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Oxidation resistance and constitution of compounds of groups IIIA and IVA with d-transition elements

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The thermal oxidation resistance of compounds of types RCo, R_3Ni and RCu, where R is a rare earth element, has been tested by an isochronal method. It is found that the ratio T_p/T_m of the oxidation parameter to the melting point decreases from about 0.75 to 0.6 with increasing atomic number, indicating a relaxation of chemical binding, and displays 'saw-tooth' variability as we pass from a compound of one element to another. This variability may be due either to weaknesses from valency-induced changes with elements such as terbium, or to deep-seated changes between odd- and even-Z elements. In a further development of the work, contours for T_p/T_m of 0.6 and 0.7 have been charted on synoptic diagrams characterized by a constant row of 4f/5d elements on one ordinate and a variable 3d element (V to aluminium) on the other. We note that the largest area of high ground is found for cobalt compounds, followed by nickel, then copper; and that with copper only elements from barium to gadolinium contribute, in contrast with cobalt and nickel (lanthanum to at least thulium). Evidently a strong transition metal contribution to bonding in cobalt compounds has weakened in the copper counterparts, and s–d resonance/attenuation across the composite divide from the 4f element into the copper d-shell is only possible for the lighter rare earths.

1. Introduction

Two papers which deal with the properties of compounds with components from Groups III and IVA have already appeared [1, 2], and the justification for another may reasonably be queried. The reason for the interest is that we are probing the properties of compounds whose components are on the boundary of the transition metal zone in the Periodic Table. Work many years ago [3] showed that non-metals (including Groups II, III, and IVB) break down in oxidation at temperatures of approximately 1.0 T_m, and typical metals at about 0.5 T_m. By studying borderline cases and, in this context, even yttrium and cobalt are limit components, we may hope to elucidate more clearly the principles involved.

The first paper [1] gives the discovery of high values of T_p/T_m (that is, of effect) in the compound Y_9Co_7 and some results on the persistance of these values with changes on the yttrium and cobalt sites. The second [2] gives more nearly complete data for compounds of selected Group IIIA/IVA elements (gadolinium, yttrium, cerium, lanthanum, titanium and zirconium) with d elements (mostly 3d). In this second part, use was made of synoptic diagrams to plot the incidence of T_p/T_m values and facilitate theoretical inferences, and as a result it became apparent that high values of effect were more likely to be found in the boomerang-shaped zone illustrated schematically in Fig. 1. An explanation was offered in terms of trends xy and yz in the figure which are related to bonding across the transition metal and composite divides, respectively. However, this latter work gave information for only six elements as common components, and it became of interest to know how changes would evolve with other Group IIIA/IVA elements, and in particular for changes along the 4f series. To have continued at the depth of detail employed in [2] would have necessitated a prohibitively long period of work, and so the expedient was adopted of making compounds for test of only the following three types, which together would characterize the shape of the zone of high effect in synoptic diagrams; the three were RCo, R_3Ni and RCu (where R is a Group IIIA/IVA element), and they are marked by points A, B and C, respectively, in Fig. 1.

The presentation and discussion of the results for the three types constitute the first half of the present paper. When these were complete, it became apparent that there was diagnostic advantage in transforming the procedure of synoptic mapping employed previously (that is, changing from 'constant IIIA/IVA against variable 3d component' to 'variable A component against constant 3d element'), and so the second half of this paper presents data and discussion on a succession of synoptic diagrams from Mn → 4f to Zn → 4f elements, inclusive.

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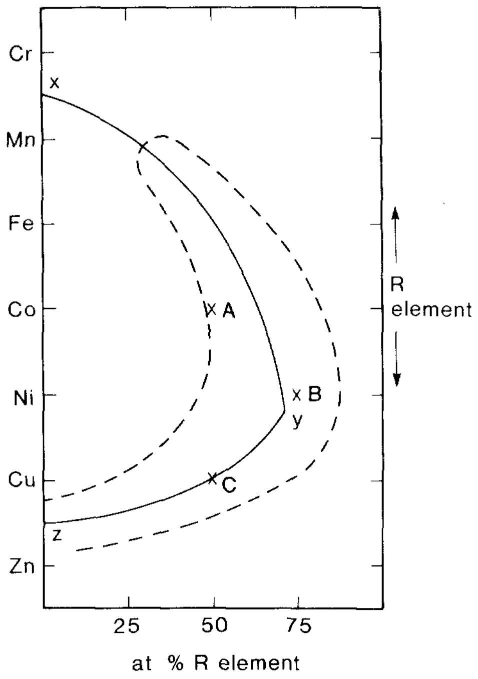


Figure 1 Schematic diagram showing (a) maximum area from [2] of T_p/T_m greater than 0.6 (inside dashed line); (b) hyperbolae for average Group number 1.5, xy across the transition metal divide, yz across the composite divide; and (c) composition types A, B and C (see text).

