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The oxidation resistance and constitution of Y_9Co_7 and nearly-related compounds

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The ratio of the thermal oxidation parameter to the decomposition point (T_p/T_m) is of the order of 0.85 for Y_9Co_7, indicating a high degree of chemical binding. The persistence of high values of this ratio has been investigated with respect to (a) other compounds in the Y–Co system, (b) replacement of cobalt in Y_9Co_7 by other d-elements, and (c) replacement of yttrium by other rare-earth elements. High ratios are found for (a) Y–Co compounds where Y/Co > 0.5, (b) Y–3d compounds with cobalt and nickel only, and (c) RE–Co compounds generally. However, there are differences in level of the ratio amongst the rare-earth compounds, from which it is inferred that the highest values coincide with full electron shells, that is, without participation of 4f electrons. Additional work is described on an effect of preparation arc-melting current on the T_p value for Y_9Co_7, and on compounds of the same pattern where both components are changed.

1. Introduction

In recent years much interest has been shown in the physics of the intermetallic phase Y_9Co_7, since it would seem [1] that it may be, depending on the temperature, either superconducting or magnetic in some sense. Extensions to our overall knowledge of the material are possible using other means. The author has presented evidence [2] on the probable valencies of the components in this phase, using a diagnostic method based simply on the systematics of incidence of compounds. Another approach related to the latter is to retain the systematic Periodic Table background, but to bring experiments to bear, as has been done in this paper, in such a way as to yield a parameter from which the degree of chemical reactivity and its variation with composition may be assessed. Because the method and argument concerning the parameter are fundamental to the appreciation of the work, it is convenient to begin with a description of the oxidation test employed rather than with alloy preparation.

2. Oxidation test

The method of testing involved heating single as-cast samples in air to successively higher temperatures (constant time of 4 h at each temperature) until the temperature corresponding to a weight change (in this work a gain) of $1\,\mathrm{mg\,cm^{-2}}$ per 4 h could be interpolated [3]. This temperature is termed T_p. It has been shown [4] that, for oxidation of typical metallic structures, T_p is of the order of $0.5\,T_m$ (where T_m is the appropriate melting point on the Kelvin scale), but that for certain classes of compounds where stronger bonding has been inferred (nml or non-metal linked), T_p approximates to or approaches T_m. Prior to this work, a $0.5\,T_m$ relation appeared to be the norm for compounds between transition metal components, and so it was only when it was found that T_p for Y_9Co_7 was significantly in excess of $0.5\,T_m$ that the ploy of using the oxidation test as an experimental probe in the transition metal context suggested itself. (For brevity, the incidence of values of T_p/T_m greater than $0.5\,T_m$ will be referred to as the effect.) From this point the method of procedure was to change in turn the components on the yttrium and cobalt sites. However, before we could do this it was necessary to standardize the melting procedure, since it had been found empirically that the properties of Y_9Co_7 were more than usually affected by such details.

2.1. Effect of melting current

This is not the place for a dissertation on argon-arc practice, but some background is necessary. In the most general terms, and depending on the alloy under preparation, repeated meltings at arc currents of 60 to 125 amps are necessary for small samples weighing not more than two grammes such as are employed herein. A median sequence, between turnings-over of the sample button, of 60/80/100/125 (nominal d.c. amps at the generator) is often sufficient to ensure as good a homogeneity as can be achieved, since longer arc exposures are not necessarily beneficial, in view of possible selective volatilization. In the case of Y_9Co_7, it was found that rather more exposure to amperages above 100 was necessary in order to avoid the presence of spurious ferromagnetism. The details of the mechanism are obscure, but the ferromagnetism is certainly not due to gross cobalt in the casting. It had become the practice to use extra meltings of (4 × 150) or (6 × 125) amps in order to avoid this intrusion, though in retrospect this appears to represent overkill for the present purpose, as will become evident from experiments in which Y_9Co_7 was melted under different conditions.

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TABLE I Summary of oxidation tests on Y_9Co_7

Sample	Aggregate amps used in melting	T_p	T_p/T_m
A	360	610	0.88
B	490	700	0.97
C	960	570	0.84
D	1600	480	0.75

Sample A was magnetic to a pocket magnet; samples B, C and D were non-magnetic when hung on a chemical balance and tested with a much larger permanent magnet.

The results are presented in Table I from which it will be noted that variation of the parameter exists, T_m rising to a maximum with increased current, then falling. However, if we consider the ratios of these different 9/7 samples as a whole, it is equally clear that they are all much higher than is described by a 0.5 T_m relationship. We therefore conclude that, whilst the effect of melting practice is important, all samples show the effect in quite high degree, and we feel able to go forward confidently to investigate the effect of compositional variations. Henceforth the degree of arc exposure aimed at was the B regime of Table I, though there are in practice many occasions when it overshoots towards C, due to pecularities of the particular melt.

Since a metastable phase Y_3CO_2 is known to be present in as-cast Y_9Co_7, a second portion of sample D was tested after heat-treatment *in vacuo* for 6 days at 500° C. The T_p value was 490, that is, the difference is of the same order as the test accuracy. Elsewhere, only the reactivity of cerium was felt to impose the refinement of a heat treatment ($CeCo_2$, Table V, sub-eutectic → sub-peritectic soakings).

