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The oxidation resistance, hardness and constitution of metallic aluminides

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The majority of the binary intermetallic compounds of aluminium with metals from the First and Third Long Periods and with Mg, Y, Pd, Ag, Th and U have been prepared, hardness tested and oxidized in air at successively higher temperatures. From the oxidation results the temperature corresponding to a weight change of 1 mg cm^{-2} over 4 h was determined by interpolation. The compounds with the highest temperature parameters (over 900° C) are formed with Cr → Cu, Ir → Au and Gd → Dy from the 3d, 5d and 4f transition series respectively, and, for d-transition compounds, at or near the equi-atomic compositions. Hardness is highest (over 800 kg mm^{-2}) for compounds of the same metals except that high values are general amongst 5d compounds. Throughout the Third Long Period, and for Fe, Co and Ni, hardness (and, for rare earth compounds, the temperature parameter also) is most often highest where Al/M is equal to or approximates to 2/1. A brief survey of melting points and structures is presented, in addition to a classification of compounds in terms of the ratio of the temperature parameter to compound or oxide melting points, the use of synoptic diagrams relating incidence of oxidation mode to Al/M ratio and atomic number, and a division of the Periodic Table consonant with the behaviour of these and other compounds. Appendices include hardness data for many unalloyed transition elements, and oxidation and hardness data for the three pseudo-binary systems Al(Ni, Pd), Al_2(La, Gd) and Al_2(Gd, Lu).

1. Introduction and experimental

A previous paper [1] presented data on the oxidation resistance and hardness of a wide selection of binary intermetallic compounds. Some useful generalizations emerged, but it became clear that for the relation between oxidation mode, hardness and constitution to be more systematically demonstrated it would be necessary to simplify the experimental scheme in some manner. Approximately half the compositions tested had been aluminium-containing compounds, notably those of vanadium, nickel and lanthanum, and in the present work the number of these has been greatly extended, to the exclusion of other compounds, so that the majority of the aluminides of the metals of the First and Third Long Periods, together with some other compositions, have been prepared and tested.

Starting materials were high-purity metals as detailed previously [2]. The aluminium used throughout was Johnson Matthey "Specpure" grade. All alloys were prepared in an argon-arc furnace, generally as buttons of surface area 0.2 to 2 cm^2. Weight losses were usually of the order of 0.3%. Compounds rich in aluminium were cast into sticks [3] to facilitate conversion to the desired compound in the subsequent peritectic equilibration. Except where such treatment was necessary, samples were oxidation-tested without further preparation. Testing consisted of heating the sample in air to successively higher temperatures (usually 200, 400, 600° C upwards) for a fixed time of 4 h at each temperature until the temperature corresponding to a weight change (usually a gain) of 1 mg cm^{-2} over 4 h could be interpolated from the results [2]. This temperature is termed T_p. At the end of testing, or after test at 1000° C if T_p was over 1000° C, samples were mounted, metallographically polished, hardness tested, etched and re-examined. Hardness testing was carried out using a Vickers microscope attachment with 50 g load. In the case of the most refractory aluminides, buttons were broken out of their mounts and testing continued as necessary. Within the time scale of this study, it has not been possible to ensure single-phase alloys throughout, but care has been taken to weight all the data referred to in the tables and notes, both against each other and in the context of nearby compounds, when interpreting the results.

2. Results and discussion

Initially we shall survey briefly the data on melting points and structures of the aluminides of the First and Third Long Periods [4, 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 [1, 2].

Surveys of melting point and other properties are facilitated by plotting the compositions of known compounds on a synoptic diagram of the type shown in Fig. 1. For the moment only the points in Figs. 1 to 3 are relevant. In the First Long Period (Fig. 1) a "900°C melting point contour" will take the form of a bulge to the left from the transition metal ordinate, and within this bulge will be included all compounds except a few which are rich in aluminium. A 1350°C contour takes the form of two bulges away from the transition metal ordinate to $\frac{2}{3}$ to $\frac{3}{4}$ the distance to the aluminium ordinate, the two bulges being nearly separated at manganese. Notably high melting points occur for Al_5V_8, CoAl and NiAl. In the 5d transition series (Fig. 3) the 900°C contour is similar, except that for gold only Al_2Au has a melting point exceeding this figure; for the 1350°C contour there is no counterpart to the manganese re-entrant. At the lower atomic number end (Fig. 2) a ridge at the Al_2M composition is continued at approximately 1500°C the whole length of the rare-earth series; the melting points of other rare-earth aluminides

