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Site occupancy of alloying elements in the $L1_2$ structure determined by channeling enhanced microanalysis in γ/γ' Co-9Al-9W-2X alloys

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Knowledge about the sublattice site preference of alloying elements in the $L1_2$-γ' phase of novel Co-base superalloys is a necessary pre-requisite to understand their influence on the properties of the alloys in general and the γ' phase in particular. In the present study, the atomic site occupancy of the alloying elements in the $L1_2$-γ' structure in Co-9Al-9W-2X quaternary alloys after long-term annealing at 900 °C for 5000 h was determined using the atom location by channeling enhanced microanalysis (ALCHEMI) technique in combination with energy-dispersive X-ray spectroscopy (EDX) composition analysis in a transmission electron microscope (TEM). The experimental ALCHEMI data were evaluated by comparing them with those calculated by the program 'Inelastic Cross Section Calculator' (*ICSC*). The results show that Co mainly occupies one sublattice site and Al/W are located at the other sublattice site in the $L1_2$ unit cell in the ternary alloy. The additional elements Ti, V, Mo and Ta which partition strongly to the γ' phase tend to occupy the Al/W sublattice site, and Cr which partitions more to the γ phase also favors the Al/W sublattice site, while Ni weakly partitions into the γ' phase and favors the Co sublattice site. The results of this study can provide evidence to the predictions on the site preference in literature based on the phase composition or on theoretical studies.

1. Introduction

The reports about an ordered $L1_2$ precipitate (Co_3(Al, W)) phase in the ternary Co-Al-W system in 2006 which can be stable up to temperatures of 950 °C have attracted significant research interest [1]. The low mismatch between the fcc γ-Co solid solution phase and the $L1_2$ γ'-Co_3 (Al, W) phase helps to establish a microstructure with a high volume fraction of coherent cuboidal γ' precipitates embedded in a continuous γ matrix [2]. This opens for Co-base alloys the perspective to benefit from the same precipitation hardening mechanism that works so efficiently in Ni-base superalloys. However, recently the γ' phase has been reported to be metastable in the ternary Co-Al-W system [3]. In order to increase the temperature capability and stabilize the $L1_2$-γ' phase, additional elements such as Ni, Ti, Ta, Nb, Mo and V are alloyed to the ternary Co-Al-W system [4–6]. It is found that Mo, V, Nb, Ta and Ti partition to the γ' phase and thus increase the γ' solvus temperature of Co-Al-W superalloys, while, Fe, Mn and Cr partition to the γ phase and decrease the amount of the γ' phase [1,7,8]. With increasing Ni content in the Co-Ni-Al-W system, the γ' solvus temperature increases and the $\gamma+\gamma'$ two-phase region is broadened [9]. The partitioning and site preferences of additional elements effects the γ' solvus temperature and lattice mismatch between the γ and γ' phases and can strongly influence the electronic bonding, antiphase boundary and stacking fault energy as well as the resistance to dislocation motion [4]. It is important to investigate these basic structural properties to understand the effects of different alloying elements on a wide variety of alloy properties. Thus, knowledge about the partitioning behavior and site occupancy of alloying elements is a valuable prerequisite to further optimize and develop these novel γ/γ' Co-base superalloys.

The atomic site preference of several alloying elements in the γ' phase of Co-base superalloys has been predicted theoretically utilizing first principles and thermodynamic calculations [4,10–12]. However, direct experimental investigations are relatively rarely found in the literature. Some researchers tried to use atom probe tomography (APT) to determine the lattice site occupancy of the alloying elements, but the individual atomic layers in the atom

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maps could not be resolved due to the limited spatial resolution in pulsed laser mode [13,14]. In other APT work in the voltage operation mode it could be shown that Al, W and Mo or Ta occupied the same atomic planes, but the pure Co planes were still not resolved in the APT reconstruction [15]. Recently, in a Co-12Ti system investigated by APT in the pulsed laser mode, the additions of Mo and Cr were reported to preferentially occupy the Ti sublattice site based on the element-specific spatial distribution maps along the [001] direction of the γ' phase [16]. Using a combination of aberration corrected high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) with a four-quadrant FEI Super-X detector the site preferences of Co, Al, W, Ti and Ta in the $L1_2$-γ' unit cell in Co-base superalloys have been investigated experimentally [17]. However, it should be mentioned that the alloys investigated in these studies were only annealed for a short time. Thus, the measured phase compositions and atomic site occupancies might deviate from those under equilibrium conditions.

The method of atom location by channeling-enhanced microanalysis (ALCHEMI) which was first developed by Taftø and Spence [18,19], has been widely used to determine the crystallographic sites, distribution and chemical nature of substitutional impurities in alloys, such as TiAl alloys [20], Ni-base alloys [21], B2-(Ni, Fe)Al phase [22] and Nb-Cr-X Laves phase [23]. It is a transmission electron microscopy (TEM) technique based on the orientation-dependence of characteristic X-ray emissions of alloying elements [24]. Because the initial formulations of ratio ALCHEMI did not consider the effect of delocalization of the inner-shell ionization event and anti-site defects, significant errors and unphysical site occupancies can result [25–27]. To solve these problems, approaches such as using correction factors [26,28], statistical analysis of the data acquired from a variety of orientations [29,30] or incorporating the anti-site defect concentration into the formulation [31] have been developed. Recently, the characteristic X-ray intensities were measured at various electron incidence directions and by comparison with the X-ray intensities calculated from first principles, or with the inelastic scattering cross-sections calculated by the *ICSC* program developed by Oxley and Allen [32] it was possible to determine the atomic site occupancies in thermoelectric materials [33] and the dopant cation site in oxygen separation membrane materials [34].

