EFFECT OF NEUTRON IRRADIATION; TEMPERATURE AND NIOBIUM ADDITIONS ON THE MICROHARDNESS OF NUCLEAR MATERIALS

G. Lucki and V.L. Galli
Instituto de Pesquisas Energéticas e Nucleares
São Paulo - Brasil

ABSTRACT

Data about the effects of neutron irradiation on the microhard~~e~~ness of stainless steel of type AISI 321 with 0.05; 0.10; 0.20; 0.50; and 1.00 wt.% Nb additions are presented with the purpose of contribution to the technology of fabrication and characterization of materials intended to perform in nuclear environments. The samples have been irradiated with fast neutron ($E \geq 1$ Mev) inside IPEN's reactor core in argon atmosphere and temperature range of 200-600 ^{o}C (isothermal annealing during $\simeq 7$) hours with fluences of 10^{17} n/cm^{2}. Identical isothermal annealings have been performed without irradiation. Present work also reports the Vickers microhardness of ZrNb(97.5 - 2.5wt.%) alloy and zircaloys 2 and 4 before irradiation.

Apresentado na:
VII - Inter-American Conference on Materials Technology - 1981 - Outubro - Cidade do México. México

INTRODUCTION

Starting from several experimental evidences (1-4), Nb additions in steels have established a reputation of improving the mechanical and electrical properties as well as having a better corrosion resistance in agressive environments, such as nuclear power reactors.

The aim of this work is, firstly to establish the experimental procedures for the fabrication (in laboratory scale) of steels with Nb additions , and secondly, to perform a characterization of this Nb dopped steels, and any other nuclear material by means of all experimental methods at our disposal at the Radiation Damage Dept. of IPEN. Specifically, in present work, the characterization was carried out by means of microhardness on AISI 321 stainless steel with 0.05; 0.10; 0.20; 0.50; 1.00 wt.% Nb; Zr; Zr-Nb (97.5 - 2.5wt.%) alloy, zircaloys 2 and 4, and Ni-Cr (80-20 wt.%) alloy; and electrical resistivity on AISI 321 stainless steel with 0.05 and 0.10 wt.% of Nb.

The analysis of these properties permits the detection of structural changes and also the prevision of the limitations of a material vis a vis its applications in nuclear technology.

MATERIALS AND METHODS

The materials studied were: Zr, Zr-Nb (97.5-2.5 wt.%) alloy, Zircaloys 2 and 4 and austenitic stainless steel of type AISI 321 with Nb additions and a Ni-Cr (80-20 wt.%) alloy.

The composition of these materials is the following:

a) Stainless steel of type AISI 321 (wt.%)

Cr - 17.88
Ni - 11.02
Ti - 0.39
C - 0.08

b) Ni - Cr (80-20 wt.%) (wt.%)

Ni - 79.500	P - 0.012
Cr - 18.800	S - 0.005
C - 0.140	Ti - 0.260
Si - 1.020	Al - 0.060
Mn - 0.030	N - 156 ppm

The Nb additioned in the AISI 321 stainless steel was provided by physics Dept. of the University of Campinas Brasil with the following characteristics:

a) Alumino-thermal reaction of Nb_2O_5 - CBMM - Cia Brasileira de Metalurgia e Mineração

b) Six electrical beam meltings in vacuum (10^{-5} torr in the last melting)

c) Analysis (ppm)

Ag - 3
Si - 35
W - 50
Ni - 10
Sn - 3
B - 5

Co - 40
Ta - 800
C - 80
Pb - 5
Fe - 10
Ti - 5

O_2 - 105
Mo - 35
S - 4
H_2 - 8
Mg - 3
Al - 40

Microhardness HV is generally expressed as the ratio of the load to the contact area of the indentation and can be computed by the following formula:

$$HV = 1854.4\ P/d^2\ (\mathrm{kgf/mm^2})$$

Where P is given in grams-force and d in micrometers.

A constant load was applied in the interior of the grains outlined by chemical etching.(7) The lenght of diagonal was measured trugh a Carl Zeiss model III photomicroscope. The microhardness was obtained from the mean value of 10 diagonals for each sample. The above described is the constant load method.

