Ideal strength and deformation-induced phase transformation of hcp metals Re, Ru, and Os: A first-principles study

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ABSTRACT

The intrinsic mechanical properties, deformation-induced transformation, and electronic deformation mechanisms of hexagonal close-packed metals Re, Ru, and Os were systematically studied by density functional theory. The ideal strength, elastic moduli, and toughness parameter were fully presented. Os has the largest ideal strengths and moduli over Re and Ru. Although Re has larger moduli than Ru, its strength is smaller. Thus larger modulus does not mean larger strength. The toughness was predicted to be Re > Ru > Os, reversing brittleness. The ideal shear strength of the easiest slip direction is proposed to qualitatively predict the hardness. A hcp → fct → fcc phase transformation was achieved during $[1\,1\,\overline{2}\,0]$ uniaxial tension. The corresponding energy barriers are 0.29, 0.32, and 0.42 eV/atom for Re, Ru, and Os, respectively. The electronic mechanism underlying yielding was clarified to be bond breaking accompanying disappearance of "pseudo-gap". The flow of electron accumulation between charge depletion accommodates the structural transition.

1. Introduction

The application of materials in high stresses/pressures acquires great advancement in ultra-strength, superhardness, and high creep strength [1,2]. Recently, the large atomic number hexagonal closed-packed (hcp) *d*-transition metals were successful used to synthesize superhard materials combined with light covalent elements, such as B, O, C and N [3–5]. These hcp metals in particular including Re, Ru, and Os have large elastic modulus, which is an essential factor to compose transition metal diborides with superhardness. These hcp transition metals also have high valence-electron density of Re (0.476 electrons/Å^3), [6] Ru (0.593 electrons/Å^3), [7] and Os (0.572 electrons/Å^3) [8–10]. By optimizing valence-electron density and covalent bonding, ultra-incompressible superhard material can be synthesized at ambient conditions [4].

On the other hand, Re and the platinum-group metals Ru, Os have been added as important alloying elements to the nickel-based superalloys, greatly improving their high-temperature mechanical properties, such as creep resistance and fracture strengths [11,12]. Re was experimentally observed to be rich near the dislocation core after creep test. It was considered as hard obstacle hindering the movement of dislocation, resulting in enhancement of the power-law creep resistance governed by

dislocation activity [13]. These hard transition metals also serve as ideal solid solution elements to directly improve the modulus and strength of superalloy [14]. So the study on their intrinsic mechanical properties and deformation mechanism should definitely provide fundamental information on the future application of these important strong metals. The information may be valuable implication not only to synthesize even harder material as cutting tool, but also enlighten the discovery of the next generation nickel-based superalloys.

The ideal or intrinsic strength of material dominated by atomic bonding is the minimum stress required to yield or break a perfect crystal. The strength of a real crystal can be affected not only by structural factors, such as dislocation, grain boundary, crack, and other defects, but also affected significantly by temperature and strain rate [15,16]. However, the ideal strength provides an upper limit of stress that the material can sustain before failure. The ideal strength therefore has been recognized as an essential mechanical parameter of material [17]. By virtue of the progress made in modern computational techniques, first-principles calculations based on density-functional theory (DFT) have been successfully used to obtain the ideal strength quantitatively. These ideal strength calculations with full atomic relaxation was pioneered by Price et al. [18] and the group of Šob [19–21]. After that they flourished to various systems in various groups [22–30,34,35,37,31–33,37,36,38–42]. So far, the ideal strength of most metals and some intermetallic compounds, and even more complex structures have been studied and the results were summarized in two review papers [43,44]. In particular, ideal strength of fcc metals such as Al [22,25,27,29,32], Ni

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[21,29,45,38], Cu [22,27,29,32,45,38], Ag [29,45], Ir [46,47,45,38], Pt [45,38], Pd [45], and Au [29] have been thoroughly studied. While the bcc metals, for example, Li [48], Na [48,46], K [48], V [48,33], Cr [48,21], Fe [29,48,21], Rb [48], Nb [24,48,33], Mo [24,29,48], Ba [48], Ta [48,49], and W [29,19,48,46] have also been fully recognized. But to our knowledge, the ideal strength and intrinsic deformation studies on hcp metals were rarely reported in the literature. Only the results of light hcp metals Mg [29], Ti [29], Co [21], and Zn [29] could be found. It is surprising that the ideal strength data of important heavy hcp metals Re, Ru, and Os are still lacking. Herein we will fill in the blank in this study.

Up to date there have been considerable investigations both experimentally and theoretically on the elastic properties of Re [6,50,51], Ru [51–53] and Os [51,8–10,54–56]. Especially when dispute arises since Cynn et al. claimed that Os has the lowest experimentally determined compressibility [8]. From then on a number of experiments and theoretical works clarified that Os has smaller bulk modulus than diamond [9,10,54–56]. However, there exists no report on ideal strength of these hcp d-transition metals. As we know, strength and hardness are estimated involving non-linear response of stress to strain in experiment. Although modulus measured within elasticity sometimes correlates with hardness, it cannot provide more information on the plastic deformation of material [57]. Fortunately, the first-principles ideal stress–strain relationship going beyond elastic limit could provide more intrinsic mechanical response than the elastic parameters.

