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Self-diffusion of transition metals in (Ti,W,Cr)B_2 solid solutions

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The self-diffusivities of Ti and Cr were determined in ($Ti_x W_y Cr_z$)B_2 ceramics which are a model system for the development of in-situ reinforced boride ceramics by tailored precipitate formation. Homogeneous solid solutions of composition ($Ti_{0.3}W_{0.5}Cr_{0.2}$)B_2, ($Ti_{0.5}W_{0.3}Cr_{0.2}$)B_2, and ($Ti_{0.4}W_{0.5}Cr_{0.1}$)B_2 were studied in the temperature interval between 1100 and 1500°C, using ion implanted stable ^{49}Ti and ^{54}Cr isotopes and secondary ion mass spectrometry (SIMS). The diffusivities of each element obey an Arrhenius law. The Cr diffusivities of all three compounds can be fitted to a unique Arrhenius line with an activation enthalpy of 3.5 eV and a low pre-exponential factor of 2×10^{-7} m^2/s. The Ti diffusivities are smaller by 1–2 orders of magnitude than the Cr diffusivities, showing, however, higher activation enthalpies of 3.9 eV and approximately the same pre-exponential factors. The consequences of the results for the formation kinetics of precipitates in supersaturated ($Ti_x W_y Cr_z$)B_2 solid solutions are discussed. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

The system TiB_2-WB_2-CrB_2 is a model system for the investigation of in-situ reinforced transition metal boride ceramics, which are expected to show improved toughness and creep resistance in comparison to TiB_2 [1–7]. The compound TiB_2 forms homogeneous solid solutions with WBi_2 and CrB_2 over a wide composition range at high temperatures (1600°C–2000°C) while at temperatures below 1600°C a miscibility gap occurs [1, 2]. This enables the de-mixing of a supersaturated host matrix and the formation of tungsten rich W_2B_5 precipitates embedded in a ($Ti_xW_yCr_z$) host matrix. Under certain conditions the precipitates form elongated particles with a high aspect ratio [1], which are well suited for the reinforcement of boride ceramics. In order to produce reinforced ceramics with a tailored microstructure, it is of importance to understand and to quantitatively describe the diffusion controlled changes which occur during precipitation and grain growth. The knowledge of the material transport mechanisms offers ways to optimise microstructures and consequently materials properties. Up to now, only the very basic principles are known on the atomic transport properties of these materials. Measurements on the self-diffusion of Ti and Cr in a precipitated two-phase sample with nominal composition ($Ti_{0.3}W_{0.5}Cr_{0.2}$)B_2 were recently carried out [4]. This material was separated into a matrix phase of composition ($Ti_{0.4}W_{0.3}Cr_{0.3}$)B_2 with TiB_2 structure and a precipitation phase of approximate com-

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TABLE I Chemical composition of transition metals, lattice constants, activation enthalpy of diffusion, and pre-exponential factor for different $(Ti_xW_yCr_z)B_2$ compositions. The error attributed to the chemical composition is typically 10%, to the lattice constants about ± 0.005 Å, and to $\ln(D_0)$ about ±4.

Material	Transition metal composition (at.%)			Lattice constants(Å)	ΔH^{Ti} (eV)	D_0^{Ti} (m^2/s)	ΔH^{Cr}(eV)	D_0^{Cr} (m^2/s)
	Ti	W	Cr					
$(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$	31.3	48.9	19.0	$a = 3.019$, $c = 3.155$	3.9 ± 0.6	5×10^{-7}	3.5 ± 0.5	2×10^{-7}
$(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$	47.7	32.1	20.2	$a = 3.017$, $c = 3.166$	3.9 ± 0.5	9×10^{-8}	3.5 ± 0.5	2×10^{-7}
$(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$	40.0	49.5	10.5	$a = 3.038$, $c = 3.176$	3.9 ± 0.5	9×10^{-8}	3.5 ± 0.5	2×10^{-7}

position $(Ti_{0.03}W_{0.92}Cr_{0.05})B_2$ crystallising in the W_2B_5 structure with a phase content of about 30%.

