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The oxidation resistance and hardness of some intermetallic compounds

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Thirty-nine intermetallic compounds have been oxidation-tested in air. These include all the known compounds in the Al-V, Al-Ni and Al-La systems, three compounds each from the Al-Mn and Cu-Zn systems, four zinc-rich transition-metal phases, six inter-transition metal Laves phases, and the equiatomic compounds of antimony with aluminium, indium and nickel respectively. From the oxidation results the temperature corresponding to a weight change of 1 mg cm^{-2} (4h)$^{-1}$ was determined by interpolation. An attempt is made to classify the compounds in terms of the ratio of this temperature to the melting point of the appropriate compound or its oxidation product. The hardness of the compounds and of additional Al-3d compounds has been estimated, and in conjunction with the oxidation data forms the basis for some observations on the nature and incidence of binary intermetallic compounds of high atomic ratio.

1. Introduction

The oxidation resistance of the elements has been compared [1] in terms of a parameter T_p, where T_p corresponds to that temperature which effects a weight change in air of 1 mg cm^{-2} over 4 h. A classification of the elements was proposed, in which, *inter alia*, certain elements were grouped as "metal-linked" or "oxide-linked", depending on whether T_p approximated to 0.5 T_m^{metal} or 0.5 $T_m^{\text{oxide of element}}$ respectively (where T_m is the appropriate melting temperature). In further work [2], the incidence of oxide-linked oxidation in binary alloys of chromium with metals of the First Long Period was studied. Alloys of chromium with iron, nickel and cobalt showed consistent behaviour in plots of T_p versus composition, with the exception of a 50/50 chromium-cobalt alloy. The incidence of an intermediate phase was suspected as the cause of an unexpectedly low value of T_p, and indeed the relevant temperature/weight gain curve can be interpreted in terms of a transient increase in oxidation due to the phase sigma Cr-Co at a temperature of about 500°C ($\sim$0.5 $T_{\text{decomp}}{}^{\sigma}$). This matter brought into focus the more general question of the oxidation resistance of intermetallic compounds. Consequently, numerous samples of such compounds were prepared and tested, with the results described below. The hardness of these and of additional Al-3d compounds was also estimated, and proved helpful in attempting to interpret the results.

2. Experimental

The raw materials were the purest commercially available, and details have already been given [1]. Many of the alloys were already available, having been made in connection with studies of physical properties at low temperatures (e.g. [3]); others were specially made. Most of the alloys were prepared by argon-arc melting; the remainder (those containing zinc, also InSb) by melting in evacuated silica capsules and quenching in water. Aluminium-rich peritectic compositions were cast into sticks [4] of $\sim$1.5 mm × 1.5 mm cross-section to reduce the grain size and thereby facilitate conversion to the desired compound in subsequent heat-treatment; such treatments were carried out for 2½ days at appropriate temperatures in the range 665 to 700°C followed by air-cooling, and it proved possible to heat-treat in air all aluminium alloys except Al_3V and Al_8V_5. Peritectic heat-treatments appeared to be unnecessary with Al-La compounds. Zinc-rich peritectic compositions,

TABLE I Some properties of intermetallic compounds

Compound	Structure	Melting point (°C)	T_p (°C)	Hardness (kg mm^{-2})
Al_8V_5	gamma brass	p1670	550*	650
Al_3V	tetr. Al_3Ti	p1360	570	460
Al_6V	hexagonal	p736	790	440
Al_7V	monoclinic	p688	730	370
$Al_{10}V$	cubic complex	p670	790	320
Al_3Mn	triclinic	p990	970	620
Al_4Mn	hexagonal	p882	830	600
Al_6Mn	orthorhombic	p710	970	490
$AlNi_3$	$AuCu_3$	p1395	1320	460
AlNi	CsCl	c1638	1400	410
Al_3Ni_2	hexagonal	p1133	1200	1040
Al_3Ni	orthorhombic	p854	780	430
$AlLa_3$	$AuCu_3$	c720	570	210
AlLa	CsCl	p859	390	500
Al_2La	$MgCu_2$	c1424	590	620
Al_4La	tetr. $BaAl_4$	p1222	590	440
Al_3Ti	tetragonal	p1340	870	560
beta Cu-Zn	CsCl	p870	760	180
gamma Cu-Zn	gamma brass	p830	780	600
epsilon Cu-Zn	disordered cph	p598	490	180
delta Zn-Mn	hex. complex	p420	410*	290
zeta Zn-Mn	monoclinic	p428	460	220
zeta Zn-Fe	monoclinic	p530	570	180
zeta Zn-Co	monoclinic	p566	490	180
$ZrCr_2$	$MgZn_2$	c1675	500	1210
$ZrFe_2$	$MgCu_2$	c1610	480	1070
$NbCr_2$	$MgCu_2$	c1740	780	1400
$NbFe_2$	$MgZn_2$	c1655	610	1150
$NbCo_2$	$MgCu_2$	c1570	570	1270
sigma Cr-Co	tetr. complex	1260	600	920
$MgNi_2$	C36 hex.	c1145	790	530
$MgCu_2$	C15 cubic	c819	390	510
Cu_5Ca	hexagonal	c935	180*	100
AlSb	ZnS	c1065	480	550
InSb	ZnS	c530	470	210
NiSb	NiAs	c1153	390*	1040
UC	NaCl	2390	170	770
U_6Fe	tetragonal	p810	180	510
SiC	SiC	c2700	1440	

