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by

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ABSTRACT

Canonical tight binding electronic band structure calculations were combined with a cluster variation configurational free energy, the effective pair interaction parameters of which were evaluated by the generalized perturbation method. Only d-orbitals were included and the numbers of d electrons per atom were taken to be 3 for the pure A element and 8 for pure B. A phase diagram was constructed incorporating, for the first time, both fcc and bcc lattices and their simple ordered superstructures. The calculated diagram agreed reasonably well with those determined empirically for Ti-Rh or Ti-Ir.

The task of calculating alloy phase diagrams from first principles is both practical and challenging: practical because the study of alloy properties depends critically on the knowledge of the relevant phase diagrams, challenging because the necessary calculations must combine, at a high level of accuracy, both quantum mechanical and statistical thermodynamical contributions. Recently, electronic band structure calculations have been used, in conjunction with appropriate statistical mechanical models, to derive portions of phase diagrams virtually from first principles. Recent examples include the calculation of the Cr-Mo miscibility gap[1] and of important features of binary semiconductor systems[2]. The purpose of this note is to present the results of a calculation of the phase diagram of a transition metal binary alloy exhibiting both fcc and bcc solid solutions and ordered intermetallic compounds. The prototype system chosen was Ti-Rh (or Ti-Ir).

The computational scheme employed is summarized briefly, below. Details of the calculations will be given elsewhere[3,4]. Starting assumptions are that atoms of two types, A and B, occupy the sites of either a bcc or fcc lattice with constant lattice parameter. No displacements, either static (elastic) or dynamic (vibrational) are allowed. It is further assumed that, for the transition elements considered, ferromagnetic ones excluded, only d electrons are responsible for bonding. The band structure is calculated in a tight binding (TB) scheme featuring canonical Slater-Koster parameters: $dd\pi = \frac{1}{2}|dd\sigma|$, $dd\delta = 0$, $dd\sigma = -1.385$. For the fcc electronic density of states (DOS), these values give a d-band width of 11.08 in canonical units (c.u.), with $1c.u. \approx 4.5eV$ for a typical d-band width of 5eV. The only element-specific

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parameters to enter the calculations are thus the number of d-electrons for element A (N_A) and for element B (N_B), and the diagonal disorder δ_d proportional to the magnitude of the d-band energy difference between A and B. Since identical canonical Slater-Koster parameters are used for all elements, no non-diagonal disorder is present. Charge transfer is not taken into account. Since differences of energy between ordered and disordered states are required, only band structure energy terms will be considered, under the assumption that double counting and electrostatic terms will cancel approximately. Of course, the resulting one-electron TB canonical band model with s and p electron contributions neglected is not expected to yield correct structural predictions for all pure elements across the transition metal series[5].

The statistical mechanical model employed is the cluster variation method (CVM)[6] in the tetrahedron approximation: nearest neighbor (nn) regular tetrahedron for fcc, irregular tetrahdron for bcc, comprising nearest and next nearest neighbor (nnn) lattice vectors. The CVM requires, as input, the energy of the completely disordered states $U_0{}^{\phi}$ for both lattices [$\phi=\alpha$(fcc), $E=\beta$(bcc)], representing the infinite-temperature state frozen in at absolute zero. The quantity $U_0{}^{\phi}(c)$, function of the atomic concentration of B ($c=c_B$), is evaluated in the single-site coherent potential approximation (CPA)[7]. The required Green's functions are calculated by the recursion method[8,9]. The CVM further requires, at the very least, in the tetrahedron approximation used here, nn effective pair interactions $V_1{}^{\alpha}$ in the fcc case, and $V_1{}^{\beta}$(nn), $V_2{}^{\beta}$(nnn) effective pair interactions in the bcc case. These concentration-dependent interactions are obtained by the generalized perturbation method (GPM) of Ducastelle and Gautier[10]. Relevant formulas are given elsewhere[3,9].

Minimization of the CVM free energy must be performed for the disordered phases and also for various expected ordered superstructures of the parent

lattices. Ordered superstructures of fcc are designated as α', α'', ...,
superstructures of bcc are designated as β', β'', ... For the scheme of pair
interactions used here, the ground states of order (superstructures) are fully
known[11],[12]: the $L1_2$ (Cu$_3$Au prototype) and $L1_0$ (CuAu I prototype) structures
are possible candidates for fcc, and the B2 (CsCl), B32 (NaTl), and DO$_3$(Fe$_3$Al)
structures for bcc.

