REACTION KINETICS BETWEEN FIBER AND MATRIX

COMPONENTS IN METAL MATRIX COMPOSITES

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Abstract

Interdiffusion and interdiffusion controlled intermediate phase formation in metal matrix composites can be of interest for the prolonged application of these systems at high temperatures. Methods are discussed that address the kinetics of interdiffusion in systems that exhibit solid solution intermixing or the formation of a third intermediate phase at the fiber/matrix interface, or both. The tungsten fiber reinforced niobium and tungsten fiber reinforced superalloy systems are employed as model systems for experimentation and discussion. In an effort to impede interdiffusion, the concept of ion implanted diffusion barriers have been examined. Preliminary results on the feasibility and effectiveness of ion implanted diffusion barriers are presented.

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Introduction

The current search for advanced materials to surpass the high temperature capabilities of the present single crystal superalloys has concentrated attention on metal matrix composites (MMCs) (1,2,3). The inherent advantages of composite materials, however, do not come without some potential liabilities. For example, when one considers composites for ambient temperature applications, factors such as fiber/matrix adhesion must be considered. When one extends the question to short term high temperature applications, thermal-mechanical compatibility must also be considered. For long term high temperature applications, thermally activated processes such as interdiffusion and interfacial reactions between the reinforcing fibers and the matrix can become challenging concerns. These latter issues have been the focus of recent work at Columbia University and the NASA-Lewis Research Center (3,4).

Interdiffusion promoted effects on metal-matrix composite properties has been documented. Phenomena of this type include dissolution of the reinforcing fibers, formation of intermediate phases at the fiber/matrix interface, and, in the case of refractory metal fibers, the diffusion triggered recrystallization of the heavily worked fibers. These phenomena and their effect on composite properties must therefore be understood before the advantages of metal matrix composites can be fully utilized.

Results and Discussion

The Tungsten Fiber Reinforced Niobium System. In order to gain the most fundamental understanding of interdiffusional kinetics in fiber reinforced MMCs, we chose the single phase, or entirely mutually soluble, W/Nb system for initial study. Planar and cylindrical interface diffusion couples of W/Nb were fabricated. The cylindrical interface composites employed 218CS commercial tungsten wire and were made using the arc-spray technique developed at the NASA-Lewis Research Center (5). The planar interface couples were made by diffusion bonding of bulk materials. These diffusion couples were annealed in vacuum at 1800K and 1500K for 50 to 500 hours. Composition profiles for the annealed couples were obtained using a calibrated EDS microprobe at 1 micron intervals.

Composition dependent interdiffusion coefficients were obtained from the profiles of the planar interface composites using Boltzmann-Matano analysis. This technique allows the simple extraction of diffusion coefficients by setting the flux balance point to x=0, the Matano interface. Diffusion coefficients can then be determined numerically from the composition profile such that:

$$D(C,T) = \frac{-1}{2t} \left[\frac{dC'}{dx} \right]^{-1} \int_{C_0}^{C} x dC'$$
 (1)

Experimentally determined diffusion coefficients are shown in Figure 1. For this system in this temperature range the interdiffusion coefficient may be assumed to be independent of composition. The magnitude of the coefficients is considerably higher than what was expected based on Arrhenius extrapolations from the higher temperature data of Hehemann and Leber (6).

In order to assess the accuracy of the experimentally determined interdiffusion coefficients numerical solutions to Fick's second law (Eqn. 2) were employed. The code originally developed by Tenney and Unnam (7) was

adapted for this purpose. These numerical solutions calculate composition

$$\frac{\delta C}{\delta t} = \frac{1}{r^n} \frac{\delta}{\delta r} r^n D(C, T) \frac{\delta C}{\delta r}$$
 (2)

profiles for planar, cylindrical, or spherical geometry composites (n=0, n=1, n=2) with finite boundary conditions.

