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Proposed selection rules for suitable binders in cemented hard metals with possible applications for improving ductility in intermetallics

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The results of a selective study of the literature on transition metal binder–hard metals and the parameters that determine the choice of suitable binders are reported. Thermodynamic and kinetic considerations have played a major role in the selection of suitable binders, with the electron theory of metals playing a minor role. It was deduced from the study that the electronic configuration of metals could be a major controlling factor in the thermo-kinetic reactions that take place during sintering in hard metal systems. A set of rules for binder metal selection is proposed based on this study. A modification of these rules would seem partly to explain ductilities currently obtained in certain intermetallics. The application of these rules would point to suitable binder metal(s) selection possibilities that are currently unexplored and predict alloy selection that could improve the ductility of brittle intermetallics.

1. Introduction

The term "hard metals" is generally used to classify a group of high-hardness and high melting point substances, which exhibit a metallic character based on their thermal and electrical conductivities, high strength at elevated temperatures and chemical stability at room temperature. A classification based on their chemical composition would imply that they are inorganic non-metallic compounds, whereas transmission electron microscopy studies show that they are deformed at appropriate temperatures by the same mechanisms as in metals, i.e. by dislocation mechanisms. Typical representatives of these materials would be the refractory carbides, borides, nitrides and silicides of transition elements of Periods IV, V and VI of the Periodic table of elements. The most popular and widely used of these compounds are the cemented carbides.

The cemented carbides were developed in the laboratories of Osram in Germany by Schröter [1, 2] and first produced commercially by Fried Krupp in 1927. The original and still the most important cemented carbide consists of tungsten carbide and cobalt, with a structure of tungsten carbide grains embedded in a cobalt matrix. Cemented carbides combine very high hardness and wear resistance of their carbide phase with sufficient mechanical and thermal shock resistance provided by the metallic binder phase to make them useful for many applications involving large mechanical and thermal stresses. Additions of other carbides, such as TiC and TaC, to the base WC–Co system has provided a range of hard metals with extensive applications. The unpredictable situation of the world supply of cobalt has led to research attempts directed at other carbides such as TiC, which do not require a cobalt metal binder. It is known that during the sintering of tungsten carbide and cobalt powders [2], a liquid phase is formed by the reaction between the tungsten carbide and cobalt. This paper focuses on this kind of reaction and how it affects the choice of suitable binders for hard metal systems.

2. Structure of hard metals

Hägg [3] suggested that the principal factor determining the structure of the interstitial phases formed by reaction of the transition elements of Periods IV, V and VI of the Periodic table with carbon, boron, nitrogen, silicon and hydrogen was the relative sizes of metal and metalloid atoms. Hägg predicted that if the ratio of the radii of metalloid to metal atoms was less than 0.59, the metal atoms would be arranged in a simple close-packed structure. This suggestion was confirmed by several workers [4–6] with the experimental results of Ehrlich [4] indicating that TiB_2 has a C32 type structure with $a = 0.302$ nm, $c = 0.321$ nm and $c/a = 1.06$ nm. Norton *et al.* [6] also showed experimentally that the borides of titanium, zirconium, vanadium, cadmium and tantalum corresponding to the formula MeB_2 (Me = metal atom) have isomorphous crystal structures with the metal atoms arranged in a simple hexagonal lattice having an axial ratio greater than unity.

Further experimental studies by Norton and

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Mowry [6] on the carbides of titanium, zirconium, vanadium, cadmium and tantalum showed that the monocarbides of these elements are isomorphous and have a sodium chloride type structure. Similar results were found for the other interstitial phases of transition elements. Whenever the radius ratio exceeded the critical value of 0.59, the structure was found to be complicated. Hägg concluded that the critical radius ratio $r = 0.59$, can be interpreted as an indication of the maximum expansion which can be tolerated in the lattice. This was based on the observations that for radius ratio values greater than 0.59, metal atoms are in contact with the non-metal atoms rather than with each other.

3. Theories on the electronic structure of transition metals and their compounds

The Engel–Brewer (EB) rules attempt to correlate a very large number of phases existing in metals and alloys with their electronic configurations and to predict the existence of phases for which experimental data were not available [7]. The initial work of Engel [8] in the period 1939–1949 was subsequently clarified and expanded by Brewer [9–17]. The essential feature of the EB rules predict that equilibrium crystal structures depend on the total number of unpaired (S + P) electrons, with the crystal structures and numbers of unpaired (S + P) electrons as shown in Table I. An extension of these rules to include transition metals and binary systems gave non-integer values of the number of electrons per atom as shown in Table II. These ranges are in agreement with the Hume-Rothery rules [19]. Engel [8] proposed that all the unpaired d-electrons in transition elements take part in metallic bonding, by assuming that the empty d-orbitals of one element provide a sink for the excess electrons from another alloying element and thus contribute to bonding.

