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COORDENADORIA DE CIÊNCIA E TECNOLOGIA DE MATERIAIS
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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11.049 (Pinheiros)
Cidade Universitária "Armando de Salles Oliveira"
SÃO PAULO — BRASIL

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ABSTRACT

The void formation in metals and alloys during irradiation with high energy particles is a problem of interest in Physics and of paramount importance in Nuclear Technology. Voids are formed as a consequence of vacancies and result in swelling as well as in changes of mechanical, electrical and magnetic properties of materials used in power reactor.

~~In this work~~ Isothermal annealings have been performed between 400 and 500°C with and without fast neutron (1 MeV) irradiation. Pure FeNi (50 – 50 at %) was irradiated in the Melousine reactor in Grenoble and FeNiMO (50 – 50 at % + 50 ppm) in the IEAR 1 reactor at the Instituto de Energia Atomica in São Paulo. The toroidal shaped specimens were fabricated from Johnson Mathey zone refined ingots and were initially annealed at 800°C during 1 h in hydrogen atmosphere and then slowly cooled (4 h) inside the furnace.

Magnetic After Effect Measurements (MAE) permitted the evaluation of activation energies during fast neutron irradiation (1.54 eV) and without irradiation (3.14 eV) for pure FeNi and respectively (1.36 eV) and (2.32 eV) for FeNiMo. Since the time constants of relaxation process are inversely proportional to the vacancies concentration a quantitative evaluation of vacancies supersaturation was made; it decreases from the value 730 at 410°C to the value 40 at 490°C for pure FeNi and from 765 to 121 for FeNiMo in the same temperature range.

INTRODUCTION

To improve the technology of the commercial fast reactors it is necessary to know the mechanism of the agglomeration of vacancies and consequently the mechanism of void formation in neutron irradiated materials at high temperatures. The first step consists in the study of the equilibrium concentration of vacancies with and without irradiation during isothermal annealings giving us informations about activation energies and influence of fast neutrons irradiations and impurities on the magnetic properties of FeNi alloys. In a metal at a given temperature, vacancies are created at a certain rate. The equilibrium concentration of vacancies is a function of temperature and is supposed to obey an Arrhenius type law.

Since vacancies supersaturation is a necessary condition for the formation of voids, some words must be said on the possible mechanisms of void formation during an irradiation. Vacancies occur in most metals and alloys with any type of irradiation that displaces atoms. Presently the experimental studies employ neutron, ion or electron irradiation, each of which has its advantages and disadvantages. Our samples were irradiated with fast neutrons with instant flux of 2,3 10^{13} n/cm^{2}sec at the Melousine reactor of the Centre d'Etudes Nucleaires de Grenoble and in core of IEAR 1 swimming pool reactor of the Instituto de Energia Atômica de São Paulo with an instant flux of 5.10^{12} n/cm^{2}sec. The agglomeration of vacancies is a function of number of atoms displaced and temperature.

Radiation produced voids were first detected in neutron irradiated stainless steel(2) and quickly

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(**) Instituto de Energia Atômica — São Paulo — Brasil

(***) Centre d Etudes Nucleaire de Grenoble — France followed by their discovery in other metals and alloys. The result of void formation is the swelling expressed as a relative volume change V/V, as well as in changes of mechanical, electric and magnetic properties. The effect of swelling becomes critical in commercial fast reactors and it is for this reason that there is an intensitive research effort in many countries trying to interpret the mechamisms of void nucleation and growth which are a consequence of radiation damage in solids.

Some basic ideas are now generally accepted, namely: void formation occurs at temperatures where both vacancies and interstitials are mobile. During a steady irradiation at a constant temperature an equilibrium state is reached in which the losses (annihilation) of point defects are equal to the creation rate, the rate of loss being proportional to point defect concentration and mobility. The mobility of interstitials being greater than that of vacancies, the interstitial concentration is generally lower than that of vacancies. For this reason the study of vacancies super-saturation must be made at temperatures high enough for vacancies mobility. At lower temperatures the vacancies lose their mobility and are annihilated by interstitials which are still mobile. On the other hand the annealing temperature must be low enough for the thermal concentration of vacancies be lower then that of radiation induced vacancy concentration. Otherwise there would be no supersaturation of vacancies. The temperature range for void formation in stainless steel, for fast neutron irradiation, is approximately 360 - 650°C(6). We admit the same temperature range for FeNi alloys vis a vis its mechanical similarity with stainless steel.