*Calculated on a weight *loss*.

See Notes on next page.

1. In column 3, prefix "c" indicates congruent melting compound, "p" a peritectic compound.

2. All compounds were stable in air for at least several months. (Comment not applicable to the uranium alloys which oxidized completely during testing.) White efflorescence on $AlLa_3$ specimen; tarnish film but no gross attack on microspecimens of the same.

3. The nominal compositions of the Cu-Zn compounds were 48, 60 and 80 at. % respectively. The silicon carbide specimen was in the form of a spiral section from a commercial heating element.

4. The use of "extrapolated congruent" melting points [12] was considered, but did not appear to offer advantage.

5. Presence of second phase. Chromium-cobalt (sigma) contained an appreciable amount [2]; $Al_{10}V$, Al_7V and Al_6V each contained $\not>$ 5% of an adjacent compound – other aluminium-rich 3d compounds, up to 2% of aluminium solid solution; zeta ZnMn contained approximately 2% of zinc solid solution; the results for $AlLa_3$ are derived from data on two samples, one slightly aluminium-rich, the other slightly lanthanum-rich – the microstructure of the samples was consistent with the existence of $AlLa_3$ [15] and probably with the interpretation of the AlLa equilibrium proposed by Gscheidner [16].

6. The stoichiometries 10/1, 7/1 and 6/1 in the Al-V system are used for simplicity.

7. Alumina films were evident on as-cast aluminium-rich alloys with transition elements of the First Long Period (Al_3Sc, Fig. 2, had a bright surface).

8. An attempt was made to prepare the reported compound Al_6Ti [10], but without success. The compound Al_6Fe [17] was found in chill-cast [4] sticks, but not in a 2g button (for hardness see Fig. 2). Only Al_6V of the cast alloys posed any difficulty in the casting operation; this was possibly because Al_3V is the phase of primary separation.

9. Only in two instances do the actual temperature/weight increase curves (not illustrated) call for comment. Firstly, beta CuZn, NiAl, and possibly gamma CuZn, gave curves rather similar to elemental chromium [1]. Secondly, the zeta zinc-rich intermetallics, and also epsilon CuZn, lost weight at about 200°C, from which a T_p of approximately 200°C could be construed. However, there was evidence that this was strongly dependent on the surface finish (which was variable) of the samples, and pending a complete reinvestigation, T_p has been estimated from the marked increase in weight at 400 to 600°C. The delta ZnMn lost weight monotonically with increasing temperature.

10. Hardness values are the average from not less than three impressions; load 20g for Al_3Ni and Al_6Fe only.

11. The hardness of the *3d*/*4d* Laves phases appears to vary directly with proximity to group VI, in conformity with the maximum in mechanical properties found there [18]. Such phases are much less susceptible to thermal shock and fracture by the arc in arc-melting than Al_2La; one is reminded of Raynor's suggestion [6] of a subdivision of Laves phases into those with complete or incomplete *d*-shells.

after casting, were heated in silica capsules for 3 to 4 weeks at temperatures in the range 420 to 530°C. Congruent compounds were tested in the as-cast condition. Identity of composition was ensured by weight checks during processing and by metallographic examination, supplemented by microprobe analysis in case of doubt. Single samples of each composition, of surface area 0.2 to 2.5 cm^2, were oxidation-tested. The T_p value for pure aluminium is high (1340°C), and the possibility of spurious values of T_p on aluminium alloys due to alumina-rich skins, has, it is hoped, been avoided by ensuring that a high proportion of the surface consisted of a fracture, or, alternatively, had been freshly abraded.

