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Microstructure, phase stability and element partitioning of γ-γ' Co-9Al-9W-2X alloys in different annealing conditions

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Abstract

The phase stability, γ' precipitate morphology and element partitioning behavior in dependence on temperature and alloying composition have been systematically investigated in Co-9Al-9W-2X alloys using electron microscopy, energy-dispersive X-ray spectroscopy (EDX) and high-energy X-ray diffraction (HEXRD). The results show that the decomposition of the γ' phase is promoted by adding some quaternary elements which increase the γ' solvus temperature (except V). A larger lattice misfit in the Mo, V, Ti, Nb or Ta containing alloys can explain that coarser γ' particles with a more cuboidal morphology were found in these alloys. Additional alloying elements and the annealing temperature show a stronger influence on the partitioning behavior of W between the γ and γ' phases compared to that of Co and Al. The partitioning tendency towards the γ' phase decreases with increasing temperature for all investigated alloying elements except Cr.

Keywords

Co-base superalloys; Gamma prime precipitation; Thermodynamic properties; Transmission electron microscopy, TEM

1. Introduction

Conventional Co-base superalloys are widely applied in corrosive environments at high-temperatures, like in aircraft turbines, due to their excellent hot corrosion and oxidation resistance as well as their superior thermal fatigue resistance [1]. In comparison with most Ni-base superalloys, Co-base alloys show low strength at high-temperatures, because the $L1_2$-γ' phase does not form, which is the major

strengthening phase for Ni-base superalloys [1]. The recent discovery of the $L1_2$ γ'-Co_3(Al, W) phase in the Co-Al-W ternary system has attracted great interest due to the potential to design a new class of high-temperature Co-base superalloys [2]. In order to stabilize this phase and increase the microstructure stability, alloying elements such as Ni, Ti, Mo, V, Nb, Ta, Si, Zr and Hf were added into the ternary system. The influence of these elements on the γ' solvus and liquidus temperatures has been well investigated and reported in literature [3-7]. Ooshima et al. [3] investigated the microstructures of the Co-9Al-7W base alloy after addition of various quaternary elements (X = Sc, Ti, V, Cr, Fe, Ni, Hf, Zr, Nb, Mo Ta, and Re) and observed two-phase microstructures consisting of the γ and γ' phases for most of the quaternary alloys after annealing at 850 °C for 96 h. Unfortunately, in literature the studied alloys were often annealed for short times and thus only limited information on long-term stability of the γ/γ' microstructure is available [3, 8-10]. In our recent study [11] it was found that the γ' phase in Co-9Al-9W-2X alloys decomposed into the B2 or $D0_{19}$ phases depending on the alloying additions after annealing at 900 °C for 5000 h. Additionally, it has to be taken into account that the partitioning behavior of quaternary alloying elements in Co-base superalloys can affect the γ' solvus temperature and the volume fraction of the γ′ phase [2, 3, 6]. It also can change the lattice mismatch between the γ and γ′ phases and thus influence the morphology and coarsening kinetics of the γ′ precipitates in these alloys [3, 10, 12-14]. The partitioning behavior of alloying elements can be influenced by alloy composition and annealing treatments [15]. Alloying elements redistribute between the γ and γ' phases with increasing temperature and this can alter the lattice mismatch and the γ/γ' interfacial energy, and thus the γ' particle morphology when the temperature is changed [10, 16-18]. Therefore, it is necessary to investigate the elemental partitioning in dependence on temperature in these alloys to further optimize and develop these γ' strengthened Co-base superalloys.

In our study quaternary Co-9Al-9W-2X alloys were long-term annealed at different temperatures to test the microstructure stability. Meanwhile, the partitioning behavior of the alloying elements in different phases in dependence on temperature was investigated by energy-dispersive X-ray spectroscopy (EDX) in the scanning electron microscope (SEM) and transmission electron microscope (TEM). High energy X-ray diffraction (HEXRD) was also used to measure the lattice parameters of the γ and γ' phases to understand the effects of additional alloying elements on the lattice mismatch and thus on the morphology of the γ' phase.

2. Experimental

The investigated Co-9Al-9W and Co-9Al-9W-2X (Cr, Ni, Mo, V, Si, Ti, Nb and Ta) alloys (atomic percent throughout the paper, at.%) were prepared by arc-melting under argon atmosphere and re-melted at least eight times to achieve chemical homogeneity. From weight-loss comparison between the starting elements and final ingots it is assumed that the actual composition of the alloys is close to nominal composition as the weight-loss was negligible. The cast specimens were firstly homogenized at 1300 °C for 12 h in vacuum before being annealed at 850 °C for 1000 h (water quenching), 900 °C for 200 h (air cooling) and 5000 h (water quenching or furnace cooling) or 950 °C for 1000 h (water quenching), respectively. The water quenched specimens were used to investigate conditions which resemble the situation at the annealing temperature as closely as possible (preserve microstructure and element distribution). All the annealing treatments were performed in air. The specimens for annealing treatments had a size of around 15*15*15 mm^3 and the microstructure investigated was close to the

center to avoid possible influences from the surface. The influence of alloying elements on the γ' solvus temperature was investigated by the differential scanning calorimetry (DSC) technique. DSC measurements were conducted using a Dynamic High-Temperature Calorimeter Netzsch Pegasus 404C and performed up to 1600 °C with a heating rate of 20 °C/min under Argon atmosphere (99.9999% purity). The specimens had a cube shape with dimensions of around 1×1×1 mm^3.

