RADIATION DAMAGE IN AUSTENITIC STAINLESS STEEL

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ABSTRACT

The purpose of this work is to contribute to the technology of fabrication and characterization of special stainless steels with Niobium additions by means of microhardness and electrical resistivity studies before, during and after fast neutron irradiation.

Effects of radiation in a wide range of temperatures in austenitic stainless steel of type AISI 321 with 0.05 and 0.1 wt.% Nb were investigated after neutron irradiation with fluences about 10^{17} n/cm^2 employing the Vickers microhardness testing technique, which is sensitive to the microstructure changes produced by irradiation, as well as thermal and mechanical treatments.

Our results indicate that radiation damage peaks occur around 480ºC for the austenitic stainless steel without Nb addition; around 500ºC with 0.05 wt.% Nb and around 570ºC with 0.1 wt.% Nb for the same material which is in agreement with the result obtained by means of electrical resistivity technique.

INTRODUCTION

There are some papers on the applications of Ni-Fe-Cr austenitic stainless steels at high temperatures (power reactor, electric light and power stations etc.) but little is repported about microstructure changes and consequently modifications in the mechanical properties of these material during irradiations. The mechanisms of hardening, corrosion resistance increase and of swelling under irradiation of steels are properties of interest in the nuclear technology.

This work is a contribution to technical developments of fabrication and characterization of special steels with Nb microalloying, employing the Vickers microhardness technique, which is sensitive to the microstructure changes produced by irradiation, as well as thermal and mechanical treatments. Although this technique presents empirical results these are usefull by the relation that can be established with other properties of interest such as electrical resistivity, and other which can be measured only by more expensive and complicated techniques[1].

The Nb additions in these type of steels can represent an advance in the properties of hardening, corrosion resistance, swelling resistance (under irradiation) and other mechanical properties.

The study of these properties allows us to analyze and forsee limitations in using these materials as well as to compare with electrical resistivity measurements before, during and after fast neutron irradiation, for a better material characterization.

MATERIALS AND METHODS

The material studied was an austenitic stainless steel of type AISI 321 from local production with the following composition:

Cr - 17.88 wt.% Ti - 0.39 wt.%

Ni - 11.02 wt.% C - 0.08 wt.%

The Nb came from the laboratories of University of Campinas - Brasil with the following characteristics:

a) Alumino-Thermal reaction of Nb_2O_5- CBMM-Cia. Brasileira Metalurgia e Mineração.

b) Six electrical beam melts in a vacuum of 10^{-5} torr in the last melt.

c) Analysis

Ag - 3ppm	Co - 40 ppm	O_2 - 105 ppm
Si - 35 ppm	Ta - 800 ppm	Mo - 35 ppm
W - 50 ppm	C - 80 ppm	S - 4 ppm
Ni - 10 ppm	Pb - 5 ppm	H_2 - 8 ppm
Sn - 3 ppm	Fe - 10 ppm	Mg - 3 ppm
B - 5 ppm	Ti - 5 ppm	Al - 40 ppm

The microhardness is defined by:

$$HV = P/A$$

where HV - microhardness
P - load
A - contact area

In the case of Vickers tetragonal pyramid

$$HV = 1854.4\ P/d^2$$

where P - applied load in grams-force (gf)
d - diagonal basis pyramid in μm
HV - microhardness in kilograms-force by square millimeters (kgf/mm^2).

A constant load of 25 gf was applied in the interior of the grains outlined by chemical etching and the corresponding diagonal of the pyramid basis indentation was measured with a Carl Zeiss, model III Photomicroscope. The microhardness was obtained from the average value of the pyramid diagonals measured for each sample.

The electrical resistivity was measured using the classical four wire method, on wireshaped samples.

EXPERIMENTAL PROCEDURE

Experimental facilities were developed at our laboratories for the fabrication of metallic alloys of nuclear interest, in laboratory scale.

Three lots of samples were prepared:

lot 1 - stainless steel of type AISI 321 without Nb additions;

lot 2 - stainless steel of type AISI 321 with 0.05 wt. % Nb;

lot 3 - stainless steel of type AISI 321 with 0.10 wt.% Nb.