Samples were tested in static air according to a procedure described previously [1]. Heating was carried out for 4 h at each of successively higher temperatures until the temperature for a weight change of 1 mg cm^{-2} could be interpolated from the results. The standard temperatures were at 200°C intervals, starting at 200°C, but intermediate temperatures in the range 400 to 800°C were much used. Hardness testing was carried out with a Vickers microscope attachment, using a 50 g load unless otherwise stated.

3. Results and discussion

The oxidation results in the form of T_p values are given in Table I, together with hardness figures and brief notes on the compounds.

Discussion will principally take the form of attempting to classify the compounds as either (a) oxide-linked – $T_p \sim 0.5\ T_m^{oxide}$, (b) metal-linked – $T_p \sim 0.5\ T_m^{metal}$, or (c) non-metal linked – $T_p \sim 1.0\ T_m^{metal}$, beginning with (a). However, it may be not inappropriate before proceeding further to point to the generally high level of T_p values and the relevance of this to present and future practical applications.

Any singling out of compounds as oxide-linked is made difficult by the lack of basic information on melting ranges and in some cases by uncertainty in predicting the likely oxide composition. However, as a first step, it may not be unreasonable to assume the oxide film on alloys of aluminium with First Long Period transition metals to approximate to alumina.

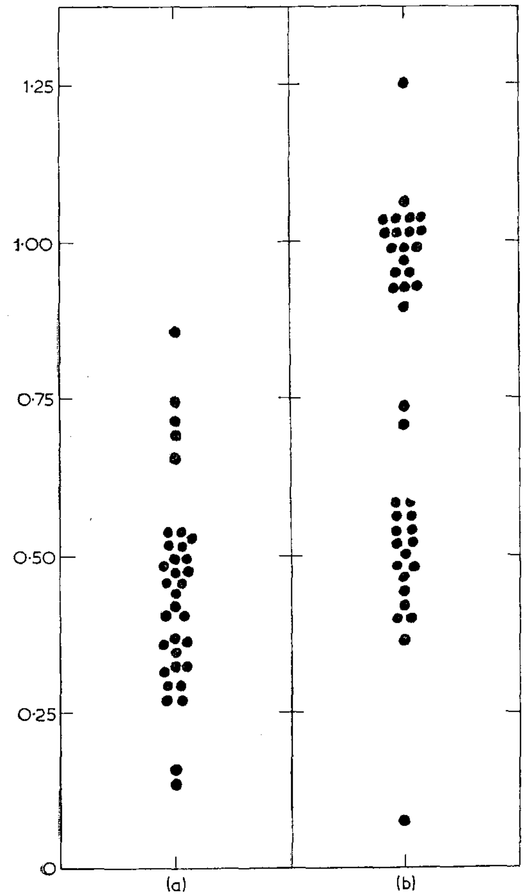

Figure 1 The distribution of values of (a) T_p/T_m^{oxide} and (b) T_p/T_m^{metal}. Points for Al-V compounds are not included in (a) because of the uncertainty regarding oxide composition.

The value of 0.5 $T_m^{Al_2O_3}$ is approximately 900°C and, depending on the degree of correspondence, some of the aluminium compounds listed in Table I could be classed as oxide-linked, though not without ambiguity. More progress may be made by calculating the ratios T_p/T_m^{oxide} (approx) and T_p/T_m^{metal} (from the data in Table I) and plotting nomograms as in Fig. 1a and b. In Fig. 1a we find a spread of ratios of T_p/T_m^{oxide} from 0.25 to 0.55, which could be interpreted in terms of a mixed population of alloys, those near ratio 0.5 conforming to an oxide-linked mode. In Fig. 1b we find a clear two-fold division between a group of alloys of $T_p/T_m^{\text{metal}} \sim 0.5$ and a second group for which $T_p/T_m^{\text{metal}} \sim 1.0$. The low ratio group includes all the inter-transition metal Laves phases, three of the Al-La intermetallics, Al_8V_5, AlSb, NiSb and U_6Fe. The high ratio group includes ten aluminium-rich Al-V, Al-Mn and Al-Ni compounds, four zinc-rich compounds with Mn, Fe or Co, the three brass phases, InSb and $AlLa_3$. The structures of high ratio are generally of low symmetry (cf. the low ratio group). If the ratios T_p/T_m^{metal} as in Fig. 1b are spread out two-dimensionally with hardness on the abscissa (not illustrated), the low ratio subdivides into (a) the inter-transition metal Laves phases of hardness 1070 to 1400 and (b) the remainder of hardness 440 to 650.