In the present study now, investigations on the self-diffusion of Ti and Cr in homogeneous diboride solid solutions with different transition metal concentrations are carried out in order to investigate the influence of the Cr and W concentration on diffusion. Three types of samples with composition $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$, $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$, and $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ were characterised. In order to quantify the low tracer diffusivities of the constituent elements a high spatial resolution in depth profiling is necessary. Thus, the diffusion measurements were performed with ion implanted stable isotopes as tracers and secondary ion mass spectrometry (SIMS).

2. Experimental procedure

The samples were produced by reaction sintering of TiB_2, WB_2, and CrB_2 powders (H. C. STARCK, Germany). The reaction sintering process was carried out in a uniaxial graphite hot press under a pressure of 60 MPa at 1800°C for 30 min under argon atmosphere, according to optimised conditions. Afterwards, the specimens were homogenised at 2000°C for 8 h at ambient pressure under argon atmosphere. The samples were further examined by X-ray diffractometry (XRD), secondary electron microscopy (SEM) and electron beam micro analysis (EBMA/EDX) in order to characterise phase content and microstructure. The XRD investigations were carried out with a SIEMENS D5000/Kristalloflex diffractometer in the $\theta/2\theta$ modus using CoK_α radiation (0.1789 nm) at 40 kV and 40 mA. The SEM experiments were made on a CamScan 44 apparatus with a tungsten cathode and the EBMA experiments on a Cameca SX-100 apparatus with an EDX detector operating with an acceleration voltage of 20 kV.

Three types of samples with nominal composition $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$, $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$, and $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ were prepared. The composition of the different samples was chosen such that the Ti/Cr ratio and the Ti/W ratio was varied in order to investigate the influence of these elements on the diffusion behaviour. For the diffusion measurements small slaps (about $8 \times 8 \times 2$ mm^3) were cut from the interior of the hot pressed samples, polished with diamond paste down to a minimum particle size of 1 μm, and cleaned with ethanol. The so prepared samples were implanted with a mass separated and scanned 54Cr$^+$ (5×10^{15} ions/cm^2) or $^{49}Ti^+$ (1×10^{16} ions/cm^2 ion beam of 50 keV. After tracer deposition, the implanted samples were diffusion annealed in the temperature range between 1100 and 1500°C in argon atmosphere (1 bar) for times between 20 min and 100 h. Tracer depth profiles (implantation and diffusion profiles) were measured by secondary ion mass spectrometry (VG SIMS-Lab), using a scanned O_2^+-ion primary beam (7 keV, 100 nA), with a quadrupole mass spectrometer. Depth calibration was obtained by measuring the crater depth with a surface profilometer (Alphastep 500, TENCOR), assuming a constant sputter rate.

3. Results

Investigations with XRD, REM, and EDX revealed that all three types of samples were homogeneous polycrystalline $(Ti_xW_yCr_z)B_2$ solid solutions, which crystallised in the TiB_2 structure with space group P6/mmm [5]. The chemical composition of the transition metals determined by EDX and the lattice constants determined from X-ray diffractograms by refinement with the program Powder Cell for Windows 2.4 (PCW) [8] are given in Table I. After diffusion annealing between 1100 and 1500°C all samples were re-investigated with XRD to ensure that no precipitation phase had been formed. Significant precipitation first occurred during annealing at 1550°C for several hours.

In Figs. 1 and 2 typical depth profiles of ^{49}Ti and ^{54}Cr are exemplarily shown before and after annealing at elevated temperatures. All diffusion profiles show a broadening of the Gaussian implantation profile due to diffusion of the corresponding elements into the solid state. The diffusivities, D, are obtained from the diffusion profiles by least-squares fitting the data to the following solution of Fick's second law [9]:

$$c(x,t) = \frac{A}{\sqrt{2\pi(\Delta R_p^2 + 2Dt)}} \exp\left(-\frac{(x-R_p)^2}{2\Delta R_p^2 + 4Dt}\right). \tag{1}$$

