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A first principles study of cohesive, elastic and electronic properties of binary Fe–Zr intermetallics

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ABSTRACT

Density functional theory (DFT) based first-principles investigation has been performed to study the cohesive, elastic and electronic properties of Fe–Zr binary intermetallics across the composition range. Our initial calibration of underlying DFT approximations provides good agreement of lattice parameters and bulk moduli with experimental results. Ground state stability analysis indicates C15-Fe_2Zr Laves phase to be the most stable and t-$FeZr_2$ to be more stable than c-$FeZr_2$. All Fe–Zr intermetallics are mechanically stable as estimated from their calculated elastic constants. The calculated elastic moduli, in general, decrease with increasing Zr concentration. Anisotropies in bulk, shear and Young moduli are also presented. All the binary intermetallic phases exhibit *G/B* value of less than 0.57 and hence are ductile due to the presence of dominant metallic bonding arising from Fe *d*–Zr *d* interactions with a small component of covalent character.

1. Introduction

Iron–zirconium system is an important alloy system in nuclear industry. The Zr-rich Fe–Zr alloys (Zircaloy) are widely employed as cladding materials and other structural components in light and heavy water nuclear reactors owing to their superior mechanical and corrosion properties and low neutron absorption cross section [1–5]. Similarly, both Fe-rich and Zr-rich Fe–Zr alloys are one of the promising materials for immobilization and disposal of high level metallic solid waste originating from the electrometallurgical treatment of the spent nuclear fuel [6,7]. Fe–Zr interactions play an important role not only in Zr-rich Zircaloy for evaluating reactor safety, particularly, in the joining region between Zircaloy and carbon-steel based structural components, but also in Fe-rich (SS-15 wt.%Zr) and Zr-rich (Zr-8 wt.%SS) where the presence of Laves phases is prominent and essential for incorporation of highly radioactive and long-lived constituents of metallic waste [8–11].

Application domain of the Fe–Zr binary and related ternary derivatives is not limited to only nuclear industry. Fe–Zr alloys can be easily be formed into glasses over a wide range of composition [12,13]. The Fe–Zr alloys are potential getter materials for the storage of hydrogen and its isotopes, in particular, $FeZr_2$ alloy is used for the purpose of tritium storage due to its favorable properties like good gravimetric storage capacity, fast kinetics of hydrogen absorption–desorption and low equilibrium pressure at room temperature [14]. The presence of Laves phases in the Fe based aluminides imparts strength making these materials suitable for structural applications at high temperatures [15–18].

The Fe–Zr binaries are, thus, an important common-base subsystem of industrially important materials. A knowledge of electronic, thermodynamic, mechanical and elastic properties of these binaries will form the basis to study ternary and higher order alloys of Fe–Zr system. In view of their technological importance, there have been a number of experimental studies [8–11,19,20] and relatively very few theoretical studies [21–25] carried out to determine these properties for binary Fe–Zr alloys and their ternary or quaternary derivative alloys. Surprisingly, there exists no systematic study to determine ground state cohesive, mechanical and electronic properties of ordered intermetallics of Fe–Zr system across the composition range, the knowledge of which will help understand the nature of bonding and hence fundamental interatomic interactions as a function of composition leading to the origin of these properties.

Fig. 1 shows Fe–Zr phase diagram as taken from Jiang et al. [26]. It consists of seven intermetallics, *viz.*, $Fe_{23}Zr_6$ ($Mn_{23}Th_6$ prototype) [27,28], C14-Fe_2Zr ($MgZn_2$ prototype) [6,10], C15-Fe_2Zr (Cu_2Mg prototype) [27,29], C36-Fe_2Zr ($MgNi_2$ prototype) [27,30], t-$FeZr_2$ ($CuAl_2$ prototype) [27,31], c-$FeZr_2$ ($TiNi_2$ prototype) [27,32] and $FeZr_3$ (Re_3B prototype) [27,33] across the composition range. Among these, C14-Fe_2Zr, C15-Fe_2Zr, C36-Fe_2Zr and t-$FeZr_2$ (C16) are the Laves phases. Table 1 gives the crystallographic information

