First-principles calculations on the stacking fault energy, surface energy and dislocation properties of NbCr$_2$ and HfCr$_2$ ☆

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ABSTRACT

First-principles calculations have been performed to investigate the site preference, generalized stacking fault energies and surface energies of the additive elements M (V, Zr, Mo) in NbCr$_2$ and M (V, Ta, W) in HfCr$_2$. Additionally, the core width and the Peierls stresses of $1/6\langle\overline{1}2\overline{1}\rangle\{111\}$ dislocations in both NbCr$_2$ and HfCr$_2$ with and without the addition of ternary atoms are firstly investigated within the improved Peierls-Nabarro theory. Our results show that V preferentially occupies Cr site in both compounds, while M (Zr and Mo) occupies the Nb site in NbCr$_2$ and M (Ta and W) the Hf site in HfCr$_2$. Furthermore, when Mo occupies Nb site in NbCr$_2$ and Ta or W the Hf site in HfCr$_2$, the ductility is found to be improved and the Peierls stresses of $1/6\langle\overline{1}2\overline{1}\rangle\{111\}$ dislocations decrease for both NbCr$_2$ and HfCr$_2$.

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1. Introduction

Laves phases are considered as high temperature structural materials owing to their attractive characteristics, such as high melting point, low density, outstanding creep resistance, corrosion potential and antioxidant properties [1–8]. There are three types of structures in Laves phases: cubic C15 (fcc), hexagonal C14 (hcp) and dihexagonal C36 (hcp) [9]. The distinction of the three types of structures is resulted from the various stacking sequences of the quadruple atomic layers. Especially, C15 Laves phase is expected to show better plastic deformability than the hexagonal C14 and dihexagonal C36 Laves phases because of the fact that more slip systems existing in fcc structures [10]. Therefore, various theoretical and experimental researches have been focused on C15 Laves phase, including electronic structure, elastic properties, defect microstructures, phase stability, deformation behavior, phase transformation and thermal properties [11–20]. However,

C15 Laves phase can't be widely used due to their extremely brittle properties at ambient temperatures. Because Laves phases possess complex structures, in general, dislocation motion is very difficult, which may be the main reason for their low temperature brittleness. Therefore, it is necessary to improve the low temperature ductility of C15 Laves phase.

It has been reported that the brittleness can be improved by addition of the third element. Among the C15 Laves phases, NbCr$_2$ and HfCr$_2$ show interesting promise for high-temperature structural applications, especially for the NbCr$_2$. Therefore, the effects of ternary additions on the physical and mechanical properties of NbCr$_2$ have been widely investigated [21–28]. For example, from the experimental aspect, Takasugi et al. [21] investigated the high temperature deformability of C15 Laves phase NbCr$_2$ alloyed with V, Mo and W by using high-temperature compressive tests, and their results demonstrated that Mo decreases the yield stress of NbCr$_2$, but V and W increase its yield stress. Thoma et al. [23] employed the resonant ultrasound spectroscopy (RUS) to study the influence of alloying on properties in the NbCr$_2$-TiCr$_2$ C15 Laves phase field, they found that the hardness and elastic properties of NbCr$_2$ increase with Ti additions. From the theoretical aspect, Yao et al. [25] have studied the site occupancy behaviors of ternary additions of M (Ti, V, Mo, Zr and W) in NbCr$_2$ Laves phase by using the full-potential linearized augmented plane-wave (FLAPW) method within the generalized gradient approximation (GGA), and their calculations indicated that V, Mo and W preferentially

substitute the Cr sites, but Ti and Zr preferentially occupy the Nb sites in NbCr$_2$. Li et al. [28] investigated the effects of M (V, W, Mo, Hf, Ta, Zr) additions on the ideal cleavage fracture of NbCr$_2$ employing the first-principles method, and they found that V on Cr site and M (W and Zr) on Nb site can increase the strength of NbCr$_2$, however, M (W and Mo) on Cr site and M (Mo, Ta and Hf) on Nb site have the opposite change trend. Obviously, all of these researches are meaningful for the application of C15 Laves phase NbCr$_2$.

