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***In situ* transmission electron microscopy studies of the kinetics of Pt-Mo alloy diffusion in ZrB₂ thin films**

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Using *in situ* high-temperature (1073–1173 K) transmission electron microscopy, we investigated the thermal stability of Pt and Mo in contact with polycrystalline ZrB₂ thin films deposited on Al₂O₃(0001). During annealing, we observed the diffusion of cubic-structured Pt_{1-x}Mo_x (with $x = 0.2 \pm 0.1$) along the length of the ZrB₂ layer. From the time-dependent increase in diffusion lengths, we determined that the Pt_{1-x}Mo_x does not react with ZrB₂, but diffuses along the surface with a constant temperature-dependent velocity. We identify the rate-limiting step controlling the observed phenomenon as the flux of Mo atoms with an associated activation barrier of 3.8 ± 0.5 eV. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4820581>]

Fabrication of advanced structural materials systems such as thermal barrier coatings^{1–4} and ultra-high temperature ceramic^{5–7} components often requires joining or sintering of dissimilar materials. For example, refractory oxides are bonded to metallic super alloys in thermal barrier coatings, and sintered composites of refractory borides⁸ and carbides⁹ are attractive for aerospace applications. The common methods employed to improve the wettability and adhesion at the heterogeneous ceramic-ceramic and metal-ceramic interfaces involve physical and chemical modification of the interfaces via deposition of a low-melting and/or a reactive metal.^{10,11} Given that the operation life-time and performance of any of these structural materials systems depend on the thermo-mechanical and chemical stabilities of the interfaces, a fundamental knowledge of the interfacial thermodynamics and reaction-diffusion kinetics is valuable. Here, we focus on the thermal stability of ZrB₂ in contact with metals such as Pt and Mo.

Motivation for the present study stems from the fact that refractory borides such as ZrB₂ and related alloys are used in airframe leading edges and reentry vehicles due to their ultra-high melting temperatures (>3000 K) and excellent high-temperature strength.^{6,12} Typically, these structural components are prepared out of ceramic powders, which are mixed with metals or metal silicides to promote sintering and to enhance their functionality.^{8,11,13–19} Growth and characterization of ZrB₂ thin films are also of interest for potential applications as decorative coatings and diffusion barriers in microelectronics.^{20,21}

In this letter, we report results from *in situ* transmission electron microscopy (TEM) studies of thermal stability of ZrB₂ thin films in contact with Pt and Mo. Cross-sectional TEM (XTEM) samples were prepared using focused ion beam (FIB) milling of polycrystalline ZrB₂ thin films sputter-deposited on Al₂O₃(0001) substrates and attached to

Mo TEM grids using Pt. *In situ* TEM images, selected area electron diffraction (SAED) patterns, and electron energy loss spectra (EELS) were acquired during annealing at temperatures T_a up to 1173 K. At $T_a > 1173$ K, we observe changes in the TEM image contrast corresponding to the formation of an interface in the ZrB₂ layer. We find that this interface moves unilaterally along the film away from the end of the sample attached to the TEM grid at a constant temperature-dependent velocity. Using a combination of SAED, EELS, and energy dispersive spectroscopy (EDS) data, we identify the diffusing material as face-centered-cubic (*fcc*) Pt_{1-x}Mo_x alloy with $x = 0.2 \pm 0.1$. And, the activation barrier associated with this process is 3.8 ± 0.5 eV. Based upon our results and the discussion in the following paragraphs, we suggest that the rate-limiting step controlling the observed Pt_{1-x}Mo_x alloy transport along the ZrB₂ thin film is the flux of Mo atoms.

All our experiments are carried out on electron-transparent XTEM samples of ZrB₂/Al₂O₃(0001). Polycrystalline ZrB₂ layers, ~85-nm-thick, are grown on Al₂O₃(0001) at 773 K by magnetically unbalanced magnetron sputter deposition from a stoichiometric ZrB₂ target (99.5% purity and 150 mm in diameter) using Ar (99.999% purity) discharge in a modified Leybold-Univex 300 system (base pressure $\sim 7.5 \times 10^{-7}$ Torr) equipped with a circular unbalanced planar-magnetron (152.4 mm in diameter, Gencoa PP 150). The substrates are centered parallel to the target and separated by 9 cm, the Ar pressure is 3 mTorr, and the target power density is 3.5 W cm^{-2} yielding a ZrB₂ deposition rate of 0.56 nm s^{-1} . The incident metal J_{Zr} and ion J_{Ar+} fluxes and the ion energy E_{Ar+} bombarding the growing film are maintained constant such that $J_{Ar+}/J_{Zr} = 0.6$ and $E_{Ar+} = 30 \text{ eV}$. The deposition system and the general film growth conditions are described in more detail in Refs. 22 and 23.