Scanning electron microscope (SEM) investigations were performed using a LEO Gemini 1530. SEM specimens were prepared by electro-polishing with a solution of 26 ml perchloric acid (70%), 359 ml 2-butanol and 625 ml methanol at 30 V and -30 °C.

High-energy X-ray diffraction (HEXRD) experiments conducted at the HEMS beam line run by the Helmholtz-Zentrum Geesthacht at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg were used to analyze the phase constitution and the lattice parameters of the γ and γ' phases. The X-ray beam had a cross section of 1×1 mm^2 and a photon energy of 100 keV (wavelength 0.1240 Å). Specimens with a size of 10×10×3 mm^3 were investigated in transmission geometry with the incident beam normal to the 10 mm x 10 mm surface. To improve grain statistics of the coarse-grained material the specimens were rotated by ± 30° around an axis perpendicular to the beam. A two-dimensional PerkinElmer XRD1621 detector continuously recorded the diffraction rings during the rotation. Diffractograms were obtained by integrating the diffraction patterns azimuthally over the Debye-Scherrer rings. The lattice constant of the γ' phase was obtained by evaluating the (001) and (011) superlattice reflections. By fitting the respective sub-peaks to the overall shape of the (002), (022) and (111) peaks using Pseudo-Voigt functions, the lattice constant of the γ phase and the lattice mismatch between the γ and γ' phases could be determined.

A Philips CM200 transmission electron microscope (TEM) operated at 200 kV was used for TEM investigations. TEM foils with a diameter of 2.3 mm were ground to a thickness below 120 μm and thinned by twin-jet polishing at 25-35 V and a temperature of -40 °C with the same solution as for SEM specimen preparation. The particle size of the γ' phase was measured using the line intercept method in two different <100> directions and averaged from 5 different regions when viewed along the <001> zone axis. The volume fraction of the γ' phase in the alloys was roughly estimated by evaluating the area fraction of the γ' particles in the γ+γ' regions and ignoring other intermetallic phases such as the B2 and $D0_{19}$ phase which occurred with low volume fractions. The TEM images used for analysis were recorded along the <001> zone axis and analyzed using the ImageJ software. Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDX) in the SEM and TEM instruments. The spectrums in SEM-EDX were recorded with the EDAX system and analyzed using the TEAM software. Those in TEM-EDX were recorded by the Oxford instrument X-mas EDX analysis system and analyzed by the Oxford Inca software. In TEM-EDX the compositions of the γ and γ' phases were averaged from at least ten different regions with a similar dead time and a tilt angle around 20° that was chosen to get a sound X-ray signal (around 50000 counts for the Co-Ka peak). When recording EDX spectra, it was taken care to be away from low symmetry diffraction conditions to exclude channeling effects. The concentrations of the elements Co, Al and W were quantified by using an alloy standard Co-2Al-2W. The composition of the standard alloy was determined based on the concept of minimizing the weight loss between raw materials and final ingot.

3. Results and discussion

3.1 γ’ solvus temperature

The γ’ solvus temperature of the Co-9Al-9W and Co-9Al-9W-2X (at.%) alloys is shown in **Table 1**. The ternary Co-9Al-9W alloy has a γ’ solvus temperature ($T_{\gamma'}$) of 974 °C. The addition of Cr or Ni (2 at.%) did not change $T_{\gamma'}$ obviously. The other alloying elements Mo, Si, V, Ti, Nb or Ta increased $T_{\gamma'}$ in the order of Mo < Si < V < Ti < Nb < Ta. The increase in $T_{\gamma'}$ by addition of 2 at.% Ta is most significant resulting in $T_{\gamma'}$ = 1065 °C. The increase of the γ’ solvus temperature by adding V, Ti, Nb and Ta has already been reported in literature [3, 4, 7]. For the elements Cr, Ni, Mo and Si, the effect on the γ’ solvus temperature does not completely correspond with the literature data [3, 4, 7]. Addition of 2 at.% Si, Mo or Cr to the quaternary Co-9Al-8W-2Ta alloy was found to decrease $T_{\gamma'}$ [4], while 2 at.% Cr, Ni or Si addition decreased and 2 at.% Mo did not influence $T_{\gamma'}$ of the Co-8.8Al-9.8W baseline alloy [7]. Our results agree roughly with the study of Co-9Al-7W-2X alloys by Ooshima et al. [3]. The inconsistencies between the different studies could be due to many factors, such as the difficulty to determine small changes in the γ’ solvus temperature as caused by adding Cr, Ni, Mo and Si, deviations from the intended chemical composition among the different investigated alloys, different parameters of DSC measurements (heating rates), analysis conditions (determination of peak onset, maximum, etc.) and alloy conditions (cast or heat-treated).

