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Ab-initio study of structural, electronic and elastic properties of cobalt intermetallic compounds

Nikita Acharya *, Bushra Fatima, Sunil Singh Chouhan, Sankar P. Sanyal [1]

Department of Physics, Barkatullah University, Bhopal 462026, India

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ABSTRACT

The structural, electronic, elastic, bonding and thermal properties of CoX (X = Ti, Zr and Hf) have been investigated using ab initio full potential linearized augmented plane wave (FP-LAPW) method within generalized gradient approximation (GGA). The ground state and electronic properties such as lattice constant (a_0), bulk modulus (B), pressure derivative of bulk modulus (B') and density of states at Fermi level $N(E_F)$ are reported with experimental and available theoretical results. Electronic and bonding patterns of these compounds have been analyzed from band structure, Fermi surfaces and contour plots. The elastic constants (C_{11}, C_{12} and C_{44}) and mechanical properties are also estimated. From the elastic constant, it is inferred that these compounds are mechanically stable in B_2 phase. Ductility for these compounds is further analyzed by calculating the ratio of B/G_H and Cauchy's pressure (C_{12}–C_{44}). Our calculated results reveal that all these compounds are ductile in nature.

1. Introduction

The intermetallics are a fascinating new group of materials; due to their unique physical and mechanical properties and occupy an intermediate position between metallic and non-metallic materials [1]. They exhibit interesting mechanical and thermal properties such as high tensile strength, good ductility, high corrosion resistance and thermal stability [2–8], which are generally attributed to difference in the chemical bonding that binds the atoms together. Intermetallic compounds have emerged with vast potential for application in a wide range of technologically important areas [9]. The enormous potential of intermetallics especially aluminides stems from their many attractive properties, such as high oxidation and corrosion resistance and relatively low densities, combined with their ability to retain strength and stiffness at elevated temperatures [10,11]. Due to long range ordering and specific properties, the intermetallic alloys are assumed to fill an existing gap between structural ceramics and classical metallic alloys [12]. In intermetallic compounds the absence of '*d*' like orbital near the Fermi level accounts for the observed ductility in 90% of these compounds [7].

The intermetallic compounds CoTi, CoHf and CoZr composed of VIII group elements have unique functional and structural properties. They crystallize in B_2 structure and have low ductility at low temperature in spite of relatively simple crystal structure [13]. Hafnium (Hf) is primarily used in the control and safety mechanisms of nuclear reactors, because of its high cross-section for neutron absorption and its high corrosion resistance. It is also used extensively as an alloying element in nickel-, niobium- and tantalum-based super alloys, which are designed to withstand high temperature and pressure [14]. Some intermetallic compounds of Hf and the transition metal Fe, Co, Pd and Pt have been investigated as hydrogen storage materials because of their capability to form hydrides with high hydrogen to metal ratio at room temperature [15]. CoTi, CoZr or CoHf have attracted attention because they show a yield strength anomaly with increasing temperature [16]. It is also observed from a recent study that, these B_2 type intermetallics (CoTi, CoZr and CoHf) exhibit no phase transition up to their melting temperatures [17]. Thus these intermetallics are expected to prove as new materials having both functional and structural properties [13].

Cheng et al. [18] have investigated the elastic properties and electronic structure of FeTi, CoTi and NiTi using first principles method. Kellou et al. [19] have reported the electronic properties, bulk surfaces and interfaces of FeTi, CoTi and NiTi alloys using FP-LAPW method. Freeman et al. [20] have reported the electronic structure and mechanical behavior of aerospace materials using FP-LAPW method. Gupta [21] has calculated lattice constant and

* Corresponding author. Tel.: +91 755 4224989; fax: +91 755 2491823.
E-mail addresses: acharyaniks30@gmail.com (N. Acharya), sps.physicsbu@gmail.com (S.P. Sanyal).
[1] Address: Condensed Matter Physics Laboratory, Department of Physics, Barkatullah University, Bhopal, M.P. 462-026, India. Tel.: + 91 755 4224989; fax: + 91 755 2491823.

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other parameters of various systems of Co-Hf-Zr. Uğur et al. [22] have investigated the structural, electronic and vibrational properties of ordered intermetallic alloys CoZ(Al, Be, Sc, Zr) from first principles total energy calculation. The tensile properties of recrystallized B_2 CoZr intermetallic alloys were studied by Kaneno et al. [13] using X-ray diffraction technique. Levy et al. [14] have carried out studies on hafnium binary alloys using both experimental and theoretical techniques. The methodology of single crystal growth and microstructure analysis of CoTi (Zr) have been investigated by Zhang et al. [16]. The application of tight binding electronic theory to phase stability and mechanical property have been performed by Jindo and Sluiter [17] using generalized recursion and TB-LMTO methods. Agosta et al. [23] have investigated the elastic moduli of polycrystalline ZrCo as a function of temperature using Resonant ultrasound spectroscopy technique (RUS). Mechanics of ductility in CoTi and CoZr B_2 intermetallics has been reported by Wollmershauser et al. [24] using experimental technique. Jha et al. [25] have reported the puzzling phonon dispersion curves and vibrational mode instability in superconducting $MgCNi_3$ using plane wave self consistent field (PWSCF) method. Structural, electronic, magnetic and dynamical properties of mononitrides FeN and CoN have been performed by Soni et al. [26] using first principles calculation.