Another way to measure the microhardness is the variable load method: owing to the fact that microhardness value is always measured after removal of the load, the diagonal d is thus incorrect by an amount d_o which represents the elastic recovery of the material; we can take it into account making an assesment of elastic recovery d_o possible, microhardness then becomes:

$$HV = 1854.4\ p/(d+D)^2\ (\mathrm{kgf/mm^2})$$

where $D = d_0 \pm \Delta d$ (Δd - experimental error)

$D \simeq d_0$ for $d << d_0$

The variable load method was used for the samples of Ni-Cr (80-20 wt.%). The microhardness of all other samples have been measured by the constant load method.

EXPERIMENTAL PROCEDURE

The indentations for Zr, Zircaloys 2 and 4, Zr-Nb (97.5-2.5.wt.%) alloy were made in the original material as received from the factories and the microhardness was obtained from the mean value of ten diagonals measured after an applied constant load of 25 gf.

The Nb additions in the austenitic stainless steel of type AISI 321 were made in an induction furnace at a temperature of 1,450 °C in argon atmosphere followed by an annealing at 1,300 °C during two hours to improve Nb solubility in the lattice.(

Nine lots of AISI 321 stainless steel with different Nb addition were prepared:

lot 1a - AISI 321 stainless steel wothout Nb addition, after fabrication.

lot 1b - AISI 321 stainless steel without Nb addition with a reduction in its cross section of 85% by means of wiredrawing. Annealed at 1,000 °C during 2 hours in argon atmosphere and quenched after the cold work.

lot 2a - AISI 321 stainless steel with 0.05 wt.% Nb addition, after fabrication.

lot 2b - AISI 321 stainless steel with 0.05 wt.% Nb addition with a reduction in its cross section of 85% by means of wiredrawing. Annealed at 1,000 °C during 2 hours in argon atmosphere and quenched after the cold work.

lot 3a - AISI 321 stainless steel with 0.10 wt.% Nb addition, after fabrication.

lot 3b - AISI 321 stainless steel with 0.10 wt.% Nb addition with a reduction in its cross section of 85% by means of wiredrawing. Annealed at 1,000 °C during 2 hours in argon atmosphere and quenched after the cold work.

lot 4 - AISI 321 stainless steel with 0.20 wt.% Nb addition, after fabrication.

lot 5 - AISI 321 stainless steel with 0.50 wt.% Nb addition, after fabrication.

lot 6 - AISI 321 stainless steel with 1.00 wt.% Nb addition, after fabrication.

The annealing at 1,000 °C during 2 hours in lots 1b 2b and 3b were made to relieve the internal stresses due to cold work.

After these treatments, the samples from these lots were exposed to isothermal annealing with fast neutron irradiation during approximately 7 hours, with fluences of 10^{17} n/cm^2 in argon atmosphere at a pressure of 1 atm and temperature range of 200-550 °C for lots 1a, 2a, 3a, 4, 5 and 6 and in the range of 300-600 °C for lots 1b, 2b, and 3b. Identical isothermal annealing have been performed without irradiation.

A constant load of 25 gf for the microhardness measurements (10) was applied in the interior of the grains outlined by chemical etching with the solution having the following composition:

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

The microhardness was obtained by the mean value of ten diagonals measured after the removal of the load of 25 gf for each sample (constant load method).

The Ni-Cr (80-20 wt.%) alloy lot was reduced 85% in its cross section by means of wiredrawing. Five samples were prepared for microhardness measurements (variable load method).

Sample 1 - original material as supplied.

Sample 2 - hardened after the wiredrawing.

Sample 3 - annealed at 900 °C during 2 hours, in vacuum and slowly cooled down in furnace, during 6 hours.

Sample 4 - annealed at 900 °C during 2 hours in vacuum

Sample 5 - annealed at 900 °C during 2 hours in vacuum and quenched. Irradiated at 566 °C for 4 hours and at 520 °C during 3 hours. Annealed after irradiation at 550 °C.

All the irradiations were performed in the core of IPEN's reactor, with an instant fast neutron flux of 5×10^{12} n/cm^{2}.s.

