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The oxidation resistance, hardness and constitution of some intermetallic compounds containing zinc

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The majority of the binary compounds of zinc with the metals from titanium to copper inclusive has been prepared, hardness tested and oxidized in air at successively higher temperatures. A zinc–ruthenium and some zinc–gadolinium compounds have also been tested. From the oxidation results, the temperature corresponding to a weight change of 1 mg cm^{-2} over 4h was determined by interpolation. The highest temperature values (700 to 800° C) were found for Zn_8Cu_5, Zn_3Ni and Zn_3Co, and the highest hardnesses (about 600 kg mm^{-2}) for Zn_8Cu_5, Zn_3Ni and ZnCo. A short survey of melting points and structures is presented, and the results are briefly discussed in terms of a previous hypothesis concerning combination of elements of groups IIB and IIIB with those of groups IIIC and IB.

1. Introduction

A recent paper [1] presented oxidation and hardness data for a wide selection of binary metallic aluminides. In this and previous work [2–4], oxidation resistance was summarized as a parameter T_p, defined as the temperature corresponding to a specimen weight change of 1 mg cm^{-2} over 4h, and hardness [4] was measured by an indentation micro-test. Analysis of the data showed that the majority of compounds oxidized so that either $T_p \sim 0.5\,T_m$ (where T_m = the melting point on the absolute scale of the compound or an oxide product) or $T_p \sim 1 \times T_m$. Such a classification into "0.5" and "1.0" modes is important both practically and theoretically. Clearly, for a given melting point, a compound conforming to the latter mode will normally have the advantage in thermal oxidation resistance, although in practice one of many other properties, for example, thermal shock resistance, may be the determining factor. At the same time, it has become apparent that the incidence of compounds of the latter mode (referred to as nml or non-metal linked, because it was first found [2] for non-metallic elements) may probably be predicted from the positions of the components in the Periodic Table. In brief, a hypothesis was advanced that nml mode occurs where the components are near to, and on opposite sides of, certain divides in the Table. In this paper interest is on the vertical division between groups IB and IIB, which will be referred to as the composite divide, for a reason which will become apparent. Zinc, like aluminium, is an element near to and to the right of the composite divide and is, therefore, an appropriate fixed component in a comparative survey. However, because zinc compounds are probably not of such immediate practical interest as aluminides, and also because the pattern of results proved to be similar to that in the case of aluminides, this work was limited essentially to compounds of elements of the 3d transition series.

2. Experimental

Details of starting materials have been given previously [2]. Zinc of 5N purity (Koch-Light Labs Ltd) was used throughout. Except where stated in Table notes, the procedure was as follows. The cleaned and weighed components (total weight generally 0.7 to 2g) were sealed in evacuated silica capsules (6 mm bore) and heated for

30 or 60 min at temperatures in the range 850 to 1150° C (the actual setting was related to the appropriate liquidus, but most often was 1000° C), after which the capsule was quickly lowered into water. At this stage, all preparations with chromium to nickel inclusive where Zn/M was greater than unity were treated for $2\frac{1}{2}$ days at 420° C; this was done as a routine measure–the intention was to achieve peritectic equilibration but it is not implied that it is necessary in every case. This treatment was carried out in the original capsules where these remained sound.

After breaking out, all samples were cut transversely by spark machining at points 6 mm apart. The resulting cylinder was used as the oxidation specimen; it was ground (220 grit paper) on one face and metallographically polished on the other, and no treatment was carried out on the cast barrel surface. Oxidation testing was done in air for 4h at successively higher temperatures (200, 400° C upwards) until the temperature corresponding to a weight increase of 1 mg cm^{-2} could be interpolated from the results. Sometimes, weight losses of this order were experienced at 200° C, but testing was continued until weight gains overall were obtained; in these instances the final weight increase occurred over only a relatively small temperature increment, so that the T_p value would not be greatly different had the weight loss stage not been present. The lower fragment of the original casting, used for microscopic examination and hardness testing, was mounted so that the polished face was adjacent to an end of the oxidation specimen. Previous suspicions [4] regarding an effect of surface finish on oxidation appear to have been unfounded, since the present results gave a consistent pattern with those already reported. Former results have, therefore, been consolidated in the main tabulation.

3. Results and discussion

Initially, we shall survey the data on melting points and structures [5], after which the oxidation and hardness results will be discussed in themselves, followed by a second presentation in terms of the method of oxidation classification employed earlier [2, 4]. For brevity, comparison with the behaviour of aluminides, though of much interest, has been largely eschewed.