It is not necessary to repeat the details of the alloy preparation and air oxidation test procedures, since these have been given many times. It suffices to say that the oxidation parameter T_p gives a measure of the turnover point of the temperature/weight change curve – the temperature in effect of the release of the kinetic trigger in the body of the solid undergoing oxidation. The Periodic Table divided by vertical lines has also been frequently presented, as has the hypothesis of s–d resonance and attenuation. Complete tables of T_p values are not given, but only results (Table I) not quoted previously. The sources for phase diagram data were Hansen and Anderko, and supplements [4] and Massalski [5].

TABLE I Summary of new oxidation tests

Composition	T_p(° C)	T_m	T_p/T_m
BaCu	190	570c	0.55
La_2Zn_{17}	390	974c	0.53
Ce_2Zn_{17}	270	980c	0.43
$PrCo_2$	320	934p	0.49
Pr_3Co	360	588c	0.74
Pr_3Ni	380	500c	0.84
PrCu	390	583p	0.77
$NdFe_2$	520	1130p	0.57
$NdCo_2$	360	965p	0.51
Nd_3Co	300	645c	0.62
NdNi	340	780c	0.58
Nd_3Ni	300	590c	0.66
$NdCu_2$	410	840c	0.61
NdCu	460	675p	0.77
Nd_2Zn_{17}	370	951c	0.53
NdZn	300	923c	0.48
$SmMn_2$	370	930p	0.53
$SmFe_2$	400	900p	0.57
$SmCo_2$	240	1074p	0.38
Sm_3Co	390	695c	0.68
SmNi	320	1079c	0.44
Sm_3Ni	370	684p	0.67
$SmCu_2$	490	850c	0.68
SmCu	440	724p	0.72
SmZn	350	950c	0.51
Tb_3Ni	340	(784p)	(0.58)
TbCu	330	(900)	(0.51)
$DyMn_2$	400	930c	0.56
DyNi	390	1248c	0.44
Dy_3Ni	460	782p	0.69
DyCu	380	955c	0.53
Ho_3Ni	440	(800p)	(0.66)
HoCu	410	(900)	(0.58)
$ErMn_2$	470	990p	0.59
$ErFe_2$	470	1300c	0.47
ErNi	390	1255	0.43
Er_3Ni	440	845p	0.64
ErCu	360	(900)	(0.54)
Tm_3Ni	460	(890)	(0.63)
TmCu	350	(900)	(0.53)

c, Congruently formed compound; p, pertitectic. Parentheses, supposed melting/decomposition temperatures. $SmCo_2$ showed a weight loss on oxidation, all others a weight gain. TmCu showed a tendency to a 'chromium' type of curve. T_p for $NdFe_2$ was extrapolated.

2. Results and discussion

2.1. Changes of T_p/T_m with R element in RCo, R_3Ni and RCu

The results are summarized graphically in Fig. 2. A mass of supporting data is necessary for discussion of this. It is convenient to begin with a statement of variations of the following properties with respect to atomic number of rare earth element, in the following order (i) melting points of elements; (ii) melting points of compounds; (iii) T_p and T_m for elements; and (iv) T_p and T_m for compounds.

The melting points for the elements rise monotonically from about 900° C for lanthanum to about 1600 for lutetium, if one excepts breaks at europium and ytterbium which are ascribed to, or are consistent with, valency changes. (Since compounds of these two elements were not studied in the present work, connecting lines on diagrams herein take no account of them.) However, there is also a slight dip for the melting point of cerium, although the weight of opinion is in favour of a valency of greater than three in its compounds. The melting points of compounds follow the same trend, though the gradients are in general not so steep – from 500 to 800° for our light rare earth compounds, to 800 to 950 for the heavies, melting points increasing for families of compounds in the order $R_3Ni \rightarrow RCu \rightarrow RCo$. The rise in general of T_p values for elements and compounds is less (the gradient is less) than for melting points, and in addition more of a saw tooth character comes into the plot. Again the family order for compounds is generally the same. The data that are available for scandium and yttrium (not illustrated) suggest similarities to gadolinium and with each other, here and elsewhere.