Transition metal elements are characterized by the overlap of their outer s-orbital with the inner d-orbital leading to a broadening of the overlapping bands. A review carried out by Schwartz and Neckel [20] summarized that all the three main types of bonding operate in refractory transition metal compounds, namely:

(i) metallic contributions with a finite density of states at the Fermi energy, E_f;

(ii) ionic bonding caused by a charge transfer from metal to non-metal atom;

(iii) covalent bonds with particularly strong interactions between non-metal (p) and metal (d) valence states.

TABLE I Engel–Brewer rules for different crystal structures

	Structure	Number of electrons per atom
1.	bcc	One electron
2.	cph	Two electrons
3.	fcc	Three electrons
4.	Diamond structure	Four electrons

TABLE II Engel–Brewer rules for transition metals and binary systems

	Structure	Number of electrons per atom
1.	bcc	1.0–1.5
2.	cph	1.7–2.1
3.	fcc	2.5–3.0

Pauling [21–25], based on considerations from structural chemistry, suggested that for the series potassium, calcium, scandium, titanium, vanadium, chromium, the metallic valence rises from 1 to 5.78 and remains at 5.78 for manganese, iron, cobalt and nickel but begins to fall with copper. These numbers represent the number of orbitals which are actually used for the formation of shared electron pairs. Pauling concluded that because only one s and three p orbitals are available, the bond numbers deduced from observed atomic diameters demand the participation in bond formation of at least some of the five d-orbital electrons. Ishizawa and Tanaka [26] determined the Fermi surface of transition metal carbides and borides by the de Haas-Van Alpen (dHVA) effect technique. Their studies were conducted on TiB_2 and WC at low temperatures. They calculated an electron concentration of carriers of 0.023 per unit cell for TiB_2. This low concentration of carriers is characteristic of a semi-metal, which agreed with an earlier report, from calculations on ZrB_2, with the same AlB_2 structure as TiB_2, conducted by Tanaka *et al.* [27]. Ishizawa and Tanaka defined WC to be semi-metallic with an electron concentration of 0.01 per unit cell. The conduction band and valence band in these compounds were found to overlap slightly.

Xu and Freeman [28] very recently studied band filling and structural stability of the transition metal trialuminides YAl_3, $ZrAl_3$ and $NbAl_3$ using a total energy local-density approach. The variation of structural stability with transition-metal constituent was explained in terms of band filling of the bonding states in the rigid sense, with valence electrons gradually filling the bonding states on going from YAl_3, $ZrAl_3$ to $NbAl_3$. This led to a phase transition from the cubic $L1_2$ structure (for YAl_3). It was suggested that this criterion may also explain the variation of the structural stability of other transition-metal compounds, like transition-metal carbides, nitrides, silicides, etc., that are dominated by covalent interactions between the transition-metal d and metalloid p states.

3.1. Observations

3.1.1. Hard metals

The theoretical analyses and experimental observations indicate that the unfilled inner d-shell of transition metals of Periods IV, V and VI (Fig. 1) of the Periodic table are involved in both bonding and chemical reactions in these metals. However, their high melting points necessitate powder metallurgy methods of fabrication of components and the use of suitable sintering additives. These additives also act as binders to activate the sintering process, usually

4	21 Sc $4s^2$ $3d^1$	22 Ti $4s^2$ $3d^2$	23 V $4s^2$ $3d^3$	24 Cr $4s^1$ $3d^5$	25 Mn $4s^2$ $3d^5$	26 Fe $4s^2$ $3d^6$	27 Co $4s^2$ $3d^7$	28 Ni $4s^2$ $3d^8$	29 Cu $4s^1$ $3d^{10}$	30 Zn $4s^2$ $3d^{10}$
5	39 Y $5s^2$ $4d^1$	40 Zr $5s^2$ $4d^2$	41 Nb $5s^1$ $4d^4$	42 Mo $5s^1$ $4d^5$	43 Tc $5s^2$ $4d^5$	44 Ru $5s^1$ $4d^7$	45 Rh $5s^1$ $4d^8$	46 Pd $5s^0$ $4d^{10}$	47 Ag $5s^1$ $4d^{10}$	48 Cd $5s^2$ $4d^{10}$
6	71 Lu $6s^2$ $5d^1$ $4f^{14}$	72 Hf $6s^2$ $5d^2$ $4f^{14}$	73 Ta $6s^2$ $5d^3$ $4f^{14}$	74 W $6s^2$ $5d^4$ $4f^{14}$	75 Re $6s^2$ $5d^5$ $4f^{14}$	76 Os $6s^2$ $5d^6$ $4f^{14}$	77 Ir $6s^2$ $5d^7$ $4f^{14}$	78 Pt $6s^1$ $5d^9$ $4f^{14}$	79 Au $6s^1$ $5d^{10}$ $4f^{14}$	80 Hg $6s^2$ $5d^{10}$ $4f^{14}$