XTEM specimens are prepared via FIB milling using Ga⁺ ions in a FEI Nova 600 Nanolab DualBeam FIB system equipped with a scanning electron microscope (SEM) and facilities for electron- and ion- beam induced deposition of

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Pt, W, and C. Prior to milling, the sample surface is first covered with a thin (≈ 120 nm) film of amorphous carbon deposited using 5 kV and 6.3 nA electron beams to minimize Ga^+ irradiation induced damage to the sample surface. Additional carbon layers up to a nominal thickness of $1.5\ \mu\text{m}$ are deposited using 30 kV and 0.3 nA Ga^+ ion beams. After Ga^+ ion milling, the sample is removed from the substrate and attached *in situ* in the FIB to a molybdenum lift-out TEM grid by ion-beam-assisted deposition of platinum from trimethyl platinum ($\text{C}_9\text{H}_{16}\text{Pt}$), a metalorganic precursor. Using EDS inside a FEI Nova 230 SEM, the composition of bare TEM grid is found to be 100 at. % Mo and that of FIB-deposited Pt to be ~ 58 at. % Pt and ~ 42 at. % Ga. Final thinning of the $\text{ZrB}_2/\text{Al}_2\text{O}_3(0001)$ sample to electron transparency is carried out using 10 kV Ga^+ beams. Fig. 1(a) is a typical SEM image of the as-prepared sample showing the overall sample geometry.

The XTEM sample is mounted in a Gatan 652 double-tilt heating holder and air-transferred into a 200 kV, LaB₆, Philips CM20ST TEM (base pressure $\sim 10^{-7}$ Torr) for initial characterization. The sample is heated over a period of 3 h to $T_a = 773$ K in intervals of 100 K and held at each T_a for approximately 20 min. This procedure helps remove volatile adsorbates and Ga incorporated during FIB milling from the sample surface. Previous studies have shown that FIB-induced Ga segregates onto the surface in the form of spherical droplets.^{24–29} Within an hour of annealing at $T_a \sim 773$ K, most of the smaller Ga droplets disappear from the transparent regions of the sample via Ostwald ripening and are absorbed by larger droplets located at the thicker ends of the sample.³⁰

In situ annealing at higher temperatures T_a between 1073 and 1173 K are carried out in the double C_s -corrected Linköping FEI 80-300 Titan³ scanning TEM (STEM) equipped with EDS and EELS spectrometers. In a typical experiment, the desired temperature is set and after reaching the set T_a , the sample is allowed to thermally equilibrate with its local environment before collecting the data. This occurs within 15 min at which point the thermal drift in the images is minimal (~ 1 nm/s at T_a between 1073 K and 1173 K). The temperatures are measured by a thermocouple built into the holder and is expected to be accurate to within ± 50 K.

TEM images are acquired in bright-field mode at regular intervals of 1 s and 5 s during annealing at $T_a \geq$ and < 1123 K, respectively. Typical image widths and pixel resolutions varied between 100 and 500 nm and 0.5 and 1.0 nm/pixel,

respectively. TEM image magnifications ($13\text{ k}\times$ – $44\text{ k}\times$) and image acquisition times (0.1–0.5 s) were varied to check for the electron beam induced damage in the sample. We do not observe any such effects. SAED and EELS measurements are collected during annealing at high temperatures and also after cooling the sample to room temperature. EDS data are obtained at room temperature from selected points and along the lines of interest on the sample. TEM images are processed using the Gatan Digital Micrograph software. EDS and EELS are analyzed using the FEI Tecnai Imaging and Analysis software.

Figure 1(b) is a low-magnification STEM image of the ZrB_2 thin film supported by $\text{Al}_2\text{O}_3(0001)$ at the bottom and covered with amorphous carbon at the top. In this imaging mode, the ZrB_2 and the top C layers appear brighter and darker than the Al_2O_3 substrate due to mass contrast mechanism. SAED patterns acquired from the ZrB_2 layers indicate that the film is polycrystalline exhibiting the expected hexagonal structure. At the ZrB_2 - Al_2O_3 interface, we note the presence of an 8-nm-thick layer that is darker in contrast compared to Al_2O_3 . From the recorded EELS data, we find that this interfacial layer is primarily composed of B and O. Complementary SAED patterns acquired from the interface indicated that the layer is amorphous. Based upon these results, we suggest that the interfacial layer is amorphous boron oxide. While the reasons leading to the formation of boron oxide at the interface are not clear, it is likely that this layer is a consequence of sputter deposition of ZrB_2 ; similar results have also been reported during the growth of ZrB_2 on Si and SiC substrates.³¹