The additions of Nb were made in an induction furnace at a temperature of 1450ºC in argon atmosphere.

The ingots of the three compositions were wiredrawn with 4 mm^2 cross section area and cut in pieces 2 mm long.

These materials were initially annealed at 1000ºC in argon atmosphere during 3 hours for normalization.

The main purposes of annealing and normalizing steel are the following:

1. improvement of the mechanical properties;
2. improvement of the machinability;
3. increasing ductility, particularly to restore the normal condition of steel after cold working;
4. to remove chemical non-uniformity;

5. to alter the microstructure and develop a structure more desirable for hardening[1];

6. to relieve internal stresses.

After the normalization process, all samples were exposed to thermal treatments, with and without fast neutron irradiations in the range of 300 to 700°C in argon atmosphere at a pressure of 1 atm.

The irradiations were performed in the core of the IPENR-1 reactor, with an instant fast neutron flux of $5 \times 10^{12} n/cm^2.s$. All integrated fluxes were of the order of $10^{17} n/cm^2$.

For the microhardness measurements the samples were polished and etched with "aqua regia" in the proportion as follows:

nitric acid - 1 part
chloridric acid - 5 parts
distilled water - 6 parts

Isothermal annealing were performed inside (in situ) and outside the reactor core, on square cross section wires (1 mm^2), during which the relaxation of electrical resistivity was measured. This parameter is extremely sensitive to structural changes, and permits "in situ" measurements where significant structure variations occur. In figure 1 isothermal relaxation kinetics can be seen at temperatures of 478°C (in situ) and 482°C after fast neutron irradiation. From a series of such relaxation curves the time constant τ, and ratios between them, were calculated to obtain the damage curves (τ_a/τ_d) as well as the supersaturation curves (τ_b/τ_d) where:

τ_a - time constant for a relaxation process after irradiation;

τ_b - time constant for a relaxation process before irradiation;

τ_d - time constant for a relaxation process during irradiation.

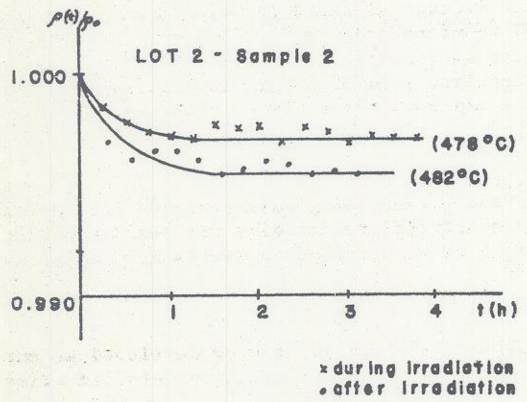

Figure 1 Kinetics of the samples from lot 2 (0.05 wt.% Nb), during and after irradiation.

RESULTS AND DISCUSSION

Microhardness Measurements

Althought the effect of Nb additions in the material properties is not directly observable, the microhardness and metallografic studies contribute to a better understanding of the effects and mechanism of precipitation in the samples irradiated with fast neutrons.

For the non-irradiated samples of the three compositions, no structural changes occur during the annealing time, as can be seen from figure 2.

In figure 3, for the irradiated samples, there is a range of temperature where vacancy supersaturation and the mechanisms of phase transformation and annealing out of deffects, provide a damage peak characterized by a minimum in the microhardness parameter, that are resultant from these processes alltogether.

