder than the NC75 alloys. The most important factors, that contribute to the room temperature hardness of the alloys are solid solution strengthening, the volume fraction of the precipitates, their size and their shear resistance against different types of dislocations. As the difference ΔH between both alloy series is larger on the Ni-rich section of the diagram, where the Cr is strongly enriched in the γ matrix, it is believed that the higher hardness level is mainly caused by additional solid solution strengthening due to Cr. As it is less enriched in γ in the Co-rich alloys, ΔH decreases almost linearly from 1.1 GPa to about 0.2 GPa. Additional solid solution strengthening, in this case due to Co, is also believed to be the reason for the increase of H between the sole Ni-base alloys (NC0_{0Cr} and NC0_{8Cr}) and the alloy variants with $f_B = 25$ %. The higher difference of NC0_{0Cr} and NC25_{0Cr}, however, might also be caused or supported by the difference in the actual W content of approximately 1 at.% (compare Table I). The decrease of hardness that follows at higher Co contents might again be caused by a decreasing level of solid solution strengthening in the γ phase, because both Cr and W are decreasingly enriched there. As the γ' volume fraction is even increasing to some extent ($\text{NC25}_{8\text{Cr}} < \text{NC50}_{8\text{Cr}} < \text{NC75}_{8\text{Cr}}$, $\text{NC25}_{0\text{Cr}} < \text{NC75}_{0\text{Cr}} < \text{NC50}_{8\text{Cr}}$) in these alloys, it could however also be caused by a decreasing shear resistance of the precipitates.

In creep, it has already been observed that deformation mechanisms change across the range of compositions between Co- and Ni-base alloys [7, 15, 27, 28]. In Co-Ni-base alloys, antiphase boundaries have been observed that extend completely through the precipitates [15] and in single phase $\text{Co}_3(\text{Al}, \text{W})$ it was found that the complex stacking fault energy is particularly low [29]. This findings imply, that the precipitates of the Co-rich alloys can be sheared more eas-

Figure 8. γ'/γ partitioning behavior of the Cr containing alloys ERBO-NCX_{8Cr} (solid symbols) compared to the alloys without Cr investigated by [17] (hollow symbols).

ily by full and partial dislocations respectively, which lowers their contribution to the hardness.

The increase of hardness values between $f_B(\text{Co}) = 75$ % and 100 % could be influenced by secondary γ' precipitates, which were found in the APT measurements of alloy NC100_{8Cr}. If the supersaturation is high enough, i.e. a sufficiently higher amount of γ' is stable at low temperatures compared to the aging temperature of 900 °C, secondary precipitates can form during cooling. Although APT was only conducted with the Cr containing alloys, where secondary precipitates were only found in NC100_{8Cr}, precipitates might well be present in the corresponding Cr free alloy variant as their γ' solvus temperature is similar.

The compressive creep curves of all alloys tested at 900 °C and 250 MPa are shown in Figure 10. Additionally the times to 0.2 and 0.5 % plastic creep strain are given in Table II. Evidently there is a large variation in the creep performance of both alloy series. In the series without Cr (Figure 10a), the Ni-base alloy NC0_{0Cr} shows by far the worst creep behavior and the optimum creep resistance is achieved by the Co-rich NC75_{0Cr}.

The Cr containing alloys (Figure 10b) show quite the opposite behavior: The Co-base alloy NC100_{8Cr} shows the worst performance and the Ni-rich alloy NC25_{8Cr} has the highest creep strength. In Figure 11, where the minimum creep rate is shown as a function of Co content, the creep properties can be compared in a more descriptive way.

