JOURNAL OF MATERIALS SCIENCE 26 (1991) 3309–3312

Abnormal weight changes of intermetallic compounds when heated

H. E. N. STONE*
Blackett Laboratory, Imperial College, London SW7 2AZ, UK

Monotonic weight gains are most usual when intermetallic compounds are heated in air to successively higher temperatures, but about 15% of compositions exhibit other behaviour in which mainly losses were partial or dominant. From a specimen population of binary phases with components drawn from many parts of the periodic table, it was found that abnormality was markedly found when components came from the early B Groups. It is suggested that the high volatility of phases such as beta brass and related structures may be responsible.

1. Introduction

From the nature of the topic, a long introduction is necessary in order to give adequate background; thereafter, it will be found that the conclusion becomes quickly evident.

A monotonic weight increase is the norm when an intermetallic compound is heated in air to successively higher temperatures. The vast majority of rather more than 1000 such compounds made and tested by the author in the period 1970–1988 displayed that behaviour. However, a number of them, amounting to about 150, showed departures from this. These were mostly cases in which losses were either partial or dominant, but some showed weight increase/temperature curves at constant time which, although monotonic, would not conform to a simple equation. The situation may be understood in more detail by reference to Fig. 1, which expresses schematically the various types of Δw–T curves. Curve G represents normal behaviour with continued smooth weight uptake. L is the converse of G with continued loss. LG is a hybrid curve which starts as a loss type but then reverts to an increase. There is also a converse, GL, of the latter, for which less than 10 exemplars were found, and which is omitted from Fig. 1 for clarity. Curve Cr represents the variant from continuous increase already mentioned, so called because it was first found in the element chromium [1]; it is thought that the initial part ending at the point x is linked to agitation of the substrate lattice, and final turnover to that of the oxide scale Cr_2O_3. Curve NM represents behaviour for many non-metals, a typical example being elemental silicon; it is arguable whether it is to be considered as two lines with a discontinuity, or as a limiting case of G.

It must not be supposed that the presence of abnormality correlates necessarily with poor heating/oxidation resistance, although a really big swing to L before G in type LG could indicate significant weakening of specimen integrity for a particular practical application. The equiatomic AgCd suffers from a swing to 0.4 mg at an L stage, although terminal gain, presumably by oxidation, is shown to occur at over 0.90 of the melting point, but integrity, at least as shown by shape retention, is maintained. It is more difficult to characterize curves NM, Cr, LG and GL by a single parameter such as T_p [2] (the temperature for a weight change of 1 mg in 4 h) than curves G and L. However, such considerations, and also the study of the mathematical scaling of curves relative to ordinate and abscissa in Fig. 1, are not relevant to this paper, which is concerned with the identification of the alloy components which give rise to abnormal behaviour. We are not concerned either with the direct observation of surface structures at the microscopic level, though clues as to mechanism, by oxidation or vaporization, of metal or oxide, will be noted in passing; this situation arises from historical reasons which limited the approach and the manner in which information was collected, as follows.

In research of 1972 [1] a direct heating/oxidation comparison of most of the solid elements was made possible by the use of the one parameter T_p. The method was extended in subsequent years to a miscellany of intermetallic compounds, and the greater part of the results have been reported (for a lead into the literature, Stone [2]). (Most compositions have been binaries, and this paper is limited to them in order to simplify the systematizing procedure.) As a result, extensive lists of T_p values have been accumulated, which are the experimental basis for many papers based on discussions of T_p/T_m (where T_m is the melting point Kelvin) values. Over the same period, notes were made regarding the incidence of abnormal behaviour. They have been recorded as footnotes in published papers, but until now have not been the subject of systematic analysis because of the paucity of information at any one time. This paper sets out to remedy that deficiency.

There are two inherent but not insurmountable difficulties in the procedure herein. The indications G, LG etc. are to some extent subjective. This is amelior-

---

* Retired – private address: 27 Cornwall Road, Uxbridge, Middlesex, UK.

