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**In situ** transmission electron microscopy studies of the kinetics of Pt-Mo alloy diffusion in ZrB$_2$ thin films

I. Jouanny,$^{1}$ J. Palisaitis,$^2$ C. Ngo,$^1$ P. H. Mayrhofer,$^3$ L. Hultman,$^2$ P. O. Å. Persson,$^2$ and S. Kodambaka$^{1,4,*}$

$^1$Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, California 90095, USA
$^2$Department of Physics, Chemistry, and Biology (IFM), Linköping University, S-581 83 Linköping, Sweden
$^3$Institute of Materials Science and Technology, Vienna University of Technology, A-1040 Vienna, Austria

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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 ZrB$_2$ thin films deposited on Al$_2$O$_3$(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 ZrB$_2$ layer. From the time-dependent increase in diffusion lengths, we determined that the Pt$_{1-x}$Mo$_x$ does not react with ZrB$_2$, 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 borides$^{8}$ and carbides$^9$ 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 ZrB$_2$ in contact with metals such as Pt and Mo.

Motivation for the present study stems from the fact that refractory borides such as ZrB$_2$ 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 ZrB$_2$ 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 ZrB$_2$ thin films in contact with Pt and Mo. Cross-sectional TEM (XTEM) samples were prepared using focused ion beam (FIB) milling of polycrystalline ZrB$_2$ thin films sputter-deposited on Al$_2$O$_3$(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 ZrB$_2$ 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 ZrB$_2$ thin film is the flux of Mo atoms.

All our experiments are carried out on electron-transparent XTEM samples of ZrB$_2$/Al$_2$O$_3$(0001). Polycrystalline ZrB$_2$ layers, ~85-nm-thick, are grown on Al$_2$O$_3$(0001) at 773 K by magnetically unbalanced magnetron sputter deposition from a stoichiometric ZrB$_2$ target (99.5% purity and 150 mm in diameter) using Ar (99.999% purity) discharge in a modified Leybold-Univex 300 system (base pressure ~7.5 x 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 ZrB$_2$ 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 $E_{Ar^+} = 30$ 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...
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 μm 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 (C₃H₇₃Pt), 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 ZrB₂/Al₂O₃(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 ≈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. In situm annealing at higher temperatures \( T_a \) between 1073 and 1173 K are carried out in the double Cs-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 \( T_a \geq < 1123 \) 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 k×−44 k×) 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 ZrB₂ thin film supported by Al₂O₃(0001) at the bottom and covered with amorphous carbon at the top. In this imaging mode, the ZrB₂ and the top C layers appear brighter and darker than the Al₂O₃ substrate due to mass contrast mechanism. SAED patterns acquired from the ZrB₂ layers indicate that the film is polycrystalline exhibiting the expected hexagonal structure. At the ZrB₂-Al₂O₃ interface, we note the presence of an 8-nm-thick layer that is darker in contrast compared to Al₂O₃. 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 ZrB₂; similar results have also been reported during the growth of ZrB₂ on Si and SiC substrates.

Figures 2(a)–2(c) are representative bright-field TEM images acquired from the ZrB₂ 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 ZrB₂ 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. The observed phenomenon is qualitatively similar to silicidation of nanowires in contact with a metal. 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

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**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, ZrB₂ layer, a thin boron oxide layer, and Al₂O₃ substrate from top to bottom, respectively.
find fainter diffraction spots corresponding to hexagonal 
ZrB$_2$, suggesting that the newly formed cubic phase coexists 
with the ZrB$_2$ film, likely as a surface coating. EDS data 
aquired 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 $80 \pm 10$ at. % Pt and 
$20 \pm 10$ at. % Mo. These results suggest that the observed 
contrast is due to a fcc Pt$_{1-x}$Mo$_x$ alloy with $x = 0.2 \pm 0.1$.

The observation of a crystalline Pt$_{1-x}$Mo$_x$ alloy phase 
superposed on ZrB$_2$ film is surprising since neither Pt nor 
Mo were present in or on the as-deposited ZrB$_2$ 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 ZrB$_2$ at these 
temperatures. The EDS line intensities of Pt and Mo (see, for 
example, Fig. 2(e)) are fairly homogenous across the film, 
diagnostic 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 ZrB$_2$ film, and not on the top 
carbon layer or on the Al$_2$O$_3$ 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 
ZrB$_2$ 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. 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$_x$ 
roll formation along the ZrB$_2$ 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 irra-
diation 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. 2](image-url) (a)–(c) Representative bright-field TEM images acquired from ZrB$_2$/Al$_2$O$_3$(0001) sample as a function of time $t_a$ during annealing at temperature $T_a = 1123$ K. The ZrB$_2$ 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 ZrB$_2$/Al$_2$O$_3$ interface, likely formed during sputter deposition of the ZrB$_2$ thin film. The darker contrast visible in the images is due to the diffusing Pt-Mo alloy whose length $L$ along the ZrB$_2$ 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 a face-centered cubic lattice. The green dotted and solid circles indicate ZrB$_2$ with the ZrB$_2$ 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 $80 \pm 10$ at. % Pt and 
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in measuring (or attaining) the set temperature and/or due to 
time-dependent variation in the rate of mass transport along

![FIG. 3](image-url) (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 $3.8 \pm 0.5$ 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 $t_{sa}$, 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. $1/T_a$ shown in Fig. 3(b), using linear least-squares fit to the data, we extract an activation energy of $3.8 \pm 0.5$ eV.

We interpret these results as follows. The observed transport 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, 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/Al$_2$O$_3$ interfaces. Our TEM, SAED, EDS, and EELS data do not reveal the presence of Pt or Mo on the top carbon surface, bottom Al$_2$O$_3$, or the ZrB2/C and ZrB2/Al$_2$O$_3$ 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 lattice. For both surface and bulk diffusion controlled kinetics, $L$ is expected to vary nonlinearly with $t_{sa}$, i.e., $dL/dt_a$ will not be constant. Moreover, the measured activation energy is considerably higher than the values expected for surface diffusion of Pt and Mo. 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 Al$_2$O$_3$(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 on 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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32See supplementary material at http://dx.doi.org/10.1063/1.4820581 for a set of TEM movies showing the contrast changes at four different temperatures.