The results may also be discussed in terms of families of compositions. Firstly, in three binary systems, Al-La, Al-V and Al-Ni, all the intermetallic compounds have been tested. In the Al-La system, the Laves phase Al_2La has the highest melting point and the flanking intermetallics have lower melting/decomposition points. The trend of hardnesses (Table I) is roughly the same as that of melting points, which may indicate parallelism between hardness and melting point with heat of formation. The values of T_p for Al_4La, Al_2La and AlLa (and La itself [1]) are consistent with a metal-linked mode of oxidation. For the remaining compound in this system, $AlLa_3$, T_p approaches 1.0 T_m^{metal}. (Two modes of oxidation [1] – the 0.5 × boiling point criterion for the element aluminium, and the empirical relation characterizing room temperature-reactive metals such as lanthanum – appear to be inapplicable in the context of these compounds.) Oxidation in the Al-V system follows a different pattern. For the three compounds richest in aluminium – $Al_{10}V$, Al_7V and Al_6V – T_p is consistent with either an oxide or a non-metal linked mode. The value of T_p for Al_8V_5 is consistent with either metal linked oxidation or failure by loss of pentoxide; T_p for Al_3V is intermediate between that for Al_6V and Al_8V_5. The compounds Al_3Mn, Al_4Mn and Al_6Mn have high T_p/T_m^{metal} ratio as with $Al_{10}V$ etc., and the same is true for Al-Ni compounds, for zinc-rich intermetallics with Mn, Co, Fe, and also for the brass phases. The T_p values for beta and gamma brass could be interpreted as either oxide or non-metal linked, though if the former is true it is difficult to understand why T_p for epsilon brass is not also $\sim$ 800°C. (But see note to Table I concerning weight loss.)

Reference has already been made to the consistent T_p behaviour of the 3*d*/4*d* Laves phases; in contrast, $MgNi_2$ and $MgCu_2$ have values of T_p/T_m^{metal} intermediate between 0.5

