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Influence of alloying additions on $L1_2$ decomposition in γ-γ′ Co-9Al-9W-2X quaternary alloys

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Abstract

The influence of alloying elements on the formation of the intermetallic phases B2 and $D0_{19}$ via $L1_2$ decomposition during long-time annealing was investigated in Co-9Al-9W-2X alloys using electron microscopy. It is found that the type, shape and location of these intermetallic phases strongly depend on the alloying elements, which could be mainly attributed to different formation energies. Ti promotes B2 phase formation contrary to Mo, Nb and Ta which stabilize three-phase γ+$D0_{19}$+B2 domains. Nb greatly destabilized the γ’ phase and is not suggested for alloy design in the Co-9Al-9W system.

Keywords

Superalloy; $L1_2$ phase; annealing; decomposition; transmission electron microscopy (TEM)

Discovery of an ordered $L1_2$-γ' precipitate phase in the ternary Co-Al-W system by Sato et al. [1] attracted significant interest because of the possibility to develop a new class of load bearing Co-base high-temperature alloys. The microstructure with coherent cuboidal γ' precipitates embedded in a continuous γ matrix is morphologically identical to that of Ni-base superalloys suggesting that new Co-base superalloys may possess good high-temperature mechanical properties [2-5]. Such novel Co-base superalloys may offer a number of advantages with respect to corrosion resistance and castability when compared with Ni-base superalloys [6].

The γ' solvus temperature in the Co-Al-W ternary system is quite low (~ 1263 K) [1] compared to that (~ 1620 K) of CMSX-10, a third generation single-crystal Ni-base superalloy [7]. The γ' phase is not stable at all temperatures in the ternary system and co-exists with γ, B2 and $D0_{19}$ phases [8, 9]. In order to increase the γ' solvus temperature and thus improve the microstructural stability, alloying elements, such as Ti, V, Ta, Nb, Mo and Ni have been added into the ternary system. Such elements increase the γ' solvus temperature in the following order: Ta>Nb>Ti>V>Mo>Ni [10]. Other literature reports contradictory data on the effects of Nb and Ti, but actually the difference between ΔT_{Nb} and ΔT_{Ti} (for 2 at.% element addition) is only in the range of 10 °C or less [11, 12] which may explain the ambiguity of the results. However, after extended annealing other intermetallic phases, such as B2-CoAl and $D0_{19}$-Co_3W also occur and deteriorate the mechanical properties [13]. Unfortunately, in literature the studied alloys were often annealed for short times and thus limited details on the formation of these phases [10,

13-15] were reported. Additionally, investigations of the influence of alloy composition on these intermetallic phases and their formation mechanisms are rare [10, 13-15], although their morphology and distribution critically determine the mechanical properties. In the present study, phase transformations in Co-9Al-9W-2X alloys with different alloying elements were investigated. It is believed that this study can be instructive for alloy design and help understand phase transformations in these alloys.

The investigated Co-9Al-9W and Co-9Al-9W-2X (Ti, Mo, Nb and Ta) alloys (at.%) were prepared by arc-melting under argon atmosphere and re-melted at least eight times to obtain chemical homogeneity. The cast buttons were homogenized at 1300 °C for 12 h and subsequently annealed at 900 °C for 5000 h. Due to rapid decomposition of the γ' phase in the Co-9Al-9W-2Nb alloy after annealing at 900 °C for 5000 h, this alloy was also annealed at 850 °C for 1000 h. It is reported by Lass et al. [16] that decreasing the temperature accelerates the dissolution of the γ' phase in the ternary Co-Al-W system and after annealing at 850 °C for 4000 hours only very little γ' existed. Thus, here the annealing treatment at 850 °C was restricted to 1000 hours to ensure that the γ' phase has not completely decomposed. Scanning electron microscopy (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. For electron back-scattered diffraction (EBSD) investigations a TSL analysis system fitted to the Gemini microscope was employed. EBSD specimens were prepared by vibration polishing. A Philips CM200 transmission electron microscope (TEM) operated at 200 kV and a FEI Titan 80-300 TEM with a Cs image corrector operated at 300 kV were 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. Elemental analysis was performed using EDS in the TEM mode and concentrations of the elements Co, Al and W were quantified with a Co-2Al-2W alloy standard.

