Fe3Pd ferromagnetic shape memory alloys

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Fe₃Pd alloys are potentially useful ferromagnetic shape memory materials with a maximum predicted strain of up to 6.8%. Currently, however, there are difficulties with fabrication of the desired fct-ordered martensitic phase. The experimentally observed ground state of Fe₃Pd is a nonreversible bct phase, and a rapid quench is required to form the martensitic. This quench freezes substitutional disorder into the crystal, reducing the maximum obtainable strain to about 1%. Thus, discovering how to stabilize an ordered fct phase of Fe₃Pd is of paramount importance if this is to become a usable shape memory material. Electronic structure calculations indicate the ordered fct phase can be energetically stabilized by decreasing the c/a ratio below the equilibrium value. This might be achieved by doping with materials containing a lone valence p-electron, such as B or Al. Furthermore, a rigid band analysis suggests that addition of electrons to the system through alloying slightly favors the ordered phase. © *2003 American Institute of Physics.*
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INTRODUCTION

Shape memory materials have found widespread application in engineering and medicine, and recently there has been a great deal of interest in the search for ferromagnetic shape memory (FSM) alloys capable of large reversible strains under an applied magnetic field. Fe₇₀Pd₃₀ is a relatively new FSM material that has exhibited strains of 1%, although an analysis of the various crystal structures suggests a maximum strain of 6.8% is theoretically possible.[1] The fct phase of these alloys has a fairly large saturation magnetization (1200–1500 emu/cm³) and magnetocrystalline anisotropy (MCA) (0.30 MJ/m³). We have previously reported that small additions of Pt can more than triple the MCA of the martensite.[2] Large saturation magnetizations and MCA allow the growth of a single magnetic domain by ensuring a large driving force can be applied to the twin boundaries with an external magnetic field. Fe₃Pd-based FSM alloys thus have significant potential for eventual industrial applications.

However, there are fabrication difficulties associated with this material. Although the desired phase is fct martensite, the ground state of Fe₃Pd is experimentally found to be a nonreversible bct phase. A fairly rapid quench is required to obtain the metastable fct phase. The quench must be fast enough to prevent formation of the bct phase and precipitation, and yet slow enough to allow atomic diffusion over at least a unit cell. This quench produces a disordered crystal; consistent with laboratory samples that have a substantial degree of substitutional disorder, x-ray diffraction data have shown no superlattice peaks. A direct consequence of disordering is that experimentally measured MCA values are found to be an order of magnitude smaller than calculated bulk values. Although it is the ordered, high-MCA phase that is desired for FSM applications, the substitutionally disordered fct phase has a lower energy than the ordered phase; the material is naturally disordered. Finding a method of lowering the energy of the ordered phase below that of the disordered phase is thus imperative if the quench is to produce a well-ordered, high anisotropy phase. This article is a report upon our efforts aimed at achieving this goal. We have focused on alloying as a possible route, exploring the relation between the electronic structure and ordering energy.

First-principles calculations reveal a sensitive dependence of the energy difference between the ordered and disordered phases, $\Delta = E_{\text{ord}} - E_{\text{dis}}$, on the tetragonality of the cell. We found computationally that the ordered phase is energetically favored when c/a is less than about 0.936, a value 3.6% smaller than the calculated equilibrium value. One possible way to induce a decrease in c/a might be to alloy with small amounts of B or Al, as the highly directional nature of a single p-bond may contribute to unidirectional cohesive enhancement between the Fe–Fe and Fe–Pd layers. An alternative strategy is to alloy with elements that add or remove electrons within a rigid band picture and to use the density of states (DOS) as a guide. We found that additional valence electrons added to the system seem to decrease the energy difference between the phases.

CALCULATIONS

First-principles calculations were performed on both ordered and disordered fct Fe₃Pd. The ordered material has a $L1_2$ structure with Fe atoms at the face centers and Pt atoms at cube corners. The disordered phase was treated within the coherent potential approximation,[3] with 75% Fe and 25% Co

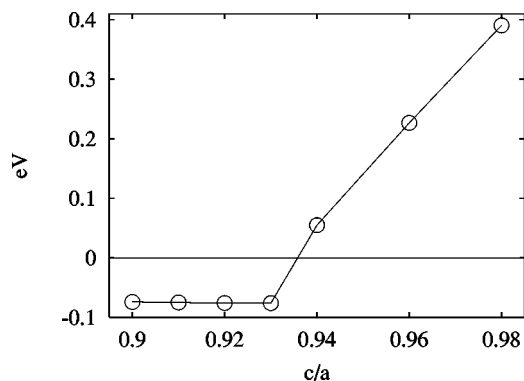a) Electronic mail: astern@tulane.edu

FIG. 1. Energy difference in eV between ordered and disordered phases of Fe$_3$Pd, vs. c/a, for fixed cell volume. The ordered phase is stable for c/a less than about 0.936, and the disordered phase is energetically favored for c/a greater than 0.936.

