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The mutual alloying behaviour of some B-group elements

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The mutual alloying characteristics of the block of elements approximately represented by Groups IIB, IIIB and IVB are described. They are predominantly elements which mutually display insolubility in some form or other. Variations from such typical behaviour, chiefly the occurrence of compounds of line type or with variable composition, occur on the periphery of the block, and these are the subject of supplementary comment. A hypothesis regarding retrograde solubility is presented.

1. Introduction

Previous papers have analysed the alloying behaviour of various groups of elements in the Periodic Table, and, in particular, a study [1] was made of the behaviour of the later transition metals with each other. Between these elements and the high Group number non-metallic elements lies a block of distinctive mutual alloying character which for convenience may be labelled B_1B_1 type. The alloying behaviour in a B_1B_1 system such as Zn–Ga is quite different from that in an A_2A_2 system (i.e. Cu–Ni), and this difference needs to be explained by any general alloying theory. Unfortunately this obvious division has not so far, it would seem, been presented adequately and recognized as such. It will not be possible in a short paper to present any theoretical model; nor is that desirable, since there has been no delineation of the limits in the Periodic Table of this B_1B_1 behaviour and the changes that occur in progressing from the block to adjacent areas in the Table. In short, this paper will simply attempt to clear the ground for future work. In view of this, and because for other reasons the subject matter favours a piecemeal approach, discussion is classificatory and descriptive. We will first state the nature of the distinctive behaviour and afterwards consider what variations from that norm occur in that general area of the Periodic Table. We base our studies on the well-known collection of phase diagrams [2].

2. Typical behaviour of the early B-group elements

This is predominantly a block of elements which mutually display insolubility in some form or other. Certainly, many other elements in Groups IA, IIA, the First Long Period, and also silver, carry the immiscible label, but nowhere else is insolubility so generally and mutually dominant as around our present block of elements, although variations in the degree of insolubility exist, in that eutectic systems occur often between elements in adjacent Periods, whereas liquid immiscibility systems are more generally found for components with greater separation in the Periodic Table. The insolubility is perhaps due to the lack of suitable electron partners which would either (a) facilitate s–d resonance as in transition–transition systems with consequent solubility, or (b) allow complete chemical combination as in B_1B_2 systems (see Section 3.3).

If we ask ourselves which elements are to be considered as belonging to the B_1B_1 block, this is answered by direct recourse to the appropriate phase diagrams. The question may be answered formally by considering a portion of the Periodic Table (Fig. 1), and noting that their "western"

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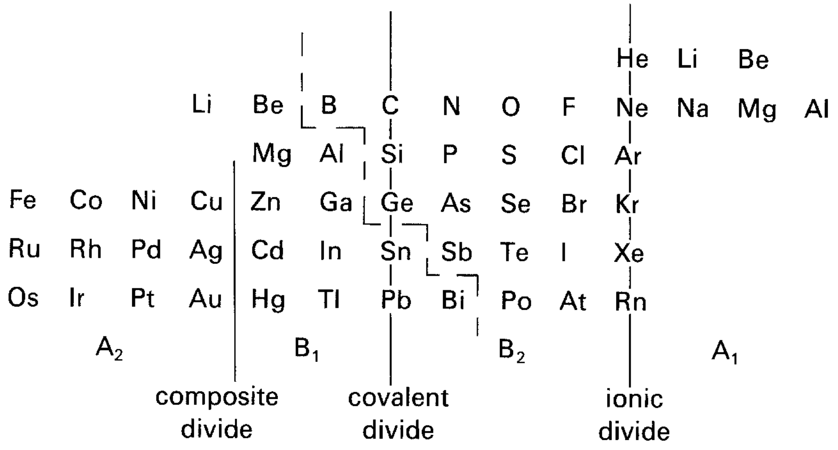

Figure 1 The Periodic Table dissected by divides into blocks, B_1 etc. The dashed line represents a boundary between metals and non-metals.

margin is the composite divide, and the eastern is a compromise between the covalent divide and the stepwise line which conventionally divides metals and non-metals. In practice the margins are not clear cut, and this characteristic is taken account of in the remainder of this discussion.

3. Variations from typical behaviour

We shall consider these in turn as they occur on the periphery of our block of elements, starting at the left-hand side as the long Periodic Table is usually presented, thence moving clockwise.

3.1. Near the composite divide

The boundary of the B_1 zone is most well-defined here. However, the Cu–Ag system, a eutectic, may formally be claimed as an example of B_1B_1 behaviour, whereas the Mg–Cd with its solutions and superlattices suggests an A_2A_2 classification.

