Conference Paper

Effect of β-Quenching on Oxidation Resistance of Zirconium Alloy ZrNbMoGe for Fuel Cladding Material

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Abstract

Effect of ß-quenching of Zr-2.5Nb-0.5Mo-0.1Ge alloy used for advanced fuel cladding material of Pressurized Water Reactor (PWR) was investigated. The aim of this research is to improve the mechanical and corrosion properties through modification of the alloy with regard to high reactor burn up. The quenching process was conducted by heating the sample at temperature of 950 °C and soaking 2.5 hours, followed by quenching in water at room temperature and then continued with annealing process at 500 and 600°C. The change of hardness and oxidation resistance were characterized using optical microscope and scanning electron microscope (SEM). The effect on the oxidation resistance was investigated by the high temperature oxidation test using the MSB (Magnetic Suspension Balance) at 700 °C for 5 hours. The hardness increased from 217 VHN to 265 VHN after quenching due to grain refinement and precipitation hardening. The oxidation rate followed the typical parabolic growth characteristic. The formation of thin layer was considered to be a stable oxide ZrO_2 that influenced the oxidation characteristic and increasing the hardness of the alloy.

Keywords: cladding material, zirconium alloy, quenching, hardness, oxidation.

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1. Introduction

The advanced fuel cladding materials based on ZrNbMoGe alloy which termed for high performance for reactor application with high burn up has been investigated at PSTBM-BATAN. The niobium containing zirconium alloy has been used successfully as fuel cladding materialin Pressurized Water Reactor (PWR) typed nuclear power plant sex hibiting high burn up [1]. Addition of Nb reduced the risk of nodular corrosion, decreased the hydrogen uptake and increased the ductility, toughness and creep resistance of the alloy [2, 3]. Molybdenum was also added to improve the hardness, phase homogeneity and corrosion resistance [4], while the addition of germanium was designed to improve the stiffness of the fuel cladding [5]. The investigation showed that the ZrNbMoGe alloy scan satisfy the requirement of high material hardness and high oxidation resistance for application as reactor fuel cladding material [6]. However, a properly heat treatment process during in got production is necessary to carry out to improve the mechanical properties for subsequent manufacturing process. With regard to the workflow of fuel cladding material manufacturing both of quenching and annealing processes should be investigated [7].

Quench treatment of zirconium alloy was performed firstly by heating the material into the β-phase temperature ranges followed by rapid cooling into room temperature to produce a controlled precipitation during the subsequent aging. Based on the metallurgical consideration, during β-quenching zirconium alloy matrix transforms from a β-bcc phase to an α-hcpphase which obviously has different microstructure when treated at different cooling condition [8]. The change of microstructure was mostly indicated by the formation of a Wildman structure consisting of α-phase plates and the precipitation of small secondary phases in the grain boundaries [9]. The α to β allotropic transformation takes place at 865°C. β phase is stable up to 1860°C, while α phase exhibits strong anisotropy which plays an important role during deformation [10]. It was reported that new Nb containing Zirlo alloy is characterized by its single martensitic structure obtained by water quenching [10]. Further, β-quenching has also significantly improved the corrosion resistance of zirc alloy due to the existence of small second phase [10].

The temperature and time of the quenching and heat treatment process of the new. ZrNbMoGe alloy are the main parameter that needs further investigation. The aim of this work is to investigate the effect of β-quenching on Zr-2,.5Nb-0.5Mo-0.1Ge alloy according to the microstructure, hardness and high temperature oxidation characteristics.

2. Experiments

As shown in flow chart in Fig. 1 (a) this work mainly contains the following activities: the material synthesis, the quenching and annealing, the hardness testing, oxidation experiment and the microstructure characterization. Fig. 1 (b) presents the quenching and annealing process diagrams. The annealing is performed at two different durations, 2 and 3 hours.

The ZrNbMoGe alloy was manufactured by melting of zirconium, niobium, molybdenum and germanium sponges using arc melting furnace in the argon atmosphere at temperature around 1850 °C. The mixture was 96.9 wt.%, 2.5 wt.%, 0.5 wt.%, 0.1wt.% for Zr, Nb, Mo and Ge respectivelly. Regarding to reach a homogeneous microstructure, the sample was remelted five times and slowly cooled in air to room temperature. The β-quenching was carried out by heating the samples 10°C/minutes, followed by soaking at 950 °C for 2.5 hours and immediately cooled in water. The sample was then annealed at 500°C and 600 °C for 2 hours to release the residual stress.

