Anisotropic elastic properties and phase stability of B2 and B19 CuZr structures under hydrostatic pressure

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ABSTRACT

B2 CuZr exhibits a stress-induced martensitic transformation from a B2 to a B19 structure during tensile deformation, and that is believed to be the reason for the pronounced ductility and work hardening of CuZr-based bulk metallic glass (BMG) composites. In order to gain a better insight into the structural transformation of CuZr precipitates, the phase stabilities as well as the anisotropic elastic and thermodynamic properties of both B2 cubic (CsCl-type) CuZr and B19 (β-AuCd-type) CuZr structures under hydrostatic pressures up to 30 GPa are investigated by first principles calculations. Moreover, the effects of the hybridization between the electronic orbitals of the constituent atoms on the variation of the elastic properties of the B2 CuZr structure are discussed. The results show that the Young's modulus (E), bulk modulus (B) and shear modulus (G) increase significantly with increasing pressure. Noticeably, for pressures up to 30 GPa, the B2 CuZr structure shows a stronger anisotropy along the (1 1 0) plane than for the (1 0 0) plane. Under high pressure, the stability of both B2 CuZr and B19 CuZr phases decrease while the Helmholtz free energy (F) and the formation enthalpy (H) of B2 CuZr increase monotonically. However, the different stability decreasing trajectories of both B2 and B19 CuZr phases result in a high propensity of martensitic transformation from the B2 to B19 structure. Our results may have implications for better understanding the phase stability of B2 and B19 CuZr structures under high pressure and can shed light on the structure-property relationships of BMG composites reinforced with shape-memory crystals.

1. Introduction

Bulk metallic glasses (BMGs) have been investigated extensively as potential structural and functional materials as they possess a unique combination of mechanical properties, i.e., high strength together with a large elastic regime [1–4]. Composites consisting of *in-situ* precipitated soft crystalline dendrites in a BMG matrix were developed to overcome the macroscopically brittle failure of monolithic BMGS in tension [5–7]. For bcc β-Ti dendrite-reinforced ZrTiNbCuBe composites, pronounced necking without work-hardening is typically observed [8]. In contrast, by introducing second phase precipitates which undergo a stress-induced martensitic transformation into BMGs, pronounced work hardening and significant ductility can be achieved successfully [9,10]. As has been shown by a number of investigations over the years [11–13], the B2 cubic (CsCl-type) CuZr phase synthesized by rapid solidification or casting is often utilized to improve the mechanical properties of Zr-based BMGs. Some available literature also

demonstrated that both B2 CuZr and B19 CuZr structures in CuZr-based BMG composites can be observed simultaneously during the deforming process [14,15]. Under tension, the B2 CuZr precipitates undergo a martensitic transformation from a B2 to a B19 structure, which is the mainly reason for the enhanced plasticity and work hardening observed in BMG composites. Obviously, the characteristics of B2 and B19 CuZr phases under high pressure are of fundamental importance for the properties of CuZr-based BMGs. However, detailed investigations on the chemical bonding and the elastic and thermodynamic properties of B2 and B19 CuZr crystalline precipitates under high pressure are still scarce and further investigations are required. As we known, first principles methods can be used to calculate the elastic and thermodynamic properties of materials with high accuracy [16]. Hence, such theoretical methods allow obtaining useful data for gaining a better insight into the intrinsic properties of B2 and B19 CuZr structures under different hydrostatic pressures.

This paper presents a detailed study of the stability, the elastic and

thermal properties of B2 and B19 CuZr structures under high hydrostatic pressures using plane wave pseudo potential density functional theory (DFT) and the corresponding Debye model. The first-principles methods employed in this work allow to obtain elastic constants (C_{ij}), Young's modulus (E), shear modulus (G), Poisson's ratio (υ) as well as thermal properties, i.e., Debye temperature (Θ), formation enthalpy (H), heat capacity (C_v) and Helmholtz free energy (F) under different hydrostatic pressures (ranging from 0 to 30 GPa).

2. Computational details

Based on DFT implemented in the CASTEP code, an ultra-soft pseudopotential (USPP) was employed in all calculations to reveal the interactions between the electrons and the core. For Cu and Zr atoms, the valence configurations are $3d^{10}4s^1$ and $4s^24p^64d^25s^2$, respectively. Generalized Gradient Approximation (GGA) together with the Perdew Burke Ernzerhof (PBE) parameterization were utilized for the exchange correlation function [17]. In the Brillouin zone sampling, $10 \times 10 \times 10$ and $8 \times 12 \times 8$ Monkhorst Pack schemes were utilized for k point separation of B2 CuZr and B19 CuZr structures, respectively, while the kinetic energy cutoffs were set to 450 eV and 550 eV for plane wave expansions. The other parameters for optimizing the crystal structures of the B2 and B19 CuZr structures were as follows: the separation of the reciprocal space was $0.01 \, Å^{-1}$, and the SCF tolerance was 5.0×10^{-7} eV/atom. Moreover, the maximum ionic force displacement and stress were 0.02 eV/Å, 5.0×10^{-3} Å and 0.03 GPa, respectively. According to the forming process, the applied pressure on the particles can reach up to 30 GPa [18]. Therefore, the effect of an external pressure ranging from 0 to 30 GPa was investigated. The B2 and B19 CuZr crystal structures were built based on the experimental crystallographic data of CuZr intermetallic compounds [19,20]. A cubic structure with a space group of PM3M for the B2 cubic CuZr structure (Fig. 1 a) and an orthorhombic structure with a space group of PMMA for the B 19 CuZr structure (Fig. 1 b) are shown in Fig. 1. The atomic coordinates in the unit cell of the B 19 CuZr structure are Cu (0.250, 0.000, 0.25004) and Zr (0.25, 0.5, 0.75001).