The first broad feature of Fig. 2 is the drift downwards with increasing atomic number, for compounds from 0.7 to 0.8 at low Z to 0.5 to 0.7 for thulium. Values of T_p/T_m for the elements, though showing much variation, stay at about the same level and therefore approach the values of compounds at high Z. Thus there appears to be a factor operative which

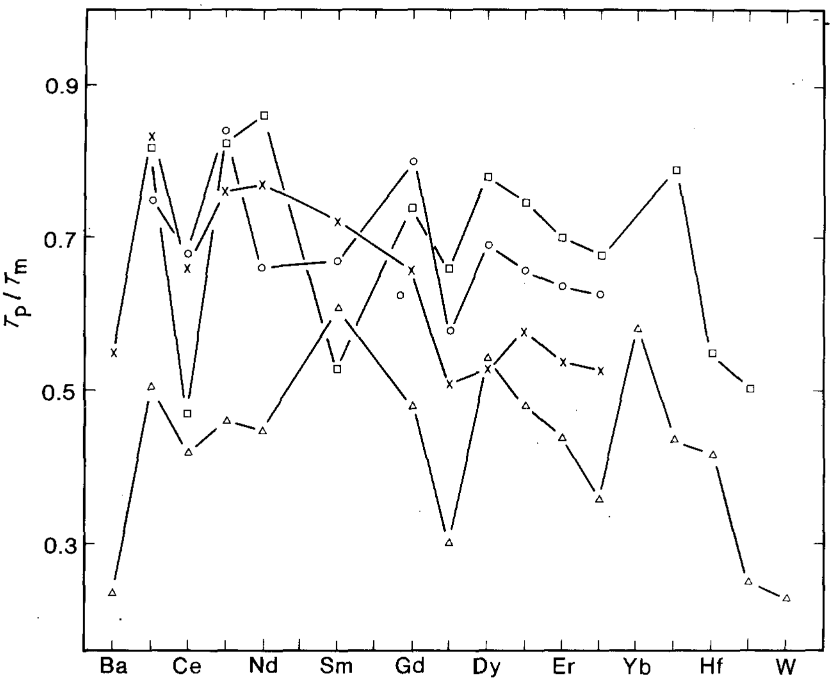


Figure 2 T_p/T_m against number Z for four families of compositions. △, elements; □, RCo; ○, R_3Ni; x, RCu, where R is a 4f metal, barium, hafnium or tantalum. All tests in as-cast state except [2] some cerium compositions.