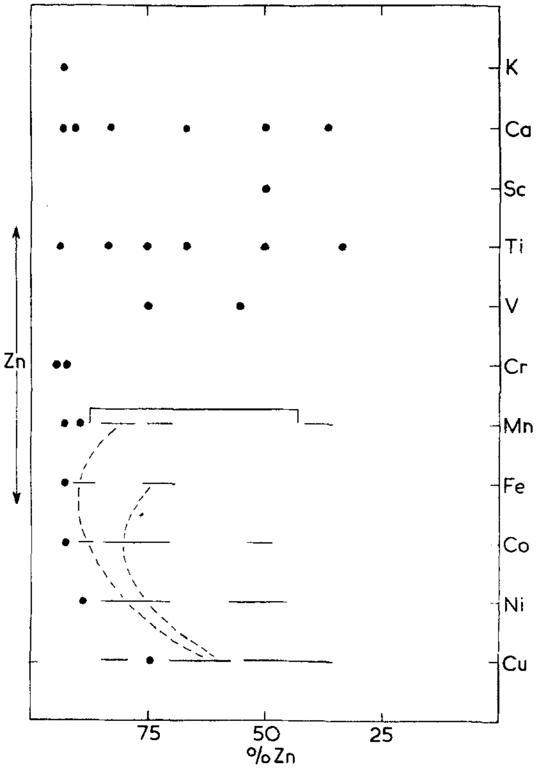

Figure 1 Summary diagram indicating compositions of intermetallic compounds in binary systems of zinc with metals from potassium to copper inclusive. The left-hand edge or ordinate stands for zinc throughout; zinc increases from right to left. Each compound is represented either by a dot, or, for compounds of appreciable variability of composition, by a horizontal bar. The bar/bracket for the Zn–Mn system indicates the range of stability of the epsilon phase, which exists in equilibrium only at elevated temperatures. The dashed lines link phases having the gamma-brass structure.

Surveys of melting points and other properties are facilitated by plotting the compositions of known compounds on a synoptic diagram of the type shown in Fig. 1. Notable in the pattern of incidence is the tendency to bunch towards the left-hand (zinc) ordinate, and indeed the Zn/3d ratio is as high as 13/1 for several compounds. Melting points of approximately 900° C tend to be recorded in mid-diagram; they increase monotonically from that of zinc to that of the transition metal. (An exception is $Zn_{12}Ca$, which melts at 920° C.) Several caesium chloride structures appear. Another feature is the contrast between the compounds of manganese to copper, taken together, which are generally of variable composition, with the compounds of potassium to vanadium. But, most of all, the pattern of structures is dominated by the presence of several gamma-brass phases in compounds with manganese to copper inclusive. Further, these phases appear to occur along two trend lines separating at the prototype gamma-brass and as such they are indicated in Fig. 1. If extrapolated, these curves would probably intersect the transition metal ordinate at points between vanadium and manganese.

The oxidation results, in the form of T_p values, supplemented by a code for the type of temperature/weight change curve, are presented in Table I. In general, the level of values is moderate, the highest (700 to 800° C) being found at or near a line joining gamma-brass to Zn_3Ni (Fig. 1). Initial oxidation weight losses greater than $1\,mg\,cm^{-2}$ over 4h were recorded for $Zn_{15}Ti$, the chromium compositions, $Zn_{13}Fe$ and Zn_9Fe. No manganese compound lost more than the value just mentioned; also, during the preparation of manganese-rich compounds, no distillation of metal into the upper parts of the capsule occurred, in contrast with the usual mirror effect.

Hardnesses (Table I) are highest (about 600 $kg\,mm^{-2}$) along a line gamma-brass → Zn_3Ni → ZnCo → Mn not dissimilar to one of the gamma-brass trends (i.e. the right-hand dashed line, Fig. 1). There is also a band of moderate hardness (200 to 400) which continues past Zn_3Ni towards Zn_3Ti. Low hardness is found for compounds richest in zinc, and for CuZn and NiZn.

