JOURNAL OF MATERIALS SCIENCE 28 (1993) 3145–3148

Correlations between the electronic state and mechanical properties of some transition metal compounds/alloys

A. A. OGWU, T. J. DAVIES
Manchester Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester M1 7HS, UK

It is observed that changes in the mechanical state of solids can alter their electronic state and vice versa. The d-state electrons in transition metal compounds/alloys are found to influence mechanical properties in a range of materials that include intermetallic compounds, hard metals, cryogenic alloys, etc. We have attempted to represent these effects graphically as a field map based on axes of the number of d-state electrons in the compounds. Specifically identifiable properties are found in different regions in this property field map.

1. Introduction

The electrical and mechanical properties of a solid are both related to the nature of the bonding in the solid. The bonding in a solid determines the type of cohesion that would exist in the solid, as well as whether the solid would be an electrical insulator, semi-conductor or metallic conductor. Many recent publications have indicated that the application of mechanical force in the form of a compressive pressure is capable of inducing an insulator–metal transition in nominally fully insulating materials. The most recent articles on this subject are those of Gilman [1] and Cahn [2] on the metallization of silicon, in which the experiments of Pharr *et al.* [3] on the indentation of silicon were analysed. All these authors observe that the combination of pressure and shear that exists under a mechanical indentor could cause a semi-conductor to transform to a metal. Gilman [4], based on his earlier proposal that dislocation motion at low temperatures in silicon could be explained in terms of stress-induced tunnelling of bonding electrons into anti-bonding states, further proposed that the compression of silicon during indentation with a diamond indent would cause a narrowing of the band gap, thereby increasing the probability of electrons tunnelling from the valence band (bonding states) into the conduction band (anti-bonding states) resulting in metallization. Gilman [1, 4] also indicated that metallization and dislocation motion are closely related through their mutual dependence on the excitation of bonding electrons into antibonding states and the existence of a correlation between glide activation energies and the average band gaps in solids.

A more spectacular example of metallization is the transformation of hydrogen from its normally gaseous state to a near-metal state by the applications of local pressures in a mechanical anvil [5]. This transformation is described by Mao and Hemley [5] in terms of an insulator-to-metal transition. Mao *et al.* [6] have already found hydrogen to exist in the hexagonal close packed (hcp) structure at pressures around 300 kbar, with lattice positions occupied by hydrogen molecules. It is believed that as the pressure is increased, hydrogen would form an atomic metal in which hydrogen "atoms" would occupy lattice sites instead of hydrogen molecules, leading to a complete delocalization of electrons and a full metallization of hydrogen.

The influence of electronic states on the mechanical behaviour of highly ordered "crystallographic" structures such as intermetallic compounds has also attracted considerable interest in recent times. The results of Nicholas [7] on ordered intermetallic compounds have shown that there is a change in the electron density of state per unit volume curve when such a material undergoes a transformation from a disordered to an ordered state, due to splitting of the brilloiun zone of the disordered state, leading also to an alteration of the shape and size of the fermi sphere of the disordered state relative to the ordered state. In a study of a similar nature, Baker [8] proposed that the addition of boron to Ni_3Al alters the chemistry and bonding of the grain boundaries and this allows unpaired dislocations to slip easily, leading to an improvement in ductility. Commenting on the general theme of such effects, Imayev and Imayev [9] argued that there is a change in the type of interatomic bonding which occurs during the transition from pure metals to intermetallic alloys, resulting in a weakening of the metallic bond and strengthening of the covalent bond.

2. Discussion

We [10] have proposed on empirical grounds a set of conditions based on the Engel–Brewer rules [11] for

0022–2461

improving the ductility of transition metal-based intermetallics, when compositional and phase diagram data are taken into consideration. Many examples were cited from the literature to support the association of these conditions with an improvement in the ductility of ordered intermetallic compounds when the alloying electron addition is determined by theory considerations. We have also put forward a possible correlation between γ_{APB} (the anti-phase boundary energy) in ordered transition metal-based intermetallic compounds and d^+, the sum of the number of unfilled d-state electrons in each constituent transition metal of the compound of the form

$$\gamma_{APB} \propto \frac{1}{d^+} \tag{1}$$

Modifications are expected to Equation 1, by the presence of group IIB elements with filled d-orbital states (as defined by the Engel–Brewer theory) and non-transition metals in the intermetallic compounds. In this case Al_3Ti is given as an example, which changes from its normal tetragonal structure to a cubic Cu_3Au type structure on alloying with the $3d$ elements Fe, Ni, Cu or Zn [12].