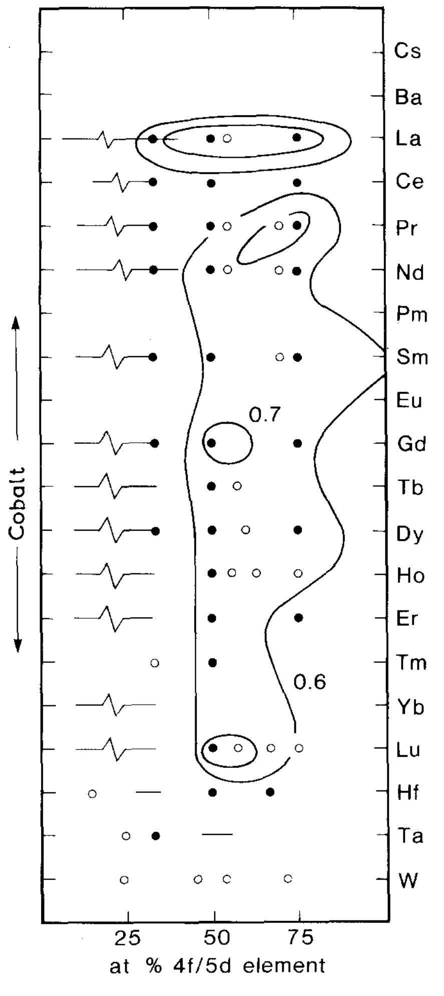


Figure 3 Synoptic diagram showing condensed phase information for systems of cobalt with lanthanum to tungsten successively, with superimposed contours for T_p/T_m = 0.6 and 0.7. ○, compounds; ●, tested compositions. Jagged bar indicates the existence of more than two compounds in a limited composition range, simple bar a single compound of variable composition. No markings other than ● indicate no information. Present evidence suggests that no truly equiatomic compounds RCo exist, only 6/7 (praseodymium, neodymium) and 3/4 (terbium, holmium) (but Co_2Dy_3).

decreases from the start of the lanthanide series. It may be objected that this is not a real effect, but is a consequence of the lanthanide contraction, but this is to ignore the consideration that the latter is built into the rise in melting points, at least for the elements. The other main feature is the saw tooth character or local Z variability. Since T_p/T_m for compounds roughly follows that for elements, we associate low values of the one with a weakness introduced by the element into the compound structure, and since in the cases of cerium and terbium this is quite likely to be oxidation to a higher valency state, we suggest that the weakness is due to the latter. However, the fact that T_p/T_m does not drop anywhere below 0.5 (compare with the values for the elements terbium, tantalum and tungsten) suggests that degradation of the structure by loss of volatile species is a stage not reached in our sample compounds. The saw-tooth character may, alternatively, be due to more deep-seated changes between even- and odd-Z elements, as happens with certain properties along the 3d series.

2.2. Synoptic diagrams for lanthanides against 3d elements

Relatively few additional oxidation tests were necessary before it became possible to effect this graphical transformation. As a result we arrive at a sequence of synoptic diagrams with the series of 4f elements on one ordinate and a constant 3d element on the other, and on which values of T_p/T_m for compounds are the basis for drawing contour lines at ratios of 0.6 and 0.7. As in [2], we review firstly the incidence of compounds in the various synoptic diagrams, and then the incidence of the contours, since it was a principal finding there that the former gave only limited hints as to the location of the latter. In passing, one notes too that incidence of high effect appears to bear no relation to the types of compound crystal structure.

Vanadium is immiscible in the liquid state with all

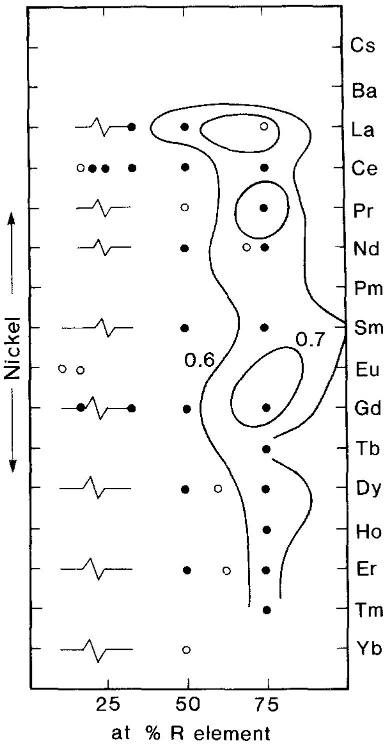


Figure 4 As Fig. 3, but for nickel against 4f elements.

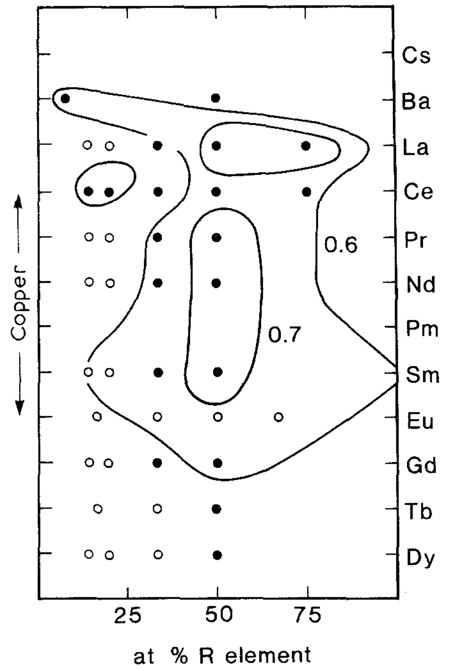


Figure 5 As Fig. 3, but for copper against 4f elements with barium.