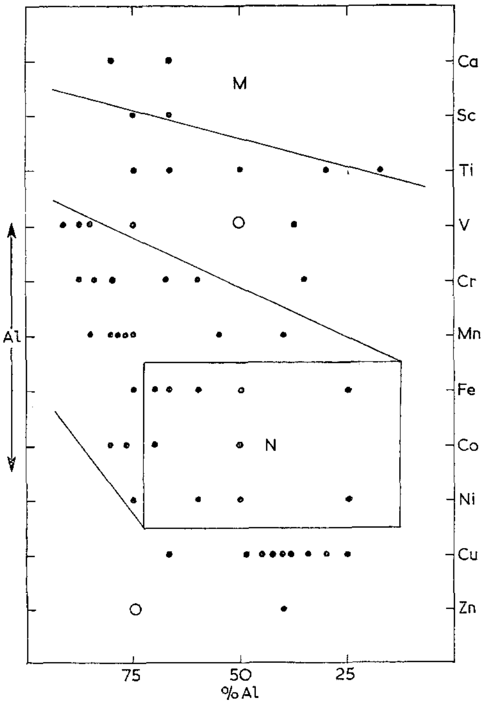

Figure 1 Summary diagram indicating compositions of reported intermetallic compounds in binary systems of aluminium with metals from calcium to zinc inclusive; with a superimposed grid dividing zones of different oxidation mode. The left-hand edge or ordinate stands for aluminium throughout; aluminium content increases from right to left. Each compound is represented by one dot. Zones are marked thus: M = metal-linked oxidation of compounds; O = oxide-linked oxidation of compounds; N = non-metal linked oxidation. The zone above and to the left of the latter is ambiguous between O and N.

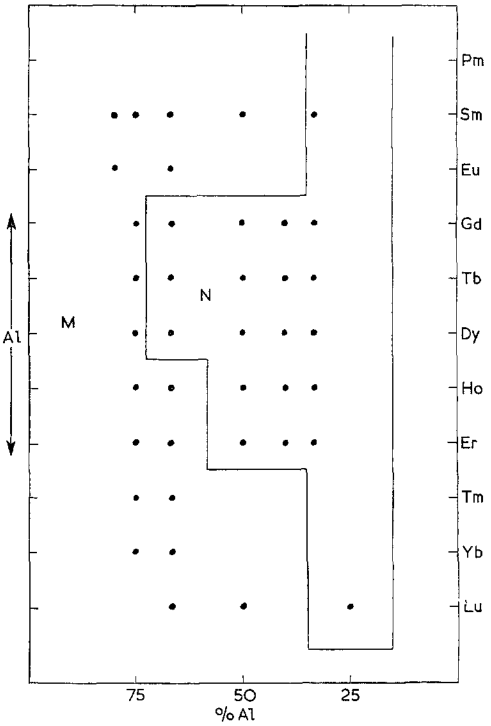

Figure 2 As Fig. 1, for metals from samarium to lutetium inclusive. $AlTb_3$ and $AlEr_3$ are probably metal-linked, but no indications have been made, for the sake of clarity. AlM_3 compounds of nml mode may occur for rare-earth metals of lower atomic number than promethium (see Table II).

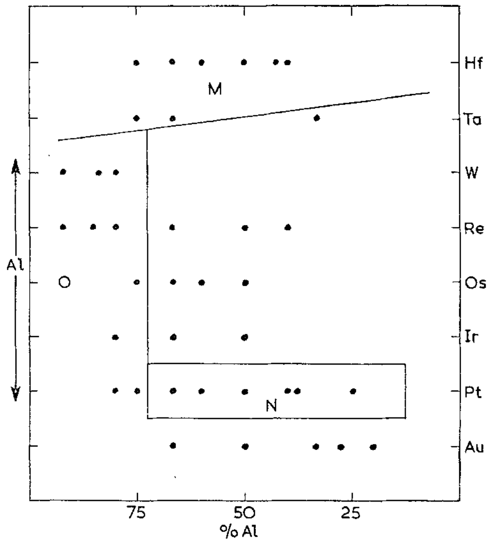

Figure 3 As Fig. 1, for metals from hafnium to gold inclusive. No classification is intended for gold compounds; rhenium, osmium and iridium compounds in the unmarked zone tend to behave like the respective transition metal.

fall away on both the aluminium and rare earth metal sides.

Certain tendencies are apparent in the occurrence of particular structures. The caesium chloride type occurs for AlFe, AlCo and AlNi. Further from the transition metal ordinate (Fig. 1) there are gamma-brass structures with V, Cr, Mn and Cu. The most aluminium-rich compounds from vanadium to nickel have low symmetry. Compounds of Ca, Sc and Ti crystallize generally in structures different from those of V to Cu. In the Third Long Period (Fig. 3) the CsCl structure occurs apparently in AlRe, AlOs and AlIr (but not AlPt); the gamma-brass structure occurs in Al_4Pt and Al_2Au_5, and the calcium fluoride in Al_2Pt and Al_2Au. The compounds $Al_{12}W$ and $Al_{12}Re$ crystallize in a body-centred array of icosahedra [6], whilst the other aluminium-rich compounds of tungsten and rhenium appear analogous to those of vanadium, chromium and manganese. Hafnium compounds parallel those of titanium. The rare earth aluminides [7-10] (Fig. 2) are dominated by the occurrence of a series Al_2M of $MgCu_2$ type from lanthanum to lutetium inclusive. On the Al-rich side it appears that Al_4M (or $Al_{11}M_3$) and Al_3M compounds occur from La to Sm, but that only Al_3M compounds occur at higher atomic numbers. Other features include a series of monoaluminides.

In all the compounds under discussion, marked composition ranges of stability only occur from titanium to zinc (also palladium), being particularly prominent in AlCo and AlNi.

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 Tables I to IV. The overall pattern of oxidation and hardness trends, the aspect which will perhaps be of most interest to the reader interested in practical applications, may be described thus.

