## Atom Probe Tomography Investigation on the Effect of Ni Additions on the Site Occupation and Partitioning Behavior in Co-Based Superalloys

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Single crystal Ni-based superalloys have been the material of choice for the hot section turbine blades of jet engines due to their excellent creep and oxidation behavior [1]. However, this class of alloys is reaching its high temperature capability limit, and the demand for improved engine efficiency, requiring higher operating temperatures, is begging for materials that can replace Ni-based superalloys. In 2006, Sato et al. [2] reported a  $\gamma'$ -strengthened Co-Al-W-based alloy, which possesses significantly improved properties over conventional Co-based alloys. Since then, different research groups have studied the effect of alloying additions on the creep behavior and have shown that the creep properties of some Co-Al-W-based single crystal alloys are comparable to those of Ni-based superalloys [3]. However, these novel Co-based superalloys still face major application restrictions, e.g., a lower  $\gamma'$  solvus temperature, microstructural instability at high temperature, and higher alloy density compared to commercial Nibased superalloys. Research focused at improving these shortcomings suggests that CoNi-based alloys are superior with respect to their Ni-free counterparts, as the Ni expands the  $\gamma$ - $\gamma'$  two-phase field, thereby improving the stability and the temperature capability of the alloys [4]; however, a higher concentration of Ni alters the L1<sub>2</sub> formation behavior to be similar to that of Ni-based superalloys. With that respect, only a few studies exist on the preferred site occupancy in the L1<sub>2</sub> lattice of Co-based alloys [5], mainly due to the difficulty of these measurements, although this sort of information is very useful for alloy design as well as behavior modeling. In this study, we compare the elemental partitioning and the site occupation in a Ni-free and a Ni-rich Co-based superalloy, as studied by atom probe tomography (APT).

Single-crystal Co-7Al-8W-4Ti-1Ta in at.% (Alloy TaTi) and 7 component variant with 30 at.% Ni and 5 at.% Cr (Alloy NiCr) were subjected to a standard heat treatment of 900°C and 1000°C, respectively, for 50 h to ensure an equivalent  $\gamma'$  volume fraction of ~80%. Several APT samples were prepared using an FEI Helios Nanolabs 600i focused ion beam (FIB). The microtips were polished with Ga<sup>+</sup> ions down to a ~50 nm radius using a final energy of 5 kV and a current of 16 pA. APT was conducted using a CAMECA LEAP<sup>®</sup> 5000 XR and running conditions set as: base temperature of -243°C (30 K), 40 pJ laser pulse energy, pulse repetition rate of 200 kHz, and evaporation rate of up to 1.0%. Electron back scattered diffraction (EBSD) was used to measure the exact deviation from the [001] direction of the sample, while post-APT tip image processing was utilized to estimate an evaporation field of 47.9 V/nm. The data was analyzed using IVAS 3.8.2 software from CAMECA Instruments Inc.

Fig. 1 (a) and (e) show the typical  $\gamma$ - $\gamma'$  microstructure of Alloy TaTi and NiCr, respectively, while Fig. 1 (b) and (f) show respective 3D reconstructions (where only Co, W, and Ni ions are displayed). Fig. 1 (c) and (g) are magnified views showing the {001} atomic planes. Chen et al. [6] used atomic elemental mapping in a HRTEM to show that the Co atoms occupy the A sites in Alloy TaTi, while the Al, W, Ti

and Ta occupy the B sites. The APT results confirm this behavior, and it should be noted that based on the composition it appears that there would also be some Co anti-sites. A proximity histogram across one  $\gamma$ - $\gamma'$  interface, Fig 1 (d), confirms the previously reported partitioning, but also shows Co and Al segregation to the interface. Meanwhile in the NiCr alloy, the partitioning follows a more classical Nibased alloy behavior, where Al, Ta, and Ti partition to the  $\gamma'$  phase, while Co, Ni, and Cr partition to the  $\gamma$  phase, with the only exception being W partitioning to the  $\gamma'$  phase. Some anti-site formation is also required for correct stoichiometry, which would likely be Co atoms, judging by the behavior of Ni-based alloys. In this alloy, Co and Ni occupy the A sites, while Cr, W, Al, Ta, and Ti occupy the B sites, as shown Fig. 1 (g). To illustrate the site occupation of Ni and Cr in the CrNi alloy more quantitatively, a spatial distribution map (SDM) along the z direction was calculated and the results for select elements are shown in Fig. 1 (h). The Co and Ni show representative peaks at the {002} plane locations, i.e., the A sites, while Cr follows the behavior of Ti and shows peaks only at the {001} plane locations ~0.365 nm apart, which is the lattice constant of the  $\gamma'$  phase. In Ni-based alloys, the occupation of the Cr atoms is typically in the A sites, although modeling of pure Ni<sub>3</sub>Al suggests that it would occupy the B sites [7]. These results provide a more complete model of the crystal structure of the L1<sub>2</sub> phase in these new Cobased and CoNi-based superalloys, which can be utilized for different modelling purposes [8].

## References:

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**Figure 1.** (a) microstructure, (b) 3D reconstruction, (c) resolved {001} atomic planes, and proximity histogram from a 6 at.% W isoconcentration surface of Alloy TaTi; (e) microstructure, (f) 3D reconstruction, (g) resolved {001} atomic planes, and (h) SDM-z of Alloy NiCr.