



HAL
open science

Microstructural evolution of α or β quenched zirconium alloys during isothermal agings, between 20 °C and 750 °C

P. Merle, K. Loucif, R. Borrelly

► **To cite this version:**

P. Merle, K. Loucif, R. Borrelly. Microstructural evolution of α or β quenched zirconium alloys during isothermal agings, between 20 °C and 750 °C. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-519-C7-522. 10.1051/jp4:1993783 . jpa-00252203

HAL Id: jpa-00252203

<https://hal.science/jpa-00252203>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Microstructural evolution of α or β quenched zirconium alloys during isothermal agings, between 20 °C and 750 °C

P. MERLE, K. LOUCIF and R. BORRELLY

Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux, URA 341, Bat. 502, INSA, 69621 Villeurbanne cedex, France

Abstract : In Zircaloy and zirconium alloys, after quench from the upper limit of the α domain a small quantity of iron, chromium or nickel remains in solid solution and then precipitates during further isothermal aging. This precipitation is studied between 450°C and 600°C, using thermoelectric power (TEP) and resistivity measurements. It is shown that precipitation kinetic is strongly reduced by the presence of oxygen and tin.

After quench from the β domain (1030°C) five stages of evolution are detected by TEP measurements in Zircaloy-4, the more important being :

- a low temperature evolution (<400°C) attributed to local atomic rearrangements
- the precipitation of iron and chromium initially dissolved. The amplitude of TEP variation shows that β quench do not permit to allow larger amount of iron and chromium in solution tha for α quench
- the recrystallization of the initial martensitic structure.

Introduction :

In Zircaloy, after quench from the upper limit of the α domain, a small part of the added elements : Fe, Cr, Ni in solid solution, precipitates during isothermal agings at low temperature. The same phenomenon can take place after quench from the β domain. In this case substructure rearrangements can be also observed. These evolutions are expected to have an influence on the mechanical or chemical properties. To study a such fine microstructural change a very sensitive method of investigation is required. In this study we have essentially used thermoelectric power measurements which is particularly well adapted to this problem as it was shown in a previous paper [1,2]. Some experiments have been made using also electrical resistivity measurements at the temperature of liquid nitrogen.

In the α quenched alloys the precipitation kinetics have been determined between 450°C and 600°C as a function of the composition of the alloys. In the β quenched Zircaloy-4 the more complex evolution has been studied between 320°C and 750°C.

Experimental method :

TEP is measured at 20°C on small parallelepipedic samples (70 x 4 x 1 mm³) relatively to pure aluminium [3]. The resistance variation $\Delta\rho / \rho_0$ is measured at the temperature of liquid nitrogen after removing the superficial oxydised layer occuring during aging. A correction based on mass determination takes into account the section reduction of the sample.

Samples are initially annealed at high temperature in a pure argon atmosphere, then

water-quenched. Isothermal agings are performed so as to avoid as much as possible the oxydation of the specimen. The TEP variation is followed using the method of cumulated aging-times. The chemical composition of the studied alloys is given in table I.

Table 1 : chemical composition of alloys (wt ppm)

| Alloy | Ni | Sn | Fe | Cr | O | Ni | C |
|------------|----|-------|------|------|------|-----|-----|
| Zr-Fe | 1 | | 36 | | 320 | | |
| Zr-Fe | 2 | | 277 | | 70 | | |
| Zr-Fe | 3 | | 556 | | | 70 | |
| Zr(D) | 4 | <30 | 410 | 55 | 850 | | 40 |
| Zr-Sn-O-Fe | 5 | 13100 | 337 | | 1050 | | |
| Zr-Sn-O-Cr | 6 | 12800 | | 275 | 1320 | | |
| Zircaloy-2 | 7 | 15000 | 1500 | 1000 | 1300 | 600 | 75 |
| Zircaloy-4 | 8 | 14800 | 2100 | 1200 | 1100 | <50 | 100 |

Aging of α quenched alloys :

Precipitation of iron and chromium gives rise to an increase of TEP and to a decrease of resistivity, due essentially to the variation of the concentration of these elements in solid solution.

Figure 1 shows the curves of TEP and resistivity variation due to isothermal agings at temperature between 450°C and 600°C, after quench from 805°C.