the lanthanides so far as is known, and there is no information with regard to chromium. With manganese, although phase diagrams of immiscibility are reported for barium, lanthanum and cerium, compounds are formed with neodymium, samarium and gadolinium to erbium, inclusive, three in number, at least for gadolinium to erbium, with RMn_2 having the highest proportion of rare earth. With iron, compounds are known to be formed with cerium to lutetium inclusive, two in number with light rare earths, three with heavies, with $R(3d)_2$ again being the richest in rare earth. Compounds of cobalt are prolific, from 2/17 to 3/1 across the binary diagrams, and from lanthanum to tantalum inclusive, and the case of nickel is similar. Many compounds are formed by copper and zinc, although compounds of R_3Cu and R_3Zn stoichiometry appear not to exist.

That the incidence of compounds contrasts with incidence of effect is well brought out, the first thing to note (Table I and [2]) being an effective cut-off in values of T_p/T_m more than 0.6 for compounds with the elements vanadium to iron inclusive, with the sole exception of $GdMn_2$, whereas many compounds of cobalt, nickel and copper have high values. Synoptic diagrams charting the incidence of high effect for

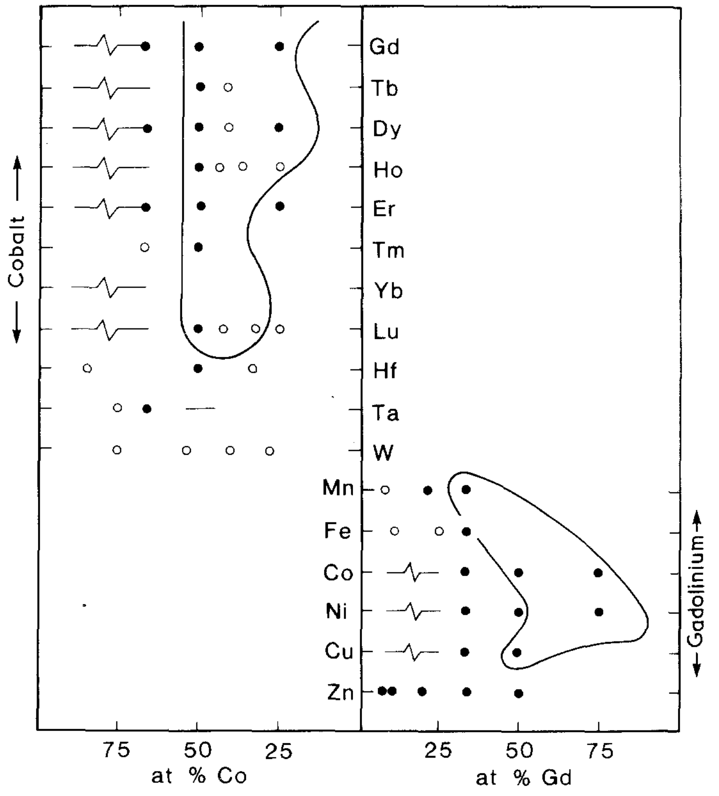


Figure 6 Double synoptic diagram for cobalt against 4f/5d and gadolinium against 3d elements, assembled from Fig. 3 herein and Fig. 2 in [2]. Only lines for $T_p/T_m = 0.6$ are shown. Samarium structures, Co–Zn compounds and superlattices have been omitted from the top right and lower left quadrants. Other conventions as for Fig. 3.

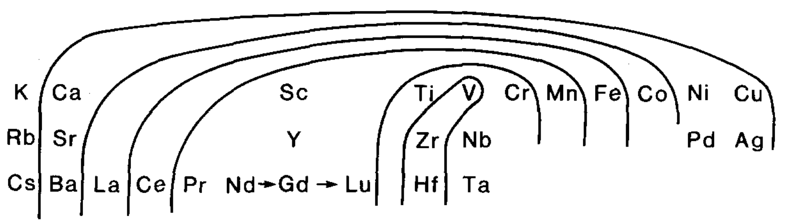
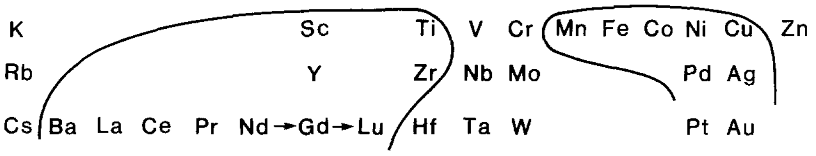


Figure 7 Limits of formation of compounds as we pass along the Periods; for example, lanthanum first forms compounds with cobalt, cerium with iron, and so on.

