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Coarsening behaviour and interfacial structure of γ' precipitates in Co-Al-W based superalloys

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ABSTRACT

This work discusses the effects of alloying on the coarsening behaviour of the $L1_2$ ordered γ' phase and the structure of the γ/γ' interfaces in three Co-Al-W base superalloys aged at ~90 °C below the respective solvus temperatures: Co-7Al-7W, Co-10Al-5W-2Ta and Co-7Al-7W-20Ni (at.%). The coarsening kinetics are adequately characterised by the classical Lifshitz-Slyozov-Wagner model for Ostwald ripening. Co-7Al-7W exhibited much slower coarsening than its quaternary derivatives. Alloying can be exploited to modify the coarsening kinetics either by increasing the solvus temperature by adding tantalum, or by adding nickel to shift the rate controlling mechanism towards dependence on the diffusion of aluminium rather than tungsten. Lattice resolution STEM imaging was used to measure the widths of the order-disorder (structural) and Z-contrast (compositional) gradients across the γ/γ' interfaces. Similarly to nickel base superalloys, the compositional gradient was found to be wider than the structural. Co-7Al-7W-20Ni had much wider interface gradients than Co-7Al-7W and Co-10Al-5W-2Ta, which suggests that its γ' phase stoichiometry is less constrained. A possible correlation between temperature and misfit normalised r vs. $t^{1/3}$ coarsening rate coefficients and the structural gradient width has also been identified, whereby alloys with wider interfaces exhibit faster coarsening rates.

1. Introduction

Interfaces play a fundamental role in determining the properties of materials [1–3]. This is particularly true in regard to their effect on the mechanical behaviour of multi-phase alloy systems. Superalloys, widely used in the manufacture of high-temperature turbine components for jet engines, are no exception [4]. Their microstructure consists of a *fcc* solid solution matrix, γ, strengthened by an intermetallic phase, γ', with an $L1_2$ ordered structure. The volume fraction of the γ' is as high as 80% in some alloys.

The γ/γ' interface is an important physical boundary that interacts with the dislocations responsible for the plastic deformation of the alloys. Depending on the specific stress-temperature regime experienced by these materials [5], the dislocations either pass through the interface to shear the precipitates [6], or become trapped in the interface and are forced to circumvent the precipitates via thermally activated climb and cross-slip [7].

The lattice misfit between the γ and γ' is the most thoroughly studied interfacial property in superalloys. The associated strain field has been exploited by metallurgists to attain strength improvements [8]. However, excessive strains destabilise the microstructure by promoting directional coarsening (rafting) at elevated temperatures [9,10]. Furthermore, addition of certain refractory elements to increase the lattice misfit favours the formation of brittle topologically close packed phases that denude the microstructure of strengthening γ' precipitates [11].

The γ/γ' interface is a dynamic entity which evolves over time when superalloys are subjected to service conditions. The diffusion mediated processes that are active at the high operating temperatures allow the interface to migrate and alter its morphology. This not only concerns rafting regimes, but other deformation modes as well. Recent studies have shown the interface interacting with matrix dislocations, wrapping around them to form characteristic ridges and thus reducing the local elastic strain fields in the crystal [12–15].

Modern atom probe tomography (APT) techniques allow detailed studies of the elemental partitioning between γ and γ', revealing new information about the interface in the form of compositional gradients. The diffuse nature of these gradients is in

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accordance with the Cahn-Hilliard [16,17] model for spinodal decomposition, which occurs cooperatively with chemical ordering during precipitation of the intermetallic phase [1].

A study of alloy René 88DT using APT and atomic resolution Z-contrast scanning transmission microscopy (STEM) by Srinivasan et al. [18] has revealed two markedly different interfacial widths corresponding to the compositional and the order-disorder (structural) gradients. This has raised the fundamental question about the treatment of the γ/γ' interface in mathematical models of physical processes such as precipitate coarsening and dislocation-precipitate interactions.

In this study we examine the γ/γ' interface structure in alloys based on the Co-Al-W system which, since their discovery by Sato et al. [19] in 2006, have attracted significant research interest as successor candidates to nickel-base superalloys, particularly since adequate oxidation resistance has been demonstrated through alloying and coating [20–22]. Using high-resolution (HR) STEM imaging we examine the effects of alloying and heat treatment on interfacial gradient widths in three model alloys and consider the correlation with the observed γ' coarsening kinetics.

2. Experimental methodology

2.1. Material preparation

A ternary base alloy, Co-7Al-7W [base], and two quaternary derivatives, Co-10Al-5W-2Ta ['2Ta'] and Co-7AL-7W-20Ni ['20Ni'](at.%) were investigated. The alloys belong to the same stock as the batch #1 specimens studied by Yan et al. [23], produced in the form of 50 g finger-shaped polycrystalline ingots by vacuum arc melting using back-filled argon. The ingots were homogenised at 1300 °C for 24 h, then encased in rectilinear mild steel cans with titanium powder oxygen scrubber and super-solvus hot rolled at 1150 °C to 3 mm.