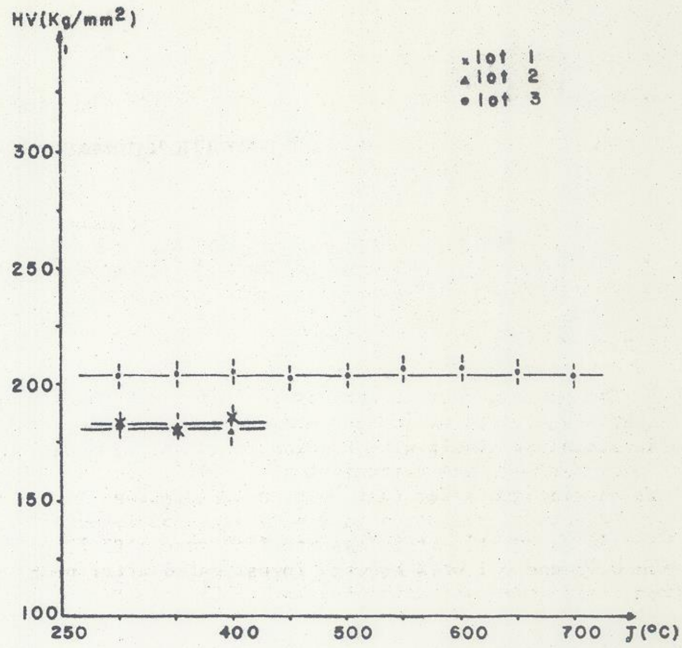

Figure 2. Microhardness vs. annealing temperature for the non-irradiated material (lot 1 - without Nb, lot 2 - with 0.05 wt.% Nb and lot 3 - with 0.1 wt.% Nb).

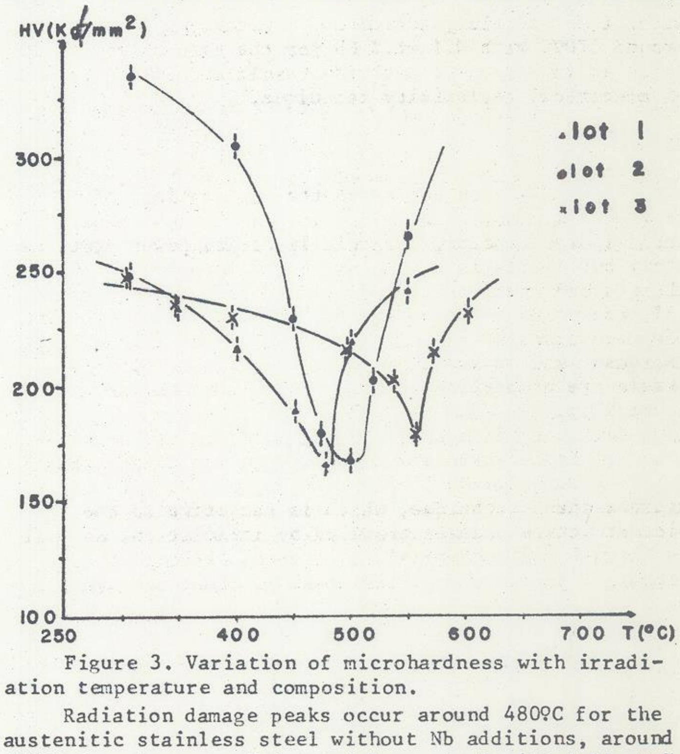

Figure 3. Variation of microhardness with irradiation temperature and composition.

Radiation damage peaks occur around 480°C for the austenitic stainless steel without Nb additions, around 500°C for the austenitic stainless steel with 0.05 wt.% Nb and around 570°C for the austenitic stainless steel with 0.1 wt.% Nb.

The precipitation of Nb particles in the austenite has the function of inhibiting the swelling, because it maintains minor vacancies concentration, minor vacancies supersaturation and slowing in this way the radiation damage process.[1,2]

By means of this technique, it is possible to study and forsee with satisfatory reliability the limitations of use of the materials of interest and determine the temperature range where the fast neutron radiation damage becomes more pronounciated.

Electrical Resistivity Measurements

During Irradiation. During irradiation, in the range between 400ºC and 600ºC, the relaxation of resistivity is supposed to be due to two competitive processes:

a) radiation damage process; when Frenkel pairs (point defects) are produced together with the formation of dislocation structures, new phases in the material and precipitates, as a consequense of enhanced diffusion conditions created during irradiation. This can result in a vacancy supersaturation[2][3] and in void formation and swelling respectively, and also in the austenite decomposition;

b) annealing of point defects produced during irradiation; when the excess of vacancies is anihilated by vacancy-interstitial recombination, and the structures mentioned in a) are annealed out recovering the initial state. These mechanisms do not necessarily represent the recovery of the metastable austenitic phase in this temperature range, and that can be considered as a consequense of the radiation damage.

