

Chemical bonding and crystal structure of Zr-based intermetallic high-temperature shape memory alloys

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The present paper is dedicated to an analysis of the influence of chemical bonding in intermetallics of the ZrCu–ZrNi–ZrCo row on the relative stability of the crystalline phases competing in the process of martensitic transformation. Electronic structure analysis has shown that the amount of bonding Co–Co (Ni–Ni, Cu–Cu) states in the binary ZrCo, ZrNi and ZrCu intermetallic compounds is highest for the B2 phase in the case of ZrCo, but for the *Cm* phase in the case of ZrCu, whereas similar values were obtained for the three low-symmetry model structures in the case of ZrNi. These results are compared with the phase formation in binary and quasi-binary intermetallics ZrCo–ZrNi–ZrCu as observed by X-ray powder diffraction.

Intermetallics / Martensitic phase transformation / Electronic structure / Crystal structure

Introduction

The group of intermetallic compounds of the *AB* type undergoing B2↔low-symmetry phase martensitic transformations, is considered competitive amongst novel functional materials – high-temperature shape memory alloys [1,2]. Their application is hindered because of the significant plastic deformation resulting from the crystallographic scheme of the B2→B19' martensitic transformation. The martensitic transformation in the B2 ZrCu intermetallic, belonging to this group, results in the formation of two monoclinic martensites, the crystal structures of which are attributed to space groups $P2_1/m$ (B19' type) and *Cm* [3]. The stability of the B2 austenite with respect to martensitic transformation can be enhanced by additions of Co, replacing Cu up to binary ZrCo, which retains B2-type structure upon cooling to the temperature of liquid helium. The replacement of Cu by Ni destabilizes the B2 phase so that binary ZrNi crystallizes from the liquid into a B33 phase. In other words, a competition between B2 austenite (*Pm-3m*), B19' ($P2_1/m$) and B33 (*Cmcm*) martensites, and a martensite belonging to space group *Cm*, takes place for multi-component quasi-binary shape memory intermetallics based on compounds of the ZrCu–ZrNi–ZrCo row. It has already been shown [4], with the help

of high-precision FLAPW calculations, that the total energy of the ordered B2 crystal structure, modeling ZrCu austenite, decreases when the symmetry is lowered, resulting in the formation of B19' and *Cm* martensitic phases. It has also been shown that the origin of the instability of the ZrCu austenitic phase model and formation of the B19' and *Cm* martensite phase models lies in the possible existence of two types of local short-range order in ZrCu: the first local short-range order type is determined by Cu–Zr interatomic interactions, and the second one by Cu–Cu interactions. It was concluded that Co–Co, Ni–Ni, and Cu–Cu interactions control the phase formation within the ZrCo–ZrNi–ZrCu intermetallic compound row [4]. The present paper is dedicated to further exploration of the structural instability in this row of intermetallic compounds, through an analysis of the influence of chemical bonding on the relative stability of the crystalline phases competing in the process of martensitic transformation.

Experimental and calculation details

Crystal structure analysis was performed with Rietveld refinements (Maud program [5]) of X-ray powder diffraction data collected using a DRON-3M

diffractometer with Cu $K\alpha$ radiation. The results of LCAO (linear combination of atomic orbitals) modeling of the electronic and crystal structures, obtained using the SIESTA program package [6], were subjected to an analysis of the bonding-antibonding states, based on the chemical bond indicator Crystal Orbital Hamilton Populations (COHP) [7]. The calculations were carried out in the generalized gradient approximation (GGA) for the exchange-correlation functional [8]. A zeta-polarized basis set, which included double $4s$ -, $4p$ -, $4d$ -, $5s$ -orbitals plus a $5p$ -orbital for Zr, double $4s$ -, $3d$ -orbitals plus a polarized $5p$ -orbital for Cu, and double $3d$ -, $4s$ - $4p$ orbitals and one $4p$ -orbital for Ni and Co, was used. The basic functions and the electron density were presented on a uniform grid in real space to calculate the total energy and matrix elements. The cut-off energy was chosen to be 200 Ry. 500 k -points were used throughout the Brillouin zone. All the calculations were carried out in the non-spin-polarized approximation.

