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Preparation of Insoluble Zirconate from Egyptian Zircon via Alkali Fusion Process to Enhancement Al Alloy Performance

H. Mashaal

Nuclear Materials Authority, Cairo, Egypt

Abstract

In this paper, Egyptian zircon was decomposed through the alkali fusion process to obtain the insoluble product (sodium zirconate) for developing the performance of Al alloy. For this purpose, Egyptian zircon was mixed with NaOH at specific ratios on the stainless steel crucible for starting the opening process. Several parameters such as NaOH /Zircon ratios, fusion temperature, and fusion time were investigated to obtain the optimum conditions to prepare sodium zirconate. Next the Al alloy was melted and sodium zirconate particles were added while stirring. Characterization of zircon opening products was performed by X-ray Diffraction, Scanning Electron Microscopy, and Energy Distributed X-ray. Also, the effect of insoluble product of the zircon opening product on the performance of Al alloy was evaluated via hardness and wear resistance tests. The results demonstrate that the optimum alkali fusion parameters to obtain high recovery of sodium zirconate were as follows; 1.5 $NaOH/ZrSiO_4$ ratio, 650 ◦C as fusion temperature, and 3 hr as fusion time. On the other hand, adding 5% of sodium zirconate to Al molten metal leads to increasing in the hardness value and the wear resistance over than the value of Al alloy.

Keywords: Zircon; Alkali fusion; alkali ratio; Al alloy; sodium zirconate.

1. Introduction

Zirconium metal and compounds are attracting increasing interest because of the growing number of applications. Zircon is the main source of all zirconium compounds. It is a heavy mineral with excellent properties like; high hardness, high melting point, high chemical stability. This allows zircon to be utilized in important applications including; ceramics, refractory industries, foundry, abrasives, TV glass, electronics, pigments, and catalysts [1-4]. In Egypt, widespread placer deposits of black sand are intermittently distributed along the northern coast. These deposits contain huge reserves of the six common economically important heavy minerals; zircon, ilmenite, rutile, monazite, magnetite, and garnet [5-8]. Zircon is a non-magnetic, non-conducting material so, it can be easily concentrated by means of gravity, magnetic and electrical separation. High grades are suitable for the extraction of zirconium metal and chemicals while Low grades zircon can be used in foundry and other applications[9-11].

Zircon is very stable and refractory mineral (ΔG° 1400 K = 1489.1 kJ/mol). Hence, its decomposition requires harsh conditions to overcome the strong bond between SiO_2 and ZrO_2 [9, 12]. For this purpose, several methods like; caustic fusion, lime fusion, fluorosilicate fusion, carbiding, thermal dissociation and chlorination can be used. Also, mechanochemical treatment can be used [1, 13-16]. Among all methods, alkali fusion of zircon presents good versatility, simplicity and effectiveness [4, 15, 17].

Abdelkader et al. [15] used a mixture of KOH and NaOH to achieve high recovery with low temperature and short fusion time. Song et al. [18] carried out a two-step alkali fusion for zircon. Where 1.3 alkali/zircon ratio was divided to 0.7 and 0.6 at 700℃ fusion temperature and 0.5h fusion time for each step. Also, Eldesouky et al. [19] used alkali fusion process followed by different steps for the production of high purity zirconia. Literatures show that researchers were interested with producing a high purity compounds with high recovery and low production cost as possible. Unfortunately, the attention of researchers was focused on the preparation of zirconium oxychloride or zirconia for different applications while the intermediate products of zircon opening was not fully explored. Consequently, this current study aims to obtain a high recovery of sodium zirconate from Egyptian zircon to utilize it in development of Al alloy performance.

*Corresponding author e-mail: h.mashaal23@gmail.com (Heba Mashaal).
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2. Materials and Methods

2.1 Zircon

The chemical composition of zircon concentrate ($ZrSiO_4$), separated from the Egyptian black sand heavy mineral from Egyptian Nuclear Materials Authority (ENMA) is shown in Table 1. Zircon is the most abundant zirconium ore and the main source for commercial production of zirconium and its compounds.

Table 1. Average chemical composition of the concentrated Egyptian zircon

Compound	ZrO_2	SiO_2	HFO_2	Al_2O_3	Fe_2O_3	TiO_2	Other
%	63.07	31.23	2.27	0.87	0.77	0.82	Bal.