The highest T_p values were recorded (a) in the First Long Period, for many compounds of Fe, Co and Ni, in a block centred on AlCo (Table I, Fig. 1), and (b) in the Third Long Period, for most of the platinum and gold compounds (Table III, Fig. 3). Values of T_p decrease away from these zones, with decidedly large falls for the transition metal rich compounds of V, Re and Os. A high level of T_p values, of the order of 800° C, is maintained with the compounds most rich in aluminium, but it should be noted that for many of these, and for many compounds of copper and gold, T_p is in excess of the melting/decomposition point, reminiscent of the behaviour of many B sub-group elements in the original classification [2]. For the rare earth aluminides (Table II, Fig. 2), T_p is most frequently highest for the Al_2M compounds, falling away on the flanking intermetallics, but with superimposed tendencies (a) for T_p for Al_2Gd to Al_2Er inclusive to be higher than other Al_2M compounds, and (b) for AlM_3 as a class to be higher than might be expected from the general level.

With regard to the type of oxidation curve, the Al–3d compounds with few exceptions showed the more usual continued weight gain behaviour (Table I). There was a tendency to a "chromium" variation of curve [2, 11] in many compounds of Cr, Fe, Co and Ni. Amongst the Al–5d compounds (Table III), many compositions with Re, Os, Ir and Pt showed continued losses or losses followed by gains, and such behaviour was also sporadically encountered amongst the rare earth aluminides (Table II).

Hardnesses amongst the Al–3d compounds (Table I) are highest (about 1000 kg mm^{-2}) along the series AlCu–Al_3Ni_2–Al_5Co_2–Al_3Fe–Mn; at lower atomic numbers the maximum hardnesses are lower, and for V, Cr and Mn compounds there is a monotonic fall in hardness for a considerable distance towards that of pure aluminium [1]. In the Third Long Period (Table II, and III) there is (except for Hf) a maximum at the composition Al_2M from La to Ir inclusive, the actual values being about 700 for 4f aluminides (higher from Al_2Gd to Al_2Dy) and about 1100 for 5d compounds. The flanking compounds have concomitant lower hardnesses. In both Periods compounds rich in aluminium have hardnesses of roughly 400. The hardness of the equiatomic compounds of Fe, Co and Ni is noticeably less than that of AlOs, AlIr and AlPt.

As a brief summary, one could say that (a) for 4f aluminides, the hardness, melting points and T_p values move in the same sense, (b) for 3d aluminides, melting points and T_p move together, (c) in the 5d series, hardness and T_p are, to some extent, connected.

Further comment will be centred on the classification of compounds as either (a) oxide-linked – $T_p \sim 0.5\ T_m^{\text{oxide}}$, (b) metal-linked – $T_p \sim 0.5\ T_m^{\text{metal}}$, or (c) non-metal-linked (nml) – $T_p \sim 1.0\ T_m^{\text{metal}}$, and with this in mind, a short list of the most probable oxidation modes for each compound has been suggested in Tables I to IV which in turn becomes the basis for maps of the "most likely" mode zones presented in Figs. 1 to 3.

A not unexpected feature is the boundary line (upper parts of Figs. 1 and 3) between metal- and oxide-linked zones, which may be considered as

TABLE I Some properties of binary aluminium compounds (Sc–Cu)

Compound	T_p (°C)	Type of $T/\Delta w$ curve	Oxidation mode	Hardness (kg mm^{-2})
Sc 3/1	880e	G	o	320
2/1	590	G	m	250
1/3	580	G		450
Ti 3/1	870	G	o	560
1/1	810e	G	o	410
"1/3"	830e	G	o or m	350
V 10/1	790	G	o or n	320
7/1	730	G	o or n	370
6/1	790	G	o or n	440
3/1	570	G	m or o (of V)	460
8/5	550	L	o (of V)	650
Cr 7/1	810	G	o or n	410
4/1	700	G	n	550
8/5	960	G	o or n	880
1/2	1020e	G	o or n	630
Mn 6/1	970	G	o	490
4/1	830	G	o or n	600
3/1	970	G	o or n	620
"1/1"	1000	L	o or n	990
"1/3"	600	G	o (of Mn)	1310
Fe 6/1	850	LG	o or n	410
3/1	1300	G	n or b (of Al)	1000
5/2	1320	G	n or b (of Al)	830
1/1	1360	G	n or b (of Al)	590
1/3	1240	G	n	360
Co 9/2	760	G	o or n	350
5/2	1170	G	n	1000
1/1	1440e	G	n or b (of Al)	680
Ni 3/1	780	G	o or n	430
3/2	1200	G	n	1040
1/1	1400	G	n or b (of Al)	410
1/3	1320	G	n or b (of Al)	460
Cu 2/1	920	G	o	500
"1/1"	970	G	o or n	960
1/3	960	G	o or n	160

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TABLE II Some properties of binary aluminium compounds (Ba–Lu)