EXPERIMENTAL PROCEDURE AND RESULTS

The temperature range explored extends form 400°C to 514°C which corresponds to a typical temperature range (from 0.3 T_m to 0.5 T_m where T_m is the melting temperature) in which void formation was detected. In our specific experiment the temperature is limited by 514°C and 320°C respectively Curie point and Order disorder transformation temperature.

The mechanism which permits the detection of the vacancies movement is the establishment of *short range order. It is supposed that the migration of vacancies permits the reorientation of atom pairs* (E.G. FeFe NiNi or FeNi). The spontaneous magnetization commands this reorientation and progressively establishes the short range order which tends to materialize the geometry of the internal magnetic anisotropy. After demagnetization, during the relaxation process at a given temperature, the Bloch walls are agitated by a weak (~1mOe) alternating (35 Hz) magnetic field. As a consequence of this a progressive immobilization of Bloch walls occurs permitting the detection of an exponential decrease of the initial permeability. This is a well known experimental technique called Magnetic After Effect (MAE) and it permits an easy evaluation of the time constant and activation energy from the experimental curves of permeability disaccommodation(3) (5).

The directional short range order once established during an isothermal annealing must be completely destroyed before a subsequent annealing is made at a given temperature in sense to have reproducible experiments. The sample treatment obeys the following sequence:

a) the sample temperature is increased to a temperature above the Curie point where it is thermally demagnetized.

b) a demagnetizing alternating magnetic field is applied until the sample reaches the pre established annealing temperature, assuring thus the maintenance of the disorded state.

c) the annealing temperature once stabilized, the sample is demagnetized and a weak (~1 mOe) alternating (35 Hz) magnetic field is aplied which permits a reversible displacement of the *Bloch walls (Rayleigh region) and the measurement of the corresponding disaccommodation* process.

The samples with primary and secondary windings were placed in a device with a furnace having a controlled atmosphere which can be used for annealings out or inside the reactor core. The experimental apparatus is a classical set for MAE measurements, consisting basically of:

1 – Lock in amplifier
2 – Temperature regulator
3 – Annealing furnace with controlled atmosphere

The samples were of toroidal shape 0.3 mm thick, having an external diameter of 17.4 mm. The initial thermal treatment consisted of an annealing at 800°C during 1 hour in hydrogen followed by a slow cooling (~ 4 h inside the furnace. The samples were made at the Centre d'Etudes Nucleaires de Grenoble starting from metals refined by zone melting.

The time constants were calculated by means of the Brissoneau method(1),(2) from the most representative isothermal annealing. The initial permeability obeys the following phenomenological law,

$$\frac{\frac{1}{\mu} - \frac{1}{\mu_0}}{\frac{1}{\mu_\infty} - \frac{1}{\mu}} = 1 - e^{-\frac{t}{\tau}}$$

where

μ – initial permeability
μ_0 – initial value of μ
μ_∞ – final value of μ
t – time
τ – time constant of the disaccommodation process

Figure 1 shows the effect of vacancy diffusion during irradiation with fast neutrons. This particular behaviour of μ during irradiation induces a great relative error on the values of μ_0; on the other hand it is very difficult to obtain stable values of μ_{00} without irradiation. For instance, this fact made disregard an experimental point at 420° without irradiation of FeNiMo (50 – 50 at % + 50 ppm) due to the deterioration of a thermocouple which impeded the stabilization of M and hence the determination of M_{00}. The activation energy of FeNi (50 – 50 at %) without irradiation was also determined by the magnetic anisotropy method giving results comparable to the one obtained by MAE (fig. 2).