Further, a fundamental understanding of the plastic deformation is very necessary for improving the ductility of materials and the plastic deformation is usually carried out by nucleation and slip of dislocations [29]. There has been a great deal of interest in describing the dislocation core structure because it determines the mobility of the dislocation [30,31]. It is widely accepted that the generalized stacking fault (GSF) energy of a material is critical to analyze the dislocation core structure [32]. Generally, the famous classic Peierls-Nabarro (P-N) model combined with the GSF energy can give a quantitative description of the dislocation core structure [33,34], however, there are still some basic issues that need to be clarified in the classic P-N theory. The major drawback of the classic P-N model is that the crystal is treated approximately as an elastic continuum body and the discrete effect is neglected [35]. Actually, displacement varies so rapidly at the dislocation core and the classic P-N model need to be modified. Afterwards, the modified P-N equation has been derived based on the lattice dynamics [35]. Because Laves phases possess complex structures, the plastic deformation is very complicated. So far, the deformation mechanisms in Laves phases have been received little attention. Recently, Ma et al. [36] investigated the deformation mechanism in C15 Laves phases MCr$_2$ (X = Nb, Zr, Hf) alloys based on the GSF energy curves obtained from ab initio calculations. However, the dislocation core structure of NbCr$_2$ and HfCr$_2$ with and without ternary additives has never been reported. And the dislocation core structure plays a key role in determining the mechanical properties of a material. It can be served as a prediction for the design and development of high performance materials. In this work, the core structure of the $1/6\langle\overline{1}2\overline{1}\rangle\{111\}$ synchro-Shockley partial dislocations in NbCr$_2$ and HfCr$_2$ with and without a ternary atom M (M = V, Zr, Mo, Ta, W) is firstly investigated by using the modified P-N theory combined with GSF energies. The remainder of this paper is organized as follows. In Section 2, we describe the calculation model and the details of first-principles methods. In Section 3, the site occupancy behaviors of the ternary additives by calculating formation energy are investigated, and we compare our results with available theoretical and experimental results. All of the various criteria including Pugh's ratio, Cauchy pressure and Poisson's ratio are given for predicting the brittle/-ductile behaviors of NbCr$_2$ and HfCr$_2$ with and without ternary additives. The brittle/ductile behaviors are also presented in terms of Rice criterion based on the cleavage decohesion process energy (G_c) and unstable stacking fault (USF) energy (γ_{us}). The core structure and Peierls stresses of $1/6\langle\overline{1}2\overline{1}\rangle\{111\}$ synchro-Shockley partial dislocations in NbCr$_2$ and HfCr$_2$ with and without a ternary atom M (M = V, Zr, Mo, Ta, W) have been given by adopting the improved P-N dislocation equation. Finally, the conclusions are drawn in Section 4.

2. Model and computational details

2.1. Model of calculation

C15 Laves phase with space group $Fd\overline{3}m$ (227) possesses a complex structure containing six atoms in the primitive unit cell. The chemical formula is LS_2, where S and L represent smaller and larger

