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SOME ASPECTS ON THE EVOLUTION OF THE RECOVERY AND RECRYSTALLIZATION OF ZIRCONIUM - NIOBIUM ALLOYS

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ABSTRACT

In this paper we will present results detailing the recovery and recrystallization processes in Zr-Nb alloys (Zr with 0.25wt% ; 0.5wt% ; 1.0wt% ; 1.5wt% Nb), by means of isochronal heat treatments, microhardness measurements, optical and transmission electron microscopy. One of the principal deal is to correlate the increasing presence of new phases in the metallic matrix (alpha-Zr ; beta-Nb ; beta-Zr phases), changing recovery and recrystallization processes and also the final microstructure (grain size refinement, presence of fine and coarse precipitates, second phases, etc). The behavior of the recrystallization of the Zr-Nb alloys is different regarding to the pure Zirconium. The recrystallization in the two phase alloys will occur by nucleation and/or growing of the beta zirconium and by poligonization of the alpha zirconium.

INTRODUCTION

The zirconium alloys are widely used as structural and fuel cladding materials for water cooled reactors(1,2). As requirement in the nuclear industry, some properties such as mechanical and corrosion resistance would be - enhanced. This cladding is always cold-worked and subsequently heat treated to produce a structure suitable for reactor applications and also during the reactor operation it could experience microstructural and property changes due to temperature transients (normally at 300° C, but in a loss-of-coolant accident may be arrive at 1000° C). The zircaloy is one of the most used alloy for this purpose. The binary Zr-Nb alloy was also developed because its corrosion behavior would be better as the zircaloy series and has a similar mechanical resistance. For example, the aged Zr-1wt% Nb is remarkable similar to the 20% cold worked zircaloy 2. The martensitic transformation from the beta phase (BCC structure) to the metastable Nb-saturated "transformed alpha" with hcp structure is the responsible for the increasing of the mechanical properties (3,4).

It is the aim of this paper to show a study of the recovery and recrystallization of the 60% cold-worked Zr-Nb alloys utilizing microstructural observations (optical and electron microscopy) and microhardness tests.

EXPERIMENTAL DETAILS

The material used in this study was a serie of Zr-XwtXNb alloy ingots where X= 0.25 ; 0.5 ; 1.0 ; 1.5 . The ingots was initially sliced in a series of rectangular sheets of 3x0.8x0.5 cm each one. The samples were annealed in an argon atmosphere at 650° C for one hour, followed by a cold water quenching. Then, after a chemical cleaning, the samples were 60% cold rolled (in thickness). After cold rolled, the samples were heated, in an argon atmosphere, in the temperature range 300 - 1050° C for one hour and cooled to room temperature.

The microstructure was analyzed by optical and transmission electron microscopy for a better understanding related to the influence of the refinement of grain size in the rolling process and also in the recrystallization. The suitable specimens for optical metallography, after a conventional mechanical polishing were chemical etched using a solution containing 3ml HF + 10ml H_2SO_4 + 45 ml H_2O + 45 ml HNO_3. The 3 mm discs for TEM were prepared in a double jet electrolytic polisher using 90% of methanol plus 10% of perchloric acid mixture at - 15°C (p.d. = 12 V). TEM analysis of the samples were conducted at 200 kV accelerating voltage in a JEOL JEM 200 C microscope. Conventional imaging techniques as well as selected area diffraction techniques were used in characterizing the samples.

Each stage of the process was mechanical characterized by microhardness - (Vickers ; load = 200 g).

RESULTS AND DISCUSSION

The cold-work promotes a hardening in the material with a consequent increase in the strength; the figure 1 shows an increase in the microhardness related to the cold-rolling process in the Zr-Nb alloys that, of course, is related with the increasing of crystal defects as point defects, dislocations, dislocations loops, etc. The heat treatments of the cold-worked alloys promote the recovery and recrystallization processes. As we can see in the figure 2, the microhardness values show a similar behavior with the pure zirconium (5,6,7) related to the involved recovery process (goes to 450° C). The ending of the recovery temperature apparently shows a slight difference between them. It indicates that the mobility energy of the defects does not change significantly for the Zr-Nb alloys, although they had an unlike microstructure, compared with the pure zirconium (figures 3,8,9,10).The figure 3 shows a microstructure of the one of the as-cast Zr-Nb alloys and the figure 4 shows a heat-treated and 5% cold worked Zr-1.0wt% Nb (both by TEM). The electron micrograph of the figure 5 brings a microstructure of the recovery process on a 60% cold worked Zr-0.25wt% Nb (T = 450° C for 1h).