Fig. 1 shows an overview of the microstructures of the Co-9Al-9W-2X alloys after heat-treatment. They have a similar γ+γ' based microstructure (cuboidal γ' precipitates homogeneously distributed in a γ matrix) together with other intermetallic phases, such as B2-CoAl and $D0_{19}$-Co_3W. The amount, shape and location of these intermetallic phases depend strongly on the alloy composition. Although it is found in this study that the alloying elements increase the γ' solvus temperature by the order of Ta>Nb>Ti>Mo, they lead to a faster formation and higher fraction of the intermetallic phases compared to the microstructure of the Co-9Al-9W alloy. In the Co-9Al-9W-2Ti alloy, after annealing at 900 °C for 5000 h the B2 phase is observed to exist at grain boundaries and in the grain interior, easily recognizable by its darker appearance in the back-scattered electron image (Fig. 1a, b). Its morphology is irregular at grain boundaries, while needle- or disc-shaped inside grains. By comparing the microstructure after a shorter annealing time (200 hours), the B2 phase is found to first form at grain boundaries and then appears within the matrix after extended annealing. Needle- or disc-shaped B2 particles in the grain interior are seldom reported in Ti-containing Co-base superalloys [11, 17, 18]. In the Co-9Al-9W-2Mo alloy a configuration of alternating $D0_{19}$ and γ phases together with B2 particles is detected at grain boundaries, which could result from a decomposition of the γ' phase into this γ+ $D0_{19}$+ B2 mixture. The B2, γ and $D0_{19}$ phases show dark, grey and bright contrast, respectively in the back-scattered electron images (Fig. 1c, d). Moreover, needle- or plate-shaped $D0_{19}$ phase is found inside the grains with a very high aspect ratio and has four different orientations. Additionally, some of the needles/plates originate from grain boundaries and are interlocked with others. Domains of γ, $D0_{19}$ and B2 or γ and $D0_{19}$ are also detected in the alloys Co-9Al-9W-2Nb (Fig. 1e, f) and Co-9Al-9W-2Ta (Fig. 1g, h), respectively.

They frequently appear inside the grains and at grain boundaries of the Co-9Al-9W-2Nb alloy, but only at grain boundaries in the Co-9Al-9W-2Ta alloy.

Fig. 2 shows the TEM and EBSD investigation of the B2 phase in the Co-9Al-9W-2Ti alloy. Diffraction patterns in Fig. 2a hint that no orientation relationship (OR) exists between the B2 and the γ+γ' phases, no matter where the B2 phase is located. This is different to the study by Petrushin et al. [19], where the Kurdjumov-Sachs OR between the γ' precipitates and B2-(Co, Ni)Al phase was found. Generally, it has been found for metallic alloys that the experimentally observed orientation relationships between phases of different Bravais lattices as also the Kurdjumov-Sachs OR can be explained by purely geometrical atomic row matching between the two structures [20]. Atomic row matching is only possible in certain ranges of lattice parameter ratios of the involved Bravais lattices [20]. The ratio $a_{\gamma'}/a_{B2}$ is around 1.234 in the present study, which was determined from the analysis of diffraction patterns. 1.234 is below the minimum ratio of 1.25 reported for a number of fcc/bcc systems with Kurdjumov-Sachs OR [21] and accordingly it is understandable that these two phases in the present work assume no OR. The discrepancy between Petrushin et al. [19] and the present work could be attributed to a different alloy composition influencing the lattice constants of both phases. The random orientation of the B2 phase is further confirmed by the EBSD measurements (Fig. 2b). The orientation of the B2 phase is nearly the same for particles located at the same grain boundary, while it varies in the grain interior.

Fig. 3 shows domains of either γ, $D0_{19}$ and B2 or γ/γ' and $D0_{19}$ phases at grain boundaries. In the Co-9Al-9W-2Mo alloy (Fig. 3a) there exists the Blackburn orientation relationship (OR) between the $D0_{19}$ and the γ+γ' phases: [11-20]-$D0_{19}$ // [101]-γ/γ' and (0001)-$D0_{19}$ // (11-1)-γ/γ' as determined by diffraction analysis. But no OR has been identified between the B2 and γ phases. This is different from measurements by Makineni et al. [22] that the γ and B2 phases obey the Kurdjumov-Sachs OR, while

