PHASE TRANSFORMATIONS OF E110G Zr-ALLOY OBSERVED BY "IN SITU" XRD

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Abstract

The high-temperature phase transformations of E110G Zr-alloy were investigated by using "in situ" X-ray diffraction methods. The Zr-Nb E110G alloy is nowadays used for protective layers of nuclear fuel rods in PWR a BWR nuclear reactor. For the examination of interstitial oxygen and nitrogen influence on phase transformation the samples of pure Zr were used. The measurements proceed in evacuated high-temperature chamber being a part of automatic powder diffractometer. Experimental samples were heated at different maximum exposure temperatures and then cooled down at temperatures 1000 °C, 900 °C, 850 °C, 800 °C and 30 °C. At all these temperatures the diffraction patters were collected.

1. Introduction

Materials on the basis of zirconium are already used more than fifty years in area of nuclear energetics. Due to combination of high corrosion resistance in the air, water and also in any aggressive environments, e.g. H_2SO_4, HCl, KOH, NaOH, good mechanical properties and very low absorption cross section for thermal neutrons, Zr-alloys are an ideal material for protective layers of nuclear fuel rods. For this application the Zr-alloys can be used in pressurized water reactors (PWR) and boiling water reactors (BWR). There are two basic types of materials used as claddings. The first group of materials is represented by alloys of zirconium and tin, which are called Zircaloys, Tab. 1. Four types of these alloys were developed in the USA from a first half of 1950s, [1-4].

The second basic type of Zr-based materials was developed practically at the same time in USSR and later also in Canada for CANDU reactor. As a main alloying element the niobium was used. The main cladding material was designated as E110 (Zr+1%Nb) and its properties are constantly improved. In the present the modified E110G alloy is used for fuel rods protective layers, Tab. 2. From late

Table 1. Chemical composition of Zircaloy alloys [6]**.**

Alloy	Chemical composition Wt. %			
	Sn	Fe	Cr	Ni
Zircaloy-1	2.5	-	-	-
Zircaloy-2	1.5	0.12	0.10	0.05
Zircaloy-3	0.25	0.25	-	-
Zircaloy-4	1.5	0.22	0.10	-

1990s the Zircaloys are gradually replaced by Zr-Nb alloys with regard to their much better corrosion properties, [1-4].

An important part of Zr-alloys research is a study of their behaviour during the LOCA accident. This type of reactor accident results in a rapid cooling water escape in a time shorter than 10 seconds, followed by a rapid heating of the Zr-alloy in steam environment at the temperature above 1000°C. These severe conditions lead partly to a fast high-temperature oxidation and also to a phase transformation of Zr-alloy to high-temperature -modification with body-centred cubic lattice until the reactor core is flood with water and the cladding is quenched back to -phase with HCP lattice. The temperature of Zr-alloy phase transformation is strongly influenced by free oxygen and nitrogen placed in interstitial positions of crystal lattice and also by a heating rate [5]. The theoretical value of + transformation temperature is for E110G alloy 620 °C, Fig. 1. In the real material structure the transformation temperature is very strongly influenced by oxygen and nitrogen presence. In a form of solid solutions these elements stabilize the low-temperature -phase even at high temperatures. In this work as a main experimental material the E110G alloy was used. The samples of pure Zr by Goodfellow Ltd. were used for the comparison and also for study of oxygen and nitrogen influence on high-temperature phase transformations.

Table 2. Chemical composition of E110 and E110G Zr-Nb alloys**.**

Alloy	Element							
	Nb [%]	Fe [ppm/%]	H [ppm]	N [ppm]	C [ppm]	O [ppm]	Ni [ppm]	Hf [ppm]
E110	1.0	100	25	-	-	600-700	70	100
E110G	1.0 - 1.1	0.055	3	20	100	840	-	~500
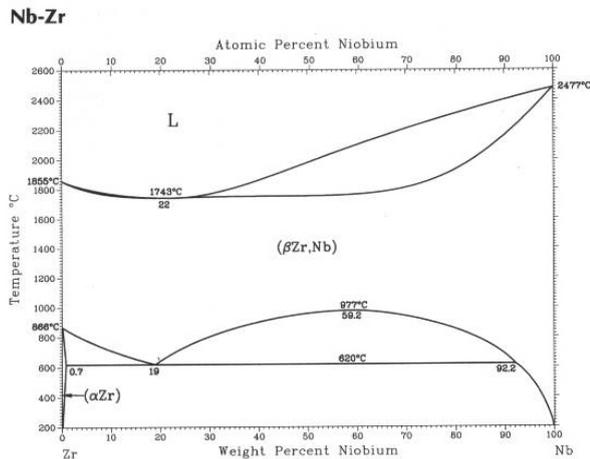
Figure 1. Zirconium – niobium binary phase diagram [6].