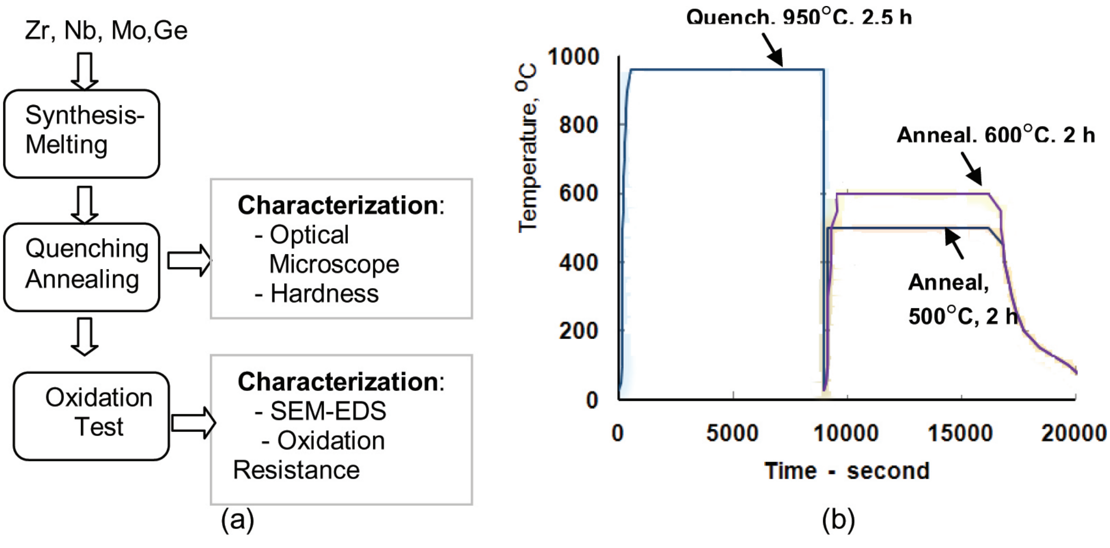

Figure 1: (a) Flow diagram and (b) quenching and annealing curve.

The sample preparation for micro structural analysis using optical microscope was performed by mechanical grinding and subsequent chemical etching in a solution of 5% H_2SO_4, 10% HF, 30% HNO_3 and 55% H_2O by volume. The hardness measurement was carried out using Vickers Hardness tester with diamond indenter at applied load of 500 grams and indentation time 15 seconds. The high temperature oxidation test was performed in the Magnetic Suspension Balance (MSB) in the High Temperature Material Laboratory of PSTBM-BATAN. The oxidation test was carried out at temperature of 700 °C for 5 hoursto simulate the operation temperature of PWR fuel cladding with the main interest on the investigation of the early stage of the oxidation. The MSB workstation consistsmainly of alumina tube, electrical resistance furnace, temperature control and balancing measurement system equipped with suspension and holding magnet. The weight gains per unit area was measured in a fix time difference and displayed as characteristic oxidation curve. The sample cross section was observed using SEM JEOL JMS2605LV. For elemental analysis energy dispersive x-ray spectroscopy (EDX) attached on SEM was used.

3. Result and Discussion

The microstructures of ZrNbMoGe as cast ingot before and after quenching and annealing process taken by optical microscope are shown in Fig. 2.

The sample as cast is obviously martensitic andrelatively has small amount bainitic structure due to high cooling rate after melting. The structure is homogenously distributed in