Figures 2(a)–2(c) are representative bright-field TEM images acquired from the ZrB_2 thin film sample during annealing at $T_a = 1123$ K as a function of time t_a . We observe a darker contrast develop along the ZrB_2 film near the end of the sample attached to the TEM grid. We find that the length L of this contrast increases with increasing t_a . This behavior is typical of all our annealing experiments carried out at T_a between 1073 and 1123 K.³² The observed phenomenon is qualitatively similar to silicidation of nanowires in contact with a metal.^{33,34} As a means to identify the origin of this contrast, SAED patterns were collected during annealing and EDS data after cooling the sample to room temperature. Figs. 2(d) and 2(e) show a bright-field TEM image and corresponding SAED pattern, respectively, acquired from the sample during annealing at $T_a = 1123$ K. Interestingly, we observe diffraction spots characteristic of an *fcc* structure and are nearly lattice-matched with Pt. In addition, we also

FIG. 1. Typical (a) SEM and (b) STEM images of a XTEM sample prepared via FIB milling and attached to a molybdenum grid by FIB deposited platinum. The STEM image in (b) shows amorphous C layer with implanted Ga, ZrB_2 layer, a thin boron oxide layer, and Al_2O_3 substrate from top to bottom, respectively.

FIG. 2. (a)–(c) Representative bright-field TEM images acquired from ZrB₂/Al₂O₃(0001) sample as a function of time t_a during annealing at temperature $T_a = 1123$ K. The ZrB₂ film surface is covered with amorphous carbon deposited prior to FIB milling and helps prevent FIB damage of the sample. The images also reveal the presence of an amorphous boron oxide layer at the ZrB₂-Al₂O₃ interface, likely formed during sputter deposition of the ZrB₂ thin film. The darker contrast visible in the images is due to the diffusing Pt-Mo alloy whose length L along the ZrB₂ film increases with time. (d) Higher magnification TEM image of the same sample at 1123 K. (e) Selected area electron diffraction pattern of the region shown in Fig. 2(d) along the Pt[110] zone axis. The black dashed circles highlight the diffraction spots due to face-centered cubic lattice. The green dotted and solid circles indicate ZrB₂ {00.1} and {11.1} planes, respectively. (f) Energy dispersive spectral line intensities of Pt, Mo, Al, and O acquired along the solid green line across the ZrB₂-Al₂O₃ interface shown in the associated STEM image of the sample.

find fainter diffraction spots corresponding to hexagonal ZrB₂, suggesting that the newly formed cubic phase coexists with the ZrB₂ film, likely as a surface coating. EDS data acquired post annealing at room temperature from the darker contrast regions revealed the presence of significant amounts of Pt along with small amounts of Mo in addition to Zr. Fig. 2(f) is a typical plot of EDS intensities of Pt, Mo, Al, and O along the line shown in the associated STEM image. For clarity, Zr spectral profile is not included in the plot. From the intensities of Pt and Mo lines measured both from EDS line scans and from selected points within the darker contrast regions, we estimate the composition as 80 ± 10 at. % Pt and 20 ± 10 at. % Mo. These results suggest that the observed contrast is due to a *fcc* Pt_{1-x}Mo_x alloy with $x = 0.2 \pm 0.1$.³⁵

The observation of a crystalline Pt_{1-x}Mo_x alloy phase superposed on ZrB₂ film is surprising since neither Pt nor Mo were present in or on the as-deposited ZrB₂ thin films prior to annealing. In our experiments, the only possible sources of Mo and Pt are, respectively, the TEM grid, which is primarily made up of Mo, and the FIB-deposited Pt intended to weld the sample to the grid. Moreover, the absence of diffraction spots from pure Mo and any intermetallics in the SAED patterns indicate that Pt and Mo prefer to exist as an alloy and that they do not react with ZrB₂ at these temperatures. The EDS line intensities of Pt and Mo (see, for example, Fig. 2(e)) are fairly homogenous across the film, indicative of uniform distribution of Pt and Mo as expected for an alloy. We also note that the Pt_{1-x}Mo_x alloy is observed only in the region around the ZrB₂ film, and not on the top carbon layer or on the Al₂O₃ substrate (see Figs. 2(a)–2(c)). Based upon these results, we suggest that the FIB-deposited Pt alloys with Mo from the TEM grid and diffuses along the ZrB₂ film. This is reasonable since the XTEM sample is in direct contact with both Pt and Mo and Pt(Mo) solid solutions are thermodynamically favorable at temperatures up to

the melting point of Pt.³⁵ Also, our suggestion is consistent with the fact that the change in contrast is unidirectional away from the end of the sample attached to the Mo grid using Pt.

