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# The variation of thermal oxidation resistance across certain binary systems

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Isochronal oxidation tests have been carried out on numerous compositions based on copper and silver with elements forward in the Periodic Table and compositions based on aluminium and zinc passing back. Variability across the various systems is such that three composition ranges may be defined; the first is the terminal solution where the oxidation parameter, $T_p$, rises from a value typical of a metal to that of a non-metal, a second where non-metal behaviour is the norm, and a third where $T_p$ rises in the liquid state to that of the later B element. The results, in particular the rise in the terminal solid solution, are discussed with respect to concepts such as s–d resonance, Fajans' rule, and the limits of the zone of influence of the composite divide. A postscript discusses the fall in oxidation resistance of molten aluminium when alloying elements are present.

## 1. Introduction

The study of oxidation variability, in addition to its practical value in predicting useful high-temperature alloys, enables us to come to grips with a central problem in chemistry and physics, namely, the distinction between mixtures and compounds. In the field of alloys, we know that silver and gold mutually form complete solid solutions in which properties change gradually from one element to the other, but that gallium and arsenic form an equiatomic compound whose properties are different in kind from the two elements. For example, an etching reagent suitable for silver or gold would suffice for any binary alloy of those metals, but tables of reagents for gallium and arsenic give no help with GaAs. Not only do intermetallic compounds react differently from their components, they frequently display a considerable degree of inertness; as examples we may cite the compounds formed across the composite divide [1] which are the subject of this paper. This divide runs vertically in the long Periodic Table between Groups IB and IIB, and so we are concerned with the compound compositions formed from the later transition (including IB) and the remaining B elements. New experiments reported mean that it is possible to gain an overview of many Cu–B element and Ag–B element systems. Of these, the Cu–Zn has been studied in most detail. The counterpart of copper and silver forward is the study of aluminium and zinc systems passing back in the transition metals; these are not new results, but help to complete the overview of variations across the composite divide.

## 2. Experimental procedure

Small samples of the compositions were either prepared by arc melting or melting in evacuated ampoules [2, 3], and then subjected these to thermal oxidation, using an isochronal scheme, so as to estimate $T_p$ (the temperature for a weight change of 1 mg cm$^{-1}$ over 4 h). Table I gives values of $T_p$ for the alloys which were specially prepared for this paper and a preliminary note [3]; the discussion is based on these and earlier results considered together. Knowing $T_p$, and the melting/decomposition point $T_m$(K), it was possible to estimate $T_p/T_m$, the stability ratio. Broadly speaking [2], the ratio of a compound or non-metallic element approximates to unity, but is about 0.5 $T_m$ for metallic alloys and elements. The relative levels of stability ratio and the mathematical

TABLE I Summary of oxidation tests. Column 1: compositions (single samples) are characterized by the atomic concentration of the second-mentioned component. Column 2: departures from normal weight increase curves are indicated by the following code; L continuous weight loss; LG loss followed by gain at higher temperature, estimated on gain; GL gain followed by loss, estimated on loss; E extrapolation; * 'chromium' type of curve [4]. High incidence of oxidation curve abnormalities is a characteristic of the present population. Column 3: c, congruent; p, peritectic; when neither is inserted, the temperature given is an average of the liquidus and solidus

| Composition | $T_p$(°C) | $T_m$(°C) | $T_p/T_m$ |
|---|---|---|---|
| MgAl92 | 600 | 590 | 1.01 |
| CuMg67 | 460 | 568c | 0.87 |
| CuAl5 | 670* | 1080 | 0.70 |
| CuAl8 | 980 | 1070 | 0.93 |
| CuAl10 | > 1000 | 1060 | > 0.95 |
| CuAl20 | > 1000 | 1040 | > 0.97 |
| CuSi6 | 650* | 1020 | 0.71 |
| CuZn10 | 460 | 1040 | 0.56 |
| CuZn20 | 620 | 990 | 0.71 |
| CuZn29 | 640* | 930 | 0.76 |

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* Now retired.