In the tables of results, the incidence of compounds is in general that preferred in Hansen's Monograph and Supplements [6]. Sources for the Y–Co system are [1, 7]. The relevant systems are for the most part cascades of peritectics. Designation is by melt composition. The use of normal compound nomenclature is dictated by convenience; nevertheless, the work was based conceptually on the existence of compounds.

Rare-earth metals were from Rare Earth Products Ltd (Widnes, Cheshire) 3N purity(yttrium 4N), the 3d metals were Johnson Matthey (Royston, Hertfordshire) Specpure grade (5N), and the precious metals 3N. Melts of weight 0.2 to 2 g were cast [8, 9] into the form of sticks of 2.3 mm diameter, giving surface areas of 0.2 to 2 cm^2. Identity of overall composition was ensured by a weight check after melting. Losses were in the range 0 to 1.5%, often about 0.2%. No surface preparation was given before oxidation testing.

The reader of previous papers in this series may well ask why only the reduced temperature with reference to T_m^{metal} has been chosen in the argument, and query the relevance of the other ratio T_p/T_m^{oxide}. The text of [10] is still relevant. There is no interpretative correspondence between 0.5 T_m^{oxide} and the T_p values in the present tables, be the oxide reference point that of Y_3Co_2 or any other oxide of a component. Barometer-charts of the type used in the earlier paper illustrate this clearly.

TABLE II Summary of oxidation tests on yttrium–cobalt compounds

Composition	T_p (° C)	T_m	T_p/T_m
Y_3Co	480	880p	0.65
Y_8Co_5	570	740p	0.82
Y_9Co_7	700	725pd	0.97
YCo	540	802p	0.76
Y_2Co_3	590	860p	0.76
YCo_2	380	1150p	0.46
YCo_5	450	1352p	0.44

p, Peritectic formation; c, congruent; pd, peritectoidal.

2.2. Effect of yttrium/cobalt ratio

In the first set of experiments with compositional variations (Table II), yttrium and cobalt are retained as the components but the atomic ratio is varied. The results show that several compounds, not only Y_9Co_7, show the effect markedly, but that it only exists for compositions richer in yttrium than YCo_2. The maximum value is given by Y_9Co_7 itself. The value of 0.65 for the phase richest in yttrium (i.e. Y_3Co), is rather lower, but it is felt that it too represents an approach to nml character, be it only partial.

2.3. Effect of d-transition metal

In a second set of experiments, yttrium was retained as the rare-earth metal, but the 3d component varied (Table III). In planning this, the point was kept in mind that, whilst the maximum in the yttrium–cobalt system occurs at 9/7 (44 at % d-transition metal), the effect, if it occurs in analogous systems, could well be subject to a drift of relevant average Group number. When we consider the results, we find that there is indeed a strong effect (0.73) for Y_3Ni, which, in conjunction with 0.67 for Y_3Ni_2, may be construed as suitable evidence. However, apart from these instances, there is no strong evidence for the effect in other than cobalt-containing compositions. A few tests were run on Y–4d compositions (foot of Table III). There is no indication of an effect here, though admittedly

TABLE III Summary of oxidation tests on yttrium-containing compounds

Composition	T_p (° C)	T_m	T_p/T_m
YMn_2	460	1102c	0.53
YFe_2	470	1125p	0.53
YCo_2	380	1150p	0.46
Y_3Ni	580	898p	0.73
Y_3Ni_2	470	835p	0.67
YNi	500	1065c	0.59
YNi_2	590	1115p	0.62
YCu	470	935c	0.59
YCu_2	430	935c	0.57
YRu	340	–	(0.48)
YRh	480	–	(0.53)
YPd	460	–	(0.51)
YAg	310	1160c	0.41

The melting points of YRu, YRh and YPd were assumed to be the same as YAg. These are ScCo, as YCo; CeCo as $CeCo_2$.
p, Peritectic formation; c, congruent.
YMn_2 and YFe_2 were magnetic to a pocket magnet.

TABLE IV Summary of oxidation tests on cobalt-containing compounds

Composition	T_p (° C)	T_m	T_p/T_m
ScCo	570	–	(0.78)
YCo	540	802p	0.76
LaCo	440	–	(0.68)
CeCo	170	–	(0.34)
PrCo	370	–	(0.59)
NdCo	480	–	(0.69)
SmCo	440	–	(0.63)
GdCo	580	880p	0.74
TbCo	500	–	(0.66)
DyCo	560	930	0.69
HoCo	500	–	(0.65)
ErCo	580	940p	0.70
TmCo	560	–	(0.68)
LuCo	720	–	(0.79)
HfCo	690	1480c	0.55

In addition to the method of estimating the melting points of equiatomic (RE)Co compositions referred to in the text, other approximations were used where necessary and are marked by parentheses. These are: ScCo, as YCo; CeCo, as $CeCo_2$.
p, Peritectic formation; c, congruent.
GdCo was magnetic to a pocket magnet.

