MATERIALS SCIENCE & ENGINEERING A

Uphill diffusion in ternary Ni–Re–Ru alloys at 1000 and 1100 °C

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Abstract

The rates of interdiffusion of Re and Ru at 1000 and 1100 °C in binary diffusion couples with single phase face centred cubic (fcc) microstructures have been characterised and compared to their respective rates in the presence of one another in ternary Ni–Re–Ru couples. The diffusivity of Re in Ni at 1000 °C (6.12×10^{18} m²/s) and at 1100 °C (9.31×10^{-17} m²/s) was found to be an order of magnitude slower than that of Ru at both temperatures (5.01×10^{-17} and 4.71×10^{-16} m²/s at 1000 and 1100 °C, respectively). The interdiffusion coefficient of Re was found to be unaffected by the presence of Ru in the ternary Ni–Re–Ru alloy (6.08×10^{-18} and 9.16×10^{-17} m²/s at 1000 and 1100 °C, respectively). That of Ru was modestly reduced by the presence of Re to 3.45×10^{-17} and 2.36×10^{-16} m²/s at 1000 and 1100 °C, respectively. Uphill diffusion of Ru was evident in the diffusion zone of the Ni–Re–Ru/Ni–Ru couples under all annealing conditions despite the absence of a Ru concentration gradient. The uphill diffusion of Ru was opposite to and of the same order of magnitude of Re, the principal diffusing element. This suggests Re lowers the chemical potential of Ru thus promoting uphill Ru diffusion to equilibrate the chemical potential gradient. Lowering of the chemical potential of Ru by Re is consistent with thermodynamically stable Re–Ru bonding which may contribute to the enhanced microstructural stability and high temperature creep performance documented in Ru-bearing Ni-base single crystal superalloys.
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1. Introduction

In the quest to improve the performance and efficiency of the gas turbine engine, a large body of research and development has been devoted towards enhancing the maximum operating temperature of the turbine blade. Turbine blades, which are required to operate for long times at elevated temperatures under high centripetal forces and in aggressive atmospheres, are currently manufactured from single crystal Ni-base superalloys.

Single crystal Ni-base superalloys have been through three generations of development; the major advance of the third generation alloys was achieved through rhenium (Re) additions which contributed to significant gains in creep capability over earlier generation alloys [1–3]. However, the difference between the crystal structures and atomic sizes of Re (hcp) and Ni (fcc) limits the solubility of Re in Ni. Moreover, the low diffusivity of Re, which partitions strongly to the dendrite core during solidification, makes compositional homogenisation of the microstructure during solution heat treatment inherently difficult [4,5]. In certain instances local supersaturation of the γ-matrix phase caused by residual Re microsegregation is relieved by the precipitation of deleterious topologically close-packed (TCP) phases following prolonged exposure to elevated temperatures [2,6,7]. The major detriment accompanying the formation of TCP phases is the associated depletion of the important strengthening elements, such as Cr, Mo, W and Re, from the desired alloy phases and their concentration in the brittle intermetallic TCP phases; this adversely affects the mechanical properties, most notably the high temperature creep rupture strength [6,8–10].

Recent initiatives to address these microstructural stability concerns have involved the addition of the refractory platinum group metal ruthenium (Ru) to single crystal Ni-base superalloys. Preliminary studies have indicated that alloys containing both Re and Ru are less prone to TCP phase precipitation than alloys bearing solely Re [10–14]. However, the mechanism(s) by

which Ru enhances microstructural stability remains debatable [6,10–12,15,16]. Furthermore, Ru additions have been documented to enhance the creep response of Ni-base single crystal superalloys at temperatures below which TCP precipitation is prevalent [13] and in alloys resistant to microstructural instabilities [17]. Creep deformation occurs at a rate dictated by diffusional rearrangements at dislocation cores [18] and the growth rate of TCP particles is controlled by the bulk volume diffusion of TCP forming elements towards the growing precipitate interface. In both instances, the creep strength and stability of the two phase γ/γ' microstructure are intrinsically governed by diffusional processes. It is therefore of interest to investigate how the diffusivity of a solute through the Ni-solvent is affected by potential interactions with a dissimilar solute as a means of explaining a possible contribution to the above mentioned benefits of Ru additions to high Re-content single crystal Ni-base superalloys.