For the samples of Ni-Cr (80-20 wt.%) loads from 10 to 100 gf were applied in the interior of the grains outlined by electrolytic etching with the following solution:

glacial acetic acid - 112 ml
perchloric acid - 28 ml
distilled water - 80 ml

RESULTS AND DISCUSSION

Radiation Damage research consists essentially on testing materials, before, during, (in pile) an after irradiation with suitable high energy particles. This sequence is not always possible due mainly to experimental particularities; such is the case of microhardness (HV) which cannot be directly measured during irradiation. On the other hand, electrical resistivity (ρ) can be followed in all three cases, giving valuable informations on the critical structure changes in the enhanced diffusion conditions, ocurring exclusively during irradiation. This procedure (in that sequence) provides a complete set of informations allowing thus a good characterization of the material studied.

Initially all materials are tested as supplied from factory, or with a normalized heat treatment if prepared in our laboratory. Figure 1 represents the initial microhardness of Nb, Zr, Zircaloys 2 and 4, Zr-Nb (97.5-2.5 wt.%) and Ni-Cr (80-20 wt.%), as supplied. The evaluation of irradiated samples is presently underway, with exception of Ni-Cr (80-20 wt.%) (fig. 5). Figures 2, 3 and 4 show remarkable results for samples of same composition AISI 321 with 0.05 and 0.10 wt.% of Nb, but with different heat treatment.

The samples (lots 1b, 2b and 3b), show practically a constant Hv for each composition, but with increasing values directly proportional to Nb addition (fig.2). During fast neutron irradiation (fig.3) three distinct radiation damage peaks are determined at 490, 500 and 570 ^{o}C, obtained by means of electrical resistivity, These results are in good agreement with those obtained by means of microhardness, where analogous peaks can be identified after irradiation (fig.4). Thus the figure 3 and 4 are the representation of the same damage process put in evidence by two different methods. It must be said that, apart the paper of Pokrovskij (11), this is the first time that a characterization of structural material in nuclear environments is succesfully achieved by means of microhardness. This method if compared with others is more practical and convenient.

Figure 5 shows the microhardness behaviour after several mechanical and thermal treatments of the NiCr (80-20 wt.%) alloy. It can be seen that the fast neutron irradiation produces a relative hardening (curves 4 and 5), even at relatively low dose (10^{17} n/cm^{2}). The samples 1 (as supplied) and 2 (hardened by wiredrawing) present, as expected, the highest microhardness.

New lots of AISI 321 stainless steel with the following Nb additions 0.05 - 0.10 - 0.20 - 0.50 and 1.00 wt.% were prepared with a different experimental procedure. These lots (1a, 2a, 3a, 4, 5 and 6) were not submitted to cold work and stress relieve heat treatment at 1,000 ^{o}C in argon atmosphere, but were in the initial state as fabricated in our laboratory. The variation in behaviour of microhardness curves in figure 6 are attributed to the absence of cold work and subsequent stress release annealing. Other samples from the same lots were irradiated with fast neutron (10^{17} n/cm^{2}) (fig.7) at same temperatures as the previous samples (fig. 6). Figure 7 shows as expected, a wider amplitude of microhardness variation. The general trend shows an increase of microhardness at higher temperatures for irradiated and non irradiated samples.

It is worthiwhile to stress that a very small change in experimental procedure (mechanical and therma) produces a striking variation in the behaviour of microhardness in material of the same composition.

Presently, irradiation experiments are being performed with the purpose of evaluation of the material shown in figure 1.

REFERENCES

(1) Keown, S.R. - "Niobium as a microalloying element in steel". 3º Congresso Brasileiro de Engenharia e Ciência dos Materiais, Rio de Janeiro, December 1978.

(2) Ehrlich, K., and Gross, R., Proceedings of the symposium on fuel and fuel elements for fast reactors, Brussels, july 2-6, 1973

(3) Camargo, M.U.C., Lucki, G., Proceedings of the V Inter-american Conference on Materials Technology, pp. 525-530, november 6-10, 1978, São Paulo, Brasil.

(4) Lucki, G. and Galli, V.L., Proceedings of the VI Inter-american Conference on Materials Technology, pp. 79-83, august 12-15, 1980, San Francisco, U.SA.

(5) Camargo, M.U.C., "Radiation damage studies in stainless steel of type AISI 321 with Nb additions subjected to heat and mechanical treatments and fast neutron irradiations". M.Sc. Thesis march, 1979, São Paulo, Brasil.