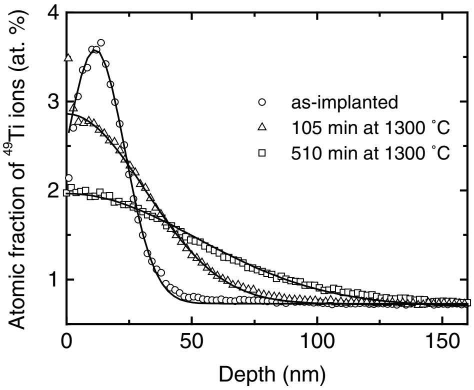

Figure 1 ^{49}Ti isotope depth profiles for ion implanted $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ ceramics as a function of annealing time at 1300°C. Not all symbols are shown for clarity. The solid lines are least-squares fits of the experimental data to Equation (1).

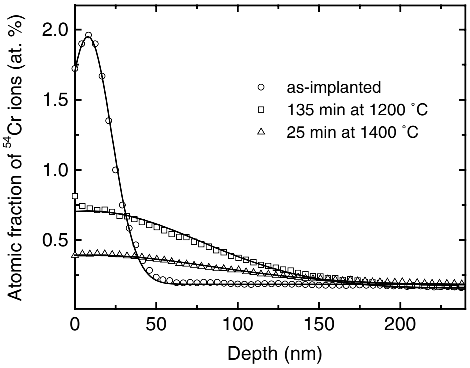

Figure 2 ^{54}Cr isotope depth profiles for ion implanted $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ ceramics at 1200 and 1400°C. Not all symbols are shown for clarity. The solid lines are least-squares fits of the experimental data to Equation (1).

Here, c is the tracer concentration, t is the diffusion time, A is the implanted dose, R_p is the projected range, and ΔR_p is the straggle of the implantation profile. Fig. 3 shows the self-diffusivities as a function of reciprocal temperature as obtained from the depth profiles. The diffusivities of both elements can be described by an Arrhenius relation according to

$$D = D_0^i \exp\left(-\frac{\Delta H^i}{k_B T}\right) \qquad (2)$$

where D_0^i denotes the pre-exponential factor and ΔH^i the activation enthalpy of diffusion for element i, and k_B is the Boltzmann constant. The determined activation enthalpies and the pre-exponential factors are given in Table I.

Fig. 3 and Table I exhibit that the diffusivities of Ti in $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$ and in $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ are lowest and are also identical, if compared for the same temperature. Consequently, they were fitted with a unique Arrhenius straight line with an activation enthalpy of $\Delta H^{Ti} = 3.9 \pm 0.5$ eV and a pre-exponential factor of $D_0^{Ti} = 9 \times 10^{-8}$ m^2/s. However, the Ti diffusivities of the $(Ti_{0.3}W_{0.2}Cr_{0.2})B_2$ compound are slightly, but not significantly enhanced (about a factor of five), leading to the parameters $\Delta H^{Ti} = 3.9 \pm 0.6$ eV and $D_0^{Ti} = 5 \times 10^{-7}$ m^2/s. The Cr diffusivities of all three compounds are about 1–2 orders of magnitude higher than those of Ti and can be fitted with a unique Arrhenius line with $\Delta H^{Cr} = 3.5 \pm 0.5$ eV and $D_0^{Cr} = 2 \times 10^{-7}$ m^2/s. It has to be noted, that a fit of the Cr diffusivities for each material separately leads to the same parameters within error limits.

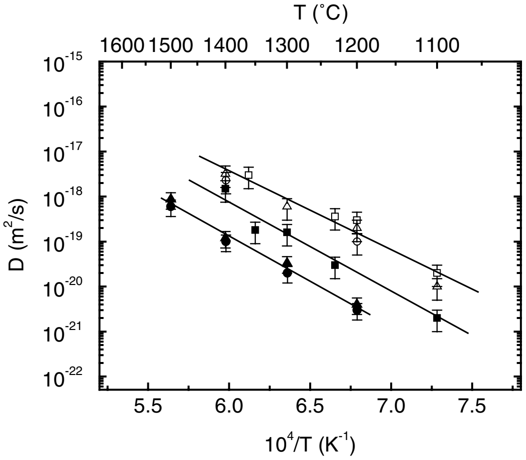

Figure 3 Ti and Cr diffusivities as a function of reciprocal temperature in transition metal diboride ceramics. Open symbols refer to Cr diffusivities and closed symbols to Ti diffusivities, respectively, in $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ (circles), $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ (squares), and $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$ (triangles).