Li				
Na	Mg	Al	Si	
I	S	VL	L	
	Zn	Ga	Ge	As
	V	L	L	L
	Cd	In	Sn	Sb
	V	V	L	L
	Hg	Tl	Pb	Bi
	VL	L	L	L

Figure 2 Sketch of the alloying behaviour of lithium with the elements of the B_1 block. L = system with line compounds, V = variable stoichiometry compound, S = solid solutions.

3.2. Lithium, sodium and magnesium

Lithium forms compounds (Figs. 2) with two groups of B_1 elements. The first group are exemplified by its line compounds with arsenic, tin, antimony, thallium, lead and bismuth formed possibly "across the ionic divide" (Fig. 1). The second group comprises systems with aluminium, zinc, cadmium, indium and mercury, in which a 1/1 phase of variable stoichiometry and frequently of sodium thallide structure occurs in addition to one or more line compounds. Such variability is reminiscent of equiatomic or near-equiatomic structures in brass-like systems. Sodium (Fig. 3) exhibits phase diagrams containing line compounds with the generality of B_1 elements.

With regard to magnesium, this complexity of behaviour is such that it would require a whole paper to do the subject justice. Some notes have

Na	Mg	Al	Si		
	I	I	L		
	Zn	Ga	Ge	As	Se
	L	L	L	L	L
	Cd	In	Sn	Sb	Te
	L	L	L	L	L
	Hg	Tl	Pb	Bi	
	L	VL	VL	L	

Figure 3 As Fig. 2, but for sodium. I = insolubility without the presence of compounds.

Na	Mg	Al	Si	P	
I		V	L	L	
	Zn	Ga	Ge	As	Se
	L	L	L	L	L
	Cd	In	Sn	Sb	Te
	S	SV	L	L	L
	Hg	Tl	Pb	Bi	
	L	L	L	L	

Figure 4 As Fig. 2, but for magnesium.

already been published [3], and it suffices here simply to observe the following in conjunction with Fig. 4. Magnesium forms normal valency compounds [4] with elements of Groups IVB and VB and, in some cases, line compounds with elements of Groups IIB and IIIB, although the Mg–Cd and Mg–In diagrams are redolent of A_2A_2 systems, as already noted. The author (*pace* previous adverse criticisms) remains of the opinion that the Mg–Al is a primitive or emerging type of brass-like (i.e. A_2B_1) system, with magnesium functioning as transition metals are inferred to do in such a context.

3.3. Compounds B_1B_2

These compounds, of which GaAs is an example, are one of the fundamental groups. Because they are very numerous, there is a little difficulty in illustrating their incidence. However, a combined average Group number/average Period number (AGN/APN) plot as shown in Fig. 5 gives a fair impression of their incidence. This figure has been constructed with the straightforward average Group numbers, and for most of the points this poses no complication. But consider the case of magnesium, for which we calculate *inter alia* the AGN of Mg_2Si as $2\frac{2}{3}$; if we accept a suggestion from Section 3.2 on another type of bonding behaviour of lithium and magnesium, we would then count Si as minus 4, Mg as plus 2, in which case the AGN works out at zero, i.e. that of a noble gas.

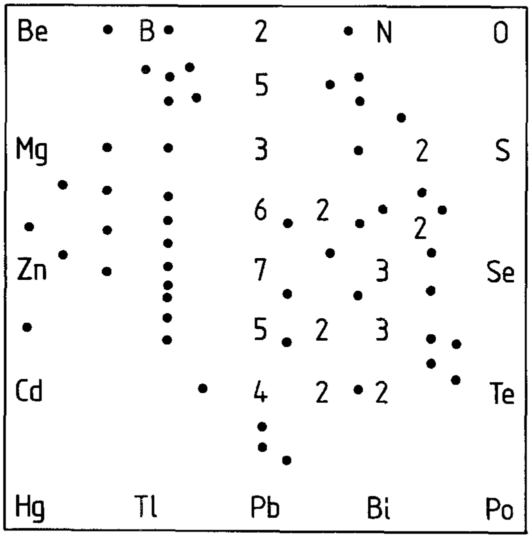

Figure 5 Plot of AGN/APN of line compounds formed between elements on and inside the square Be–O–Po–Hg of the Periodic Table. Multiple points are replaced by numbers.