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TABLE I *Continued*

| Composition | $T_p$(°C) | $T_m$(°C) | $T_p/T_m$ |
|---|---|---|---|
| CuZn33 | 780 | 920 | 0.88 |
| CuZn37 | 900 | 900 | 1.00 |
| CuZn41 | 860 | 890 | 0.97 |
| CuZn45 | 760 | 880 | 0.90 |
| CuZn49 | 760 | 870 | 0.90 |
| CuZn53 | 690 | 860 | 0.85 |
| CuZn57 | 700 | 840 | 0.87 |
| CuZn61 | 700 | 830 | 0.88 |
| CuZn65 | 690 | 820 | 0.88 |
| CuZn69 | 690 | 750 | 0.94 |
| CuZn73 | 690 | 700 | 0.99 |
| CuZn90 | 530 | 500 | 1.04 |
| CuGa10 | 840 | 1010 | 0.87 |
| CuGa20 | 1060E | 915p | 1.12 |
| CuGa67 | 440 | 254p | 1.35 |
| CuGe12 | 470 | 823p | 0.68 |
| CuSe33 | 390 | 1110c | 0.48 |
| CuIn10 | 790* | 710p | 1.08 |
| CuIn15 | 840GL | 710p | 1.13 |
| CuIn20 | 840E* | 710p | 1.13 |
| CuIn40 | 770* | 310p | 1.79 |
| CuSn8 | 780 | 798p | 0.98 |
| CuSn13 | 730 | 798p | 0.94 |
| CuSn15 | 720 | 798p | 0.93 |
| CuSn45 | 560 | 415p | 1.21 |
| CuSb10 | 600* | 645 | 0.95 |
| CuSb20 | 500LG | 645 | 0.84 |
| CuTe33 | 160 | 1125c | 0.31 |
| AgAl10 | > 1000 | 870 | > 1.11 |
| AgZn10 | 590* | 870 | 0.76 |
| AgZn20 | 700LG | 800 | 0.91 |
| AgZn29 | 820LGE | 740 | 1.08 |
| AgZn37 | 700E* | 710p | 0.99 |
| AgGa10 | 1000 | 830 | 1.15 |
| AgGa20 | 930 | 611p | 1.36 |
| AgGa25 | 880 | 611p | 1.30 |
| AgGa60 | 400L | 326p | 1.12 |
| AgCd10 | 710LG | 920 | 0.82 |
| AgCd20 | 700LGE | 870 | 0.85 |
| AgCd30 | 590 | 810 | 0.80 |
| AgCd40 | 810LG | 736p | 1.07 |
| AgCd80 | 310 | 343p | 0.95 |
| AgIn10 | 630* | 880 | 0.78 |
| AgIn20 | 720* | 693p | 1.03 |
| AgIn25 | 810* | 693p | 1.12 |
| AgIn67 | 670 | 166p | 2.15 |
| AgSn3 | 710 | 940 | 0.81 |
| AgSn6 | 880 | 900 | 0.98 |
| AgSn12 | 790 | 724p | 1.07 |
| AgSb5 | 780LG | 860 | 0.93 |
| AgSb9 | 810LE | 702p | 1.11 |
| AgSb17 | 530L | 558p | 0.97 |
| NiZn40 | 700 | 1040p | 0.74 |
| CoAl20 | 940* | 1400 | 0.73 |

scale 0.5 to 1.0 are the parameters around which the discussion will be based. In some cases the ratio for some B elements is well above unity, and this circumstance, and the question of alloy components for Cu and Ag, Al and Zn, requires some preliminary explanation and discussion.