Phase diagrams (AB) were calculated for N_A = 3, 4, 5 and N_B = 7, 8, 9 d
electrons per atom and for diagonal disorder values δ_d = 0.6, 0.8, and 1.0.
Here, only the case N_A=3, N_B=8 will be examined. The reason for that
particular choice is as follows: recent LMTO electronic band structure
calculations[13] have shown that, across transition metal series, the number of s
electrons in elemental crystals remains approximately constant at about 1.3.
Hence, the case (3,8) corresponds roughly to a binary alloy with A = Ti, Zr, or
Hf, and B = Rh or Ir (the ferromagnetic Co element being excluded). Ordering
maps based on a rectangular DOS model[14] show that such binaries should
display ordering tendencies over the whole concentration range, making these
systems particularly interesting to study by the CVM. Only for the (3,8)
combination does the simple TB approximation used here predict bcc stability
for pure A and fcc for pure B. The value δ_d = 0.8 was selected because the
calculated phase diagram appeared to agree more closely with the
experimentally determined systems than did those obtained with δ_d = 0.6 or
1.0.

When the TB-CPA-GPM-CVM computations described briefly above were
carried out with the selected parameters, resulting $U_\alpha(c)$ curves for both fcc
and bcc disordered solid solutions had the expected shapes[3],[9] and so did the
$V_1^\alpha(c)$ curve (nn effective pair interaction for fcc as a function of
concentration). For bcc, the values of V_1^β and V_2^β varied strongly as a

function of c, probably as a consequence of performing the GPM calculation only to lowest order in the pair interactions. Nevertheless, the ratio V_2^β/V_1^β remained at values located between 0 and $^2/_3$, thereby guaranteeing relative stability of the B2 over the B32 superstructure[12].

When free energies of both fcc and bcc disordered and ordered phases were combined, the diagram of Fig. 1 was obtained. It is apparent that phase equilibria are dominated on the A (Ti) side by the bcc lattice, on the B (Rh) side, by the fcc lattice. The fcc + bcc ($\alpha+\beta$) two-phase region located at about 60% B must necessarily persist to infinite temperatures. In the center of the phase diagram, the B2 phase (bcc superstructure) overwhelms the L1$_0$ (fcc superstructure) for geometrical reasons: for dominant nn pair interaction, ordering is optimized in the bcc lattice (B2 ordered structure) whereas it is frustrated in the fcc lattice, the characteristic feature of that lattice being the equilateral nn triangle for which only AAB or ABB partial order can be achieved. The ordered B2 (β') phase is found in two regions of the diagram: somewhat off-center (50 to 60% B) and way off stoichiometry. That latter feature may well be an artifact of the type of approximation used here for calculating nn and nnn bcc pair interactions. Second-order transitions (dashed lines), allowed by the Landau rules, are predicted at the top of the central B2 region and between the disordered β and the strongly off stoichiometric β'. The α' superstructure (L1$_2$), located about the A$_3$B is separated from the parent disordered fcc (α) by first-order transitions, as expected. The locus of equality between the B2 and metastable L1$_0$ phases has also been plotted as a dot-dash curve in Fig. 1. The temperature scale was fixed by adopting the canonical d-band width of 5eV.

Available experimental data on the Ti-Rh and Ti-Ir systems have been examined recently by Murray[13] and the resulting "assessed" phase diagram

Zr-Rh and Zr-Ir are quite similar in their essential features. At first glance, theoretically (Fig. 1) and experimentally determined (Fig. 2) phase diagrams seem to differ significantly. It must be recognized, however, that the scope of the present computation is a limited one: only the two basic lattices, fcc and bcc were considered along with their allowed superstructures, i.e. a total of 11 possible phases was entered in the calculation. Out of these, the minimization procedure correctly predicts, at approximately correct location: the βTi phase, the βTiRh (β' in Fig. 1, correct B2 structure), and the TiRh$_3$ (α' in Fig. 1, correct L1$_2$ structure). The region marked "αTiRh" on the experimentally-determined phase diagram (Fig. 2) is separated from βTiRh by a dot-dash curve which pertains to a diffusionless transformation. It is known that αTiRh is a metastable phase, of uncertain crystal structure, but described generally as "distorted L1$_0$".

Experimentally observed, but imperfectly characterized phases Ti$_2$Rh (Laves phase), Ti$_3$Rh$_5$ and TiRh$_5$ could not be predicted by the present model since these phases have crystal structures not contained in the set of possible superstructures of fcc or bcc, and were therefore not included in the calculation.