Compound	T_P (°C)	Type of $T/\Delta w$ curve	Oxidation mode	Hardness (kg mm^{-2})
Ba 4/1	270	L	m	180
La 4/1	590	G	m	440
2/1	590	G	m	620
1/1	390	G	m	500
1/3	570	G	n	210
Ce 2/1	410	G	m	730
1/1	270e	G	m	440
1/3	280	G	m	300
Pr 2/1	710	LG	m	720
1/1	440e	G	m	470
1/3	390	G	m or n	210
Nd 4/1	560	G	m	510
2/1	630	G	m	720
1/1	400	G	m	420
1/3	390	G	m or n	190
Sm 4/1	590	G	m	370
2/1	550	G	m	690
1/1	440	G	m	510
1/3	440	G	m or n	400
Eu 4/1	730	LG	m	200
2/1	600	G	m	560
Gd 3/1	590	G	m	430
2/1	970	G	n or o	900
1/1	590	G	n or m	550
1/3	500	G	n or m	270
Tb 3/1	470	G	m	420
2/1	980	LG	n or o	910
1/1	540	G	m	570
1/3	410	G	m	290
Dy 2/1	970	L	n or o	890
1/1	760	G	n	750
1/3	750	G	n	330
Ho 2/1	700	LG	n or m	770
1/1	780	G	n	
1/3	750	G	n	320
Er 2/1	720	G	n or m	790
1/1	610	G	n or m	710
1/3	180	L	m	400
Tm 2/1	540	G	m	750
1/1	320	L	m	740
1/3	750e	G	n	340
Yb 3/1	440	LG	m	500
2/1	390	G	m	660
Lu 2/1	630	G	m	850
1/1	530	G	m	710
1/3	670	G	n	360

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an extension of a division of the elements noted previously [2]. The boundary tends to lower atomic number with increasing aluminium content in the 3d series, somewhat in the reverse sense in the 5d series. A notable feature of Fig. 1 is the zone of nml mode which occurs for compounds of Fe, Co and Ni. From this zone, extending predominantly in the direction of the aluminium-rich Al–V compounds (but perhaps also including one or more copper compounds), is a zone ambiguous between nml and oxide-linked (alumina). Of the remaining compounds

TABLE III Some properties of binary aluminium compounds (Hf–Au)

Compound	T_P (°C)	Type of $T/\Delta w$ curve	Oxidation mode	Hardness (kg mm^{-2})
Hf 3/1	770	G	m	510
2/1	670	G	m	670
1/1	710	G	m	980
"2/3"	560	G	m	810
Ta 3/1	760	G	m	600
2/1	630	G	m	1020
1/2	500	G	o (of Ta)	470
W 12/1	780	G	o or n	490
5/1	760	G	o or n	470
4/1	750	G	o or m	440
Re 12/1	900	G	o	390
6/1	780	G	o or n	310
4/1	960	G	o or n	470
2/1	500	L	m or Re	1020
"1/1"	480	L	m or Re	970
Os 3/1	930	LG	o	660
2/1	230	L	Os	1160
1/1	500	L	Os	830
Ir "4/1"	880	LG	o or Ir	610
2/1	820	LG	o or Ir	1430
1/1	960	L	o or Ir	1190
Pt 4/1	960	LG	o	540
3/1	960	LG	o or n	770
2/1	1370	G	n or b (of Al)	760
3/2	1380	G	n or b (of Al)	740
1/1	1200	LG	n	920
2/3	1250	LG	n	640
1/3	1250	LG	n	480
Au 2/1	1300	G		340
1/1	1020e	G		250
1/2	1020e	G		250
2/5	970	G		390
1/4	1250	G		390

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TABLE IV Some properties of binary aluminium compounds (misc.)

Compound	T_P (°C)	Type of $T/\Delta w$ curve	Oxidation mode	Hardness (kg mm^{-2})
Mg "6/1"	510	G	b (of Mg) or n	100
"1/1"	560	G	b (of Mg) or n	150
Y 2/1	590	G	m	720
1/3	500	G	m	390
Pd 3/1	930	LG	o or n	670
3/2	770	G	o or n	630
1/1	720	G		750
1/2	1040	G		680
Ag 1/2	1000	LG		220
1/3	1090	LG		110
Th 2/1	450	G	m	370
1/2	400	G	m	490
U 4/1	510	G		340
3/1	390	G		520
2/1	350	G		700

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Notes to Tables I-IV

1. The incidence of compounds and their probable formulation is, in general, that preferred in Hansen's Monograph and Supplements [4]. In stoichiometric ratios (column 1), aluminium is included in the numerator throughout. Nominal compositions approximate to the quoted ratio. Quotation marks indicate a binary melt of that ratio. In the absence of such marks, heterogeneity may still be present – see the metallographic notes.

2. Possible oxidation modes:
o = oxide-linked (alumina-linked, unless qualified)
m = metal (generally compound)-linked
n = non metal linked
(these, together with T_p, are defined in the text)
b = $T_p \sim 0.05\ T_{\text{boiling point}}^{\text{metal}}$.
Use of chemical symbols (e.g. Re, Os, Ir) on their own indicates behaviour similar to the appropriate pure metal.

3. Type of curve (column 3): G = gain, LG = loss at lower temperatures followed by gain at higher temperatures, etc. For type LG, the T_p values in the second column were estimated from weight gain parts of curves. e = extrapolated value.

4. As previously, single samples only were tested, but subject to a repeat if the first test was rejected as suspect.

5. Etching was often difficult, probably because of either (a) precious metal content, or (b) the complexed nature, in the sense of bonding, of many compounds; however, either the finely ground pre-polished face [16, 17] or polishing relief [18] often gave indications of second phase.

