A STUDY OF PHASE STABILITY IN INVAR Fe-Ni ALLOYS OBTAINED BY NON-CONVENTIONAL METHODS

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It is known that thermodynamic equilibrium in Fe-Ni alloys, ir composition at temperatures below 450 °C, is difficult to achieve because of the diffusion rate at low temperatures. One of the ways in which we car transformation which may be responsible for invar behavior is to i) materials of similar composition obtained by non-conventional meth allow the enhancement of diffusion at temperatures where atomic mobil the laboratory time scale; ii) materials which have been treated for of time (geological time scale) in the same temperature range, such meteorites. In this context we have studied the phase stability o in mecanically alloyed powders, ion beam mixed multilayers and in meteorites.

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I - INTRODUCTION

The invar alloys, which are based on the composition Fe-36% Ni, h zero thermal expansion coefficient over a substantial temperature ran high temperature properties and parameters (lattice parameter, elect magnetization and elastic moduli) show anomalies which have bee experimentally. These observations indicate that there is a phase inst Ni phase system at the invar composition. Several authors suggested a low temperature miscibility gap to explain the anomalies and have variety of phase diagrams for the Fe-Ni system.

The Fe-Ni phase diagram proposed by Romig and Goldstein in 198 showed two major phases, α and γ, and a two phase $\alpha+\gamma$ region. Using this phase diagram, for a typical invar alloy, heat treatment in the γ-phase occurs at 800 °C. The alloy will enter the two phase region at about 450 °C during the cooling process.

The low temperature portion of the Fe-Ni phase diagram was recen [2, 3] based on meteoritical evidence and electron irradiation of alloys. The authors concentrated on the composition range from 0 to 5 on temperatures below 450 °C (fig. 1). Both the stable and metastable p boundaries are defined. They observed an asymmetrical miscibility g metastable below 390 °C and is caused by the presence of a tricritical poin produced by magnetic interactions. One can apply this phase diagram di alloys of ~36 wt% Ni. This phase diagram is not simple and the low tem phase transformations are not still well understood.

The major experimental difficulty in studying these alloys is the rate of the Fe-Ni system at these low temperatures. As cooling occurs coefficient of Ni decreases, for example, from $5x10^{-16}$ cm^2s^{-1} at 600°C to $1x10^{-21}$ cm^2s^{-1} at 500°C . At 300°C it takes more than 10^4 years for one atomic jump to occur.

One of the ways in which we can study phase transformations whic responsible for invar behavior is to investigate materials of simi prepared by non-conventional methods which are known to enhance diffu allowing equilibrium to be reached in short times. So, to accelerate t equilibrium-like state we studied samples prepared by non-conventional as: i) Fe-Ni alloys in the form of fine particles prepared by mechani Fe-Ni multilayers in a very thin modulation ion bombarded with noble g Meteorites which contain Fe-Ni alloys slowly cooled after solidificat bodies for millions of years.

II - MECHANICAL ALLOYED FE-NI ALLOYS

Mechanical alloying (MA) is a a new technique of combining meta milling of elemental powders in a high energy ball mill under an ine It circumvets many of the limitations of conventional alloying and cr of metals or metal-non metal composites that are difficult or imposs by other means.

We used MA as an alternative method to prepare Fe-Ni alloys, sin grain refinement and produces great amount of lattice defects. There expect that MA can greatly enhance the diffusivity of the powders. T details are described in ref. [4] and in this Proceedings. The longes 90h and that powder was subsequently annealed at 350°C for different times. The composition of the powder after milling was checked by EDS, indicating

no detectable difference from the starting powder.

The phase separation process during the subsequent heat treatment by X-ray diffraction (XRD), Mössbauer spectroscopy (MS) and magne measurements.

The XRD patterns of the starting and milled (10 to 90h) powders s after 10h milling, a $Fe_{60}Ni_{40}$ alloy with fcc structure is formed as indicated disappearance of the diffraction peaks from the pure metals. The diffr the powder milled 90h does not show significant difference from that in both, the structure and the linewidth. The effective crystallite si for the two milled powders.