FIG. 2. Integrated minority Fe d-bands of Fe$_3$Pd vs. c/a. Decreasing c/a populates the mixed-layer Fe orbitals at the expense of the pure-layer Fe orbitals. Note the populations are equal when full rotational symmetry is restored at $c/a = 1$.

evenly distributed on each site. Experimental as well as calculated lattice constants and magnetic properties are given in Ref. 2.

Total energies, MCA, and DOS were calculated with the layered-Koringa–Kohn–Rostoker (LKKR) density functional formalism.[4] This approach is based upon Green functions, and, by use of the coherent potential approximation, can treat both ordered and disordered alloys within the same set of approximations. Since this formalism uses the atomic sphere approximation, however, structures cannot reasonably be optimized, although total energies of different phases at the same lattice constants can be compared to each other with reasonable confidence. Therefore, in order to determine equilibrium structures for the ordered compound, structures were optimized with the density functional program VASP.[5] VASP uses all-electron frozen core projector augmented wave potentials[6] and the generalized gradient approximation to the exchange-correlation energy.[7] Apart from supercell computations, VASP cannot readily treat substitutional alloys. Accordingly these two programs provide complementary yet distinct information. The lattice constants and c/a ratios obtained from experiment[2] and from VASP were used as input to the LKKR calculations. The VASP calculations predict lattice constants of $a = 3.791$ Å and $c = 3.681$ Å, corresponding to a c/a of 0.971. Lattice constants of experimental samples with significant substitutional disorder have values of $a = 3.8375$ Å and $c = 3.5938$ Å ($c/a = 0.937$). Consistent with Vegard's law, both experiment and theory have similar cell volumes. To date, only the disordered fct phase has been observed.

The energy difference Δ between the ordered and disordered phases is found to depend strongly on the tetragonality of the unit cell. Figure 1 shows Δ as a function of c/a. In the LKKR calculations presented, the cell volume was fixed at that obtained from the VASP calculations, so that increasing (decreasing) c/a causes the basal lattice constant a to decrease (increase). The results of LKKR total energy calculations predict the ordered phase is energetically favored for c/a less than about 0.936. Note that at the calculated lattice constants for the ordered structure, the LKKR method predicts the disordered phase is energetically favored relative to
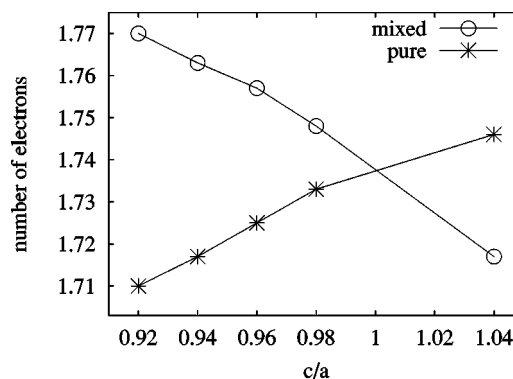
the ordered phase (i.e., $\Delta < 0$). An estimate of the (positive) contribution that the entropy of mixing E_{mix} adds to Δ can be found from the classical formula for a binary alloy with concentration c: $E_{\mathrm{mix}} = -k_B T[c \ln(c) + (1-c)\ln(1-c)]$, evaluated at $c = 0.25$. This gives roughly 0.01 eV at room temperature, which is about a 10% correction to Fig. 1.

