

## INVESTIGATION OF REACTIVITY BETWEEN SiC AND Nb-1Zr IN PLANNED IRRADIATION CREEP EXPERIMENTS - C. A. Lewinsohn (Associated Western Universities), M. L. Hamilton, and R. H. Jones (Pacific Northwest National Laboratory)\*

### OBJECTIVE

The objective of this study is to determine whether detrimental reactions will occur between silicon carbide (SiC) composites and niobium-1wt% zirconium (Nb-1Zr) during experiments intended to measure the irradiation creep properties of the composites. The experiment designed to measure the creep of SiC fiber-reinforced, chemically vapor infiltrated SiC composites under irradiation involves using a Nb-1Zr pressurized bladder in contact with a cylindrical SiC composite. Data regarding the compatibility between Nb-1Zr and SiC are not available. Therefore, the reactivity between Nb-1Zr and SiC is investigated by using a computer program (Chemsage) capable of calculating the Gibbs free energy of formation for all compounds within the program database that can exist for a given thermodynamic state (pressure, temperature, number of moles). The actual reaction that will occur, however, will be limited by the kinetics of the transport mechanisms and the chemical reactions. A series of diffusion couple experiments aimed at gathering information on the kinetic aspects of the reactivity between Nb-1Zr and SiC is described.

### SUMMARY

Thermodynamic calculations and diffusion couple experiments showed that SiC and Nb-1Zr were reactive at the upper range of temperatures anticipated in the planned irradiation creep experiment. Sputter-deposited aluminum oxide ( $Al_2O_3$ ) was selected as a diffusion barrier coating. Experiments showed that although the coating coarsened at high temperature it was an effective barrier for diffusion of silicon from SiC into Nb-1Zr. Therefore, to avoid detrimental reactions between the SiC composite and the Nb-1Zr pressurized bladder during the planned irradiation creep experiment, a coating of  $Al_2O_3$  will be required on the Nb-1Zr bladder.

### PROGRESS AND STATUS

#### Introduction

Silicon carbide fiber-reinforced silicon carbide matrix composites ( $SiC_f/SiC_m$ ) are attractive materials for fusion energy systems for a variety of reasons<sup>1-6</sup>. The radioactivation of these composite materials is expected to be very low and would in fact be dominated by the activation of impurity elements<sup>1-3</sup>. These impurities most likely can be controlled to produce a truly low-activation material, especially via the chemical vapor infiltration (CVI) forming technique. Toughening mechanisms, such as matrix cracking, crack deflection, interface debonding, crack-wake bridging, and fiber pullout, provide ceramic matrix composites (CMCs) with a greater reliability against catastrophic failure processes than unreinforced ceramics<sup>7</sup>. A fundamental understanding of the mechanisms that control the lifetime of these materials is required.

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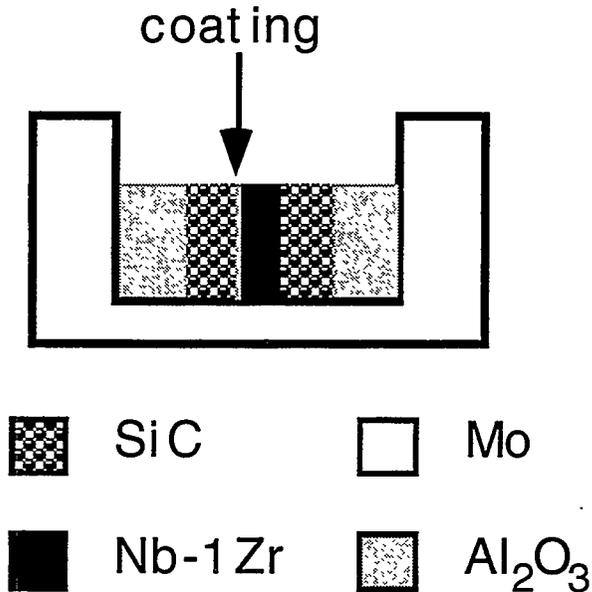


Figure 1. Schematic drawing of the fixture used for diffusion couple experiments.

Very little data for the irradiation creep of SiC is available<sup>8-10</sup>. The data indicates that the creep of SiC is enhanced by radiation and possesses a temperature insensitive regime, similar to many metals. No data exists for the irradiation creep behavior of SiC<sub>f</sub>/SiC<sub>m</sub>. Irradiation creep is one of the major processes by which the dimensional stability of structural components can be altered by radiation exposure. The thermal creep behavior of SiC<sub>f</sub>/SiC<sub>m</sub> is not very well understood, either. Therefore, experiments have been designed to measure the irradiation creep response of SiC<sub>f</sub>/SiC<sub>m</sub> composites.