Assuming that the vacancy diffusion can be expressed by an Arrhenius law

$$\tau = \tau_\infty \, e^{\frac{Ea}{kT}}$$

where

τ_∞ – time constant at infinite temperature
E_a – Activation energy
T – temperature in °K
k – Boltzmann constant

and knowing that the relationship between the concentration of vacancies and the time constant is given by

$$\frac{1}{\tau} \propto C_{vac}$$

the ratio

$$\frac{\tau}{\tau_{irrad}} = \frac{C_{vac\ irrad}}{C_{vac}}$$

gives us a quantitative information about the supersaturation of vacancies.

Table 1 shows the activation energies, time constants, with and without irradiation as well as the vacancies supersaturation of FeNi (50 – 50 at %)

Table 1

FeNi (50-50 at %)

Temp. (°C)	τ (sec) $E_a = 3.15$ eV	τ irrad. (sec) $E_a = 1.54$ eV	Supersat. of Vac.
410	2.82×10^5	3.89×10^2	724.4
442	2.51×10^4	1.22×10^2	206.5
450	1.46×10^4	9.55×10	153.1
460	7.33×10^3	4.73×10	76.7
480	1.95×10^3	3.51×10	55.6
490	1.04×10^3	2.60×10	39.8

The same values for FeNiMo (50 50 at % + 50 ppm) are compiled on Table 2.

Table 2

FeNiMo (50-50 at % + 50 ppm)

Temp. (°C)	τ (sec) $E_a = 2.32$ eV	τ irrad. (sec.) $E_a = 1.36$ eV	Supersat. of Vac.
*410	4.63×10^4	61.00	764.75
420	2.63×10^4	44.10	596.37
440	7.86×10^3	21.90	358.45
460	3.16×10^3	12.89	245.15
480	1.19×10^3	7.34	162.12

The disparity of vacancies supersaturation behaviour seen on Fig. 3 cannot be explained in a simple way however the following must be taken into account. The Mo impurity atoms due to their large size cause distortions in crystal lattice and associate themselves with vacancies forming clusters which are not easily destroyed, thus producing an imbalance in the equilibrium concentration of vacancies. For pure FeNi (50 - 50 at %) the thermal vacancies concentration tends to the values of irradiation induce of vacancies concentration reducing in this way the superasaturation. In FeNiMo the Mo atoms somehow avoid the annihilation of the surplus vacancies produced during fast neutron irradiation giving as a result a higher supersaturation at high temperatures. It is interesting to point that even a small amount of an impurity (50 ppm) produces a noticeably different behaviour on the vacancies supersaturation curve (fig. 3). Presently experiments are perfomed on FeNiMo (49 – 49 – 2 at %) FeNiSi (49 - 49 – 492 at %) and FeNi (50 – 50 at % + 50 ppm) in sense to complement the informations of this work