A very good correlation is observed between the results obtained with these two experimental techniques. For further studies only TEP has been used, owing to easiness of such a measurement [3].

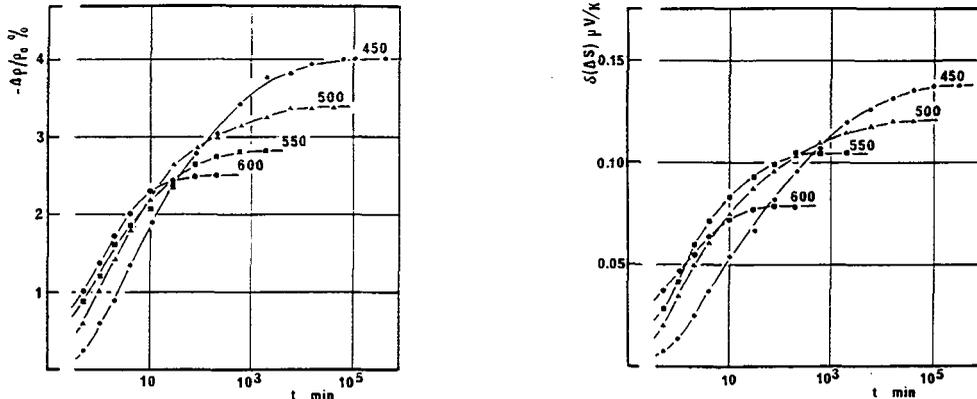


Figure 1 : resistivity (a) and TEP (b) variations due to isothermal agings at various temperatures after quench from 805 °C in Zircaloy-4.

The maximum amplitude variation of TEP curves can be associated to the amount of solute precipitated. The important variation of this amplitude according to the aging-temperature observed in the curves (Fig. 1b), corresponds to a variation of the maximal solubility of iron and chromium between 450°C and 600°C.

Assuming a proportionality between TEP variation [4] and the amount of precipitated elements, the precipitation kinetic can be deduced from TEP curves such as those given in figure 1. Thus, the time corresponding to the complete precipitation (90 % of the total variation of TEP) has been determined for various alloys (Figure 2) and at different temperatures. It is observed that this time may vary of two order of magnitude according to the various studied alloys. This effect is attributed to tin and oxygen which tends to reduce the precipitation rate.

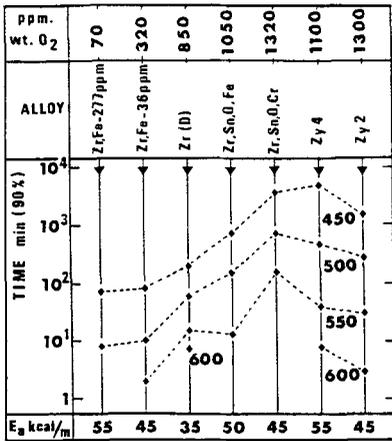


Figure 2 : Aging-time corresponding to 90 % of TEP variations by aging at 450°C, 500°C, 550°C and 600°C for various alloys, and apparent activation energy.

Aging of β quenched Zircaloy-4 :

After water-quench from 1030°C of Zircaloy-4 samples, we obtain a martensitic type microstructure, consisting in fine plates of α phase, the arrangement of which is generally designed as "basket-weave" microstructure [5]. The curves of figure 3 show TEP variations due to isothermal agings of such a structure between 400°C and 750°C.

