SOME RELATIONSHIPS BETWEEN THE ELECTRONIC AND MECHANICAL PROPERTIES OF Ti ALLOYS, DISCUSSED FROM THE STANDPOINT OF FUNDAMENTAL ALLOY THEORY*

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The results of two general theories, which when taken together enable the structure-dependence of the cohesive energy of an alloy to be related to the electronic structures (atomic and band) of the pure constituents, are applied in a discussion of solid solution strengthening in α-stabilized and β-stabilized Ti-base alloys.

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1. INTRODUCTION

The problem of finding some common ground between the metal physicist and the physical metallurgist has always been a difficult one, particularly when the electronic basis of mechanical strength in metals and alloys is under debate. Progress has been inhibited by, for example, the fact that some electronic properties of some materials are practically unaffected by mechanical deformation. Nevertheless, a proper description of a metal, as an assembly of positive ions in equilibrium with the conduction electrons, must eventually lead to an understanding of the principal interactions which control ionic motion during deformation. Accordingly we commence our discussion with an expression for the cohesive energy (E_{COH}) of a pure metal, expanded in terms of atomic potentials and structural arrangements. For an alloy, E_{COH} in this format may be regarded as being dependent on the atomic potential differences of the constituents, or some equivalent parameter. In applying this extension of the basic theory, particularly to alloys of transition metals with nontransition metals, we are guided by the results of Stern's(1,2,3) tight-binding theory of electronic structure.

Through the use of such concepts, *a postiori* qualitative explanations of various mechanical property trends in real metals (as distinct from perfect crystals) have begun to develop into useful alloy design criteria. The fundamental approach seems, at first inspection, to be applicable only to pure or single-phase materials, and as such, would be of only limited value. This difficulty can be overcome by applying the method separately to the individual components of a polyphase system. Since the particular mechanical behavior of interest in a given situation is usually dominated by the mechanical properties of only one of the component phases (e.g., brittle particles either precipitated uniformly or concentrated at grain boundaries), at least as much attention is paid to the intrinsic characteristics of such a phase as to those of the host alloy.

2. THE COHESIVE ENERGY OF METALS AND ALLOYS

2.1. Pure Metals

The cohesive, and hence the mechanical properties of metals and alloys, depend principally on the interaction of metallic ions with, and *via*, the conduction electrons. The cohesive energy is represented by E_{COH}, a component of the internal energy E, where:

$$E = E_{COH} + TS \; ; \qquad (1)$$

with S and T representing entropy and absolute temperature respectively. If constant volume conditions prevail, E_{COH} may be identified as the Helmholtz free energy.

The key statement in this approach to an understanding of electronic-property/mechanical-property interrelationships, takes the form of a series expansion of E_{COH} into components representing the contributions by (a) the electron gas itself, and (b) n-body (n = 1,2 ...) ionic interactions; thus:

$$E_{COH} = \sum_{i=1}^{n} E_i \ . \qquad (2)$$

Such an expression might well be used axiomatically(4), but has also been derived formally by Cohen(5) who pointed out how the free energy could in this way be resolved into structure-independent and structure-dependent components. The expansion for E_{COH} is dominated by E_1, which represents the contribution by the electron gas plus the self-energy of the ions imbedded in it. Being structure-independent it is this term which confers on metals and alloys their characteristic ductility. E_2 depends on pair-wise (central-force interactions, E_3 on triplet interactions, and so on. These are all structure-dependent, and therefore control the metal's resistance to deformation. The convergence of (2) depends on the strengths of the atomic potentials expressed in some suitable form.

For very weak potentials (such as pseudopotentials) the series may be terminated at n = 2(6). Within the context of the topic under discussion such a truncated form of Equation (2) has been derived by Harrison(7) and by Blandin(8) using second-order perturbation theory. Under these conditions E_{COH} is only weakly structure-dependent. A second-order perturbation expression of E_{COH} is valid, for example, for the monovalent(9) pseudopotential metals Na and K, which are for this reason plastic at all temperatures.