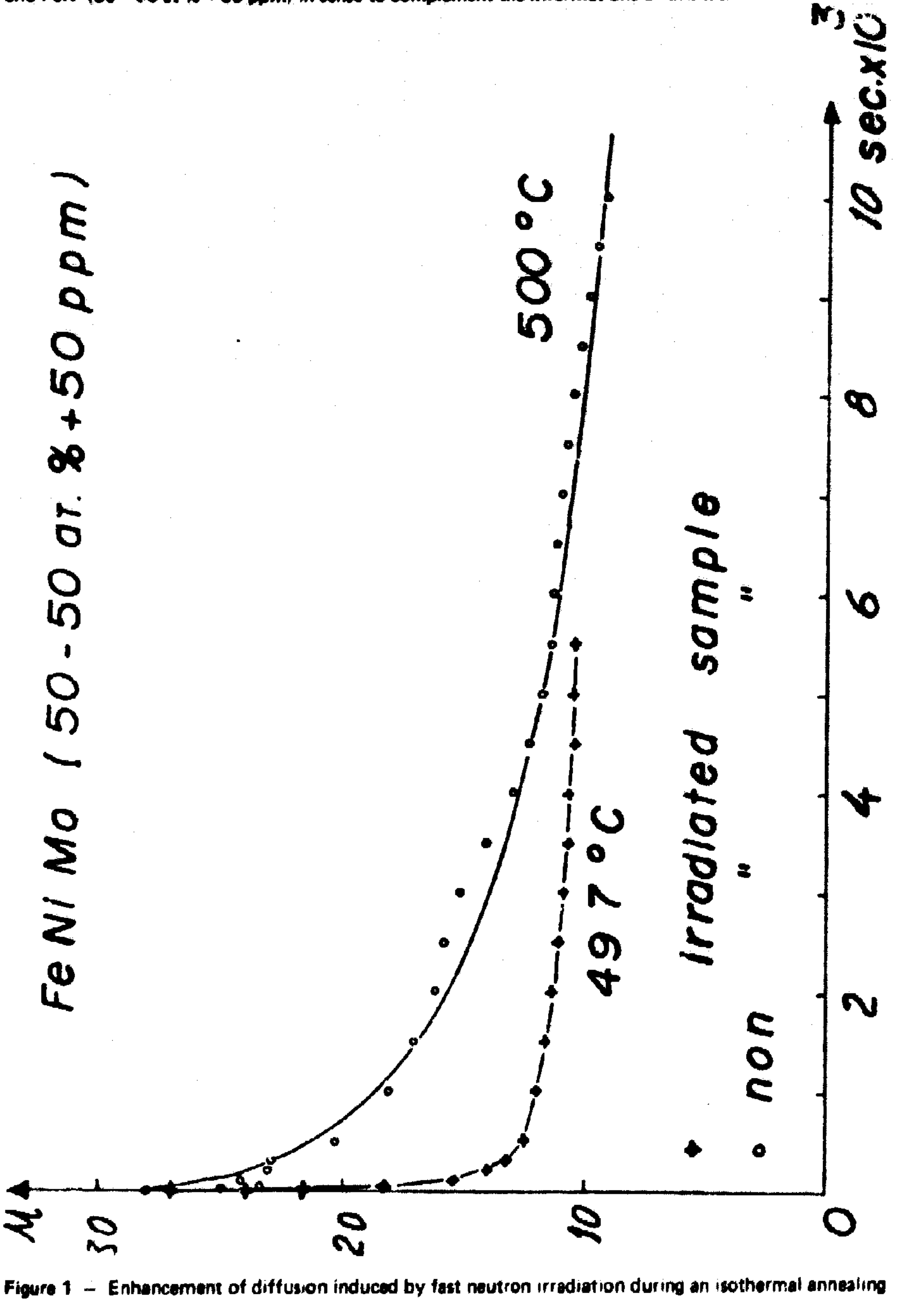

Figure 1 – Enhancement of diffusion induced by fast neutron irradiation during an isothermal annealing