During irradiation, as can be seen from figures 4 and 5, there is a temperature interval with a lower limit (400ºC), where the radiation induced vacancies are mobile, and an upper limit (600ºC), where the radiation induced vacancies concentration is much higher than the thermal vacancies concentration[4][5]. These curves characterize a temperature range where the vacancies supersaturation and phase transformations mechanisms result in a minimum peak, where the defects are preferencially annihilated.

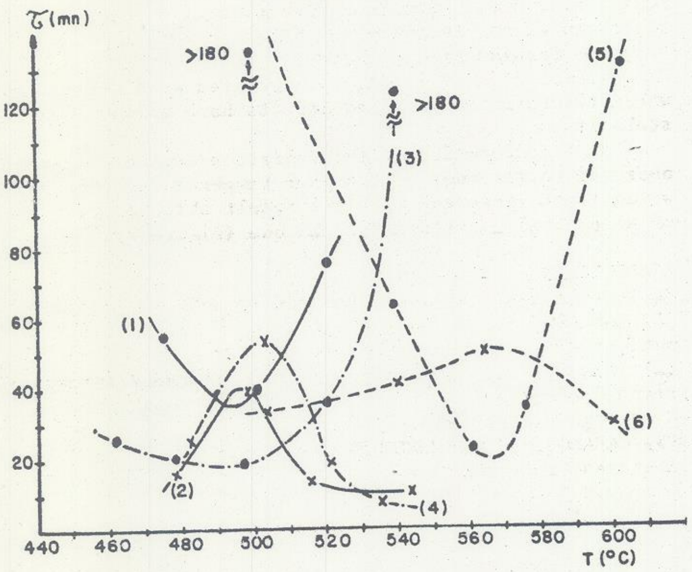

Figure 4. Variation of relaxation time vs. temperature during and after irradiation.
Curve (1) - lot 1 (without Nb) - during irradiation
Curve (2) - lot 1 (without Nb) - after irradiation
Curve (3) - lot 2 (0.05wt.%Nb) - during irradiation
Curve (4) - lot 2 (0.05wt.%Nb) - after irradiation
Curve (5) - lot 3 (0.1 wt.%Nb) - during irradiation
Curve (6) - lot 3 (0.1 wt.%Nb) - after irradiation

Before Irradiation. In this case, the curves of time constants variation (obtained from the isothermal relaxation kinetics of the electrical resistivity), follow the general pattern of the transformation of austenite in ferrite-cementite precipitates[4][6]. This transformation occurs within the same temperature limits as during irradiation. In the lower limit (around 400ºC) the temperature is not sufficient to provide the necessary mobility to the atomic species to precipitate into phases in thermodynamic equilibrium. Thus the diffusion is relatively slow and the time constants are consequently longer.

The upper limit (around 600ºC) is the phase equilibrium temperature, where the precipitates nucleii do not reach the critical growth radius, what inhibits the transformation kinetics and results in longer time constants. These arguments suggest the existence of a minimum of time constants curve, where the transformation is faster; thus defining a critical temperature of transformation. This reasoning is confirmed by the experience (figures 4 and 5).