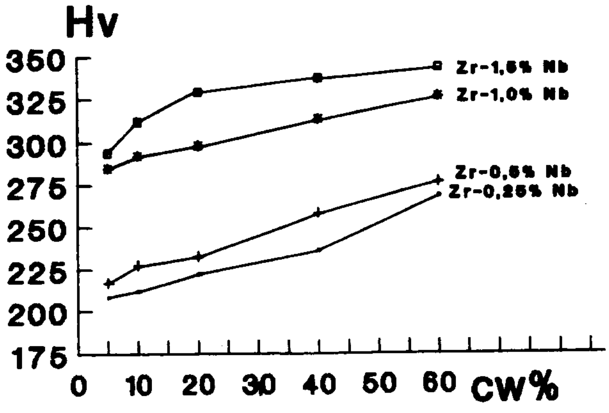

Figure 1 - Dependence of the microhardness (Vickers indentation; load = 200 g) in the four Zr-Nb alloys on the percentage of cold-work.

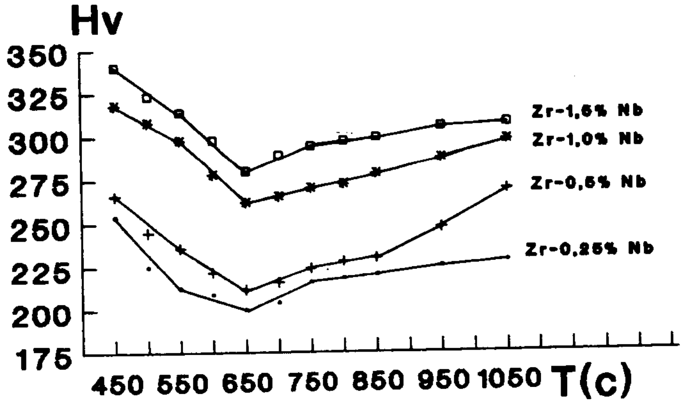

Figure 2 - Dependence of the microhardness in the four Zr-Nb alloys on the annealing temperature

In the recrystallization processes, it was found that for alloys with percentages above 0.25wt% Nb, the treatment is complete at 850° C for one hour while for the Zr-0.25wt% Nb it occurs at 650° C for 1/2 hour.

The microstructure of Zr-1.0wt% Nb in figure 6 shows the beginning of the recrystallization and, comparing with the pure Zr, there are no significant modifications when the annealing temperature achieves 550° C for one hour.

The electron micrograph of the figure 7 shows a microstructure of a Zr-0.5wt%

Nb completely recrystallized.

To verify the effect of the annealling time for the 60% cold-worked Zr-Nb alloys, additional heat treatments were performed with the following conditions: the Zr-0,25wt% Nb was heated at 600° C for 1/2 hour and the others at 650° C for 5 h and 700° C for 4 h. In the four alloys the recrystallization has occurred.

Figure 3-As-cast Zr-0.5wt% Nb, grains of alpha Zr surrounded by beta phase widmannstatten microstructure (electron micrograph)

Figure 4-Zr-1.0wt% Nb,heat treated and 5% cold worked. High density of dislocations inside the subgrains (electron micrograph)

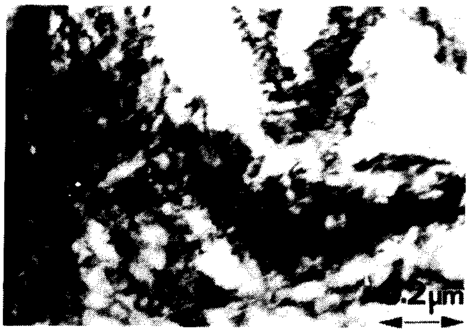

Figure 5- Zr-0.25wt%Nb, 60% cw, heat treated, T=450°C for 1h. Recovery process, decrease of the dislocation density (electron micrograph)