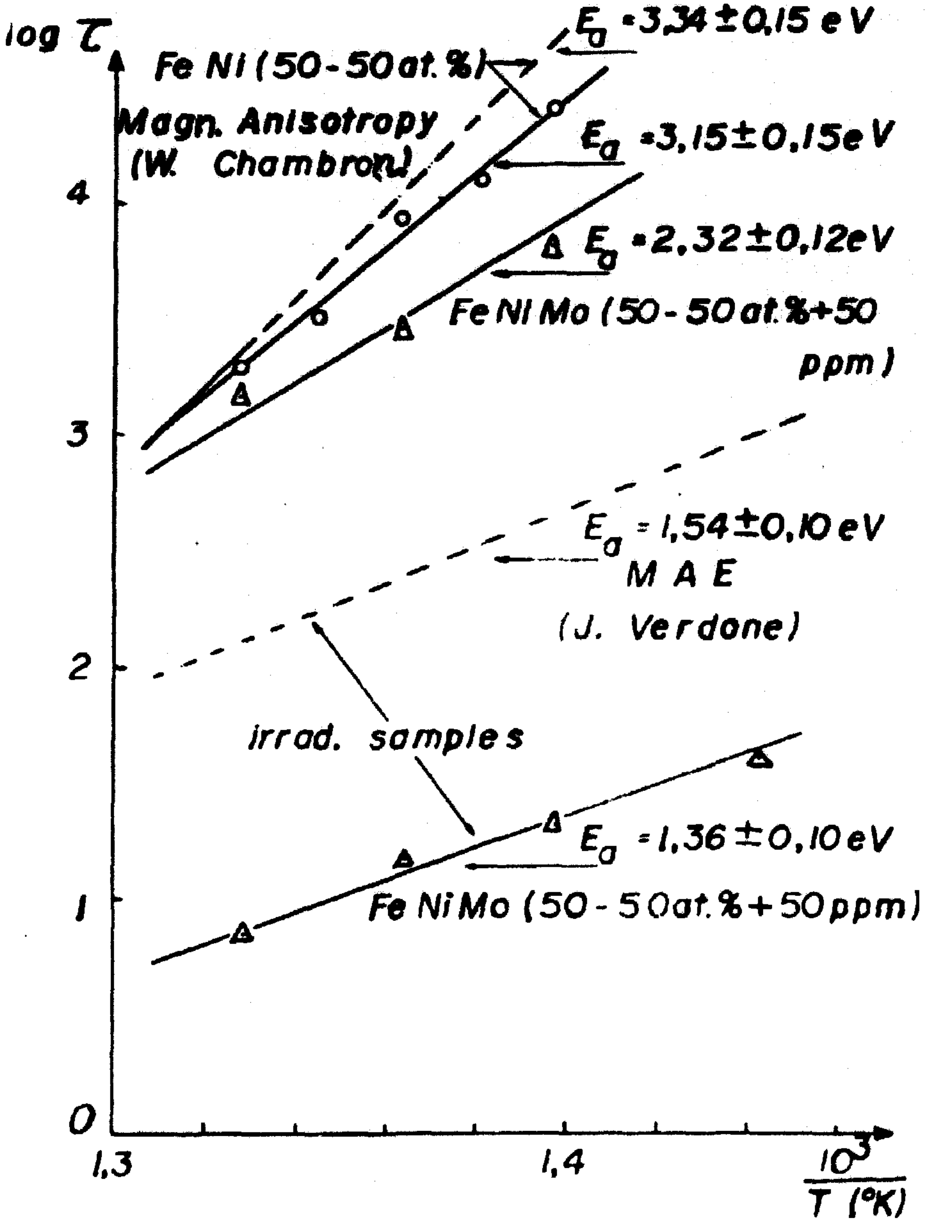

Figure 2 – Activation energies for FeNi (50 – 50 at %) and FeNiMo (50 - 50 at % + 50 ppm) with and without fast neutron irradiation