6. Presence of second phase. In the First Long Period, Al_4Cr and Al_8Cr_5, also Al_9Co_2 and AlCu, were grossly duplex ($\frac{1}{3}$ to $\frac{1}{2}$ fraction second phase). Amongst the rare earth aluminides the 1/1 melts were likewise heterogeneous. In the 5d series, Al_6Re, "AlRe" and "AlIr" were seriously duplex, Al_3Ta contained 20% solid solution, and Al_2Au and AuAl each contained 5 to 10% of each other. All other compounds contained 5% or less of other intermetallic or solid solution.

7. Aluminium-rich melts containing tungsten and rhenium were melted to a homogeneous liquid globule by the use of the "sauce" technique, that is, the high melting point metal in the form of thin sheet or powder was melted initially with a small part of the aluminium, after which more aluminium was gradually fed in, etc.

8. All compounds were stable in air for at least several months. (Comment not applicable to Al_3U, Al_2U and AlHo, which oxidized completely during testing.) A composition "$AlBa_3$" was prepared, but this gained 1 mg cm^{-2} in weight in 1 h and was immediately remelted with more aluminium to give Al_4Ba.

9. Samples appeared bright before test, with the following exceptions. Compounds of V to Ni inclusive with Al/M greater than 2/1 were covered with an alumina film; all chromium compounds had an oxide surface film, and the three alloys of copper were borderline. Compounds Al_4M (where M = Ba, Sm or Eu), also Al_3Gd and Al_3Tb, and possibly Al_3Yb and Al_2Yb, had an oxide appearance. Compounds of Ta to Pt inclusive with Al/M greater than 2/1, and possibly AuAl, tended to be covered with an alumina film. Al_2Au had the characteristic purple colour [19].

10. No complete phase diagrams for the Ta, Os, Ir, Sc and some rare earth systems have been reported, and melting points were estimated from homologous systems.

11. Previously determined values of T_p and hardness for some compounds are incorporated in the tables; elsewhere, comment and data are supplementary to that given earlier [1].

12. The experimental scheme of compositions with rare earth metals was centred on the stoichiometries Al_2M, AlM and AlM_3, although some implications of this are at variance with the extensive work of Buschow and van Vucht [8, 9]. The present, limited, evidence is on balance thought to favour the existence of at least some AlM_3 compounds of the heavy rare earths. On the other hand, the heterogeneous nature of the 1/1 melts was probably due to incomplete peritectic reaction. Melts "AlYb" and "$AlYb_3$" were prepared but the buttons contained free ytterbium and results are not reported; consequently, for europium, only Al_4Eu and Al_2Eu were prepared.

13. The Al–Mg system (Table IV) (? an sp system) provides apparently the only example from the Second Short Period of a series of compounds comparable in their close grouping with manganese and copper groups in the First Long Period.

14. The yttrium compounds (Table IV) were included in view of the possibility of an AlM_3 composition of nml mode, such as seems to occur with rare earth compounds (Fig. 3). On the whole, the evidence on AlY_3 is against this.

15. The composition "$AlAg_3$" was quickly cooled from 750° C and checked as single-phase prior to test.

16. Classification of oxidation mode for compounds of Pd, Ag and Au is difficult, though there is no mistaking the high values of T_p encountered.

17. The low value of T_p for Al_2U (? and also elemental terbium – Appendix 1) is possibly linked to an effect of acidic oxide, in spite of the weight gain recorded. This, and the low value of T_p for uranium, indicates that the boundary between tungsten and rhenium in the original classification [2] has moved back one group if one classifies uranium as a group VI element.

in the unambiguously oxide-linked zone, Al_3Sc, Al_3Ti and AlTi are probably oxide-linked (alumina).

The metal-linked zone of Figs. 2 and 3 may be regarded as firm, but the remaining features in the Third Long Period are more difficult to classify than those in the First Long Period. The difficulties are (a) the perplexing results for gold compounds (also palladium and silver – Table IV) for which no classification is offered, (b) the low T_p values of some rhenium and osmium compounds (Table III, Fig. 3), presumably from a tendency to behave like the respective 5d metal, and (c) the fact that although a nml zone is drawn (Fig. 2) for rare earth compounds, the actual values of T_p/T_m^{metal} on which this is based are of the order of 0.7 – much lower than for Fe, Co, Ni and Pt. Uncertainty in particular exists for the AlM_3 part of the nml zone in Fig. 2, partly because of the incidence of intermediate ratios of T_p/T_m^{metal}, partly also to some doubt regarding the composition of compounds [7-10]. However, the rare earth elements which form more than one possible nml compound each (Table II) are Gd, Dy and Ho, which in conjunction with the classification of most Fe, Co and Ni aluminides as nml in Fig. 1, seems significant, suggesting that the vagueness of the nml zone in Fig. 2 is in some manner analogous to magnetic coupling in rare earth metals through conduction electrons. In contrast, the fact that $AlLa_3$, and probably $AlLu_3$ are also apparently nml mode would suggest that the behaviour of these is linked to sp interactions.