Results and discussion

As mentioned above, in our previous work [4] results of high-precision FLAPW calculations of the electronic and crystal structure for the competing B2, B33, B19', and Cm phases in the compounds of the

ZrCo–ZrNi–ZrCu row were presented. However, this is not sufficient to understand why the ZrCo and ZrNi intermetallics exist as B2 and B33 stable phases, respectively, since the dependencies of the total energy on the volume per atom of the low-symmetry phases are almost identical and the partial d -electron densities of states in these compounds are very similar (but different from those in ZrCu). If we check the crystal structures of the phases that form between the intermetallics of the ZrCo–ZrNi–ZrCu row (Fig. 1), then we see that in $Zr_{50}Cu_{25}Ni_{25}$ a B19'-phase and a Cm martensitic phase coexist as in ZrCu (Fig. 1a), while in $Zr_{50}Co_{25}Ni_{25}$ B19' and B33 phases form (Fig. 1b), and in $Zr_{50}Cu_{25}Co_{25}$ only a B19' martensite forms (Fig. 1c). Once we had plotted the volume per atom against the electron concentration for all the phases competing during martensitic transformation in the ZrCo–ZrNi–ZrCu row (Fig. 2), it became clear that the high-temperature B2 austenitic phase is denser than the martensitic transformation products, in contrast to the classic TiNi shape memory intermetallic [9], which undergoes martensitic transformation at lower temperatures. In addition, the general increase in volume observed along the ZrCo–ZrNi–ZrCu row indicates weakening of the chemical bonds in this order. To understand the phase formation within this row, it is necessary to analyze the chemical bonds more in detail.