Figure 2. Heat treatment of experimental samples.

2. Experiment

For the experimental samples the heating-cooling courses with three maximum exposure temperatures 1100 °C, 1150 °C and 1200 °C were created, Fig. 2. These courses also make provision for a strong affinity of zirconium for oxygen and nitrogen. Air molecules adsorbed on sample surface caused relatively strong surface oxidation of Zr and its alloys. That is why a deaeration step at 250 °C for 60 minutes was added to heating-cooling course of all experimental samples. After the deaeration each sample was firstly heated at the temperature 860 °C which is the theoretical phase transformation temperature of pure Zr. This step displayed if the phase transformation of experimental materials proceeds already during the heating.

After that the experimental samples were heated at a maximum exposure temperature and then they were gradually cooled down at temperatures 1000 °C, 900 °C, 850 °C, 800 °C and 30 °C, Fig. 2. At all these temperatures the "in situ" X-ray diffraction was measured. This form of heating-cooling course ensures that there will be no influence of transformation temperature hysteresis for heating and cooling down. During the measurements the experimental samples were inserted in the evacuated high-temperature chamber Anton Paar HTK 1200N. This chamber uses a radiation heating without temperature gradients up to the temperature 1200 °C. Inner space of the chamber was evacuated with the aid of dry scroll pump Edwards XDS 5 and turbo-molecular pump Edwards EXT 75 system. The chamber was mounted in an automatic powder diffractometer Panalytical X'Pert Pro. This instrument is equipped with a Cu X-ray tube and an ultra-fast semi-conductor PIXcel with high resolution ability.

3. Results and discussion

For the experimental measurements two pairs and one separate sample were used. For the highest exposure temperatures 1100 °C and 1150 °C two pairs of samples were used. One sample was always made from E110G alloy and the second one was from pure Zr. For the temperature 1200 °C only E110G alloy was used.
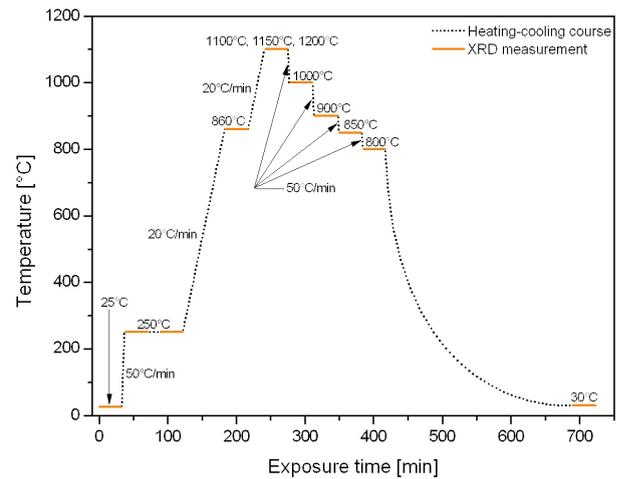
3.1 Samples Zr-1Nb_11 and Zr_29

For the samples Zr-1Nb_11 (E110G alloy) and Zr_29 (pure Zr) the temperature 1100 °C was used. Results of Zr-1Nb_11 sample show at 860 °C surface corrosion layer compound of monoclinic ZrO_2 and non-stoichiometric tetragonal $ZrO_{1,95}$, Fig. 3. This layer is unstable at higher temperatures and it disintegrates quite fast. The identified high-temperature -Zr phase is a part of this corrosion layer. Its appearance is then fixed to the corrosion layer. The phase transformation of inner volume of E110G did not proceed in consequence of interstitial oxygen and also nitrogen presence which stabilised the low-temperature -phase even at high temperatures. The interstitial nitrogen is in the structure of both investigated materials. At high temperatures it creates with zirconium the surface cubic nitride ZrN which is visible in diffraction patterns at 1100 °C, Fig. 3, 4. Creation of this layer strongly influenced also the phase transformation of pure Zr. The -Zr phase can be seen after the cooling down at 1000 °C. This is related to surface -Zr layer initially oversaturated by the