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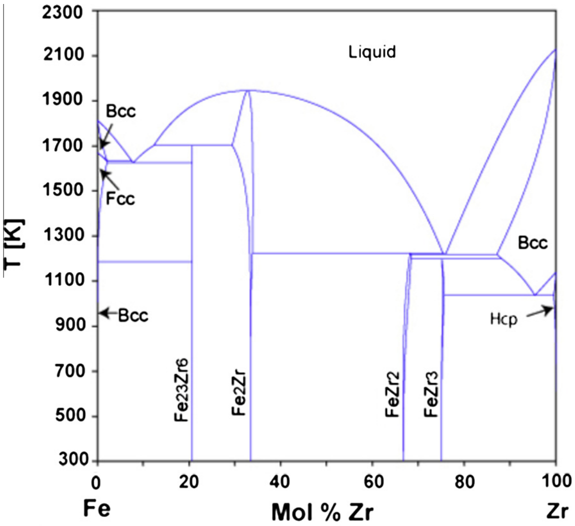

Fig. 1. Fe–Zr phase diagram [26].

of all the intermetallics of Fe–Zr alloy system. In Fig. 2, we depict the unit cells of these intermetallics. A quick look at the experimental investigations carried out on these intermetallics suggests that there are contradictory observations with regard to stability of some of these phases, *e.g.*, $Fe_{23}Zr_6$ and $FeZr_2$ phases have been reported to be equilibrium phases in some studies [34,35], whereas in other studies these phases have been reported to be stabilized only by impurities (*e.g.*, oxygen) or contaminations from crucible material [36,37]. Moreover, their suggested phase formation reactions are also debatable, *e.g.*, Liu et al. [38] suggested a peritectoid reaction $(\alpha\text{-Fe}) + Fe_2Zr \rightleftarrows Fe_{23}Zr_6$ for nucleation of $Fe_{23}Zr_6$, while Abraham et al. [20] suggested a two-step mechanism, *viz.*, $Fe_2Zr \rightarrow Fe_{23}Zr_6 + \alpha\text{-Zr}$, followed by reaction of α-Zr with α-Fe to form more of $Fe_{23}Zr_6$. At Fe_2Zr composition, three polymorphs of the Laves phase Fe_2Zr, *viz.*, C15, C14 and C36 are present in the phase diagram. The experimental studies carried out on these Laves phases suggest that these phase are stable/metastable in the given temperature-composition domain. At stoichiometric composition, Fe_2Zr crystallizes into a cubic structure (C15) and a hexagonal C36-type polymorphic structure at high temperatures with low Zr concentrations of 26.6 at.% [21,36]. Guseva et al. [39] observed formation of C14-Fe_2Zr phase in the composition range Fe – 21–23 at.% Zr annealed below 1480 °C. The c-$FeZr_2$ has been observed by some workers [36,37,40] to be a high temperature phase which undergoes eutectoidal decomposition to form Fe_2Zr + $FeZr_3$ between 780 °C and 951 °C, while others observed it to be stable down to room temperature [21,41–43]. Stein et al. [36] observed that $FeZr_3$ intermetallic phase forms by peritectoid reaction at 851 °C from the phases $FeZr_2$ and β-Zr. Though different temperatures has been reported for this invariant reaction, *viz.*, 923 °C by Servant et al. [21], 940 °C by Bhanumurthy et al. [41], 877 °C by Alekseeva et al. [37] and 885 °C by Malakhova et al. [40]. It is clear from the above that in spite of its technological importance, the Fe–Zr system is still not well-understood.