Figure 6- Zr-1.0wt%Nb, 60% cw, heat treated, T=550°C for 1 h. Beginning of the recrystallization; small α-grain (electron micrograph)

From the optical and electron microscopy, we can expect the resulting microstructure with the accomplished heat treatments of the c.w. material (alloys with niobium above 0,25wt%): (a) the microstructure of the c.w. material consists of elongated alpha Zr grains with some beta phase at the boundaries of the elongated alpha-grains; in the range 500 - 700° C, the microstructure shows a dispersion phase in the matrix starting with dispersion of beta-Nb in

alpha-Zr until a dispersion of beta-Zr in alpha-Zr plus beta-Nb with the increase in temperature; (b) between 700 and 900° C, there are a duplex microstructure, alpha-Zr + beta-Zr, and also some Nb dispersion; (c) for temperature upper to 900° C, dispersion of the alpha-Zr in the beta-Zr.
After treatments at 700° C, the beta-Zr is unstable and transforms partially to a twinned structure on cooling to room temperature (called "transformed alpha").

Figure 7- Zr-0.5wt%Nb, 60% cw, heat treated, T=850°C for 1 h. Completely recrystallized twinned grains fron β quenching (electron micrograph)

Figure 8- Zr-1.0wt%Nb, 60% cw, heat treated, T=950°C for 1 h. Twinned structure (β phase), also some α-grains (electron micrograph)

Figure 9- Zr-1.5wt%Nb, 60% cw, heat-treated, T=750°C for 2 h. α-grains; α-transformed by quenching, some number of dislocations (electron micrograph)

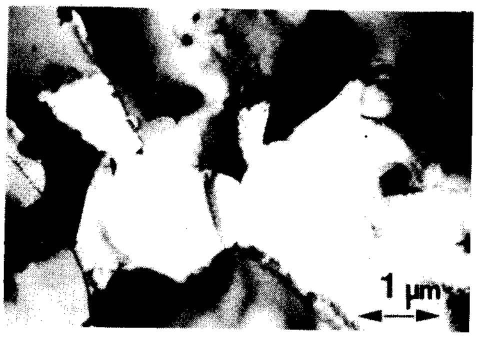

Figure 10- Zr-1.0wt%Nb, 60% cw, heat-treated, t=700°C for 5 h. Typical microstructure of a recrystallization in two phases, β-phase growing in a triple junction of α (electron micrograph)

Table 1 shows the evolution of the grain size range (in µm) with the heat treatment of the c.w. alloy observed by optical microscope. Apparently the grain size of the Zr-Nb alloys with wt% of Nb more than 0,25 is very little influenced by the heat treatment although the TEM observations of these alloys show that subgrain size tends to grow with the increase of the heat treatment of the alloys.

The increase on microhardness observed on figure 2 for temperatures above 700° C is related to the beta-Zr phase transformation, by quenching to a very hard metastable phase Nb saturated ("transformed alpha"). The martensitic -transformation of this phase produces thermal twins (observed in figures 7, 8 and 9). This behavior is also useful for a better understanding of the phase diagrams of the zirconium-rich - Niobium alloys.

TABLE 1 - Grain Size Range (in µm) x Heat Treatment

	Zr-XwtX Nb			
T	0.25	0.5	1.0	1.5
650°C	10-12	-	-	-
750°C	27-30	-	-	-
850°C	11-15	5-8	5-8	5-8
950°C	17-23	6-9	6-9	6-9
1050°C	27-30	7-10	7-10	7-10

CONCLUSIONS

1 - The presence of a little percentage of Nb in Zr does not change the initial stages of the recrystallization process.

2 - The recrystallization kinetics of zirconium decreases with the increase of the amount of niobium (dilute zirconium niobium alloys).

3 - The presence of Nb promotes a stability of the beta-phase or transformed alpha according to the quenching temperature. It's possible in dispersion form as two phases or precipitation dispersion.

4 - The cold work followed by heat treatment and the homogenization of Nb bring a grain size refinement.

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