Structure of Palladium-Rhodium Alloys below Their Melting Points

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(Received 22 February 1993)

A new method for calculating the boundaries between two solid alloy phases has been developed. It is first principles in that the only input is the atomic numbers of the constituents, and differs from previous efforts in that no interaction potentials are introduced. It is used to calculate the miscibility gap in the palladium-rhodium phase diagram.

PACS numbers: 64.70.Kb, 71.55.Ak

The phase diagram of a binary alloy system is a two-dimensional plot that indicates the regions of concentration and temperature within which the alloy will exist in a particular phase after it has been allowed to reach thermodynamic equilibrium. Such diagrams are very useful in the development of special-purpose alloys, and it has long been a goal of condensed matter theorists to develop methods for calculating them from first principles. Of course, most binary phase diagrams have been measured and appear in handbooks, but a theoretical understanding of the electronic and statistical features that cause the alloy to exist in a particular phase is of interest in itself and is a first step in the understanding of ternary, quaternary, and higher order phase diagrams that cannot be found experimentally because of the overwhelming number of measurements that would be required. In this paper we describe a method for treating this problem that combines the coherent potential approximation for the electronic states and the Monte Carlo method of statistical mechanics in a novel way.

The coherent potential approximation (CPA) [1] has proven itself to be an excellent predictor of such global properties of metallic alloys as the delocalized one-electron states, Fermi surfaces, residual resistivities, magnetic properties, etc. Detailed predictions made with this theory for real alloy systems have been compared with experiment in a number of papers, and these papers have been reviewed in several articles [2-4]. The CPA gives the electronic states for the random substitutional alloy in which the probability for a particular type of atom appearing on a given lattice site is just the concentration of that constituent in the alloy. The theory says nothing about the partially ordered phase in which alloys can exist in certain regions of concentration and temperature, not to mention the inhomogeneous mixture of two phases which can be the structure of the alloy in other regions.

Efforts have been made to build on the successes of the CPA, but to go beyond its limitations. The CPA produces a heat of mixing for an alloy in a given phase at any concentration, a quantity that can be used in the modeling of the thermodynamics of phase diagrams. The generalized perturbation method (GPM) [5] produces effective pair, triplet, or higher order interaction potentials that can be used in an Ising-like Hamiltonian for a statistical-mechanical study of ordering in alloys. It is obtained from a perturbation theory with the CPA as the reference state. The Gyorffy-Stocks method (GSM) [6] extends the CPA to obtain correlation functions that predict the occurrence of short-range order and long-range order in alloys. These methods have been used with success in the study of alloy properties of great interest, but the accuracy with which they predict some phase boundaries can be improved upon.

The method proposed here is based on the observation that the crux of the Monte Carlo (MC) method for obtaining the equilibrium distribution of atoms in an alloy is a calculation of the energy required to replace an A atom on a particular site with a B atom when the configuration of atoms on the neighboring sites κ is specified, $\delta H_\kappa = E_B(\kappa) - E_A(\kappa)$. A random number z between zero and one is generated, and the atoms are interchanged on that site if $z < \exp(-\delta H_\kappa / 2k_B T)$. Conventionally, the interchange energies δH_κ are obtained from an Ising-like Hamiltonian using effective interaction potentials. We use another approach based on the embedded-cluster method (ECM) [7].

In the ECM, the electronic structure is calculated for an alloy with a specified arrangement of atoms on the atomic sites in the first few nearest-neighbor shells surrounding the central site. The effective scatterer calculated with the ordinary CPA for a particular concentration is placed on all the other sites. Calculations of the total energy for two such systems that differ only in that an A atom on the central site is replaced by a B atom leads to a direct evaluation of the δH_κ. For lack of a better name, we call this new approach the embedded-cluster Monte Carlo method (ECMC).