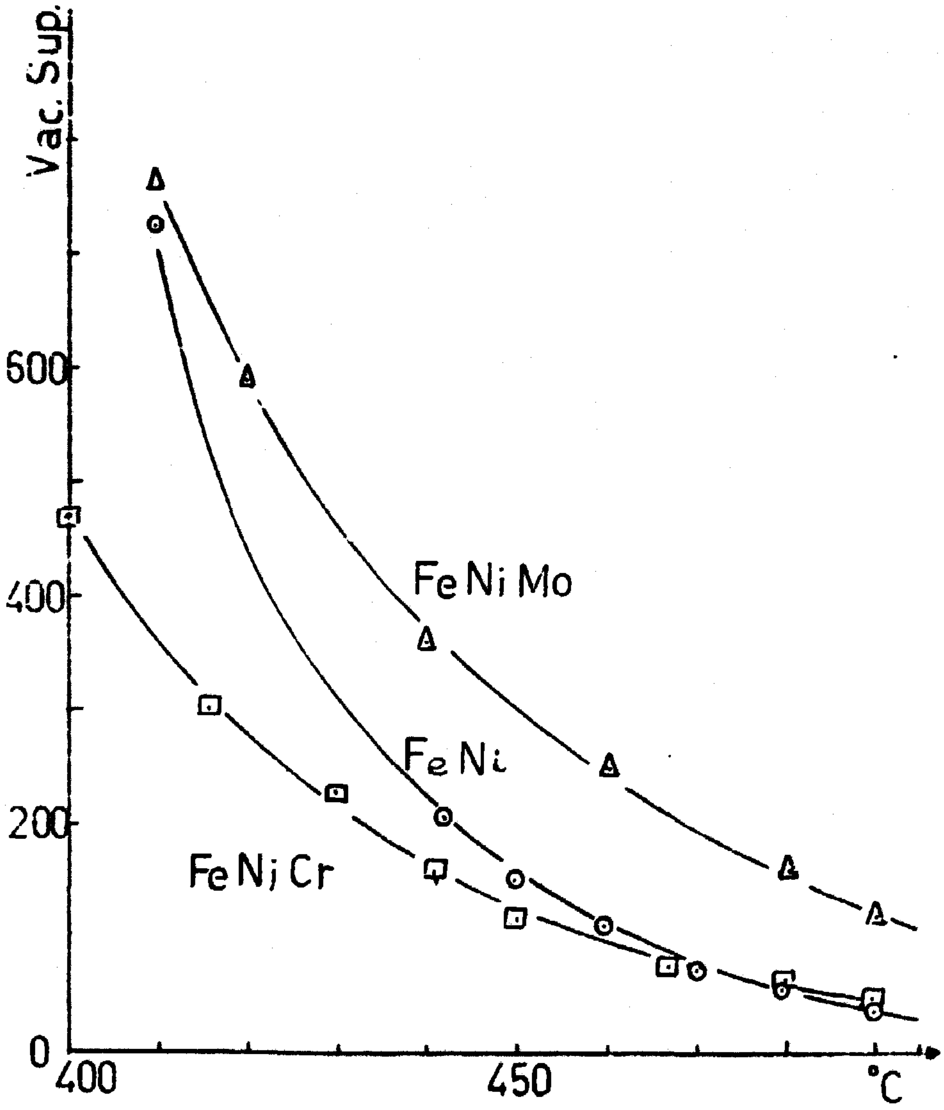

Figure 3 – Supersaturation of vacancies in FeNi (50 – 50 at %) and FeNiMo (50 – 50 at % + 50 ppm) in the temperature range of 410 – 490°C.

RESUMO

A formação de cavidades em metais e ligas durante uma irradiação com partículas de alta energia é um problema de interesse em física e de grande importância em tecnologia nuclear. As cavidades são formadas como consequência de aglomeração de lacunas e resultam em dilatação bem como na modificação de propriedades mecânicas, elétricas e magnéticas de materiais utilizados em reatores de potência.

Neste trabalho foram feitos recozimentos entre 400 e 500°C com e sem irradiação de neutrons rápidos (E ≥ 1 MeV). FeNi (50 – 50% at) puro foi irradiado no reator Melusine em Grenoble e FeNiMo (50 – 50% at +50 ppm) no caroço do IEAR 1 do Instituto de Energia Atômica, em São Paulo. As amostras de forma toroidal foram feitas de material fornecido pela Johnson Mathey refinado por fusão por zonas. O tratamento térmico inicial consistiu num recozimento a 800°C durante 1 hora em atmosfera de hidrogênio seguido de um resfriamento lento (4 h) dentro do forno.

As medidas do Efeito Magnético Posterior (EMP) permitiram a determinação das energias de ativação durante a irradiação neutrônica (1,54 eV) e sem irradiação (3,14 eV) para FeNi puro e (1,36 eV) e (2,32 eV) respectivamente para FeNiMo. Considerando que as constantes de tempo do processo de relaxação são inversamente proporcionais à concentração de lacunas, uma avaliação quantitativa da supersaturação lacunar pode ser feita: ela decresce do valor 700 a 410°C para 40 a 490°C para FeNi puro e de 765 para 121, para FeNiMo na mesma amplitude de temperatura.

REFERENCES

1. BRISSONNEAU, P. Le trainage magnétique. *J. Phys. Chem. Solids*, New York, **7**:22, 1958.

2. CAWTHORNE, C. & FULTON, J. The nature of small defects clusters. *Nature*, London, **216**:575, 1967.

3. MOSER, P. *Etude au moyen du trainage magnétique des défauts créés par irradiation dans le fer.* Grenoble, 1965 (Ph. D. Thesis)

4. NEEL, M. L. Anisotropie magnétique superficielle et sur-structure d'orientation. *J. Phys. Radium*, Paris, **4**:225, 1954.

5. ______. La théorie du trainage magnétique de diffusion. *J. Phys. Radium*, Paris, **5**:249, 1952.

6. NORRIS, D. I. R. Voids in irradiated metals (Part II). *Radiat. Effects*, New York, **15**:1-22, 1972.