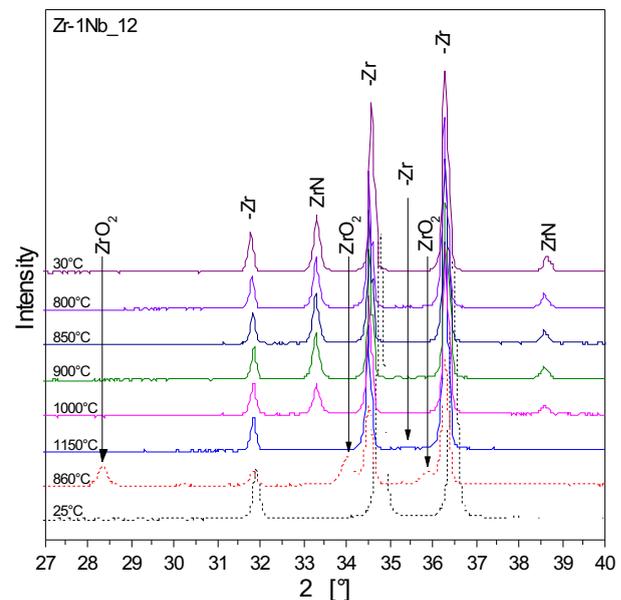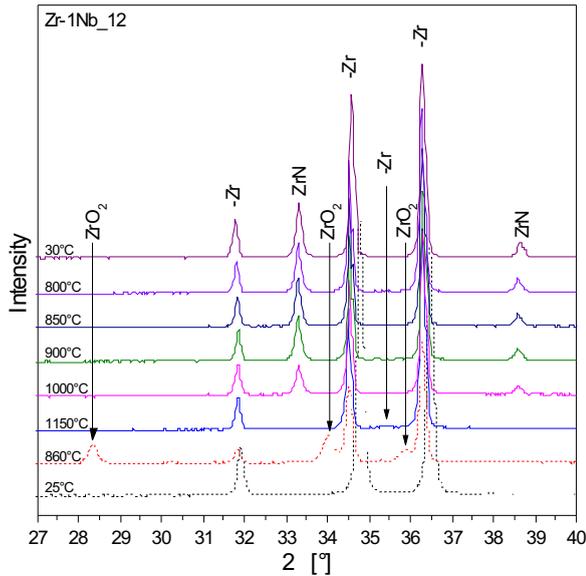**Figure 3.** Partial diffraction patterns of Zr-1Nb_1.

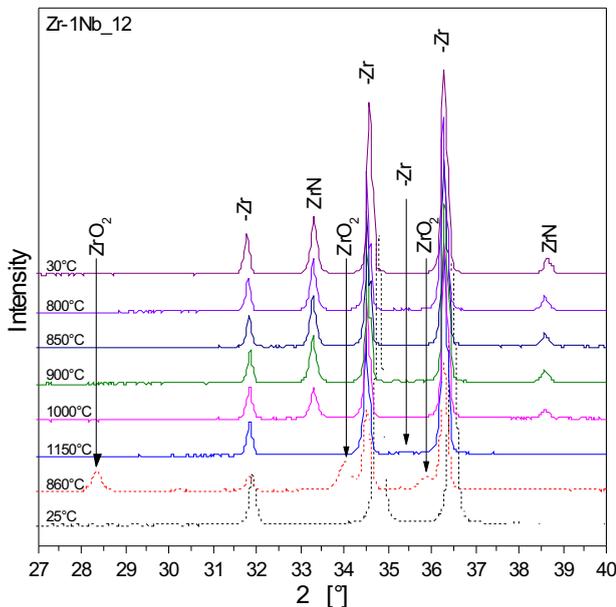**Figure 4.** Partial diffraction patterns of Zr_29.

Figure 5. Partial diffraction patterns of Zr-1Nb_12.

Figure 6. Partial diffraction patterns of Zr_32.
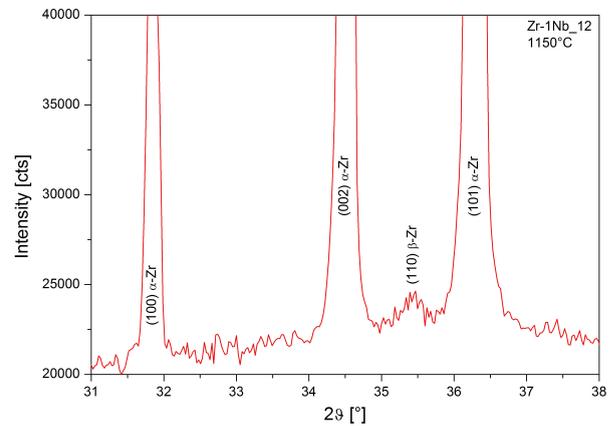
Figure 7. Detailed partial diffraction pattern of Zr-1Nb_12 at 1150 °C.

nitrogen. With the surface ZrN growth this layer was depleted of nitrogen which caused decreasing of transformation temperature. At 850 °C is the -Zr completely changed back into -Zr which corresponds with binary phase diagram, Fig. 4.

