STUDIES OF A QUASI-BINARY β-NiAl AND α-Re EUTECTIC

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Introduction

Future improvements to jet engine performance will require materials which are lower in density and can withstand higher temperatures; thus increasing the thrust-to-weight ratio and the engine efficiency. The intermetallic compound β-NiAl is a prime candidate for this new high temperature material. This intermetallic offers a low density, a high melting temperature, and excellent oxidation resistance, but exhibits poor creep resistance. The creep resistance may be improved by composite engineering with refractory metal fibers and of particular interest to the present study are the refractory composites formed by eutectic solidification. There are three known refractory metals which may be solidified as a eutectic with β-NiAl: W(1), Mo(2,3), and Cr(2-5). Another useful refractory metal addition would be Re. Indeed, α-Re fibers would offer greater high-temperature strength than either Mo or W in the temperature range of 950 to 1250°C(6). This is in part a result of the close packed hexagonal crystal structure of α-Re. The mechanical properties of β-NiAl alloyed with Re via a powder metallurgy technique have been studied by Vedula et al.(7). This study revealed that the addition of Re to β-NiAl did not produce an extended solid solution or a new phase equilibrium and the consolidated alloys exhibited microstructures of β-NiAl with a dispersion of α-Re particles. One possible explanation for this result is that Re forms a quasi-binary eutectic isopleth with β-NiAl. Thus, the purpose of this study was to determine if a composite with a matrix of β-NiAl and fibers of α-Re could be produced by eutectic solidification and if so, to determine the nature of the quasi-binary phase diagram.

Experimental Procedure

Alloys with nominal compositions between β-NiAl and α-Re were prepared by arc-melting in an argon gas atmosphere. Additions of 1 to 5 atom percent Re were prepared by first melting the Re with Ni prior to melting the ternary alloy. The total weight of each button was below 30 grams which assured a homogeneous melt. An additional alloy of 3 atomic percent Re was melted by induction heating under an argon gas atmosphere. Differential thermal analysis (DTA) of the eutectic structure was performed using a Netzsch model STA 409 analyzer equipped with a 1600°C furnace. The maximum temperature of the sample was limited to 1575 °C and no evidence of transformation was observed. Thin foil specimens for transmission electron microscopy (TEM) were prepared by twin-jet electropolishing in a solution of 70% methanol, 6% perchloric acid, 10% butylcellusolve, and 14% water, operating at 70 V and -10°C. Under these conditions the matrix was preferentially polished with respect to the Re-rich phase. The electropolishing was followed by 5 -10 minutes of ion milling to clean the surface. Electron microscopy studies were performed using the facilities of the Electron Microbeam Analysis Laboratory at the University of Michigan. A CAMECA model MBX electron microprobe analyzer, equipped with a three crystal spectrometer, was used for chemical analysis of the eutectic microstructure. Chemical analysis of the eutectic structure was performed using elemental standards and a KEVEX-8000 system. Analytical electron microscopy studies were performed using a JEOL 2000FX equipped with a Tracor-Northern TN-5502 analysis system.

Results

Three distinct phases were observed (FIG. 1a) in the arc-melted buttons: small dendrites of nearly pure α-Re, a dendritic structure of β-NiAl, and a eutectic structure consisting of β-NiAl and α-Re rods. A large area of eutectic was