(6) Suszczynski, E.F. and Cabral, U.Q.. Technical contribution number 1155 presented in XXVIII Annual meeting of the brasilian society for metals, june, 1973, Bahia, Brasil.

(7) Petty, E.R., Hardness Testing, In: Bunshah, R.F., ed Measurements of Mechanical Properties, pt. 2. New York, Interscience, 1971. (Tecniques of Metal Research, v.5, pt.2) pp. 157-221.

(8) Nolasco, C.A., Bordignon, P.J.P., Oliveira, E.Q., Technical comtribution presented in XXXI annual meeting of the brasilian society for metals, july, 4-9, 1976, Belo Horizonte, Brasil.

(9) Zakharov, B, "Heat treatments of metals". 1st. published 1962. Peace published 1962. Peace Publishers, Moscow.

(10) Butler, T.W., 5. Annual technical conference of the IMS analysis society. Chicago, Illinois, USA. 19 sep 1972. x. Gray, R.J. (ed.) Microstructural Science. Vol. I New York, American Elsevier Publishing Company, Inc. 1974. p. 15-24. Conf-720983.

(11) Pokrovskij,A.S., Malkov, V.V. - NIIAR - P - 10(276) 1976. 21p.

FIGURE CAPTIONS

Figure 1. Comparative microhardness of Zr, Zircaloys 2 and 4, Nb ZrNb (97.5-2.5 wt.%) and NiCr (80-20 wt.%).

Figure 2. Microhardness vs. annealing temperature for the non-irradiated material of stainless steel with Nb additions.
(1b) stainless steel of type AISI 321
(2b) stainless steel of type AISI 321 with 0.50 wt.% Nb
(3b) stainless steel of type AISI 321 with 0.10 wt.% Nb.

Figure 3. Variation of the ratio between the relaxation time constant after (τ_a) and during (τ_d) irradiation respectively with temperature
(1b) stainless steel of type AISI 321
(2b) stainless steel of type AISI 321 with 0.50 wt.%Nb
(3b) stainless steel of type AISI 321 with 0.10 wt.%Nb

Figure 4. Microhardness vs. irradiation temperature.
(1b) stainless steel of type AISI 321
(2b) stainless steel of type AISI 321 with 0.05 wt.%Nb
(3b) stainless steel of type AISI 321 with 0.10 wt.%Nb

Figure 5. Square root of applied load vs. diagonal of the pyramid basis for NiCr (80-20 wt.%).

Figure 6 Microhardness vs. annealing temperature for the non-irradiated material of stainless steel with Nb additions.
(•) stainless steel of type AISI 321.
(>·<) stainless steel of type AISI 321 with 0.05 wt.%Nb.
(△) stainless steel of type AISI 321 with 0.20 wt.%Nb
(⊙) stainless steel of type AISI 321 with 0.05 wt.%Nb
(⊗) stainless steel of type AISI 321 with 1.00 wt.%Nb
(×) stainless steel of type AISI 321 with 0.10 wt.%Nb

Figure 7. Microhardness vs. irradiation temperature.
(•) stainless steel of type AISI 321.
(><) stainless steel of type AISI 321 with 0.05 wt.%Nb.
(×) stainless steel of type AISI 321 with 0.10 wt.%Nb.
(△) stainless steel of type AISI 321 with 0.20 wt.%Nb.
(⊙) stainless steel of type AISI 321 with 0.50 wt.%Nb.
(□) stainless steel of type AISI 321 with 1.00 wt.%Nb.