3. Results and discussion

3.1. Structure modifications under pressure

The geometrical structures of the B2 and B19 CuZr structures under hydrostatic pressures in the range of 0 and 30 GPa were optimized, as shown in Table 1. Comparing the calculated results at zero pressure with the available experimental data in Refs. [19,20] reveals that the average deviation of the lattice parameters a of the B2 CuZr structure is about 0.03%, while the average deviations of the lattice parameters a, b

and c of the B19 CuZr structure are about 1.8%, 4.1% and 1.8% respectively. This means that our calculation models can be considered as reasonable. Obviously, the calculated lattice parameter of the B2 CuZr structure (lattice constant $a = 3.271$ Å) agrees very well with the available experimental data ($a = 3.267$ Å [19]), and the calculated lattice constants of the B19 CuZr structure (lattice constant $a = 4.535$ Å, $b = 3.430$ Å and $c = 4.533$ Å) also agree very well with the available data ($a = 4.620$ Å, $b = 3.249$ Å and $c = 4.621$ [20])). This demonstrates the accuracy of our method. Unfortunately, other theoretical and experimental results for the lattice parameters of the B2 and B19 CuZr phases under high pressure are not available in the literature for possible comparison.

The optimized volume V under applied pressure in the range of 0–30 GPa is also listed in Table 1.

With increasing the pressure from 0 to 30 GPa, the volume V of the B2 CuZr structure decreases from 34.977 to 29.154 $Å^3$, while the V of the B19 CuZr structure decreases from 70.642 $Å^3$ to 58.638 $Å^3$. The volume of the B19 CuZr structure is larger compared with that of the B2 CuZr structure. This implies that the martensitic transformation from the B2 to B19 structure is associated with a volume change which can affect the stress state in the matrix. Moreover, the volume decreasing trajectory of the B2 CuZr structure is less pronounced towards high pressures, as shown in Fig. 2. This may imply a low deformation capacity of the B2 CuZr structure under high pressure.

The relative phase stabilities of the B2 and B19 CuZr structures expressed through the deviation of the formation enthalpies ($\triangle H$) have been calculated by employing the following relation:

$$\Delta H_{CuZr} = (E_{total} - E_{bulk}^{Zr} - E_{bulk}^{Cu})/2, \tag{1}$$

where E_{total} represents the total energy of a CuZr cell under different pressure, and E_{bulk}^{Zr} and E_{bulk}^{Cu} are the energy of a Zr atom and a Cu atom in the bulk state, respectively. The results of the deviation of the $\triangle H_{CuZr}$ values under various pressures are given in Table 1. It is apparent that the $\triangle H_{CuZr}$ values of the B2 and B19 CuZr crystalline structures are negative under different pressures and increase with increasing pressure, implying that the stabilities of both B2 and B19 CuZr structures are reduced under high pressure. It should be noted that under pressures of 0 GPa the $\triangle H_{CuZr}$ of the B2 CuZr structure is smaller than that of the B19 CuZr structure, while under pressures of 30 GPa the $\triangle H_{CuZr}$ of B2 CuZr is larger than that of B19 CuZr. There must exist an intersection point of two $\triangle H_{CuZr}$ –pressure lines for the B2 and B19 CuZr structures, i.e., $\triangle H_{CuZr}$ and pressures approximately are -2 KJmol^{-1} per atom and 27 GPa, respectively. This means that the B19 CuZr structure is more stable than the B19 CuZr structure when the pressure is less than 27 GPa, and when the pressure is higher than 27 GPa, the B19 CuZr structure is much more stable. The decreasing stability of both B2 and B19 CuZr structures and the different stability decreasing
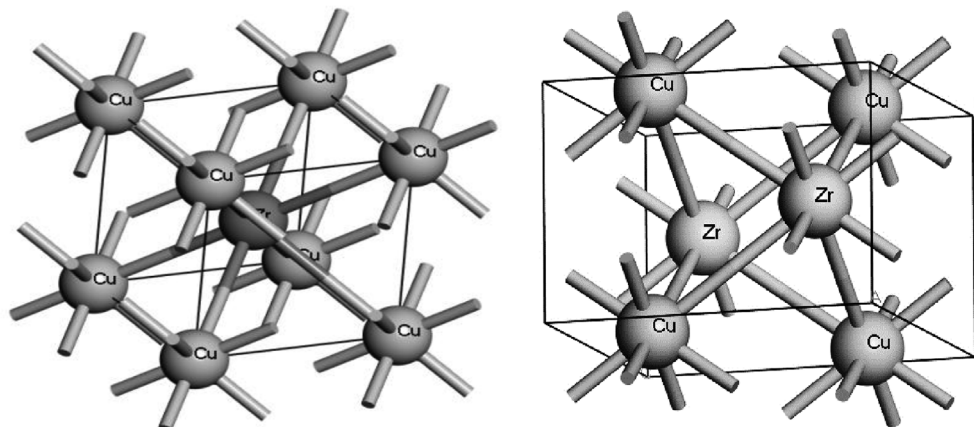

Fig. 1. Crystal structures of CuZr compounds at zero pressure: (a) B2 and (b) B19.