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Oxidation, hardness and other properties of some borides, carbides, arsenides and sulphides

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The thermal oxidation resistance, hardness and electromechanical polishing response of compounds with elements of the First Long Period have been studied, and are briefly discussed in relation to the properties of the component elements, and of other classes of intermetallic compound.

1. Introduction

Studies of the oxidation resistance and hardness of aluminides and zinc compounds of transition elements [1, 2] led to a hypothesis [3] that properties and alloying trends could be systematized in terms of "divides". To take an example, if iron is alloyed in turn with Co, Ni, Cu, etc., we find that no intermetallic compounds are formed until we come to the Fe–Zn system, and subsequently compounds are formed between Fe and Ga, and Fe and Ge. We express this by saying that a divide exists between, in this case, Cu and Zn. In similar fashion, if zinc is, in turn, alloyed with Ga, Ge, etc., compounds are formed with As and Se, but not with Ga and Ge. At a first level of understanding or analysis we can therefore separate the relevant elements into three blocks as shown in Fig. 1, which for convenience may be labelled A, B_1 and B_2 respectively. Aluminides and zinc compounds of the transition elements may thus be termed AB_1, and III/V compounds such as GaAs, B_1B_2, and it became of interest to explore in some degree the properties of AB_2 compounds for comparison with the other classes. Consequently, four series of compounds were prepared, that is, borides (TiB – NiB), carbides (TiC – Fe_3C), arsenides (TiAs – GeAs) and sulphides (FeS – ZnS), and also MnSe and MnTe. Since it is well known that many compounds may often be formed in the types of system considered, it became necessary for a cursory survey such as this to limit the number of compounds in some way, and this was done by choosing equi-atomic compositions wherever this was possible. Exceptions to this arrangement were Cr_7C_3, Mn_3C, Fe_3C, Cu_3As, Zn_3As_2 and Cu_2S, also an additional sample CrB_2. The metal/non-metal ratio has a marked effect on the probable geometry of the non-metal partial lattice (Fig. 2). It should be noted that a rigid vertical extension of the divides in Fig. 1 would place boron in category B_1. However, from considerations outlined in [4] and the operation of the diagonal rule, it was evident that the divides draw towards each other and to the left at the beginning of the Short Periods, and the question of boron's category became an additional motivation for the work.

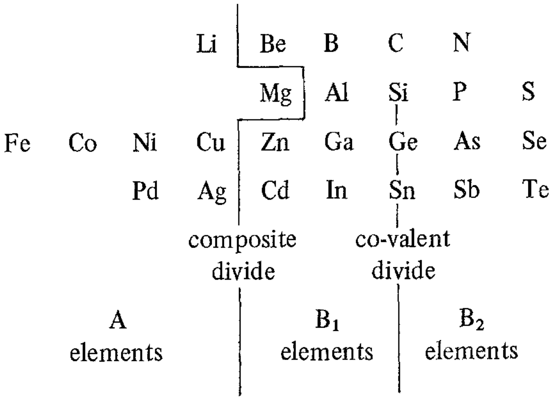

Figure 1 A part of the Periodic Table, showing the divides and blocks of elements.

2. Experimental details

The basis materials were high purity elements as detailed previously [5] except that the boron was from Koch-Light Laboratories (99.8%), and the

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For elements → (8-n Rule)	Group IVB	VB	VIB	Group VIIB	
	3-dimensional frameworks	sheets	chains	pairs	
For borides →	MB_{12}, MB_6, MB_4	TaB_2	Ta_3B_4	TaB	Ta_2B
	3-dimensional frameworks	sheet	double chains	chains	single atoms

Figure 2 The effect of the metal/boron ratio on the geometry of the boron partial lattice (adapted from [14]). Data for structures of solid elements are given for comparison.

compounds (single samples) were prepared by direct synthesis in an argon arc furnace. Such a furnace is clearly more appropriate for preparing borides and carbides than arsenides and chalcogenides, and for the latter special care was taken to cover as far as possible the non-metal with the metal component in order to reduce loss by evaporation. In spite of this, many of the preparations were very messy. Paradoxically, melting weight losses were highest for borides synthesis (~ 8%), in contrast with carbides and sulphides (~ 5%) and arsenides (~ 2%), and this is thought to be due to the high arc currents and long melting times required for the former. The buttons thus prepared appeared bright and metallic, with the exception of TiB, TiAs and MnSe which were somewhat dull. They were tested at this stage with a pocket magnet for room-temperature magnetism, and subsequently mounted for metallographic inspection.