fig. 1

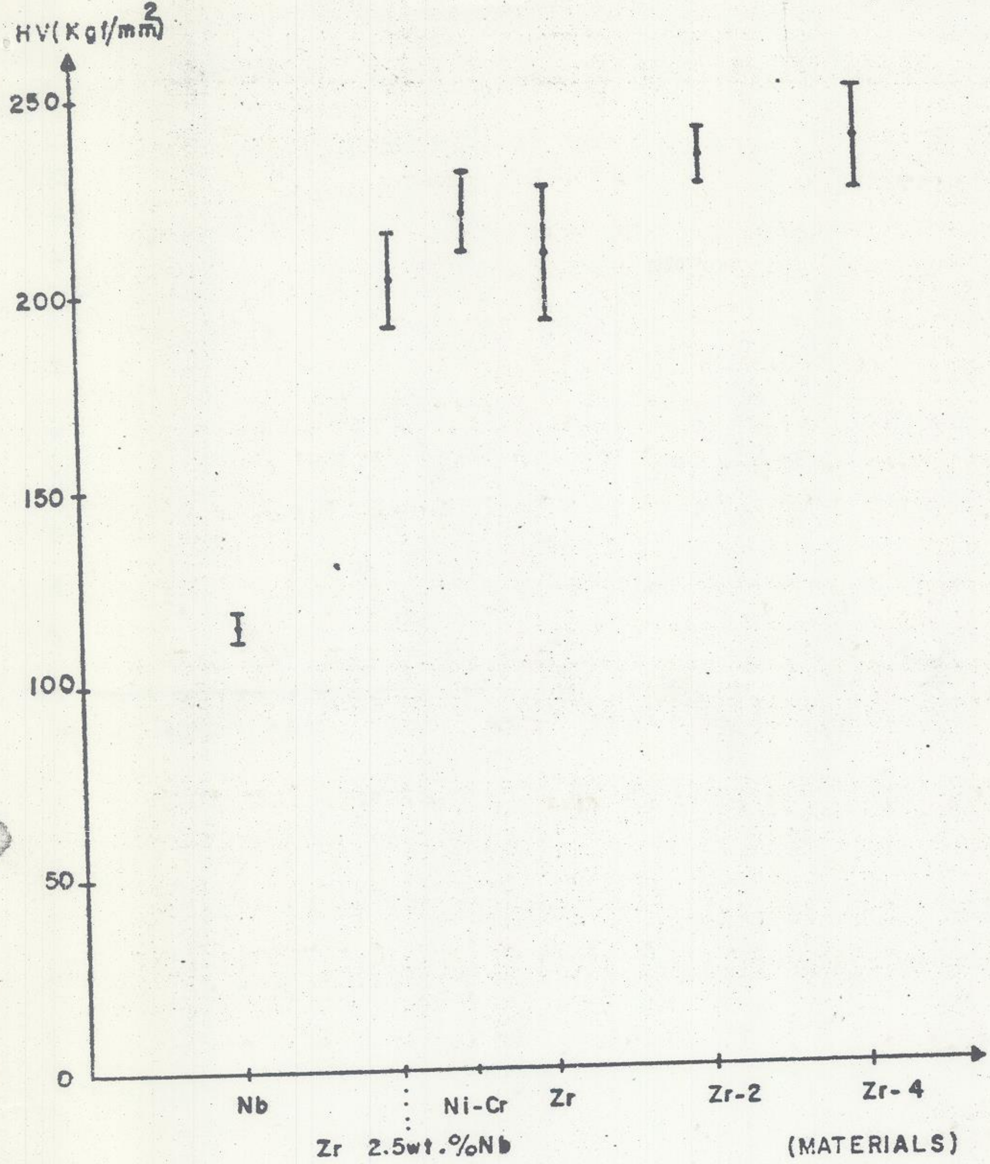
HV(Kgf/mm^2)
250
200
150
100
50
0
Nb
Zr 2.5wt.%Nb
Ni-Cr
Zr
Zr-2
Zr-4
(MATERIALS)