3.2 Phase stability

The SEM images in **Figs. 1-3**, which were taken in the back-scattered electron mode, show the microstructures of the alloys after different annealing treatments. By analyzing the HEXRD patterns, the phases existing in the alloys are found to be γ, γ’, B2 or/and $D0_{19}$.

The microstructure of the Co-9Al-9W and Co-9Al-9W-2X alloys after annealing at 850 °C for 1000 h is shown in **Fig. 1**. For the ternary Co-9Al-9W alloy (**Fig. 1**a), after 1000 h annealing, the γ’ phase is stable and the microstructure is composed of the γ solid-solution phase and cuboidal γ’ precipitates. The γ’ precipitates were coarser at grain boundaries compared to those in the grain interior. But no other intermetallic phases such as B2-CoAl and $D0_{19}$-Co_3W were detected. With the addition of 2 at.% Cr (**Fig. 1**b) or Ni (**Fig. 1**c), the microstructure was hardly affected and also exhibited cuboidal γ’ precipitates homogeneously distributed in the γ solid-solution matrix. However, with the addition of Ti (**Fig. 1**d), Mo (**Fig. 1**e, f), Nb or Ta (**Fig. 1**g, h), although the γ’ solvus temperature increased, other intermetallic phases were observed. In the Co-9Al-9W-2Ti alloy the B2 phase with a dark contrast was detected at grain boundaries, while, in the Co-9Al-9W-2Mo alloy, compounds of $D0_{19}$+γ (**Fig. 1**e) or DO_{19}+B2+γ (**Fig. 1**f) were observed at grain boundaries, which have probably been formed via the decomposition of the γ’ phase. Due to the frequent observation of the $D0_{19}$+γ compounds in the alloy, the $D0_{19}$ phase (in bright contrast) was deemed to appear first and B2 particles (in dark contrast) then should have formed later in the nearby γ phase (in grey contrast) and have surrounded the DO_{19} phase. Besides this the $D0_{19}$ phase with needle- or plate-like shape also formed at grain boundaries and grew into the grain interior. In the alloy with Nb addition, as discussed in our previous work [11], the γ’ phase was not stable and decomposed into $D0_{19}$+B2+γ compounds very fast. In the alloy with Ta addition which increased the γ’ solvus temperature most significantly, the $D0_{19}$+γ compounds could only be occasionally found at grain boundaries.

After annealing at 900 °C for 5000 h, as shown in **Fig. 2**a and **c**, the compounds of the $D0_{19}$ and γ phases also appeared at grain boundaries in the ternary Co-9Al-9W and quaternary Co-9Al-9W-2Ni alloys. In the Co-9Al-9W-2Cr alloy (**Fig. 2**b), both the $D0_{19}$ and the B2 phases were observed at grain boundaries. Again, the B2 phase seemed to form in the coarse γ phase and in contact to the $D0_{19}$ phase. With 2 at.% Si addition (**Fig. 2**d), the microstructure was significantly changed. Numerous DO_{19}+B2+γ domains which consisted of the $D0_{19}$ phase appearing bright and B2 phase appearing dark surrounded by the γ phase identifiable by its greyish appearance in the backscattered scanning electron micrographs, were found inside the γ+γ' grains. By comparing with the microstructure after 200 hours' annealing it is found that the microstructure becomes unstable by the addition of Si as the amount of these DO_{19}+B2+γ domains increases in the alloy after annealing for 5000 h. However, no B2 or $D0_{19}$ phase was observed in the Co-9Al-9W-2V alloy (**Fig. 2**e) and the γ' phase was very stable in this alloy after 5000 h annealing at 900 °C. For the Co-9Al-9W-2Nb alloy (**Fig. 2**f), most γ' phase particles decomposed into the B2, $D0_{19}$ and γ phases. The microstructure of the Co-9Al-9W-2Ti, -2Mo and -2Ta alloys after annealing at 900 °C, which has been reported in [11], is described here again for easier comparison of the microstructure with the other alloys. In the Co-9Al-9W-2Ti alloy, the B2 phase existed not only at grain boundaries but also in the grain interior with a needle- or plate-like shape. Compounds of the B2, $D0_{19}$ and γ phases appeared at grain boundaries in the Co-9Al-9W-2Mo and Co-9Al-9W-2Ta alloys. Additionally, $D0_{19}$ needles or plates with a large aspect ratio were found in the grain interior of the Co-9Al-9W-2Mo alloy.