## 3. Results and discussion

Of the Periods of the Periodic Table, we ignore the First Short and Third Long because insufficient data points in the few phase diagrams studied do not permit interpretation of the present type. Elements to the right of Si, As and Sb are also excluded because of shortage of data and sparcity of compounds – though the latter is not so true of the Cu–Te system. For silver compounds a further limitation is given by the absence of compounds in its systems with Si, Ge and As. This leaves us with consideration of the elements Al, (Si), Zn, Ga, (Ge), (As), Cd, In, Sn and Sb as components in the copper and silver systems. Si, Ge, As and Sb display normal non-metal behaviour in that they fail in oxidation tests at a stability ratio of unity. Of the rest, the high ratios for Al and Ga were ascribed [4] to the operation of a boiling point-linked criterion, and those for Zn, Cd, In and Sn to an oxide-linked criterion relative to the molten state. However, these criteria are not important for the first part of the discussion insofar as all the elements first survive (in terms of rising temperature) to more than 1.0 $T_m$. Later on, the manner in which $T_p$ for these anomalous elements is modified by alloying will be found to be of interest.

As noted before, the Cu–Zn system has been studied in more detail than any other; it is interesting intrinsically and as an archetype before approaching the generality of B systems. The $T_p$ results are shown superimposed on the phase diagram in Fig. 1. The span from 29 to 73 at % (atomic per cent is used throughout) was covered at 4% intervals. The range zero to 45% has already been presented and discussed [3]. In this region the stability ratio rises from approximately 0.5 for pure copper to 1.0 at the peritectic horizontal (37% Zn). Between 37% and 80%, $T_p$ is never far below the solidus; there appears to be a maximum inside the gamma field between 62% and 64%, and also a levelling out in the beta field which may effectively be a local maximum inside its stoichiometry range. A hypothesis for the maximum at 37% has been presented in [3], for that at 44.7% in [5], and 61.8 is a golden ratio point. However, from results presented later, it will be noted that whilst the Ag–Cd is like the Cu–Zn system, stability ratios in the Ag–Zn are generally higher. This is probably because Zn → Ag, like Al → Cu, is a stronger Fajans' rule direction across the composite divide than Zn → Cu

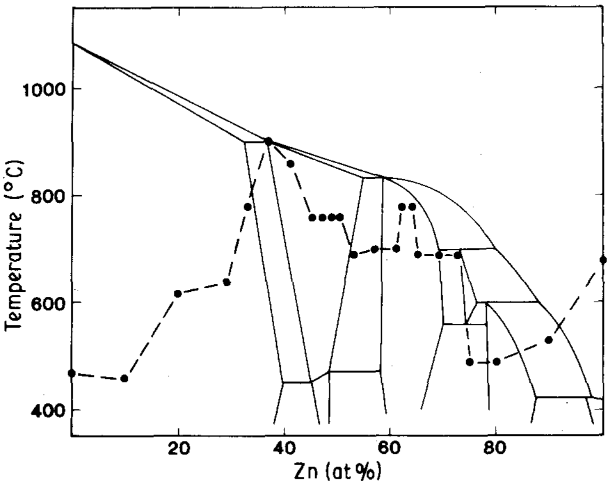

*Figure 1* The Cu–Zn system with superimposed $T_p$ trace.

or Cd → Ag. From 80% to 100% in the Cu–Zn system the $T_p$ trace changes direction, rising steeply upwards to a $T_p$ in the liquid state for zinc. We may divide behaviour across the diagram into three parts; a rise of $T_p$ in the IB-rich solid solution, a central region where the stability ratio for the intermetallic phases approaches or equals unity, and a third region where the $T_p$ of more than one of elemental Zn progressively overrides the second effect. We call these Types I, II and III, respectively, and present the remaining block of experimental data with this division in mind.

The results for copper- and silver-base binary alloys with elements to the right in the Periodic Table are given in summary form in Figs 2 and 3, respectively. The solid lines represent the liquidus, $T_p$ traces are dashed, and the extent of the Cu/Ag solid solutions is indicated at the foot of each small diagram. For copper systems, the three-fold division is approximately obeyed, with the following modifications: in the Cu–Al, Cu–Si and Cu–In systems, the onset of Type III occurs at quite high IB percentages; in the Cu–Sb, although there is a rise in the solid solution region, the Type II stability ratios are somewhat low, and in the Cu–As the ratio for $Cu_3As$ is approximately 0.5, indicative of metallic bonding. With regard to silver systems, one may comment in similar terms; stability ratios tend to be somewhat higher, especially in systems with Group IIB. So much for coinage metal systems with other B Group elements.

