Effect of High-Temperature Heating Cycle on Mechanical Strength Degradation of 95 wt% Metallic Zirconium in Alkaline Fusion Environment

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ABSTRACT

Zirconium and its alloys are metals that resist high temperatures, have good mechanical characteristics, and resist corrosion attacks. PT Timah uses metallic zirconium for tin ore smelting reactors involving alkaline fusion at a heating temperature of 800 °C in 10 minutes. Under these conditions, zirconium fails after 1000 minutes of accumulative heating. In this study, a simulation of tin ore smelting was conducted with 100 minutes each cycle. Tensile strength and Vickers hardness tests were conducted at cycles 0, 3, 6, 9, and 12 to observe the degradation that occurred. The results showed that the samples decreased their UTS and lost their elasticity as the heating cycle increased. At cycle 9, the samples experienced the largest decrease in UTS of 80% from 406.76 MPa to 81.20 MPa. The Vickers hardness of the sample surface increased from 180 VHN to 1031.42 VHN while the strain decreased from 11.90% to 3.70%.

Keywords: Zirconium, High-Temperature, Crucible, Alkaline Fusion

1.   Introduction

Zirconium and its alloys are often used for applications in highly corrosive environmental conditions because of their high corrosion resistance. Zirconium is characterized by good resistance to corrosion and oxidation, resistant to irradiation damage, has good mechanical characteristics, and is transparent to thermal neutrons making it very suitable for applications in nuclear fuel [1]. Zirconium also has good thermal conductivity which is 30% better than stainless steel alloys so it can be used for heat exchanger structures in extreme environments in a smaller and more compact size [2].

Zirconium metal has a melting temperature of around 1850 °C and is an allotropic metal element that has 2 different structural phases. Zirconium at room temperature up to 860 °C is α-Zr with a hcp (hexagonal closed pack) crystal structure and above that temperature turns into β-Zr which has a bcc (body center cubic) structure [2], [3], [4].

PT Timah Tbk and related industries use zirconium metal as a reactor for laboratory needs as a replacement for high-priced platinum. The use of other crucibles such as alumina in industries with large production or analysis needs may disrupt the lab process given the weak nature of ceramic materials against thermal shock. Zirconium metal was resistant to thermal shock, high corrosion resistance, and did not cause contamination in the analysis process.

Research on zirconium resistance to corrosive chemicals has been conducted by scientists. Rivai et al. [5] researched zirconium alloy resistance to lead-bismuth-eutectic (LBE) heavy metal fluids. This liquid is corrosive to

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metal cladding materials and nuclear reactor structures. The zirconium alloy used was Zr 97.5 wt%, Nb 1%, Mo 1%, and Ge 0.5%. Corrosion testing was carried out at 550 °C with an oxygen flow concentration of 1×10^{-6} for 312 hours. The results showed that the penetration of LBE liquid caused an exchange with the sample surface which caused pitting corrosion. A ZrO_2 (zirconia) layer with a depth of about 10 μm was formed.

In the application of zirconium concerning wear behavior, Mosbacher et al. [6] conducted Tribological properties research on ZrNb7 as a bone implant. The ZrNb7 alloy was compared with other materials, namely ZrNb2.5 oxidized in air, and CoCrMo28-6 with and without Ti4N coating. The samples were treated with 3 different methods, the first was oxidation at 600 °C for 1 hour, the second was a 3-stage heat treatment, namely heated in air at 600 °C for 1 hour, then at 700 °C for 2 hours at a pressure of 4×10^{-3} Pa, then heated again at 600 °C for 1 hour, and the third treatment was heated at low oxygen partial pressure conditions with a special furnace (pressure 1×10^{-9} Pa) at 600 °C for 6 hours. The results show that Zr with heat treatment at partial pressure is black, has the best wear resistance, and has a small hardness gradient, as well as good coating adhesion properties.

Recent research by Destiati et al. [7] researched the high-temperature corrosion behavior of Zr alloys with alkaline fusion media. The zirconium used was 90 wt % Zr, with Al, Mg, and Si alloys. The samples were subjected to benign corrosion tests using a mixture of NaOH, Na_2CO_3, S, and SnO_2. The research was carried out with an immersing test at a temperature of 800 °C for 10 minutes and repeated 100 times the heating process. The results showed pitting corrosion on the outside of the crucible and all-direction corrosion for the inside of the subtract. The corrosion structure is crack-shaped and some cracks reach the base metal. Crystal lattice strain occurred which led to an increase in dislocations resulting in strain hardening thus increasing the yield strength and UTS values, which increased by 22.5% while the strain decreased by 50%.

