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Some properties of intertransition metal compounds

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The hardness and oxidation resistance of twenty-three binary intertransition metal compositions have been estimated. Eleven of these contained titanium, and the majority of the remainder were preparations of σ phases from the First and Third Long Periods. Hardnesses ranged from 380 to 2100 kg mm^{-2}, and the values for the temperature parameter T_p (the temperature for a weight increase of 1 mg cm^{-2} over 4 h) from 360 to 750° C. The two properties are discussed in the context of the melting points of the compounds and their component elements. Attention is also given not only to the variation of these parameters within a long period, but to the similarities and differences between long periods, and the contrast between *d*-transition metal and B sub-group behaviour. Some cursory hardness–composition traverses for several intertransition metal binary systems are also presented, and these suggest the presence of compounds V_3Fe and Cr_3Fe, possibly of β-tungsten type.

1. Introduction and experimental

When the incidence of binary compounds whose components are both transition metals is considered, it becomes evident that the pattern of alloying of Group IVA metals with later elements in the same Period differs greatly from that of either Group VA or VIA metals with later elements. The first mentioned pattern is characterized by the formation of compounds of small range of stoichiometry occurring at fixed atomic ratios, for example $TiCo_2$, and the second includes compounds of wide range of composition, whose average composition is related to their position in the Periodic Table. The fixed ratio compounds (including those existing in systems whose marked characteristic is the presence of variable phases such as σ) may be interpreted as covalent structures consistent with an uncomplicated valency system, and the prime motivation for what follows arose because the method of oxidation testing developed by the author [1–5] provides in principle a means of testing this hypothesis. Results are also reported on σ phases, which were selected as representive of the other pattern. Both patterns are consistent with an interpretation of combination as necessarily occurring between elements to the left and right respectively of a transition metal divide (Table I), but variable composition phases tend to occur preferentially where components are near the divide (e.g. σ Fe–Cr), whereas fixed ratio phases more generally result from combination between elements further from the divide. Discussion of the results is conducted with reference to this divide and to the average group numbers, hardnesses and melting points of compounds and their component elements. In addition, trends in the B series of the Periodic Table are compared with those in the transition series. A concluding section describes hardness surveys on some inter-First Long Period systems.

Alloy buttons were prepared by argon arc melting and tested for oxidation resistance and hardness using materials and methods already described [4].

TABLE I A Division of part of the Periodic Table

← A_1 →			← A_2 elements →					← B_1 →			← B_2 →
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
		transition metal divide					composite divide			covalent divide	

Their compositions are indicated in Table II, column 1. More than half the number were inter-First Long Period compositions, the rest being principally from the Third Long Period. With two exceptions, the preparation of cross-Long Period compounds was eschewed (cf [3]), the intention being to try to emphasise any possible differences between Periods. Of the five groups of compounds listed in Table II, two were of Laves phases (extended in one group to include $TiNi_3$ and "$TiCu_3$"), two of σ phase preparations, and the remaining group was of the TiM CsCl/bcc phases.

TABLE II Some properties of intertransition metal compounds

Compound	Melting Point* (° C)	T_p (° C)	Hardness (kg mm^{-2})
$TiCr_2$	1350	740	980
$TiMn_2$	1325	550	1000
$TiFe_2$	1427	660	1050
$TiCo_2$	1250	750	950
$TiNi_3$	1378	730	670
$TiCu_3$	885	660	580
TiMn	1175	680	1050
TiFe	1317	680	690
TiCo	1300	720	540
TiNi	1240	740	380
TiCu	980	670	510
MnV20	1050	360	910
FeV50	1200	370	470
CoV50	1240	410	960
NiV60	1220	410	1050
ZrW_2	2150	370	830
$ZrRe_2$	2450	380	1500
HfW_2	2650	360	1900
$HfRe_2$	3160	360	2000
TaRe70	2770	370	2100
WRe70	3000	360	2100
WOs35	2800		1700
WIr25	2540		1400