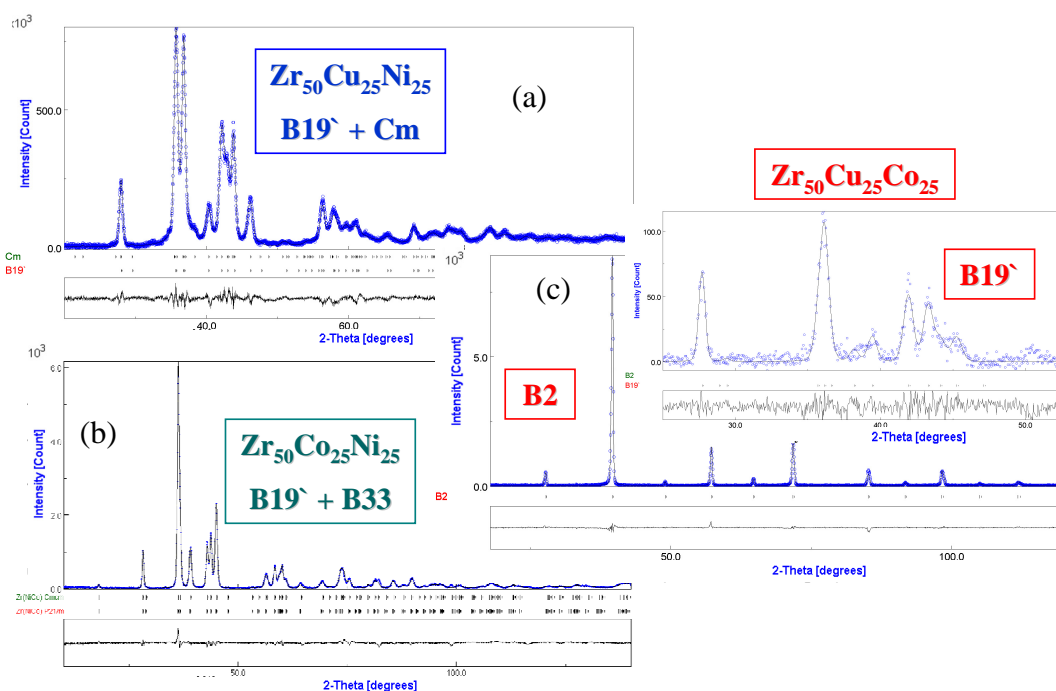


Fig. 1 Rietveld refinements of X-ray diffraction data collected for (a) $Zr_{50}Cu_{25}Ni_{25}$: the volume fraction of the $P2_1/m$ (B19') phase is 38%, that of the Cm phase 62% ($R_{wp} = 16.1\%$, $R_p = 9.6\%$, $R_{exp} = 7.99\%$); (b) $Zr_{50}Co_{25}Ni_{25}$: the volume fraction of the $P2_1/m$ (B19') phase is 60%, that of the $Cmmm$ (B33) phase 40% ($R_{wp} = 16.3\%$, $R_p = 9.15\%$, $R_{exp} = 7.72\%$); (c) $Zr_{50}Cu_{25}Co_{25}$: 100% B2 phase in the melt-spun state, while in the as-cast state (inset) 100% B19' was observed ($R_{wp} = 10.7\%$, $R_p = 7.4\%$, $R_{exp} = 7.99\%$). Dots correspond to experimental data, the line to the calculations. Reflection positions for the different phases and difference lines are also shown.

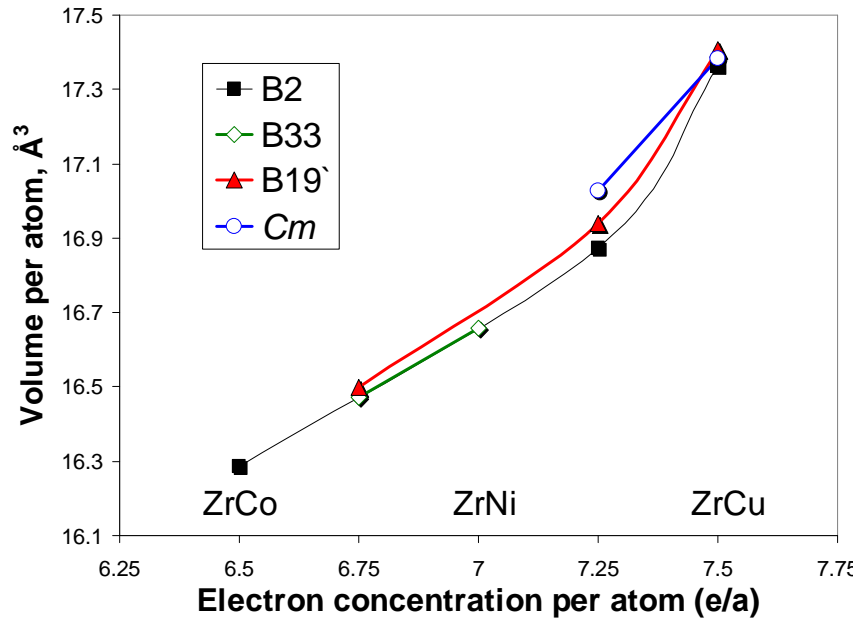


Fig. 2 Volume per atom *versus* electron concentration per atom for the phases forming in the ZrCo–ZrNi–ZrCu row (from X-ray powder diffraction).