The use of metallic zirconium as a fusion reactor is also not without problems. With the characteristics of zirconium which is high-temperature resistant, and oxidation-corrosion resistant, in tin ore smelting applications zirconium metal only lasts up to 1000 minutes. This study analyzed the degradation of tensile strength and Vickers hardness of zirconium metal due to repeated heating cycles in an alkaline fusion environment. Tests were carried out at cycles 0 (without treatment), 3, 6, 9, and 12 or with the use of crucibles at 300, 600, 900, and 1200 minutes. The results of the analysis are then used as a scientific study of the degradation of zirconium metal material strength which is one of the causes of failure.

2. Material and Methods

2.1 Materials

The sample is zirconium metal obtained from PT Timah Tbk Pangkal Pinang Laboratory. Zr Crucible is from Sigma-Aldrich, Germany, and is produced by ATI Germany Operations. The zirconium metal used has a Zr content of ± 95 wt%, some P, Al, Ca, and Fe, as well as other impurities. The XRF results are shown in Table 1.

Table 1. Composition of new zirconium crucible by XRF

No	Element	%wt
1	Zr	95.44
2	P	3.15
3	Al	0.74
4	Ca	0.32
5	Fe	0.15
6	K	0.11
7	els	0.09

The corroding media used are tin ore from PT Timah Tbk Pangkal Pinang Lab with SnO_2 ± 56 wt%, Na_2CO_3 in powder form, NaOH, and sulfur in powder form with 99.8 wt% content. Then an HCl PA 37% MERCK was used for sample immersion media at room temperature after heating in each cycle.

2.2 Methods and Characterization

Initially, the material is a cup with a thickness of 1 mm. The cup is then cut to a size of 10 mm x 10 mm to be used as a sample coupon that is immersed in the alkaline fusion mixture. The cutting was done with a 1000W Fiber laser machine. For tensile strength testing, the samples were cut following the standard size for tensile testing, which refers to the ASTM E8/E8M standard by taking the standard on the subsidized specimens and scaling down by 3 times [8].

A new zirconium crucible is prepared as a combustion reactor. Next, tin ore smelting media in the form of SnO_2, Na_2CO_3, NaOH, and Sulfur with a weight ratio of 2:13:40:17 were put into the reactor and then stirred evenly. Coupons and tensile test samples were inserted into the reactor and immersed into the mixed corrosion media. Hoffman's Muffle Furnace was prepared and set to 800 °C. After reaching the temperature, the crucible containing the sample and the corrosion medium was inserted into the furnace and heated for 100 minutes. After 100 minutes, the crucible is then removed directly using the Handling tool and waited to cool to room temperature.

The next step was to immerse the crucible into a 150 mL solution consisting of 75 mL of 37% HCl PA and 75 mL of distilled water for 50 minutes. The crucible was then removed and washed using water. Heating and immersion were then repeated for up to 12 cycles. In the 3rd cycle, 1 coupon and tensile test sample were removed for testing. The samples were then tensile tested using an RTI Series UTM machine and tested for Vickers hardness on the surface and cross-section using a BUEHLER Vickers Tester machine. For ease of identification, Zr-new was named for new zirconium samples without treatment, Zr-3, Zr-6, Zr-9, and Zr-12 for Zr metal samples subjected to treatment at cycles 3, 6, 9, and 12, respectively.