fig. 2

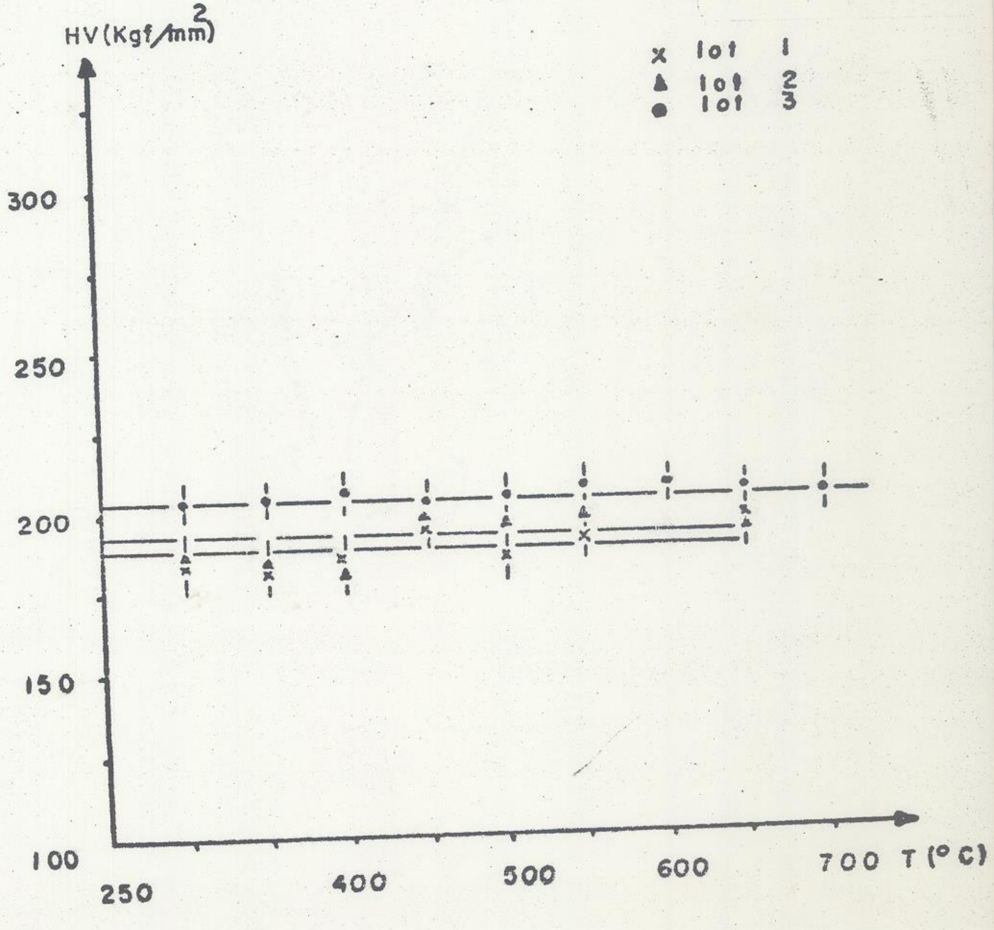
HV(Kgf/mm^2)
x lot 1
▲ lot 2
● lot 3
300
250
200
150
100
250
400
500
600
700 T(°C)

fig. 3

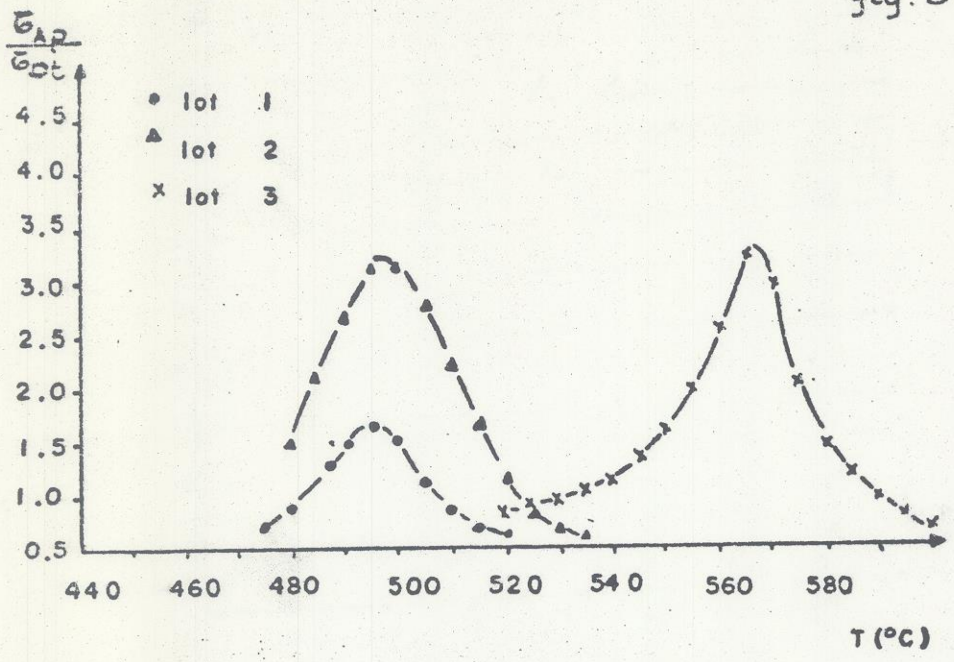
$\frac{\sigma_{Ap}}{\sigma_{ot}}$
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
● lot 1
▲ lot 2
× lot 3
440
460
480
500
520
540
560
580
T (°C)