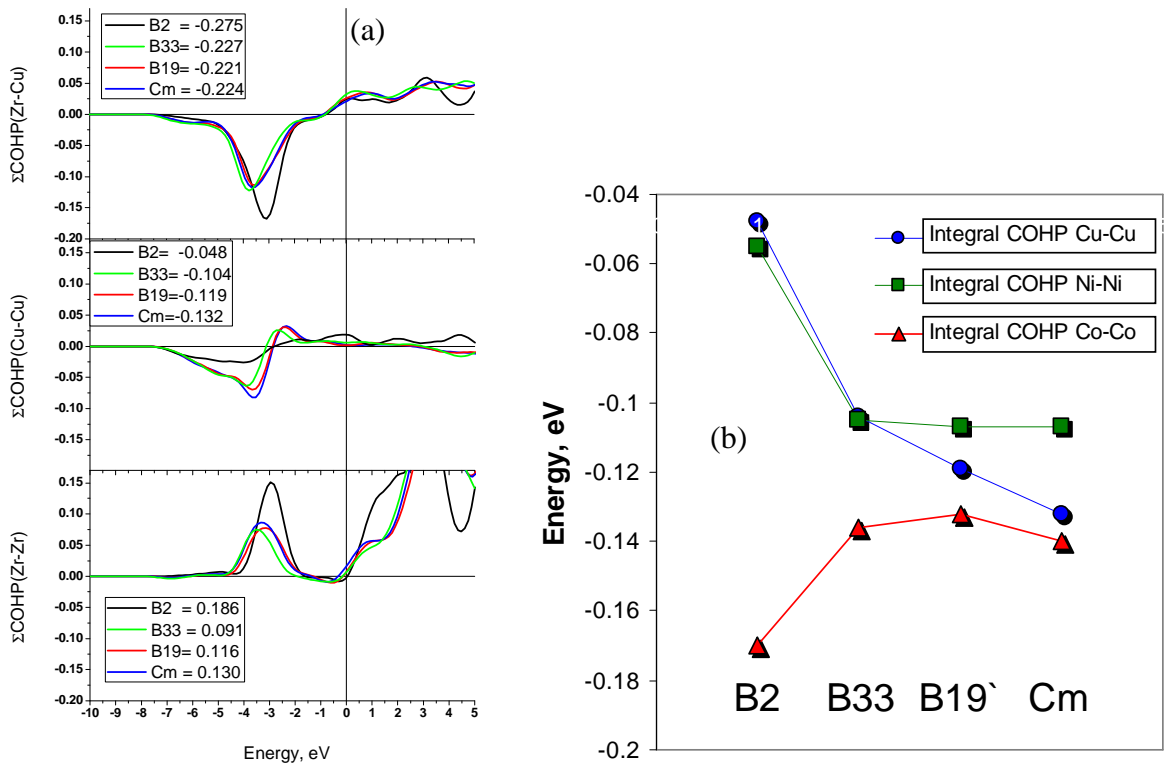


Fig. 3 (a) Integrated Crystal Orbital Hamilton Populations (Σ COHP) of the Zr–Cu, Cu–Cu and Zr–Zr bonds for ZrCu considering four different model structures; (b) Integrated Crystal Orbital Hamilton Populations of the Co–Co, Ni–Ni and Cu–Cu bonds in ZrCo, ZrNi and ZrCu.

Results of such an analysis are presented in Fig. 3. It can be seen (Fig. 3a) that the chemical bond indicator COHP, for which negative values correspond to bonding states and positive values to anti-bonding states [7], has negative values for the Zr–

Cu and Cu–Cu interactions (bonding), while for Zr–Zr it is positive (anti-bonding). Since in [4] it was shown that the Cu–Cu interactions actually control the phase formation, let us consider in more detail the Co–Co, Ni–Ni and Cu–Cu bonds in the ZrCo–ZrNi–ZrCu row

of intermetallic compounds (Fig. 3b), in order to understand the phase formation in these compounds. From Fig. 3b it is clear that the lowest negative value of the chemical bond indicator (COHP) observed for the B2 phase of the ZrCo compound indicates a higher amount of bonding states, as compared to the low-symmetry phases. For this reason the B2 phase remains stable in ZrCo, from crystallization till the temperature of liquid helium, despite the energetic favorability of the low-symmetry phases shown in [4]. In the case of ZrNi, the Ni-Ni interactions are still bonding for the B2 phase, but the COHP value strongly decreases with decreasing symmetry, following a path to the B33 orthorhombic phase, implying an increase of the amount of Ni-Ni bonding states. Further decrease of the symmetry does not change COHP. This is why the B33 phase is stable for the ZrNi intermetallic compound. In the case of the ZrCu compound, the Cu-Cu bond strengthens steadily with decreasing symmetry, which explains why the B2 high-temperature phase undergoes martensitic transformation to the B19' and *Cm* phases, bypassing B33, as the stronger Cu-Cu chemical bond adds to the favorable energy of these phases.

In the end it can be concluded that, targeting specifically the Cu-Cu (Ni-Ni, Co-Co) bond, it would be possible to tune the crystal structure formation in Zr-base high-temperature shape memory intermetallics, ensuring the most complex crystal structure after the martensitic transformation, avoiding in such a way plastic deformation during the shape

memory effect. This could enhance the functional properties of these materials to such an extent that industry might finally be able to apply them successfully.

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