First-principles prediction of superplastic transition-metal alloys

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Superplastic transition metal alloys and compounds are predicted from first principles calculations. Provided a suitable tuning of the alloying is done, materials with vanishingly low shear modulus C' have recently been identified among the $3d$, $4d$, and $5d$ elements if the valence electron average number is close to 4.24 (i.e., Ti-Ta-Nb-V-Zr-O and Ti-Nb-Ta-Zr-O alloys). The vanishingly low C' elastic constant of these bcc alloys is, according to the joint experimental and theoretical studies [T. Saito *et al.*, Science **300**, 464 (2003)], the crucial material parameter that is responsible for the superplasticity. We predict here, using first principles calculations, that superplastic alloys should also be found for alloys with drastically different valence electron concentrations, i.e., for W-Re-, W-Tc-, Mo-Re-, Mo-Tc-, and Fe-Co-based alloys.

I. INTRODUCTION

Novel materials with improved, tailor-made properties are being proposed and synthesized at an impressive rate.[1] Among many examples of materials that have been synthesized to meet one or several specific demands put on them by the application they are intended for, we mention the carbon nanotubes that have a vast range of mechanical and electrical properties,[2] multilayers that are designed to block dislocation movement so that the hardness is improved,[3] thin film materials which exhibit the supermodulus effect,[4] ultrahard oxides,[5] and materials for use in fuel cell technology.[6] In many of the studies of advanced material properties, theoretical modeling has been an important tool to help in the understanding of them and in some cases theory has been used to predict important features (e.g., a superhardness for the C_3N_4 based materials).[7] It is in particular theoretical modeling based on first principles density functional approach[8] that has been demonstrated to be a very efficient tool for studies of materials and their properties (e.g., hardness, elasticity, magnetism, superconductivity, and chemical reactivity).

The recent discovery[1] of alloys with "superproperties" (superplasticity, superelasticity, invar and elinvar behavior and ultrahigh strength) is no exception to this trend. By combining theory and experiment several alloys were identified that had these extreme properties. The theoretical work suggested one electronic parameter, the average valence electron number (electron/atom ratio), as the most critical parameter for these unique alloy properties. The observed dislocation-free plastic deformation of the Ti-Ta-Nb-V-Zr-O and Ti-Nb-Ta-Zr-O alloys in Ref. 1 was concluded to be a result of a nearly vanishing shear modulus along the $\langle 111 \rangle$ direction on the $\{011\}$, $\{112\}$, and $\{123\}$ planes, which is closely related to two particular elastic constant C' [where $C' = \frac{1}{2}(C_{11} - C_{12})$] and C_{44}. The mathematical relationship reads

$$G_{111} = \frac{6C_{44}C'}{C' + 4C_{44}}, \qquad (1)$$

where C_{44} is the shear modulus along the $\langle 001 \rangle$ direction on the $\{011\}$ plane. From first principles calculations it was found that for the superplastic alloys studied one obtained a vanishing tetragonal shear constant, i.e., C' approached zero. This means that G_{111} became very low, and superplasticity was argued to follow since the $\langle 111 \rangle$ directions on the $\{011\}$, $\{112\}$, and $\{123\}$ planes are typical slip systems for bcc crystals.[1]

The vanishing of the tetragonal elastic constant C', predicted for the presently studied alloys, suggest that they are possible candidates for having superelastic properties. However, it should be noted that superplasticity only occurs in polycrystaline materials and in fact represents a grain-boundary phenomenon.

We propose here that the vanishing tetragonal elastic constant is a result of the electronic structure of bcc crystals, in particular, of the general shape of the density of states (DOS) curve for transition metal alloys, that for a valence electron number of 4.24 (corresponding to the alloys found in Ref. 1) leads to a near instability of the bcc structure[9,10] and a vanishing C'. This identification opens the avenue for finding other alloys with "super" properties, and we demonstrate from theoretical calculations that alloys with a valence electron number of 6.6–6.9 (e.g., W-Re, W-Tc, Mo-Tc, and Mo-Re alloys) also have a vanishingly low C' and are likely to possess superelastic properties. We also predict that Co-rich, magnetic Fe-Co alloys in the bcc structure should have a vanishingly low C' and a bcc structure that is stable in comparison with close-packed ones, analogously to the W-Re and Mo-Tc alloys. The similarity is because the band-filling of the spin-down band is approximately the same as that of the spin degenerate band of W-Re alloys.[11] Conse-
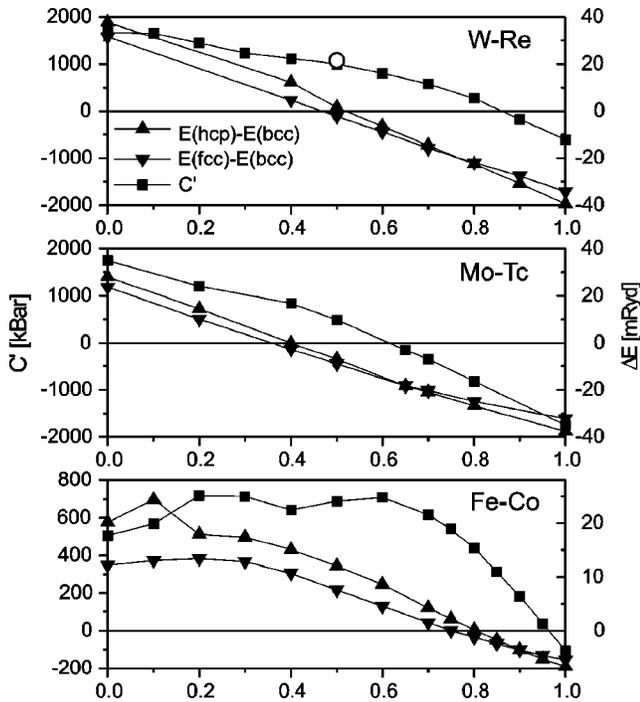
FIG. 1. Calculated tetragonal elastic constants of Fe-Co, Mo-Tc, and W-Re alloys (filled squares). The calculated energy difference among bcc, fcc, and hcp crystal structures is also shown (filled triangles and filled upside down triangles). For the W-Re alloys the elastic constant from the VCA was compared to a supercell calculation (open circle).