In the present paper, we have carried out a thorough study on the electronic and physical properties of Co-based intermetallic compounds, namely CoTi, CoZr and CoHf by computing the band structure, density of states, elastic constants and thermal properties using full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code. We have also critically examined their ductile property.

2. Method of calculation

The total energy, ground state properties and electronic band structures of cobalt intermetallic compounds, which crystallize in CsCl (B_2^- type, Pm3m, Space Group, No. 221) structure, have been computed in spin polarized calculation within GGA using full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code [27]. GGA has been used in the scheme of Perdew et al. for the exchange and correlation effects [28]. It gives accurate and larger equilibrium lattice parameter comparing to LDA [29,30] and has attracted much attention for its simplicity and moderate computational workloads as well as it is a straightforward substitute to improve over the LDA in ab initio total energy calculations [31].

R_{max} (in a.u.) is the maximum distance for considering neighbors [27]. The convergence parameters $R_{MT} * K_{max}$, which controls the size of the basis set in these calculations, is set to 7, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} gives the magnitude of the largest **k** vector in the plane wave expansion. The valence wave functions inside the spheres are expanded up to $l_{max} = 10$ while the charge density is Fourier expanded up to $G_{max} = 12$ (a.u.)$^{-1}$ [32]. The self consistent calculations are considered to converge when the total energy of the system is stable within 10^{-4} Ry. Energy to separate core and valence state is −6.0 Ry. A dense mash of 1000*k* points is used and the tetrahedral method [33] has been employed for the Brillouin zone integration.

3. Result and discussion

The structural properties are very imperative in analyzing the behavior of material. We have performed the spin polarized calculations to obtain the total energy of CoTi, CoZr and CoHf intermetallic compounds using FP-LAPW method. To determine the ground state properties of these intermetallics, the total energies are fitted to Birch Murnaghan's equation of state [34]. The variation of total energy as a function of volume has been plotted in Fig. 1(a–c). The calculated total energies and their corresponding volumes are used to calculate the ground state properties such as lattice constant (a_0), bulk modulus (B) and its pressure derivative (B'). The results are listed and compared with other theoretical and experimental values in Table 1. It may be seen from this table that our values agree well with other theoretical and experimental results. From Fig. 1, one can notice that, all the three intermetallics of Cobalt are stable in B_2 phase and that, as one goes from Ti → Hf with Co, CoHf requires less energy to be stable in B_2 phase as compared to CoTi and CoZr. It may be due to low electronegativity of Hf atom. The order of energetic stability of CoTi, CoZr and CoHf from high to low is: CoTi > CoZr > CoHf.

The calculated electronic band structure along the principle symmetry directions of CoTi, CoZr and CoHf intermetallic compounds are presented in Fig. 2(a–c) respectively, where Fermi level (E_F) is considered at origin. To further understand the elemental contributions to the electronic structure, we have calculated the total and partial density of states for these compounds at ambient pressure and presented them in Fig. 3(a–c) respectively. For CoTi as shown in Fig. 2(a), the lowest lying bands around −7.8 eV at Γ-point are mainly due to Co '*s*' like states and the bands above this and below the Fermi level around −2.2 eV and −2.8 eV are due to '*d*' states of Co and Ti. From Fig. 3(a) the hybridization between '*d*' states of Co and Ti from lowest band up to above the Fermi level can also be seen. The finite DOS at Fermi level $N(E_F)$, is found to

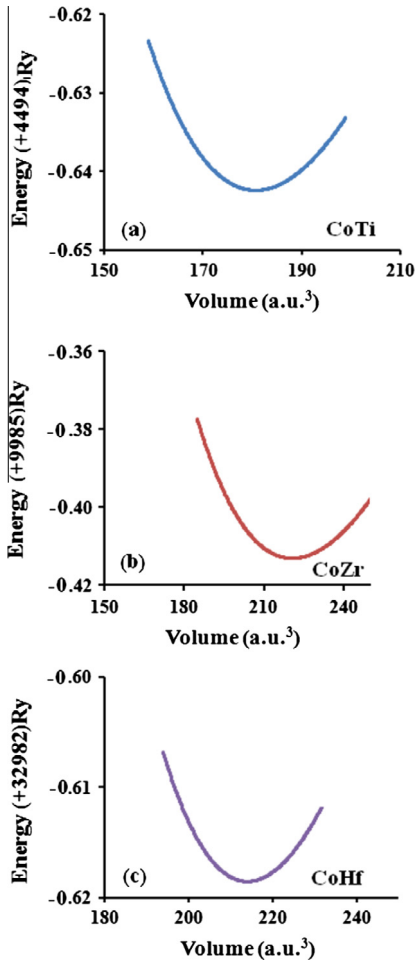

Fig. 1. Energy v/s volume curve for CoTi (a), CoZr (b), and CoHf (c).