* or decomposition point

2. Results and discussion

The pattern of incidence of different structures has been discussed elsewhere [6]. Results for the principal parameters investigated are given in Table II, and supplementary data and matter, with an explanation of the oxidation parameter T_p, are included in the notes appended to the table. We begin by discussing the hardnesses. For the first group in Table II, Laves phases in the First Long Period, hardness is at a maximum for $TiFe_2$. If the compositions of these TiM_2 are weighted according to Group Number (counting Ti as 4, Fe, Co and Ni as 8, 9 and 10 respectively), it will be found that $TiFe_2$ may be expressed as $6\frac{2}{3}$, which may be identified with the position of the transition metal divide (between Groups VIA and hardness decreases progressively from TiMn (except for TiCu) with increasing Group Number. The data on zirconium- and hafnium-containing Laves phases are too fragmentary to detect trends, though it may be noted that the general level of hardnesses, ignoring ZrW_2 (see notes, Table II), is higher than that of $TiMn_2$ just as the hardnesses of the *elements* of the Third Long Period are greater than those of the First Long Period excepting manganese [4, 7], and the same may be said of the levels of hardness of the groups of σ phases (i.e. TaRe70 etc. versus MnV20 etc.). The average Group Number (or e/a ratio) of these intertransition metal phases tends to a typical value (cf. the Laves phases) and thus the values for the σ phases of Table II range only from 6.4 to 7.0, but note that the divide position as deduced from these values is again near $6\frac{2}{3}$.

Notes to Table II

Hardness was by microindentation at 50 g load.

(1) The incidence of compounds is based on data in Hansen's Monograph and Supplements [13]. Compounds (column 1) are described in one of two ways. In the case of the σ preparations. Mn V20 indicates (for example) a content of 20 at. % of vanadium; other preparations are described by chemical formulae.

(2) To determine the oxidation parameter T_p, the sample, usually in the form of a small button, is subjected to successive heatings in air at 200, 400° C etc., upwards, for a fixed period of 4 h at each temperature, until a weight change of 1 mg mm^{-2} can be interpolated from the results. Single samples only were tested. All the weight increment/temperature curves showed continuing weight increases $TiCr_2$ and TiMn had an "oxide" type of surface finish as-cast, the remainder were more obviously metallic. FeV was magnetic, but the remainder were not.

(3) The preparations $TiCu_3$, FeV50 and WOs35 had obviously two-phase structures. Minor amounts of second phase were probably present in $TiCr_2$, $TiCo_2$, HfW_2 and WIr25. The low hardness figure for ZrW_2 presumably indicates second phase, but etching attempts to show this were not successful. Some specimens as-polished had an appearance (outline of bright needles against dark backgound porosity) which may be described as martensite pattern; these were $TiMn_2$, MnV20, CoV50, $ZrRe_2$, HfW_2 and $HfRe_2$, and, to a lesser extent, TiMn, NiV60 and WRe50.

(4) The values of T_p/T_m (where T_m is the melting temperature) for compounds from the First Long Period are somewhat greater than 0.5 for the Laves phases, somewhat less for the σ phases.

(5) The two Ti–Cu compositions have quite high ratios of T_p/T_m, which may perhaps be explained in terms of a vestigal effect of the composite divide [9], and the Ti–Cu alloys may well repay further study.

With regard to melting points (Table II), the compound $TiFe_2$ has the highest value for TiM_2 Laves phases. The variation of this property has the same trend as for TiM_2 hardnesses, and is to be contrasted with the changes in the melting points of the elements of the Long Periods, with their characteristic "break in the property" [8] at Group VIIA, a break which is especially marked at manganese in the First Long Period. Incidentally, whilst inter-Third Long Period Laves phases have higher melting/decomposition points than First Long Period counterparts, there appears to be a general tendency for these to occur as peritectic rather than congruent compounds.