Behaviour for aluminium and zinc alloys passing back in the First Long Period are presented in Figs 4 and 5, respectively, plotted from earlier tabulated data [6, 7]. For aluminium passing back, the three-fold division is followed to Al–Cr; a particularly high rise

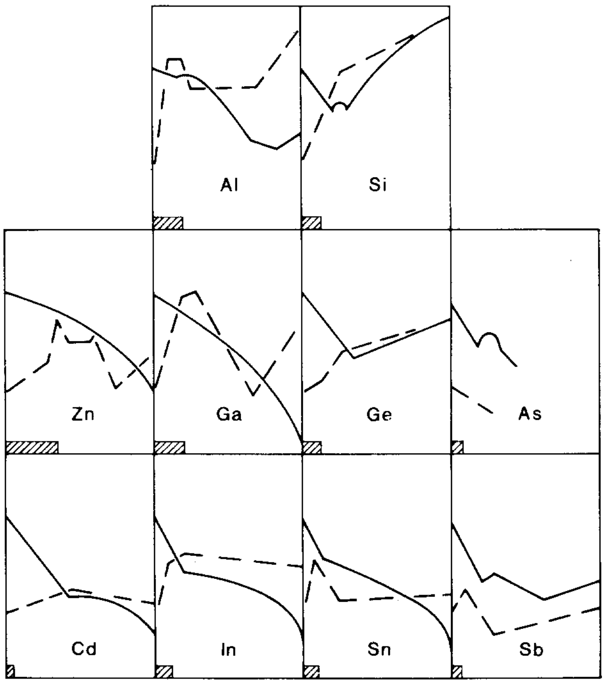

*Figure 2* Sets of phase diagrams for Cu-base alloys. (——) Approximate liquidus, (– – –) variation of $T_p$. Shaded areas lower left are an indication of the extent of solid solution. Each rectangle is characterized by its alloying element, with the abscissa running from 0%–100% and the ordinate from 0 to 1500 °C.

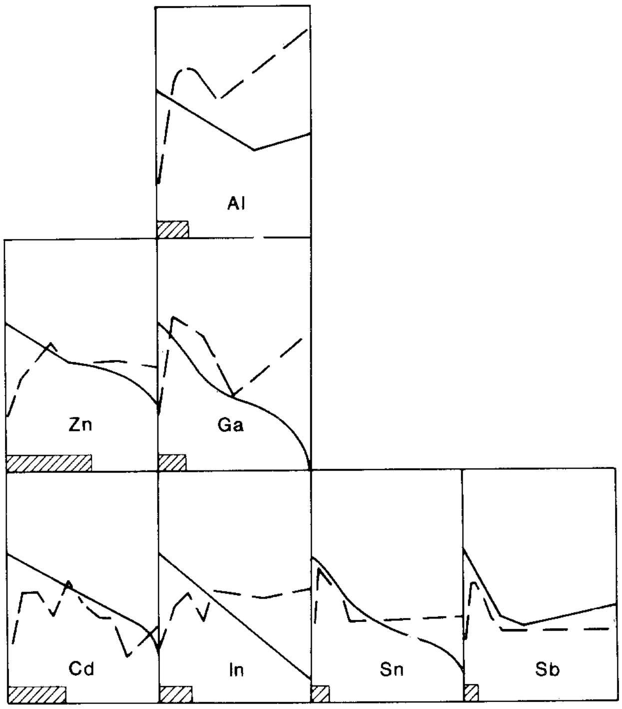

*Figure 3* As Fig. 2, but for Ag-base alloys. At the Ag-rich ends, the dashed line has been continued to a notional $T_p$ which is $0.5T_m^{Ag}$. Extrapolation to zero solute could be a method of estimating the Tammann temperature for noble metals.

