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Oxidation resistance and relative stability of some inter-4f alloys

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Ten samarium-structure alloys have been oxidation tested in air to estimate the thermal oxidation parameter, T_p, and hence the ratio T_p/T_{Sm}, where T_{Sm} is the temperature of decomposition of the appropriate structure and the ratio is a measure of the strength and type of bonding. The ratio decreases with (a) increasing distance apart in the 4f series of the components, and (b) increasing average Group number.

1. Introduction

This is an interesting little tale, long in preamble but not in discussion, because the paucity of the results does not allow it.

Characteristic compounds and patterns of compounds are formed across divides [1] in the Periodic Table, i.e. if we take components near to but on opposite sides of a divide, we expect, and usually find, similarities of crystal structure types. If we now consider the corresponding strength of bonding, as measured by T_p/T_m, the ratio of the thermal oxidation parameter, T_p, to the melting point T_m, we find structure systematics running in parallel with high T_p/T_m across the ionic, covalent and composite divides. Extensive studies across the composite divide have shown ratios approximating to unity, indicative of a high degree of non-metal type bonding, and results across the other two divides, though sparse, are in agreement. The incidence of high T_p/T_m (i.e. of high effect) and the persistence of crystal structure types extend about two elements to either side of a divide [2]. This is only a rough rule; at one extreme we find that zinc forms high-effect compounds across the composite divide passing back to vanadium, while at the other we know that KCl, a trans-ionic divide compound, is very stable, but that K_2S has a sulphide smell. Nevertheless, it is a useful one. The situation is more complicated across the transition metal divide, in that high effect is found only amongst compounds formed by components well out on the flanks, such as titanium with copper, and yttrium with cobalt [1], and there appears to be no obvious correlation with crystal structure. Now there is yet another divide in the Periodic Table, occurring in the 4f series, and placed either through samarium or near it. The ionic and covalent divides run (vertically) in the (long) Periodic Table through Groups O and IVB, respectively; the positions of the composite and transition metal divides are expressed by a division of the Period of 18 elements by golden section. Similarly, a division of the 14 4f elements by golden ratio would place the divide at an average Group number (AGN) of 8.4, counting lanthanum as 3 and samarium as 8, in good agreement with existing methods of dividing the 4f series [3–5]. The 4f divide may only be operative where both components are rare-earth elements. Certainly only one structure is formed between a light (La to Nd) and a heavy rare-earth element, that is the samarium structure, the type of the element samarium [6–10]. Because of this circumstance, the situation at the 4f divide is, in principle, diagnostically far simpler than at the other divides. The plan suggested itself, of making samples of samarium structures, the components of which would be of varying distances from the 4f divide, and correlating the effect ratio with the distance from that divide. By this means it was hoped to find out under well-controlled conditions, if the ratio and, therefore, the type of stability, falls with increasing distance from the divide or vice versa. However, there are diagnostic complications in other respects, mostly concerned with insufficient phase diagram data for inter-4f systems, so that much transformation/melting point data which are essential for this type of study had to be estimated by analogy. The elements promethium, europium and ytterbium were not admissible for other reasons. In passing, it appears to be not known yet if rare-earths beyond erbium can be components in samarium structures. Also, an La–Er alloy of samarium structure composition transforms to bcc not far below the melting point, in contrast to the element erbium.

2. Experimental procedure

Single samples of approximately samarium structure composition (Table I) were made by arc melting from 99.9% purity stock. The buttons were about 6 mm diameter; melting losses were in the range 0%–2%. All were non-magnetic at room temperature. They were subjected in the as-cast state to the well-known procedure [1] for extracting T_p, the thermal oxidation parameter (the temperature for a weight change, herein a gain in all cases, of 1 mg/cm^2/4 h). To convert this to the dimensionless parameter of type T_p/T_x on

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TABLE I Compositions, weight uptake/temperature and derived data for some inter-4f alloys. Phase diagram data are from [14]

Composition (at %)	Weight uptake mg/cm^2/4 h				T_p/T_{Sm}[b]	T_p (°C)	T_{Sm} (°C)[c]	Samarium structure[d]	Samarium count	AGN
	200 °C	400 °C	500 °C	600 °C						
Sm100[a]	0	0	–	5.2	0.82	550	734		0	8
LaGd70	0.06	0.75	0.84	1.5	0.74	550	840	65 72 80	7	7.9
LaEr50	0	0.42	0.74	1.7	0.67	550	950		11	8.5
CeGd75	0	0.76	1.0		0.78	500	720	66 71 74	6	8.5
CeEr50	0	0.06	72		0.55	380	920	40 ? 50	10	9.0
PrGd60	0.13	1.4			0.67	370	770		5	8.0
PrEr40	0	2.8			0.56	380	890		9	8.6
NdGd50	0	0.65	1.6		0.74	450	700	44 50 56	4	8.0
NdDy45	0	0.60	3.2		0.63	440	860	34 42 51	6	8.7
NdEr40	0	0.45	1.2		0.65	490	900	37 41 45	8	9.2