Palladium-rhodium alloys have the face centered cubic crystal structure for all concentrations and temperatures below their melting points. CPA calculations were carried out with a scalar-relativistic version of the Korringa-Kohn-Rostoker (KKR) CPA method [8] for three

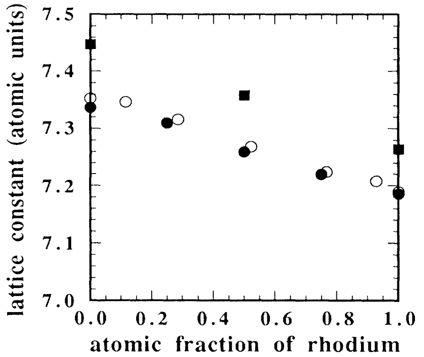

FIG. 1. The lattice constants of palladium-rhodium alloys as a function of the atomic fraction of rhodium. The solid circles are the calculations based on a scalar-relativistic version of the KKR CPA. The solid squares are calculations done with a nonrelativistic version of the KKR CPA. The open circles are the experimental measurements of Shield and Williams [9].

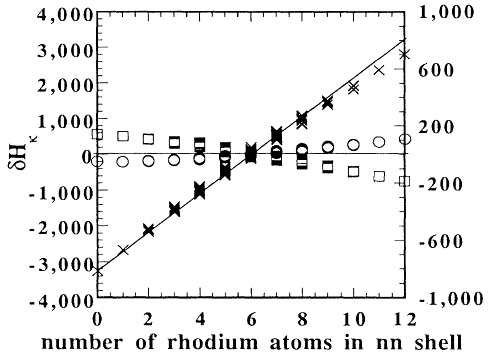

FIG. 2. The ×'s are the interchange energies for a 50% palladium-rhodium alloy plotted as a function of the number of rhodium atoms in the nearest-neighbor shell. The open circles are the interchange energies for the 25% alloy minus those for the 50% alloy, the values being read from the right-hand scale. The open squares are the interchange energies for the 75% alloy minus those for the 50% alloy, the values being read from the right-hand scale.

alloys with rhodium concentrations of 25%, 50%, and 75%. Six lattice constants were used with each concentration, for a total of eighteen self-consistent CPA calculations. From a plot of the total energies as a function of lattice constant, the equilibrium lattice constants can be found very accurately. Band theory calculations were used to obtain the lattice constants of pure palladium and rhodium. These lattice constants are compared with experiment in Fig. 1. The excellent agreement between theory and experiment is another example of the success that the CPA has in predicting global properties of alloys.

The clusters in our ECM calculations consist of the central site and its twelve nearest neighbors. There are 4096 configurations for the atoms in the nearest-neighbor shell, but, because of symmetry, it is only necessary to carry out calculations on 144 of them. Since it is required to do each calculation with an A atom and a B atom on the central site, 288 cluster calculations were done. The 144 different interchange energies, δH_κ, for the 50% alloy are shown in Fig. 2. They are the difference between the total energy of the crystal with an A atom and a B atom on the central site and a given configuration κ of atoms on the nearest-neighbor shell. We calculated these energies within the frozen potential approximation, which means that only the sum of one-electron eigenvalues was used. The amount that the δH_κ for the 25% and 75% alloys differs from the δH_κ for the 50% alloy is quite small (note the change in scale in Fig. 2) but it affects the phase boundary in an important way. The δH_κ for any concentration of interest can be found by interpolation.

The reason that the δH_κ are plotted as a function of the number of rhodium atoms in the nearest-neighbor shell, $n_{\rm rh}$, is that they are a linear function of $n_{\rm rh}$ for the frequently studied Ising model with only nearest-neighbor pair interactions. The inclusion of longer-range pair interactions will simply broaden the line. By comparison with the straight line shown in Fig. 2, it can be seen that the δH_κ calculated in the ECMC are not symmetrical about $n_{\rm rh}=6$. The other obvious point is that there are several values of δH_κ for a given $n_{\rm rh}$ because they depend on the precise configuration κ.