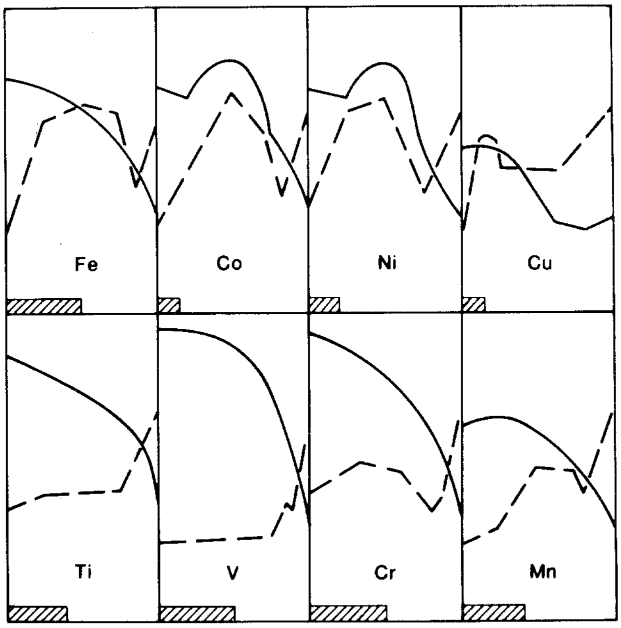

*Figure 4* Sets of phase diagrams for alloys containing Al with metals passing back the First Long Period. Otherwise as Figs 2 and 3, except that the ordinate runs from 0 to 2000 °C.

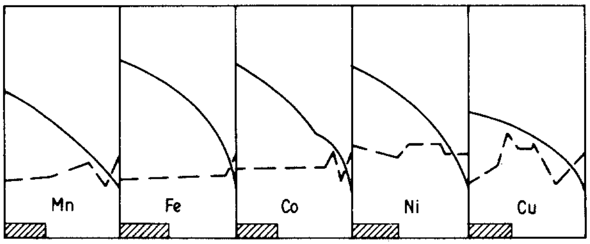

*Figure 5* As Fig. 4, but for Zn alloys.

of stability ratio occurs in the iron-rich solid solution, probably indicative of a high degree of non-metallic bonding in the 3/1 superlattice. A big change occurs as we move to Al–V, where the Type II range is limited to the compounds of high Al/V ratio, whilst in Al–Ti all compounds have stability ratios of approximately 0.5. The system Al–Ti passing back is evidently the counterpart of Cu–As. In the Al–V and Al–Ti systems, only the Type III remains unchanged. Although results for Al–Second Long Period are not comprehensive, sufficient is known to suggest that the influence passing back there only extends to palladium, in conformity with Pt in the Third Long Period [6]. For systems with Zn as common component (Fig. 5), behaviour similar to Al is found. At first sight the solid and dashed lines seem to vary differently from the Al set, but closer inspection will show that this is not so, but is a consequence of the different forms of liquidus in the two cases; continuously falling for Zn, but tending to mid-diagram maxima in Al systems. Full Type II behaviour is not so clearly marked with Zn as a common component, but overall the trends are not essentially different, considering the contrasting compound composition scalings.

Figs 2–5 all show that the rise from 0.5 to 1.0 stability ratio or near takes place generally as we move across the IB solid solutions (or, in the Al and Zn systems, across the transition metal solid solutions), and that the Cu–Zn case was not an isolated example. It lends support to the notion [3] that quasimolecular assemblages such as analogues to CuZn form with increasing solute content in the terminal solutions. It may be objected that, given high stability ratios for compounds, the increase could be explained by an argument through mixtures; that, for example, Zn itself in *Cu*–Zn solid solution is imposing large ratio, but this is to ignore the fact that, in the systems under discussion, the Cu and Zn solid solutions are not the reacting species. Indeed, the way in which the stability ratio switches (changes direction) at the junction of many Types II and III in Figs 2–5 is strong evidence that the intermetallic phases which occur in the Type II region are behaving individually, that is, like compounds.

