1. Introduction

Fe-Ni is a key system for different technologically relevant materials such as invar alloys, permalloys, inconel alloys, etc. From a fundamental point of view it is interesting for the peculiar interplay between chemical and magnetic ordering phenomena.

Fe-Ni phase diagram has been studied for more than a century. Nevertheless some uncertainty still affect low temperature phase relations mainly because of the difficulty in reaching stable equilibrium at temperatures lower than about 300°C. Atomistic calculators may complement experimental investigation of phase equilibria and thermodynamics, especially at low temperatures.

A recent critical assessment [2005Cac] pointed out the need for a complete re-evaluation of the system taking into account not only stable phase equilibria, but also metastable ordering equilibria, especially between fcc-based ordered structures. This is in progress and preliminary results have already been used in the thermodynamic assessment of the Fe-Ni-Ti ternary system [2007Cac].

The present status of the evaluation, also supported by new atomistic calculations, is presented and discussed.

4. Fe-Ni phases

Stable and metastable Fe-Ni phases modelled in this work are listed in the Table below. Liquid and bcc (c2-W, A2) have been modelled as disordered solutions. The disordered fcc (cP4-AuCu, A3) solid solution and the related ordered phases (cP4-AuCu, L10 and cP4-AuCu, L2) have been modelled as a single four sublattice phase where each sublattice corresponds to a different crystallographic site in the fcc lattice. In this way the different fcc-based structures result from the different occupancy of the four sublattices:

- (A)(A)(A)(A) cF4-Cu (A1)
- (A)(A)(A)(A) cP4-AuCu (A1)
- (A)(A)(A)(A) cP4-AuCu (L2)

Milling of several atomic species in the same sublattice can describe compositional variations in the same phase. This allowed us to correctly reproduce either first and second order transitions between ordered and disordered structures. Magnetic interactions in both bcc and fcc phases play an important role in this system and have also been considered.

5. Results: Thermodynamic modelling

Thermodynamic functions of the solid solution states have been calculated, corresponding to the magnetic (PM) and ferromagnetic (FM) states respectively. The important role of magnetism in this system is evident.

Enthalpy of formation of the solid phases at 0 K, reference states are A2-Fe and A1-Ni. The curves computed on the basis of the thermodynamic models are compared to the results of ab-initio ground state calculations. bcc ordered phases (B2, B3 and D03) have not been modelled yet.

Selected thermodynamic functions of the liquid phase compared to the available experimental information.

Thermodynamic functions of the disordered solid solutions (notice that only stable in a narrow Fe-rich composition range) calculated at 1330 K. They are compared to the available experimental data.

The present ab initio results are in agreement with previous calculations produced by several authors [2005Lec, 2005Mis, 2007Cac] using different methods. As evidenced in the Table, most binary Fe-Ni structures have been modelled as a single four sublattice phase where each sublattice corresponds to a different crystallographic site in the fcc lattice. In this way the different fcc-based structures result from the different occupancy of the four sublattices:

- (A)(A)(A)(A) cF4-Cu (A1)
- (A)(A)(A)(A) cP4-AuCu (A1)
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