These δH_κ were used in a grand canonical Monte Carlo calculation on a sample made up of 55 296 atoms to obtain the phase boundary that is compared with experiment [9] in Fig. 3. The Monte Carlo calculation is of a standard form [10], although the asymmetry of the δH_κ introduces some difficulties that are not considered in the literature. The slope of the δH_κ vs $n_{\rm rh}$ curve has the gen-

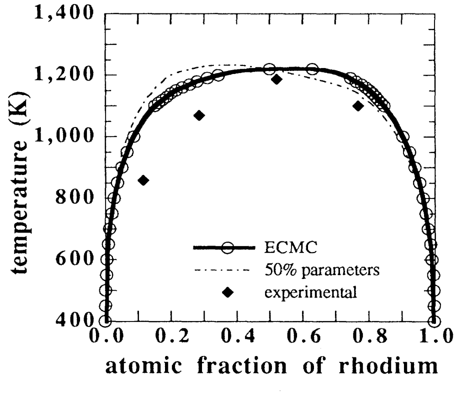

FIG. 3. The phase boundary for the palladium-rhodium alloy system calculated with the ECMC is shown by the solid line, which is a cubic spline fit to the Monte Carlo results indicated by open circles. The temperatures at which four samples with the indicated concentrations were observed to undergo transitions to the two-phase region by Shield and Williams [9] are shown by the diamond-shaped points. The light dash-dotted line is the phase boundary calculated with interchange energies for the 50% alloy.

eral form that in a magnetic analogy would correspond to a ferromagnetic interaction. In an alloy, this means that the constituent atoms prefer to be surrounded with atoms of their own kind. For this reason, the shape of the boundary shown in Fig. 3, called a miscibility gap, was expected. Above the boundary, the system exists as a homogeneous substitutional alloy, while within the boundary, it exists as a mixture of two phases. One phase is a palladium-rich substitutional alloy and the other is rhodium rich, the concentrations for a given temperature being the boundary points on the miscibility gap. The amounts of the two phases depend on the concentration of the alloy, and are given by the lever rule. The highest point on the calculated miscibility gap has a temperature T_c of 1220 K, which can be compared with the highest transformation temperature observed experimentally, 1190 K.

If the concentration dependence of the interchange energies is ignored and the phase boundary is calculated with the δH_κ for the 50% alloy shown in Fig. 2, the consequence of the asymmetry in these parameters when viewed as a function of n_{rh} is that the highest point on the miscibility gap is on the palladium-rich side, as can be seen from Fig. 3. When the concentration dependence of the δH_κ is included in the calculation, the peak of the miscibility gap is on the rhodium-rich side, which agrees with the experimental determinations [9]. The primary reason for the ultimate shape of the curve is the change in the lattice parameters with concentration shown in Fig. 1. The excellent agreement between the ECMC theory and experiment is clear from Fig. 3. The meaning of the asymmetry in the miscibility gap is that, in the two-phase region, the concentration of rhodium in the palladium-rich grains is greater than the concentration of palladium in the rhodium-rich grains.

Several other calculations of this miscibility gap have been reported in the literature. The Gyorffy-Stocks method [6] predicts a boundary that has its maximum on the palladium-rich side, and its highest point at a T_c that is about 330 K higher than ours, which makes it 360 K higher than experiment. Calculations using effective pair interactions obtained with the generalized perturbation method [5] give a miscibility gap with a maximum near 30% rhodium, and a T_c about 380 K above ours [11]. A theory based on the heat of mixing from the CPA and the ideal entropy of mixing produces a curve that has a peculiar shape [11]. If the one point that appears to be a mistake is ignored, it gives a T_c that is about 160 K higher than ours. Finally, the Conolly-Williams method [12], which obtains interaction potentials by fitting to calculated total energies of several ordered structures, gives a rather symmetrical miscibility gap with a T_c about 130 K higher than ours [13].