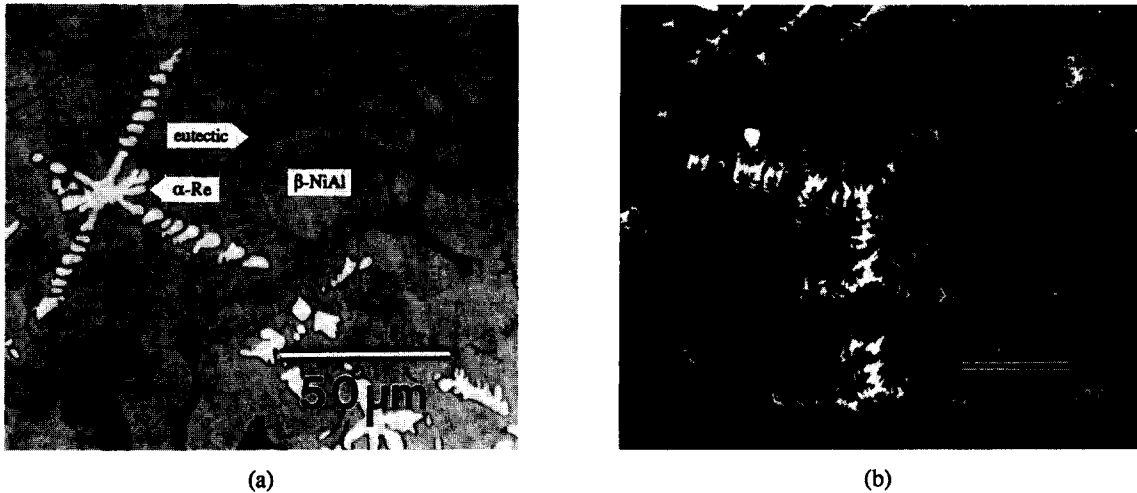<div align="center">(a)   (b)</div>

FIG. 1. (a) An optical micrograph of the arc-melted 47.5 Al -47.5 Ni -5 Re alloy showing the α-Re dendrites, the dendritic β-NiAl and the eutectic. (b) An optical dark-field micrograph of the induction melted, and slow cooled, 48.5 Al -48.5 Ni -3 Re alloy showing the α-Re dendrites and the eutectic structure.

observed in the 5% Re sample near the top of the arc-melted button, and this area was used for analytical study. In contrast, the alloy melted by induction heating and solidified in the crucible exhibited a two phase structure consisting of α-Re dendrites and a eutectic structure (FIG. 1b). Phase identification was accomplished by x-ray diffraction and analytical electron microscopy studies; thus two crystal structures, β-NiAl and α-Re, were identified. The α-Re exhibited the equilibrium close packed hexagonal (cph) lattice parameters and the β-NiAl exhibited a cubic lattice parameter of 0.2892 nm. Although the lattice parameter of β-NiAl exceeds the maximum of 0.2886 nm reported for the binary β-NiAl alloys(9), larger lattice spacings have been reported for β-NiAl when grown as a eutectic with Cr (5). The hexagonal nature of the fibers was verified by a convergent beam electron diffraction (CBED) technique (8). A high symmetry zone axis was chosen to obtain the crystal point group symmetry. An α-Re fiber was aligned such that the electron beam was parallel with the [0001] zone axis. The whole pattern and bright-field (BF) symmetry was found to be 6mm (FIG. 2a and 2b) and this indicated either a diffraction group symmetry of 6mm or $6mm1_R$. These two diffraction groups may be separated by examining the symmetry of a dark-field reflection (DF) when placed at the Bragg condition. Thus, the 2mm symmetry exhibited in FIG. 2c confirmed the $6mm1_R$ diffraction group and the 6/mmm crystal point group symmetry expected for α-Re. Some solubility of Re in the β-NiAl, and Ni in the α-Re, was observed by x-ray energy dispersive spectroscopy (XEDS). The eutectic composition in atomic percent was determined to be 47.5 Ni , 51 Al, and 1.5 Re by electron microprobe analysis. However, when this composition was arc-melted the resulting microstructure was dendritic in nature, i.e., dendrites of β-NiAl with the eutectic.