Some further elucidation arises from a study of the overall pattern of incidence of the d-transition compounds (Figs. 1 and 3) with reference to three customary parameters, namely, electronegativity, size and size ratios, and electron/atom ratio. Lines of equal electronegativity (Table V) [12] show a marked similarity to the pattern of oxidation classification of the elements [2]. We note in Table V that maxima in electronegativity occur in the vicinity of Os–Au and Ru–Pd, and there is a lesser maximum, corresponding to these, in the First Long Period; the incidence pattern of aluminides of these metals, which shows a perceptible bulge towards the aluminium ordinate (Figs. 1 and 3 – the tip of the bulge corresponds to Al_9Co_2 and Al_4Ir respectively), may be symptomatic of a dominant electronegativity effect. (The incidence of compounds in the Second Long Period is similar to that in the Third Long Period, Hf–Au.) Lines of constant parameter, in similar fashion, of (a) atomic size, and (b) electron/atom ratio, would also bulge towards the aluminium ordinate, but based more broadly at the transition metal ordinate (for example, instead of $\left(\begin{matrix}\text{Mn}\\\text{Cu}\end{matrix}\right.$ we would have $\left(\begin{matrix}\text{Ca}\\ \\\text{Zn}\end{matrix}\right)$, and indeed some such tendency is apparent (Figs. 1 and 3). A simple tabulation (Table VI) of the metals whose atomic radius is less than that of aluminium shows good correspondence with the incidence of compounds of high Al/M ratio at the low atomic number end (the high end would presumably be subject to some other limitation); however, a similar exercise for compounds of zinc, which

TABLE V Lines of equal electronegativity (after Pauling/Hume-Rothery [12])

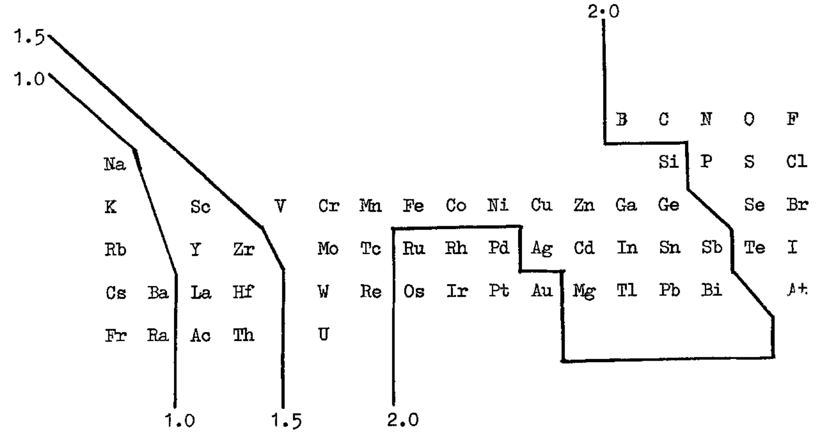


TABLE VI Metals having atomic radii less than that of aluminium

No high ratio compounds (Al/M greater than 4/1) are known to be formed by elements to the left of V, Mo and W. Nb and Ta are borderline cases.

V	Cr	Mn	Fe	Co	Ni	Cu →
Nb	Mo	Tc	Ru	Rh	Pd	
Ta	W	Re	Os	Ir	Pt	

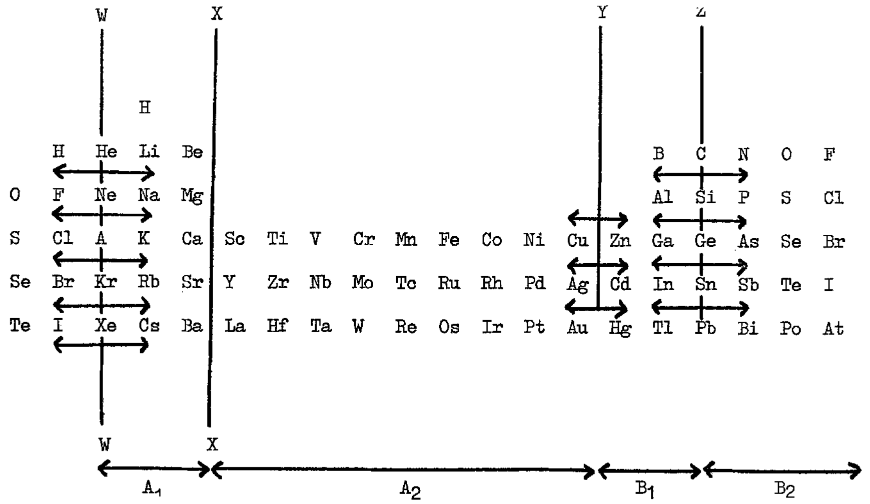
forms analogous compounds, reveals poor agreement, so that the role of a crude size limitation factor remains in doubt.

Further interpretation is necessarily speculative. Perhaps it would be most appropriate if we attempt to give a hypothesis with some regard to the simple basic mechanisms of chemical combination, as follows.