The present authors have published a description of the ECMC with some preliminary calculations [14], and also a calculation of the palladium-rhodium phase boundary based on a nonrelativistic version of the KKR CPA and ECM [15]. It can be seen from Fig. 1 that the quality of the total energy calculations and hence the predicted lattice constants is improved considerably in the scalar-relativistic case. The gross features of the miscibility gap were not changed so much, but the earlier calculations predicted a miscibility gap with its peak on the palladium-rich side. The reason for this is that, although the self-consistent KKR CPA calculations were done for 25%, 50%, and 75% alloys, the lattice constants were all kept fixed at the value for the 50% alloy shown in Fig. 1. The T_c obtained in these nonrelativistic calculations is about 40 K higher than the present one. A calculation of the miscibility gap for the copper-nickel alloy system was also reported in the earlier paper [15]. It is qualitatively correct, but the experimental situation for that alloy is not clear at the present time.

There are many reasons for incorporating the concentration dependence of the interchange energies in calculations of this sort. An obvious one is it guarantees that the correct average lattice constants are used in the calculation of the δH_κ. This is the most fundamental manifestation of the atomic size effect and can be important, as was demonstrated in the previous paragraph. Another reason is that the change with concentration of the Fermi energy, which is the chemical potential for the electrons, must be included.

For those who are accustomed to considering pairwise atomic interactions, the calculations reported here include certain of these up to fourth nearest-neighbor distances. For those who consider triplet, quadruplet, . . . , interactions, these calculations include up to dodecatuplets. A better way of looking at this theory is that it incorporates a different point of view concerning the features of the environment of an atom in an alloy that are important in determining the magnitude of the interchange energy. It should also be emphasized that the atomic interactions between the central atom and the atoms outside of the nearest-neighbor shell are not being ignored. They are treated statistically within the coherent potential approximation, which appears to do this successfully for the alloys we have treated so far.

The excellent agreement between our predicted miscibility gap and the experimental measurements gives us considerable confidence that we are proceeding in a promising direction. It can be pointed out that the palladium-rhodium system is a particularly simple one. It is one of the few alloy systems that does not show polymorphism, and there is relatively little transfer of charge or size disparity between the atoms. At the same time, there are many improvements that could be made in our ECMC to cope with more complicated systems.

The KKR CPA and ECM calculations described here make use of the muffin-tin approximation for the one-electron potentials. Although this will have little effect on a palladium-rhodium calculation, it would be desirable to remove this restriction in future calculations. Another extension of the theory that is relatively simple to implement is to use spin polarization to treat alloys that have magnetic phases. The frozen-potential approximation can be eliminated by going to the Harris approximation [16], and then to a calculation of the energy with no simplification beyond the local density approximation. These extensions are developmental in nature, and will not make the calculations more time consuming.

The inclusion of more nearest-neighbor shells in the embedded-cluster and Monte Carlo calculations is straightforward, and there is no difficulty in principal in allowing atoms in the embedded cluster to move off their average lattice sites to treat size effects. These improvements will also allow the effects of charge transfer to be included for the systems in which it is important, but they do increase the amount of computer time required for the calculations.

ECMC calculations are not computer intensive on the scale of some of the first-principles molecular dynamics calculations that are being done today, but they do strain the limits of conventional vectorized supercomputers. It would have been quite difficult to finish the calculations described here so soon without the availability of a massively parallel supercomputer.

This work was supported by the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Sciences, under Grant No. DE-FG05-89ER45392 and Subcontract No. DE-ACO5-84OR21400 with Martin Marietta Energy Systems, Inc., and by the Federal High Performance Computing and Communications program, Applied Mathematical Sciences Program, Office of Energy Research. We had help from the Southeastern Universities Research Association, Inc. (SURA). We made use of the Cray YMP computer funded by the DOE at Florida State University and the Intel iPSC/860 massively parallel supercomputer at the Oak Ridge National Laboratory. We received help in modifying our programs for parallel calculations from Dr. W. A. Shelton. We would like to acknowledge the contributions of Dr. Shelto and also Dr. F. J. Pinski, Dr. D. D. Johnson, and Dr. D. M. Nicholson in the development of the initial complex-lattice, scalar-relativistic, KKR CPA code on which our ECM was based.

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