The partitioning and site occupancy of solutes in W free Co based γ-γ′ superalloys: A combined TEM and 3DAPT study

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Microscopic characterization and microanalysis have played crucial role in the development of the new class of Co based γ-γ superalloys that does not contain tungsten [1]. The partitioning of different elements in these two phases significantly influences both the microstructural and phase stability as well as their subsequent properties including the mechanical properties. We have carried out detailed study utilizing transmission electron microscope as well as atom probe based techniques coupled with, wherever possible, insight from calculations from first principles density functional theory (DFT). In the original alloys (Co-5Mo-10Al-2 Nb/Ta alloys) the γ-A_3B ($L1_2$) precipitates are stabilized by Mo and Nb/Ta atoms that partitions preferentially to this phase, Fig.1 [1 - 3]. The microanalysis suggests that they most likely occupy the B sites in the compound.

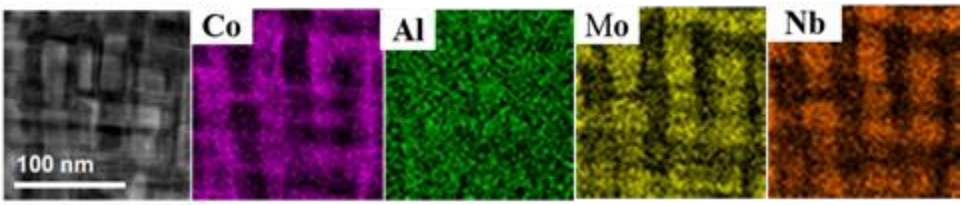

Fig. 1: *Elemental mapping for the peak aged Co-10Al-5Mo-2Nb alloy in a scanning transmission electron microscopy (STEM) nano probe mode [2].*

The addition of Ni stabilizes this class of alloys further and primarily replace Co both in γ matrix and in the 'A' sites of γ. On the other hand, the addition of Ti also has significant influence on the overall stability of these superalloys. However, Ti primarily act synergistically with Al and stabilizes the ordered precipitates as reflected by the enhanced solvus. Chromium has a unique place in the alloying landscape. The atom probe tomography (APT) results indicate that addition of 2 at. % Cr to Co-30Ni-10Al-5Mo-2Ta-2Ti alloy leads occupancy of Cr to Mo (B-site) site of γ-A_3B lattice with equal partitioning of Mo across the γ/γ interface ($K_{Mo} \cong 1.0$). With further addition of 5 at. % Cr (Cr-5 alloy) to Co-30Ni-10Al-5Mo-2Ta-2Ti alloy, microanalysis indicates partitioning of ~ 1.8at.% Cr to γ precipitates that lead to a change in the Co + Ni concentration in γ precipitates from 77.3 at.% to 75 at.% suggesting anti-site occupancy of Co (as shown in Fig. 2a). The APT measurements also permit determination of average distances of each atomic species through spatial distribution maps (SDM). Thus the combination of the knowledge of the distance between the Cr atoms in γ lattice and the microchemistry of the precipitates allow us to conclude that apart from Mo, Cr atoms also occupy Co anti-sites (B-site). Further, this phenomenon of equal Cr atoms occupancy of Mo (B-site) site and Co anti-site (B-site) occurs concomitantly with reverse partitioning of Mo atoms from γ precipitates to γ matrix (Fig. 2b and 3a). The first principles calculation provides additional support to this conclusion. However, subsequent addition of 8 at. % Cr (Cr-8 alloy) causes a partial switch in the site occupancy of Cr from B site to A site with substitution of regular Co site (as reflected in the average chromium distances obtained from 3DAPT), Fig. 3b. Thus Cr site occupancy in the ordered precipitates changes with increasing concentration from Mo to Mo + Co anti-sites at B sites and then with further increase in concentration to both Mo + Co anti-sites of B sites + Co of A sites. The

switch in site occupancy of Cr atoms and reversion of Mo partitioning result in changes in lattice parameter of g matrix and γ precipitate leading to an overall decrease of lattice mismatch between γ and γ that influence the properties of these superalloys. Thus the knowledge of partitioning can provide insight into an intelligent design of these cobalt based superalloys.

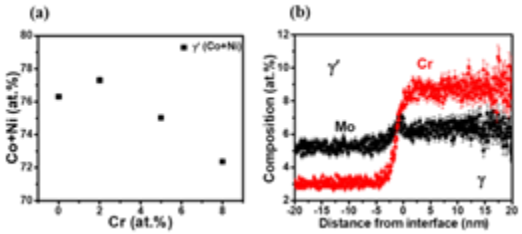

Fig. 3: *Plot showing variation in Co + Ni concentration in γ phase with Cr addition to Co-30Ni-10Al-5Mo-2Ta-2Ti alloy. (b) Concentration plot showing distribution of Cr and Mo concentration across the γ/γ interface for Cr-5 alloy aged at 900 °C for 50h.*

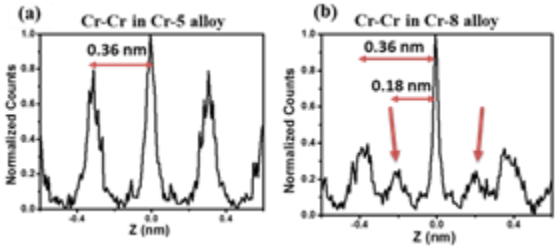

Fig. 2: *Spatial distribution map obtained along successive (100) planes in γ' phase for (a) Cr-5 and (b) Cr-8 alloy.*

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