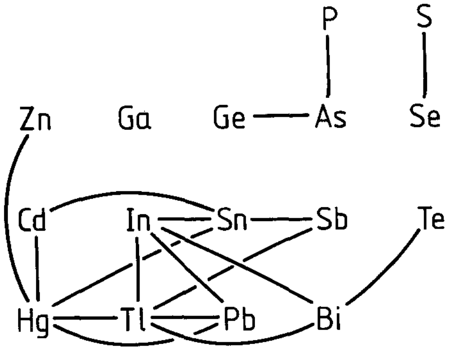

Figure 6 Systems with intermediate structures of variable stoichiometry formed between B elements.

3.4. Intermediate structures of variable stoichiometry forced between B elements

The necessity for separating these from the generality of inter-B compounds of the previous section will be reinforced if one compares the phase diagrams of the Tl–Bi and In–Sb systems. The latter is a typical normal valency B_1B_2 system, whilst the former has intermetallic compounds with decided ranges of non-stoichiometry. The latter systems occur (Fig. 6) in the Second and, especially, the Third Long Period. Away from their centre of occurrence it is sometimes difficult to differentiate them *prima facie* from some phases in Hume-Rothery or brass-like systems.

3.5. Binary systems showing retrograde solid solubility

This topic is discussed here because the incidence of this phenomenon shows a correlation with that of the variable stoichiometry phases of the last section. It is however necessary to cast the net outside the confines of the B_1 group of elements since the element in which the

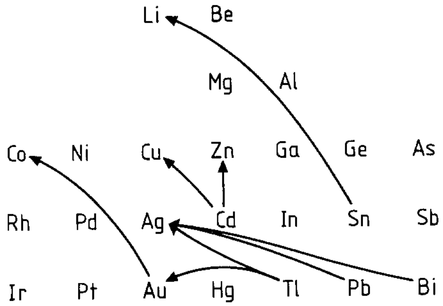

Figure 7 Binary systems in which the insolubility in one component is retrograde; the end of each system displaying such a characteristic is marked by an arrow-head.

retrograde solubility is shown is the element of lower Group number. Fig. 7 illustrates the incidence; each arrowhead points to the end of the system exhibiting retro-solubility. We associate the incidence displayed in this figure with that in Fig. 6, and it is therefore proposed that the free energy changes associated with the formation of compounds are such that a phase constitution of the type shown in Fig. 8 is about to emerge as the equilibrium constitution. In other words, the behaviour which is evident in the Pb–In system is present in an attenuated form in the Pb–Ag.

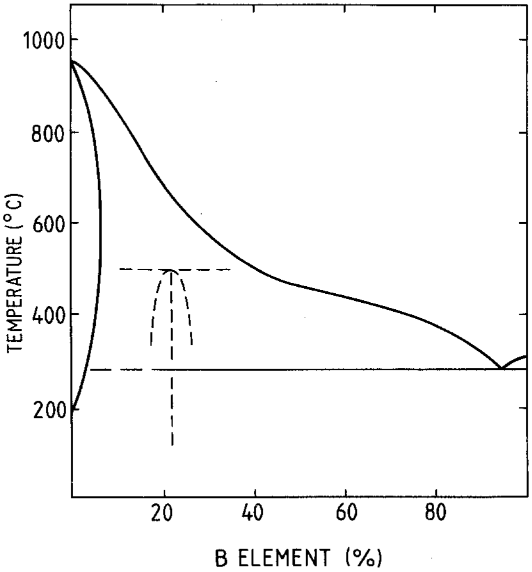

Figure 8 Phase diagram showing retrograde solubility – with modifications.

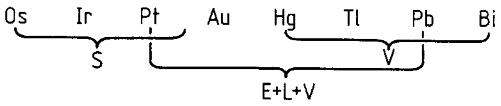

Figure 9 Diagrammatic representation of the mutual alloying characteristics of the elements osmium to bismuth inclusive. S = solid solution, V = presence of variable stoichiometry compounds, E + L + V = systems showing variously eutectic, line and variable stoichiometry compounds.

3.6. The Third Long Period

Just as lithium, sodium and magnesium form a group of individual elements at the top of the Periodic Table in our block, so we have distinctive behaviour at the foot of our block of elements. Changes occur so near to each other along the sequence of elements osmium to polonium, and so few *exemplaires* exist, that it has not been possible to date to unravel trends by hyperbola analysis [5], except for an interface regarding the valency of gold. A short description is presented in Fig. 9. Here the "S" and "V" brackets on the flanks indicate the modes of solid solution and variable stoichiometry intermediate phase formation respectively. In the centre are bracketed elements which mutually alloy, giving, sometimes eutectic systems, sometimes vaguely brass-type systems, and sometimes line compounds as in the Au–Pb system.

Acknowledgement

This survey was initiated by an enquiry from Dr A. D. Caplin regarding alloying patterns amongst pairs of B elements.

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