2.1.1 Zircon Decomposition

The general procedure to produce sodium zirconate (Na_2ZrO_3) from zircon sand mineral include; alkali fusion and water leaching. The most important step is alkali fusion as it decomposes zircon to sodium silicate (Na_2SiO_3) and sodium zirconate. There are many alkali fusion conditions directly affect on achieving a high decomposition efficiency. In this paper alkali ratios, fusion temperature, and fusion time were studied. Firstly, $NaOH/ZrSiO_4$ ratio were investigated as follows; 1:1,1.3:1, 1.5:1, and 1.7:1). Next, the effect of fusion temperatures (450, 550, 650, 750℃) was investigated. Finally, the effect of fusion time (1, 2, and 3 h) was also studied.

As general, $ZrSiO_4$ (100g) was mixed with NaOH at the specified ratios, fusion temperatures and times. The mixture was charged to a 316l stainless steel crucible which fed to the electric furnace. For $NaOH/ZrSiO_4$ experiments, the reaction temperature was adjusted as 650℃ for 3 h. Next, for temperature experiments, the optimum $NaOH/ZrSiO_4$ was applied for 3 h. Finally, for fusion time experiments the optimum alkali ratio and temperature were conducted.

The opening product (frit) consists of two major compounds Na_2SiO_3 (water soluble) and Na_2ZrO_3 (water insoluble). Thus, to obtain the Na_2ZrO_3, frit was water leached to remove the soluble one in the presence of additional NaOH to hinder the hydrolyses of Na_2ZrO_3. Next, the solution was filtrated followed by drying at 105 °C for 20 h to obtain the dried sodium zirconate.

2.1.2 Al-Alloy

The selected Al-alloy for the present investigation is the commercial alloy with the chemical composition as shown in Table 2.

Table 2. The chemical composition of Al alloy.

Element	Mn	Mg	Fe	Si	Cu	Al
%	0.51	4.13	0.24	0.33	0.12	Bal.

2.2 Developing of Al Alloy

To study the effect of Na_2ZrO_3 on the development the performance of Al alloy, Al alloy was melted firstly in electric furnace. Secondly, heat treated Na_2ZrO_3 was wrapped in Al foil and incorporating into molten metal of Al alloy. The stirring was continued for five minutes after the addition of the prepared insoluble fusion product at 800 rpm speed. Finally, the molten was poured into the permanent mold and allowed to cold in the air.

2.3 Characterization

X-ray diffraction analysis was performed using Philips Machine to determine the different the product of alkali fusion of zircon. A monochromatic Cu-K radiation with $\lambda = 0.154$ nm was used. The scanning range was 10–80 (2θ) with a step size of 0.01° (2θ)/Sec.

Scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy was used to collect data about the microstructure of the materials. The samples were first ground on a series of SiC emery papers underwater stream, followed by polishing a series of polishing cloths with alumina suspension.

For studying, the effect of Na_2ZrO_3 on the hardness of Al alloy, Vickers microhardness test using a load of 500 gf for seven seconds was conducted. Four spot readings have been conducted on each sample by Vickers microhardness machine model (LECO LM70 -USA). Also, the wear behavior of Al was evaluated by using a pin-on-disc wear apparatus at room temperature according to ASTMG99-04 standard. The polished surface of the samples was held against a rotating disc made of hardened chromium steel. The test was conducted for 40 min at a sliding speed of 0.6 m/sec and normal load of 5 kg. The specimens after each test were dried, cleaned with a soft brush and weighed with a micro-balance. The mass loss value of the samples was determined using an electronic balance of 0.001 mg.

3. Results and Discussion

3.1 Opening of Zircon.

The main reactions that take place between $ZrSiO_4$ and NaOH during alkali fusion are as follows [1, 15, 20]:

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O \quad (1)$$
$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \quad (2)$$
$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3H_2O \quad (3)$$

The product of fusion is named frit which, according to the equations 1:3 consisting of Na_2ZrO_3, sodium zirconium silicate (Na_2ZrSiO_5) and Na_2SiO_3, Na_4SiO_4 beside water vapor and unreacted zircon. The decomposition recovery refers to the decomposition ratio of fused zircon to unreacted. The frit is friable and caustic powder consist of Na_2ZrO_3, Na_2SiO_3,

Na_4SiO_4, Na_2ZrSiO_5, and unreacted zircon as obtained by XRD pattern shown in Figure 1. It can be indicated that Na_2ZrO_3 is the major phase with a small fraction of Na_2ZrSiO_5. Also, EDX analysis confirmed that the major compound elements are Na and Zr as presented in Figure 2.