3.2 Samples Zr-1Nb_12 and Zr_32

For this pair of samples the highest exposure temperature was 1150 °C. At 860°C the diffraction pattern of Zr-1Nb_12 sample (E110G alloy) shows the corrosion layer again. During subsequent heating to 1150°C this layer completely disintegrated. The trace amount of -Zr phase identified at this temperature is in inner volume of alloy, Fig. 6. During the cooling down at 1000 °C the high-temperature Zr phase changed back to -Zr very fast due to oxygen and nitrogen presence. The corrosion layer of Zr_32 sample (pure Zr) is a consequence of oxygen dif-
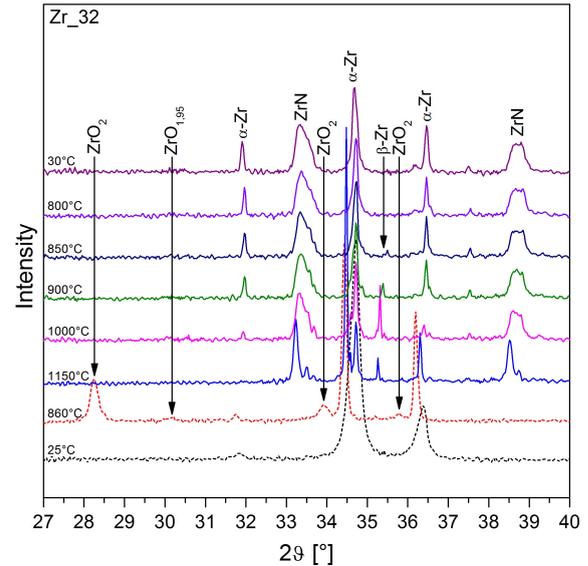
fusion to material even at room temperature, Fig. 6. Also here the corrosion layer disintegrated during the heating at 1150 °C and the (110) line of -Zr is obviously evident in diffraction pattern, Fig. 7. The increasing amount of -Zr visible at 1000 °C is again caused by ZrN layer creation as well as in case of Zr-1Nb_11 sample. At 850 °C a trace amount of -Zr could be identified in the structure but nearly under this temperature it changed to -Zr.

3.3 Sample Zr-1Nb_13

With regard to higher amount of -Zr phase which was created in Zr_32 sample after the heating at 1150 °C only a sample made from E110G alloy was used for the heating at 1200 °C. The corrosion layer created during the heating at 860 °C completely disintegrated during subsequent heating at 1200 °C, Fig. 8. The phase transformation is again influenced by interstitial oxygen and nitrogen. The relatively strong (110) line of -Zr can be identified at 1200 °C. After the cooling down at 1000 °C the high-temperature modification changed back to -Zr phase.

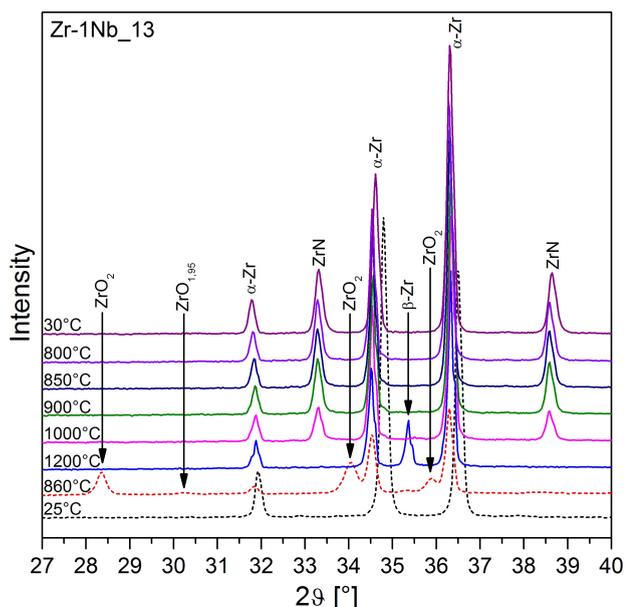**Figure 8.** Partial diffraction pattern of Zr-1Nb_13 at 1200 °C.

heating at 1150 °C. At 1200 °C the (110) of -Zr is relatively strong, but this temperature is still nearly above transformation temperature due to nitrogen and oxygen. During the cooling down at 1000 °C the -Zr phase completely changed back to -Zr in all samples of alloy. The influence of nitrogen show itself also in the case of pure Zr. The small amount of -Zr is shown in the structure during the cooling at 1000 °C after the heating at 1100 °C. This is due to depletion of undersurface -Zr layer of nitrogen which is used for surface ZrN layer creation. After that the presence of -Zr conforms the binary phase diagram.

4. Conclusions

The results show that the high-temperature phase transformation of E110G and also of pure Zr is absolutely fundamentally influenced by nitrogen and also oxygen dissolved in interstitial positions. Both these elements even in a small amount strongly increase the phase transformation temperature of experimental materials. The heating-cooling courses used for experimental samples demonstrated that for the E110G a trace amount of high-temperature -Zr phase was in inner volume of material created after the

References

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