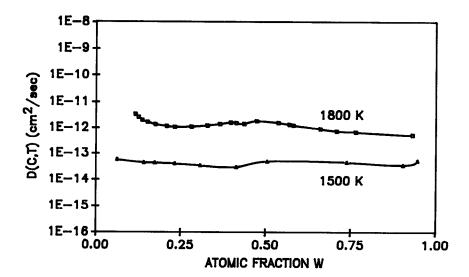


Figure 1 - Experimentally determined interdiffusion coefficients for the W/Nb system at 1500K and 1800K.

Figure 2 illustrates the good agreement between an experimentally determined composition profile for a cylindrical geometry composite and one that was calculated with interdiffusion coefficients determined from a planar interface diffusion couple. The good agreement between experimental and calculated composition profiles led to efforts to employ these same numerical solutions in order to predict the long term interdiffusional behavior of these composites.

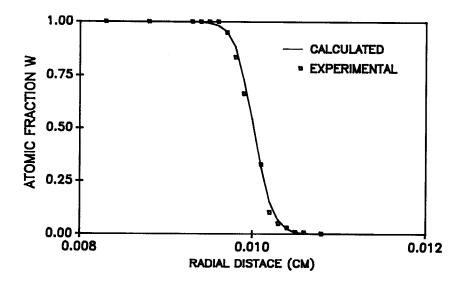


Figure 2 - Experimental and calculated composition profiles for a cylindrical geometry W/Nb composite annealed at 1500K for 500 hours.

The ability of the numerical solutions which were employed to handle finite boundary conditions also allows for the consideration of long term diffusion where the diffusion fields of individual fibers begin to overlap. Figure 3 shows a calculated time progression of the concentration profile of a cylindrical geometry W/Nb composite at 1500K. This hypothetical composite contains 200 micron diameter tungsten fibers making up approximately 40 volume percent of the composite. Recrystallization has been shown in this and other systems to follow the diffusion field of the matrix material in the refractory metal fibers (8). Accordingly, one would expect significant recrystallization of the tungsten fiber in one year at 1500K. Similar calculations and predictions can be done, of course, for other time-temperature conditions of interest.

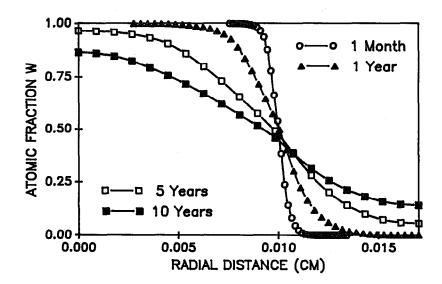


Figure 3 - Long term progression of composition profiles of a cylindrical geometry W Nb composite at 1500K.

The ability to make predictions in this manner does require a great deal of care in determining the interdiffusion coefficients. Often the accuracy in determining interdiffusion coefficients may be limited to within a factor of 2 or 3. This uncertainty can lead to a large variation in predicted composition profiles simulating long term services.

This same approach has also been used to model the behavior of the W/Nb1Zr system with equally good results (9). A pseudobinary approach of W and Nb1Zr components was found to yield good agreement between experimental and calculated composition profiles, although the ability to treat phases with more extensive alloying has not yet been established.

Similar numerical solutions have also been shown to adequately describe the moving boundary behavior of the W/Ni system in the two-phase regime above 1343 K (7).

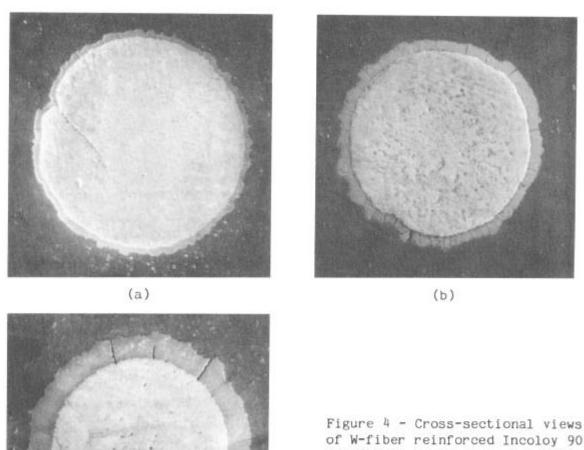
Tungsten Fiber Reinforced Superalloys (TFRS). In studying more complicated systems, we chose the TFRS systems in the 1323 K to 1473 K temperature range. At these temperatures, and after some time, this system exhibits the formation of a brittle reaction zone at the fiber/matrix interface. Matrix alloys that were initially studied included FeCrAlY, Waspaloy, Incoloy 907, Incoloy 903, and 316 stainless steel (10,11). These composites were fabricated using a 100 micron diameter ST300 thoriated