After washing the frit with cold water for three times to remove both soluble silicates and excess caustic. Most of the water soluble Na_2SiO_3, Na_4SiO_4, and unreacted NaOH dissolve in water. By filtration, the filtrate consists of the soluble substances while the residue represents Na_2ZrSiO_5 which are dried. Figure 3 shows XRD pattern of prepared Na_2ZrO_3 powder which its peaks clearly appeared with a little peak refers to of the presence of ZrO_2 (red cycle in graph). Also, EDX analysis shows the presence of Zr as major contents as shown in Figure 4. On the other hand, the presence of Si means that sodium silicate is still presence in the final product with small content. This behaviour may be attributed to the added NaOH during water leaching.

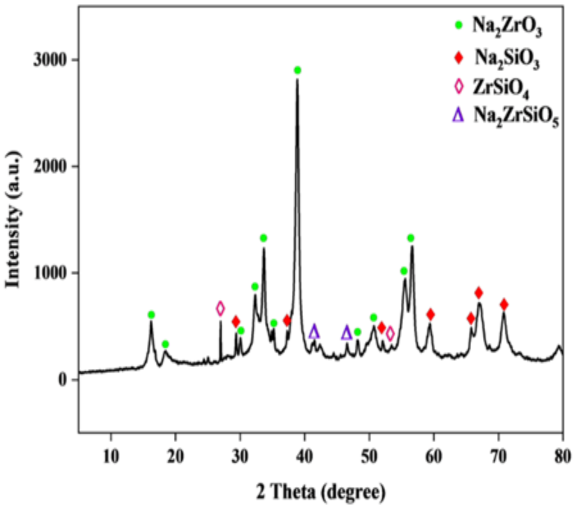

Fig.1 XRD pattern of fusion product.

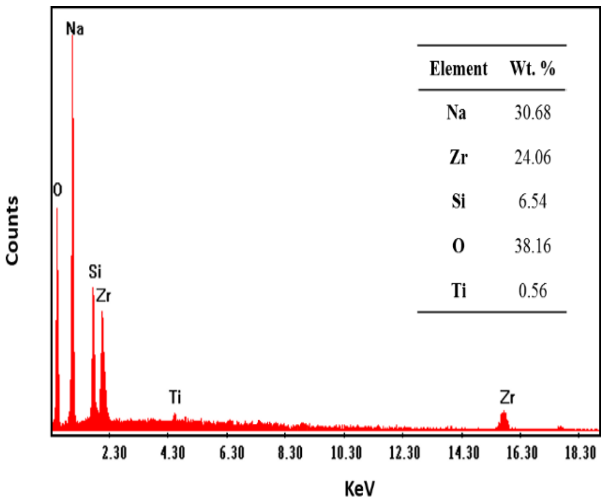

Fig. 2 EDX analysis of alkali fusion product.

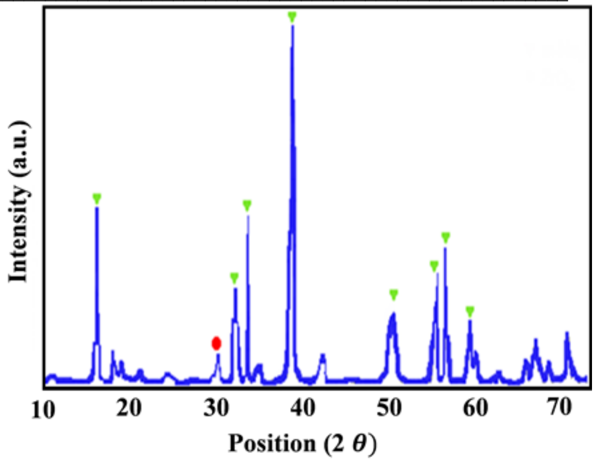

Fig. 3 XRD pattern of prepared sodium zirconate.