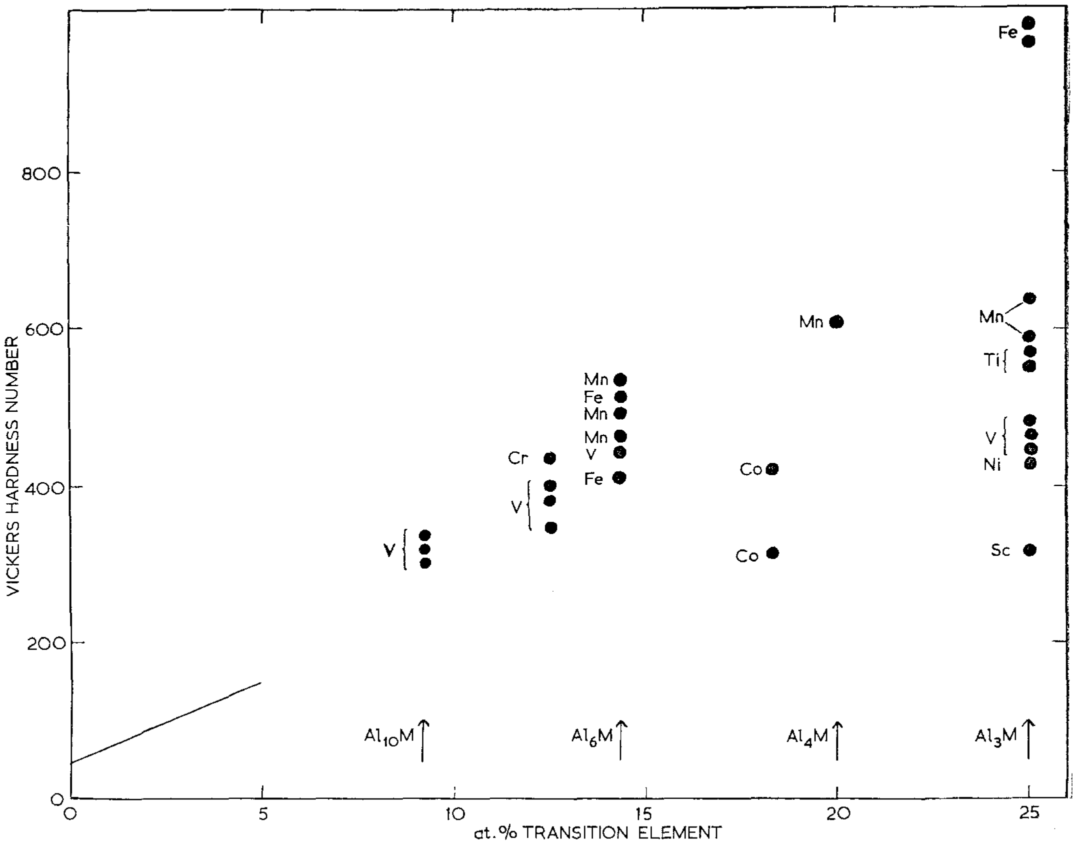

Figure 2 The hardness of aluminium binary compounds as a function of transition metal content. *Notes* The thick line near the origin summarizes results of Babić *et al* [19] on aluminium-base *solid solutions* with vanadium, chromium and manganese; the hardness increase per unit of solute is higher with titanium, iron and cobalt, and for a complete discussion of the relative effects of the transition elements, reference should be made to the original. The zinc-rich intermetallics (Table I) follow the same trend as the aluminium compounds.

and 1.0. It may be significant that the "odd" points in Fig. 1b include intermetallics of metals ($MgNi_2$, $MgCu_2$ and Cu_5Ca) of widely different electronegativities. T_p for uranium monocarbide and U_6Fe is essentially the same as for metallic uranium [5], apparently indicating that their oxidation behaviour is dominated by the presence of the uranium sub-lattice. It is suggested that AlSb and InSb are non-metal linked of the type represented by germanium and antimony in the original scheme [1], but that oxidation is prematurely initiated (i.e. considered in terms of increasing *temperature*) by sublimation of antimony. Silicon carbide is also probably non-metal linked, but with deterioration setting in at the phase field horizontal at 1427°C. Nickel antimonide, a NiAs structure of more metallic type [6] is perhaps metal-linked.

4. The hardness of compounds of aluminium with transition metals

The hardness of aluminium-rich intermetallics, some of which were not included in the Table I survey, has been plotted in Fig. 2. The obvious feature thus shown is an overall tendency for hardness to increase *pro rata* with content of transition element, which is perhaps a little unexpected. Here we have brittle compounds of low symmetry so that *prima facie* $Al_{10}V$ might (to take one example) be expected to be as hard as Al_3V. However, it has been shown [7-9] that the compounds Al_{10} and Al_6V are characterized by the persistence of a basic tetrahedral unit of structure. These strongly bonded Al_3V units arrange themselves to each other in different ways in the two compounds, the remainder of the structure in each case being filled with aluminium of more "metallic" size. It is possible that this behaviour is a general characteristic of the structures of high ratio Al/3*d* compounds, and if so, this would be consistent with a model for hardness variation in which the indenter forces apart an assembly of structure units with variable admixture of a common diluent.

Study of the equilibrium diagrams [10] of the systems Al-Ni, Al-Co → back to Al-Ti shows that the Al-Mn, Al-Cr and Al-V systems are particularly rich in aluminium-rich intermetallics, after which there appears to be a break and the Al-Ti diagram is quite different from the Al-V. Raynor [11] observed that the atomic ratio of the compounds richest in aluminium tends to vary with distance from group IIIB. However, the Al-V system, and particularly the existence of $Al_{10}V$, was not then known, and later the notion of a negative valency operating back from Al/Ga was criticized [12]. One may hazard the suggestion that the non-occurrence of high-aluminium phases in the Al-Ti system is due to an insufficiency of electrons for bonding in any possible scheme with structure units. A conceivable valency scheme for the vanadium linkages in $Al_{10}V$ would require pentavalent vanadium and monovalent aluminium [13]. However, niobium and tantalum do not apparently form high ratio compounds. The elements which form high-ratio aluminium-rich intermetallics (Table II) are those that form oxysalts (K_2MnO_4, for example) in which the transition metal is part of the anion.