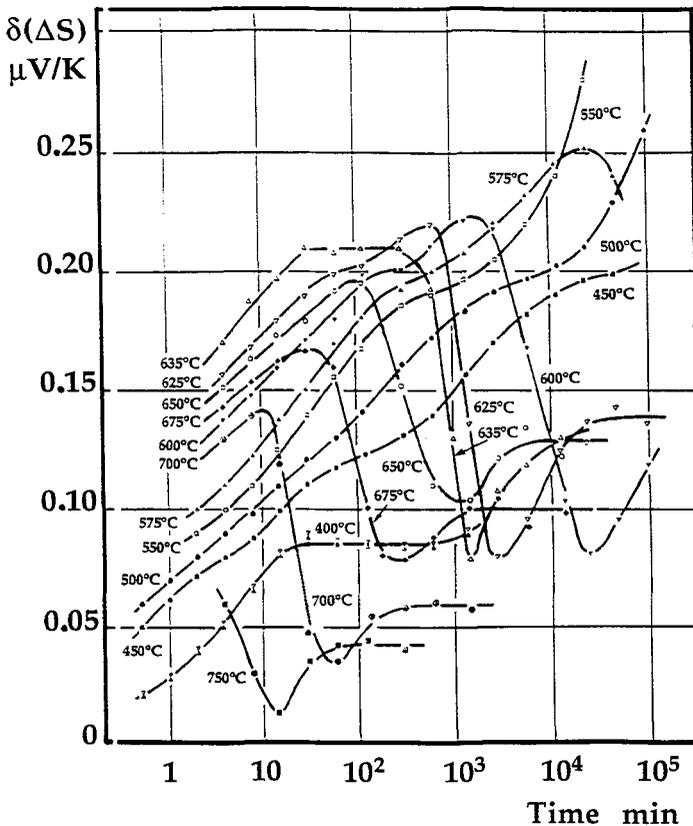


Figure 3 : TEP variation due to aging between 400°C and 750°C in Zircaloy-4 after quench from 1030°C.

It can be observed that the TEP variations are much more complex than those obtained for the α quenched alloys.

From these results it is possible to distinguish five evolution stages :

- stage I corresponding to TEP evolution at temperature below 400°C is only observed here in figure 3 at its limit temperature (400°C). It has been attributed to atomic rearrangements of interstitial elements.

- stage II is easily observed between 450°C and 650°C and corresponds to an increase of TEP up to a roughly constant value of 0.2 $\mu\text{V/K}$. It occurs in the same time range than TEP evolution in α quenched Zircaloy, and it has been attributed to the precipitation of solute elements : Fe, Cr, in solid solution after quench. Moreover it has been observed by electron microscopy that recovery of quench defects occurs during this stage. The 0.2 $\mu\text{V/K}$ amplitude of TEP increase supports the assumption that the amount of iron and chromium in solid solution after β quench is not very different than that obtained after α quench (about 150 ppm).

- stage III observed between 600°C and 700° in figure 3 corresponds to an abrupt decrease of TEP. Optical micrographs shows that this stage is due to a recrystallization of the specimen, as for a cold working materials. During this stage microhardness decreases, but electrical resistivity do not vary. This recrystallization is observed only because the β quench rate is high. For a low quench rate the phenomenon is rather different since it consists in a coarsening of the preexistent α plates.

- stage IV corresponding to a low increase of TEP after recrystallization has been attributed to a segregation of added elements on the new boundaries.

- stage V intermediary between stage II and III is observed between 500°C and 575°C. It corresponds to an abrupt TEP increase interrupted by the recrystallization. The origin of this stage has not yet be explained.

From the TEP curves, a complete T.T.T. diagram describing the various microstructural evolutions of β quenched structure in Zircaloy-4 has been established (Figure 4).

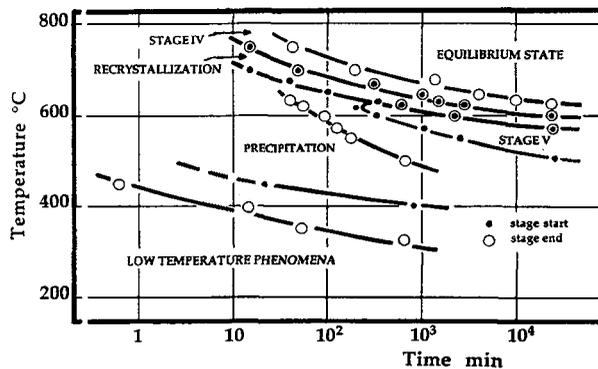


Figure 4 : T.T.T. diagram showing the different stages of evolution of β quenched Zircaloy-4

Bibliography :

- 1) BORRELLY R., MERLE P. and ADAMI L., J. Nucl. Materials, 170, (1990), 147.
- 2) LOUCIF K., BORRELLY R. and MERLE P., J. Nucl. Materials, 189, (1992), 34.
- 3) BORRELLY R., BOUVIER-VOLAILLE, Traitements thermiques, 221, (1988), 43.
- 4) LOUCIF K., Thèse de Doctorat, Déc. 1992, INSA de LYON.
- 5) WOO O. T. and TANGRI K., J. Nucl. Materials, 79, (1979), 82.