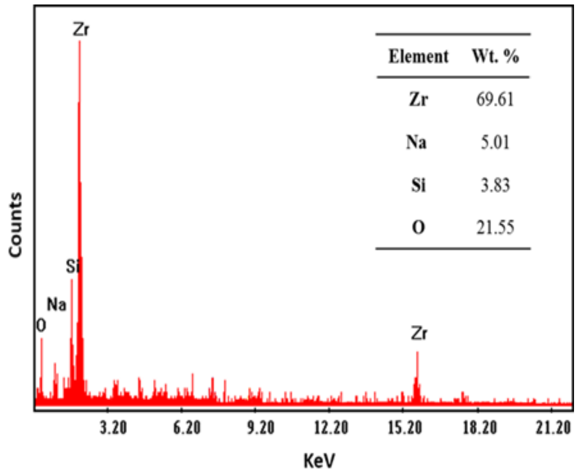

Fig. 4 EDX analysis of sodium zirconate.

3.1.1 Effect of Fusion Temperature

To study the relationship between fusion temperature and zircon decomposition, the following conditions; 1.5 $NaOH/ZrSiO_4$ ratio and 2 h fusion time were applied. The fusion temperatures were in the range of 450 to 750 °C in 100 °C step. Figure 5 shows the influence of fusion temperature on the decomposition efficiency. It is clearly noted that, decomposition of zircon increases with growing fusion temperature. However, the increasing of the degree of decomposition is sharply increased by increasing temperature from 450°C to 650°C and slightly increased at 650°C. Also, high temperature leads to the reaction of liquids with the body of the crucible as indicated by the greenish colour. Thus, the fusion temperature of 650°C will drive to select as the optimum temperature.

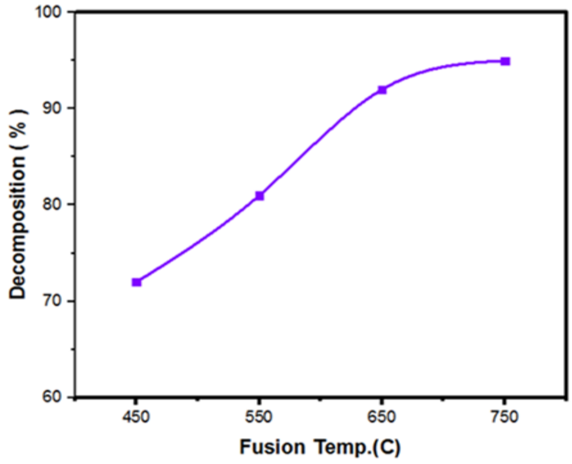

Fig. 5 Decomposition efficiency versus alkali fusion temperature.

3.1.2 Effect of Zircon to Alkali Ratio

Figure shows the relation between $ZrSiO_4$/NaOH ratio and decomposition efficiency. It is clear that, soda ratio and the decomposition degree of zircon is directly corelated. This relation seems to be linear in the range of 1 to 1.7, where the slope of decomposition line was highly for the ratio of 1 up to 1.3 which means the great effect of increasing NaOH. Beyond 1:1.3 the decomposition degree was less effect by increasing NaOH ratio as indicated by less line slope. On the other hand, at lower ratios the amount of NaOH is not enough to react with all $ZrSiO_4$. As a result, decomposition efficiency was low about 85%. When the ratio increased, the decomposition efficiency also increased up to 1.7 ratio up to 93.5%. However, at 1.5 and 1.7 ratios more decomposition was achieved while the removal of the product from the crucible will be very difficult which requires further milling. Thus, 1.3 NaOH/$ZrSiO_4$ was selected as the most suitable ratio for the breakdown in this study.

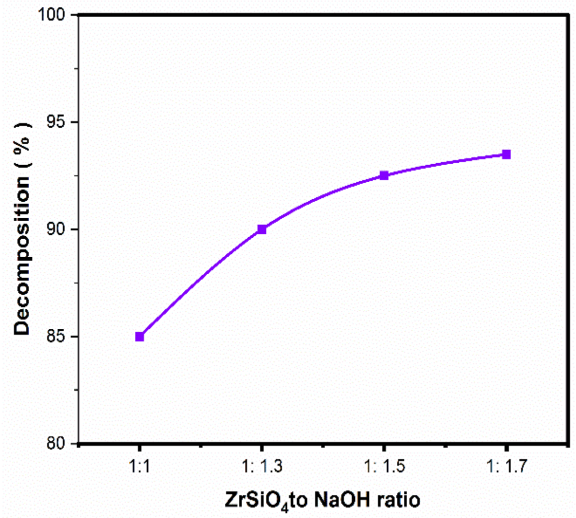

Fig. 6 Decomposition efficiency versus NaOH/$ZrSiO_4$ ratio

3.1.3 Effect of Fusion Time

The results of investigated fusion time on the breakdown of zircon with NaOH from 1 to 3 h were presented in step of 0.5 h as shown in figure 7. The reaction temperature applied during this test was 650ºC while the reaction mixture kept as 1:1.4 NaOH/$ZrSiO_4$ ratio. This figure demonstrates the increasing of zircon decomposition as fusion time rose.