If the atomic potentials are strong, perturbation theory may no longer be used and we return to the full expression for E_{COH}, entering the regime of interest to us here, in which third- and higher-order terms become significant. The resistance to deformation of a pure metal may thus be related to the strength of its atomic potential; one measure of which, as Cohen has suggested(5), being E_g/Δ, the ratio of a low-lying band gap to the width of the unperturbed energy band.

In this paper we employ these concepts, formerly applied in discussions of phase stability in metals and alloys, to gain a fundamental understanding of solid-solution strengthening in Ti-base alloys.

2.2. Alloys

As the above discussion indicates, strengthening in metals is accompanied by a breakdown of perturbation theory. This is the clue which leads to an understanding of solid-solution strengthening in alloys. As Stern(2) has pointed out, perturbation theory may be used in describing the electronic structures of alloys formed between two simple metals only if V_{12}/Δ is small, where V_{12} is the difference in the atomic potentials of the components. Thus V_{12} for an alloy plays the same role as E_g for a pure metal. By selecting solute elements whose potentials differ considerably from that of the host we can control the convergence of Equation (2) and consequently the degree of solid-solution strengthening.

When dealing with alloys, it may be more convenient to go directly to factors which govern the validity of perturbation theory, and hence which from this standpoint control the convergence of Equation (2) rather than to take the intermediate step of considering individual atomic potentials or their relative differences in the format V_{12}/Δ. This is because many alloys of interest are those formed between nontransition metals and transition metals. It is difficult to assign to a transition metal a meaningful "atomic potential", particularly one that would be valid in a mixed alloy. On the other hand it is more straightforward to consider directly, and perhaps in a more fundamental way, the strong perturbation of electron states that result when a nontransition metal is alloyed with a transition metal.

3. ELECTRONIC STRUCTURES OF ALLOYS

The atoms of a pure simple metal (metal 1) of valence Z each contribute Z electrons to the conduction band. Similarly for a pure simple metal (metal 2) of valence Z + 1. But this is no longer true when metal 2 is dissolved in metal 1; since screening or charge-neutrality considerations require the extra valence electron to be more-or-less localized in the vicinity of the metal-2 atoms. This example, discussed initially by Mott(10) and developed into theories of metallic virtual bound states by Friedel(11) and into the theory of "charging", through the work of Stern(1,2,3), shows clearly that the perturbation approach and the rigid-band model are inapplicable to alloys of simple metals differing in valence. The theory of charging implies more than just a cell-by-cell neutralization of net charge by screening. If charging is "large"(1) the theory requires in addition a drastic alteration in band shape as the electrons are redistributed in energy. Thus, for example, the screening electrons of atom 1 may be assigned mostly to low-lying states in the band, and conversely for atom 2. Such an arrangement would imply the existence of a minimum in the n(E) (density-of-states *versus* energy) curve. In contrast to the motion of "neutral pseudo-atoms"(12) which carry their "own" screening electrons with them, the movements of atoms under conditions of large charging are resisted by the energy barriers associated with redistribution of the screening charge in space and energy with each change of local environment. This strong structure-dependence of electron states which accompanies large charging is expressive of solid-solution strengthening.

Three results from the above theory, particularly important in this context are summarized below.

3.1. Transition-Metal Binary Alloys (T_1-T_2 Alloys)

Charging is particularly small in alloys between adjacent transition elements near the middle of a long period(3,13). Excellent agreement with the rigid-band model has in fact been demonstrated by McMillan(14) for adjacent binary alloys from the sequence Hf-Ta-W-Re. We would not expect to find such good adherence to rigid-band principles for Ti-rich alloys with nearby transition elements, but nevertheless such alloys may still be classed as "low perturbation".