It is interesting at this point to make a brief comparison with the hardness and melting points of elements and compounds near the covalent divide (Table I). The hardness of some B Group elements and compounds are presented in Table III. The hardness of the *d*-transition metals has been recorded elsewhere [4, 7], but it may be said that the transition elements with maximum hardness in their Periods are Mn–Ru (or Tc?)–Os–Np, whereas the corresponding series for B sub-Group elements is B (or diamond)–Si–Ge–Te (Table III). The hardness of GaAs is in fair agreement with that for Ge, and that of $TiFe_2$ with α manganese, so that in one sense GaAs is a counterpart to $TiFe_2$. Agreement for InSb and CdTe appears to be poorer, though this involves the difficulty of comparison with a value extrapolated from Si–Ge–? for grey tin. The B Group elements of maximum melting point in their respective Periods are C–Si–Sb–Pb, that is, not very different from the corresponding maximum hardness series. Around the covalent divide, melting points and hardnesses increase towards the centre of the B Groups and towards the top of the Periodic Table; around the transition metal divide these properties increase generally towards the middle of the transition series and towards the bottom of the Table.

TABLE III The hardness of some elements and compounds

Be	B	C				
270	3700	36				
Mg	Al	Si				
54	30	850				
Zn	Ga	Ge	As	Se	GaAs	
44	14	550	170	110	670	
Cd	In	Sn	Sb	Te	InSb	CdTe
21	< 3	6.9	74	87	210	270
Hg	Tl	Pb	Bi			
	5.5	5.5	12			

Notes to Table III

The hardness of lithium is less than 3 kg mm^{-2}. Frozen mercury is obviously soft and this is confirmed [7]. The hardness of diamond is variously quoted as 8,500 or 10,000 [7, 14]. Loads in the range 5 to 200 g were used as necessary. Indentation serious encountered by the author, and for these elements selected impressions were used.

Turning now to consideration of T_p values, we find firstly that the compounds of the Second and Third Long Periods (Table II) oxidise at quite low temperatures in relation to their melting points. One may tentatively suppose that gross oxidation is initiated by attack on the more oxidizable components tungsten and rhenium [4], which form volatile acid oxides. In view of the weight gains reported, however (Table II, cf. [1]), oxidation would then probably have to continue with weight increase presumably on the titanium component. In the case of the First Long Period compounds, it is difficult to classify these unambiguously in terms of any one 0.5 T_p oxidation mode [1], simply because of similarities in the values of the relevant melting points. Probably they are metal-linked, that is, the counterpart of the $T/\Delta w$ curve is the thermal characteristic of the *substrate* lattice, though this question is not central to the conclusion which now follows. What is clear from the First Long Period T_p values (Table II) is that the compounds are *not* non-metal linked. The significance of this finding as regards the Laves phases becomes apparent in relation to the proposition, stated in the introduction, that if we have covalent binding, we should, by analogy with compounds formed "across the covalent divide" (Table III and [3]), except the non-metal linked (that is, $T_p \sim 1 \times T_m$) type of oxidation behaviour. It would therefore appear that the term covalent is inadmissable in the present context. However, there remains a possibility that non-metallic behaviour will be most evident in the compounds at atomic ratios consistent with the electron requirements of homo- and hetero-polar bonds. The hypothetical condition is self-evident in the case of the Laves phases where the necessary atomic ratio would be two, but because in practice any nominal composition such as those reported on in Table II will deviate slightly from actual, due to impurity contents and preparation losses, it follows that any critical examination of the possibility would require close examination of selected systems across a range of B/A ratios. This problem is one for future investigation, and indeed it was this interpretation of the experimental situation on which the decision was based to limit the number of preparations in the present programme to those in Table II. Meanwhile, the exigencies of low temperature investigations have provided data on a related compound, the cubic Laves phase UCo_2. An account of the physical property results from these investigations is given elsewhere [10]. In brief, it may be said that a maximum (cusp point) occurs in a plot of residual resistivity (at liquid helium temperatures) versus U/Co at a critical nominal ratio near 2, and this point has counterparts in casting and electromechanical polishing tests, though there appears to be no singularity in hardness variations, nor does the "critical" compound display other than metal-linked oxidation behaviour [11]. In a general way we may perhaps say that low temperatures favour a more chemically bound structure, and that high temperature oxidation testing by its very nature would be unlikely to give indications for the more metallic combinations of elements. This subject appears to be of much interest, and further work is desirable.

3. Hardness and constitution in some inter-3d systems

This section records the results of some tests on intertransition metal systems which were carried out some four years before those described in the main body of this paper. The work was initiated when a maximum in hardness was found at the 25%-Fe composition in a series of V–Fe alloys, and was continued to include other systems, with the results given below.