tungsten wire (1.5% thoria) by a powder metallurgical technique. These composites were annealed in vacuum for 50 to 500 hours. Figure 4 illustrates the growth of the "reaction zone" phase at the fiber/matrix interface. The formation of the reaction zones was found to be long range diffusion controlled (10) and the kinetics to be highly matrix chemistry dependent (11).

In order to quantitatively assess the kinetics of reaction zone formation, the moving boundary equations were solved simultaneously with Fick's second law, yielding the expression for the diffusion coefficient of the reaction zone phase (Eqn. 3). Assuming the interfacial concentrations

$$D_{rz}(T) = 1/2 \left[(C_{f|rz} - C_{rz|f}) / (C_{rz|f} - C_{rz|m}) \right] K_{f}(T)^{1/2} K_{rz}(T)^{1/2}$$
(3)

(where $C_{f\mid rz}$ would be the W concentration on the fiber side of the fiber/reaction zone interface, for example) can be considered roughly constant for the different matrix alloys studied, this result indicates that the diffusion coefficient is proportional to the product of the roots of parabolic rate constants for the total growth of the reaction zone and the component of the reaction zone which displaces the fiber (12).



of W-fiber reinforced Incoloy 903 composites annealed at 1373K for (a) 25 hours, (b) 100 hours, and (c) 400 hours.

By ranking the different alloys studied in order of these kinetic constants, it was determined that the kinetics of reaction zone growth decreased with decreases in Fe and Co content, and the corresponding increase in Ni content. Based on this kinetic data from conventional superalloy matrices, a new matrix alloy (Alloy 89) was designed and fabricated which totally eliminated Fe and Co. The kinetic constants were determined for this composite and the results for all of the matrix materials studied are shown in Table 1. As is evident, by eliminating these stable reaction zone formers, the kinetics of reaction zone formation have been greatly reduced.

Table 1. Product of the square roots of the parabolic rate constants for various TFRS composites annealed at 1366K and their corresponding Fe, Co, and Ni contents in atomic percent.

Matrix	Fe	Со	Ni	$[K_{rz}^{1/2}K_{f}^{1/2}]$ (cm ² /sec)
FeCrAlY	71	0	0	3.5x10 ⁻¹²
SS 316	70	0	12	2.9×10^{-12}
Incoloy 907*	57	13	25	1.7×10^{-12}
Incoloy 903 Î	42	15	38	0.8x10 12
Waspaloy	0	13	56	0.3x10 -
Alloy 89	0	0	66	0.05×10 ⁻¹²

^{*}Annealed at 1373K.

This decrease in reaction zone growth kinetics may, however, be accompanied by increasing the rate of recrystallization of the W-fibers when considering long term composite properties. Work by Larsson (13) has shown that increasing the Ni content in the matrix leads to accelerated fiber recrystallization. This may be due, at least in part, to the ability of the reaction zone to limit the flux of Ni into the tungsten fiber.

Ion Inplanted Diffusion Barriers. In an effort to investigate means by which interdiffusion between fiber and matrix components can be halted, or at least slowed, work has been performed to evaluate the feasibility of ion implanted diffusion barriers. The Pauling rules dictate that materials with considerable differences in atomic radii, valence, or electronegativity will have limited solubility in each other, or will have little driving force for interdiffusion. Based on this principle, it might be expected that interdiffusion in composites may be impeded by creating a layer at the fiber/matrix interface which is very different than either of the two component phases. This preliminary work is an attempt to create such a interdiffusionally incompatible zone by means of ion implanting large alkali ions into the surface of one of the components prior to fabrication.