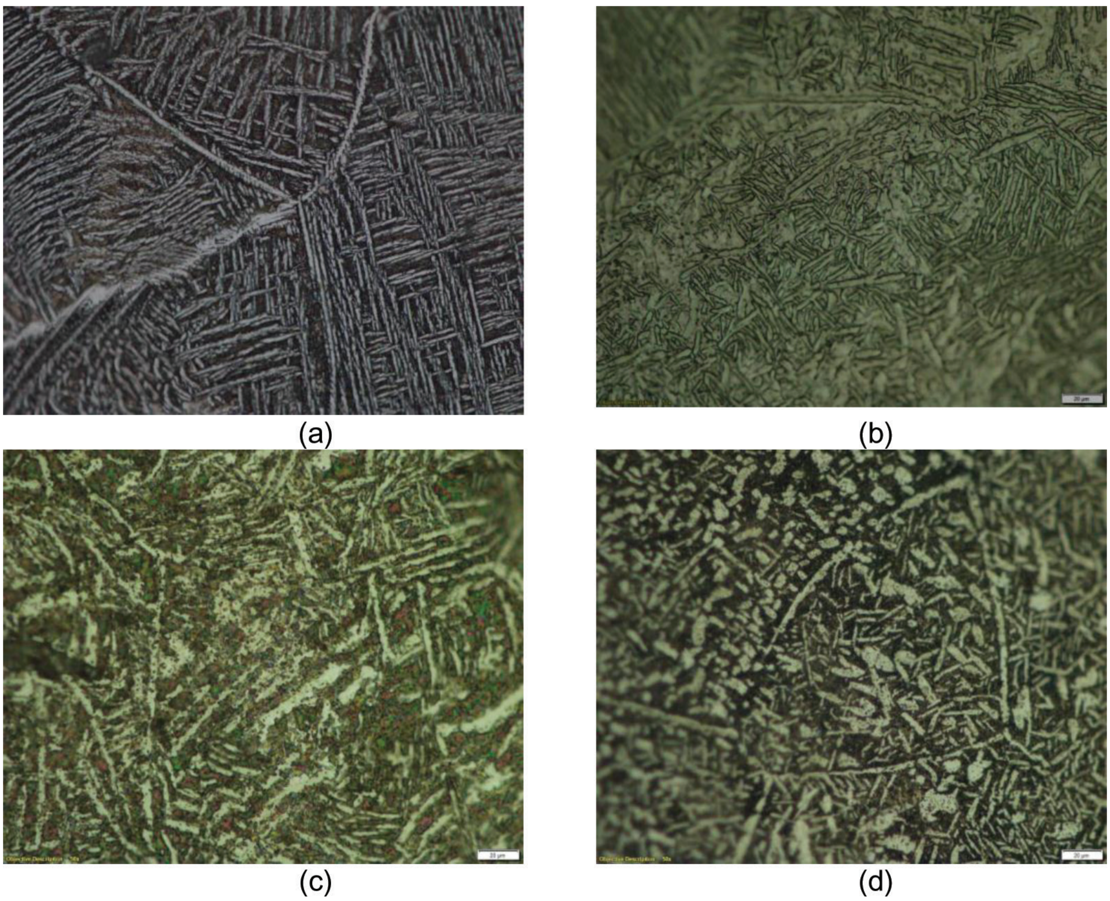

Figure 2: Microstructure of as cast in got (a), after quenching (b), after quenching continued with annealing 500°C –2 hours (c) and 600°C – 2 hours (d).

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the entire matrix volume with the characteristic lath martensite as commonly occur in Zr-Nb alloys [9,10]. After quenching, again the structure consists of martensite similar to those as cast but with more finer grains. The annealing process carried out after quenching causes a re-crystallization which leads to the grain coarsening as obvious in Fig. 2 (c) and (d). At higher annealing temperature the grain coarsening becomes faster. Previous investigation on the same alloy, the SEM-EDS analysis supported by the XRD analysis confirmed the presence of hard Zr-Ge precipitates in grains and grain boundaries [11]. This precipitation occurred during melting and significantly increase the hardness of the alloy. However, after quenching and annealing the precipitation hardening can not be observed. This could be due to applied temperature in this experiments which was lower than those during melting.

Fig. 3. shows the result of hardness measurement after and before treatment. The hardness increases significantly from 217 VHN as cast to 265 VHN after quenching process.

The change of hardness was considered to be mainly caused by the microstructure change as explained and shown above (Fig. 2). The annealing following quenching process decreases the hardness due to grain coarsening which is strongly depend on the temperature as seen in Fig.2 (c) and (d).

Figure 4 shows the oxidation characteristic curve of ZrNbMoGe in got before and after quenching and annealing process. The weight gains resulted from the oxidation in air are plotted as a functionof the oxidation time.

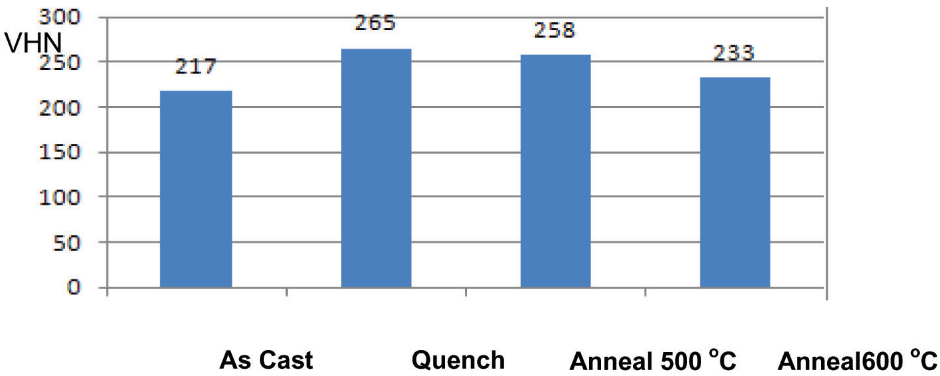

Figure 3: Hardness of ZrNbMoGe alloy before and after quenching-annealing.