3. Results and Discussions

3.1 Tensile degradation

The tensile test results for the Zr-new metal sample and the Zr-3, Zr-6, Zr-9, and Zr-12 samples are shown in Figure 1. In the Zr-12 sample, tensile testing could not be carried out because the sample had buckled and lost its integrity, causing fracture and damage before the sample was tested. From the results, it was known that the Zr-new sample has a tensile strength (UTS) of 406.76 MPa with a strain capability of up to 11.90%. This strain capability is confirmed by macroscopic observation of the tensile test sample in Figure 3-a which shows necking in the area around the fracture. After heating up to cycle 3 or 300 minutes, the UTS dropped by 53% to 190.94 MPa. The decrease in the UTS strength value which reached half resulted in a significant decrease in its strain capability where Zr-3 had an elongation value of 4.33% and can be seen in Figure 3-b where the Zr-3 sample did not experience necking in the area around the fracture.
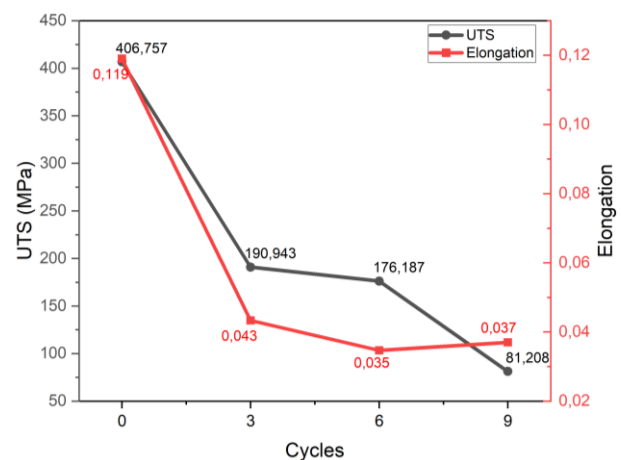

Figure 1. UTS vs Elongation results

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The decrease in UTS continues to occur in the next cycle, namely in the Zr-6 and Zr-9 samples. Each sample had a UTS of 176.18 MPa, and 81.20 MPa, respectively. In general, elongation in Zr-3, Zr-6, and Zr-9 did not change much with strain values ranging from 3-4%. However, Figure 3. b-d shows the difference in fracture shape where Zr-6 and Zr-9 have straight fractures indicating that the samples are more brittle.
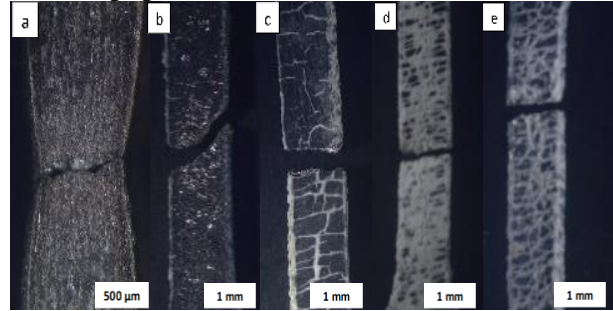

Figure 3. Macroscopic photographs of fault area, a. Zr-new, b. Zr-3, c. Zr-6, d. Zr-9, dan e. Zr-12
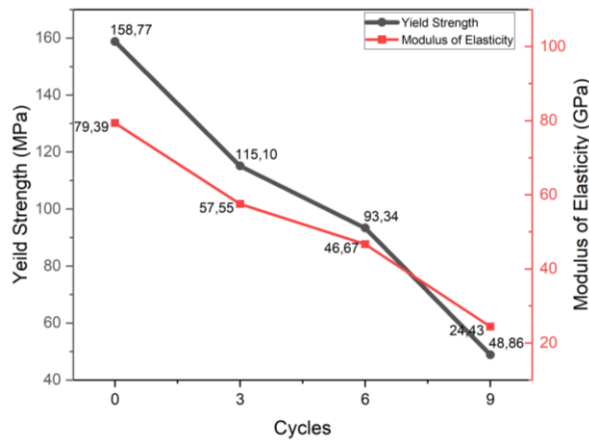

Figure 2. Yield strength vs Modulus of elasticity results

The embrittlement of the material can also be seen in Figure 2. Zr-new, which initially had a yield strength of 158.77 MPa, decreased gradually as the heating cycle increased. Zr-3, Zr-6, and Zr-12 decreased by 27.50%, 41.21%, and 69.23% respectively from the yield strength value of Zr-new. This decrease in yield strength caused the elastic modulus of the samples to decrease significantly. From the test results, it is known that the Modulus of Elasticity values of Zr-3, Zr-6, and Zr-9 are 57.55 GPa, 46.67 GPa, and 24.42 GPa respectively, or decreased by 27.50%, 41.21%, and 69.23% from Zr-new which has a Modulus of Elasticity value of 79.38 GPa.

