Interdiffusion in the Carbides of the Nb-C System

J. WOODFORD and Y.A. CHANG

Interdiffusion coefficients in Nb2C and NbC1−x were measured using bulk diffusion couples in the temperature range from 1400 °C to 1700 °C. Marker experiments were used to show that carbon is the only component undergoing significant diffusion in both carbides. Carbon concentrations were measured by difference using electron probe microanalysis, and interdiffusion coefficients were taken from Boltzmann–Matano analyses of the resulting concentration profiles. This analysis clearly showed that, in NbC1−x, interdiffusion coefficient varies with carbon concentration, and is expressed by

\[ D(NbC_{1-x}) = 3.84 \times 10^{-9} \exp(23.24x) \exp\left(-\frac{28,450 \pm 850}{T}\right) \text{ m}^2/\text{s} \]

where \( x \) is the site fraction of vacancies on the carbon sublattice. The interdiffusion coefficient in Nb2C is given by

\[ D(Nb_2C) = 2.04 \pm 0.57 \times 10^{-9} \exp\left(-\frac{35,520 \pm 2190}{T}\right) \text{ m}^2/\text{s} \]

Parabolic layer growth coefficients were estimated from the Nb|C diffusion couples as well. They are given by

\[ K_p(NbC) = 2.65 \times 10^{-7} \exp\left(-\frac{37,600 \pm 1400}{T}\right) \text{ m}^2/\text{s} \]

\[ K_p(Nb_2C) = 1.57 \times 10^{-5} \exp\left(-\frac{36,400 \pm 3100}{T}\right) \text{ m}^2/\text{s} \]

The value of \( D \) in NbC1−x was found to be consistent with literature values for the tracer diffusivity of C in NbC1−x via the thermodynamic factor, which was determined in two ways.

I. INTRODUCTION

In an effort to enhance the high-temperature stability of a Ti-alloy/Al2O3 fiber metal-matrix composite, we have been evaluating different fiber-coating schemes.[1] One such scheme is the sequence Al2O3 fiber|C|Nb metal|Y2O3|Ti-alloy matrix. We are, thus, interested in the kinetic stability of the NbC interface; this is best determined by finding the diffusivity of carbon in Nb2C and NbC1−x.

Several researchers[2,3,4] have prepared excellent reviews of the properties of the different phases in the Nb-C system. A brief overview of some of the intermediate phases will now be given. The Nb sublattice in Nb2C has the hexagonal close-packed structure, with C atoms occupying some of the octahedral interstitial sites. Storms[3] reported a possible low-temperature orthorhombic form, but further research[3] has not confirmed this. At the temperatures covered in the present study, NbC has a narrow range of solubility. The NaCl structures is in NbC1−x, with C atoms occupying octahedral sites in a face-entered cube Nb sublattice; \( x \), the site fraction of vacancies on the C sublattice, can be as high as 0.3 over the temperatures considered here[6] (Figure 1). Although an \( \epsilon \)-carbide near that composition was observed by Crane and Osterrm, it is not clear whether the \( \epsilon \)-carbide is a stable phase. The work of Viswanadham and Wert[5] suggests that it is not, and Storms and Krikorian[6] also failed to find such a phase. The phase diagram in Reference 6 shows it as a tentative phase.

Huang[10] has successfully modeled the major features of the Nb-C phase diagram (Figure 2). For the purposes of the model, the third carbide phase was ignored, as were all of the order-disorder transitions. At the temperatures of interest in this study, the only difference between the model results and the phase diagram given in Reference 6 was the shape of the low-carbon boundary on the NbC1−x phase field, about which there is some doubt.

Figure 3 contains plots of previously determined interdiffusion coefficients in NbC1−x.[11,12,13] All of these were determined by parabolic analyses of NbC1−x layer growth in NbC bulk diffusion couples and, therefore, represent average values for the interdiffusion coefficient \( D \) across the width of the NbC1−x phase field. Brizes et al.[12] were able to obtain a partial carbon concentration profile in the
Fig. 1—The Nb-C phase diagram.

Fig. 2—Nb-C phase diagram.

Fig. 3—Plot of literature data for interdiffusion coefficient in NbC\textsubscript{1-x}. Numbers denote the reference for the given data. Data are included from the present study at the extremes of concentration.

Fig. 4—$^{14}$C and $^{95}$Nb tracer data in NbC\textsubscript{1-x} from the literature. Each set of data is labeled with a reference number and either mole fraction carbon (for $^{14}$C tracers) or “Nb” and mole fraction carbon (for $^{95}$Nb tracers). Data obtained from the present study and Huang’s thermodynamic factors are also plotted.

NbC\textsubscript{1-x} layer by using X-ray diffraction to measure lattice parameter variation with position. Powder samples were ground off of the NbC\textsubscript{1-x} layer and analyzed. The lattice parameter was then correlated with carbon concentration. On the basis of the partial concentration profile, it was predicted that $D$ should decrease with an increasing carbon concentration in NbC\textsubscript{1-x}. This behavior is also exhibited by the $^{14}$C tracer diffusivities and was observed by van Loo and Bastin in TiC\textsubscript{1-x}.

Yu and Davis\textsuperscript{[15]} found that carbon tracer diffusivity in single-crystal NbC\textsubscript{1-x} varied considerably with carbon concentration, even undergoing a significant change in activation energy between different values of x. A number of other researchers\textsuperscript{[16-20]} have measured $^{14}$C and $^{95}$Nb tracer diffusivities in polycrystalline NbC\textsubscript{1-x} and Nb\textsubscript{2}C, and the NbC\textsubscript{1-x} results are plotted in Figure 4. Most of the data are quite consistent. The exception is the work of Gel’d and Liubimov,\textsuperscript{[18]} who appear to have consistently underestimated activation energies relative to the other investigators. This may be attributed to their use of sintered materials with void densities described to be on the order of 10 to 15 pct, leading to the possibility of rapid surface diffusion paths within the material.

Based upon their $^{14}$C tracer results, Yu and Davis\textsuperscript{[15]} postulated two different mechanisms for carbon diffusion in NbC\textsubscript{1-x}. At lower carbon concentrations, they claimed that carbon atoms diffuse directly to adjacent vacant sites \textit{via} intervening vacancies on the Nb sublattice (Figure 5). At higher carbon concentrations, they proposed a mechanism in which a carbon atom diffuses to a vacant site in the (110) direction \textit{via} a two-step process: first, a shorter (111) jump to an unoccupied tetrahedral site on the Nb sublattice followed by an immediate (111) jump to a vacant site on the C sublattice (Figure 6). In support of their choice of mechanisms, they point out that the Nb vacancy formation energy, 253 kJ/mol, determined by Storms \textit{et al.}\textsuperscript{[21]} is similar.