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Experimental assessment of the Ru–Al–Ni ternary phase diagram at 1000 and 1100 °C

B. Tryon *, T.M. Pollock

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States

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Abstract

Knowledge of phase equilibria in the Ru–Al–Ni ternary system is relevant to the development of new single crystal Ni-based superalloys as well as to new high temperature protective coating systems for these alloys. A series of diffusion couple investigations have been performed across the Ru–Al–Ni ternary system in order to establish phase fields and possible diffusion paths. A continuous B2 phase has been shown to exist across the Ru–Al–Ni ternary between the RuAl and NiAl phases at temperatures of 1000 and 1100 °C. Ternary isothermal sections for Ru–Al–Ni at 1000 and 1100 °C are presented.

Keywords: Ruthenium aluminide; Nickel aluminide; Interdiffusion; Ternary phase diagram

1. Introduction

Developments in thermal barrier coating (TBC) technology for Ni-base superalloys have resulted in B2 Pt-modified NiAl-based bond coatings with improved coating system durability relative to conventional NiAl bond coat systems [1–9]. It is interesting to consider further improvements in the high temperature capability of this class of bond coats by the substitution or addition of other B2-type compounds, such as RuAl, with improved high temperature properties compared to NiAl [10].

Ru is also being investigated as an alloying addition to bulk Ni-base single crystal superalloys for improvement of high temperature capabilities [11–17]. The diffusion of various alloying additions to Ni-base systems, including diffusion of some platinum group metals (PGMs), has recently been investigated [16–19]; however, there has been less attention focused on diffusion of Ru and the resultant formation of Ru-rich intermetallic precipitates [16–23]. Detailed information regarding the phase stability and diffusional characteristics of the Ru–Al–Ni ternary system is needed for tailoring the properties of continually advancing Ru-modified superalloy and TBC systems [24].

To investigate stable phases present and high temperature diffusion paths, diffusion couples were fabricated across the Ru–Al–Ni ternary system among the following compounds: δ-Ru, RuAl, NiAl, γ′-Ni_3Al, and γ-Ni. Experiments were performed to examine the composition and structure of compounds across this ternary to determine useful thermodynamic and diffusional information about the Ru–Al–Ni ternary system. A new version of the ternary Ru–Al–Ni phase diagram is presented, and the implications of these observations for processing of RuAl-based bond coatings are discussed.

2. Experimental procedures

A select series of diffusion couples were fabricated across the Ru–Al–Ni ternary system at temperatures of 1000 °C (1273 K) and 1100 °C (1373 K). The couples fabricated are listed in Table 1.

Single crystal NiAl castings, high purity polycrystalline γ-Ni (99.999%), and near stoichiometric polycrystalline γ′-Ni_3Al were sectioned into blocks in order to fabricate the diffusion couples. The portions of the blocks which formed the diffusion couple surfaces and the opposing loading surfaces were ground flat and parallel. The diffusion couple surfaces were hand polished to a mirror-like finish with 1 μm alumina slurry. The dimensions of each block were approximately 4 mm × 4 mm × 3 mm in length, width, and in thickness, respectively.

* Correspondence to: 3062 H.H. Dow Building, 2300 Hayward Street, Ann Arbor, MI 48109, United States. Tel.: +1 734 615 5164; fax: +1 734 615 5168.
E-mail address: btryon@umich.edu (B. Tryon).

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Table 1
Fabrication conditions for Ru–Al–Ni system diffusion couples

Specimen	Joining conditions			Heat treatment	
	Temperature (°C)	Time (h)	Load (MPa)	Temperature (°C)	Time (h)
RuAl–NiAl	1000	24	20	'As joined'	–
RuAl–NiAl	1000	24	20	1000	336
RuAl–NiAl	1000	24	20	1100	336
Ni–RuAl	1000	24	20	'As joined'	–
Ni–RuAl	1000	24	20	1000	336
Ni–RuAl	1000	24	20	1100	336
Ru–NiAl	1000	24	20	'As joined'	–
Ru–NiAl	1000	24	20	1000	336
Ru–NiAl	1000	24	20	1100	336
Ru–Ni_3Al	1000	24	20	'As joined'	–
Ru–Ni_3Al	1000	24	20	1000	336
Ru–Ni_3Al	1000	24	20	1100	336
RuAl–Ni_3Al	1000	24	20	'As joined'	–
RuAl–Ni_3Al	1000	24	20	1000	336
RuAl–Ni_3Al	1000	24	20	1100	336