The most flagrant shortcoming of the calculated diagram is, of course, the absence of liquid-phase equilibria. Here, for the sake of illustration, we constructed an empirical liquid free energy function, based on a sub-regular solution model[17] the parameters of which were fitted[4] to provide the correct pure Ti and pure Rh melting temperatures and the βTiRh congruent melting temperature. Experimentally determined[18] values of Ti and Rh entropies of melting were included. The fitted free energy was then combined with calculated crystalline phase free energies to produce the phase diagram of

Fig. 3. The agreement between theory and experiment is now much more striking.

In conclusion, we have shown that, with a canoncial TB scheme, it was possible to calculate a reasonable phase diagram for the Ti-Rh (or Ti-Ir) system. More importantly, we have shown that stable and metastable phase equilibria in this class of binary systems can be understood on the basis of competition between fcc and bcc solid solution tendencies, each lattice contributing its own set of candidate ordered superstructures. The model is currently being improved upon and will be tested on other systems.

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Figure Captions

Fig. 1   Calculated phase diagram for Ti-Rh-like binary systems.   The miscibility gap between fcc and bcc disordered phases persists to infinite temperatures (in the absence of melting).

Fig. 2   Assessed Ti-Rh phase diagram acording to Ref. 15.

Fig. 3   Phase diagram calculated as in Fig. 1 but with fitted free energy curve for the liquid phase included.   Phases are: L = liquid, α = fcc (disordered), α' = $L1_2$, β = bcc (disordered), β' = B2, α'' = $L1_0$ (metastable).

