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P.E.A. Turchi
M. Sluiter
G. M. Stocks

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A COMPARATIVE STUDY OF SHORT RANGE ORDER IN Fe-Cr AND Fe-V ALLOYS AROUND EQUIATOMIC COMPOSITION

P.E.A. TURCHI¹, M. SLUITER¹ AND G. M. STOCKS²

1. LLNL, Condensed Matter Division, P.O. Box 808, Livermore, CA 94550

2. ORNL, Metals and Ceramics Division, P.O. Box 2008, Oak Ridge, TN 37831-6114

ABSTRACT

Configurational energies have been calculated for equiatomic Fe-Cr and Fe-V alloys possessing the high temperature bcc crystalline structure, within a first principles electronic band structure approach. In agreement with experimental facts, a tendency towards order, with a B2 ordered structure of CsCl type, is found for FeV whereas phase separation characterizes FeCr. These results suggest that the nature of short range order in the high temperature bcc solid solution is not the primary driving force for describing the structural transformation from bcc to sigma which takes place in both alloys upon decreasing temperature.

INTRODUCTION AND METHODOLOGY

It is well known that both Fe-Cr and Fe-V alloys exhibit a structural transformation from a bcc solid solution to a complex Frank Kasper phase, of sigma (or D8_b) type, in a broad range of concentration around equiatomic composition, upon decreasing temperature [1]. Hence, precursor phenomena taking place in the high temperature phase which could assist and explain such structural transformation are of particular interest. These phenomena address the more general problem of phase formation of alloys based upon complex structures. Among the potential precursors, one can mention chemical short range order and local atomic displacements. With this primary motivation in mind, we report in this paper a preliminary study of the tendencies towards order or phase separation for the two selected bcc-based alloys at equiatomic composition. Because we will mostly concentrate on high temperature behavior, well above the extrapolated line of magnetic transformation in the bcc phase (estimated at 350 K and 540 K for FeV and FeCr respectively), we will ignore short range order associated with magnetic interactions. In other words, for alloys either maintained at high temperature or quenched from high temperature, correlations due to magnetism are supposed to be negligible.

Our study is based on the generalized perturbation method (GPM) [2] applied to the Korringa-Kohn-Rostoker (KKR) multiple scattering formulation of the coherent potential approximation (CPA) [3]. This treatment allows us to express the

ordering energy of an alloy, that is the energy difference between a particular atomic configuration and the chemically random state (as described by the CPA) in terms of pair and multi-site interactions. To lowest order in perturbation, the ordering energy of an alloy $A_{1-c}B_c$ takes, at $T = 0$ K, the simple form:

$$\Delta E_{\text{ord}}(\{q_s\}) \approx \sum_s q_s V_s, \quad q_s = \frac{c}{2} (n_s^{\text{BB}} - c n_s) \quad (2)$$

where n_s^{BB} and n_s refer to the number of BB pairs and total number of pairs associated with the s -th neighbor shell, respectively. V_s is an s -th neighbor effective pair interaction (EPI).

As clearly justified from electronic structure calculations, this ordering energy is driven by a Hamiltonian of the Ising type with interactions which are concentration dependent. Once these EPI are known, it is a simple matter to find the most probable ground state at $T = 0$ K by referring to ground state studies of the Ising model. For bcc-based systems, the most complete results were established for interactions extending up to the fifth neighbor shell (with $V_4 = 0$) [4].

RESULTS

For both systems, the electronic structure calculations were performed on the basis of charge self-consistent KKR-CPA potentials, up to an angular momentum index equal to 3. The total DOS of FeV and FeCr bcc-based disordered alloys, displayed in Figure 1, show very similar features and weak disorder broadenings as expected from a tight binding picture [5]. In other words the main difference, if any, between both alloys, comes from a difference in the average number of valence electrons, N , i.e. in the location of the Fermi energy E_F . Both alloys exhibit a very small charge transfer from V (Cr) to Fe of about 0.11 (0.07) electron, consistent with the proximity of the species in the periodic table.

Figure 1 Total DOS (solid curve) and average number of valence electrons N (dashed curve) of: a) $\text{Fe}_{50}\text{V}_{50}$ and b) $\text{Fe}_{50}\text{Cr}_{50}$. E_F is the actual Fermi energy.

The EPI were calculated within the KKR-CPA-GPM framework [3]. The results are summarized in Figure 2. It is clear that the EPI converge fairly rapidly as a function of distance and indicate distinct behaviors as far as ordering tendencies are concerned. Indeed, with these EPI and the ground state properties of the Ising model [4], the following conclusions can be drawn: FeV exhibits a clear tendency towards order with a B2 superstructure of CsCl type, whereas FeCr shows a tendency towards phase separation.

Figure 2 EPI (in mRy/atom) as a function of distance (in units of the bcc lattice parameter) for Fe₅₀V₅₀ (---O---) and Fe₅₀Cr₅₀ (---□---).