Fig. 3 shows the microstructure of the alloys after annealing at 950 °C for 1000 h. In the ternary Co-9Al-9W (**Fig. 3**a) and quaternary Co-9Al-9W-2Ni (**Fig. 3**c) alloys the $D0_{19}$ phase formed only at grain boundaries together with coarse γ phase regions nearby, which is similar to the microstructure after annealing at 900 °C. But for the Co-9Al-9W-2Cr alloy (**Fig. 3**b), like the situation after annealing at 850 °C, the microstructure is composed of the γ and γ' phases. In the Co-9Al-9W-2Ti alloy (**Fig. 3**d), as for the microstructure after annealing at 900 °C, the B2 phase was observed at grain boundaries and in the grain interior. Different to the microstructure at 850 °C, the B2 phase occurred in the grain interior when the annealing temperature was increased. In the Co-9Al-9W-2Mo alloy (**Fig. 3**e), compounds of either the $D0_{19}$, B2 and γ or the $D0_{19}$ and γ phases were again found at grain boundaries and $D0_{19}$ needles or plates with a large aspect ratio grew from grain boundaries into the grain interior. In the Co-9Al-9W-2Ta alloy (**Fig. 3**f), again $D0_{19}$+γ compounds were only occasionally observed at grain boundaries.

From the results shown above, it could be inferred that with the addition of alloying elements, such as Mo, Ti, Nb and Ta which can increase the γ' solvus temperature, the formation of other intermetallic phases, such as B2 and $D0_{19}$ is promoted compared to the ternary Co-9Al-9W alloy. While adding 2 at.% Cr or Ni which has no benefit with respect to the γ' solvus temperature, does not deteriorate the γ/γ' microstructure. This could be very important especially regarding Cr which is added to improve the oxidation resistance of the Co-base superalloys [19, 20]. V has a moderate effect on increasing the γ' solvus temperature and the microstructure of the V containing alloy was stable.

3.3 γ' particle size and morphology

TEM images in **Figs. 4**-**6** show the γ+γ' microstructure in the ternary Co-9Al-9W and quaternary Co-9Al-9W-2X alloys after different annealing treatments. All images were recorded along the <001>

orientation. From analyzing the diffraction patterns, the orientation relationship $[100]_{\gamma}$ // $[100]_{\gamma'}$ and $(001)_{\gamma}$ // $(001)_{\gamma'}$ between the γ and γ' phases was found, which has been commonly reported in literature [2]. The particle size and volume fraction of the γ' phase are plotted in **Figure 7** as a function of alloy composition and annealing temperature.

After annealing at 850 °C for 1000 h (**Fig. 4**), most γ' particles were found to have a cuboidal shape in the ternary Co-9Al-9W and the quaternary alloys with Cr or Ni addition. Their average γ' particle size was similar and amounted to 137 ± 46, 172 ± 63 and 143 ± 45 nm for the Co-9Al-9W (**Fig. 4**a), Co-9Al-9W-2Cr (**Fig. 4**b) and Co-9Al-9W-2Ni (**Fig. 4**c) alloys, respectively. But in the alloys Co-9Al-9W-2Mo (**Fig. 4**d), Co-9Al-9W-2Ti (**Fig. 4**e) and Co-9Al-9W-2Ta (**Fig. 4**f), part of the γ' particles were elongated along one direction and not regular cuboids anymore. This could be explained by the coagulation and coalescence between the cuboids [15, 21]. In these alloys, the particle size increased to 201 ± 107, 209 ± 96, 244 ± 82 and 218 ± 89 nm for the Co-9Al-9W-2Mo, Co-9Al-9W-2Ti, Co-9Al-9W-2Nb and Co-9Al-9W-2Ta alloys, respectively. Additionally, the volume fraction of the γ' particles was found to be lower in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni (about 70 %) than in the Co-9Al-9W-2Mo, Co-9Al-9W-2Ti, Co-9Al-9W-2Nb and Co-9Al-9W-2Ta (around 85 %) alloys.