3.2. Transition-Metal/Nontransition-Metal Binary Alloys (T_1-B Alloys)

For isolated transition-metal ions dissolved in simple metals, the amplitudes of the d wavefunctions are large in the vicinity of the impurity. These are referred to as virtual bound states(11). Together with some extra broadening of the d-states this picture carries over to concentrated alloys, with the result that we again find maximal d-wave-function amplitudes at the transition-metal-ion sites. The tendency of the d wavefunctions to stay away from the nontransition-metal sites leads to an approximate representation of the alloy as a "diluted" or "expanded" transition metal lattice. This model is substantiated by several pieces of experimental evidence. For example, as a result of NMR studies of the V-Al system, Van Ostenburg, et al(15), were able to demonstrate that the d-band electrons tended to avoid the Al cells. It is useful to interpret this as strong scattering of the d wavefunctions by the Al ions. In addition, the above authors were able to conclude that the valence electrons of the Al appeared to contribute to a low-lying band; a suggestion which later appeared(1) as a part of Stern's tight-binding theory of disordered alloys. Although somewhat more refined, the conclusions reached by Lye(16) with regard to the electronic structures of intermetallic components of Ti with the nonmetallic "p-s" elements C, N, and O, based on the results of band-structure calculations for TiC, are also in general agreement with these ideas.

For a T_1-B alloy, therefore, the picture which emerges is one of strong noncentral interactions between the ions, resulting in a pronounced structure-dependence of the corresponding E_{COH}.

3.3. Influence of Order-Disorder on Electron States

Stern's theory(1) shows that in the presence of small charging an electron energy band splits into two when the alloy orders. On the other hand, when $V_{12}/\Delta >> 1$ the model yields a band gap in both the disordered and ordered states of the alloy. The real situation will presumably be less well defined than this; nevertheless, as some of us have pointed out elsewhere(4), it is clear that various degrees of electronic structure change can be expected to accompany order-disorder. It can be argued that in general (there is at least one exception) the disordered alloy will tend to be the more ductile.

4. APPLICATION TO ALLOYS OF TITANIUM

4.1. Alloys of Ti With a Nearby Transition Metal (Ti-T_2 Alloys)

As indicated in 3.1., Ti-base transition-metal-binary (Ti-T_2) alloys may be classified as "low-perturbation". If T_2 is close to Ti in the transition-metal block of the periodic table, many of the properties of Ti-T_2 alloys are determined by the average electron-to-atom ratio, $\mathfrak{z}$. For example, when $\mathfrak{z}$ exceeds a threshold value of about 4.4 the bcc (β) structure remains stable during quenching. We Therefore regard T_2 solutes as structural (β) stabilizers rather than solid-solution strengtheners, although some degree of strengthening may be contributed by their presence. Having obtained a suitable β-stabilized binary alloy, a second solute species may then be selected solely on the basis of its strengthening properties. This will generally be a nontransition element.

4.2. Alloys of Ti With Nontransition Metals -- Low-Concentration Ti-B Alloys

Significant solid-solution strengthening is achieved by adding nontransition metals (designated B-metals) to Ti. As indicated in 3.2., Ti-B alloys are characterized by a relatively high density of occupied d-states at the Fermi level. The d-wavefunctions are strongly scattered from the B-ions, which are themselves screened by electrons occupying states in the lower part of the band. During alloying, as the Ti-lattice becomes diluted or "expands", the influence on the Fermi density-of-states, $n(E_F)$, of a decreasing d-band width tends to be compensated for by a decrease in the average volume-density of d-states. The resultant relatively small concentration-dependence of $n(E_F)$ with alloying, in low-concentration Ti-Al alloys, has already been demonstrated(17).

It is possible to enumerate several important consequences of the rearrangement of electron states which accompanies the addition of B-metals to Ti.

4.2.1. The Cohesive Energy

Of primary concern to us here is the fact that the readjustment of the energy state of B which accompanies its solution in Ti can be designated as a "strong interaction" between B and its Ti neighbors. The increase in structure-dependence of E_{COH} through the necessity of including high-order terms in Equation(2) is an expression of solid-solution strengthening. Listed below are some of the various physical property measurement techniques which may be employed in studying the magnitude of this interaction strength.

4.2.1(a) Relative Vapor Pressure. The application of this technique in the determination of thermodynamic activities and pairwise interaction parameters is discussed elsewhere in these proceedings(18).

