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Cohesive strength of zirconia/molybdenum interfaces and grain boundaries in molybdenum: A comparative study



Olena Lenchuk*, Jochen Rohrer, Karsten Albe

Institut für Materialwissenschaft, Technische Universität Darmstadt, Jovanka-Bontschits-Str. 2, 64287 Darmstadt, Germany

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ABSTRACT

We present calculations within density functional theory on the thermodynamic stability and mechanical properties of t-ZrO₂(001)/Mo(001) interfaces. The interfacial strength is evaluated by applying energy-based (work of separation) and stress-based (theoretical strength) criteria for different cleavage planes. The lowest energy for crack propagation is obtained for a cut creating a stoichiometric ZrO₂(001) surface. Our results reveal that molybdenum grain boundaries contaminated with oxygen are less stable against brittle fracture than pure Mo GBs. Addition of Zr, however, can strengthen Mo grain boundaries that contain oxygen by forming an ultrathin zirconia film between Mo grains. The stress required to cleave an ultrathin zirconia film is equal to that required for a pure Mo GB.

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1. Introduction

Molybdenum-based multiphase materials are currently attracting interest for high-temperature structural applications, for example in gas-turbine energy-conversion systems. Key properties of materials suitable for such applications are sufficient oxidation- and creep resistance at elevated temperatures as well as adequate strength, ductility and fracture toughness at ambient conditions [1–4]. Simultaneously meeting all these requirements with a single-phase material is challenging, but can be realized in multiphase materials. In Mo-Si-B composites, for example, the silicide phases help to improve oxidation resistance, while boron enhances the growth kinetics of the protective borosilicate glass layer and molybdenum helps to improve ductility and fracture toughness [2,3,5–9].

A number of experimental studies have revealed that addition of Zr leads to an increase of the room temperature (RT) fracture toughness, strength, as well as ductility (to a minor degree) in Mo [10–14] and Mo-based alloys [2,15–20]. The working hypotheses concerning the physical origin of the improved mechanical properties of the material include (i) reduction of the grain size, (ii) reduction of oxygen concentration at the grain boundaries (GBs) due to the formation of ZrO₂ (zirconia) precipitates and (iii)

improvement of the GB cohesive strength due to the presence of Zr at the GBs [15].

Thus, in order to design a composite material with the desired combination of properties, a detailed understanding of the influence of Zr microalloying is necessary. Recently, we have investigated the influence of solutes (Zr, Si) and of oxygen on the cohesive strength of GBs in molybdenum in twist and tilt bicrystals by means of electronic-structure calculations based on density functional theory (DFT) [21]. We have identified that Zr and Si preferably segregate to the grain boundaries if the low-energy insertion sites are available. At the same time, both species act as weak embrittlers of the Mo GBs and in the presence of oxygen show even more detrimental influence on the GB cohesion. The embrittling behavior of Zr in molybdenum GBs has been also identified by Scheiber et al. in the tilt $\Sigma 3(110)[\bar{1}11]$ GB [22], by Tran et al. in the $\Sigma 5(100)$ twist and $\Sigma 5(310)$ tilt GBs [23], and by Gibson [24]. Thus, the experimentally observed improvement of fracture toughness, strength and ductility in Mo cannot be simply explained by grain boundary strengthening due to segregation of Zr and other possibilities need to be considered.

In general, oxides and metals often form interfaces with enhanced strength compared to the individual constituent phases. For example, Nb and α -Al₂O₃ form a stable interface with high adhesive strength due to strong bonds with a high degree of ionic character [25,26]. Strong adhesion is also found for interfaces between Al₂O₃, ZrO₂, HfO₂ oxides and other transition metals

* Corresponding author.

E-mail address: lenchuk@mm.tu-darmstadt.de (O. Lenchuk).

[27–29]. Also, zirconium tends to capture oxygen and form ZrO_2 . Zirconia precipitates of nanometer size have been found experimentally at GBs and in the grain interior [2,14,15,20,30]. However, there is no data available on the strength and stability of zirconia/molybdenum interfaces. This is why, we used DFT calculations to investigate the thermodynamics and mechanical properties of ZrO_2/Mo interfaces. We study the interface to thick ZrO_2 layers corresponding to precipitates and also thin ZrO_2 films embedded between Mo grains.