There are very few theoretical studies which have been carried out for determination of phase stability and mechanical properties of the Fe–Zr intermetallics. Thermodynamic modelling using the CALPHAD methodology on the phase stability/transformation of Fe–Zr intermetallics have been performed by Pelton et al. [44], Servant et al. [21] and by Jiang et al. [26]. Servant et al. [21] confirmed the existence of $Fe_{23}Zr_6$ intermetallic through their thermodynamic modelling, while CALPHAD approach adopted by Jiang et al. [26] could not give any new information on the relative stabilities of these intermetallics. Mihalkovič et al. [22] calculated enthalpy of formation at 0 K of Fe-rich glass forming alloys, *viz.*, Fe, B, Y and Zr binaries and ternaries within the plane wave (PW) based density functional theory (DFT) formalism using the projector augmented wave (PAW) potentials and generalized gradient approximations with Perdew and Wang exchange correlation functional. Their study, which did not include C14-Fe_2Zr and c-$FeZr_2$ intermetallics, showed that the C15-Fe_2Zr, t-$FeZr_2$ and $FeZr_3$ are the most stable phases at their respective compositions. However, they did not discuss other cohesive and mechanical properties of Fe–Zr intermetallics. Recently, Tao et al. [23] employed PW–PAW methodology to study phase stability and mechanical properties of both c-$FeZr_2$ and t-$FeZr_2$ intermetallics along with $AlZr_2$ (both Ni_2In and Al_2Cu prototype), and Al_2FeZr_6 ($InMg_2$ prototype) phases and found all the phases to be thermodynamically as well as mechanically stable and ductile. Zhang et al. [24] studied the electronic and magnetic structures of Laves C15-Fe_2Zr phase using the full-potential linear augmented plane wave (FP-LAPW) method. Their findings suggested that the long-range 3*d*–4*d* exchange interactions lead to anti-parallel coupling giving rise to ferrimagnetic ordering in C15-Fe_2Zr. Chattaraj et al. [25] employed first principle approach to study the structural, electronic, elastic and thermodynamic properties of $FeZr_2$ and $FeZr_2H_5$ and found that both compounds are thermodynamically as well as mechanically stable.

It is clear that though a number of experimental and theoretical studies have been carried out to determine the phase stability and phase field of most of the Fe–Zr intermetallics, the elastic and electronic properties of these intermetallics are almost non-existent. The elastic properties of both Fe-rich and Zr-rich Laves phases constitute an important piece of information as they appear frequently in several important alloys, e.g., in SS-15% Zr and Zr-8% SS alloys which, as mentioned earlier, are promising materials for metallic waste immobilization. Similarly, the elastic anisotropy, which is an important parameter to understand induction of micro-cracks, has not been reported for any of these intermetallics. Moreover, in the literature, there exists contradictory observations with regard to stability of some of these phases, *e.g.*, $Fe_{23}Zr_6$ and $FeZr_2$ phases and their formation mechanisms. Since the stability, elastic and magnetic properties of these intermetallics are intimately related to the nature of bonding operative in them, it was surprising to see that the electronic properties leading to understanding of fundamental interatomic interactions are hardly discussed in the literature.

In this work, we present a systematic study of ground state cohesive, magnetic, elastic and electronic properties of all these binary intermetallics of Fe–Zr system across the composition range to obtain their thermodynamic and mechanical stability as well as to study the effect of the nature of bonding on these properties. The paper is organized as follows: In the next section, we present the computational methodology employed to study cohesive and mechanical properties of these binary intermetallics. Next, we present results and discussion of our calculations of above properties. Finally, the main conclusions of our work are presented.

2. Computational methodology

We employed DFT *spin-polarized* plane wave based method using projector augmented wave (PAW) [45] potentials as implemented in Vienna *Ab-initio* Simulation Package (VASP) code [46] for calculations of ground state properties of all Fe–Zr intermetallics, *viz.*, bcc Fe, C15-Fe_2Zr, C14-Fe_2Zr, C36-Fe_2Zr, $Fe_{23}Zr_6$, c-$FeZr_2$, t-$FeZr_2$, $FeZr_3$ and hcp Zr (Table 1 and Fig. 2). The PAW potentials provided in VASP explicitly treat [3*d*4*s*] state of Fe and