Figure 1 Transition metals of Groups III–VIII with elements of Groups IB and IIB.

resulting in the formation of a liquid phase, i.e. liquid-phase sintering, which reduces the sintering temperature to an industrially feasible value. For an adequate bond to exist between the activator and transition metal or transition metal compound, the following requirements are important:

1. chemical reaction at the interface between transition metal/compound and the sintering activator, with a sufficient solubility of transition metal compound in the activator to promote wetting;
2. interdiffusion in both systems;
3. surface keying;
4. a favourable thermal expansion relationship between both systems on cooling.

It is likely that the inner d-shell configuration of a transition metal plays an important role in the selection of a suitable sintering activator. In the case of a transition metal or compound with an unfilled inner d-shell in the state d^x, a transition metal binder in state d^y would be the most suitable (x and y represent the number of electrons in the unfilled d-shells) where the condition

$$x + y = 11 \qquad (1)$$

is satisfied.

It is visualized that at the physical interface between transition metal or compound and the sintering activator/binder, the bonding attained would be that of a low melting point Group IB elements, i.e. a filled d-shell of ten electrons and one s-shell electron. This relationship is also possible for carbides of transition metals because of their semi-metallic bonding. The following conditions would accompany the requirements of Equation 1.

1. Whenever transition metals meet the requirements of Equation 1, the element of Period IV would be better than those of Period V, and the Period V elements would be better than those of Period VI as binders for the Period VI elements, based on the increasing order of melting points.
2. A selection of transition metal or compound and binders that give $x + y = 10$ or $x + y = 12$ could provide good bonding, but inferior to those meeting the condition $x + y = 11$.
3. It would be possible to use a combination of two or more elements to satisfy the requirements of Equation 1. However, using more than two elements would lower the effectiveness of the binding process. When one of the two combined elements comes close to satisfying the requirements of Equation 1, then improved bonding occurs.
4. Group IIB elements are not suitable as binders for transition metals or their compounds, because of their completely filled d and s shell orbitals.

Evidence for the validity of the above proposals exists in the literature. Some examples are chosen as illustrations. The tungsten carbide–cobalt (WC–Co) hard metal system is an obvious candidate to be tested to meet the requirements of Equation 1.

Tungsten has an unfilled $5d^4$ orbital, i.e. $x = 4$ and cobalt has an unfilled $3d^7$ orbital, $y = 7$. In this case $x + y = 11$, is satisfied. As an example of a pure metal, tantalum is chosen. This has an unfilled $5d^3$ orbital. Based on Equation 1, the most suitable sintering additive/binder would be nickel with an unfilled $3d^8$ orbital. For this system, $x = 3$ and $y = 8$ and the requirements of Equation 1, is satisfied, i.e. $x + y = 11$. This is in good agreement with the results of German and Munir [29] as shown in Figs 2 and 3. According to the Engel–Brewer theory [7], Table III, copper promotes two electrons from the d-orbital to the outer p-orbital, with a total of three (s + p) electrons and therefore crystallizes in the fcc structure. This promotion of two electrons in copper makes it the next most suitable sintering additive to tantalum and this is indicated in German and Munir's results on fine tantalum powders where the reactions proceed to completion at a fast rate. Cobalt would meet the requirement $x + y = 10$ and is next to copper in suitability. Zinc is seen to be a very poor activator in this system based on our proposed rules and the EB theories which shows (Table III) that zinc does not normally promote electrons out of the d-orbital.

Samsonov and Yakovlev [30, 31], using electron concentration models, selected cobalt, iron and nickel as sintering additives for niobium and obtained an enhanced sintering effect. From the requirements of Equation 1 and the stated conditions, cobalt would be the most suitable sintering aid, because in this case $x + y = 11$ is satisfied. Iron gives $x + y = 10$ and nickel gives $x + y = 12$; both are also Period IV elements, and would be the next most suitable sintering activators (to cobalt) for niobium within the proposed rules. The results of Meredith and Milner [32] as shown in Fig. 4 concur with the requirement of Equation 1 and the four stated conditions. For titanium