3.2 Micro-Vickers Hardness Testing

The heating process of a metal allows the metal to oxidize [9], [10]. In the case of zirconium metal, an oxide layer will form in the form of ZrO_2 which has a hardness of up to 1300 VHN [6], [11], [12]. The Vickers hardness test results on the surface of zirconium metal are shown in Figure 4. From the measurement results, the new zirconium metal (Zr-new) has a surface hardness of 213.67 VHN. The Vickers hardness of the surface of samples Zr-3, Zr-6, Zr-9, and Zr-12 increased significantly with an average hardness of 1031.424 VHN. This increase of up to 383% indicates the presence of an oxide layer in the form of ZrO_2. The presence of oxide on the surface can also be confirmed in Figure 3 where there is a white layer on the surface of the sample which is identical to zirconia (ZrO_2) [12], [13].
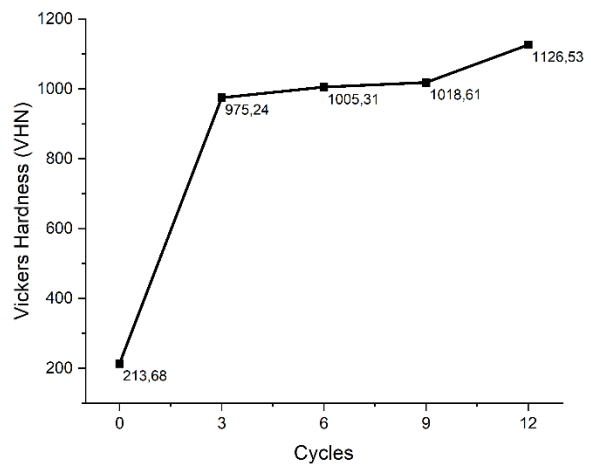
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Figure 4. Surface Vickers hardness result

Vickers hardness examinations of cross-sectional sections of the samples were performed at depths of 20 μm, 50 μm, and at the base metal shown in Table 2. The results show that the Zr-new samples have uniform Vickers hardness at all examination locations. The base metal hardness for the heated samples in all cycles also did not change significantly. At the sub-surface location of 20 μm, there is an increase in Vickers hardness in all samples subjected to heating. The value of the increase in Vickers hardness increases as the cycle increases, where Zr-9 and Zr-9 experience an increase of up to 3 times. This indicates that with the increase in heating cycles, the presence of a ZrO_2 oxide layer is increasingly formed deeper into the substrate [7].

Table 2. Cross-sectional Vickers Hardness

Cycles	Vickers Hardness (VHN)		
	Base metal	Sub-Sur20	Sub-Sur50
0	213.68	224.13	213.12
3	211.27	414.77	244.61
6	220.48	431.65	274.75
9	216.98	606.31	313.33
12	209.56	729.91	321.52

3.3 Discussion

The tensile test results when correlated with the Vickers hardness test results present data on the degradation of zirconium metal material due to 12 heating cycles that occurred at 800 °C for 100 minutes. At the initial stage of heating up to the 3rd cycle, the Zr-3 sample experienced oxidation phenomena with an increase in material hardness reaching 975.24 VHN which is identical to zirconia compounds [11] [12] [13]. This increase in surface hardness causes embrittlement of the material so that its yield strength and strain decrease drastically [5] [6] [7]. The embrittlement of the sample material

continues until the next heating cycle, namely in the Zr-6, Zr-9, and Zr-12 samples. The addition of heating cycles made an increase in surface hardness and increased oxygen deposition into the subtract. This is evidenced by the cross-sectional Vickers hardness which shows an increase in Vickers hardness at the same depth level in each sample. Ultimately, this material embrittlement continues to be accompanied by a decrease in material strength (UTS) in Zr-9 and Zr-12. With this phenomenon, it is not surprising that industry reports suggest that zirconium metal material deterioration occurs at an average time of 900 to 1000 minutes of accumulative heating.

4. Conclusion

Based on the results analysis, repeated heating of the zirconium metal caused a degradation of its tensile strength. The metal experienced the greatest decrease in the Zr-9 sample while in Zr-12 the sample was damaged and could not maintain its integrity so it could not be tested. In Zr-9 there was a decrease in UTS up to 80%, a decrease in yield strength, elongation, and Young's modulus up to 69%.

The samples were embrittled compared to Zr-new as seen from the fracture area. The Vickers hardness test results of the sample surface also confirmed the embrittlement with a significant increase reaching an average hardness of 1031.424 VHN. The hardness is a representation of the presence of a ZrO_2 oxide layer on the sample surface. This oxide layer is also confirmed to be deposited on the sample causing strain hardening and hardness increase up to 200% in the base metal close to the surface at a depth of 20 μm.

The degradation of tensile properties and embrittlement of the samples happened significantly at 900 minutes of accumulative heating, so it was correlated with industrial reports.

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