0022–2461/91 $03.00 + .12

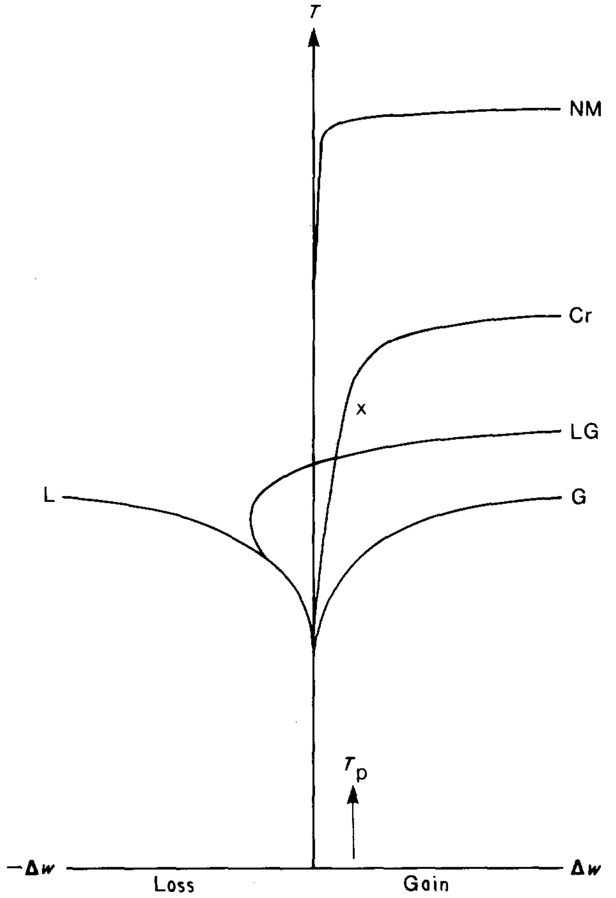

Figure 1 Typical and abnormal isochronal heating curves for overall gain or loss versus temperature. For curve descriptions see text.

ated in so far as the data were collected under sensibly uniform experimental conditions. Statistically it is likely that the general trend is correct, even though individual curves may have been misjudged. Secondly, whilst the range of compounds is catholic, there is not a uniform sampling across the periodic table. To counter this, we present the distribution of total population and abnormal population in comparative fashion, as follows.

2. Results and discussion

The incidence of total components across the periodic table is given in Table I. As compared with a perfectly flat incidence there are

(i) a big gap at the ends of the table where many compounds of inorganic chemistry would otherwise come;

(ii) isolated gaps indicative of radioactive and dangerous elements;

(iii) relatively few components in the second and third long periods for Groups VA to Rh/Ir inclusive; and

(iv) very high counts for aluminium and the lanthanide elements, deriving from personal interests and those of the author's former research group, respectively.

The distribution of the four modes of abnormality is recorded in Table II, which, like Table I, gives raw numbers only, the form which will be the most useful as source material to the specially interested reader. However, in attempting to distil a simple hypothesis from the data, it is more exact to consider the ratios of instances to total population, and these, though not tabulated, form the basis for the following comments:

1. The components giving rise to type Cr tend to come preferentially from the B sub-groups, including Groups III and IV in the short periods, with a passing back in the first long period excluding chromium and adding zirconium; the lanthanides are little representated.
2. The type LG distribution is not so very different from (1), but the B groups are not so strongly represented; also there is a stronger presence passing back in the second and third long periods and amongst the lanthanides, although the latter incidence is uneven.
3. Type L incidence is as for (1) and (2), but the passing back in the first long period stops at manganese; also the group Re, Os, Ir occurs, probably a consequence of compounds of these elements behaving like the elements (cf. compounds of Groups VIB herein).
4. The GL type was numerically the poorest represented, as already noted; the component distribution is nearly limited to the triangle Cu–Si–Sn, but with outliers at Cr, Co and S; no lanthanide components occur, which is interesting in view of the relative volatility of some of the lanthanide elements.

We tentatively conclude that there is a general tendency for abnormality to occur where components come from B groups and their congeners in the short periods. It is remarkable too that although the lanthanide elements are well represented in the total population, only 25 abnormal exemplars were noted.

We may refine the classification procedure by plotting the average group and period numbers (AGN and APN, respectively) of the compounds in the periodic table. For this purpose, the abscissa is a simple positional scale along the 18 of the long periods, with the lanthanide elements at 3 throughout. For the ordinate, the first long period is counted 4, the third 6, the lanthanides 7 etc. The results are shown in Fig. 2; in view of the often high density of points it was not possible to differentiate between the classes of abnormality, so that the figure needs to be supplemented by the following description.