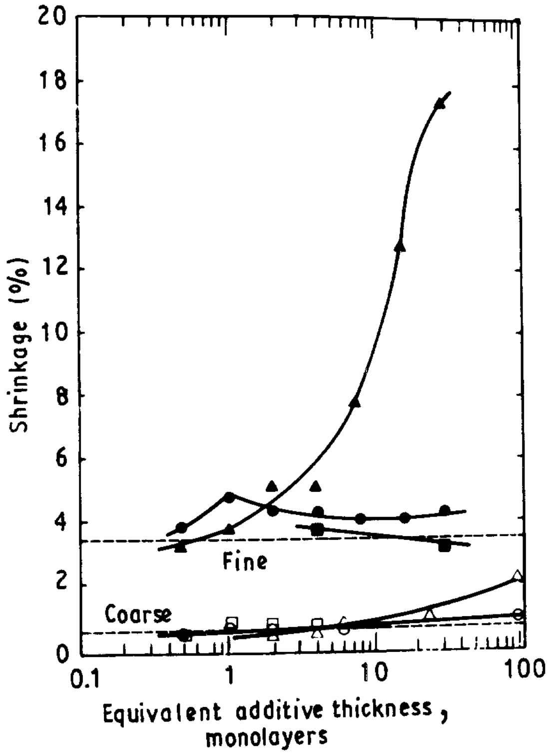

Figure 2 Influence of activator type and thickness on linear shrinkage for tantalum powders sintered for 1 h at 1500 °C. (▲, △) Ni, (●, ○) Pd, (■, □) Pt, (– – –) untreated. After German and Munir [29].

monocarbide TiC, nickel with an unfilled $3d^8$ comes closest to satisfying Equation 1. Cobalt has an unfilled $3d^7$ orbital and is quite close to nickel as a suitable sintering activator/binder for TiC. The results of Meredith and Milner [33] indicate that TiC is more soluble in nickel than in cobalt. Our current experimental work on activated sintering of transition metal compounds (to be published later) are based on the arguments proposed in this paper; preliminary results indicate good correlation between theory and experiment.

3.1.2. *Intermetallics*

These compounds are generally characterized by the following properties which make them suitable candidate materials for high temperature applications.

(a) Strong bonding which does not generally degrade with temperature.

(b) Ordered structures with low self-diffusion leading to good creep resistance.

(c) High moduli of elasticity which decreases slowly with temperature.

(d) Low specific density.

(e) Good oxidation resistance.

However, as a class of materials they are brittle. This limited ductility has caused difficulty in fabricating and applying these materials in a range of fields including the aerospace industry and consequently tremendous effort has been put into improving the ductility of intermetallics. Excellent critical reviews of the current understanding of the properties of intermetallics have been reported in the literature by Yamaguchi and Umakoshi [34], Varin and Winnica [35] and Cahn [36]. The factors found to be responsible for the limited ductility are:

1. a limited number of slip systems;
2. a large slip vector;
3. restricted cross-slip;
4. difficulty in transmitting slip across grain boundaries;
5. intrinsic grain-boundary weakness associated with ordering energies in the intermetallics.

Many researchers [37–41] have reported that the brittle intergranular failure may be more readily correlated to differences in valence states of the