<div align="center">Discussion</div>

The solidified microstructures (FIG.1) may only be explained by a quasi-binary isopleth between β-NiAl and α-Re. The dendritic nature of the arc-melted alloys may be explained by undercooling of the eutectic liquid and a disparity in the growth velocity between β-NiAl and α-Re during solidification. This was not entirely unexpected since the water cooled hearth of the arc-melter may induce a relatively fast cooling rate; and the growth of α-Re is expected to be slow with respect to β-NiAl. The slow growth is a result of a long diffusion distance associated with the low α-Re volume fraction (0.019 based on the eutectic composition), facetted growth of the α-Re, and the slow diffusion of Re. Typically, this results in a region of eutectic growth which is skewed towards the high melting point phase(10). Thus, an alloy of eutectic composition may exhibit a dendritic microstructure when severely undercooled. These undercooled alloys should also exhibit solute trapping and Re-rich precipitates were observed in the dendritic microstructures (FIG. 3). This dendritic structure was not observed in the slowly cooled hypereutectic 3% Re alloy which was induction melted. The eutectic melting point was not quantified in this study, but may exist above 1575°C. This aspect of the phase diagram is still under investigation and directional solidification experiments are currently being pursued.
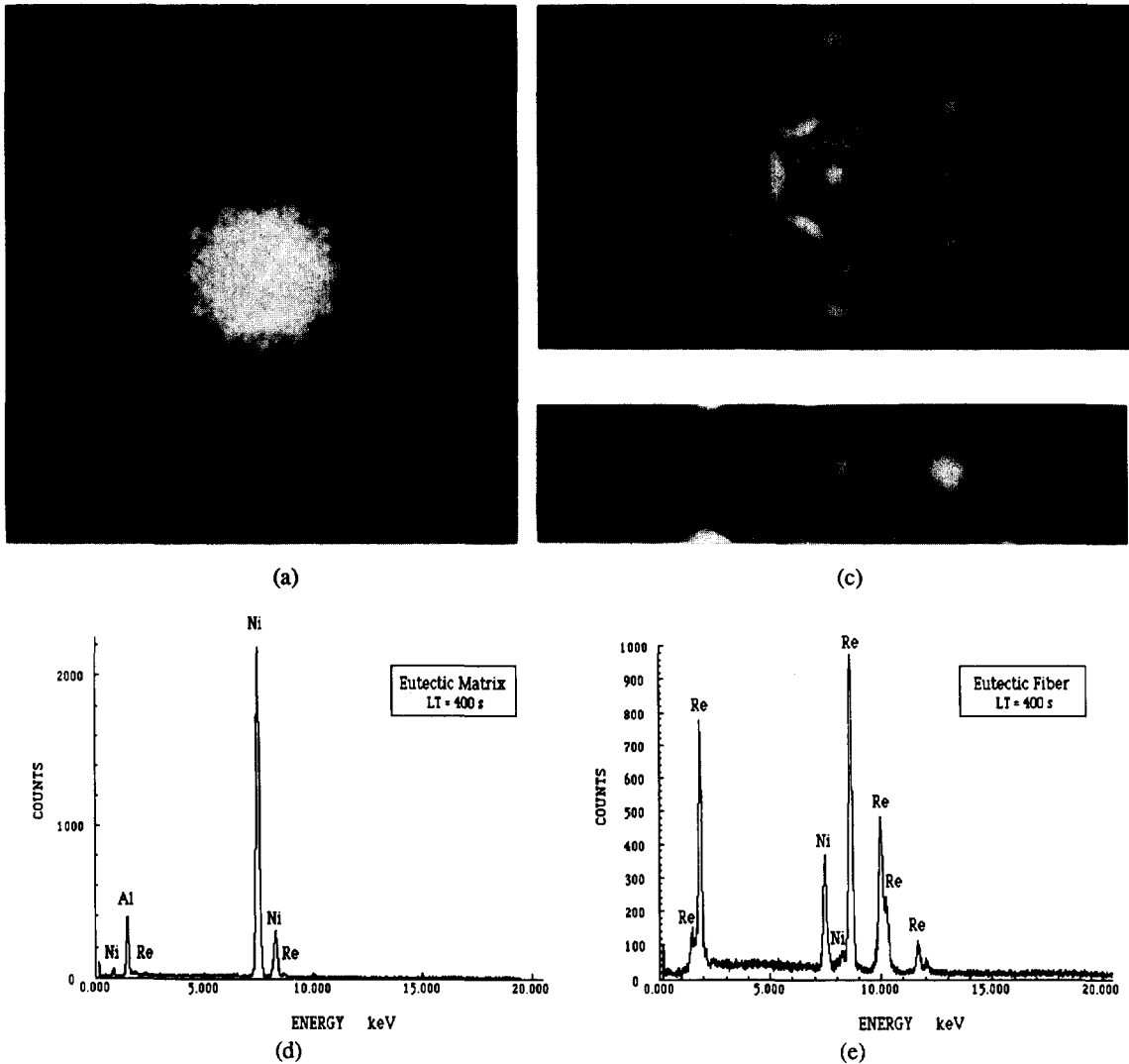
FIG. 2. Analytical data for the α-Re eutectic. (a) A [0001] ZAP showing 6mm symmetry in the whole pattern. (b) The zero order layer symmetry. (c) A dark-field reflection showing 2mm symmetry when placed at the Bragg condition. (d)XEDS spectrum of the eutectic matrix. (e) XEDS spectrum of the eutectic fiber.