Another interesting topic is the martensitic transformation due to ordered, small movement of atoms in crystal. It has been observed in many elements and alloys. Deformation could be served as the driving force to overcome the activation barrier between two stable structures. Because hcp and fcc symmetry are very intimate to each other, many stress-induced phase transformations occur between them. For example, a fcc → hcp transformation takes place in solid Xe between 5 and 70 GPa [58,59]. While the reversed hcp → fcc stress-induced transition has also been observed in Si and Co under pressure [60,61]. A ab initio work has shown that Os could experience a hcp → fcc phase

transformation by cooling [54]. Here, we will show a deformation-induced hcp → fct → fcc phase transformation by [$11\bar{2}0$] uniaxial tension.

This paper was arranged like this. First, we will present the elastic properties and electronic structure of Re, Ru, and Os at equilibrium. Next, we provide the stress–strain curves and the ideal tensile and shear strengths, exploring the relation between hardness and theoretical strengths. Then, the deformation-induced phase transformation under [$11\bar{2}0$] tension will be clarified in detail. Finally, the electronic mechanism underlying the intrinsic mechanical properties and phase transformation was fully analyzed.

2. Calculation details

The first-principles calculations presented here are based on DFT, and have been carried out using the Vienna *ab initio* Simulation Package (VASP) [62,63]. The generalized gradient approximation (GGA) using the Perdew–Wang (PW91) version [64] is adopted for parametrization of the exchange-correlation functional. The interaction between ion-core and electron is described by projector augmented-wave (PAW) method [65,66]. The cutoff energy of atomic wave functions is set to be 400 eV. The energy difference of Re unit cell is less than 0.02% compared with cutoff energy of 450 eV. The k-points in Brillouin zone (BZ) is chosen depending on the size of the adopted supercell. The convergence of elastic modulus and ideal strength with respect to both the cutoff energy and k-points has been verified. The full relaxation is done until the force on every atom is less than 0.01 eV/Å. The symmetry constraint on the deformed supercells are turned off during structural relaxation. This leads to a high accuracy stress tensor and strained structures.

Fig. 1(a) and (b) shows the unit cell and the redefined orthorhombic supercell of hcp metal adopted in our calculation. The unit cell is used to calculate the elastic properties and the [0001] tensile stress–strain curves. While the latter supercell with specific crystal directions is adopted to simulate the tension in [$1\bar{1}00$], and [$11\bar{2}0$], as well as shear modes (0001)[$1\bar{1}00$], (0001)[$11\bar{2}0$], and ($1\bar{1}00$)[$11\bar{2}0$]. Monkhorst–Pack grids [67] of $12 \times 12 \times 8$, and
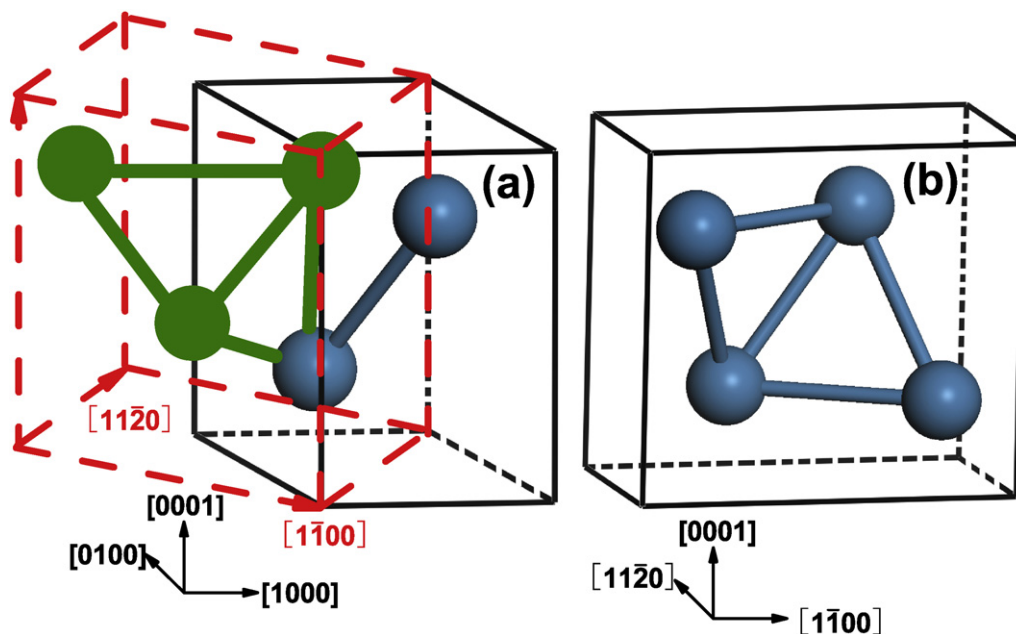

Fig. 1. Schematic model of hcp metal with specific crystal directions. (a) The black profile is the hexagonal unit cell, which contains two atoms. The red profile is the redefined orthorhombic supercell. (b) The redefined orthorhombic supercell of hexagonal lattice, in which the three orthogonal lattice vectors represent [$1\bar{1}00$], [$11\bar{2}0$], and [0001]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)