Buttons weighing ~ 1 g were prepared in an argon arc furnace from high purity metals; these were then mounted without further treatment, and hardness tested (200 g load) near the surface that had been adjacent to the copper hearth. Most of the results are plotted in Fig. 1 which shows hardness/composition traverses for three binary systems. In addition, data for the system Co–V were:

Cobalt %	0	25	50	75	100
Hardness kg mm^{-2}	190	440	1080	490	250

and there is also a maximum (1340 kg mm^{-2}) at 75% manganese in the Cr–Mn system.

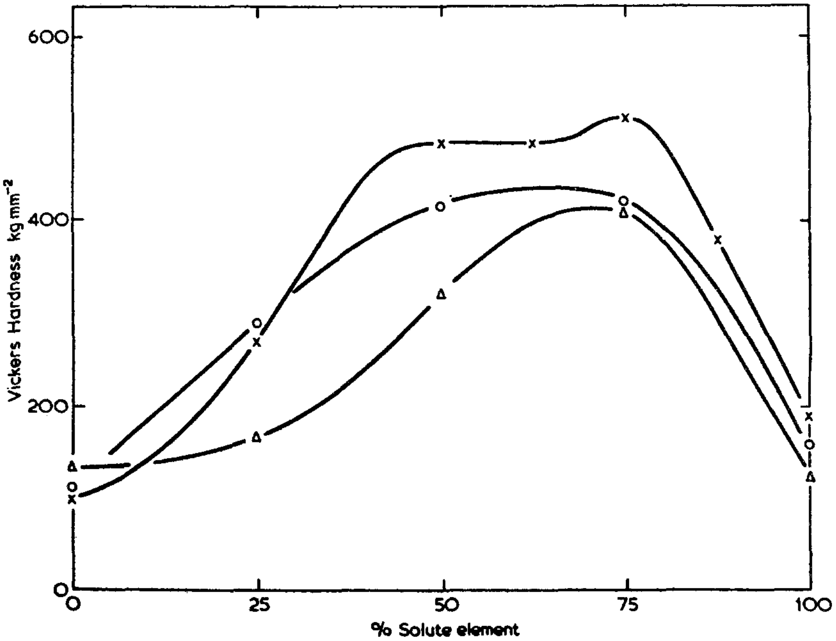

Figure 1 Hardness versus composition for some intertransition metal systems: × = alloys of V in Fe; ○ = alloys of V in Cr; △ = alloys of Cr in Fe. Compositions in wt % in this section of the paper. Load 100 g for V–Fe; 200 for V–Cr, Cr–Fe and Co–V. The specimens used for the chromium-containing systems were subsequently oxidation tested as described in [2]. The data for Cr–Fe are in good agreement with those reported and collected by Sully and Brandes [15]. For phenomena near "Cr_3Fe" see also [13] and [16].

Hardness at any composition will be derived in part from solid solution stiffening, but with modifications perhaps more usually positive, due to the incidence of intermetallic compounds. For an uncomplicated solid solution, the hardness/composition curve will probably be dome-shaped, with no point of inflexion. In Fig. 1 there is evidence of departures from such a curve for alloys of V–Fe (25 and 50%Fe) and Cr–fe (25%Fe). A high maximum is found in Co–V, but the V–Cr curve may be construed as simple. From a survey of possible types of structure [12] it would appear most likely that the evidence for V/Fe 50/50 and Co/V 50/50, as for Cr/Mn 25/75, is indicative of the presence of σ phase. In the iron-chromium systems the formation of σ has probably been inhibited because of its low temperature of formation and the rate of cooling from the melt. Such incidence of σ phase is not surprising; of more interest is the evidence of maxima at the compositions V–25%Fe and Cr–25%Fe (any possible maximum at V–25%Co would obviously be obscured by the hardness ascribed to σ). In these cases, further study of the possibilities of incidence of structures [6, 12] suggests that the maxima are perhaps the effect of previously unreported compounds V_3Fe and Cr_3Fe, examples of the Cr_3Si (β-tungsten) structure. Such structures are known in analogous systems nearby which contain both fixed ratio and variable composition phases.

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