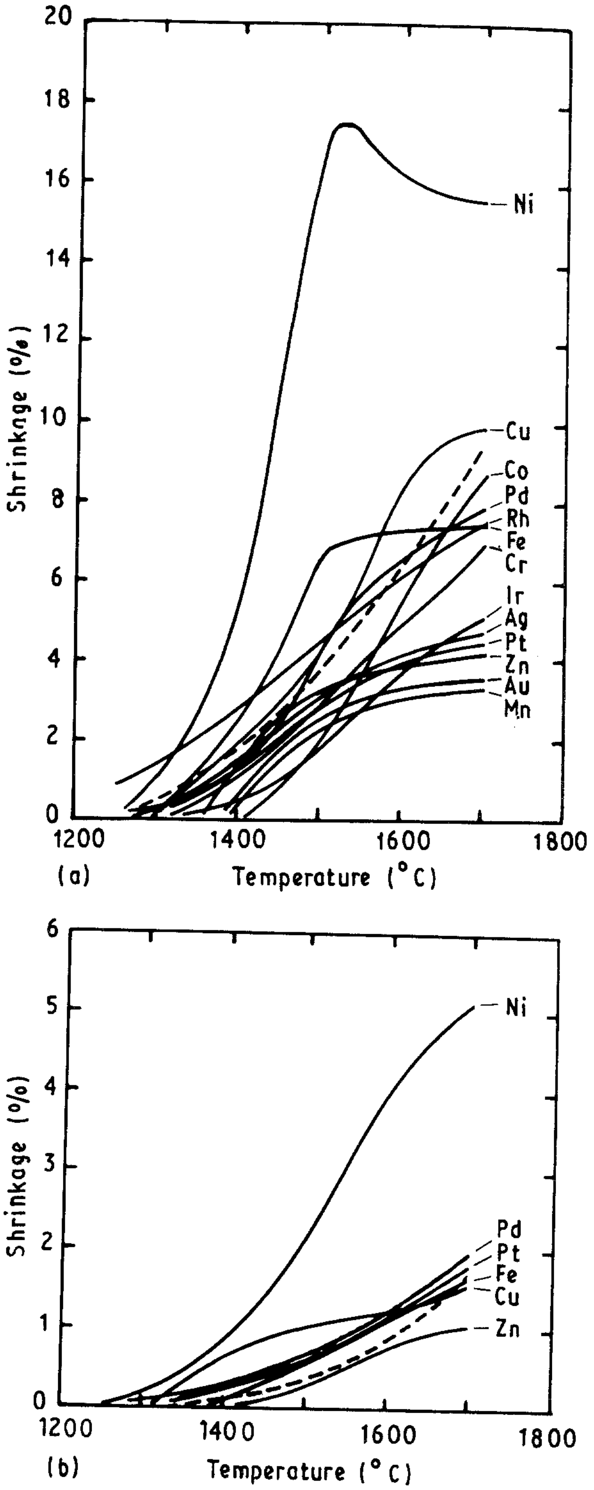

Figure 3 Shrinkage dependence on isothermal sintering temperature for 1 h, for tantalum treated with various additives: (a) fine, (b) coarse tantalum powder, 100 monolayers, (———) treated, (– – –) untreated. From German and Munir [29].

TABLE III Electronic configurations, promotion energies, and crystal structures

Element	Configuration	Promotion energy, (kcal mol^{-1})	Crystal structure[a]	Element	Configuration	Promotion energy, (kcal mol^{-1})	Crystal structure
Na	s	0[b]	bcc	Nb	d^4s	0	bcc
Mg	s^2	0	–		d^3sp	48	–
	sp	63	cph	Mo	d^5s	0	bcc
Al	s^2p	0	–	Tc	d^5s^2	0	–
	sp^2	83	fcc		d^6s	7	–
K	s	0	bcc		d^5sp	47	cph
Ca	s^2	0	–	Ru	d^7s	0	–
	sp	43	–		d^6sp	72	cph
	ds	51	bcc	Rh	d^8s	0	–
Sc	ds^2	0	–		d^6sp^2	128	fcc
	dsp	45	cph	Pd	d^{10}	0	–
	d^2s	33	bcc		d^7sp^2	140	fcc
Ti	d^2s^2	0	–	Ag	$d^{10}s^1$	0	–
	d^2sp	45	cph		d^8sp^2	133	fcc
	d^3s	19	bcc	Cd	$d^{10}s^2$	0	–
V	d^3s^2	0	–		$d^{10}sp$	87	cph
	d^3sp	47	–	Ba	s^2	0	–
	d^4s	6	bcc		ds	26	bcc
Cr	d^5s	0	bcc		sp	35	–
	d^4sp	71	–	La	ds^2	0	–
	d^4sp^2	165	–		dsp	38	cph
Mn	d^5s^2	0	–		d^2s	8	bcc
	d^5sp	53	–		sp^2	44	fcc
	d^6s	49	bcc	Hf	d^2s^2	0	–
Fe	d^6s^2	0	–		d^3s	40	bcc
	d^6sp	55	–		d^2sp	51	cph
	d^7s	20	bcc	Ta	d^3s^2	0	–
	d^5sp^2	92	fcc		d^4s	28	bcc
Co	d^7s^2	0	–	W	d^4s^2	0	–
	d^6sp^2	119	fcc		d^5s	8	bcc
	d^7sp	67	cph	Re	d^5s^2	0	–
	d^8s	10	–		d^6s	34	–
Ni	d^8s^2	0	–		d^5sp	54	cph
	d^9s	1	–	Os	d^6s^2	0	–
	d^8sp	74	–		d^7s	15	–
	d^7sp^2	120	fcc		d^6sp	67	cph
Cu	$d^{10}s$	0	–	Ir	d^7s^2	0	–
	d^8sp^2	120	fcc		d^7sp	75	–
Zn	$d^{10}s^2$	0	–		d^6sp^2	162	fcc
	$d^{10}sp$	93	cph	Pt	d^9s	0	–
Sr	s^2	0	–		d^7sp^2	156	fcc
	ds	52	bcc	Au	$d^{10}s$	0	–
	sp	41	–		d^8sp^2	159	fcc
Y	ds^2	0	–	Hg	$d^{10}s^2$	0	–
	d^2s	31	bcc		$d^{10}sp$	106	–
	dsp	43	cph				
Zr	d^2s^2	0	–				
	d^3s	14	bcc				
	d^2sp	42	cph				

[a] Stable crystal structure at ambient pressure.

[b] Ground state has zero promotion energy; other values are the lowest energies for each configuration as given by Brewer [7].