In Fig. 4 the Ti and Cr diffusivities of the homogeneous $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ solid solution are compared to the diffusivities obtained for a two-phase compound with nominal composition $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$, which was investigated in Ref. [5]. This type of material was annealed for 6 h at a temperature of 1600°C prior to the diffusion experiments, which led to the precipitation of about 30% W_2B_5 secondary phase. During the precipitation process the matrix is depleted in tungsten and an average matrix composition of $(Ti_{0.4}W_{0.3}Cr_{0.3})B_2$ is established. The diffusivities given in Fig. 4 can be attributed to this matrix phase, as recently shown [5]. As obvious, the diffusivities of homogeneous and precipitated ceramics are identical within error limits for each element.

4. Discussion

An extrapolation of the measured Cr and Ti diffusivities to the melting point of the ceramics at about 2100°C [1] yields relatively low values of about 10^{-15}–10^{-16} m^2/s at T_m. This is more typical for semiconductors than for metals [10] and reflects the influence of covalent bonding in these materials. The empirical ratio $\Delta H/T_m \approx 1.5 \times 10^{-3}$ eV/K is, however, in good agreement with typical values obtained for metals [10]. This shows that the activation enthalpy is not anomalously low in these materials. In contrast, the pre-exponential factors in the order of 10^{-7}–10^{-8} m^2/s are relatively low in comparison to those commonly found for self-diffusion

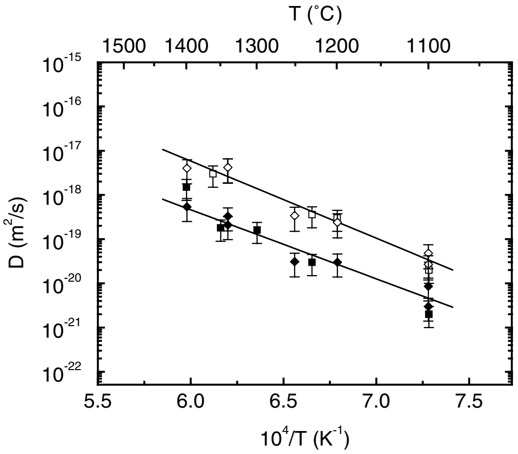

Figure 4 Ti and Cr diffusivities as a function of reciprocal temperature in homogenous $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ (squares) and in a two-phase sample with nominal composition $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ (diamonds), composed of a $(Ti_{0.4}W_{0.3}Cr_{0.3})B_2$ matrix phase and a $(Ti_{0.03}W_{0.92}Cr_{0.05})B_2$ precipitation phase (after Ref. [5]). Open symbols refer to Cr diffusivities and closed symbols to Ti diffusivities, respectively.

in metals (typically 10^{-4}–10^{-6} m^2/s [10]). Using the relation $D_0 = fa^2\nu_0 \exp(\Delta S/k_B)$ [10], where $f \approx 1$ is the correlation factor, $a \approx 0.3$ nm the jump distance, $\nu_o \approx 10^{12}$ s^{-1} the effective attempt frequency, and k_B the Boltzmann constant, the entropy of diffusion can be calculated to be about $\Delta S \approx 0$ for the present materials. Considering the error limits which can be attributed to ΔS of ± 4 k_B (Table I), this value is small but not unreasonable. However, the relatively small entropy change seems to be the reason for the low diffusivities at T_m and can be attributed to the fact that the characteristic vibration frequencies of the lattice are not much disturbed during diffusion and point defect formation.