The MS of the starting powder and the ones milled for different h an alloying process in the initial stage of the milling showing se indicating a mixture of phases with different compositions. This is d interdiffusion, i.e., Fe diffuses in Ni matrix and Ni diffuses in Fe the coexistence of Fe-rich and Ni-rich alloys. This behavior is mechanically alloyed FeCr system. After 10h milling, an homogeneous formed and further milling does not change the alloy structure. This c the spectra of the powders after 10h milling. All of them have the hyperfine field (31T) and similar hyperfine field distribution, typica alloy (40%).

The powder milled for 90h was submitted to annealing at ~350°C (T_a) for different times (fig. 2). After 20h annealing, segregation starts to c appearance of a non-magnetic phase, a singlet (IS=-0.15 mm/s) that co fcc γ-phase with ≤30% Ni. After 100h annealing, segregation becomes more c with formation of a magnetic component (H=20T) superimposed to the no phase. This is an intermediate stage in which Fe concentration is lowe non-magnetic phase but is higher than that in the initial alloy. Afte the non-magnetic phase increases and the magnetic spectrum shows a structure. The spectrum can be fitted adding a component with H=29T ar mm/s. These parameters are typical of the Fe-Ni 50-50 ordered phase s $L1_0$. This seems to be a sign of formation of the ordered phase in t process.

Using MA as an alternative method we obtained a defective nano-c Fe-Ni disordered alloy which submitted to long annealing at 350 ^{o}C, showed phase segregation with formation of γ-phases fcc with different Ni composition [4].

III - ION - BEAM MIXED Fe-Ni MULTILAYERS

It is known that irradiation with energetic particles is an eff enhancing atomic diffusion in metals, thereby reducing the time requ phase equilibrium. Extensive studies have shown that Fe-Ni invars un segregation after enough irradiation (neutrons or electrons) to enhan It has also been found that the alloys with composition in the range callled invar anomalies occurs are those with the greatest response to

One of the alternative ways of achieving a state closer to thermodinamical equilibrium (which for this system means atomic orderi segregation), is to use ion bombardment in Fe-Ni multilayers.

We investigated the effect of noble gas (He, Ne, Ar and Xe) multilayers with nominal composition $Fe_{0.63}Ni_{0.37}$ through CEMS.

The Fe-Ni multilayers were prepared using e-gun source in a u
vacuum system at the Institute for Chemical Research, Kyoto University
during the deposition was better than $5x10^{-8}$ Torr. In these conditions it was produce
multilayers with total thickness of 1020 Å and a very thin modulation Λ = 3.3Å (Fe +
0.18Å Ni) or a nominal composition $Fe_{0.63}Ni_{0.37}$. The ion irradiations were done at th
HVEE 400-kV ion implantor of the Institute of Physics, Universidade Fe
Grande do Sul [6].

Typical CEMS spectra of films irradiated using Ne ions (70keV) ar
fig. 3. The as-deposited sample as well as the $5x10^{15}$ Ne/cm^2 irradiated sample,
display only the typical sextet of bcc alpha-phase. From $1x10^{16}$ Ne/cm^2 on, it is
clearly seen the formation of two γ-FeNi phases with different Ni composition
one corresponding to a magnetic phase atomically ordered - Fe50Ni50 -
QS=0.15 - 0.20 mm/s) and another one corresponding to a non-magnetic p ≤ 30
at.%. With increasing doses the ordered phase increases up to 18% wh
magnetic component presents a remarkable enhancement up to 10^{17} ions/cm^2,
accounting for 40% of the spectrum at this dose $\sim$ 50%. An increase of the doses
did nor lead to any alteration of the spectra, suggesting that there is

The same effect but less effective was observed by irradiation
similar doses. The two phase region (ordered + non-magnetic), obtained
He irradiated samples, is the same already observed in particle irrad
[7] and meteorites [8,9], in which it has been considered as the equil

The non-magnetic phase formed by Ne irradiation shows an ins
vanishing completely when further irradiated with Xe. If we change
irradiation, first Xe and then Ne, phase segregation does not occur,
magnetic phase is not obtained and the CEMS spectra displays the same

of hyperfine fields produced by Xe irradiation, showing that the phas Xe predominates over the others.

Irradiation of Fe-Ni multilayers, in the invar region, with a se (He, Ne, Ar and Xe) allowed us to evaluate the formation/stability of formed by ion irradiation [6]. Our results can be interpreted as evi lighter ions (He, Ne) phase separation is obtained and equilibrium li system is achieved, whereas for heavier ions (Ar, Xe and Kr) the mi predominant.