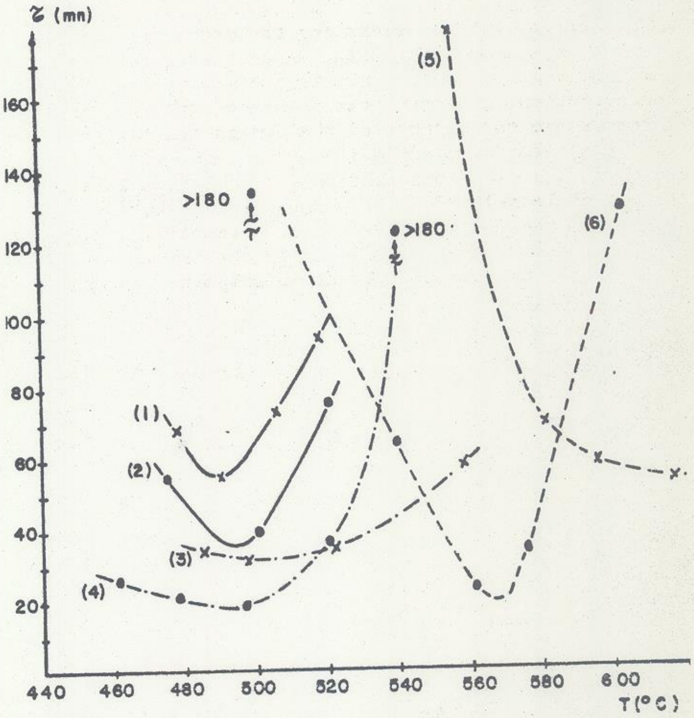

Figure 5. Variation of relaxation time vs. temperature before and during irradiation.
Curve (1) - lot 1 (without Nb) - before irradiation
Curve (2) - lot 1 (without Nb) - during irradiation
Curve (3) - lot 2 (0.05wt.%Nb) - before irradiation
Curve (4) - lot 2 (0.05wt.%Nb) - during irradiation
Curve (5) - lot 3 (0.1 wt.%Nb) - before irradiation
Curve (6) - lot 3 (0.1 wt.%Nb) - during irradiation

After Irradiation. The upper and lower temperature limits (within the range from 400ºC to 600ºC), define a temperature interval where the radiation induced defects have the maximum stability. In other words, where the recovery process is slower (figure 4), thus resulting in longer time constants represented as a maximum peak (figure 4)[7][8].

Vacancies Supersaturation. Austenitic stainless steels are material of recognized swelling resistance, in which the critical void formation occurs at fluences of $10^{22}n/cm^2$ [9]. For this reason it is expected that the vacancies supersaturation values measured on stainless steels be much lower than those of other alloy, like FeNi, which has been extensively studied by many authors[2][5][9][7]. The vacancies supersaturation curves were calculated for the samples from the lots 1, 2 and 3 (figure 6), and represent the ratios between the vacancies concentration (C) during (C_d) and before (C_b) irradiation, since from Arrhenius equation, it is known that the time constant of relaxation process is inversely proportional to the defect concentration: $\tau \alpha 1/C$; $\tau_b/\tau_d = C_d/C_b$. The results obtained are in good agreement with those of Ehrlich and Gross[6], for stainless steels with Nb additions.

In figure 6, two particular regions can be seen, as a result of the competition between the creation and anihilation of point defects. On curves of lot 1 (without Nb) and of lot 2 (with 0.05 wt.% Nb) a small plateau can be observed in the range from 475ºC to 500ºC, where a damage peak occurs around 500ºC. An analogous behavior for void formation exists in the results of Ehrlich and Gross[6]. At temperatures above 500ºC, for curve of lot 1 there is an increasing predominance of thermal vacancies concentration and for both curves (lot 1 and lot 2) the dislocations structure produced during irradiation start acting as fixed sinks for the vacancies with the consequent decrease in vacancies concentration produced by irradiation in comparison to thermal vacancies concentration. Comparing the figure 6 with the figure 7, a remarkable coincidence of the damage and supersaturation peaks can be observed. Only at temperatures higher than 500ºC a different tendency of variation exists for curves of lots 1 and 2, when the supersaturation decreases faster for curve of lot 2 containing 0.05 wt.% Nb. This can be attributed to the formation of fixed sinks by precipitates of Nb compounds (probably Niobium Carbides).