the $D0_{19}$ phase has the Blackburn OR with γ in the three-phase microstructure. This discrepancy might again be explained by the different chemical compositions of the B2 and γ phases, which can affect the lattice mismatch between these two phases. Features with alternating $D0_{19}$ and coarse γ lamellae are found in the Co-9Al-9W-2Nb alloy (Fig. 3b). In these coarse γ lamellae, twins and stacking faults are observed. Diffraction patterns show that the Blackburn OR, [0001]-$D0_{19}$ // [111]-γ and (11-20)-$D0_{19}$ // (01-1)-γ exists between $D0_{19}$ and γ phases. However, in the Co-9Al-9W-2Ta alloy the OR between the $D0_{19}$ phase and the surrounding γ grains is lost as evidenced by Fig. 3c. A thin lath of the γ' phase is observed inside the $D0_{19}$ phase and the Blackburn OR exists between them.

Numerous DO_{19} precipitates with a very large aspect ratio are frequently detected inside grains in the Co-9Al-9W-2Mo alloy (Fig. 4). They have the Blackburn OR [11-20]-$D0_{19}$ // [101]-γ/γ' and (0001)-$D0_{19}$ // (11-1)-γ/γ' with the matrix. When viewed along the [101] direction, four sets of $D0_{19}$ phase projections can be observed due to four $(111)_{\gamma'}$ habit planes. Additionally, it is interesting to note that one $D0_{19}$ precipitate always intersects with several others (Fig. 4a). In region A precipitate 1 and 2 are viewed edge-on ([11-20]-$D0_{19}$), while in region B, precipitate 3 is inclined to the TEM foil and shows contrast similar to that of stacking faults. By examining the microstructure at atomic resolution (Fig. 4b), it is clear that the stacking sequence of the close-packed planes in γ' (ABCABC) changes to ABAB in the hexagonal $D0_{19}$ needle/plate. The interface between them is coherent as no misfit dislocations occur. Additionally, the interface is very flat and no obvious growth ledges are found (Fig. 4c). Another case in Fig. 4d shows a layer of γ' phase remaining between two $D0_{19}$ precipitates (Fig. 4d).

Table 1 shows the phase compositions determined by TEM-EDS. In the Co-9Al-9W-2Ti alloy, the B2-CoAl phase has a higher Ti content compared with the γ and γ' phases, which suggests that Ti can promote its formation. Unlike Ti, Mo is depleted in the B2 phase but enriched in the $D0_{19}$ phase. The

order of the Mo partitioning in the phases is as follows: $D0_{19}$ > γ' > γ > B2. The concentrations of W and Mo are decreased in the newly formed γ phase inside the domains compared with the γ matrix. In the Co-9Al-9W-2Nb/Ta alloys, Nb and Ta also partition to the $D0_{19}$ phase. The chemical composition of the $D0_{19}$ phase indicates that Mo, Nb and Ta prefer to take the W-site in the $D0_{19}$ crystal when considering the stoichiometry Co_3W.

Omori et al. [11] calculated the formation energy of Co_3X with $L1_2$ and $D0_{19}$ structures and CoX with the B2 structure by first-principle methods. If these formation energies of binary compounds are taken as measure for the thermodynamic stability of the multicomponent phases at medium temperature some of the experimental results can be understood. Compared to Al and W the $L1_2$ phase is more stable in the Ti and Ta containing $L1_2$ compounds [11], what might be considered as stabilizing effect when adding these elements to ternary alloys. In the same sense Ti strongly stabilizes the B2 phase in agreement with the observations, Mo destabilizes the $L1_2$ phase and particularly the B2 phase what could explain that it facilitates the formation of the $D0_{19}$ phase. The $D0_{19}$ phase should slightly be stabilized by Ti, Nb and Ta which agrees with the experimental observations for the Nb and Ta containing alloys and does not contradict the observations for the Ti containing alloy due to the strong stabilizing effect of the B2 phase by Ti. However, it was found in the present study that Nb significantly destabilizes γ' and leads to its rapid decomposition, similar to the addition of Ru in the Co-Al-W system [23] but with a slower transformation rate. This does not agree with the above mentioned expectations and also work in literature [24]. Through addition of Ta the γ' phase also decomposes with time but this decomposition is similar or only slightly faster than in the Co-9Al-9W alloy. Here it should be noted that apparently the phase formation kinetics plays an important role in the investigated alloys as also observed for ternary Co-Al-W alloys [8] and hinders the formation of the thermodynamic equilibrium even after 5000 h at

900 °C.

