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COMPARISON OF THE MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF ZIRLO AND OTHER ZIRCONIUM ALLOYS

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ABSTRACT

The metallic materials employed in water cooled reactors must have several requisites, depending on their use. Some materials are used as cladding of nuclear fuels, preventing the contact of the cooling water with the fuel, and also avoid the release of fission products produced in the fuel during irradiation. Others are used as structural materials, to support the reactor core and avoid the distortion of the fuel elements under the action of several forces. The materials therefore should present good corrosion resistance, good mechanical properties and when used as a fuel cladding, should also present good thermal conductivity. Regarding nuclear properties, it is necessary that the cladding material presents low absorption cross section for thermals neutron. Zirlo is winning importance as cladding tubes material of nuclear fuels. The most promising aspects of this alloy are: low corrosion rate, best creep properties under irradiation, increase of mechanical resistance and capability of resisting the highest burn-ups. This work compares briefly zirlo with other zirconium alloys concerning mechanical properties and corrosion resistance.

1. INTRODUCTION

The metallic materials employed in water-cooled reactor cores must possess several requirements, which depend on its application. Some materials are used as cladding of nuclear fuels, preventing the contact of the cooling water with the fuel, and also avoid the release of fission products produced in the fuel during irradiation. Others are used as structural materials, to support the reactor core and to avoid the distortion of the fuel elements under the action of several forces. The materials therefore should present good resistance to the corrosion, good mechanical properties and when used in the fuel cladding, should also present good thermal conductivity. Regarding nuclear properties, it is necessary that the cladding material presents low absorption cross section for thermal neutrons [1].

Zirlo is winning importance as cladding tubes material of nuclear fuels. The most promising aspects of this alloy are: low corrosion rate, best creep properties under irradiation, increase of mechanical resistance and capability of resisting the highest burn-ups [2].

The objective of this paper is to compare briefly zirlo with other zirconium alloys concerning mechanical properties and corrosion resistance.

2. ZIRCONIUM AND ITS ALLOYS

2.1. Properties of corrosion of zirconium alloys

The zirconium corrosion resistance is affected by its pureness and the kind of present superficial film, but generally its resistance is very good. This resistance is given by the formation of an adherent oxide, of the ZrOx type.

The addition of alloy elements to the zirconium improves the resistance to corrosion, counterbalancing the harmful effect of impurities such as nitrogen, oxygen and carbon. There are two phases in the corrosion process. In the initial phase, the corrosion rate decreases with the time, followed by a second one, in which the corrosion rate increases with the time. The first phase is characterized by the formation of an adherent film, of dark color, whereas in the second phase, the product is not adherent and of clear color [1].

When impurities are present in high amounts, the zirconium resistance to the corrosion is significantly affected. The effect of nitrogen is significantly increased when present in levels above 0.004% approximately. For high amounts of nitrogen, the corrosion is increased. This harmful effect of nitrogen can be controlled with the addition of tin. As the nitrogen, the carbon is harmful for the zirconium. The effect of carbon can also be controlled by the addition of tin. The addition of tin to the zirconium modifies the resistance to the corrosion, with the smallest corrosion rate being found in the range of 0,5 to 1% of Sn [1].

When Fe, Ni and Cr are added in the range of 0,1%, they tend to improve the resistance to corrosion. Additions above 0,5% presents little improvement, and increasing this amount, the resistance to corrosion in water tends to decrease. It is found that the effect of these alloy elements is additive. Given that the addition of Sn to the Zn is not entirely effective, Fe, Ni and Cr were added to get better resistance to the corrosion.

The mechanism of zirconium corrosion in the absence of impurities or alloy elements is the diffusion of oxygen ions, by means of gaps, from the water/oxide interface to the oxide/metal interface. This process is halted when there is a break in the oxide layer, as it becomes thicker. Hence, the time for breaking the oxide layer is controlled by the diffusion of oxygen ions in the oxide layer. If nitrogen is present in the metal, it can occupy atom positions of oxygen in the crystalline oxide net and lead to an increase in the number of gaps and then to a bigger diffusion of oxygen. If tin is present in the metal, it is incorporated in crystalline oxide net, in zirconium atom positions. If both Sn and N are present, they tend to associate, decreasing the number of gaps, and then decreasing the diffusion of ions of oxygen [1].