Our studies [13, 14] on transition metal-based hard-metal systems has also revealed a correlation between suitable metal binder selection for "hard" metals (metal carbides cemented with a metal alloy phase) and the number of d-state electrons present in the transition metal compound and binder. Earlier studies on transition metal diborides by Samsonov *et al.* [15] has shown that a change in the number of d-electrons in the transition metal correlates with changes in the boron-metal structures and with changes in the physical and thermodynamic properties of the compounds. Friedel's work [16] on bonding in transition metal elements, showed that the d-band structure is composed of bonding and anti-bonding orbitals, whereby the filling of the bonding band results in stabilization and cohesion with increasing melting points for the early transition metals and the filling of the anti-bonding states reduces stabilization and lowers the melting point of the second half of the transition metal row of elements. Dempsey [17] found a similar relationship for the carbides, borides and nitrides of transition metals generally classified as hard metals. The origin of the split in the d-states is believed to be related to the symmetry of the d-wave functions in transition metals and the symmetry of the crystal structure of the compounds; this effect is generally more pronounced in transition metal complexes, i.e. crystal field splitting and Jahn–Teller distortion [18]. For binder selection in hard metals [12, 13] based on considerations similar to the above, our studies of unfilled d-state electron states in metal carbide/binder led to the proposal of a set of rules based on the Engel–Brewer theory for binder selection in hard metals [10].

Attention has been given to a probable close relationship [19, 20] between the energy band gap in semi-conducting and insulating solids and their thermodynamic properties like heats of formation and chemical potential. Li [21] has recently proposed a relationship between the work of adhesion, the electron density of liquid metals and the band gap energy of ceramics during the bonding at a ceramic–metal interface, based on an electron theory approach; the basic assumption is that the adhesion arises from the transfer of electrons from the metal to the ceramic valence band. Experimental evidence to support this proposal is reported in the work of French [22] and Ohuchi and Kohyama [23] using both theoretical calculations and experimental techniques such as valence band X-ray photo-emission spectroscopy (VBXPS) and vacuum ultraviolet spectroscopy (VUV). Li [21] also observed that semi-conducting materials (in which the energy gap $E_g \leqslant 4$ eV) are usually wetted ($\theta < 90°$) by liquid metals, but insulating materials ($E_g > 4$ eV) are not wetted ($\theta > 90°$) by non-reactive liquid metals.

Although at first contact it might not seem that the d-electron state has direct bearing on the performance of high-temperature solid lubricants, it is, however, explicit in the alloying of solid lubricants like MoS_2 and graphite to improve their endurance limit in service. The layered structure in these compounds is such that strong covalent σ-bonds exist within the layers, while weak π and van der Waal's bonds exist between the layers; this is the essential property which is required for lubricating behaviour. Intercalation of the sulphides and selenides of groups IV, V and VI transition metals with silver and copper [24] had two noticeable effects which led to an improvement in their lubricating properties. There was a modification of crystal structure in NbS_2 and NbSe when these were intercalated with silver, as well as an increase in the interlameller spacing. These effects can be related to the Engel–Brewer (E–B) rules which indicates that group IB elements, i.e. copper, silver and gold can promote two electrons out of the d-state, thereby achieving a d^8 electronic configuration and increasing the number of free electrons within the layers and therefore modifying the bonding. The endurance of MoS_2 films co-sputtered with nickel has also been shown to be superior to that of sputtered MoS_2 films both in air and in an inert atmosphere [25]. The MoS_2–Ni films are denser than sputtered MoS_2 films; similar improvements were found for co-sputtered MoS_2–Au films.

An instance of the interaction of d-electrons with mechanical behaviour is found in the well-established brittle fracture of transition metal alloys; this can be related to the electronic configuration of the elements involved. The large change in impact transition temperature [26] in low carbon steels when the nickel content is increased from 0% to 5%, may be related to an increase in free electron concentration, as follows: iron (Fe) has an unfilled d^6 electronic configuration, and alloying with nickel with an unfilled d^8 electronic configuration results in an increase in the number of free electrons. This increase in free electron concentration ensures the presence of a sufficient number of free electrons above the Fermi energy level, E_f, when these materials are tested at Cryogenic temperatures. Low-temperature conditions lead to a condensation of electrons into lower energy levels with the Pauli exclusion principle being obeyed because electrons are fermions, i.e. they obey the Fermi–Dirac statistics. The presence of the extra electrons due to nickel addition in the conduction band of the steel, would facilitate dislocation motion at low temperatures, therefore improving the low-temperature ductile–brittle transition temperature of the steel, provided the conduction band is not more than half-filled; Gilman [1, 4] has already identified a relationship between dislocation motion and the presence of electrons in the conduction band of silicon. The successful use of copper and aluminium alloys under cryogenic conditions may also be explained in terms of the large initial free-electron concentrations which results in a sufficient electron concentration above the Fermi energy level at cryogenic temperatures to permit dislocation motion.