Arc-melted buttons of RuAl and δ-Ru were fabricated from high purity stock of Ru (99.98%) and Al (99.999%). The RuAl was slightly Ru-rich in order to achieve a single phase microstructure. Arc-melted materials were cut into blocks measuring approximately 4 mm × 4 mm × 3 mm in length, width, and in thickness, respectively, for diffusion couple fabrication.

All of the diffusion couples were fabricated by joining one Ru-containing block (δ-Ru or RuAl) with one Ni-containing block (γ-Ni, γ′-Ni_3Al, or NiAl) under a constant load of 20 MPa in a vacuum furnace at 1000 °C for 24 h. Details of the joining conditions and annealing treatments for each couple are listed in Table 1. One couple from each pairing was retained in its "as joined" condition for analysis while the remaining couples were sealed in quartz tubes backfilled with high purity argon gas for annealing at the elevated temperatures detailed in Table 1. Specimens were ramped to and from the joining and annealing temperatures at a rate of approximately 1 °C/min to minimize any detrimental effects due to thermal expansion mismatches.

The "as joined" and annealed specimens were mounted and polished using standard metallographic preparation methods. Samples were observed with scanning electron microscopy (SEM) and electron microprobe analysis (EMPA). Composition profiles were generated by EMPA using a CAMECA SX100 Electron Probe Microanalyzer. The electron interaction volume of the beam was established to be 1–2 μm^3. The accelerating voltage and beam current were set at 20 kV and 10 nA, respectively. Corrections to the measurements were made with the CAMECA PeakSight software utilizing a PAP model. The calibration of the instrument was checked against nominally pure γ-Ni, NiAl, RuAl, and δ-Ru as standards. Count times were set at 10 s for the peak positions and 5 s for each background position.

The microprobe step size of the profile varied from 1–10 μm depending on the microstructural features and extent of the interdiffusion zone of a given sample. A number of line scans (a minimum of two) were taken across the interfaces of each couple at different positions across the sample. Compositional information from each line scan was analyzed in comparison with corresponding micrographs. This measure was taken in order prevent reporting data which sampled near phase boundaries where the reported compositions would be erroneous due to the sampling of more than one phase despite the small interaction volume.

3. Results

3.1. RuAl–NiAl couples

Interdiffusion was quite slow between RuAl and NiAl as shown by the backscattered electron (BSE) images and composition profiles in Fig. 1. After 336h at 1000 °C, the total extent of the interdiffusion between the nearly stoichiometric B2 compounds is only 10–12 μm and approximately 20 μm after the same amount of time at 1100 °C. Kirkendall voids are evident on the NiAl half of the diffusion couple, as shown in Fig. 1(b and c), indicating a net flux of Ni to the RuAl half of the couple at 1100 °C. EMPA data confirm that the Al level remains relatively constant from the RuAl side to the NiAl side of the couple. Some change in contrast is displayed in the interdiffusion regions of the BSE images between the two phases due to differences in atomic mass of Ni compared to Ru. The leading front of the interdiffusion zone is not perfectly planar due to the polycrystalline character of the RuAl material.

The composition profiles between RuAl and NiAl, displayed in Fig. 1 show a relatively 'smooth' and continuous transition occurs across the interdiffusion zone between the RuAl and NiAl phases following high temperature annealing. This is unexpected since the currently accepted phase diagram for this temperature range displays a miscibility gap between NiAl and RuAl [25–27]. The absence of an abrupt jump in the composition profile indicates a continuous B2 phase with interdiffusion.