TABLE V Summary of oxidation tests on miscellaneous compounds

Composition	T_p (° C)	T_m	T_p/T_m
YCo_2	380	1150p	0.46
$CeCo_2$	170	1035p	0.34
$CeCo_2$ (ht)	360	1035p	0.48
$GdCo_2$	360	1060p	0.47
$TaCo_2$	670	1593p	0.51
Sc_3Fe	680	–	(0.83)
Y_3Co	480	880p	0.65
Ce_3Co	170	480c	0.59
Gd_3Co	400	780p	0.64
Y_3Ni	580	898p	0.73
Gd_3Ni	570	775p	0.80

The melting point of Sc_3Fe was assumed to be the same as that of Y_3Co. p, Peritectic formation; c, congruent. Compounds Sc_3Fe, $GdFe_3$ and $GdCo_2$ were magnetic to a pocket magnet.

inference is made difficult by assumptions on melting points.

2.4. Effects of rare-earth component

In the third stage the procedure was to retain cobalt but change the rare-earth element. Here a simplification with regard to composition was made. We know from Table II that the position of maximum effect in the yttrium–cobalt system occurs at the atomic ratio 9/7. However, in view of inadequacies in our knowledge of all the possible phase relationships, it was decided to standardize on the equiatomic ratio, instead of the 44 at % of Y_9Co_7. The penalty in departing from the peak in the Y–Co system is not too great, and there is perhaps an advantage, for work with as-cast samples, in moving away from the position of the rare-earth rich eutectic. Further, results were calculated on the assumption that unknown melting/decomposition points fell on a straight line given by notional points of CeCo = 800° C, HfCo = 1000° C.

The results are given in Table IV. Note firstly the saw tooth type of variation of the *absolute* values of T_p for the heavy rare-earth equiatomic compounds, which recalls similar behaviour in other properties of these heavies, that is, their thermal oxidation behaviour [3, 4] and their price. In interpreting results by our method of reduced temperature ratios, the reference point for high effect is the 0.76 of YCo in Table II, and our basis level either a formalized 0.5 or the 0.46 of YCo_2. There are three features worthy of comment in Table IV. These are the high effects in ScCo and LuCo, the nil effects in CeCo and HfCo, and the intermediate levels found with the other compositions. A simple interpretation is to assume that the first named is a full-shell effect which works through a higher degree of order in the chemical bonding. A figure of 0.68 for LaCo,though somewhat low, is not completely inconsistent in this regard. Following this argument, the intermediate effect will be due to a partial breakdown of such bonding because of the intervention of the 4-f electrons, and the nil effect to completion of this process. In particular, the nil effect for CeCo is thus due to tetravalency on the cerium, which brings the latter into the same effective Group as hafnium. Low values of effect in compounds with elements from Groups IVA and VA were found some time ago [5], and the sharp drop in effect from LuCo to HfCo is particularly convincing.

2.5. Other compositions

Table V presents some data from samples which do not fit into the series of the other tables. Note (a) that the Gd–3d results show a similar pattern to the Y–3d of Table II (but compare the hypothesis of the last section), and (b) that there is quite a tendency for A_3B compositions to show some degree of effect. Amongst the latter, the effect in Ce_3Co, though modest, indicates superiority in oxidation resistance to heat-treated $CeCo_2$; Ce_3Co is stable at room temperature (c.f. metallic cerium).

3. Conclusion

The chief results from the work are two-fold. On the one hand, the effect is found predominantly with cobalt as the 3d component. At the same time, within the Y–Co system, the incidence of the effect is by no means so restricted, a fact which may be consistent with the presence of a common structural unit. Secondly, we have the finding, in contrast, that the rare-earth component may be changed in general without the effect completely disappearing. Some interesting differences in the level of effect between rare-earth elements pose interesting questions. It may well be that they have a bearing on the subtle physical properties for which Y_9Co_7 has become well known. Finally, the finding of high values of effect amongst inter-transition metal compounds has not until now been substantiated. In investigations in previous years [4, 5] they were the only set of compounds formed directly across a divide which did not show high effect. The present work suggests, after all, that, given the right combination of elements, nml mode is possible, thus giving consistency to the application of the Periodic Table.

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References

1. A. K. GROVER, B. R. COLES, B. V. B. SARKISSIAN and H. E. N. STONE, *J. Less-Common Metals* **86** (1982) 29.
2. H. E. N. STONE, *J. Mater. Sci. Lett.* **4** (1985) 799.
3. *Idem, J. Mater. Sci.* **7** (1972) 1147.
4. *Idem, ibid.* **10** (1975) 923.
5. *Idem, ibid.* **12** (1977) 1416.
6. M. HANSON 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).
7. A. E. RAY, *Cobalt* **1** (1974) 14.
8. H. E. N. STONE, *J. Physics (E)* **4** (1971) 1058.
9. *Idem, Metallurgia and Metal Forming* **44** (1977) 105.
10. *Idem, J. Mater. Sci.* **9** (1974) 607.

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