2.2. Mechanical behavior of tubes and plates of zircaloy

The mechanical properties of zircaloy tubes and plates depend to a large extent on the crystallographic texture obtained during the conformation processes. This texture leads to an anisotropy in the mechanical properties. The making of curves of yield and tensile strength can be carried out by means of plain deformation and uniaxial tests, when the samples possess sufficient dimensions, as in the case of the plates. In the case of thin wall tubes, the data are gotten by simultaneous strain of internal and external pressure and an axial strain [1].

The mechanical anisotropy of tubes and plates of zirconium alloy comes from the fact that the deformation in the direction of axis *c* can occur, in most cases, only by maclagem that needs a bigger stress, in comparison to the prismatic slides. Then, in the direction where a bigger concentration of basal polar regions exists, the mechanical resistance is bigger. There is also anisotropy in relation to the tensile and compressive stress, due to the different systems of maclagem involved [1].

2.3. Creep in zirconium alloys

The creep is a deformation under the action of a stress that is normally below of the yield strenght, and is dependent on the time and temperature.

The deformation by creep normally starts to become intense with temperatures above 0,5 T_M , where almost all the deformation occurs in the secondary phase [1].

In materials used in nuclear reactors, small deformations in the range of temperature of 0,3 T_M to 0,5 T_M are also taken into account, and these deformations occur mainly in the primary and secondary phases.

Under high temperatures (> 1100 ºC) the creep strain in zircaloys is intensified, even for low stress level as 1 N/mm^2 , and at 1150 ºC was verified a deformation of about 20% in approximately 100 minutes [1].

2.4. Nuclear applications of zirconium alloys

2.4.1. Zircaloy 2

The chemical composition (% in weight) of zircaloy 2 is:

Element	%
Zr	Remaining
Sn	1,2 – 1,7
Fe	0,07 – 0,2
Cr	0,05 -0,15
Ni	0,03 – 0,08

The Zircaloy 2 resistance to corrosion in high temperature water is much superior when compared with the metallic Zr. A highly adherent oxide film is formed on this alloy at a cubical rate at first, but after an initial period it undergoes a transition to linear behavior. Differently of the oxide film of the metallic Zr, the oxide film on Zircaloy 2 remains dark and adherent through the transition and even after the transition.

In water solutions, the reaction of corrosion between water and zirconium liberate hydrogen, part of it being absorbed by zircaloy. Hydrogen absorption is important as zirconium and its alloys become brittle due to the formation of precipitated hidretos of zirconium. Embrittlement is revealed as a decrease of ductility, and the embrittlement degree depends on the amount of absorbed hydrogen, on the crystallographic texture of the zirconium and on the orientation of hidreto plates in relation to the applied tensile stress direction. As little as 30 ppm of absorbed hydrogen can make the zirconium brittle if hidreto plates are perpendicular to the tensile directions [3].

2.4.2. Zircaloy 4

The chemical composition (% in weight) of zircaloy 4 is:

Element	%
Zr	Remaining
Sn	1,2 – 1,7
Fe	0,18 – 0,24
Cr	0,07 -0,13
Ni	-

The Zircaloy 4 composition differs from that of Zircaloy 2 by the fact that it does not have nickel and presents an amount of Fe lightly superior. Both variations aim at reducing the hydrogen absorption. The corrosion behavior of Zircaloy 4 is very similar to the Zircaloy 2, but the hydrogen absorption for Zircaloy 4 is significantly lower, particularly when the metal is exposed to water at the temperature of 360 ºC. At this temperature, the hydrogen absorption for Zircaloy 4 is less half of the Zircaloy 2 [3].

2.4.3. Zr-2,5Nb

The Zr-2,5Nb resistance to corrosion is smaller than that of Zircaloys 2 and 4. However, Zr-2,5Nb is an acceptable alloy for many applications, being a central example its use in pipes of pressure in the primary circuits of the reactors of type CANDU [3].