Information on the atomic radii of the transition metals can be deduced from the lattice constants given in Table I. Using the compound $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ as a reference material, the substitution of Cr atoms by Ti atoms leads to an increase of the a and c lattice constants for the $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ compound ($\Delta a/a \approx \Delta c/c = 6 \times 10^{-3}$). This is a strong indication that the atomic radius of chromium is smaller than the atomic radius of titanium in these compounds. In contrast, the lattice constants of the compounds $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ and $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$ are nearly the same within error limits, which is a hint that the atomic radii of tungsten and titanium are very close together. Using these results for the interpretation of the diffusion data, the enhanced Cr diffusion in comparison to the Ti diffusion is very probably due to the smaller atomic radius of chromium. The Cr atoms can migrate more easily on the transition metal sublattice as indicated by the smaller enthalpy of diffusion. However the slightly enhanced diffusion of Ti in $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$, compared to the other compounds, is unexplained up to now. Unfortunately, the diffusion of tungsten could not be measured with the present method, because the natural abundance of the rarest tungsten isotope, ^{180}W, of only 0.13% is not sufficient to produce a measurable isotope profile by ion implantation. Nevertheless, the similarity of the atomic radii of titanium and tungsten suggests that both elements have also similar diffusivities.

From the present results the following conclusions can be drawn on the formation kinetics of W_2B_5 precipitates in supersaturated $(Ti_xW_yCr_z)B_2$: (a) The observation that the Ti diffusivities are lower than the Cr diffusivities for all three compounds shows that the latter element cannot be the controlling species in diffusional growth during precipitation. Following the above argumentation on W diffusion, Ti can be assumed to be the rate controlling species. (b) The fact that indicates the diffusivities of all three compounds are identical (in case of Cr) or nearly identical (in case of Ti) indicates that in a first approximation the diffusivities are concentration independent in the composition range spanned by the three materials. Since for diffusion controlled growth processes of precipitated particles the relation $d_p \sim D^{1/2}$ is valid (d_p is the particle diameter), a difference of five in the diffusivities is reflected only very weakly in the growth rates. This means the rate constants of crystallite growth should be almost identical for the three materials. (c) The identical diffusivities found for the $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ single phase solid solutions and for the two-phase ceramic show that the diffusivities do not change significantly during the precipitation process, neither if the matrix composition changes from $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$ to about $(Ti_{0.4}W_{0.3}Cr_{0.3})B_2$. As a consequence for the modelling of the precipitation process, the tracer diffusivities can be assumed to be constant during precipitation at a given temperature.

5. Summary

In the present study the self-diffusivities of Ti and Cr in $(Ti_xW_yCr_z)B_2$ materials with compositions $(Ti_{0.3}W_{0.5}Cr_{0.2})B_2$, $(Ti_{0.5}W_{0.3}Cr_{0.2})B_2$, and $(Ti_{0.4}W_{0.5}Cr_{0.1})B_2$ were investigated using ion implanted stable ^{49}Ti and ^{54}Cr isotopes and secondary ion mass spectrometry (SIMS). The Cr diffusivities of all three compounds were found to be faster than the Ti diffusivities by 1–2 orders of magnitude in the whole temperature range investigated. The diffusivities of each element can be described by an Arrhenius law, where the Cr diffusivities of all compounds can be fitted with a unique Arrhenius line with an activation enthalpy of 3.5 eV and a low pre-exponential factor of 2×10^{-7} m^2/s. The Ti diffusivities exhibit a larger activation enthalpy of 3.9 eV for approximately the same pre-exponential factor. The lower diffusivities of titanium are attributed to a larger atomic radius of Ti in comparison to Cr. Since the diffusion controlled kinetics of precipitate formation in supersaturated $(Ti_xW_yCr_z)B_2$ solid solutions is important for the improvement of fracture toughness of boride ceramics by in-situ reinforcement, the following conclusion are drawn from the present diffusion measurements: First, the element chromium can be excluded as the species controlling the crystallite growth during precipitation. Second, the diffusion controlled growth processes during precipitation should not depend on chemical composition in the composition range spanned by the three materials investigated, and third, the diffusivities do not change during precipitate formation.

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