Another feature of the rise in the Type I region of which one would like to inquire in more detail, is the rates of rise given by the various solutes. Unfortunately, the spread of data points suitable for a cursory assessment of a whole diagram does not enable trends to be elucidated with any degree of accuracy for a more limited composition spread, although a few comments can be made. Information on zinc passing back is completely inadequate; and that for aluminium systems is sparse, though what exists suggests that the rise is quite high in systems passing back to chromium. For Cu- and Ag-base solid solutions, plots of rise of $T_p$ against at % solute (not illustrated) show that whilst Group IIB elements do raise the level well, they are inferior to other elements, notably Al, Ga and Sn. Mention of these elements is particularly interesting in conjunction with the finding that the locus of most effective elements for Hume–Rothery-type phase diagram formation moves in the Periodic Table from Zn up to Al, then down to Sn. This locus will be the resultant from two tendencies, a strength of ion effect, and a low charge effect, with Fajan's rule operating. For example, although the first effect for Sn will be small, because of the difference between atom and ion size, it can have a strong low-charge effect because of its ability to become divalent. The apparent inferiority of Group IIB may, of course, be a consequence of the method of plotting. With further information it could be profitable to try alternative ways of plotting the solid solution rises. However, it is not self-evident to the author that re-scaling the abscissa either to an average Group number or conventional e/a ratio basis would be a proper proceeding. If s–d resonance is the reason for 0.5 stability ratios, the appearance of the latter on our diagrams will only be possible when the solute element can show valencies (meaning, at this point, s electron donor numbers) of 1 to 2 or $2\phi$-1 in dilute terminal solid solution. The elements that can do this are strictly limited; they are the elements constituting the zone of influence of the composite divide. Although there is continuum behaviour in solid solutions, in general as we move out of these zones we will encounter discontinuities, such as where the terms Type I and Type II cease to have the meaning here ascribed to them, as in the Al–Ti and Cu–As systems. Another consideration: very high B element weighting would be expected to impose unity stability ratio, but we must be aware of a lattice factor. Hume–Rothery compounds such as gamma brass are homogeneous electronically to a finer degree than for example NiAs type. In the latter, at least for axial ratios which are not very high, we probably have a dual lattice electronically, with a resultant short-circuiting effect of the metal sub-lattice on the stability ratio. Such could be the explanation for the 0.5 ratio for $Cu_3As$ herein.

That concludes the main business. It is convenient to bring together, as a postscript, some previously scattered data on the oxidation of molten Al. Al, as we have learnt, is one of those elements which not only shows non-metal behaviour, but has a stability ratio well in excess of unity. Indeed, its $T_p$ value is 1340 °C, and this high value, and the practical importance of Al alloys, makes it interesting to consider what happens when alloying elements are added. The results, in the form of the percentage of alloying element necessary

TABLE II Part of the Periodic Table. The figures denote the solute content which reduces $T_p$ from 1340 °C (for pure Al) to 1000 °C

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Mg | (Al) |
| | | | | | | | | | | 4 | |
| | | Tr | V | Cr | Mn | Fe | Co | Ni | Cu | – | |
| | | 16 | 5 | 8 | 12 | 10 | 10 | 16 | 28 | | |
| – | Y | – | – | – | – | – | – | Pd | Ag | | |
| | 15 | | | | | | | 19 | 45 | | |
| Ba | Ce | – | – | W | Re | – | – | Pt | Au | | |
| 8 | 11 | | | 4 | 6 | | | 18 | 70 | | |
| | | Th | – | U | | | | | | | |
| | | 12 | | 10 | | | | | | | |

to decrease the $T_p$ to 1000 °C, are presented in Table II. Points to note are the concentration of values in the range 4–19 at % inclusive, with the exception of the coinage metals which are much higher. The latter is presumably a simple dilution effect of increasingly more noble metals. The high decrease in $T_p$ brought about by Mg, V, W and Re is presumably due to a strong destabilizing effect which destroys the tenuous, but normally protective, alumina film. Unfortunately, the results of Table I are not of immediate help to the man on the foundry floor with his pot of molten alloy, because they were obtained under quiescent conditions. They will, however, provide him with an upper bound to behaviour, to the degree of oxidation which is unlikely to be bettered.

## Acknowledgement

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