When the annealing temperature was increased to 900 °C, the Co-9Al-9W (**Fig. 5**a), Co-9Al-9W-2Cr (**Fig. 5**b) and Co-9Al-9W-2Ni (**Fig. 5**c) alloys still had a similar γ' particle size after 5000 h annealing time which was 392 ± 183, 382 ± 134 and 398 ± 200 nm, respectively, while Co-9Al-9W-2Mo (**Fig. 5**d), Co-9Al-9W-2Ti (**Fig. 5**e), Co-9Al-9W-2Ta (**Fig. 5**f) and Co-9Al-9W-2V (**Fig. 5**g) had a coarser particle size of 548 ± 187, 510 ± 158, 497 ± 187 nm and 534 ± 252 nm, respectively. It was also found that the γ' phase resembled more clearly a cuboidal morphology with less rounded corners in Co-9Al-9W-2Mo, Co-9Al-9W-2Ti, Co-9Al-9W-2Ta and Co-9Al-9W-2V compared to the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni alloys. This could be mainly attributed to the lattice misfit between the phases γ and γ', which will be discussed later. In addition, the volume fraction of the γ' particles was still higher in the Mo, Ti, V or Ta containing alloys (80-85 %) than in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni alloys (65-68 %). In the specimens which were furnace cooled subsequently to the heat treatment numerous secondary small γ' particles nucleated in the γ channels during cooling, as examples show for the Co-9Al-9W-2Ni (**Fig. 5**h) and Co-9Al-9W-2V (**Fig. 5**i) alloys. The particle size of the secondary γ' phase in the γ channels appears to be larger in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni than in the Co-9Al-9W-2Mo, Co-9Al-9W-2Ti, Co-9Al-9W-2Ta and Co-9Al-9W-2V alloys.

After annealing at 950 °C for 1000 h (**Fig. 6**), the γ' particle sizes of Co-9Al-9W (353 ± 149 nm), Co-9Al-9W-2Cr (404 ± 124 nm), Co-9Al-9W-2Ni (363 ± 145 nm) were still smaller than those of Co-9Al-9W-2Mo (479 ± 156 nm), Co-9Al-9W-2Ti (500 ± 213 nm) and Co-9Al-9W-2Ta (425 ± 157 nm). It is also found that the corners of the γ' precipitates in the alloys became more rounded with increasing annealing temperature. This could be due to the fact that the γ' phase in some of the alloys starts to dissolve at this temperature and the dissolution occurs preferentially at the cuboidal corners [22]. Another possible explanation could be that the lattice misfit and in consequence the coherency strain decreases at higher temperatures causing a more rounded γ' precipitate morphology [10]. The difference of the γ' volume fraction between the different alloys is more pronounced at this temperature. The volume fraction of the γ' particles was measured to be 40-50 % in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni alloys. It is about 65 % in the Co-9Al-9W-2Mo alloy and 75-80 % in the Co-9Al-9W-2Ti and Co-9Al-9W-2Ta alloys, which seems to be in relation to the order of γ' solvus temperatures. Compared to the situation after annealing at 850 °C for 1000 h, γ' particles grew and clear signs of

dissolution of the γ' phase are evidenced by the decreased volume fraction and wider γ channels at 950 °C after 1000 h annealing. Additionally, small secondary γ' particles (not considered for the above mentioned volume fraction measurement) were also observed in the γ channels of all alloys which should have formed during the cooling process (transferring from the furnace to water) due to the decreasing solubility of solute elements with temperature.

3.4 Lattice parameters and mismatch

Table 2 shows the lattice parameters of the γ and γ' phases and the mismatch in the alloys with different quaternary element additions after annealing at 900 °C for 200 h (cooled in air). The HEXRD patterns were taken at room temperature and analyzed by using the software package XPLOT (ESRF). It is noteworthy that the measured lattice parameters of the phases in the specimens which were cooled down in air after annealing, could deviate from those at high temperature or after longer annealing times. Due to the coherent interfaces between the γ and γ′ phases the measured lattice parameters are constrained [12, 23]. The mismatch δ is defined by $\delta=2(a_{\gamma'}-a_{\gamma})/(a_{\gamma'}+a_{\gamma})$, where $a_{\gamma'}$ and a_{γ} are lattice parameters of the γ and γ' phases, respectively. $a_{\gamma'}$ was determined by fitting the (001) and (011) superlattice reflections of the γ' phase. Then, the (002), (022) and (111) reflections were used to determine a_{γ}. This was done by fitting the respective sub-peaks of the γ and γ' phases to the overall shape of these reflection peaks using Pseudo-Voigt functions and holding the already determined $a_{\gamma'}$ constant. **Figure 8** shows examples in the Co-9Al-9W, Co-9Al-9W-2Ni and Co-9Al-9W-2Nb alloys where the experimental (011) and (022) reflection peaks were fitted to determine the lattice parameters of the γ and γ' phases. In the ternary Co-9Al-9W alloy, the lattice parameters were measured to be 3.577 and 3.601 Å for the γ and γ' phases, respectively, resulting in a lattice mismatch of around 0.67%. These values show agreement with those reported in literature [2, 24, 25]. The addition of Ni to the ternary alloy only slightly decreased the lattice parameters and also the lattice mismatch. That the lattice parameters of the γ and γ' phases as well as the lattice mismatch decrease with increasing Ni content, has also been found in Co-xNi-10Al-7.5W alloys with a much higher Ni concentration (x=10-70 at.%) [16]. This has been attributed to the fact that W partitioned into the γ phase with increasing Ni addition [16]. Adding Cr reduced the lattice parameters of both phases but the lattice mismatch kept unchanged. Increasing the Cr content to 8 at.%, the lattice mismatch has been reported to decrease in a Co-9Al-9W-8Cr alloy investigated by Povstugar et al. [26]. The addition of the other alloying elements Mo, V, Ti, Nb or Ta had varying influences on the lattice constants. It increased the γ' lattice constant except for the addition of Nb and decreased the lattice constant of the γ phase, resulting in an increased lattice mismatch compared to the ternary alloy. The higher lattice mismatch between the γ and γ' phases in these alloys induces a higher elastic strain energy that could influence significantly the γ' morphology [21]. This is probably be the main reason for the formation of γ' particles with a more cuboidal morphology in the Mo, V, Ti, Nb or Ta containing alloys. Other factors, for example the change in the elastic modulus of the γ and γ' phases and their interfacial energy which are induced by additional alloying elements, also could influence the morphology of the γ' precipitates.