atoms, respectively [37]. In this paper, elastic constants calculations of C15 Laves phases NbCr$_2$ and HfCr$_2$ with and without ternary additives are performed by employing a 24-atom supercell. The crystal structure of pure C15 Laves phase NbCr$_2$ with 24 atoms are shown in Fig. 1(a), which has the chemical formula Nb$_8$Cr$_{16}$. When one Nb atom is replaced by a ternary atom M (M = V, Zr, Mo), the chemical formula will be expressed as Nb$_7$MCr$_{16}$ and the concentration of the alloying atom M is about 4.17 at.%. Similarly, when one Cr atom is substituted by a ternary atom M, the chemical formula is changed into Nb$_8$Cr$_{15}$M with the same M concentration. HfCr$_2$ is the same with NbCr$_2$, only the doping elements are different. The crystal structure of C15 Laves phase is similar to that in fcc, the atom arrange sequence in the $\{111\}$ plane can be defined by repeated XYZ stacking $\cdots \overbrace{A\alpha c\beta}^{X}\ \overbrace{B\beta a\gamma}^{Y}\ \overbrace{C\gamma b\alpha}^{Z} \cdots$ and each unit X(Y or Z) is furthermore constructed by a four layer group. The capital Latin letters (A, B, C) represent the S atoms, which form the single layer with a kagome lattice; the Greek letters (α, β, γ) represent the L atoms and the lower case Latin letters (a, b, c) represent the S atoms, which form the triple layers stacking sequence of $\alpha c\beta$ ($\beta a\gamma$ or $\gamma b\alpha$). Fig. 1(b) shows the side view of the C15 structure along the $\langle111\rangle$ direction. Considering the geometry and energy, it is very difficult to form the stacking fault in C15 Laves phase via a conventional slip. It is found that the $1/2\langle\overline{1}10\rangle\{111\}$ dislocation can be formed through the simultaneous shear of two sublayers along different directions, which has been called as synchroshear [38,39]. Taking the unit X ($A\alpha c\beta$) as an example, Fig. 1 (c) shows the top view of the atomic arrange during the synchroshear. Obviously, when the β atoms move toward c with Burgers vector $\boldsymbol{b_1} = 1/6\langle\overline{1}2\overline{1}\rangle$ (red arrow), at the same time the c atoms must move toward β with Burgers vector $\boldsymbol{b_2} = 1/6\langle\overline{2}11\rangle$ (black arrow) to avoid the overlapping of the β and c atoms within the slip plane. Finally, the stacking sequence of the X unit ($A\alpha c\beta$) will be turned into X′ unit ($A\alpha b\gamma$), and similarly the forms of Y unit ($B\beta a\gamma$) and Z unit ($C\gamma b\alpha$) are turned into Y′ unit ($B\beta c\alpha$) and Z′ unit ($C\gamma a\beta$), respectively. Consequently, the stacking fault $\cdots$ $\overbrace{A\alpha b\gamma}^{X'}\ \overbrace{B\beta c\alpha}^{Y'}\ \overbrace{C\gamma a\beta}^{Z'} \cdots$ is generated.

2.2. Calculations of first-principles

The present calculations based on the density functional theory (DFT) are performed using the Vienna ab initio Simulation Package (VASP) program [40–42]. The exchange-correlation potential is described by the GGA with the well established Perdew-Burke-Ernzerhof (PBE) version [43] and the ion-electron interaction is described by the projector augmented wave (PAW) method [44,45]. The cut-off energy of plane wave basis set is chosen to be 500 eV. For calculation of GSF energies and cleavage decohesion process energies, a periodic supercell consisting of 36 atoms with 24 atomic planes in the $\langle111\rangle$ direction is employed (see Fig. 2). In Cr-Nb(Hf)-M solid solutions, a ternary atom M (M = V, Zr, Mo, Ta, W) substitutes one Cr or Nb (Hf) atom, so the concentration of the solute atom is about 2.78 at.% for the whole system. In order to avoid interactions between faults in two neighboring slabs, about 15 Å thick vacuum region is added in the direction normal to the slip plane on the basis of our test. Brillouin zone (BZ) integrations are performed using the Monkhorst-Pack special k-point scheme [46]. A $11 \times 11 \times 11$ special k-point mesh is employed for determining the optimum lattice and elastic constants, while the GSF energies and cleavage decohesion process energies calculations employ $9 \times 9 \times 1$ grid meshes for C15 Laves phases NbCr$_2$ and HfCr$_2$ with and without ternary additives. The convergence of energy and force is set to 1.0×10^{-6} eV and 1.0×10^{-4} eV/Å, respectively.