4.2.1(b) The Electrical Resistivity. As pointed out above, it is possible to relate the solid-solution-strengthening capacity of B, when dissolved in Ti, to the scattering potential presented by B-ions to d-wavefunctions. Thus the relative magnitudes of the specific resistivities(19) of various metals when dissolved in Ti, can be used as indicators of the degrees of charging, and consequently of solid-solution strengthening. The composition-dependences of resistivity of several Ti-T_2 and Ti-B alloys are shown in Figure 1. It is seen immediately that the specific resistivity common to various T_2 ions in Ti is about an order of magnitude smaller than those for B-metals; a result consistent with Sections 4.1 and 4.2. Furthermore the resistivity data suggest that the interaction strengths between various B-metals and Ti, and hence the solid-solution-strengthening abilities of the B-metals in Ti-B alloys, increase in the sequence Al → Ga → Sn. This has indeed proved to be the case for Al and Ga additions to Ti, as indicated in Figure 2.

4.2.2. Phase Stability

In contrast to transition-metal solutes, additions of which increase the d-electron density and lead eventually to β-stabilization; the "p-s" elements (particularly the B-metals) by "diluting" the Ti lattice in the manner outlined in Section 3.2, yield solid solutions which remain "Ti-like" as alloying proceeds. This is the mechanism of α-stabilization.

In other papers(20) we have usually defined an electron-to-atom ratio ($\mathcal{Z}$) scale by considering the average number of valence electrons (i.e., the atomic d, s electrons for Ti; and the p, s electrons for Al). However, the dilution concept referred to above, together with the conclusions of other workers(21), suggest that a more physically meaningful $\mathfrak{z}$-type scale, valid for both Ti-T_2 and Ti-B alloys, might result if we restricted ourselves to a consideration of the average density of only the d-electrons.

4.2.3 Ternary Solid-Solution Strengthening

For a given total solute concentration we would generally expect to observe an improvement in solid-solution strengthening in going from a binary to a ternary (Ti-B_1-B_2) alloy, as the binary Ti-B_i-type interactions become augmented by interactions (B_1-B_2) between the solute atoms themselves. An example of this is given in Figure 2 which illustrates a "secondary" solid-solution strengthening of Ti-Ga accompanying the substitution of Al for half of the Ga formerly present. In that figure it is interesting to note that the Ti-xAl-xGa curve lies above that for Ti-Ga, rather than between those for Ti-Al and Ti-Ga as might otherwise have been expected. Numerical values of the pair-wise interaction parameters appropriate to the Ti-Al, Ti-Ga, and Al-Ga interactions respectively, are presented elsewhere in these proceedings(18).

Finally we note that these principles of solid-solution strengthening can be extended to β-stabilized (i.e., Ti-T_2) alloys, which may thus be strengthened through additions of the elements B_1, B_2, etc.

4.3. Alloys of Ti With Nontransition Metals -- High-Concentration Ti-B Alloys

The strong spacial correlations which characterize the structures of Ti-B alloys lead eventually, as the alloys become more concentrated, and hence as the atom-ratio n_{Ti}/n_B becomes smaller, to long-range-ordered sturcutres. A good example of this effect is to be found in the Ti-Al system. At, say, 700° C Ti-Al alloys with Al concentrations of 21 through 25 at.% assume the long-range-ordered α_2 structure(22). The influences of such ordering on the electronic transport and density-of-states properties of Ti-Al are described elsewhere(4,17,23), the experimental results being consistent with a considerable reduction of $n(E_F)$ with ordering, particularly in Ti_3Al.