As a further example, we have found it convenient to represent these apparently diverse relationships in the form of a two-dimensional plot (Fig. 1) with the number of d-state electrons in the transition metal element rows representing both axes; this allows the separation of the different effect of d-state electrons on transition metal alloys/compounds into regions in a property field diagram. One may recall previous classifications of structure types of compounds based on the classical coordinates electronegativity difference, ΔX, the atomic size difference, ΔY, and the average number of valence electrons per atom, $\bar{Z}$, conducted by Villars [27–30]. Villars maps had limitations, such as the inability to accommodate certain crystal structures, because the coordinates had a classical rather than a quantum origin. Classical coordinates cannot be used to describe fully the behaviour of atoms and molecules. In a far more substantial way, Pettifor [12] has proposed a two-dimensional way of arranging the structures of compounds, based on the coordinate termed the Mendeleev number which follows the ordering of elements in the Periodic Table, and therefore has a defined link with the quantum nature of atoms in compounds. Pettifor's structure maps based on the Mendeleev number have enjoyed a great deal of success in predicting the structures of many compounds. In this field map that we propose it is clear that the d-state electron orbital arises directly from the quantum-mechanical nature of atoms and the use of the valence electrons that occupy this orbital removes a deficiency which would have existed if classical coordinates had been used (Fig. 1). In order to explain how different regions are identifiable in our property diagram, we have to recall two important findings from our studies on transition metal-based hard metals and intermetallic compounds [10, 13, 14].

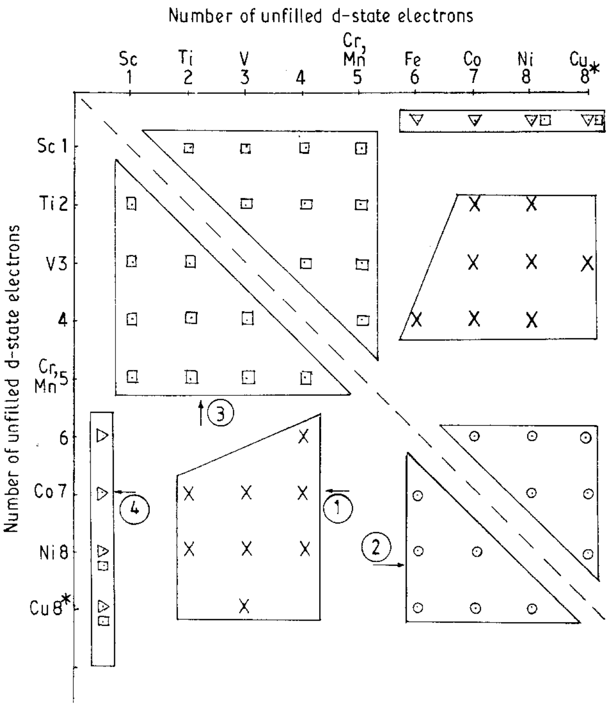

Figure 1 A property field map for transition metal alloy/compounds. * According to the Engel–Brewer theory, group IB elements copper, silver and gold promote two electrons out of the d-state, thereby achieving a d^8 electronic configuration.

1. We assumed that for a transition metal or compound with an unfilled inner d-shell in the state d^x, a transition metal binder in the state d^y would be the most suitable (x and y represent the number of electrons in the unfilled d-shells) where the condition

$$x + y = 11 \qquad (2)$$

is satisfied, along with other necessary chemical and thermodynamic requirements.

2. For a transition metal compound (using transition metal aluminide intermetallics as prototypes), with the transition metal having an unfilled d-shell shell in the state d^x, alloying with another transition metal with an unfilled d-shell in the state d^y (by replacing some of the aluminium by the alloy element leading to non-stoichiometric compound formation in the case of the aluminide) where the condition

$$x + y = 19 \qquad (3)$$

is satisfied, leads to an improvement in ductility, when taken along with other requirements, above 1.

In Fig. 1, the axes are made up of the number of d-state electrons in the transition element rows. Periods IV, V and VI transition elements can be placed on the axes interchangeably.

The significance of the different sections in the property field map in Fig. 1 are as follows.

Region 1. This represents the combination of the carbides, borides and nitrides of the early transition metals (hard metals) and their most suitable binder metals from the later part of the transition metal element row, e.g. WC–Co.