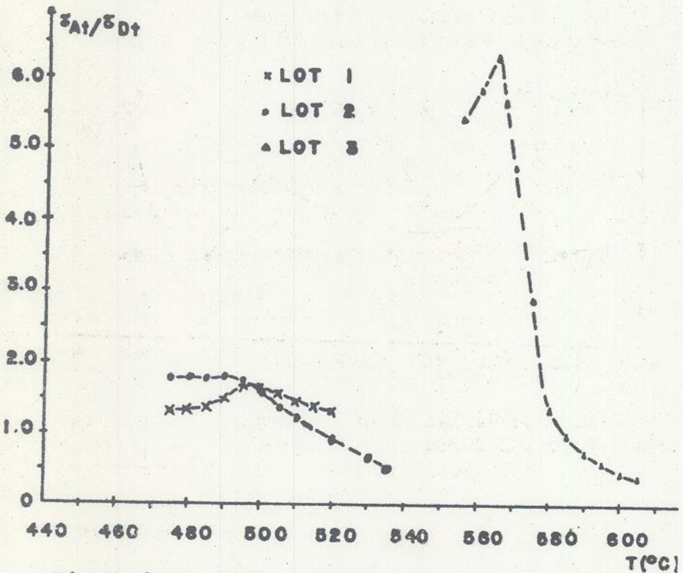

Figure 6. Variation of vacancy supersaturation with the irradiation temperature and composition.

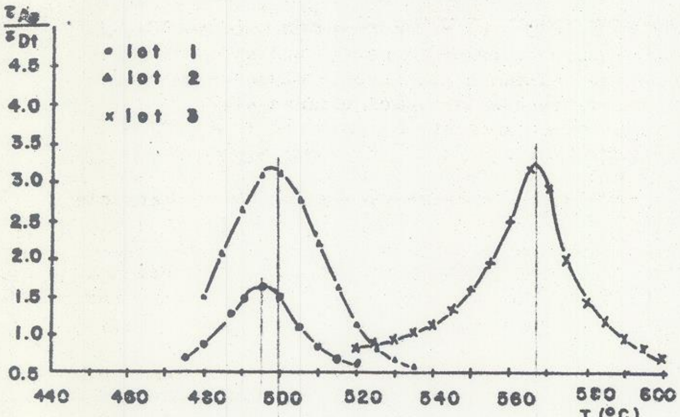

Figure 7. Variation of the ratio between the relaxation time constant after (τ_a) and during (τ_d) irradiation respectively, with temperature.

As for the sample with 0.1 wt.% of Nb (figure 6), its supersaturation maximum also coincides with that of damage curve in figure 7. The translation of the critical phenomenon to higher temperature (565ºC) is attributed to the greater amount of Nb addition. Apparently, at a sufficiently higher temperature (between 500ºC and 600ºC) the fixed sinks start losing their efficiency due to increasing thermal agitation bringing as a consequence an increase in point defects concentration in the lattice, and a charp maximum in vacancies supersaturation at higher values than the maxima for the other compositions. However the curve of lot 3, shows a very steep decrease at temperatures higher than 565ºC, thus confirming the predominance of thermal vacancies concentrations at high temperatures.

CONCLUSIONS

The following conclusions can be drawn from the results discussed.

1. Small additions of Nb in an austenitic alloy increases its microhardness mainly after a convenient cold work and heat treatments.

2. In spite of the fact that AISI 321 stainless steel is stabilized by Ti (0.39 wt.%), the addition of Nb in small quantities (0.05 wt.% and 0.1 wt.%) performs as an efficient microalloying element, suggesting that the same stabilizing efficiency can be reached with reduced Nb additions.

3. During fast neutron irradiation, a temperature interval was characterized (for each composition) giving an experimental evidence of existence of a minimum of relaxation time constants of the electrical resistivity due to combined effects of vacancies supersaturation, recovery and phase transformation (Niobium Carbide Precipitates).

4. After irradiation, temperatures were determined where the radiation induced defects have maximum stability.

5. A dislocation in the radiation damage peak was observed to the region of higher temperatures (figure 3) which is in agreement with the result obtained by means of electrical resistivity technique (figure 7).

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