TABLE II Atomic ratios of reported intermetallic compounds. x in Al_xM (for x greater than 3 only)

V	*Cr*	*Mn*	*Fe*	*Co*	*Ni*
11					
7	7				
6	5.5	6	6		
	4	4		4.5	
		3.8			
		3.3		3.25	
	Mo	*Tc*	*Ru*	*Rh*	*Pd*
	12	12	12		
	6	6	6		
	5				
	4	4		4	
			3.25	3+	
	W	*Re*	*Os*	*Ir*	*Pt*
	12	12			
	5	6			
	4	4	3.25		4

5. Conclusion

We have seen how hardness data on aluminium compounds are consistent with a model for crystal structure characterized by localized lattice variations from metallic bonding. Also, oxidation tests, although ambiguous in many instances, tend to suggest that some compounds (excluding AlSb, InSb and SiC from consideration) oxidize in the non-metal mode. As a generalization over the results as a whole, it is tentatively proposed that such intermetallics and oxidation behaviour are likely to be found *where one component is near to the limit of the metal elements in the Periodic Table.* For this purpose, elements normally regarded as metals classify as the non-metallic component. For example, AlNi – probably non-metal linked because of the presence of aluminium; $ZrFe_2$ – probably not, because here both elements are much further to the left. A cursory survey of Hansen's original monograph [10] shows that the incidence of the major elements for high ratio phases occurs as shown in Table III. The zone of the Periodic Table in which these elements occur can be characterized in several ways. Hume-Rothery [14] places Zn, Ga, Cd, In, Sn, Hg, Tl and Pb in a separate class intermediate between non-metals and the majority of metals, a class notable for a degree of divergence from the full metallic state (vestiges of 8-N behaviour, incomplete ionization, non-typical crystal structures). The zone is a part of the Table where

TABLE III Elements forming the major component in high-ratio compounds. For compounds X_aY_b, where X is any one of the elements noted below; the figure beneath each symbol is an estimate of the number of systems in which high-ratio phases are found (ratio $a/b = 4/1$ is the border-line).

		Li	Be			
		3	6			
			Mg	Al		
			3	16		
Co	Ni	Cu	Zn	Ga		
2	2	5	11	3		
			Cd	In	Sn	
			5	1	10	
			Hg	Tl	Pb	Bi
			5	0	3	4

ionic and atomic radii are out of step (cf. K → Ca →). Another characteristic is the presence of several amphoteric elements. Further work will be necessary to determine which of these or other considerations is the principal determinant of oxidation mode.

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References

1. H. E. N. STONE, *J. Mater. Sci.* **7** (1972) 1147.
2. *Idem*, *ibid* **8** (1973) 1009.
3. A. D. CAPLIN, G. GRÜNER and J. B. DUNLOP, *Phys. Rev. Letters* **30** (1973) 1138.
4. H. E. N. STONE, *J. Phys. (E)* **4** (1971) 1058.
5. *Idem*, unpublished work.
6. G. V. RAYNOR, Paper 3A, "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds", N. P. L. Symposium No. 9, 1958 (HMSO, London, 1959).
7. P. J. BROWN, *Acta Cryst.* **10** (1957) 133.
8. J. F. SMITH and A. E. RAY, *ibid* **10** (1957) 169.
9. F. LAVES, in "Intermetallic Compounds" (edited by J. H. Westbrook) (Wiley, New York, 1966) p. 129.
10. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) and supplements.
11. G. V. RAYNOR, *Progr. Metal Phys.* **1** (1949) 1.
12. W. HUME-ROTHERY and B. R. COLES, *Adv. Phys.* **3** (1954) 149.
13. P. GROSS, *Discuss. Faraday Soc.* **4** (1948) 206.
14. W. HUME-ROTHERY, R. E. SMALLMAN and C. W. HAWORTH, "The Structure of Metals and Alloys" (The Metals and Metallurgy Trust, London, 1969) p. 47.
15. A. IANDELLI, Paper 3F, "The Physical Chemistry of Metallic Solutions and Intermetallic Compounds", N.P.L. Symposium No. 9, 1958 (HMSO, London, 1959).
16. K. A. GSCHEIDNER JUN, "Rare Earth Alloys" (van Nostrand, Princeton, 1961) p. 103.
17. E. H. HOLLINGSWORTH, G. R. FRANK JUN and R. E. WILLETT, *Trans. Met. Soc. AIME* **224** (1962) 188.
18. N. P. ALLEN and W. E. CARRINGTON, *J. Inst. Metals* **82** (1953) 523.
19. E. BABIĆ, E. GIRT, R. KRSNIK, B. LEONTIĆ, M. OČKO, Z. VUČIĆ and I. ZORIĆ *Phys. Stat. Sol.* (to be published).

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