We evaluate the adhesion and the theoretical strength of ZrO_2/Mo interfaces and compare them with pure, Zr- and O-containing twist $\Sigma 5[001]$ Mo GBs. We find that the pure GB is the most stable against brittle fracture. The thick zirconia precipitate and the two monolayer (2 ML) thin zirconia film both fracture creating the stoichiometric $\text{ZrO}_2(001)$ surface. Intergranular and transgranular fractures for the thick precipitate are both possible. Only strength of the ultrathin zirconia film (1 ML) is comparable to that of the pure GB.

The paper is organized as follows. In Section 2 a brief description of the zirconia/molybdenum models and computational details are given. We report our findings and discuss the results in Section 3. The summary and conclusions are given in Section 4.

2. Method

2.1. Background and atomistic setup

In bcc metals the principal fracture plane is the (001) plane [31–34]. We therefore consider $\text{Mo}(001)$ as the dominant Mo surface orientation on which ZrO_2 may grow. The most stable ZrO_2 polymorph at the characteristic synthesis conditions ($T = 1500\text{ }^\circ\text{C} - 1980\text{ }^\circ\text{C}$, 1 atm) is tetragonal $t\text{-ZrO}_2$ [35]. Thus, we focus our work on $\text{Mo}(001)/t\text{-ZrO}_2(hkl)$ interfaces. Based on the computed lattice parameters, we investigate the mismatch between $\text{Mo}(001)$ and $t\text{-ZrO}_2(hkl)$ for $h, k, l \leq 3$ and the planar atomic density at $t\text{-ZrO}_2(hkl)$ surfaces. In the following, we use $a_{\text{ZrO}_2} = 3.626\text{ \AA}$, $c_{\text{ZrO}_2} = 5.225\text{ \AA}$ for $t\text{-ZrO}_2$ (see [supplementary information](#)) and $a_{\text{Mo}} = 3.15\text{ \AA}$ for molybdenum. A minimal mismatch reduces the mechanical stress at the interface while a maximum planar atomic density increases the number of atom pairs that bond across the interface. We find that an optimum is achieved for a $(\sqrt{5} \times \sqrt{5})\text{Mo}(001)/(2 \times 2)t\text{-ZrO}_2(001)$ system. Moreover, $t\text{-ZrO}_2(001)$ exhibits one of the highest surface energies among all zirconia (hkl) surfaces with $h, k, l \leq 1$ [36–38]. Because of the large number of dangling bonds at the $t\text{-ZrO}_2(001)$ surface, which are saturated at the interface with $\text{Mo}(001)$, chosen interface is corresponding to a very stable interface configuration. For details we refer to the [Supplementary Materials](#) section.

[Fig. 1](#) shows the unit cell of $t\text{-ZrO}_2$. Along the [001] direction, the stacking sequence can be described as $\text{R}[\text{O}-\text{Zr}-\text{O}]-\text{R}$, where $\text{R} = \text{O}-\text{Zr}-\text{O}$. This structure suggests three possible terminating surfaces, namely a metallic Zr surface layer ($\text{R}-\text{O}-\text{Zr}$), a stoichiometric Zr-O surface layer ($\text{R}-\text{O}-\text{Zr}-\text{O}$) or an O-rich O layer ($\text{R}-\text{O}-\text{Zr}-\text{O}-\text{O}$). For $t\text{-ZrO}_2$, the stoichiometric configuration is preferred (see [supplementary information](#)), independent of the environment. For the interface, we consider all three terminations.

[Fig. 2](#) schematically illustrates our atomistic setup. We consider (a) zirconia precipitate on a molybdenum grain and (b) zirconia thin films embedded between molybdenum grains. Since the thickness of the zirconia precipitates, observed experimentally, is in the nanometer range and thus considerably smaller compared to the grain size of molybdenum (micrometers), the dimensions of the interface cell along the [100] and the [010] directions are fixed to the lattice constant computed for molybdenum, independent of the number of zirconia layers.