N.B. Promotion energy is the energy required to place electrons in the outermost (s + p) orbital from the inner shell during bonding according to the Engel–Brewer Theory [7].

constituent atoms in the intermetallic and their respective atomic sizes than with ordering energy, yield strength or solidification morphology. Following Aoki and Izumis' [42] discovery that the ductility of Ni_3Al can be increased by microalloying with boron, it has been suggested that boron has a strong tendency to segregate to the grain boundaries [43], thereby facilitating the accommodation of slip dislocations at grain boundaries [44] and enhancing the cohesive strength between grains. Imayev and Imayev [45] argued that there is a change in the type of interatomic bonding which occurs during the transition from metals to intermetallics, resulting in a weakening of the metallic bond and strengthening of the covalent bond. In general, most of the current attempts to improve the ductility of intermetallics are based on partially modifying the bonding from being mainly covalent to a more metallic nature by macro-alloying with substitutional ternary elements.

Court *et al.* [46] suggested that enhanced slip activity observed in niobium-alloyed Ti_3Al arises from the weakening of the covalent bonds between titanium atoms. According to their model, strong covalent bonding is developed between the titanium atoms in

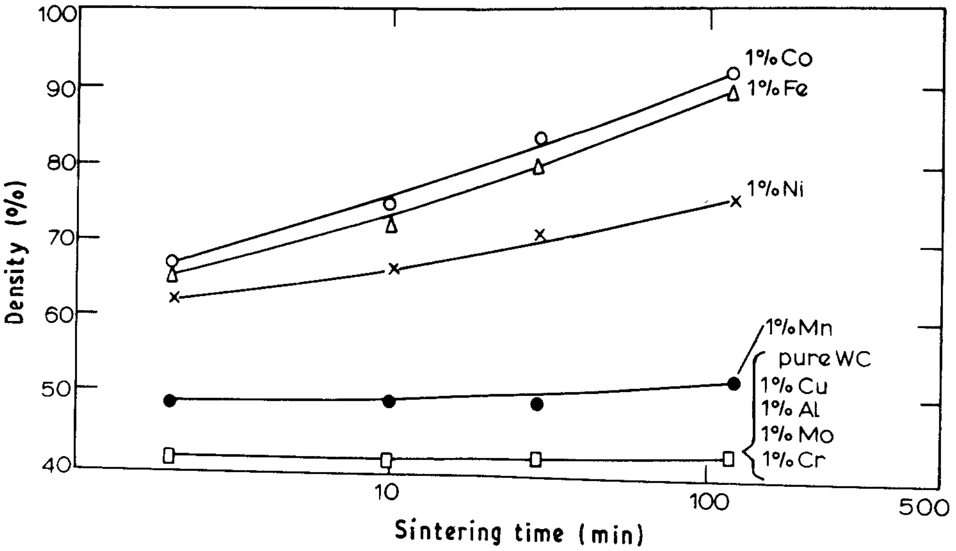

Figure 4 The effect on densification of tungsten carbide of adding 1 vol % of a range of metallic powders. After Meredith and Milner [32].

planes that contain sheets of only titanium atoms (e.g. $\{11\bar{2}0\}$). These covalent bonds immobilize dislocations by increasing the depth of the Peierls valleys of the dislocations, with segments lying approximately perpendicular to the planes containing sheets of titanium atoms. If niobium atoms substitute for titanium atoms and reduce the covalency, the mobility of the dislocations would increase.

Morinaga *et al.* [47] investigated the electronic structure of TiAl and concluded that the existence of a directional $\text{Al}_{\text{p state}}$–$\text{Ti}_{\text{d state}}$ covalent bond causes this compound to be brittle. It was also suggested that alloying of TiAl with the elements which weaken p–d interactions, but enhance d–d interactions would be quite effective in improving the ductility of TiAl.

Our extended study of the literature indicates an emerging pattern for improving the ductility of intermetallics. Using transition metal aluminides as the prototypes, the following conditions would seem to be singularly associated with an improvement in ductility in transition metal aluminide intermetallics.

1. For a transition metal aluminide, with the transition metal having an unfilled inner d-shell in the state d^x, alloying with another transition metal in the state d^y (by partial replacement of aluminium by the alloying element, leading to non-stoichiometric compound formation) where the condition

$$x + y = 19 \qquad (2)$$

is satisfied, leads to substantial improvement in ductility.

2. Where a single alloying element cannot satisfy the requirement of Equation 2, it would be possible to use a combination of two or more transition metal elements to achieve ductility. For example, when two alloying elements in states d^y, d^z are used, the requirement of Equation 2 would be that $x + y + z = 19$, forming a non-stoichiometric compound. The improvement in ductility in this case would be inferior to that obtained for the $x + y = 19$ condition. There could also be two metal systems satisfying $x + y = 18$, $x + y = 17$ etc., that would provide greater ductility than the $x + y = 19$ case.