In **Section 3.3** the γ' precipitate coalescence was found to be less pronounced at a higher temperature. With increasing temperature, as shown in the investigations by Pyczak et al. [23, 24], the lattice mismatch between the phases γ and γ' reduces. Thus a smaller elastic strain energy together with wider

γ channels between the γ' precipitates where elastic strains can relax in a larger volume results in a less pronounced coalescence phenomenon at higher temperatures [10]. Meanwhile, the γ' precipitates become less cuboidal and their corners are more rounded due to the resultant reduced strain energy at higher temperature. It was also found that the particle size of the γ' phase was smaller in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni alloys compared to that in the Mo, V, Ti, Nb and Ta containing alloys at all investigated annealing temperatures. This could be due to faster diffusion in the latter alloys which would accelerate precipitate growth and coarsening. It is also possible that an increased interface energy in the Mo, V, Ti, Nb and Ta containing alloys fastens the coarsening rate of the γ' particles. As mentioned in [10], the lattice mismatch between the γ and γ' phases can influence the interfacial energy and induce this effect.

3.5 Temperature dependence of the chemical composition and element partitioning behavior

As stated above adding quaternary alloying elements can influence the lattice parameters of the γ and γ' phases and by this the lattice mismatch due to their different atomic size and partitioning behavior. But also a number of other important alloy properties as stability of the γ' phase, mechanical strength of the phases γ and γ', etc., are affected by the partitioning behavior of alloying elements. In order to determine the partitioning coefficients in dependence on temperatures, the chemical composition of the phases in all alloys after different annealing treatments was measured. All specimens used for chemical composition analysis were quenched in water to preserve the high-temperature microstructure and element partitioning. The concentration of alloying elements in the four phases (γ, γ', B2 and DO_{19}) is given in atomic percent throughout the paper and detailed values are shown in **Table 3** in supplementary materials. The γ and γ' phase composition in some alloys after annealing at 900 °C has already been published in [11, 27] but the results are included in **Table 3** for better comparison with the other results. The phase compositions of the alloys after annealing at 900 °C for 5000 h were also plotted in the isothermal section of the Co-Al-W phase diagram at 900 °C which was reported by Omori et al. [7], as shown in **Fig. 9**. The phase compositions determined in the quaternary alloys were projected into the Co-Al-W triangle. It can be seen that the phase compositions measured in the ternary alloy agree rather well with the phase diagram published by Omori et al. [7]. The influence of the quaternary elements on the phase composition will be discussed in the following.

In **Table 3** it is obvious that the concentration of W in the γ solid-solution phase increased with temperature in all alloys. For the ternary Co-9Al-9W alloy, the W content in the γ phase was 4.5% at 850 °C, and rised to 5.7% at 900 °C and 7.3% at 950 °C. This could be due to the temperature dependence of the W solubility in the γ-Co matrix [28] which increases with temperature as it is usual in terminal solid-solution phases. With the addition of Cr or Ni, the W concentration in the γ phase did not deviate greatly from that in the ternary alloy (**Fig. 9**). But it decreased on adding other alloying elements in the order of Mo < V < Ti < Ta (Nb). Interestingly, the influence of alloying elements on the W content in the γ phase had a similar order as that for increasing the γ' solvus temperature. With respect to the Al concentration in the γ phase, the variation was smaller than for W (**Fig. 9**) and it did not show a clear tendency when considering the scatter of measurement data. However, the concentrations of both Al and W in the γ' phase were hardly affected by increasing temperature in all the alloys. By varying the quaternary element, the W concentration in the γ' phase in the quaternary alloys except for Co-9Al-9W-2Ni was slightly reduced compared with that in the ternary alloy and the

change was again as for the γ phase stronger than for the Al concentration (**Fig. 9**). This means that in these quaternary alloys the W content has a more severe influence on the γ/γ' phase fraction ratio than the Al content what has to be taken into account with respect to alloy design.