In this study, the atomic location of alloying elements in the $L1_2$-γ' unit cell in Co-9Al-9W-2X (X = Ti, V, Cr, Ni, Mo and Ta) alloys after long-term annealing was investigated by planar ALCHEMI. To the authors' knowledge, this is the first work which applies ALCHEMI to γ-γ' Co-base superalloys and also the first experimental investigation of the site preferences of a wide selection of elements in the γ' phase. Additionally, the experimental results have been compared with calculated inelastic ionization scattering cross-sections using the *ICSC* program [32]. Finally, by quantifying the experimental ALCHEMI data with aid of the measured chemical composition of the γ' phase after annealing at 900 °C for 5000 h, the site occupancy of the alloying elements in the $L1_2$-γ' unit cell has been confirmed. It is believed that this work can be instructive for both theoretical and experimental studies on the alloy design for the new type of γ-γ' Co-base superalloys.

2. Inelastic scattering cross-section calculation by *ICSC*

The program *ICSC* (Inelastic Cross Section Calculator) developed by Oxley and Allen [32] was applied to calculate the inelastic scattering cross-sections of alloying elements, which were compared with the experimental characteristic X-ray intensities. Based on the formulas in Refs. [32,35], the ionization cross-section σ contains contributions from dynamically scattered electrons and also "dechannelled" electrons (mainly thermal diffuse scattering). In the current calculations, the unit cell of the $L1_2$ γ'-Co_3(Al, W) phase is defined as a cube with Co atoms occupying the face-centered sites, while Al and W occupy the corner sites equally. In order to simplify the calculation, the additional element Ti, V, Cr, Ni, Mo or Ta was treated as an impurity in the $L1_2$ phase because its contribution to the thermal diffuse scattering is not significant. When calculating the inelastic scattering cross-sections, with or without including the root-mean-square thermal atomic displacements of the quaternary elements, no significant differences were noticed in the simulated inelastic scattering cross-sections. Thus, only the root-mean-square thermal atomic displacements of Co, Al and W atoms which at about room temperature are 0.0060 [25], 0.0095 and 0.0019 Å^2 [36], respectively were imported into the program for calculating the thermal diffuse scattering coefficients. Because the ionization scattering factors for X-ray emission in the program were only parameterized for $6 \leq Z \leq 50$ for K-shell ionization and $20 \leq Z \leq 60$ for L-shell ionization, the cross-sections for W and Ta could not be calculated.

Experimental parameters such as electron voltage, specimen thickness and convergence angle influence the inelastic scattering cross-sections of the alloying elements, and thus affect the enhancement or attenuation of the emission of characteristic X-rays. Fig. 1 shows the calculated normalized inelastic scattering cross-sections of the base element lines Co-K and Al-K. The cross-sections were plotted as a function of scattering conditions along the 002 Kikuchi band with a maximum Bragg angle of 20.9 mrad for ±006 reflections in the <001> zone axis of the $L1_2$ γ'-Co_3(Al, W) phase. In order to make the channeling effects of the alloying elements easily visible in the $L1_2$ phase, the cross-sections were firstly normalized by the cross-sections under kinematical condition and then normalized by the cross-section of the Co-K line, namely (σ_d/σ_k)-X/(σ_d/σ_k)-Co_K (X is alloying element). Thus, the normalized Co-K cross-section remains unity while the normalized cross-section of other elements, such as Al can show the channeling effects when the scattering condition changes. When changing the (a) convergence angle, (b) voltage, and (c) specimen thickness, the channeling intensity varies. If the convergence angle is increased from 2 to 4 mrad (voltage kept at 200 kV and specimen thickness at 100 nm), the channeling effect of the normalized Al-K cross-section is less pronounced. As increasing the convergence angle, the ionization cross-sections slightly decrease and the channeling intensity of the normalized Al-K cross-section is also slightly reduced. This stems from the fact that the channeling condition is fulfilled for a planar incident electron wave and thus a bigger convergence angle causes a higher deviation of the incident beam from such an ideal planar wave character, resulting in a reduced channeling intensity [37,38]. On increasing the electron voltage (convergence angle kept at 4 mrad and specimen thickness at 100 nm), the normalized cross-section profiles of the Al-K line change obviously, especially for scattering conditions between the (00−2) and the (002) reflections. Increasing the electron voltage, the peak at $k_x/g_{001} = 0$ gradually becomes lower and broader and disappears finally. From the calculations it is found that the effects from delocalization on the cross-section increase with acceleration voltage and are stronger for the characteristic X-ray emission with lower energy [24,26,35]. A lower voltage can reduce the delocalization effects and show better channeling effects. But for better statistic it is recommended to use a higher voltage to get more X-ray counts and improve the peak/background ratio. Thus choosing an acceleration voltage of 200 kV could balance the effects from delocalization and X-ray counts. Also the normalized cross-section of Al-K still shows similar channeling features at 200 kV as at 80 kV voltage. Varying specimen thickness can also influence the normalized cross-section profiles and the channeling intensity is less pronounced with