At 0.5 h decomposition efficiency was low (87%), while at 2 h the efficiency significantly increased to 93%. Beyond 2 h, the increased of decomposition of zircon was augmented up to 95% at about 2.5 h of fusion time. Further increase in time to 3 h, a slight increase to about 96% was reached. Consequently, and from an economic considerations 2.5 h fusion time is considered as the optimum time in this study.

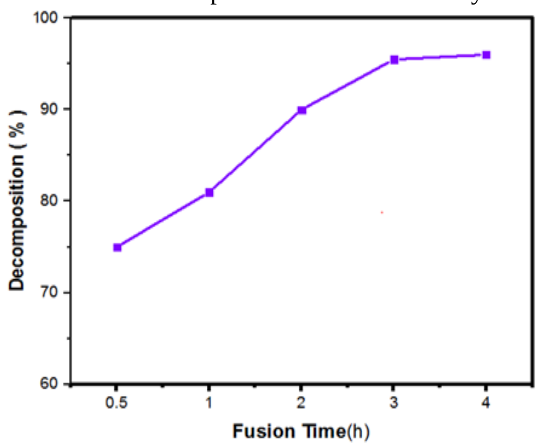

Fig. 7 Decomposition of zircon versus fusion time

3.2 Hardness and Wear Behavior

The average hardness value of bare alloy and alloy incorporated with 5% Na_2ZrO_3 was 62 and 73 HV respectively as shown in Table 3. The Hardness value for the alloy incorporated with Na_2ZrO_3 is 18 % higher than that of the bare alloy. The increase of hardness can be attributed to the presence of the hard ceramic Na_2ZrO_3 particles. Therefore, the strong and rigid Na_2ZrO_3 particles severely restrict deformation of the softer Al matrix. Also, the wear resistance increased by adding 5% Na_2ZrO_3 to Al alloy as compared with the bare alloy as showing in Table 3. This action can be due to decreasing the contact surface area of alloy where the added particles act as a load carrier and protect the surface from frictional forces. Also, the weight loss decreases due to the lubricating behavior of the emerging oxide layer [21].

Table 3. The hardness and wear resistance value

sample	Hardness (HV)	Weight loss (mg)
Al alloy	62	63
Al+5%Na_2ZrO_3	74	38

4. Conclusion

1- Alkali fusion was usefully technique to prepare sodium zirconate.
2- High recovery of sodium zirconate was successfully obtained at the following conditions; 1.5:1 as $NaOH/ZrSiO_4$ ratio, fusion temperature (650 ◦C), and fusion time (3 hr).
3- The addition of sodium zirconate to Al alloy leads to increasing in the hardness value by 18% over than value of Al alloy.
4- The wear resistance of Al alloy was increased by addition of sodium zirconate.

Conflicts of interest: There are no conflicts to declare.