IV - METEORITES

Meteoritic metal contains a unique complicated microstructure. observed that in slowly cooled meteorites their metallic microstructur by a series of complex phase transformations occurring below 400 ^{o}C. These microstructures can be observed in the 3 main groups of meteorites: meteorites = chondrites (from the mantle of parent bodies); b) in meteorites (from mantle/core interface or from collision mixing); a meteorites (from Fe-rich Fe-Ni cores of parent bodies).

The study of meteoritic metal is an attempt to determine the diagram experimentally. Meteoritic metal is basically an Fe-Ni alloy 5 to 60 at% Ni with small amounts (< 1 wt%) of Co, P, S, and C. Becau have cooled slowly over millions of years (1 to 1.000 million years) i bodies, meteoritic metal contains a characteristic structure whic completely duplicated in the laboratory due to the slow diffusion p temperatures. Therefore, meteorites are useful as indicators of the phase transformation which occur in Fe-Ni alloys. The microstructur

temperature phase transformation products in meteoritic metal are si
stony-iron and iron meteorites. Differences in the microstructure ar
function of cooling history at low temperature.

It should be noted that the metallic phases of meteorites, pro
temperature phase transformations, are sub-micron in size due to t
diffusivity of the system. Therefore for this particular phase equili
X-ray diffraction technique is of little use due to the crystallograph
resultant phases. Mössbauer spectroscopy, on the other hand has playe
in the meteorite work. In particular Mössbauer measurements gave the f
evidence for the existence of the superposition of a ferromagnetic a
$Fe_{50}Ni_{50}$ phase - tetraenite - (H= 29T; QS=0.20 mm/s) and a non-magnetic ph
with Ni ~30% (fig. 4).

The non-magnetic phase usually referred to as "paramagnetic ph
recently reported by Rancourt and Scorzelli [10] as a possible equilib
Fe-Ni system. We propose that this phase, with estimated composition
a low spin γ-Fe-Ni phase (γ_{LS}), that in synthetic irradiated alloys and met
always occurs in a fine epitaxial intergrowth with ordered FeNi. Sin
seen in coexistence with tetraenite (having different degrees of atomic orde
depending on the sample) it has been proposed that this γ_{LS} phase always occurs in
close microstructural association with tetraenite.

This phase is only observed by Mössbauer spectroscopy because tetraenite
(ordered FeNi) and γ_{LS} (proposed to be called antitaenite) have practically
indistinguishable lattice parameters. Therefore, the γ_{LS} phase is not readily observable
as a distinct phase by TEM or X-ray diffraction.

So, the proposed γ_{LS}/tetraenite intergrowth that is a common state in slow cooled iron meteorites, is present in metal particles of cho has also been observed in synthetic irradiated alloys, mechanically a and ion irradiated thin films, can be considered as indicative of the equilibrium state of Fe-Ni at the invar composition.

FIGURE CAPTIONS

Fig. 1 - FeNi phase diagram proposed by Reuter et al [2] based on the iron meteorite structure and electron irradiated alloys.

Fig. 2 - Mössbauer spectra at room temperature of 90h milled $Fe_{60}Ni_{40}$ alloy powders submitted to annealing at 350 °C for the indicated times.

Fig. 3 - CEM spectra of Fe-Ni multilayers: a) as deposited; and Ne i doses b) 5×10^{15} Ne/cm^2; c) 10^{16} Ne/cm^2; d) 5×10^{16} Ne/cm^2; e) 10^{17} Ne/cm^2.