In the Co-9Al-9W-2Ti alloy, only the intermetallic B2 phase forms after annealing. Due to the low nucleation energy barrier at grain boundaries, the B2 particles first form at grain boundaries. With respect to the B2 phase in the grain interior, a needle-or disc-like shape was observed. As the interface between B2 and the matrix phase is incoherent, the precipitates have this shape to balance the opposing effects from the interfacial energy and strain energy due to the volume misfit [25]. It should be noted that the B2 phase appears to have preferred orientations in grains but no orientation relationship is identified probably due to a ratio of lattice parameters which does not allow atomic row matching.

With regard to the multiphase domains at grain boundaries in Co-9Al-9W-2Mo/Nb/Ta alloys, $D0_{19}$ is found to be the first phase to form. Because the formation of the $D0_{19}$ phase rejects Co and Al into but absorbs W and X (Mo, Nb and Ta) from the γ' phase, a γ solid-solution phase will be generated nearby. During further transformation, the $D0_{19}$ phase further depletes the newly formed γ phase in W and X (Mo, Nb and Ta) and B2 appears to accommodate the rejected Al.

By glide of 1/3<112>(111) Shockley superpartial dislocations in the γ'-$L1_2$ structure a superlattice intrinsic stacking fault (SISF) is formed, which results in an embryonic state consisting of four basal planes of the hcp $D0_{19}$ structure [26, 27]. The SISF energy (ΔE_{SISF}) of the γ' phase in Co-base superalloys is related to the difference in energy between the $L1_2$ and $D0_{19}$ structures. By density functional theory calculation, additions of Ta, Nb and Ti were found to raise ΔE_{SISF} (Ti could reach the highest ΔE_{SISF}), while Mo decreased it strongly [27-29]. It is reported for a Co-Al-W-Ta alloy that W and Ta segregate to but Co and Al are depleted from the SISF [27]. Such chemical fluctuations near to stacking faults can lower the energy and favor the formation of the $D0_{19}$ phase as the local composition

is closer to the stoichiometry of Co_3W [27]. Thus presumably, in the Co-9Al-9W-2Mo alloy the formation of the $D0_{19}$ precipitates in the grain interior follows this path: the DO_{19} structure nucleates at the site of a SISF and then by atom diffusion the $D0_{19}$-Co_3(W, Mo) phase with equilibrium composition is formed. The growth is very fast along the longitudinal direction because the process only involves further separation of the partial dislocations. In contrast, thickening can proceed with growth ledges but these were not frequently observed probably due to the difficulty in nucleating new ledges at the interface [26]. However, thickening can also take place via merging of two nearby $D0_{19}$ precipitates, as shown in Fig. 4d. Thus, the precipitates have a very large aspect ratio with a length several orders of magnitude greater than their thickness. It is interesting to note that $D0_{19}$ precipitates intersect with several other $D0_{19}$ precipitates and seem to initiate their formation. An explanation could be that in the vicinity of an existing stacking fault ($D0_{19}$ phase), stair-rod dissociation of dislocations will take place [30]. Through cross-slip of such a dislocation another stacking fault will form from the interface of the $D0_{19}$ phase onto the intersecting slip plane [31]. By repeating the process mentioned above, another $D0_{19}$ precipitate forms.

In summary, the phase transformations and orientation relationships were investigated in Co-9Al-9W-2Ti/Mo/Nb/Ta alloys after long-term annealing. It is found that the type, shape and location of the B2 and DO_{19} phases strongly depend on the alloying elements, which is probably due to their different effects on the formation energies of the B2 and DO_{19} phases. The addition of Ti promotes the formation of the B2 phase in the grain interior but prevents the formation of three-phase γ+$D0_{19}$+B2 domains, which were found in the Co-9Al-9W-2Mo/Nb/Ta alloys. Mo facilitates the formation of the $D0_{19}$ phase, which occurs as needles/plates with a very large aspect ratio. Nb significantly destabilizes the γ’ phase and most of the γ’ particles were transformed into γ, B2 and $D0_{19}$ phases. Ta greatly increases the γ’

solvus temperature but does not destabilize the γ/γ′ microstructure to the same extent as Ti, Mo and Nb.

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