It is possible that a little second phase was present in Mn_3C, Fe_3C and MnSe, and probable that there was rather more in CoS and NiS, but otherwise samples appeared to be single phase. Several preparations as-polished had an appearance (outline of bright needles against dark background porosity) which may be described as martensite pattern; these were the borides and carbides of V, Cr and Mn, and all the arsenides with the exception of MnAs.

After several days had elapsed, the mounts of MnB and MnAs suffered cracking, especially the latter, probably due to expansion of the compound. At this stage the compounds were tested for hardness using a Vickers microhardness attachment with 50 g load and not less than three impressions. They were also tested for response to the electromechanical polishing (EMP) technique, using the 12/19 electrolyte (12% thiosulphate, 19% thiocyanate), since previous results [6] had shown that AA solid solutions were often polished, but not AB_1 compounds. Polishing currents (specimen anode) were mostly of the order of 60 mA, but higher (600 mA) for the sulphides.

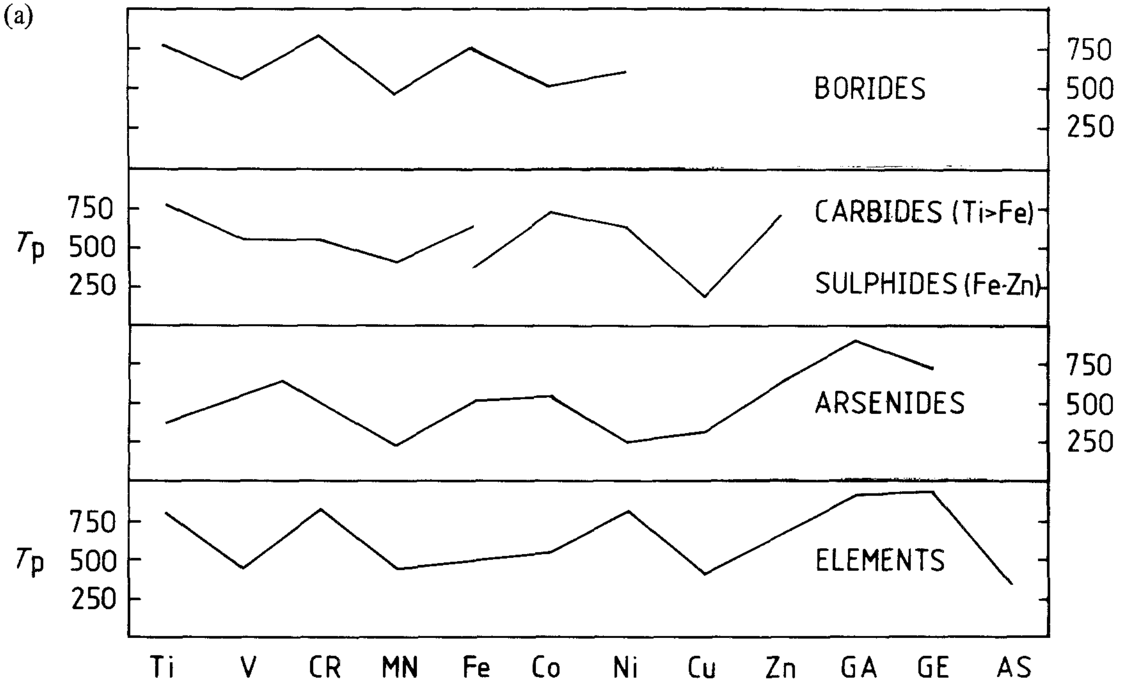
After metallographic inspection, hardness and EMP testing, samples were carefully broken out of their mounts. This operation was relatively easy, because the copper-loaded mounting resin (Struers) is brittle; traces of resin remaining may be removed with chloroform. Samples were then tested for thermal oxidation resistance by the isochronal method used previously [5]; they were heated in air for 4 h at each of successively higher temperatures (200, 400° C etc., upwards) until the temperature corresponding to a weight difference of $1\,mg\,cm^{-2}\,4\,h^{-1}$ (a parameter termed T_p) could be interpolated from the results.