The experiment designed to measure the creep of SiC<sub>f</sub>/SiC<sub>m</sub> composites under irradiation involves using a Nb-1Zr pressurized bladder in contact with, and surrounded by, a cylindrical SiC composite<sup>11</sup>. Data regarding the compatibility between Nb-1Zr (Nb-1Zr) and SiC (SiC), at elevated temperatures, are not available. Therefore, efforts were made to investigate the thermodynamic stability of Nb-1Zr and SiC and also to investigate the kinetics of possible reactions. The results of this work are presented in this report.

#### Experimental Technique

An experimental approach was used to determine the kinetic stability of an Al<sub>2</sub>O<sub>3</sub> coating with Nb-1Zr and β-SiC. β-SiC refers to the cubic polytype of SiC, also known as 3C, which composes the matrix of the SiC<sub>f</sub>/SiC<sub>m</sub> composites of interest to this study. Fixtures, procedures, and analytical methods were designed and verified for these experiments. The fixtures consisted of a molybdenum holder and alumina inserts to hold a sandwich of Nb-1Zr between two pieces of β-SiC (Fig. 1). The Nb-1Zr was the same material as that which will be used to form the pressurized bladders. The β-SiC was fabricated by chemical vapor deposition, so that it would be similar to the matrix of the composite, and supplied by Morton Advanced Materials, Woburn, MA. One side of the Nb-1Zr was coated with a 1 μm thick layer of Al<sub>2</sub>O<sub>3</sub>. The coating was deposited, at room temperature, by

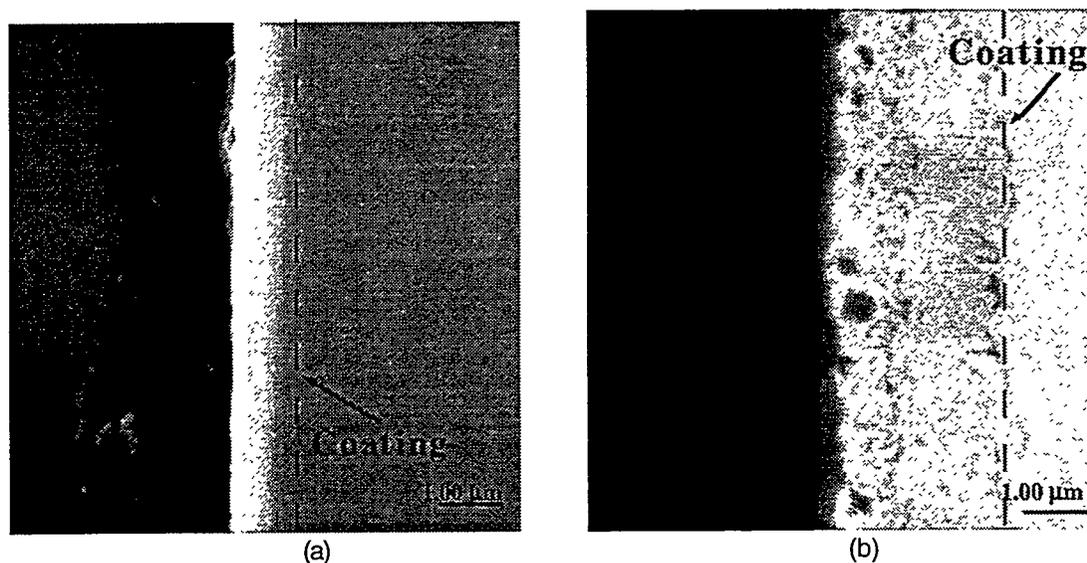


Figure 2. SEM micrograph of the  $\text{Al}_2\text{O}_3$  coating (a) before and (b) after treatment at 400 h at  $1000^\circ\text{C}$ , in flowing argon. Dashed line indicates approximate edge of coating.

electron-beam sputter deposition at PNNL. The purpose of the alumina spacers (Fig. 1) was to obtain a clamping stress on the sandwich, due to differential thermal expansion. The clamping stress was designed to be of the order of 200 MPa, or slightly higher than the maximum stress anticipated in the creep experiment. The samples and fixtures were heated for various times in a resistively heated furnace, under flowing argon gas ( $< 50 \text{ Pa O}_2$ ). The diffusion couple specimens were examined via scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and Auger electron spectroscopy (AES).