fig. 4

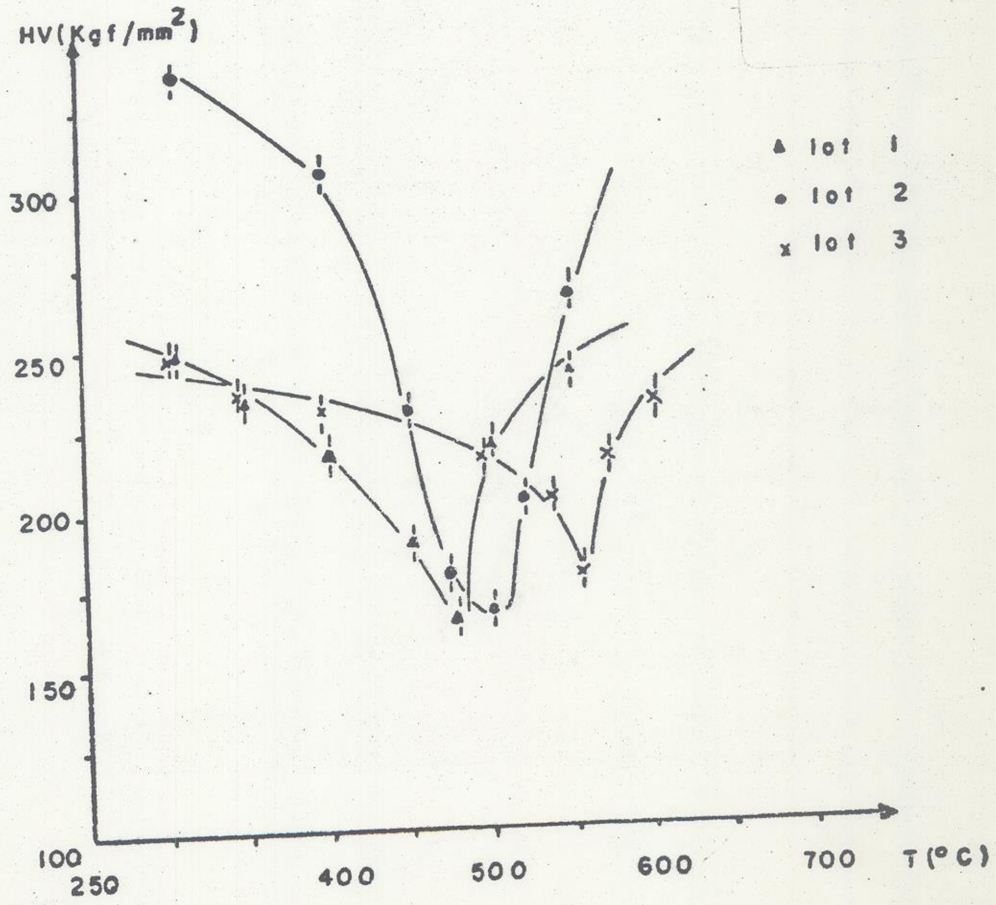
HV(Kgf/mm²)
300
250
200
150
100
250
400
500
600
700
T (°C)
▲ lot 1
● lot 2
× lot 3