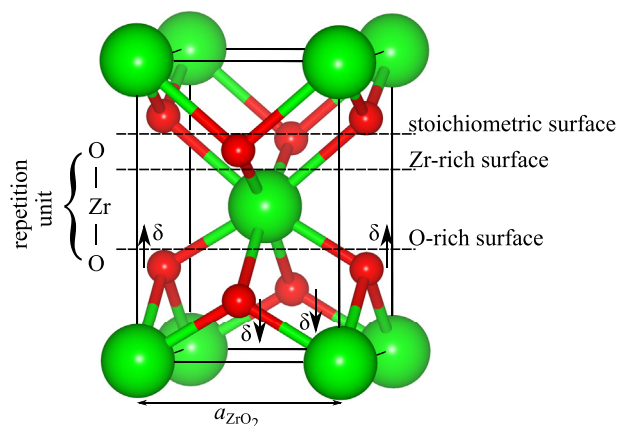


Fig. 1. The atomic structure of tetragonal zirconia ($t\text{-ZrO}_2$). The arrows indicate the displacement of the oxygen pairs along the [001] axis from the plane located in between two Zr planes by an amount δ . Red and green spheres represent oxygen and zirconium atoms, respectively. Black dashed lines correspond to the cleavage planes required to create a stoichiometric, Zr-rich and O-rich (001) zirconia surfaces. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

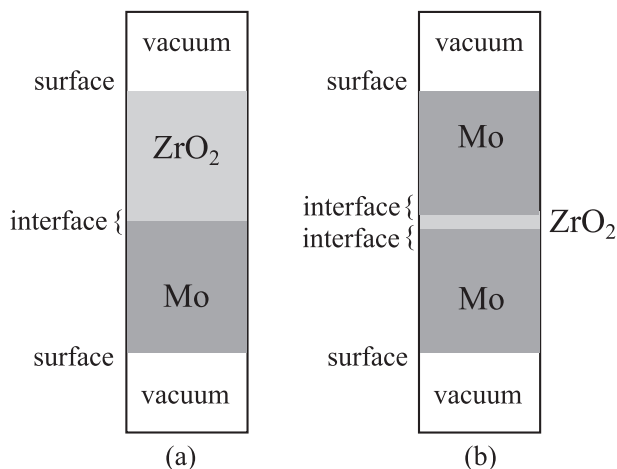


Fig. 2. Schematic model structures for (a) zirconia precipitate on a molybdenum grain and (b) zirconia thin films embedded between molybdenum grains. We consider (i) a one monolayer zirconia film (further on called an ultrathin film) and (ii) a two monolayer (2 ML) zirconia film.

For describing the interface with a precipitate ([Fig. 2\(a\)](#)), we use a slab geometry representing a $\text{Mo}(001)$ grain in contact with a $\text{ZrO}_2(001)$ precipitate. These systems contain one interface, one $\text{Mo}(001)$ surface and one $\text{ZrO}_2(001)$ surface. The latter is always terminated stoichiometrically while the interfacial composition varies. The slab consists of fifteen Mo layers and seven stoichiometric zirconia layers.

For modeling the case of thin films ([Fig. 2\(b\)](#)), we use a sandwich geometry containing two interfaces and two $\text{Mo}(001)$ surfaces. The supercells consist of thirty Mo layers (fifteen on each side) and (i) a monolayer (further on called an ultrathin film) or (ii) two monolayers (further on called a 2 ML thin film) of stoichiometric zirconia. A monolayer of stoichiometric zirconia contains four zirconium atoms and eight oxygen atoms.

[Fig. 3](#) shows the geometry of the zirconia/molybdenum interface on the atomic scale. The $\text{Mo}(001)$ substrate is characterized by three high-symmetry positions and the $\text{ZrO}_2(001)$ surface is characterized by two high-symmetry positions for Zr and two for O.

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