Just as one may write the formulae of the beta, gamma and epsilon phases in the well-known copper-zinc system as CuZn, $\mathrm{4CuZn.CuZn_4}$ and $\mathrm{CuZn_4}$, so one may formulate compounds in the Al–Ni system as NiAl, $\mathrm{3NiAl.NiAl_3}$ and $\mathrm{NiAl_3}$, and for the Al–Fe system, FeAl, $\mathrm{2FeAl.FeAl_3}$, $\mathrm{FeAl.3FeAl_3}$ and $\mathrm{FeAl_3}$. The phase $\mathrm{Co_2Al_5}$ may be formulated using a hypothetical $\mathrm{CoAl_3}$, but the remaining two compounds in the cobalt system have ratios of Al/Co greater than three and obviously the procedure cannot be extended from 1/1 beyond 3/1 Al/Co. However, the compound $\mathrm{MnAl_6}$, an example of a high-ratio compound, may be written through an extension of this procedure as $\mathrm{Al_2^{I}/Al_2^{III}\ Al_2Mn^{II}}$), with the aluminium before the bar as donor, and this formulation may correspond to bond lengths in the structure [5]. Evidently the extended procedure may not be able to represent all compounds of ratio greater than 3/1, as is shown by the structure of $\mathrm{Al_{10}V}$ which contains part of the aluminium in a clathrate-type environment [13]. Also, the seemingly anomalous hardness of $\mathrm{Al_{12}W}$ and $\mathrm{Al_{12}Re}$ (Table III, cf. $\mathrm{Al_5W}$ and $\mathrm{Al_6Re}$) may be due to completely different (that is, non-ionic) bonding in their bcc/icosahedral structure [6] from that suggested for $\mathrm{MnAl_6}$. It appears that the procedure may not be extended beyond vanadium, the structures of scandium and titanium compounds following different laws.

The above procedure implies an ionic relation between, for example, nickel and aluminium in NiAl, presumably with aluminium as the donor and the "hole in the d-band" as receptor, and if this be accepted one may note this formally in the Periodic Table by indicating a divide (Y in Table VII) analogous in some measure to the vertical line WW through the noble gases. Line Y is also in agreement with the general alloying behaviour of neighbouring elements – witness the formation of compounds of Cu forward with Zn, Ga etc, but not back (Fe, Co, Ni ←), and the converse behaviour of zinc. Lines WW and Z represent the established divides across which strong ionic salts and compounds of adamantine structure respectively occur. An additional line XX has been inserted (and retained from Wells [14]) which, although not a divide, appears to delimit (with Y) the zone within which both

TABLE VII The Periodic Table: a scheme for the classification of binary compounds



			H																
	H	He	Li	Be											B	C	N	O	F
O	F	Ne	Na	Mg											Al	Si	P	S	Cl
S	Cl	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Te	I	Xe	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At

components of the metal-linked intertransition metal phases previously discussed [1] may be located. (In the terminology of Table VII the latter would be termed A_2A_2 phases.)

However, it must be stressed that it is the positions of the constituent elements with respect to the appropriate divide which is thought to be significant with regard to the incidence of nml oxidation mode. The arrows in Table VII which broaden the divides are schematic indications only, and it is likely that the effective zones on the sides of the divides, between which any two elements will give nml compounds, will vary between Periods. The width of the broadening may probably be ascertained by study of the relevant equilibrium diagrams supplemented by experiment, though clearly, to take the present example, aluminium in its compounds gives nml behaviour back to iron or further in the First Long Period, but only to platinum in the Third Long Period. Gallium is of interest in this connection because it is nml in both GaNi (T_p 1200°C, hardness 430) and GaAs (T_p 900°C, hardness 670) [15], i.e. in compounds across Y (A_2B_1) and Z (a B_1B_2 compound) respectively. As indicated above, one would, on the basis of existing results, expect examples of metal- or oxide-linked, but not nml mode, where both components are distant from a divide and/or are from the same zone in Table VII. However, the complete population of intermetallic compounds will probably contain a higher proportion of non-metal-linked type than exists among the pure elements as a body.

Appendix 1. Values of T_p for some elements

Eu	Tb	Ho	Tm	Lu
360	210	560	390	580
Th	U			
410	170			

Metallic purity 3N (Koch-Light Laboratories Ltd).

Appendix 2. Vickers hardness of some metallic elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
130	120	160	140	1400	130	250	120	60	44
		Nb	Mo	Tc	Ru	Rh	Pd	Ag	
		130	220	—	460	240	64	48	
		Ta	W	Re	Os	Ir	Pt	Au	
		200	490	320	720	360	74	59	

Also:

Al	La	Gd	Th	U
30	52	120	98	320

Notes:

The hardness of a Mn–25% Cu alloy (stabilized gamma-Mn?) was 140 [15].

Except for Al and Zn (cast and annealed), all samples were arc-melted, button size as in main work. In each case, the flat underside of the button was mechanically polished for test; load not more than 200 g. Hardness figures are consistently higher than in published data [20, 21]; however, a limited number of retests on a standard Vickers hardness machine (load 1 kg) gave results generally agreeing with the above. The above hardnesses provide a background of reference for the evaluation of the data on the aluminides. To the more general question of the hardness of the elements and their compounds in relation to the Periodic Classification, a few comments may be offered, based on fragmentary evidence [1, 15]. The hardness of Group IV elements and 3:5 compounds across the divide Z (Table VII) is most frequently high. The scratch hardness of ionic salts occurring as minerals is given as $2/2\frac{1}{2}$ on Moh's scale [22], which may be equated with 50 to 80 on the (Vickers) indentation scale [23], and the writer has obtained 30 as the Vickers hardness of fused common salt; from this one concludes that such salts are typically soft. The hardness of the aluminides is more akin to that of the Group IV elements and compounds, but the comparative softness of AlM (where M is Fe, Co or Ni) as compared with the equiatomic compounds with metals from the same Groups in the Third Long Period, is consistent with a more ionic character for AlNi etc – with a common donor (aluminium), one would expect such for the bond with the smaller "anion", by Fajan's rule.