The few GL points occur more or less evenly in that part of Fig. 2 for AGN less than 8. For the other abnormalities, segregations were by no means complete. There are somewhat fewer of type LG at less than 10.6 AGN. From AGN 3.0 to 10.5 there is a fairly strong tendency for the lower points in the left-hand "tail" of Fig. 2 to be L type and lanthanide-containing, and the upper to be Cr type; the provenances of the latter are predominantly borides, carbides and sulphides, in which the Cr behaviour is perhaps due to appropriate electronic modification of the A element by the B element [3].

The obvious and interesting finding from Fig. 2 is the bunching of points between AGN 10.5 and 12.5, which corroborates the discrete-element periodic table

TABLE I Distribution across the periodic table of the components of the binary intermetallic compounds studied (in addition there were Li 4, Ca 1 and Ba 3)

										B	C			
										7	6			
									Mg	Al	Si	P	S	
									10	143	35		5	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
6	47	22	19	34	34	73	53	81	80	13	21	10	1	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	
33	9	0	2		3	2	7	49	16	13	23	17	2	
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
	8	5	8	9	4	5	11	27			2	2		
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
16	18	9	18		12	2	23	5	7	5	10	5	2	3

TABLE II Distribution across the periodic table of components of compounds showing abnormality[a]

										B	C			
										3,0	2,0			
										0,0	0,0			
									Mg	Al	Si	P	S	
									0,0	2,16	1,0		0,0	
									0,0	12,0	0,2		1,0	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
0,0	8,3	2,2	2,2	2,6	0,3	4,2	2,2	12,4	5,24	1,3	3,0	0,0	0,0	
0,0	3,0	0,0	0,1	3,0	1,0	6,1	3,0	6,2	5,2	2,0	1,1	9,0	0,0	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	
1,1	4,0	0,0	0,0		0,1	0,0	0,1	8,8	0,3	6,0	2,3	1,7	0,0	
0,1	0,0	0,0	1,0		0,0	0,0	0,0	2,0	5,0	0,1	1,1	2,0	0,0	
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
	0,0	0,0	0,0	0,0	0,1	0,3	2,5	1,2			0,0	0,1		
	0,0	0,0	0,0	2,0	2,0	1,0	0,0	2,0			0,0	0,0		
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1,0	0,0	0,1	2,0		0,0	0,1	0,2	0,1	0,0	0,1	2,0	0,0	0,1	0,0
0,0	3,0	0,0	0,0		1,0	0,0	2,0	0,0	3,0	0,0	3,0	1,0	0,0	0,0

[a] As key, note the following expanded entry for zinc: { Zn
5Cr, 24LG
5L, 2GL. In addition there were nil Li, 1 × Cr for Ca and 1 × L Ba.

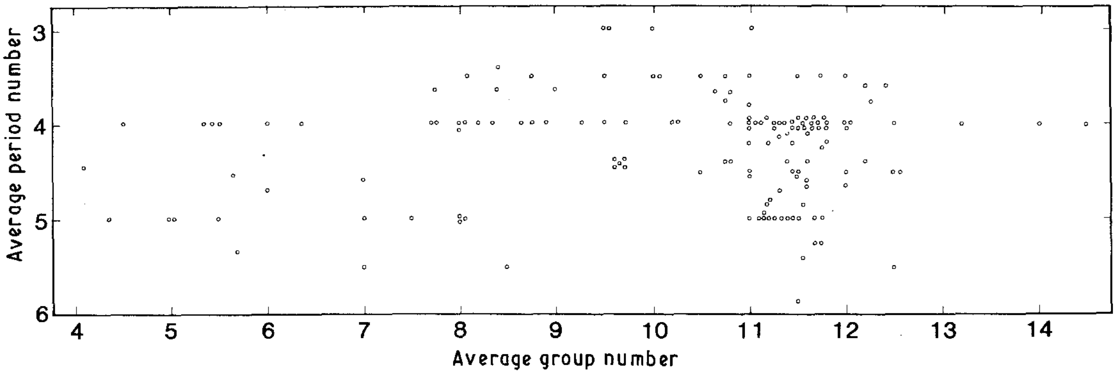

Figure 2 Distribution in the periodic table of abnormal compounds. Placing is determined by using as coordinates their average group numbers and average period numbers (see text). Three inter-f alloys, all of type Cr, lie at lower left at coordinates (3, 7).