2. Experimental procedure

The experimental procedure and data analysis employed in this paper are based on the work detailed by Karunaratne and coworkers [19–21]. Pure Ni, two Ni-base binary alloys (Ni–10 wt.% Re and Ni–10 wt.% Ru) and one Ni-base ternary alloy (Ni–10 wt.% Re–10 wt.% Ru) were prepared in the form of 400 g ingots by vacuum induction melting. Consistent with the equilibrium binary phase diagrams [22], the alloying levels used in this study were insufficient to result in the precipitation of secondary phases within the single phase fcc-γ microstructures at the temperatures under investigation. No ternary phase diagrams are currently published for this system. The ingots were

annealed at 1310 °C for 48 h to ensure homogenisation and a relatively large grain size, >500 μm (Fig. 1).

Bars approximately 7.8 mm × 7.8 mm in cross-section were machined from the ingots using electro-discharge machining (EDM) from which slices 3.5 mm in thickness were cut. One face of each slice was polished to a 1 μm finish and subsequently cleaned with acetone in an ultrasonic bath for 5 min. The slices were then assembled into diffusion couples using a ThermecMastor-Z thermo-mechanical simulator. Bonding between the polished surfaces of the constituent slices was achieved by heating the couple to 1200 °C at a rate of 10 °C/s in a high vacuum environment and holding for 3 min under an applied compressive load of ~2 MPa at which point the load was released and the specimen was gas quenched to below 100 °C.

The following four types of diffusion couples were fabricated [wt.%]:

(1) Ni–10Re/Ni;
(2) Ni–10Ru/Ni;
(3) Ni–10Re–10Ru/Ni–10Ru;
(4) Ni–10Re–10Ru/Ni–10Re.

The binary couples 1 and 2 were designed to measure the diffusivity of Re and Ru respectively in pure Ni while the ternary couples 3 and 4 were designed to measure the same rates in the presence of constant Ru and Re, respectively. The rates of interdiffusion were characterised at 1000 °C for times of 360 and 480 h and at 1100 °C for 144 and 360 h. This enabled the independence of diffusivity with time for each element to be checked and compared with the interdiffusion coefficients documented in [19,20]. Prior to annealing, the couples were sealed
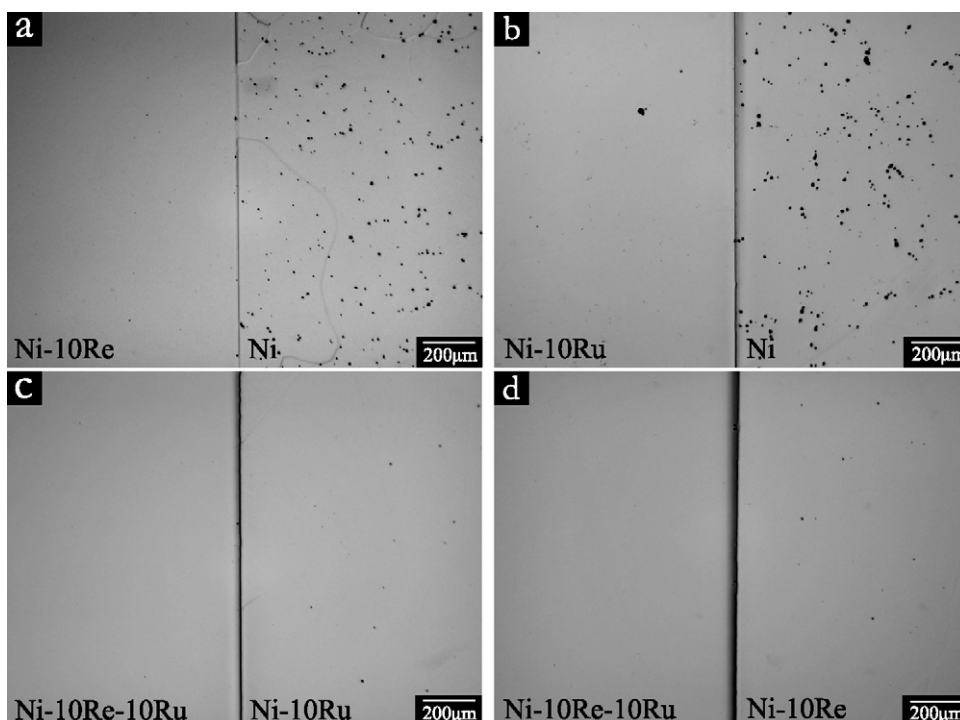

Fig. 1. Optical micrographs of the diffusion couples investigated: (a) Ni–10Re/Ni; (b) Ni–10Ru/Ni; (c) Ni–10Re–10Ru/Ni–10Ru; (d) Ni–10Re–10Ru/Ni–10Re following an anneal of 360 h at 1100 °C. Note the planar bond interface and the large grains size of the constituent alloys.