4.3.1 Influence of Order-Disorder on Electronic Structure and Mechanical Characteristics

Referring to previous sections (the above, and Section 3.3) and elsewhere(4) the results of both theory and experiment indicate that changes in electronic structure are expected to accompany order-disorder in most alloys except those characterized by small value of

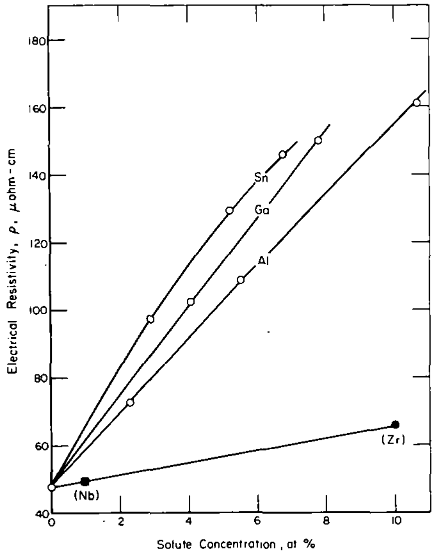


Fig. 1. Composition dependences of resistivity for Ti-T_2 and Ti-B alloys. The data for Ti-T_2 alloys are from S. L. Ames and A. D. McQuillan Acta. Met. 4 619 (1956). The results show that the interaction strengths of various solute elements with Ti proceed in the sequence T_2, Al, Ga, Sn.

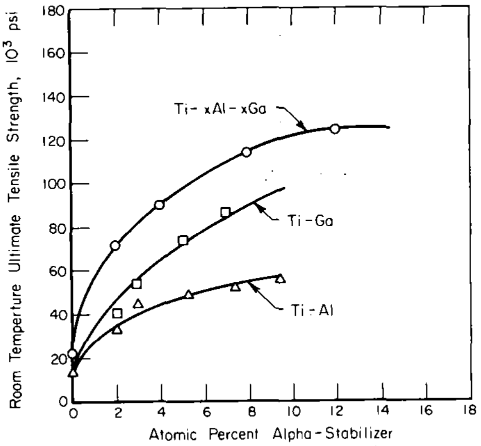


Fig. 2. The solid-solution strengthening capacities of B-metals dissolved in Ti increase in the sequence Al, Ga, in agreement with the data of Figure 1. In addition it can be seen that "secondary" solid-solution strengthening results in a ternary alloy (Ti-Al-Ga) which is stronger than Ti-Ga.

the parameter V_{12}/Δ. For example, in Ti_3Al the ordered α_2 structure supports, and is supported by, a significant degree of bond directionality(23,24).

It follows that deformation of a long-range-ordered structure results in a reduction in the order-parameter, and consequently a change in the electronic structure. This is not necessarily true for a disordered alloy, deformation of which merely results in another disordered structure. As a result, an ordered alloy tends to resist deformation to a greater extent than it otherwise would, if in the disordered state(25). A classical exception to this is Mg_3Cd(26) whose deformation properties require individual treatment.

Thus it is generally possible to alleviate the brittleness associated with a given intermetallic compound by destroying the long-range order. Two methods of disordering, or partially disordering, binary compounds are available: (a) isothermal disordering through the addition of a third atomic species; (b) thermal disordering by heating through the order-disorder critical temperature, T_c. Examples of these are as follows.

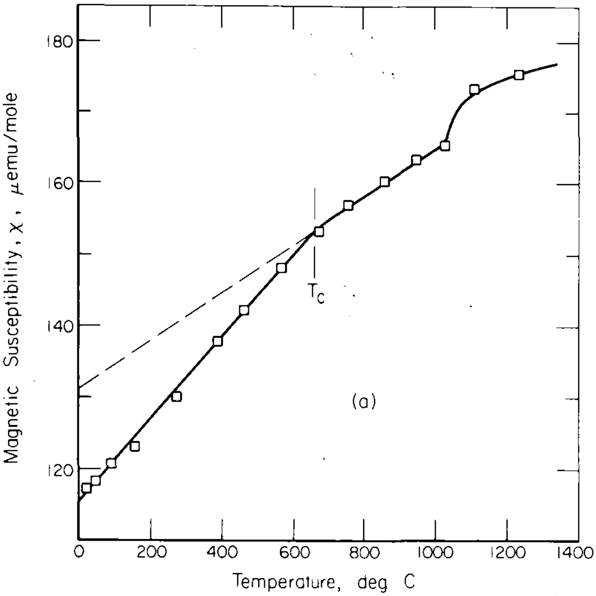
4.3.1.(a). A significant reduction in the brittleness associated with Ti_3Al is achieved by the substitution of Ga for some of the Al, within the "ordered" lattice. This procedure also results in a reduction in T_c from 850° C for Ti_3Al to 640° C for "$Ti_3Al_{1/2}Ga_{1/2}$".