### Results

Previously<sup>11</sup>, the thermodynamic stability of Nb-1Zr and  $\beta$ -SiC was calculated at the lower end of the range of temperature of interest:  $800^\circ\text{C}$ ,  $10^5 \text{ Pa}$  total pressure, in pure helium. At this temperature, a niobium carbide ( $\text{Nb}_6\text{C}_7$ ) and a silicide ( $\text{NbSi}_2$ ) had a negative Gibbs free energy of formation, as did zirconium carbide ( $\text{ZrC}_4$ ), according to the following reaction,



The Gibbs Standard Free Energy of Reaction,  $\Delta G^\circ$ , is  $-27.2 \text{ kJ}$ . These results indicated that a diffusion barrier coating must be placed between the Nb-1Zr and the SiC to prevent a detrimental reaction from occurring during the creep experiments. Based upon the results of additional thermodynamic based calculations,  $\text{Al}_2\text{O}_3$  was selected as the most suitable coating material.

An experimental approach was used to determine the kinetics of the reactions between Nb-1Zr and SiC and to evaluate a  $1\mu\text{m}$  thick, sputter-deposited coating of  $\text{Al}_2\text{O}_3$  as a diffusion barrier coating. After heat treatment for 400 h at  $1000^\circ\text{C}$ , the alumina coating appeared much coarser, and the width of the coating was approximately  $3\mu\text{m}$  (Fig 2). Mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ , or  $2\text{Al}_2\text{O}_3\text{-SiO}_2$ ) may have formed as a reaction product between the SiC and  $\text{Al}_2\text{O}_3$  coating, or

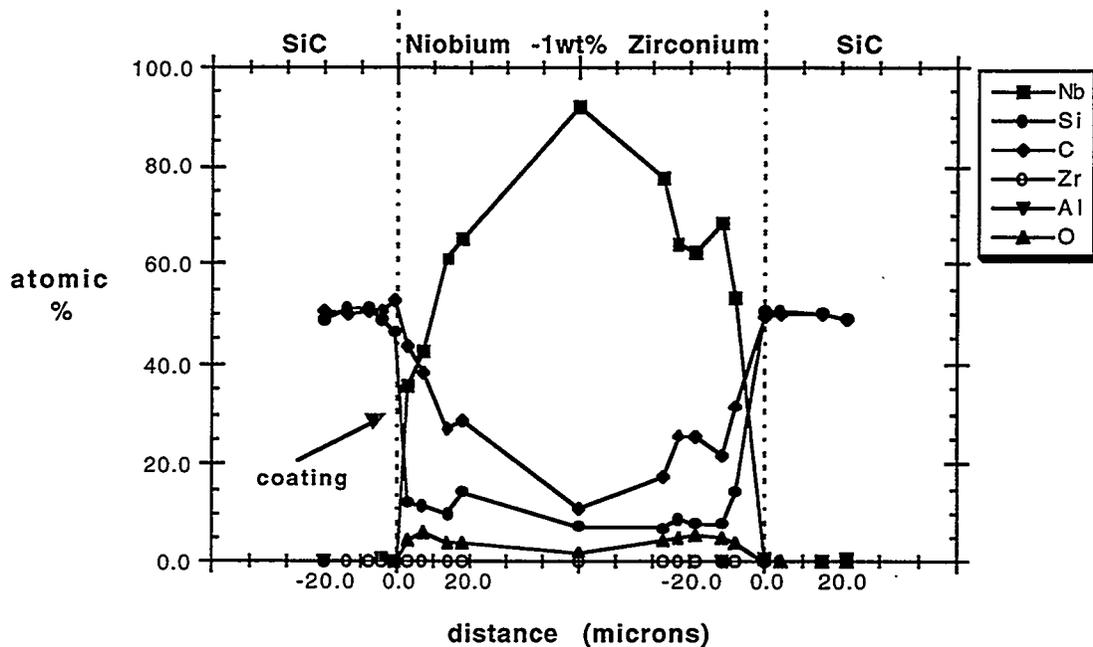


Figure 3. AES profile of a diffusion couple profile after 400 h at 1000°C.

the  $\text{Al}_2\text{O}_3$  coating may have coarsened by grain growth. Neither hypothesis has been investigated further. The temperature, 1000°C, was chosen to evaluate the highest possible temperature expected in the irradiation creep experiment. Therefore, the results of these studies would actually overestimate the rates at which diffusional processes would occur during the creep experiment.