The concentrations of the base elements in the other intermetallic phases are also shown in **Table 3**. In the B2-CoAl phase, the ratio between the Co and Al contents is around 2. About 2-3% W and different amounts of the additional alloying elements (1.1% Cr, 0.3-0.7% Mo or 4.3% Ti) were also detected in this phase. Its chemical composition agrees with that measured by APT in a Co-9.5Al-7.5W-0.05B alloy [29]. For the $D0_{19}$-Co_3W phase, the fraction of Co is about 75.0% and the chemical composition indicates that around 3.0% Al and a fraction of other alloying elements occupy the W-site.

The partitioning behavior of alloying elements in different phases is shown in **Fig. 10** (detailed values are shown in **Table 4** as supplementary material). The partitioning coefficient K-γ'/γ, K-B2/γ or K-DO_{19}/γ is defined by the concentration of an alloying element measured in the γ', B2 or DO_{19} phase divided by the concentration measured in the γ matrix. A value larger than one indicates that the corresponding element prefers to partition into the γ', B2 or DO_{19} phase, while the element enriches in the γ matrix when the coefficient is less than one.

Fig. 10a shows that Co has a weak tendency to partition into the γ phase while Al slightly partitions into the γ' phase in all the alloys. The partitioning coefficient K-γ'/γ for Co and Al did not change significantly with varying additional alloying elements and annealing temperature. But it should be mentioned that Al partitioned nearly equally between the γ and γ' phases in the Co-9Al-9W-2Ti, Co-9Al-9W-2Nb and Co-9Al-9W-2Ta alloys. This was also observed in a Co-9Al-9W-2Ti (or Ta) alloy investigated by means of APT [8]. The partitioning behavior of W in these alloys is quite different to that of Al and Co as W partitioned preferentially into the γ' phase. The coefficient K-γ'/γ is 2.12 after annealing at 900 °C for 5000 h in the ternary Co-9Al-9W alloy. It is similar to the values reported by Omori et al. [7] in a Co-9Al-10W or Co-10Al-10W alloy after annealing at 900 °C for 168 h determined by utilizing electron probe microanalysis (EPMA). But it is lower than the values (2.6-2.7) obtained by APT in a Co-9Al-9W alloy after annealing at 900 °C for 200 h [8] and in a Co-10Al-10W alloy after annealing at 900 °C for 96 h [10]. The coefficient K-γ'/γ of W decreased significantly with increasing annealing temperature. Furthermore, the coefficient of W changed when quaternary alloying elements were added. Cr and Mo which are in the same group (VIB) with W, and Ni tended to decrease the partitioning coefficient K-γ'/γ of W, while Ti, Nb and Ta which significantly increase the γ' solvus temperature, increased it. At a higher temperature, the change of the partitioning coefficient K-γ'/γ of W by the addition of quaternary elements was less pronounced for Ni, Cr or Mo addition but even stronger when Ti or Ta was added.

Here it should be noted that the partitioning coefficient K-γ'/γ especially for W changed with annealing time at constant temperature in the same alloy. For prolonged annealing, the concentration of W decreased in the γ matrix but increased slightly in the γ' precipitates resulting in an increased partitioning coefficient. W is known to be a slow diffuser and the formation of other intermetallic phases takes place during extended annealing. These factors can influence the partitioning behavior of the alloying elements during annealing and should be taken into consideration.

The partitioning behavior of the additional quaternary elements among the γ, γ', B2 and $D0_{19}$ phases in dependence on temperature is shown in **Fig. 10**b. Cr preferentially partitions to the γ matrix with partitioning coefficients K-γ'/γ, K-B2/γ and K-DO_{19}/γ of 0.62, 0.38 and 0.38, respectively, after an annealing at 900 °C for 5000 h. The partitioning behavior of Cr between the γ and γ' phases showed no obvious change when varying the annealing temperatures. Ni partitioned into the DO_{19} phase and