Classification of compounds as oxide-, metal-,

TABLE I Some properties of binary zinc compounds

Compound		T_p(° C)	Type of $T/\Delta W$ curve	Oxidation mode	Hardness (kg mm^{-2})
Ti	15/1	560	LG	n or o (of Ti)	110
	5/1	540	LG	n	180
	3/1	520	LG	m	470
	2/1	570	G	m or o (of Ti)	460
V	3/1	540	LG	n or o (of V)	240
	5/4	540	LG	n or o (of V)	150
Cr	17/1	620	LG	n or o	210
	13/1	620	LG	n or o	190
Mn	13/1	460	LG	n	220
	9/1	520	LG	n	290
	4/1	580(540)	LG(LG)	n	120(320)
	3/1	680(520)	LG(LG)	n or o	500(180)
	2/1	620	G	n or o	180
	2/3	550	G	n or o (of Mn)	180
Fe	13/1	570	LG	n or o (of Fe)	180
	9/1	550	LG	n or o (of Fe)	330
	3/1	540	LG	n or o (of Fe)	440
Co	13/1	490	LG	n	180
	8/1	750	G	n or o	260
	4/1	600	G	n or o	430
	1/1	620	G	n or o	670
Ni	8/1	460	LG	n	260
	21/5	750	LG	n or o	260
	3/1	800	LG	n or o	570
	1/1	800	G	n or o	140
Cu	4/1	490	G	n	180
	3/1			n or o	250
	8/5	780	G	n or o	600
	1/1	760	G	n or o	180
Ru	13/1	530	LG		170
Gd	11/1	460	LG	m	260
	17/2	420	LG	m	490
	4/1	340	G	m	
	2/1	350	G	m	500

Notes

(1) The incidence of compounds is, in general, that preferred in Hansen's Monograph and Supplements [5]. In stoichiometric ratios (column 1), zinc is included in the numerator throughout. Nominal compositions approximate to the quoted ratio. The expression "Mn 2/1" (column 1) is purely for convenience; other qualifications are given below. Single samples only of each composition were tested.

(2) Possible oxidation modes: o = oxide-linked ($T_p \sim 0.5\,T_m^{\text{oxide}}$), m = metal-linked ($T_p \sim 0.5\,T_m^{\text{metal (compound)}}$), and n = non-metal linked ($T_p \sim 1.0\,T_m^{\text{compound}}$). All compounds were stable in air for at least several months.

or non-metal-linked (for terminology, see notes to Table I and [1–4]) is in many cases ambigous because of the nearness of T_p for component elements and their oxides to the values obtained on compounds. It seems fairly clear that Zn_3Ti and Zn_2Ti are metal-linked, so that most titanium compounds (and presumably compounds of scandium and calcium also) may be included in such a zone in the upper part of Fig. 1; in the lower part (including $Zn_{15}Ti$, Zn_5Ti and all compounds of metals of higher atomic number than titanium) compounds are either oxide-linked or nml (Table I), and probably at least a substantial proportion are nml mode. Some features of the systems with chromium to copper respectively, in relation to the present parameters, are of particular interest. For example, along the equi-atomic line, compounds with copper and nickel are nml mode and soft, whereas ZnCo is of somewhat lower T_p, is much harder, and is ferromagnetic. There is no equi-atomic iron compound. These facts, and the corresponding data on aluminides, are probably consistent with the hypothesis previously advanced [1]. That is, if a necessary part of the mechanism of combination across the composite divide involves an ionic bond with a "hole in the d-band" in copper, nickel etc, it may be expected that univalent aluminium would be more versatile than divalent zinc in ability to form compounds with elements far from the composite divide. The relatively low melting points of equi-atomic compounds of zinc with nickel and cobalt in the context of their respective systems, compared with the situation with aluminides, is probably a related phenomenon arising from the energy balance before and after combination. Another feature of the hypothesis, namely the formulation of compounds formed across the composite divide in terms of simple chemical entities, poses some difficulty. Retention of MZn_4 [1] as the higher ratio (or covalent type) entity enables us to describe approximately the gamma-brass type phases. Near the zinc ordinate the delta phase (Zn/M about 8/1) may be formulated as (e.g.) $Zn_4.(FeZn_4) = Zn_2^{II}.Zn^{II}(FeZn_4)$, but less realistic valency and co-ordination numbers are implied in attempting formulations for the zeta phases (Zn/M = 13/1), and it is perhaps more helpful to place the latter (and high ratio aluminium compounds such as $Al_{12}W$) adjacent to the Zn/Al position in a qualitative scheme such as Fig. 2, which indicates changes of bond type for the class of compounds (A_2B_1, [1, 6]) under discussion.