3. By moving to lower values of the summed number of d-electrons, i.e. much less than 19, the transition metal aluminide would become less ductile.

4. It is possible to use transition metal alloy(s) from Periods V and VI of the Periodic table of elements to improve the ductility of Period IV transition metal elements by either satisfying Equation 2 or coming very close to it. These simple additive rules can indicate which transition metal(s) can be used as alloys to improve ductility, when compositions and phase diagram data are taken into consideration and, contrarily, which alloying combinations would not lead to ductility, irrespective of the compositions involved.

5. Group IB elements would also be useful as alloys for improving ductility in transition metal aluminides, because they can promote electrons out of the d-shell [7], whereas Group IIB elements with filled d- and s-orbitals are not suitable.

Some examples reported in the literature of non-stoichiometric transition metal aluminides that are in agreement with the proposed rules are given below. Kim [48] reported that a slight improvement in ductility occurs for Ti–48 at % Al when alloyed with vanadium, chromium and manganese, whereas niobium and tungsten additions decrease the ductility. The total number of unfilled d-state-electrons in V + Cr + Mn is 13 and when added to that of titanium becomes 15, which tends towards $x + y = 19$ and the ductility improves. The total number of unfilled d-state-electrons in Nb + W = 8 and when added to that of titanium gives 10, which is very far from the ideal value of 19 and the compound is brittle in this case. Wittenaver *et al.* [49] reported a tensile elongation at room temperature of about 7% in a Ti–25 at % Al–10 at % Nb–3 at % V–1 at % Mo alloy. The total number of unfilled d-state-electrons in the transition metals in these compounds is 14. Guha *et al.* [50] obtained a remarkable increase in the ductility of NiAl when the single phase was transformed into a duplex phase by macro-alloying with iron. The duplex L1_2 (Ni, Fe) (Al, Fe) and B2 (Ni, Fe) (Al, Fe) eutectic structure gave a 22% plastic strain at room temperature, with a mixture of ductile dimpling and intergranular fracture. The total number of unfilled d-state-electrons in the transition metals in this compound is 14.

Chiba *et al.* [51] successfully rolled palladium-doped Ni_3Al to 10%–40% reductions without cracking. Their experiments indicated that a recrystallized non-stoichiometric composition $Ni_3Al_{23}Pd_2$ gave the maximum ductility in an aluminium-deficient composition. The improvement in ductility was associated with a degradation of ordering energy, due to the palladium addition and deviation in aluminium content from stoichiometry. The total number of d-electrons in this compound is 18. The substantial improvement in ductility can be attributed to the closeness to the proposed peak value of the d-electron sum of 19. It was pointed out [51] that the ductility of the compound could also be improved by alloying with platinum, gold, silver and copper, which is in agreement with the rules proposed here.

4. Conclusion

A set of rules based on unfilled d-orbital states is proposed as a basis for selection of suitable binders for transition metal compounds. A modified form of these rules would assist in selecting alloy(s) for improving the ductility of transition metal-based intermetallics. While these rules may not be exclusively sufficient in both cases, they can improve the selection procedures for alloy(s) when used in conjunction with thermodynamic and phase diagram data.