weakly into the γ' phase with a partitioning coefficient K-DO_{19}/γ of 1.28 and K-γ'/γ of 1.06 after annealing for 5000 h at 900 °C. The coefficient K-γ'/γ tended to slightly decrease with increasing temperature. Mo enriched in the DO_{19} phase (K-DO_{19}/γ=2.00) and partitioned to the γ' phase (K-γ'/γ=1.26) but is nearly not found in the B2 (K-B2/γ=0.16) phase at 900 °C. Its coefficient K-γ'/γ (1.05) and K-DO_{19}/γ (1.55) decreased but K-B2/γ (0.32) increased when increasing the temperature to 950 °C. V also partitioned to the γ' phase with a similar partitioning coefficient (K-γ'/γ=1.28) as Mo. Ti, Nb and Ta which increased the γ' solvus temperature when added, strongly partitioned into the γ' phase with partitioning coefficients K-γ'/γ of 2.27 (Ti at 900 °C), 4.5 (Nb at 850 °C) and 6.75 (Ta at 900 °C). However, Ti was also enriched in the B2 phase (K-B2/γ=3.58) and Ta and Nb in the DO_{19} phase (K-DO_{19}/γ=12.25 for Ta and 8.67 for Nb). At 950 °C K-γ'/γ is 1.86 for Ti and 4.67 for Ta while K-B2/γ of Ti is 3.07 and K-DO_{19}/γ of Ta is 7.17, which clearly shows that the coefficients decrease with increasing temperature. This agrees with the study by Omori et al. [7] in Co-8Al-10W-2Ti, Co-8Al-10W-2Ta, Co-10Al-8W-2Ti and Co-10Al-8W-2Ta alloys. However, the linear relationship between the ΔT_{solvus} and $\ln_{(K\gamma'/\gamma)}$ which was found in their research, could not be confirmed by the present study.

It has been found by Omori et al. [7] by calculating phase stabilities by first-principle methods for Co-Al-W-X alloys that the partitioning of alloying elements is related to the stability of the $L1_2$-Co_3X, $D0_{19}$-Co_3X and B2-CoX phases and the quaternary element has a strong tendency to partition into the phase with larger negative formation energy. This could be the reason for the partitioning behavior of alloying elements as found in the present study although no $D0_{19}$ forms in the Co-9Al-9W-2Ti and no $D0_{19}$ and B2 phases in the Co-9Al-9W-2V alloys. Among the elements taken into consideration by Omori et al. (Al, W, Ti, V, Nb, Ta, Cr, Mo, Mn, Fe and Ni) the calculated negative formation energy of the Co_3X $L1_2$ phase was largest [7] with values of -25.9 and -23.4 kJ/mol e.g. for the alloying elements Ti and Ta which in the present study were found to strongly partition to the γ' phase. Correspondingly, also the partitioning of Ta and Nb to the $D0_{19}$ phase and of Ti to the B2 phase can be understood.

As mentioned in **Section 3.3**, secondary fine γ' particles precipitate in the γ channels during water quenching after annealing at 950 °C and during furnace cooling after annealing at 900 °C. But no such γ' precipitates are found during water quenching after annealing at 850 and 900 °C. This could be explained under the assumption that the diffusivity of the alloying elements is too low to sufficiently diffuse into the matrix channels and lead to γ' precipitation there during quenching from 850 and 900 °C. By slow cooling in the furnace from 900 °C, the alloying elements have sufficient time to diffuse and γ' particles can form. Due to the larger concentration difference of W and smaller partitioning coefficient of the quaternary elements, the secondary γ' particles grow faster in the Co-9Al-9W, Co-9Al-9W-2Cr and Co-9Al-9W-2Ni alloys than in the Co-9Al-9W-2Mo, Co-9Al-9W-2Ti, Co-9Al-9W-2Ta and Co-9Al-9W-2V alloys. The observation that γ' particles can also form during water quenching from 950 °C could be due to the larger solubility difference and longer diffusion time when quenching from a higher temperature.

4. Summary

In this study the microstructure, phase stability and element partitioning behavior in Co-9Al-9W-2X alloys has been systematically investigated. The results show that the γ' phase decomposes into other intermetallic phases such as the B2 or $D0_{19}$ phase, after annealing at 900 °C for 5000 h in all alloys except Co-9Al-9W-2V. The addition of elements such as Cr and Ni which hardly influence the γ' solvus

temperature, does not deteriorate the microstructure. But adding Mo, Ti, Nb or Ta which can increase the γ' solvus temperature promotes the decomposition of the γ' phase. Additionally, the γ' particles in these alloys approach a more cuboidal morphology and have a coarser size due to the enhanced elastic strain energy and interfacial energy caused by a larger lattice misfit compared to the ternary and Cr or Ni containing quaternary alloys. The addition of quaternary alloying elements and changes of the annealing temperature show a stronger influence on the partitioning behavior of W between the γ and γ' phases than on those of Co and Al. Cr and Mo which belong to the same group in the periodic table of elements as W and Ni, tend to decrease the partitioning coefficient of W but this change is less pronounced with increasing temperature. Ti, Nb and Ta which greatly increase the γ' solvus temperature increase the partitioning coefficient of W and the change is enhanced with temperature. The partitioning coefficients of the quaternary elements except for Cr show a tendency to decrease with increasing temperature. It is also found that with extended annealing at constant temperature the chemical composition of the phases and the element partitioning coefficient change, apparently due to slow thermodynamic equilibration. These observations should be taken into consideration when experimental data is used to derive phase diagrams and for alloy design of this class of alloys.

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