Fig. 1

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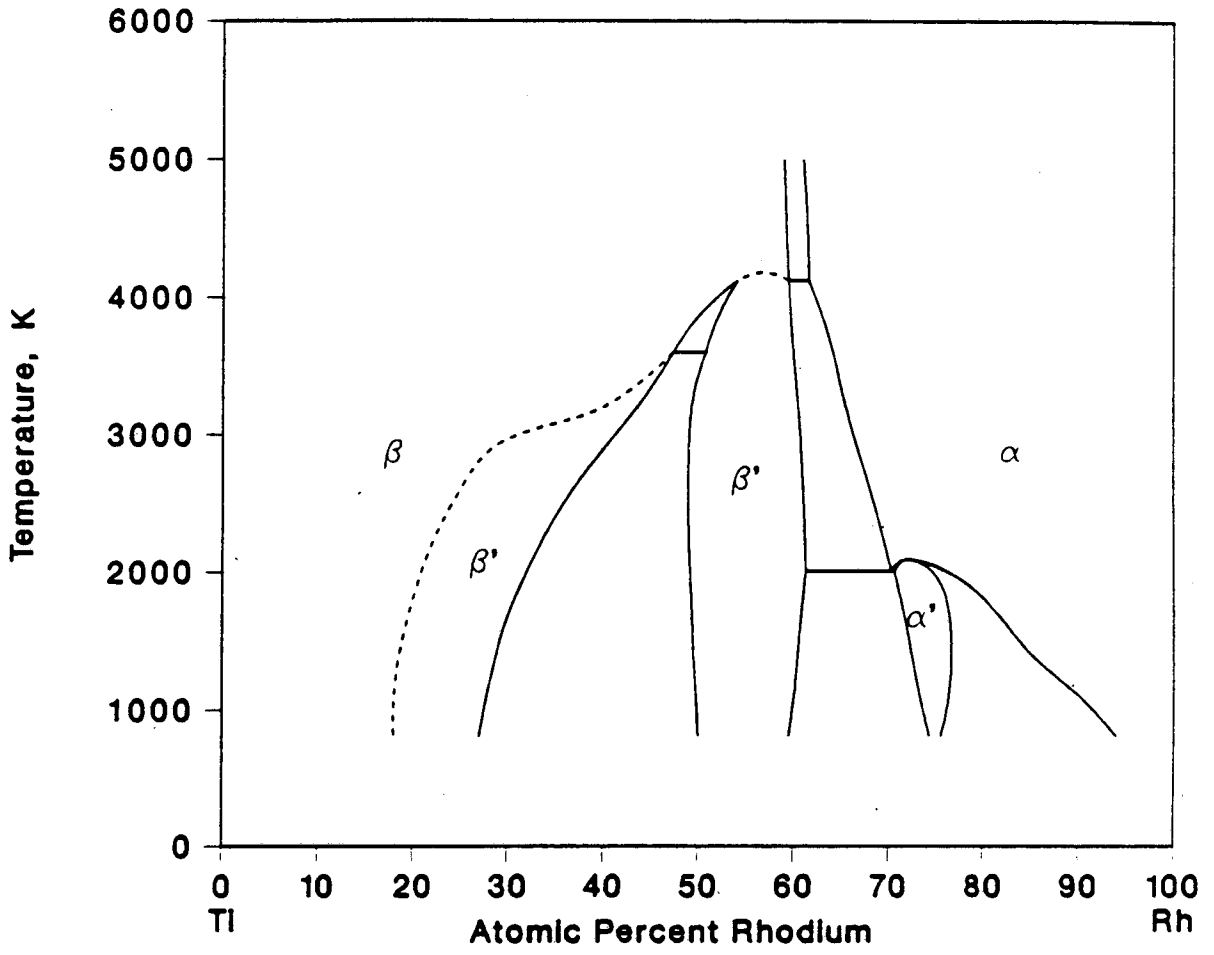
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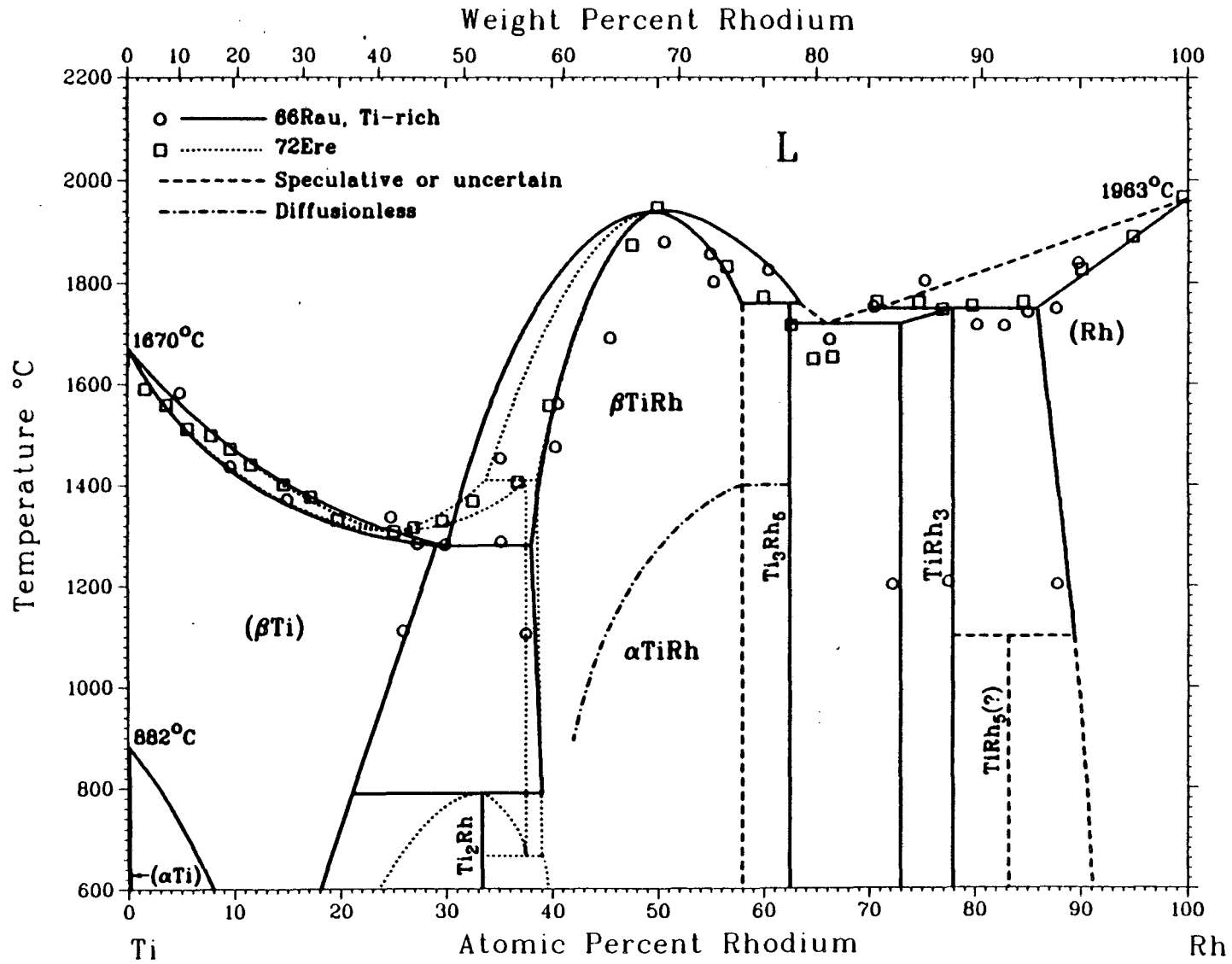
Fig. 2

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Fig. 3

XBL 875-2293