Region 2. This region represents the area where ductile intermetallic compounds are formed, with low values of anti-phase boundary energy, γ_{APB}. Intermetallic compounds such as Cu_3Au belong to this domain.

Region 3. This region represents the area where the intermetallic compounds formed would generally be brittle with higher values of γ_{APB} (anti-phase boundary energy).

However, the presence of group IIB and non-transition metals would affect the position of the compounds formed in Regions 2 and 3.

Region 4. This region represents single transition metal elements that would either serve as intercalants for improving the endurance limit of solid lubricants [Δ] or be utilized to improve the cryogenic properties of alloys or serve as cryogenic materials in their own right [□].

3. Conclusion

We have graphically represented the effect of d-state electrons on the compounds/alloys of transition metal elements for various technological applications. The various properties are found to partition into different regions within the two-dimensional plots which would probably open up a variety of useful alloy combinations for intermetallic compounds, when extended into a three-dimensional plot.

References

1. J. J. GILMAN, *J. Mater. Res.* **7** (1992) 535.
2. R. W. CAHN, *Nature* **357** (1992) 535
3. G. M. PHARR, W. C. OLIVER and D. S. HARDING, *J. Mater. Res* **6** (1991) 1129.
4. J. J. GILMAN, *J. Appl. Phys.* **46** (1975) 5110.
5. HO-KWANG MAO and R. J. HEMLEY, *Amer. Sci.* **80** (1992) 234.
6. HO-KWANG MAO, A. P. JEPHCOAT, R. J. HEMLEY, L. W. FINGER, C. S. ZHA, R. M. HAZEN and D. E. COX, *Science* **239** (1988) 1131.
7. J. F. NICHOLAS, *Proc. Phys. Soc.* **A66** (1953) 201.
8. I. BAKER, *New Sci.* **1823** (1992) 34.
9. R. M. IMAYEV and V. M. IMAYEV, *Scripta Metall. Mater.* **25** (1991) 2041.
10. A. A. OGWU and T. J. DAVIES, *J. Mater. Sci.* **27** (1992) 5382–5388.
11. N. A. GOKCEN, "Statistical thermodynamics of alloys" (Plenum Press, New York 1986) pp. 237–54.
12. D. G. PETTIFOR, *Mater. Sci. Technol.* **4** (1988) 675.
13. T. J. DAVIES and A. A. OGWU, "Developing matrices for hard metals", Proceedings of the International Conference on Advances in Hard Metals Production, Bonn, Germany, 4–6 May 1992 (MPR Publishing Services Ltd and EPM 19, Shrewsbury, UK, 1992).
14. A. A. OGWU and T. J. DAVIES, *J. Mater. Sci.* **28** (1993).
15. G. V. SAMSONOV, YU GORYACHEV and B. A. KOVENSKAYA, *J. Less Common Metals* **47** (1976) 147.
16. J. FRIEDEL, in "The Physics of Metals", Vol. 1, Electrons, edited by J. M. Ziman (Cambridge University Press, UK, 1969) p. 494.
17. E. DEMPSEY, *Phil. Mag.* **III** (86) (1963) 285.
18. A. R. WEST, "Basic Solid State Chemistry" (Wiley, Chichester, 1988) pp. 97–104.
19. A. K. VIJH, *J. Mater. Sci.* **5** (1970) 379.
20. S. A. SEMENKOVICH, in "Chemical bonds in semi-conductors and solids", Academician editor N. N. Sirota, Translation Editor Charles P. Poole Jr. (Consultants Bureau, New York, 1967).
21. J. G. LI, *J. Mater. Sci. Lett.* **11** (1992) 903.
22. R. H. FRENCH, *J. Amer. Ceram. Soc.* **73** (1990) 477.
23. F. S. OHUCHI and M. KOHYAMA, *ibid.* **74** (1991) 1163.
24. P. SUTOR, *MRS Bull.* **XVI**, No. 5 (1991) 24.
25. B. C. STUPP, "Performance of conventionally sputtered MoS_2 versus co-sputtered MoS_2 and Nickel", ASLE SP-14 (1984) pp. 217–22.
26. R. S. IRANI, *Metals Mater.* **8** (1992) 31.
27. P. VILLARS, *J. Less-Common Metals* **92** (1983) 215.
28. *Idem, ibid.* **99** (1984) 33.
29. *Idem, ibid.* **102** (1985) 199.
30. D. G. PETTIFOR, *New Sci.* **110** (1986) 48.

Received 2 September
and accepted 30 October 1992