3. Results and discussion

The results are conveyed in Figs. 3 to 6, which comprise graphical presentation of oxidation and hardness in Figs. 3a and 4, and a tubular scheme for other properties. In all cases the information is given opposite the name of the metallic component of each compound. The method of presentation leaves out MnSe and MnTe, but it may be said that they respond to oxidation and hardness tests like FeS, and also MnTe responds to EMP; T_p for CrB_2 was 1060° C, but its hardness was similar to CrB. We first discuss the oxidation data in Fig. 3a and b.

The interesting correlation from Fig. 3a is the general similarity between all five curves; the stepwise saw-tooth alternation of values familiar from previous work on the pure elements [5] is repeated, with little variation, for borides etc. Thus it appears that the sequence of oxidation is defined by the behaviour of the metallic component or partial lattice. However, when we consider Fig. 3b, we find in many cases that the type of $T/\Delta w$ curve from which the T_p values of Fig. 3a were derived, was either of loss form or a mixed

(a)



(b)

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
G	G	G*	G*	G	G*	G							Borides
G	L	G*	G*	L									Carbides
G̲L	G*		L	L	LG	L	L	L	L	L			Arsenides
				G	G	G	G	L					Sulphides
G	G	G*	G	G	G	G	G	G	G	L	L	L	Elements

Figure 3 (a) Variation of the thermal oxidation parameter T_p with atomic number of metallic component for some borides, carbides, arsenides, sulphides and elements. The experimental points are omitted for clarity. Data for elements from [5]. (b) The type of temperature/weight change curve obtained during thermal oxidation tests on First Long Period elements and compounds. G = weight gain throughout, L = loss, etc. Underling of G in GL indicates that the T_p value quoted in (a) was, exceptionally, obtained from the weight gain part of the curve. An asterisk indicates a tendency to a "chromium" variation of curve [5].

loss/gain, and since, with the exception of heavy elements such as osmium which fail at low temperatures by loss of acid oxide, the elements giving $T/\Delta w$ loss curves are generally the least metallic, it follows that the actual loss of material is of the non-metal component. Consistent with this interpretation is the fact that all the borides showed weight gain curves and for these the oxidation of the pure non-metal does not give an easily volatile product. In the present context, where we have to consider weight gains and/or losses and the possible extents of volatility or mechanical disruption for both components, it is difficult to pin-point the overall mechanism without considerably more data, but it may be self-consistent that the extent of disruption is measured by the effect on the non-metal even though the process is controlled by the oxidation of the metal. The latter, in turn, may depend on the breaking of either inter-metal or metal–non-metal bonds, whatever the bond situation as a whole may be. However, if component size plays a role, one would expect greater losses in general where the non-metal atoms are large, and this is borne out (Fig. 3b) by the extent of losses amongst arsenides. The persistence, even the increased incidence, of the "chromium" variation of $T/\Delta w$ curve [5] in borides, carbides and arsenides (Fig. 3b) is circumstantial evidence that the metallic components are behaving like uncombined metal, but with an implied modification of their electronic structure.