There is a trend towards higher creep strength with increasing Co-content for the Cr free alloy variants. This cannot be

Figure 9. Hardness dependence on the Co-content.

explained by the γ' volume fraction as it reaches a maximum at a 50 % and decreases towards the edges of the composition range. One reason for the lower creep rates could be the Co-Ni interdiffusion coefficient, which decreases towards the Co-rich section of binary Co-Ni alloys [30]. Additionally it was already shown, that the diffusivity of transition metal solutes in Co is overall lower than in Ni [31]. Furthermore, the lower stacking fault energy of Co would impede recombination and cross slip and climb of partial dislocations. The higher lattice misfit of the Co-rich alloys would also result in a finer dislocation network at the γ/γ' interfaces and form a more effective barrier for dislocation motion. All these findings imply that Co-base alloys could be expected to show lower creep rates.

Table II. Time t to plastic creep strain of 0.2 and 0.5 % at 900 °C and 250 MPa

Designation	t to 0.2 % / min	t to 0.5 % / min
NC0 _{0Cr}	2	6
NC25 _{0Cr}	31	105
NC50 _{0Cr}	15	37
NC75 _{0Cr}	30	147
NC100 _{0Cr}	22	87
NC0 _{8Cr}	21	197
NC25 _{8Cr}	1265	4485
NC50 _{8Cr}	109	337
NC75 _{8Cr}	66	169
NC100 _{8Cr}	4	12

However, for the Cr containing alloy variants the trend is reversed, as the Ni-rich NC25_{8Cr} shows the lowest minimum creep rate whereupon it strongly deteriorates until the pure

Figure 10. Compressive creep curves at 900 °C and 250 MPa for a) the alloys without Cr and b) the alloys including Cr.

Co-base alloy deforms by more than two orders of magnitude faster. In other words, the addition of Cr dramatically increases the creep strength of the Ni- and the Co/Ni-base alloy, whereas it decreases the one of the Co-base alloy. The γ' volume fraction of the Cr containing alloys is quite similar, as is their morphology at the edges of the composition range (in the pure Co- and the Ni-base alloy). Because of the almost zero misfit of NC50_{8Cr}, this alloy shows round precipitates. The changes in the microstructure are believed to be too small to explain such a large decrease in creep strength.

For the most part the arguments, which were used to explain the change in hardness might also be appropriate to describe the creep strength of the Cr containing alloy: Cr improves the solid solution hardening on the Ni-rich section of the diagram, because of its pronounced partitioning behavior. The drastically increasing creep rate with further Co additions despite a slightly increasing γ' volume fraction can probably be explained by decreasing solid solution strengthening and by precipitates that are sheared more easily because of

Figure 11. Minimum Creep Rates of all alloys at 900 °C and 250 MPa as a function of the Co fraction in the base material.

lower planar fault energies. It was discussed before that the increase of hardness, which was observed between NC75_{8Cr} and NC100_{8Cr}, could be caused by secondary precipitates that formed during cooling. The absence of the strength increases in the creep experiments could also be explained by that, as those precipitates would be dissolved, because the test temperature equals the aging temperature.

Conclusions

Two sets of Ni-base, Co-base and intermediate Co/Ni-Base superalloys with otherwise constant alloying element concentrations were investigated. One of these alloy series was free of Cr, the other one contained 8 at.% Cr. It was found, that a variety of alloy properties drastically change with the Co-content, despite qualitatively very similar microstructures:

- Solidus and liquidus temperatures are not substantially affected by the Co/Ni ratio, whereas the γ' solvus temperature decreases with increasing Co content.
- The γ/γ' lattice misfit of the Cr containing alloys is negative on the Ni-rich and positive in the Co-rich section, whereas it is deduced that all the alloys without Cr show a positive misfit.
- The γ'/γ partitioning of Co, Cr and Al is much more pronounced in alloys rich in Ni. W is enriched in γ for Ni-base alloys, distributes equally in Co/Ni-base alloys and is enriched in γ' in Co-base superalloys.

- Cr-free Co-base alloys show better mechanical properties in terms of hardness and creep strength. The addition of Cr, however, reverses this trend so that the alloys rich in Ni are superior.

This study shows that Co-base alloys cannot only be looked at as a new class of materials; their discovery rather has extended the compositional range in which superalloys can exist. This raises the possibility to vary certain alloy properties systematically over a wider range and to understand the superalloys in greater detail.

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