The ordering energy of the B2 superstructure of FeV, at T = 0 K, given by:

$$\Delta E_{\text{ord}}^{\text{B2}} \sim -V_1 + \frac{3}{4}V_2 + \frac{3}{2}V_3 - 3V_4 + V_5 + \frac{3}{4}V_6 + \dots \quad (3)$$

is of the order of -8.25 mRy/atom, a value relatively high compared with theoretical evaluations for other B2 alloys (CuZn: -2.70; NiTi: -5.71; NiAl: -22.05) [6]. These results, although established for non magnetic alloys confirm previous theoretical findings obtained for the corresponding magnetic systems, with a tight binding approach [7]. Along this line, it would be interesting to know more about the interplay between chemical and magnetic orders in these alloys. In any case, we believe our calculations, performed for the non magnetic case, take reasonably into account an experimental situation, as discussed in the introduction.

In order to understand in more details the origin of the difference in behavior between FeV and FeCr, we present in Figure 3, the EPI as a function of N. The calculations were performed according to the frozen potential approximation [6]. Although the general trend as a function of N is quite similar for both alloys, the amplitude of variation of the EPI, especially V_1 and V_2 is much smaller for FeCr than FeV. This fact can be well explained in a tight binding framework where the first EPI (V_1 for fcc, V_1 and V_2 for bcc) vary with δ^2 , δ being a measure of the

diagonal disorder effect which typically translates in a difference of numbers of valence electrons, ΔN , of the alloy species [8]. Thus, combining this ΔN effect with an increase in N from FeV to FeCr, it is then natural to find that FeV orders whereas FeCr phase separates.

Figure 3 EPI up to fifth neighbor shell (in mRy/atom) as a function of the average number of valence electrons, N , for: a) Fe₅₀V₅₀ and b) Fe₅₀Cr₅₀.

As part of a general scheme devised recently [9], one can obtain, by using an appropriate statistical treatment, among other thermodynamical properties a reliable estimate of the critical order-disorder temperature T_c , or equivalently the location of the $\langle 100 \rangle$ ordering spinodal curve, associated with the transition $B2 \rightarrow \beta$ (bcc solid solution) for FeV. Similarly one can determine for FeCr the temperature T_s where the $\langle 000 \rangle$ clustering spinodal curve is located [8]. Statistical calculations were done with the so-called C-hierarchy of the cluster variational method [10], with the centered cube and octahedron of the bcc lattice as basic clusters. The results are summarized in the following table.

Table. Characteristic temperatures (in K) for Fe₅₀V₅₀ and Fe₅₀Cr₅₀. T_i and T_m are the transition temperature from bcc solid solution to σ (as determined experimentally [1]) and the magnetic transition temperature as estimated from experiments [1], respectively. T_c and T_s refer to the temperatures of the ordering and clustering spinodal lines, respectively.

Alloy	T _i	T _m	T _c		T _s	
			Expt	Theory	Expt	Theory
FeV	1525	350	973 [11] 1123-1153 [12]	1273		
FeCr	1094	540			900 [13] 950 [13]	906

Because both bcc-based alloys exhibit a stable sigma phase in the interesting range of temperature, no direct experimental determination of equilibrium phase boundaries involving the bcc structure can be invoked. Meanwhile a few experimental studies on the bcc miscibility gap of Fe-Cr point to a value of T_s in the range 900-950 K [13] in excellent agreement with our theoretical findings. For Fe-V, less effort has been put in the determination of the B2-disordered bcc phase equilibrium; nevertheless the studies based on resistivity measurements [11] and differential thermal calorimetry [12] indicate a critical transition temperature in the range 970-1150 K, slightly below the theoretical estimation.

CONCLUSION

This preliminary study based on the KKR-CPA-GPM approach to ordering mechanisms in substitutional alloys indicates a clear change from ordering to phase separating tendency when substituting Cr to V in Fe-based alloys. This trend confirms and emphasizes the importance of the average number of valence electrons in describing properly alloy phase stability [14]. Diagonal disorder effect driven by the difference in the numbers of valence electrons of the alloy species controls quantitatively the strength of the tendency. Estimated locations of ordering and clustering spinodal curves, as obtained from a proper statistical treatment, are in good agreement with suggested experimental findings.

Unless local chemical environments in the σ phase are very different in FeCr and FeV (an unlikely assumption), it seems that bulk properties of the high temperature parent phases, and in particular atomic short range order, do not represent the major driving forces in explaining the σ phase formation. To sustain

such argument, it was recently observed that in a bcc-based FeCr sample the collective atomic motion which precludes the σ phase formation initiates at the vicinity of the free surface [15]. This fact confirms previous observations done on a FeV sample [11]. Hence, it is suggested that a comparative study of surface properties in bcc-based FeV and FeCr alloys, both experimentally and theoretically is highly desirable in order to reveal the fundamental parameters which control the initial stage of the σ phase nucleation.

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