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References

1. K. SCHRÖTER, "Hard Metals Alloys", US Pat. 1 549 615 (1925).
2. F. V. LENEL, "Powder Metallurgy and Its Applications" (Metal Powder Industries Federation, Princeton, NJ, 1980) pp. 383, 396.
3. G. HÄGG, *Z. Phys. Chem.* **B6** (1929) 221.
4. P. ERHLICH, *Engew. Chem.* **59** (1947) 163.
5. J. NORTON, H. BLUMENTHAL and S. SINDEBAND, *Trans. Amer. Inst. Mining Met. Eng.* **185** (1949) 749.
6. J. NORTON and A. MOWRY, *ibid.* **185** (1949) 133.
7. N. A. GOKCEN, "Statistical Thermodynamics of Alloys" (Plenum Press, New York, 1986) pp. 237–54.
8. N. ENGEL, *Powder Met. Bull.* **7** (1954) 8.
9. L. BREWER, in "Electronic Structure and Alloy Chemistry of Transition Elements", edited by P. A. Beck (Interscience, New York, 1963) p. 221.
10. *Idem*, in "High Strength Materials", edited by V. F. Zackay (Wiley, New York, 1965) p. 12.
11. *Idem*, in "Phase Stability in Metals and Alloys", edited by P. Rudman, J. Stringer and R. Jaffee (McGraw-Hill, New York, 1967) pp. 139–61.
12. *Idem, Acta Metall.* **15** (1967) 553.
13. *Idem, Science* **161** (1968) 115.
14. *Idem*, in "Plutonium and other Actinides", edited by W. N. Miner (Metals Society of AIME, New York, 1970) p. 650.
15. L. BREWER and P. R. WENGERT, *Metall. Trans. AIME* **4** (1973) 83.
16. L. BREWER, *J. Nucl. Mater.* **51** (1974) 2.
17. *Idem, Rev. Chim Miner.* **II** (1974) 616.
18. J. FRIEDEL, in "Electronic Structure and Alloy Chemistry of Transition Elements", edited by P. A. Beck (Interscience, New York, 1963) p. 70.
19. W. HUME-ROTHERY, "Atomic theory for students of Metallurgy" (Institute of Metals UK, 1960) Monograph and Report Series no. 3.
20. K. SCHWARTZ and A. NECKEL, in "2nd International Conference on the science of Hard Metals", Extended Abstracts, Rhodes, Greece, September 1984, Paper 3.
21. L. PAULING, *Phys. Rev.* **54** (1938) 899.
22. *Idem*, "The Nature of the Chemical Bond", 2nd Edn (Cornell University Press, New York, 1940).
23. *Idem, J. Amer. Chem. Soc.* **69** (1947) 540.
24. L. PAULING and F. J. EWING, *Rev. Mod. Phys.* **20** (1948) 112.
25. L. PAULING, *Proc. R. Soc. Lond. (A)* **196** (1948) 112.
26. Y. ISHIZAWA and T. TANAKA, in "2nd International Conference on the science of Hard Metals", Extended Abstracts, Rhodes, Greece, September 1984, Paper 2.
27. T. TANAKA, Y. ISHIZAWA, E. BANNAI and S. KAWAI, *Solid State Commun.* **26** (1978) 879.
28. JIAN-HUA XU and A. J. FREEMAN, *J. Mater. Res.* **6** (1991) 1188.
29. R. M. GERMAN and Z. A. MUNIR, *Powder Metall.* **20** (3) (1977) 145.
30. G. V. SAMSONOV and V. I. YAKOVLEV, *Z. Metallkde* **62** (1971) 621.
31. *Idem, Sov. Powder Metall. Met. Ceram.* **12** (1973) 379.
32. B. MEREDITH and D. R. MILNER, *Powder Metall.* **19** (1) (1976) 38.
33. *Idem. ibid.* **19** (3) (1976) 162.
34. M. YAMAGUCHI and Y. UMAKOSHI, *Prog. Mater. Sci.* **34** (1990) 1.
35. R. A. VARIN and M. B. WINNICA, *Mater. Sci. Engng* **A137** (1991) 83.
36. R. W. CAHN, *MRS Bull.* May (1991) 18.
37. A. I. TAUB and C. L. BRIANT, "High-Temperature Ordered Intermetallic Alloys II" (Materials Research Society, Pittsburgh, PA, 1987) p. 343.
38. A. I. TAUB, C. L. BRIANT, S. C. HUANG, K. M. CHANG and M. R. JACKSON, *Scripta Metall.* **20** (1986) 129.
39. A. I. TAUB and C. L. BRIANT, *Acta Metall.* **35** (1987) 1597.
40. T. TAKASUGI and O. IZUMI, *ibid.* **33** (1985) 1247.
41. T. TAKASUGI, O. IZUMI and M. MASAHASI, *ibid.* **33** (1985) 1259.
42. K. AOKI and O. IZUMI, *Nippon Kinzoku Gakkaishi* **43** (1979) 1190.
43. C. T. LIU, C. L. WHITE and J. A. HORTON, *Acta Metall.* **33** (1985) 213.
44. G. M. BOND, I. M. ROBERTSON and H. K. BIRNBAUM, *J. Mater. Res.* **2** (1987).
45. R. M. IMAYEV and V. M. IMAYEV, *Scripta Metall. Mater.* **25** (1991) 2041.
46. S. A. COURT, J. P. A. LOFVANDER, M. A. STUCKE, P. KURATH and H. L. FRASER, "High-Temperature ordered intermetallic alloys III", Vol. 133 (Materials Research Society, Pittsburgh, PA, 1989) p. 675.
47. M. MORINAGA, J. SAITO, N. YUKAWA and H. ADACHI, *Acta Metall.* **38** (1990) 25.
48. Y-W. KIM, *J. Metals* **41** (1989) 24.
49. J. WITTENAVER, C. BASSI and B. WALSER, *Scripta Metall.* **23** (1989) 1331.
50. S. GUHA, P. MUNROE and I. BAKER, "High Temperature Intermetallic III", Vol. 133 (Materials Research Society, Pittsburgh, PA, 1989) p. 633.
51. A. CHIBA, S. HANADA and S. WATANABE, *Acta Metall. Mater.* **39** (1991) 1799.

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