If we now consider the hardness data (Fig. 4),

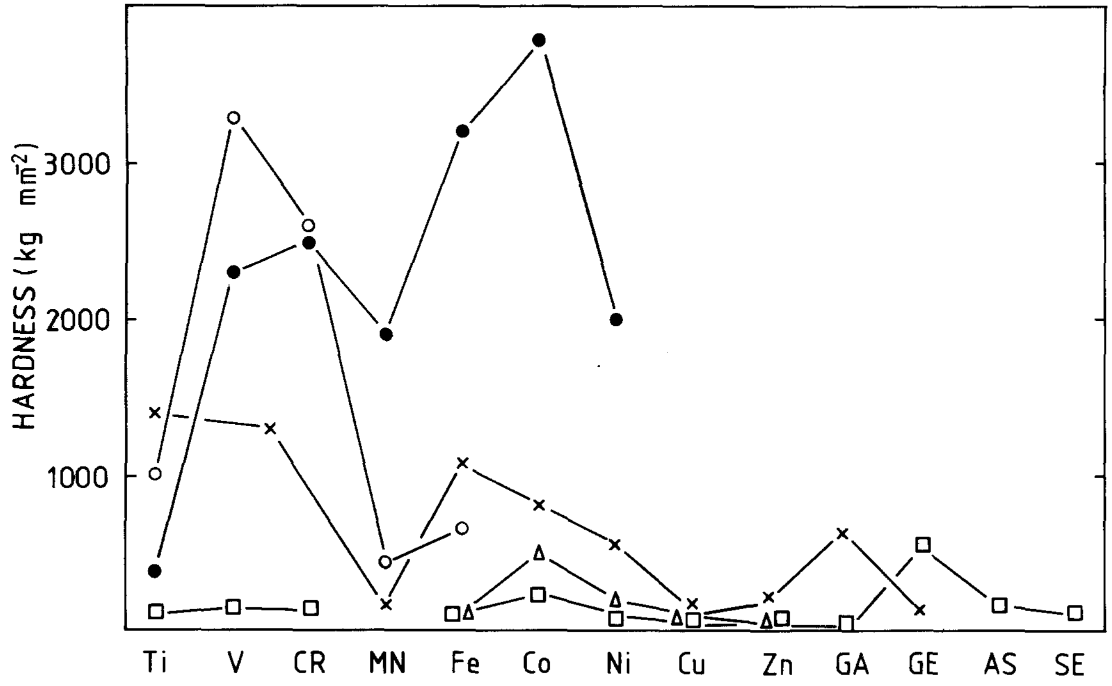


Figure 4 Hardness versus atomic number of metal component; for borides (●), carbides (○), arsenides (X) and sulphides (△). Hardness of the elements (□) (from [1, 11]) given for comparison.

two significant features are apparent as we proceed in the order elements → sulphides → arsenides → carbides → borides. In the first place, the overall level of hardness increases from about 150 for metals to ~ 2000 for borides (corroborated in [7]), that is, roughly in order of hardness of the non-metallic component. Secondly, the form of hardness/atomic number curve that develops is reminiscent of the variation of melting point and heat of sublimation with atomic number for elements of the First Long Period. It is thought that these features are consistent with a hypothesis of bonding and deformation along the following lines. Gross strength in the elements can be considered as deriving from the presence of hybridized symmetrical orbitals; the strength of these increases by Group and Period in the Long Periodic Table towards tungsten amongst the metals, boron/diamond amongst non-metals. Ductility, on the other hand, is given by the operation of s-d resonance [8]; this type of electronic process becomes more evident as we move from Third to First Long Period, and from left to right in the Period up to about Group IIB.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
x	x	x	√	√	√	x			Borides
x	x	x	x	√					Carbides
x	x		√	x	x	x	x	x	Arsenides
x	x	x	x	√	√	√	x	x	Elements

Figure 5 The response of First Long Period elements and compounds to a simple test for ferromagnetism. √ = magnetic, X = non-magnetic.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	
x	√	√	?	?	√							Borides
?	?	√	?	√								Carbides
?	?		a	√	?	√	?	x				Arsenides
				√	?	?	x	√				Sulphides
x	√	√	a	x	x	x	√	√	x	x	x	Elements

Figure 6 The response of some elements and compounds to an electromechanical polishing solution. √ = polishes, X = does not polish, ? = doubtful, perhaps mechanical polishing only from the cloth. a = attacked. For technique details see [6, 15].