In order to better understand the kinetics of Pt_{1-x}Mo_x alloy formation along the ZrB₂ film, we measured L as a function of t_a and T_a . Fig. 3(a) shows plots of L vs. t_a data obtained at different temperatures between 1073 and 1173 K. Note that there are two curves (solid and open brown circles) with different slopes at $T_a = 1173$ K. In this experiment, the L vs. t_a data were collected during annealing first at $T_a = 1173$ K (solid brown circles) followed by 1073 K, 1098 K, 1123 K, 1148 K, and again at 1173 K (open brown circles). And, we find that the rate of increase in L with t_a at 1173 K is higher the first time than during annealing at the same temperature at a later time. Since our results suggest that electron beam irradiation has little effect on the observed phenomenon, the difference in dL/dt_a at the same T_a could be due to uncertainties in measuring (or attaining) the set temperature and/or due to time-dependent variation in the rate of mass transport along

FIG. 3. (a) Plots of Pt-Mo alloy diffusion lengths L vs. annealing time t_a . Each color corresponds to data acquired at different annealing temperatures T_a between 1073 and 1173 K. (b) Arrhenius plot of dL/dt_a vs. $1/kT_a$. The solid red line is a linear least squares fit to the data, the slope of which yields an activation barrier of 3.8 ± 0.5 eV.

the ZrB₂ film. It is not clear which of these factors contribute to the observed difference. Nevertheless, at any given T_a , L increases linearly with t_a , i.e., dL/dt_a is constant. And, dL/dt_a increases with increasing T_a . From the Arrhenius plot of dL/dt_a vs. $1/kT_a$ shown in Fig. 3(b), using linear least-squares fit to the data, we extract an activation energy of 3.8 ± 0.5 eV.

We interpret these results as follows. The observed transport of Pt_{1-x}Mo_x alloy involves three basic steps: (a) transfer of Pt and Mo atoms from their respective sources to the TEM sample, (b) diffusion of the metal atoms, and (c) formation of the Pt_{1-x}Mo_x alloy. Since the formation enthalpy for Pt-rich Pt_{1-x}Mo_x alloy is negative at these temperatures,³⁶ we rule out this process as the rate-limiting step. Mass transport can occur *via* diffusion on ZrB₂ surfaces, through the bulk of the ZrB₂ film, and/or along the ZrB₂/C and ZrB₂/Al₂O₃ interfaces. Our TEM, SAED, EDS, and EELS data do not reveal the presence of Pt or Mo on the top carbon surface, bottom Al₂O₃, or the ZrB₂/C and ZrB₂/Al₂O₃ interfaces, based upon which we suggest that interfacial diffusion does not contribute to the transport of Pt and Mo atoms. Bulk diffusion of Pt and/or Mo atoms through the ZrB₂ film, although possible, is less likely since SAED patterns acquired during annealing (see Fig. 2(e)) show diffraction spots characteristic of both the metal and the ZrB₂ lattices. For both surface and bulk diffusion controlled kinetics, L is expected to vary non-linearly with t_a , i.e., dL/dt_a will not be constant.^{33,34} Moreover, the measured activation energy is considerably higher than the values expected for surface diffusion of Pt and Mo.^{37,38} Therefore, we suggest that the arrival flux of metal atoms onto the sample rather than diffusion along the ZrB₂ film is the rate-limiting step. This is plausible since the contact area between the metals and the XTEM sample is considerably small and the interfacial bonding between the metals and the XTEM sample is likely to be poor. Interestingly, although Pt is in direct contact with the XTEM sample, we do not observe pure Pt on the sample; and while there is ample amount of Mo in the form of the TEM grid, we only observe Pt-rich Pt_{1-x}Mo_x alloys and not Mo-rich phases. We attribute these two observations to limited supply of Mo from the grid followed by faster diffusion of Mo compared to Pt on the ZrB₂ surfaces.

In summary, we used *in situ* TEM and studied the thermal stability of metal-ceramic interfaces, specifically the kinetics of diffusion of Pt_{1-x}Mo_x along ZrB₂ thin films as a function of annealing time and temperature. Cross-sectional TEM samples were prepared via focused ion beam milling of polycrystalline ZrB₂ thin films sputter-deposited onto Al₂O₃(0001) substrates and attached to a molybdenum TEM grid by depositing Pt at one end of the sample. During annealing, we observed the motion of *fcc*-structured Pt-rich Pt_{1-x}Mo_x alloy along the ZrB₂ thin film. Based upon our results, we suggest that Pt and Mo form a Pt-rich solid solution and diffuse along the ZrB₂ film surface. From the measured time- and temperature-dependent changes in interface contrast, we determine that the rate-limiting step is the supply of Mo atoms from the TEM grid. Our observations suggest that *in situ* microscopy studies of high-temperature phenomena require careful consideration of the preparation procedure, composition, and geometry of the sample and holder assembly. Based upon our results, we expect that the

relative diffusivities of Pt and Mo are different and have important implications in the design of thermally stable interfaces for operation at high-temperatures.

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