[a] From Reference 13 and unpublished work at that time.
[b] T_p/T_{Sm} is the ratio of the absolute temperatures.
[c] T_{Sm} is the temperature limit of stability of the samarium structure.
[d] The composition of highest decomposition (centre figure), and the limits of the samarium structure single-phase fields where known.

which the discussion is based, it was necessary for four of the compositions to estimate T_{Sm}, the decomposition temperature of the appropriate samarium structure. This was done by plotting, in a preliminary exercise, the change points for melting, bcc transformation, samarium structure decomposition and T_p, on the same graph against samarium count on the abscissa. Not only was this a means of estimating unknown T_{Sm} values, it was also an aid in avoiding conclusions based solely on comparison using T_p/T_{Sm}. T_m and T_{bcc} temperatures were taken to be the means of the "solidus" and "liquidus" temperatures, respectively. The samarium count represents the "distance" of the alloy from the 4f divide, e.g. an alloy of neodymium and gadolimium has a count of 4, because neodymium and gadolinium are each two elements away from samarium. Because another variable exists in that the samples were not all scaled uniformly, relative to their respective samarium structure phase fields, the whole graphical exercise was repeated with the same essential temperatures plotted against the average Group numbers of the experimental alloys. These plots are not reproduced, but a description of them is given.

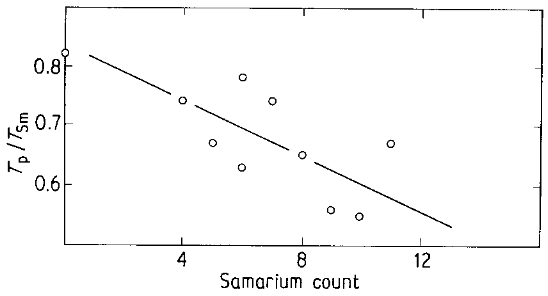

Figure 1 Effect ratio (T_p/T_{Sm}) versus samarium count.

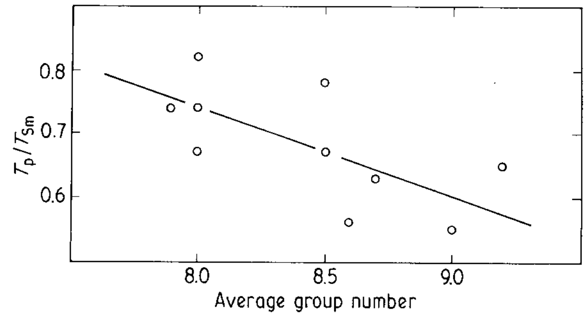

Figure 2 Effect versus average Group number.

3. Results and discussion

Temperatures T_m, T_{bcc} and T_{Sm} increase with samarium count; the best straight line for T_{Sm} passed through 950 at samarium count 11 and 800 at 4, and this was used to estimate unknown values of T_{Sm} for Table I. There was much scatter in T_p versus samarium count, although a horizontal straight line is conceivable. Slopes upward were apparent when T_p, T_{bcc} and T_{Sm} were plotted against AGN; T_m versus AGN was nearly flat. T_m and T_{bcc} would converge to an AGN of approximately 11 (corresponding to terbium). T_p falls with increasing AGN, a straight line relationship being credible. The ratio T_{bcc}/T_m was of the order of 0.9, a value typical for the light rare-earth elements. T_{Sm}/T_m was about 0.75, which is higher than for normal superlattices [11].

The heart of the matter is illustrated in Figs 1 and 2, in which effect is plotted against samarium count and AGN, respectively. In both cases it does not seem unrealistic to draw straight lines. From Fig. 1 we note that the higher the samarium count, the lower the effect becomes. Taking T_p/T_{Sm} as a measure of the strength of bonding, we infer a quite high degree of non-metal type in the element samarium, but with a decrease to metallic type with structures whose components come from near the ends of the 4f series. It is interesting that the straight line, if extrapolated, would reach 0.5, typical of metallic bonding, at an AGN of approximately 14, that of a (hypothetical) compound of lanthanum and lutetium. From Fig. 2 we note an approximately straight line relationship between effect and AGN. Here the limits of all samarium structure phase fields reported for our compounds are 7.6 and 9.6, approximately the span of the abscissa as illustrated. At AGN 7.6 we have a high effect, as is found in elemental samarium, and at 9.6 (extrapolated) the effect would fall to 0.5, so there appears to be a dependence on stoichiometry. Such dependence would appear to be analogous to that found in some brass compositions [12], where maximum effect occurs at the low atomic number end of the beta-phase field, consistent with resonance/attenuation in the sense zinc → copper (here, heavy into light rare-earth). The points in the two figures, if labelled, will be found to be not of the same order, but neither are they random one to the other. It would be rash to assert dogmatically that there is no tautology in the presentation of Figs 1 and 2. However, overall it seems that we have truly uncovered two interesting facets in the science of the lanthanide series. We are also in a better position to answer the question: samarium structure – is it a stacking variation or a compound?

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