Fig. 4 - Mössbauer spectrum at room temperature of the Santa Catharina

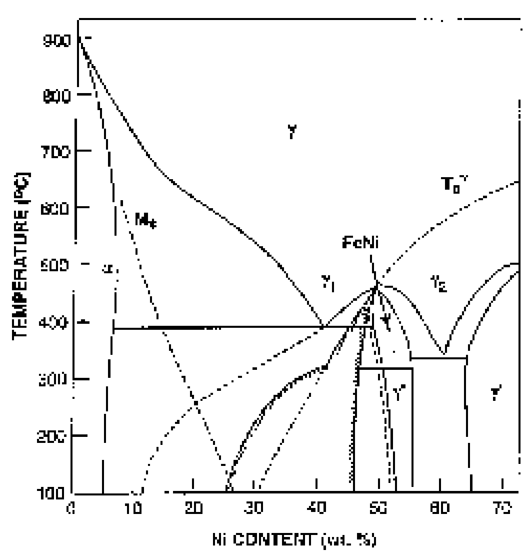

Figure 1

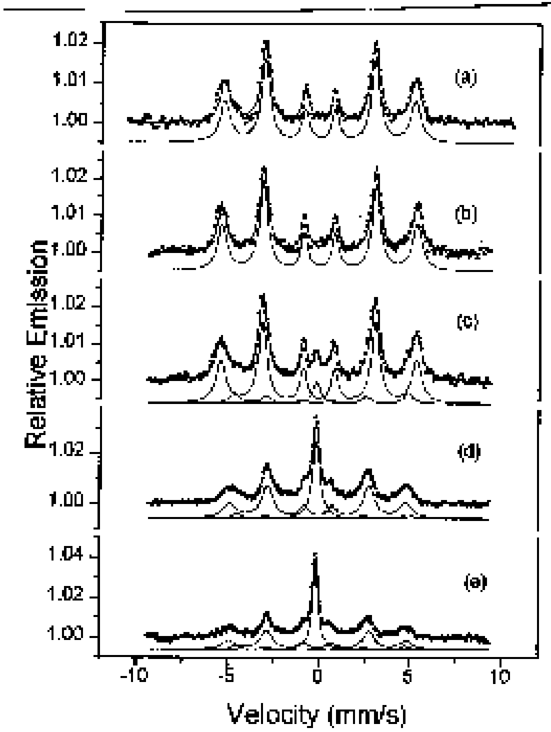

Figure 2

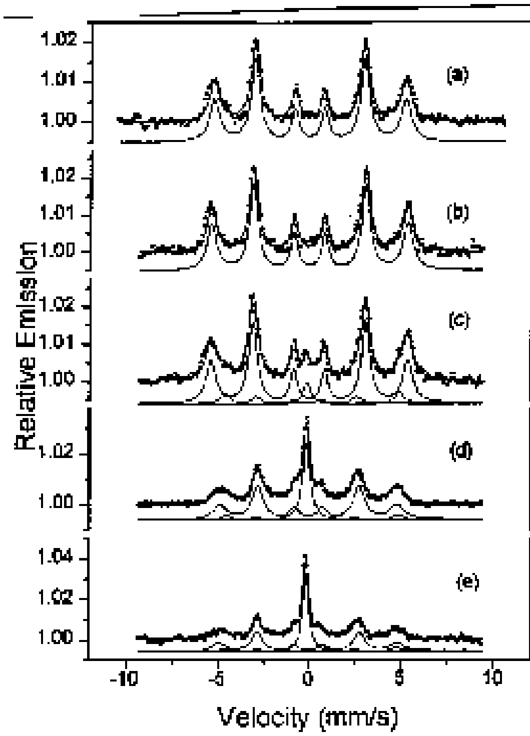

Figure 3

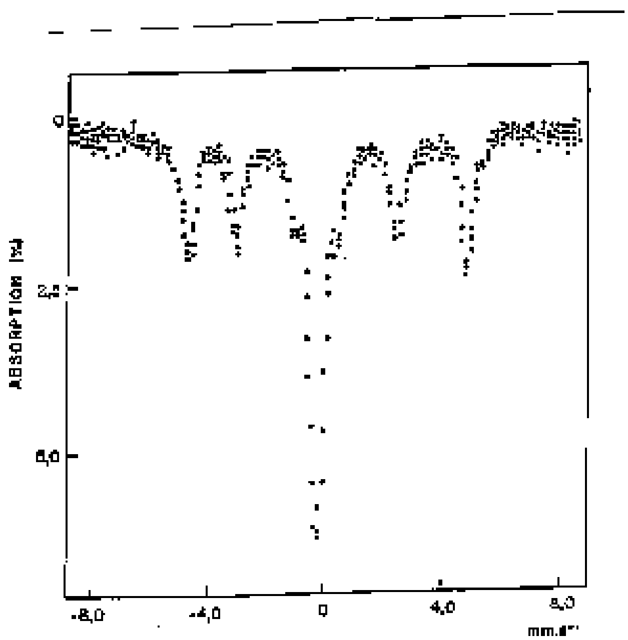

Figure 4

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