References

1. Abdel-Rehim, A.M., A new technique for extracting zirconium form Egyptian zircon concentrate. International Journal of Mineral Processing, 2005. 76(4): p. 234-243. DOI:10.1016/j.minpro.2005.02.004
2. Abd El_Kareem, A., New extraction technique of zirconium and hafnium from zircon mineral. Arab Journal of Nuclear Sciences and Applications, 2019. 52(2): p. 201-208. DOI: 10.21608/ajnsa.2019.3052.1066
3. Carter, C.B. and M.G. Norton, Ceramic materials: science and engineering. Vol. 716. 2007: Springer. https://doi.org/10.1007/978-0-387-46271-4
4. Rashed, G.M., Preparation and corrosion behavior of wrought aluminum alloy reinforced with ZrO_2 particles, in Mining and Petroleum dept., Faculty of Engineering 2021, Al-Azhar University. p. 143.
5. El-Afandy, A., M. Moustafa, H. El Nahas, A. Abdou, and M. Barakat, Geomorphology and mineralogy of the top meter black sands north west of El-Burbllus lake, Kafr Al-Sheikh Governorate, Egypt. Al-Azhar Bulletin of Science, 2016. 27(2-D): p. 59-82. DOI:10.21608/absb.2016.42888
6. Ghorbani, M., Metallogeny and distribution of minerals, in The Economic Geology of Iran. 2013, Springer. p. 87-197. DOI:10.1007/978-94-007-5625-0
7. Sakr, S., E.-A. A H, A.H. AF, and A. M E, Heavy mineral diagnosis of Ras Baghdady black beach sand: accumulations and significance. Al-Azhar Bulletin of Science, 2011. 22(2-D): p. 81-108. DOI:10.21608/absb.2011.7911
8. Moawad, I., A. El-Wakil, and W. Hamed, Determination of zirconium and hafnium in Egyptian monazite by ICP-OES. Egyptian Journal of Chemistry, 2022. 65(5): p. 1-2. DOI:10.21608/ejchem.2021.87276.4253
9. Yamagata, C., J.B. Andrade, V. Ussui, N.B. Lima, and J.O.A. Paschoal. High purity zirconia and silica powders via wet process: Alkali fusion of zircon sand. in Materials Science Forum. 2008. Trans Tech Publ. https://doi.org/10.4028/www.scientific.net/MSF.591-593.771
10. Tuyen, N.V., V.T. Quang, T.G. Huong, and V.H. Anh, Preparation of high quality zirconium oxychloride from zircon of Vietnam. 2007.
11. Lundberg, M., Environmental analysis of zirconium alloy production. 2012. DiVA, id: diva2:475527
12. Yuhelda, Y., D. Amalia, and E.P. Nugraha, Processing zirconia through zircon sand smelting with NaOH as a flux. Indonesian mining journal, 2016. 19(1): p. 39-49. DOI: 10.30556/imj.Vol19.No1.2016.364
13. Habashi, F., Handbook of extractive metallurgy. 1997: Wiley-Vch.
14. Puclin, T., W. Kaczmarek, and B. Ninham, Mechanochemical processing of $ZrSiO_4$. Materials chemistry and physics, 1995. 40(2): p. 73-81. https://doi.org/10.1016/0254-0584(94)01471-R
15. Abdelkader, A., A. Daher, and E. El-Kashef, Novel decomposition method for zircon. Journal of Alloys and Compounds, 2008. 460(1-2): p. 577-580. DOI:10.1016/j.jallcom.2007.06.032
16. Mohammed, N. and A. Daher, Preparation of high-purity zirconia from Egyptian zircon: an anion exchange purification process. Hydrometallurgy, 2002. 65(2-3): p. 103-107. DOI:10.1016/S0304-386X(02)00042-7
17. Abdelkareem, A., Thermodynamic analysis of Al alloy reinforced with zirconia particles. Open Access Library Journal, 2022. 9(12): p. 1-13. DOI: 10.4236/oalib.1109569
18. Song, J., J.-F. Fan, J.-C. Liu, R. Liu, J.-K. Qu, and T. Qi, A two-step zircon decomposition method to produce zirconium oxychloride: alkali fusion and water leaching. Rare metals, 2020. 39(4): p. 448-454. DOI:10.1007/s12598-015-0537-y
19. Eldesouky, W.S., A. Abd El_Kareem, A. El-aziz, H. Mohamed, and E.S. Mosa, Preparation and stabilization of monoclinic zirconia by yttria through mechanical alloying. Arab Journal of Nuclear Sciences and Applications, 2023. DOI:10.21608/ajnsa.2022.161293.1634
20. Liu, J., J. Song, T. Qi, C. Zhang, and J. Qu, Controlling the formation of Na_2ZrSiO_5 in alkali fusion process for zirconium oxychloride production. Advanced Powder Technology, 2016. 27(1): p. 1-8. DOI:10.1016/J.APT.2015.08.005
21. Rashed, G., M. Sadawy, A. Kandil, A. Abd Elkarim, and W. Mohrez, Influence of ZrO_2 particles on the tribological properties of almg5 alloy. Journal of Petroleum and Mining Engineering, 2021. 23(1): p. 95-103. DOI: 10.21608/jpme.2021.68312.1078