To see intuitively that ordering is induced by decreasing c/a, note that, along the [001] direction, the Fe$_3$Pd fct structure is composed of pure Fe layers separated by 50:50 mixed Fe/Pd layers. As c/a decreases below unity in an isovolume
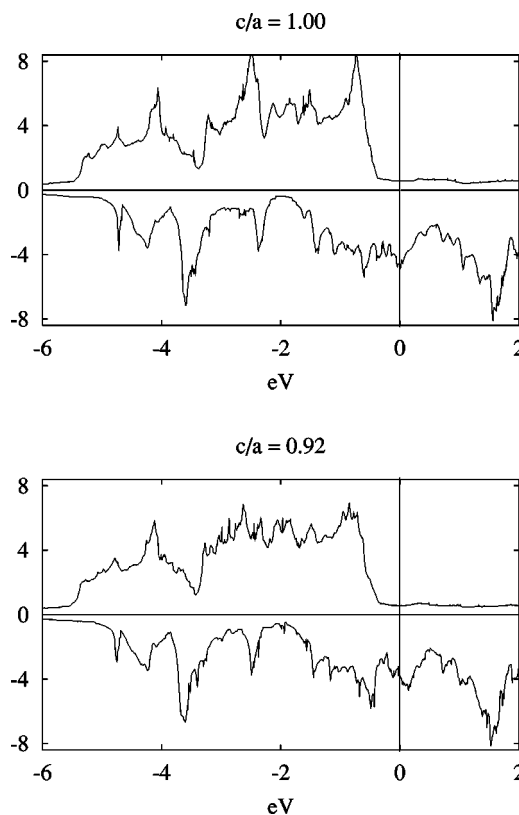

c/a = 1.00

c/a = 0.92

FIG. 3. Density of states of Fe$_3$Pd with $c/a = 1.00$ (above) and $c/a = 0.92$ (below). Note the splitting in the minority bands at E_f when the cubic symmetry is broken. This effect is almost entirely confined to the Fe d-bands. In each figure, the majority states are on top, and the minority states are on the bottom.

distortion, a increases, and the overlap of the pure-Fe/pure-Fe d-orbitals decreases relative to that of the pure-Fe/Pd d-orbitals. In terms of a pairwise bonding picture, this would increase the Fe–Pd interactions relative to the pure-layer Fe–Fe interactions. Increased Fe–Pd interactions clearly favor ordering. Evidence that d-orbital populations are changing with c/a is given in Fig. 2, which shows as a function of c/a the integrated minority d-bands for the pure-and mixed-iron atoms obtained from the DOS.

Driving the repopulation of various d-orbitals is a pseudo-Jahn–Teller instability, whereby energy levels that are degenerate when $c/a=1$ are split when c/a falls below 1, breaking the rotational symmetry of the cubic structure. This can be seen in the ordered-phase minority DOS as a splitting in the peak at the Fermi energy E_f as c/a varies from unity. This behavior is confined almost entirely to the Fe d-bands; the Pd d-bands at E_f are quite insensitive to c/a. DOS for fct Fe$_3$Pd with $c/a=0.92$ and $c/a=1.00$ are given in Fig. 3.

In an effort to induce a smaller c/a, which also has the beneficial effect of increasing the maximum shape memory effect, we have suggested various ternary additions that can provide directional cohesive enhancement. B and Al are reasonable candidates as impurity atoms since they each have a lone valence p-orbital that could naturally form bonds between the mixed and pure layers. Samples of $(Fe_3Pd)_{0.95}B_{0.05}$ have recently been prepared and show an FSM effect, but are, as yet, not fully characterized. Another approach is to add elements that change the valence electron count and impact the bonding through orbital hybridization changes. Using a rigid band model, we have found through integration of the DOS that additions of ternary atoms that increase the overall valence electron count favor the ordered structure. Calculations on Fe$_3$Pd$_{1-x}$Ag$_x$ for $x=0.0$–0.6 indeed show that additions of Ag help stabilize the ordered phase with

respect to the disordered phase. The effect is minimal, however, as $x=0.05$ lowers the relative energy of the ordered phase by only about 8 K.

CONCLUSION

Fe$_3$Pd-based FSM alloys are potentially excellent magnetomechanical materials. Large predicted strains will be realized, however, only if an as yet unseen ordered phase can be fabricated. Ordering in these systems can be understood in a straightforward way in terms of interactions between the pure Fe and mixed Fe–Pd layers. Consistent with this picture, our calculations suggest that decreasing the c/a ratio and adding electrons through alloying can energetically stabilize the ordered phase. Samples with small amounts of boron have been made and appear promising.

ACKNOWLEDGMENTS

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