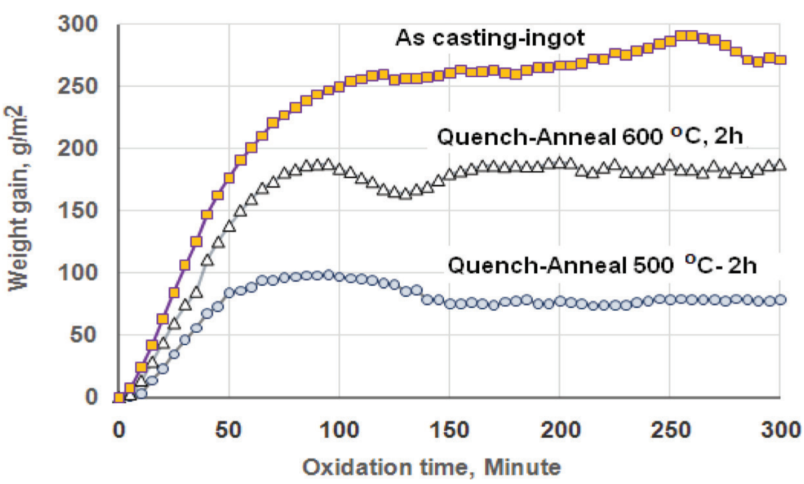

Figure 4: Oxidation characteristic curve of the ZrNbMoGe alloy oxidized in air at 700 °C.

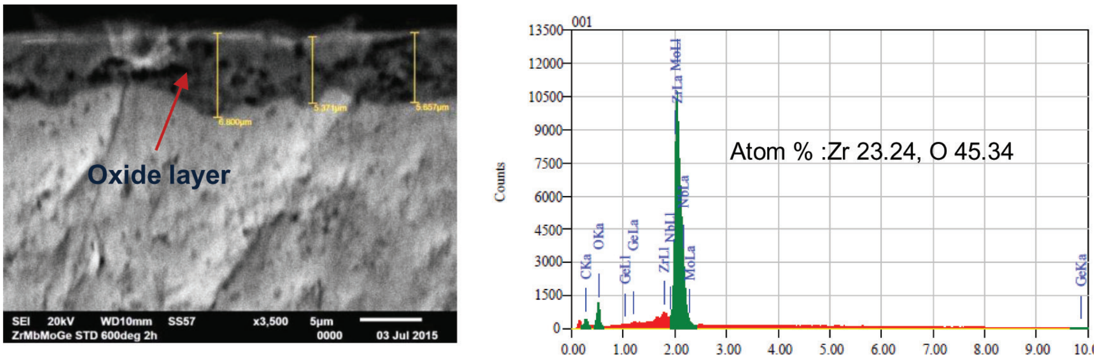

Figure 5: SEM cross section (a) and EDX spektrum (b) of ZrNbMoGe after quenching and annealing 500 °C and oxidized at 700 °C during 5 hours.

The oxidation rates of the three samples during heating up to 100 minutes follow a parabolic growth kinetics where the mass gain is proportional to the square root of time. The weight gains of all samples after100 minutes oxidation become nearly constant. However, both samples after quenching and annealing show lower oxidation rate than those of ingot samples. Decreasing of the annealing temperature from 600 °C to 500 °C resulted in better oxidation rate, as observed by the weight gain change from 190 to 90 g/m². From the charactristic of parabolic kinetics, it is obvious that the oxide formation on the samples is oxygen inward diffusion driven process inside the oxide layer. This stands in agreement with the well known high temperature oxidation characteristics of zirconium alloy [12,13]. The mechanism of high-temperature oxidation of zirconium alloy is widely accepted to be the diffusion of oxygen anions through the ZrO_2 lattice [14,15]. The metal cations transport however is fully inhibited. The lower corrosion rate of the alloy after quenching and annealing process at the early stage of the oxidation can be considered to be caused by the effect of grain coarsening on the top most of the metal surface due to annealing which in turn decreases the number of oxide crystallites formed and so the possibillities of oxygen diffusion channeling between the oxide grains.

One result of the SEM-EDX measurements on the oxide scales formed during oxidation test,is shown in Fig. 5. On all examined specimens, the oxide layer remained on the surface. Based on the EDX result, the oxide layer was identified as zirconium-oxideZrO_2.

After oxidation at 700 °C, SEM micrographs reveal the oxide layer thickness around 8 mm on the sample as cast and between 6to 7 mm on the samples after quenching and annealing. These confirmed the result of oxidation meassurements as discussed above (Fig. 4).

4. Conclusion

From this study, it can be concluded that quenching process increased the material hardness and decreased the oxidation during first stage of heating at 700 °C which is caused by the effect of grain refining during quenching and grain coarsening during annealing. This decreased the amount of oxygen diffusion channels and the oxide layer formed on the samples is a stable ZrO_2.

5. Acknowledgment

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