The tendency for zinc compounds to bunch towards the zinc ordinate (Fig. 1) on passing from copper to iron is connected with the proximity of zinc to the composite divide–the ten-

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(3) Type of curve (column 3): G = gain, LG = loss at lower temperatures followed by gain at higher temperatures. For type LG, the T_p values in the second column were estimated from weight gain parts of curves. A weight loss insufficient for classification as LG occurs at 200° C with metallic zinc.

(4) Presence of second phase. Results on the two vanadium preparations are to be regarded as much less satisfactory than all the others. Compounds Zn_5Ti, Zn_3Ti, Zn_2Mn, Zn_4Gd and Zn_2Gd were grossly duplex; $Zn_{15}Ti$ and ZnNi contained not more than 5% of another compound. Other compounds appeared to be single phase, except that $Zn_{13}Mn$ Zn_4Mn and Zn_3Mn contained traces of zinc solid solution. Etching was often difficult, as previously described [1].

(5) It is thought that only one compound exists in the Zn–Cr system (cf. Table I). The oxidation and hardness data on the "17/1" and "13/1" are similar; both samples, single phase before T_p determination, consisted after test of mixtures which from metallographic and hardness investigations could be construed as consisting of compound plus zinc and chromium solid solutions; also, X-ray powder determinations [7] showed that preparations in this composition range had one structure only, that referred to as theta in the literature [5].

(6) Compounds Zn_4Mn and Zn_3Mn were furnace-cooled from 470° C; results in parentheses refer to repeat samples water-quenched from the same temperature. The hardness changes indicate appreciable response to treatment; on the other hand, the T_p values (which for these four samples and for "Zn_2Mn" were extrapolated) do not differ greatly, probably because they reflect behaviour *at* temperature.

(7) Compound Zn_3Cu was tested at only one temperature (600° C) by dropping into a refractory boat at that temperature, leaving for the usual 4 h, after which the sample was tipped out for quick cooling. T_p was inferred to be above the test temperature, probably of the order of 800° C (weight gain); the hardness quoted was determined at room temperature.

(8) From considerations outlined in this and previous papers, it appeared likely that a high ratio compound $Zn_{13}Ru$ could exist, and from the present limited data this seems to be so.

(9) For $Zn_{11}Gd$ and Zn_2Gd, the oxidation mode could more accurately be described as "m tending to n". It would seem that, compared with the situation with aluminides, any tendency to nml type is of lesser magnitude and manifests itself at higher Zn/M ratios.

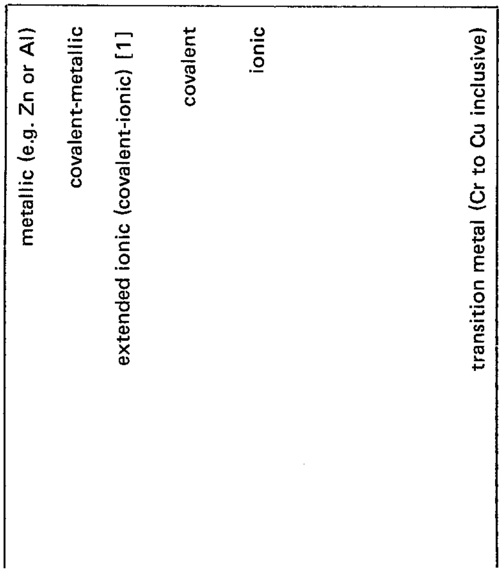

Figure 2 Suggested changes in bond type between the later transition metals and elements such as zinc or aluminium, that is, across some of the systems indicated in Fig. 1.

dency is not so great with aluminium as a common component and even less so with more distant elements. However, these considerations relate to a more general view of the zone of influence of the composite divide. It is not possible to deal adequately with this topic at this point, but it is hoped to do so in a further communication.

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References

1. H. E. N. STONE, *J. Mater. Sci.* **10** (1975) 923.
2. *Idem, ibid* 7 (1972) 1147.
3. *Idem, ibid* 8 (1973) 1009.
4. *Idem, ibid* 9 (1974) 607.
5. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) and supplements edited by R. P. Elliott (1965) and F. A. Shunk (1969).
6. A. F. WELLS, "Structural Inorganic Chemistry" (O.U.P., Oxford, 1962) pp. 971, 999.
7. J. B. DUNLOP, unpublished work.

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