In the uncombined elements, both the hybridized orbitals (which will at the start of the Periods involve unsaturated metallic resonance of the Pauling type) and s-d resonance are both present, and the element will deform in hardness test or otherwise at the (lower) s-d resonance stress in a metallic manner. However, we suppose that in the compounds the presence or operation of s-d resonance is considerably inhibited by the presence of the non-metallic atoms, and consequently flow or failure in test is limited by the much higher stresses required to operate against the strength of the hybridized orbitals. As a result, this property of the compound trends in a manner more like that of its components.

The magnetic and EMP data are given in Figs. 5 and 6, respectively. In Fig. 5 it is of interest that the three magnetic monoborides are MnB, FeB and CoB, NiB being non-magnetic, in contrast to the trio of magnetic elements. The only magnetic arsenide is that of manganese and the only magnetic carbide recorded is that of iron. Magnetic indications for sulphides are not given because the risk of traces of ferromagnetic residues in these rather more difficult preparations was considered to be too great, but the iron mineral pyrrhotite is known to be magnetic. The overall picture as the 3d elements are combined into compounds is a movement of the incidence to the left in the Period and a diminishing of incidence, depending on the nature of the compound.

As seen from Fig. 6, iron, cobalt and nickel are not polished by EMP, but this feature of the incidence is not at all apparent in the four types of compound. So far as can be estimated, there is a slight tendency for incidence to move to the left in the Period. The fact that Mn and MnAs are attacked (actually without applied emf) by the electrolyte, but not MnB and Mn_3C, suggests that essential features of the alpha manganese structure have disappeared in the latter. For comparison we note that, using other experimental probes, about 5% copper in solid solution is sufficient to "unscramble" the high hardness of alpha manganese [9, 10], whereas about 50% is necessary to produce an alloy polishable by EMP [6].

Taken together, the evidence of Figs. 5 and 6 suggests that, in band terms, the d-band is filling earlier in the Period in the compounds. One could invoke charge transfer from the non-metal atoms. However, the response of NiB in Figs. 5 and 6 could probably be explained by an assumption of nil valency electrons on the nickel sites, in effect internal compensation on the nickel partial lattice; we also know from the 3d elements that magnetism is lost by movement to lower atomic number as well as to high.

Having presented some new data on AB_2 type compounds, we conclude by briefly contrasting these with AB_1 and B_1B_2 compounds, and also with the elements themselves. Data on elements have been given elsewhere [1, 5–7, 9, 11], on AB_1 compounds in [1, 2, 6, 7], and on B_1B_2 compounds in [7, 11, 12]. With regard to oxidation, we remember that B_2-type elements tended to fail completely at approximately their melting point, but A elements followed a $0.5T_m$ (where T_m is the melting point) régime. On the other hand, compounds AB_1 and B_1B_2 tended to $1.0T_m$ in régime, presumably because compound formation had resulted in a more strongly bound structure. In contrast, the present AB_2 compounds revert to the $0.5T_m$ more typical of metals. Considering hardness, we find that AB_2 compounds are much harder than the other groups, in fact only comparable with non-metal infinite lattice structures, and this provides strong evidence for boron as a B_2 element. Finally, gross magnetism and a positive EMP response (properties found amongst the A elements) disappear in AB_1 compounds, but are noted again in AB_2 combinations, suggesting, as does the oxidation and hardness data, that the metal and non-metal partial lattices are in large measure behaving independently.

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Appendix

A note by way of postscript on the author's oxidation work on the elements may not be out of place since it has a bearing on the economy of hypotheses in these exercises in classification. The interested reader is referred to that work [5] for fuller background, in particular the temperature/atomic number plots therein. A shortcoming of the oxidation classification was that no explanation was provided for the adherence of any element to a particular oxidation régime (i.e. $0.5T_m$, $1.0T_m$ etc.). It has become clear that an element fails by oxidation, in terms of increasing temperature, at the oxidation mode or régime which provides the lowest temperature, if it is accepted that some elements (essentially the B_1 block) behave as non-metals in the solid state. This assumption, which implies a strong degree of non-metallic bonding, seems less improbable than formerly. The reader will have noted that certain intersections and conjunctions of lines in the temperature/atomic number plots [5] coincide with the positions of divides in the present Fig. 1.

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