Figure 8 Inside envelope lines to left and right, the components of compounds which show high T_p/T_m.



cobalt, nickel and copper compounds are reproduced in Figs 3, 4 and 5, respectively. The largest zones of high ratio are found with cobalt and at R/Co ratios of 1 and 3. With nickel the zone shrinks laterally, straddling only the R_3Ni compositions. From the limited data avalilable for lutetium and hafnium compounds, it would be unjustified to conclude that there is necessarily a difference between cobalt and nickel in the limit of zones at high Z. On the other hand, when we come to copper as the commom (left-hand) element, whilst there is a broad zone across the synoptic diagram at low Z (Fig. 5), this effectively finishes at gadolinium, since T_p/T_m values for equatomic compounds with terbium, dyspresium, holmium, erbium and thulium are all less than 0.6. Amongst the detail in these diagrams we note lower values in general for cerium and terbium compounds, as commented upon earlier, and the strength of gadolinium. Two 2/17 compounds of zinc showed T_p/T_m less than 0.6; there must be a strip of high ratio along the zinc ordinate because zinc itself shows that behaviour, but it cannot be very wide. No systematic data for gallium compounds are available, but if the oxidation data for rare earth aluminides is plotted from [6] (not illustrated), it will be found to be not dissimiliar to that of cobalt (Fig. 3), indicating perhaps a predominantly outer orbital role of cobalt in cobalt–rare earth compounds.

3. General discussion

In the previous study [2] it was noted and thought significant that high T_p/T_m coincides with the intersection of the transition metal and composite divide trends (Fig. 1). The finding that only $GdMn_2$ of all compounds of vanadium to iron inclusive shows a high value indicates that the strength of the transition metal divide contribution had been overestimated. Nevertheless, that a TM divide contribution exists for cobalt (the element of lower Z than the pivot element of the boomerang nickel) may be confirmed by plotting a duplex synoptic diagram as in Fig. 6. Overall, the notion of strength of high T_p/T_m deriving from a simultaneous tendency to electronic configurations across both transition metal and composite divides remains a distinct possibility. The completely new feature which has been brought out is the tendency for the limit of high ratio at high Z to decrease from cobalt/nickel to copper. This is probably because a strong transition metal contribution in cobalt compounds has weakened in the copper counterparts, a natural consequence of the distance of copper from the transition metal divide. The composite divide contribution becomes the more important, but the necessary s–d resonance/attenuation from rare-earth element into the copper d-shell to sustain this is only possible for the lighter rare earths.

Hypotheses have emerged at different times and been modified as more results came to hand, and doubtless certain matters will become clearer which are now obscured by the heat of experiment. Of one thing one can be sure, the unity in the diversity, illustrated, in conclusion, by Figs 7 and 8. The first is derived purely from published data on phase diagrams, and summarizes at what points a given element starts to make compounds as we pass along series in the Periodic Table. The second provides an overview as to which elements are components in high T_p/T_m compounds. Both figures take note of results on compounds of elements such as titanium and zirconium which were left out in the 4f-based discussion. Is it too fanciful to see in the sweep of the lines in Figs 7 and 8 an allusion to an arch bridge? If one builds good buttresses, that is, picks components from left and right in the series which mutually lap up electrons in a manner which precludes s–d resonance, one can close the arch, and attain high T_p/T_m.

Acknowledgement

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References

1. H. E. N. STONE, *J. Mater. Sci.* **22** (1987) 1749.
2. *Idem, ibid.* **24** (1989) 633.
3. *Idem, ibid.* **7** (1972) 1147.
4. 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).
5. T. B. MASSALSKI (ed) "Binary Alloy Phase Diagrams" (American Society of Metals, Metals Park, Ohio, 1986).
6. H. E. N. STONE, *J. Mater. Sci.* **10** (1975) 923.

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