The physical metallurgy of this ternary eutectic presents some interesting possibilities with respect to room temperature fracture toughness. A comparison of the coefficient of thermal expansion for β-NiAl and α-Re would indicate that the eutectic structure would be highly stressed, since β-NiAl should contract at twice the rate of α-Re from an elevated temperature. The coefficients of thermal expansion for β-NiAl and α-Re are 15.1 x 10^{-6} /°C and 6.7 x 10^{-6} / °C, respectively. However, this stressed condition may be beneficial with respect to fracture toughness. Work by Evans(11) has shown that a high residual stress at the fiber interface may contribute to fracture along the composite fiber interface and increase toughness by a fiber pull-out mechanism. This aspect was investigated by fracturing the eutectic and examining the fracture surface (FIG. 4). The secondary electron image shows that propagating cracks followed the α-Re fibers indicating that the fracture energy of the interface is less than that of the fiber or the matrix. Thus, a microstructure where the eutectic fibers are oriented parallel to the stress axis may provide improved fracture toughness by a fiber pull-out, or crack deflection, mechanism.
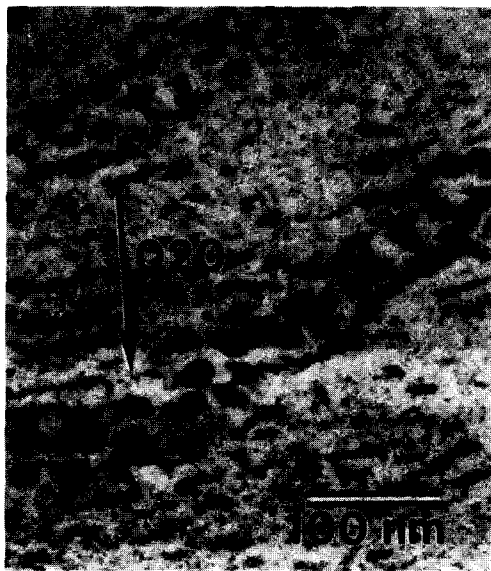
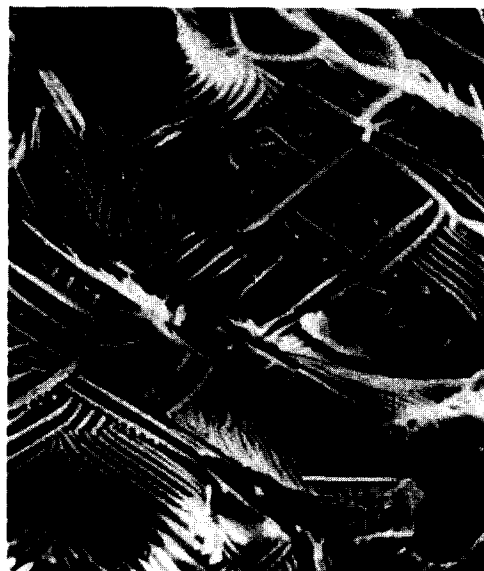FIG. 3. A bright-field transmission electron micrograph of the Re-rich precipitates observed in the dendritic β-NiAl.

FIG. 4. A secondary electron micrograph of the fractured eutectic.

Conclusions

A quasi-binary eutectic has been observed in the Al-Ni-Re ternary system. The eutectic consists of a low volume fraction of α-Re fibers in a β-NiAl matrix. The eutectic composition in atomic percent was determined to be 47.5 Ni , 51 Al, and 1.5 Re. This new eutectic structure may provide a fiber pull-out mechanism for improving the room temperature fracture toughness of β-NiAl.

Acknowledgements

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