A simple binary system was desired for a model for this work. The tungsten-nickel system was chosen due to it's well understood interdiffusion behavior and it's relative similarity to the TFRS system which is of technological interest. Diffusion couples were fabricated employing ion implanted diffusion barriers of sodium, calcium, barium, and potassium. These alkali and alkali earth ions were implanted into bulk tungsten substrates and subsequently coated by an ion-beam sputtered nickel film of approximately 100 microns in thickness. Each diffusion couple received an equal dose of the respective barrier ions of 6.4x10⁻¹¹ ions/cm² implanted with an accelerating potential of 190 keV. The substrate temperature during

the subsequent nickel deposition was estimated to be approximately 700K over the 70 hour deposition time. These diffusion couples, along with couples fabricated without an implanted layer, were annealed in vacuum at 1500K for 50 hours. Composition profiles were obtained for each diffusion couple were obtained by an EDS microprobe at 1 micron intervals across the interface.

The composition profiles for the sodium and calcium barriers diffusion couples are plotted along with the profiles of the non-implanted and as-received couples in Figures 5 and 6, respectively. The evident "saturation" of tungsten completely through the nickel "matrix" can be attributed to the very significant grain boundary diffusion induced by the characteristic microstructure of the sputtered nickel film. In spite of this problem which makes quantitative analysis of the efficacy of these barriers impossible, it is possible to make some preliminary observations for the effect of the barriers relative to the tungsten-nickel standard. As Figure 5 shows, it appears that the implanted calcium barrier did decrease the kinetics of interdiffusion in the tungsten-nickel system, although this

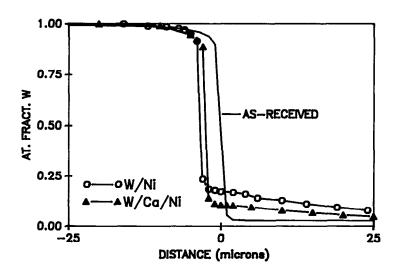


Figure 5 - Composition profile for tungsten-nickel diffusion couples with and without ion implanted calcium layer.

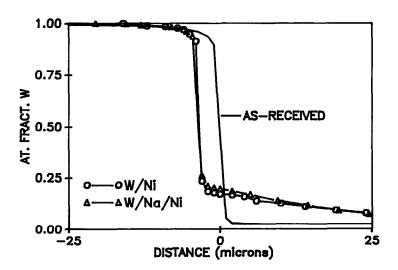


Figure 6 - Composition profile for tungsten-nickel diffusion couples with and without ion implanted sodium layer.

may be due at least in part to inhibiting the short circuit paths along the grain boundaries. The effect of the sodium barrier, illustrated in Figure 6, appears to be to promote interdiffusion in this system. Barium and potassium barriers were also found to promote interdiffusion, but to an even greater extent.

A possible explanation of this behavior may be that the distortion produced by the larger barium and potassium ions may be triggering a dynamic recovery at this elevated temperature. This process might be eliminated if lower ion doses are used. Similarly, variation of ion dose and accelerating potential may prove to yield better results for the calcium barrier by tailoring the calcium atom density and the thickness of the affected zone.

Conclusion

Understanding interdiffusion between metal matrix composite components and its affect is essential in terms of material selection for long term, high temperature applications. At very high temperatures the W/Nb (W/Nb1Zr) and the TFRS composites do show certain interdiffusional intermixing and intermediate phase formation, respectively. Diffusion mechanics have been successfully applied (and reviewed herein) to forecast these happenings.

Preliminary work in the area of developing ion implanted diffusion barriers is encouraging. Although only one of the barriers initially tested showed a moderate success, variation of implant process parameters may lead to an optimized barrier layer. Current work in this area at Columbia is utilizing hot-pressed diffusion couples in order to minimize grain boundary effects.

Efforts to develop new material systems which will be more chemically stable may include work on intermetallic/metallic composites, intermetallic/intermetallic composites which are expected to have superior interdiffusional stability due to the long range order of intermetallic phases.

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