quently, Fe-Co alloys are also suggested to demonstrate superelastic properties.

The theoretical calculations reported here are based on density functional theory in the local density approximation. The Kohn-Sham equation was solved using a full-potential linear muffin-tin orbital method.[12] The treatment of the alloy system was made using the virtual crystal approximation (VCA), the coherent potential approximation (CPA), as well as a supercell method. We made comparisons of elastic constants calculated with the VCA and with supercells, for $W_{0.5}Re_{0.5}$, and found a disagreement smaller that 5% (Fig. 1). We also compared the electronic structure of these alloys from CPA and VCA calculations and found a good agreement.

II. RESULTS

In the past the connection between structural stability and elastic constants was identified.[13–15] Further, elastic moduli in metallic systems are governed by the electronic structure; in general, one can prove that the larger the DOS near the Fermi energy, the smaller the elastic moduli C'. This modulus is especially sensitive to DOS features for crystallogeometrical reasons (it vanishes in the bcc structure in the nearest neighbor approximation and therefore the long-range part of interatomic interactions is more important).[16] Hence, in the search for alloys with vanishingly low tetragonal elastic constants it becomes useful to employ our understanding of

the general trends in the electronic structure of the d band. For this reason it seems likely that in addition to the alloys reported in Ref. 1, one should inspect the W-Re, W-Tc, Mo-Tc, and Mo-Re alloys. This is so since for these alloys the shape of the DOS curve dictates a transition from the bcc structure to a close packed structure.[9,10,16]

The factor that is most important for determining the structural stability and the elasticity of these alloys is the band filling and for this reason it is sufficient to illustrate our predictions of superplastic alloys, with calculations performed only for W-Re and Mo-Tc alloys (W-Tc and W-Re alloys are isoelectronic, as are the Mo-Tc and Mo-Re alloys). It is also of interest to investigate Fe-Co alloys since they have been shown to have similar band filling (in the spin down band) as the W-Re and Mo-Tc alloys have (in the spin degenerate band).[11] Hence it is expected that since the spin up band of the Fe-Co alloys is filled and chemically inert, the structural properties and elasticity of Fe-Co alloys should be similar to those of W-Re and Mo-Tc alloys.

In Fig. 1 we show the calculated tetragonal elastic constants for We-Re, Mo-Tc, and Fe-Co alloys, together with calculations of the structural stability. Note that just like in the Ti-Ta-Nb-V-Zr-O and Ti-Nb-Ta-Zr-O alloys, the tetragonal elastic constant can be made vanishingly small by tuning the alloy concentration. We also note that at the concentrations where C' goes to zero, the bcc crystal structure should already have transformed to another crystal structure. Hence, in order to observe novel alloys with superelastic properties one needs to consider electron concentrations of 6.6–6.9, possibly with small amounts of elements that stabilize the bcc crystal structure, in the same way as done in Ref. 1. In addition Co-rich Fe-Co alloys should be of interest.

III. CONCLUSION

To conclude, we predict several alloys that may be a base for superplastic materials, due to a vanishingly low tetragonal elastic constant C'. We argue that the elastic and structural stability are intimately connected and can both be understood from band-filling arguments. The alloys we propose to have superplastic behavior are primarily W-Re, W-Tc, Mo-Tc, Mo-Re, and Fe-Co alloys, although additional smaller components might be needed to avoid structural instabilities. It is possible that the effect under consideration will be also observed also for Cr- or Mn-based alloys, since these elements are isoelectronic with W(Mo) and Re(Tc), respectively. However, the presence of (possibly, noncollinear) magnetism in these systems, as well as the complex crystal structure of Mn systems may distort the analogy.

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