A detailed investigation of the diffusion couple was performed with AES. Spot scans were conducted along a line crossing the interfaces between the SiC and the Nb-1Zr coated with  $\text{Al}_2\text{O}_3$  and the SiC and the uncoated Nb-1Zr. The distance between spot scan positions was 4  $\mu\text{m}$  apart. From this analysis a compositional profile was constructed (Fig. 3). The concentrations of each element are not absolute since the data has not been corrected for the various sensitivity coefficients. Nevertheless, the results indicate that there is very little interdiffusion on the side of the specimen with the coating. On the other hand, on the side without the coating silicon appears to have diffused from the SiC into the Nb-1Zr and some niobium may have diffused into the  $\beta$ -SiC. These results suggest that a reaction does take place between the Nb-1Zr and the SiC.

Additional experiments were repeated for 400 h at 1000°C, in flowing argon to confirm the previous results. AES with a distance between analysis points of 0.35-0.60  $\mu\text{m}$  was used to investigate the details of the interface between the Nb-1Zr and the SiC. Although this analysis was also only qualitative, since internal calibration of the signals was not performed, the results indicate that silicon diffuses readily from the SiC to the Nb-1Zr specimen under these conditions (Fig. 4). On the other hand, silicon (or any other element) was not detected

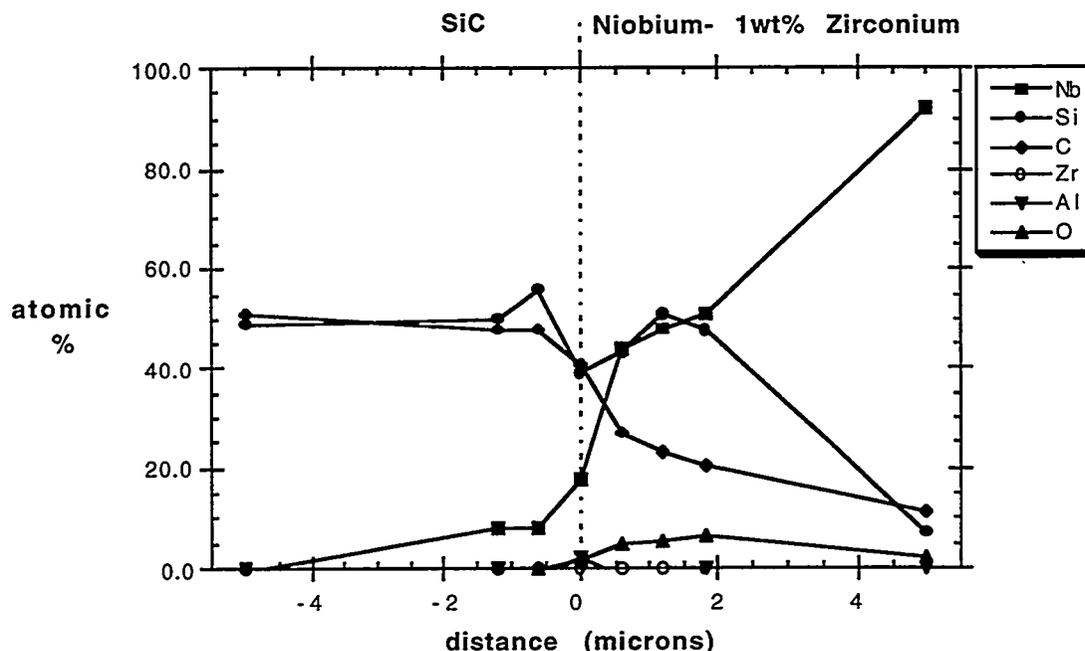


Figure 4. AES profile of a diffusion couple profile after 400 h at 1000°C, in flowing argon, showing that silicon diffuses from the SiC to the uncoated Nb-1Zr.

in higher than average concentrations in the Nb-1Zr sample that had been coated with a 1  $\mu\text{m}$  thick layer of  $\text{Al}_2\text{O}_3$ . These results confirm that SiC and Nb-1Zr are reactive under the conditions studied, and that the  $\text{Al}_2\text{O}_3$  coating is effective in preventing diffusion between the two materials.

## CONCLUSIONS

The thermochemical stability of Nb-1Zr and SiC was analyzed via thermodynamic calculations and diffusion couple experiments. Both techniques showed that the two materials were reactive under the conditions studied. A technique to deposit an  $\text{Al}_2\text{O}_3$  diffusion barrier coating on Nb-1Zr was developed. Although the coating coarsened, under the conditions investigated, the coating did not allow interdiffusion to occur. On the other hand, it appeared that, under the same conditions, the uncoated Nb-1Zr reacted with SiC. Therefore, a sputter-deposited  $\text{Al}_2\text{O}_3$  diffusion barrier coating is highly recommended for any irradiation creep experiments involving this design concept.

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