fig 5

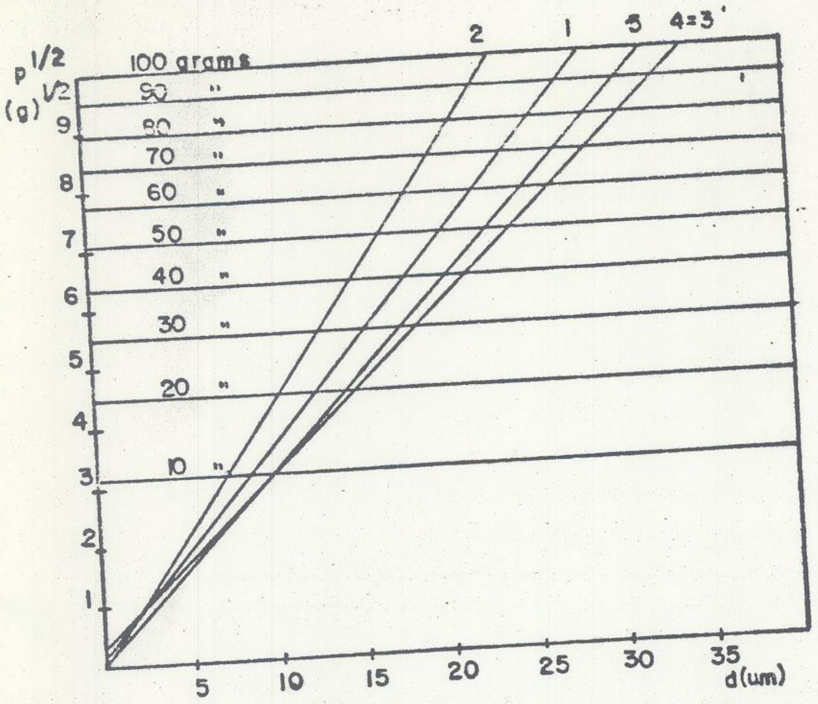
2
1
5
4=3'
$p^{1/2}$
$(g)^{1/2}$
100 grams
90 "
80 "
70 "
60 "
50 "
40 "
30 "
20 "
10 "
1
2
3
4
5
6
7
8
9
5
10
15
20
25
30
35
d(um)

fig.6

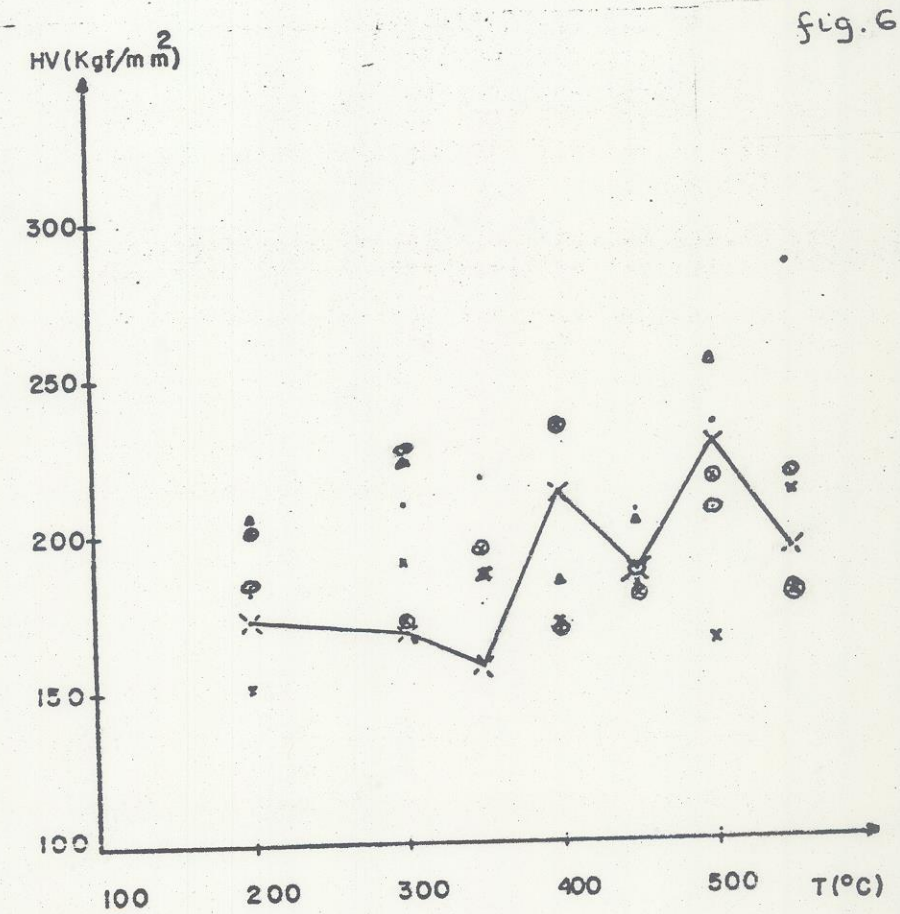
HV(Kgf/mm^2)
300
250
200
150
100
100
200
300
400
500
T(°C)

fig. 7