The rolled plates were solution treated at 1300 °C for 24 h and aged at ~90 °C below the respective solvus temperatures, measured from the cooling curve of a differential scanning calorimetry (DSC) thermogram. The DSC was carried out using a Netzsch "Jupiter" simultaneous thermal analyser. The specific details of the procedure are outlined in Ref. [23]. The solution and ageing heat treatments were terminated by furnace cooling at 1 °C min^{-1}. The duration of the ageing heat treatments was chosen to produce an optimally coarsened γ/γ' microstructure. The alloys were encapsulated in evacuated quartz tubes for all heat treatment procedures. Chemical compositions were verified using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at Incotest, Hereford, UK and are listed in Table 1 along with the solvus temperatures and heat treatment schedules.

2.2. TEM analysis of interfacial widths

To overcome problems associated with magnetic properties of cobalt, small volume specimens were prepared using the focussed ion beam (FIB) milling and in-situ lift-out technique. An FEI Helios NanoLab 600 dual beam system with an OmniProbe™ micromanipulator was employed for this purpose.

TEM evaluation of the γ/γ' interfaces required that the plane of the specimen lay normal to the ⟨001⟩ crystallographic axis. To ensure desired specimen orientation, a JEOL JSM6400 scanning electron microscope (SEM) with an Oxford Instruments HKL Nordlys electron back scatter diffraction (EBSD) detector was used to identify grains with the ⟨001⟩ pole normal to the mechanically polished surface. An indent made by a diamond hardness tester was used as a fiducial marker. The channelling contrast and differential surface erosion conveniently revealed the grain structure during ion beam imaging and thus chemical etching could be avoided.

STEM using high angle annular dark-field (HAADF) Z-contrast imaging of the interfaces was carried out using an FEI Titan^3 80–300 FEG (S)TEM with a probe C_s-corrector. A Gatan 865 Tridiem high-resolution spectrometer/imaging filter was used to perform electron energy loss spectroscopy (EELS) to investigate chemical element partitioning between the γ and γ' phases. The HAADF imaging and EELS were performed at 200 kV.

HAADF images of the crystal lattice in the interfacial regions were acquired for several precipitates in each alloy. Care was taken to avoid precipitates which may have been sectioned on a rounded corner edge, which would have caused the interfacial gradients to appear broader. To measure the widths of the interfacial gradients, 7 × 1 nm crops were taken from the lattice images across the approximate centre of the interfacial region using the ImageJ software package. The pixel brightness values were integrated/binned parallel to the interface plane to produce a scatter plot of position vs. intensity.

The plots had a sinusoidal appearance, whereby the maxima correspond to rows of strong Z-contrast. Due to the chemical ordering present in the γ', some integrated rows correspond to Co atoms only, while others correspond to Co and (Al,W). The difference in mean Z between the integrated columns causes the maxima to alternate in intensity in the γ'. The maxima do not exhibit this variation in the γ. Convoluted with the sinusoid is a sigmoid that results from the difference in mean electron scattering cross sections between the two phases. The γ' phase contains substantially more tungsten and scatters more electrons at high angles. This makes it appear brighter than γ in HAADF imaging.

To measure the width of the compositional (Z-contrast) gradient, sigmoid functions were fitted to the scatter data using the IGOR Pro software package. The fitted parameters were then used to calculate the interface width using the approach outlined by Cahn and Ardell [16,24].

The width of the structural (order-disorder) gradient was determined as follows. Signal noise was smoothed using a Gaussian filter with a 3 × 3 pixel kernel. A custom FORTRAN 95 program was used to identify the local maxima of the sinusoid. An intensity ratio was then calculated between each maximum and the maximum preceding it (from left to right). Two sigmoid functions, 'step-up' and 'step-down', were then fitted selectively to the intensity ratio vs. position data. The structural interface widths were then calculated using the same approach as that used for the compositional gradients.

2.3. SEM analysis of coarsening behaviour

To evaluate the coarsening behaviour of the three alloys, vacuum encapsulated sections of the original stock ingots were

Table 1
The three alloys used for the γ/γ' interface width study: average compositions measured using ICP-OES, γ' solvus temperatures measured using DSC, as well as the solution and ageing heat treatments, and lattice misfit between the γ/γ' phases [44].

Alloy	Composition (at.%)	γ' Solvus	Solution treatment	Ageing treatment	γ/γ' Misfit
Co-7Al-7W	Co-7.3Al-6.8W	854 °C	1300 °C/24 h	765 °C/200 h	0.57%
Co-10Al-5W-2Ta	Co-9.9Al-4.8W-1.8Ta	992 °C	1300 °C/24 h	900 °C/100 h	0.67%
Co-7Al-7W-20Ni	Co-7.3Al-7.0W-20.2Ni	881 °C	1300 °C/24 h	790 °C/200 h	0.35%