data presented earlier, but also goes further in emphasizing how many abnormal compounds occur across the composite divide [4] (roughly AGN 10.5 to 12.5). (The three points at the extreme right in Fig. 2 are from compounds across the covalent divide.) Equally striking is the absence of a concentration of compounds across the transition metal divide whose occurrence would have been marked by a population between AGN 5.5 and 7.5. This interpretation for the bunching of points may be modelled by plotting collectively the AGN and APN of the typical Hume–Rothery compounds of the zeta-hexagonal, beta and gamma brass phases (Fig. 3), using the same graphical matrix as in Fig. 2. Inclusion of other compounds in the Hume–Rothery systems, such as $AlCr_2$ and Cu_6Sn_5, would spread the distribution to left and

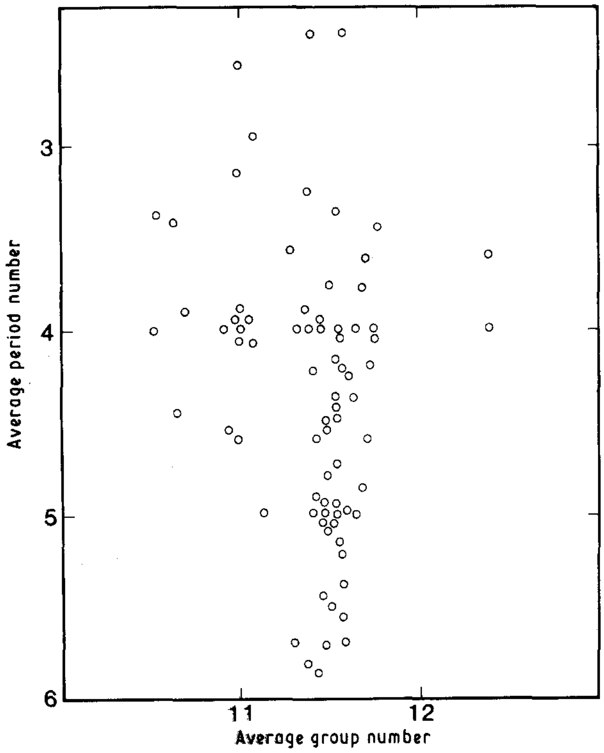

Figure 3 Distribution of Hume–Rothery zeta-hexagonal, beta and gamma brass phases plotted in the same manner as Fig. 2. Where ranges of stoichiometry exist, mid-points of phase fields are used.

right respectively to a degree where the distribution in Figs 2 and 3 between AGN 10.5 and 12.5 would be indistinguishable, except for that part of Fig. 3 for APN greater than 5. (The three points less than APN 2.8 are beryllides and lithium compounds not represented in our own population.) This particular part has 11 points, of which all but one are non-beta compositions, and this may be significant in connection with the hypothesis that concludes.

The circumstances revealed by the statistical analysis and modelling suggest that abnormality of the four types collectively is in the majority of cases intimately connected with the alloying of, for example, elements like copper with elements such as zinc; furthermore, in view of the high concentration of compositions in Fig. 2 at AGN 11.5 (the ideal for beta) or just below, beta phase may well provide the essential clue as regards mechanism. Now the remarkable characteristic of this phase at high reduced temperatures is the stability of its b.c.c. structure, its increasing composition stability with increasing temperature, and the consequent anomalous slope of the alpha–beta phase field demarcation. It has been explained by Zener [5] by the low elastic modulus along the 1 1 0 direction in the W-type lattice leading to an additional entropy of vibration, and consequently to a depressed free energy at elevated temperatures. One may suggest further that such structures, which are possibly quasi-molecular (e.g. CuZn) would be likely candidates to show volatility [6] and give heating abnormalities, with or without the incidence of atmospheric oxidation.

Acknowledgement

Thanks are due to Professor B. R. Coles for laboratory facilities.

References

1. H. E. N. STONE, *J. Mater. Sci.* **7** (1972) 1147.
2. *Idem., ibid.* **24** (1989) 633.
3. M. C. CADEVILLE and co-workers, reported by J. Friedel in "Phase Stability in Metals and Alloys", edited by P. S. Rudman, J. Stringer and R. I. Jaffee (McGraw-Hill, New York, 1967) p. 351.
4. H. E. N. STONE, *Acta Metall.* **27** (1979) 259.
5. C. ZENER, "Elasticity and Inelasticity of Metals" (University Press, Chicago, 1948) p. 37.
6. J. DROWART, in "Phase Stability in Metals and Alloys", edited by P. S. Rudman, J. Stringer and R. I. Jaffee (McGraw-Hill, New York, 1967) pp. 305–317.

Received 12 June
and accepted 5 September 1990