Appendix 3. Melting point relations [5]

If, on the appropriate equilibrium diagram, one draws a straight line between the melting points of aluminium and the transition metal, the height of the compound melting/decomposition point above this line would possibly be a measure of the ionic character; an alternative would be a simple comparison of the transition metal melting point and the melting point (°C) of a prominent compound on the diagram, as follows:

Ni 1453 AlNi 1638 difference + 185
Pd 1558 AlPd 1645 difference + 87
Pt 1773 AlPt 1554 difference − 219 .

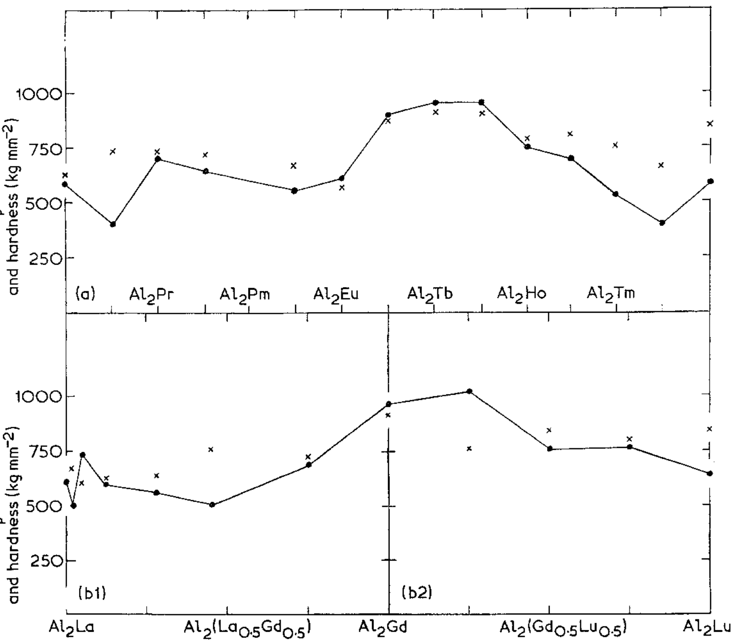


Figure 4 Oxidation and hardness of Al_2(rare-earth) compositions. (a) values of T_p and hardness for compounds Al_2M (where M is any rare-earth metal). (b) values of T_p and hardness for compositions in the pseudo-binary systems $Al_2(La \rightarrow Gd)$ (plotted in b1) and $Al_2(Gd \rightarrow Lu)$ (b2). ● = T_p (°C), × = Vickers hardness number (kg mm^{-2}).

TABLE VIII Some properties of Al(Pd, Ni) compounds

Compound	T_p (°C)	Hardness (kg mm^{-2})
AlPd	720	750
$Al(Pd_{0.88}Ni_{0.12})$	1200	420
$Al(Pd_{0.50}Ni_{0.50})$	1320	520
AlNi	1400	410

Note: weight gain type of $T/\Delta w$ curve throughout, with tendency to the "chromium" variation.

Appendix 4. Oxidation and hardness in some ternary systems

The systems studied were (a) Al(Ni, Pd), (b) Al_2(La, Gd), and (c) Al_2(Gd, Lu). The results on the first-mentioned are given in Table VIII, and are notable for a marked contra-movement of T_p versus hardness values (i.e. increase of T_p with decrease of hardness) as palladium in the AlPd structure is replaced by nickel. Results on (b) and (c) are presented graphically in Fig. 4b in adjacent fashion, so as to facilitate comparison with Fig. 4a, in which are plotted results from Table II on the properties of the separate Al_2M compounds (where M is a rare-earth metal). Comparison of Fig. 4a and b reveals a general similarity in the trend of T_p values, but with discrepancies at high and low "atomic number". In particular, the effect of replacement of lanthanum by gadolinium in Al_2(La, Gd) (Fig. 4b1) is greater than when Al_2La is "replaced" by Al_2Pr – i.e., a subsidiary maximum occurs at Al_2Pr (2/7 or 29% of the way from Al_2La to Al_2Gd) in Fig. 4a, but at 5% replacement with gadolinium in Al_2La (see Fig. 4b1). The variation of T_p with atomic number in Fig. 4a shows resemblance to the variation of magnetic moment of ions from La^{3+} to Lu^{3+} [24].

In Fig. 4a, T_p values and hardness vary together (cf. Al(Ni, Pd)), the only marked discrepancy occurring with Al_2Ce. In Fig. 4b1 and b2, hardness to a first approximation varies linearly from 620 for Al_2La to 850 for Al_2Lu, with no correlation to the T_p trend; closer inspection reveals cyclic contra-movement of the two parameters over limited composition ranges, for example ↻ near $Al_2(La_{0.5}Gd_{0.5})$, which may or may not be fortuitous. Some electron-spin resonance measurements on Al_2(La, Gd) alloys have been presented and discussed [25].

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