4.3.1.(b). Disordering can be achieved thermally by heating through T_c. At the same time we would expect to find an improvement in ductility. That this does indeed take place in "$Ti_3Al_{1/2}Ga_{1/2}$" is evidenced by Figures 3(a) and (b) which show a correlation between the order-disorder and brittle-ductile transformation temperatures. Microscopically, we have interpreted this behavior in terms of a relatively high structure-dependence of E_{COH} in the ordered phase. Thermodynamically, in considering the effect of temperature, and ultimately disordering, on ductility we return to Equation (1). For $T > 0$, E_{COH} is augmented by the "structure-independent" term TS which normally increases smoothly with temperature; but which in addition undergoes a relatively large rapid increase as T approaches T_c.

5. SUMMARY

The resistance to deformation of a metal is gauged by the extent to which the cohesive energy, E_{COH}, is structure-dependent. E_{COH} may be expanded in the form:

$$E_{COH} = \sum_{i=1}^{n} E_i \tag{1}$$



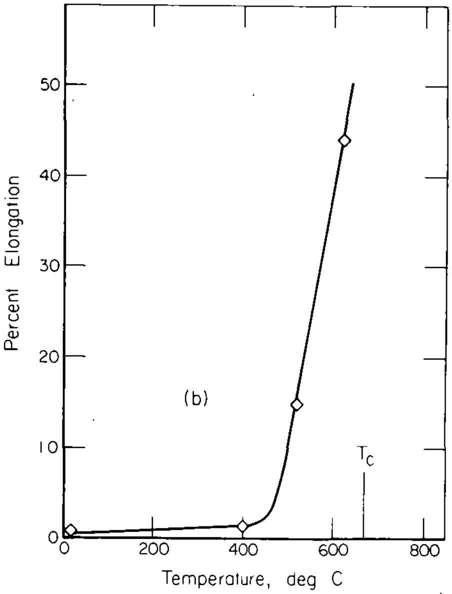


Fig. 3. (a) Magnetic determination of the order-disorder critical temperature, T_c, in "Ti_3 $Al_{1/2}$ $Ga_{1/2}$." (b) Increase in ductility in "Ti_3 $Al_{1/2}$ $Ga_{1/2}$" on approaching T_c.

in which E_n represents n-body interactions. The convergence of (1) is controlled by the strengths of the atomic potentials, in the case of pure metals; or the atomic potential differences between the constituents, in the case of alloys— in other words by the extent to which perturbation theory is valid. These principles have been employed to provide a fundamental understanding of phase stability and solid-solution strengthening in Ti-base alloys.

(a) When alloyed with B-metals the lattice remains "Ti-like" and consequently α-stable. The alloying of Ti with other transition elements β-stabilizes the lattice when the electron-to-atom ratio ($\mathfrak{z}$) becomes suitably large ($\mathfrak{z} \gtrsim 4.4$).

(b) Solid-solution strengthening may be achieved by adding B-metals either to Ti, resulting in strengthened α-alloys; or to Ti-T_2 ($\mathfrak{z} \gtrsim 4.4$) alloys, to produce strengthened β-alloys.

(c) "Secondary" solid-solution strengthening through B_1-B_2-type interactions may be achieved through the use of several B-metal additions to form Ti-B_1-B_2-etc. α-alloys, or Ti-T_2-B_1-B_2-etc. β-alloys.

(d) The embrittlement associated with "excessive" solid-solution strengthening of binary α-alloys to the point of ordered compound (e.g. α_2) formation may be alleviated by disordering, accomplished either through ternary alloying or thermally.

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