2.4.4. Zirlo

A typical chemical composition (% in weight) is given for zirlo.

Element	%
Zr	Remaining
Nb	1,0
Sn	1,0
Fe	0,2

The material of the rod has an important role, and advances for low corrosion cladding are demanded to prevent extreme corrosion. More resistant materials such as the zirlo, available at Westinghouse, show corrosion rates that are 58% smaller compared to the low Sn zircaloy 4 for irradiations up to 37800 MWD/MTU (Westinghouse, 1991). Moreover, zirlo presents a very high resistance to corrosion in water with lithium [4].

2.5. Comparison of weight gains and hidretation of zircaloy 2, zircaloy 4 and zirlo

In essays of mass gains carried out in tubes of zircaloy 2, zircaloy 4 and zirlo under atmospheric pressure at temperatures of 300 and 400 ºC, using a system with a chamber containing hydrogen gas injected at a rate of 200 cm^3/min, was verified that at 300 ºC, the zircaloy 4 pipe incubation time is the lengthiest (about 30 h), while for zircaloy 2 and zirlo tubes of them are similar (about 1000 and 800 min, respectively) (figure 1a). However, at 400 ºC the incubation time becomes very short and almost identical, indifferent of the zirconium tubes alloys (figure 1 b). It is also possible to notice that the rates of weight gains of the different zirconium tubes at both temperatures are not very different and if placed in decreasing order results: zirlo > zircaloy 2 > zircaloy 4 [5].

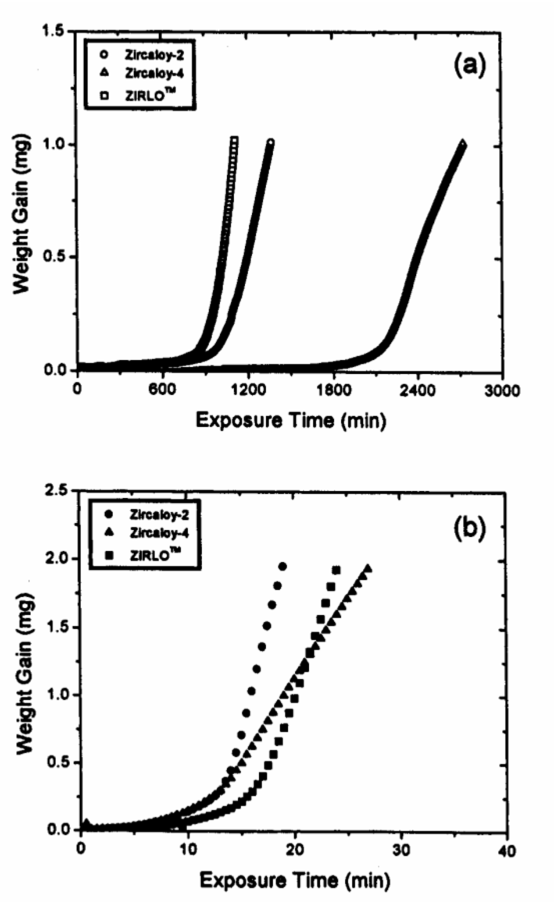

Figure 1. Comparison of the tubes weight gain of: zircaloy 2, zircaloy 4 and zirlo with the time of the reaction at the temperatures of a) 300 ºC and b) 400 ºC.

3. CONCLUSIONS

The addition of alloy elements to the zirconium improves the resistance to corrosion, counterbalancing the harmful effect of impurities such as nitrogen, oxygen and carbon.

When impurities are present in high amounts, the zirconium resistance to corrosion is significantly affected. The effect of nitrogen is significantly increased when present in amounts above 0.004% approximately. For high nitrogen amount, the corrosion is strengthened.

Comparing the zircaloys alloy (zircaloy 2, zircaloy 4, Zr-2,5Nb and zirlo), in as much as the resistance to corrosion is concerned, all of them have basically similar performances. But the zirlo alloy is gaining great importance as a potential material for nuclear fuel cladding tubes.

The most promising aspects of this alloy are: low rate of corrosion, better properties of creep to the irradiation, increase of mechanical resistance and capability of resisting the highest burn-ups.

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