The Effect of Different Molten Salt Composition on Morphology and Purity of the ZrB_2 Powder Obtained via Direct Molten Salt Reaction Method

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ABSTRACT

Zirconium Diboride (ZrB_2) powder was synthesized at low temperature via a Direct Molten Salt Reaction (DMSR) method. The influence of different salt compositions including the eutectic mixture of (KF-NaF), (KF-KCl) and (KCl-NaCl) on the morphology and purity of the reaction products was studied. The obtained samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Furthermore, the formation mechanism of ZrB_2 was investigated by DTA/TG. The results show that alongside eutectic mixture of chloride salt, the ZrB_2 powder can be obtained by eutectic mixture of the fluoride salt. In addition, the obtained ZrB_2 powder without additional salt has hexagonal prism morphology, whereas the ZrB_2 particles prepared by the eutectic mixture of fluoride salt have higher purity and particle size and hexagonal morphology as well. The synthesized ZrB_2 powder in chlorofluoride salt has lower particle size and purity and non-uniform morphology. The synthesized ZrB_2 powder is different from the starting material in term of morphology and particle size. Therefore, the dissolution–precipitation mechanism may play a dominant role in the synthesis of ZrB_2 during the DMSR process.

1. Introduction

Among ultra-high-temperature ceramics (UHTCs), ZrB_2 is thought to be one of the most attractive thermal protection material with potential applications in aerospace, bearing ceramics, cutting tools, molten metal handling crucibles, high-temperature electrodes and spray nozzles due to its unique combination of physical and chemical properties, including moderate density (6.09 g/cm3), high melting point (3200˚C), excellent chemical inertness, high thermal and electrical conductivity [1, 2]. A variety of synthesis routes have been developed to prepare the ZrB_2 powders such as borothermal and carbothermal reduction [3], mechanochemical treatment [4], chemical vapor deposition [5], sol–gel route [6] and thrombolysis of the containing gas [7]. These methods have drawbacks such as impurity, high temperature and expensive starting materials [8], therefore, finding a simple and inexpensive ZrB_2 powders with low cost and high purity is desirable because it would allow the fabrication of more cost-effective ZrB_2 ceramics. Molten salt synthesis is an alternative method that is

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used for preparation of ceramic materials with higher purity at lower temperature [9]. In this method, the reaction takes place in the molten media and higher diffusion of spices than solid state decreases the synthesis temperature and leads to increase homogeneity in terms of morphology and particles size [10].

Recently, Zhang et al. have synthesized ZrB2 from molten-salt-mediated magnesiothermic reduction method using ZrO_2, $Na_2B_4O_7$, Mg and MgCl2 as raw materials at 1200˚C after 3 hrs. They found that using excessive amounts of Mg and Na_2BO_4 leads to the conversion of ZrO_2 to ZrB_2, whereas the formation of $Mg_3B_2O_6$ as an unwanted phase was prohibited [11]. Synthesis of ZrB_2 investigated in this study processed by authors [12] offers a cost-effective way to produce the ZrB_2 powder. This method is based on the direct melt reaction in situ composite approach [13]. The ZrB_2 particles were achieved via leaching the products of metallothermic reduction of hexafluorozirconate (K_2ZrF_6), tetraflouroborate (KBF_4) and aluminum at above the melting point of aluminum (660 ˚C) for 2 h under the positive pressure of argon. Although some experiments have been carried out to produce ZrB_2 reinforcement aluminum composite via direct melt reaction, the synthesis mechanism and reaction sequence have not been clearly established [13-15].

The selection of an appropriate salt significantly influences the ability of the reaction to produce desirable powder morphologies and characteristics. The selection of the salt is highly dependent on two criteria: the melting point of the salt should be low and appropriate for the synthesis of the required phase and the salt should exhibit sufficient aqueous solubility to be easily eliminated by a simple washing after the synthesis. Furthermore, suitable choice of the salt composition may prevent the formation of volatile compounds which lead to undesirable exhalations and lowers the efficiency of the process.

The aim of this research is to study the effect of molten salt composition on purity and morphology of the obtained ZrB_2 powder via direct reaction in the molten salt method with K_2ZrF_6-KBF_4-Al as the starting material.

2. Experimental procedure

Potassium hexafluorozirconate (K_2ZrF_6 >99%), potassium tetraflouroborate (KBF_4 >99%) and aluminum (Al >98 %) (All from sigma Aldrich) were used as the starting materials, and KCl, NaCl, KF and NaF (>98%) (All from Merck) were used as salts. The starting materials were K_2ZrF_6 /KBF4 /Al mixed with 1/2/10 ratio, respectively, using an agate mortar and then mixed in 1/4 with eutectic mixture of KCl-NaCl or KF-NaF or KF-KCl. In order to understand the nature of the occurred reaction, blend mixture was subjected to DSC/TG using Bahr STA 503 equipment with linear heating rate of 5˚C/min up to 900˚C with 2 ml/min flow of argon with purity of 5.0 as an inert gas. The resultant powder batch was contained in an alumina crucible covered with a lid and placed in an alumina tube furnace with continuous purge of argon. The samples were heated up to 700˚C with 10˚C/min and held for 2 h before being cooled down to the room temperature. Afterwards, the prepared powders were taken out of the crucible, washed several times by hot distilled water until no F- and Cl - in the washing solution was detected by $AgNO_3$ [16] and then subjected to acid leaching with a dilute HCl solution to remove aluminum and residual salts in consideration with ZrB2 particles have no reaction with HCl [17].

The leached mass was repeatedly washed with hot distilled water until no evidence of Cl- was seen [16].

The fine retained powder dried at 120˚C for 2 h and characterized by X-ray diffraction (XRD, Philips pw3710) and scanning electron microscopy (SEM, Tuscan Vega II provided with energy dispersion X-EDS).

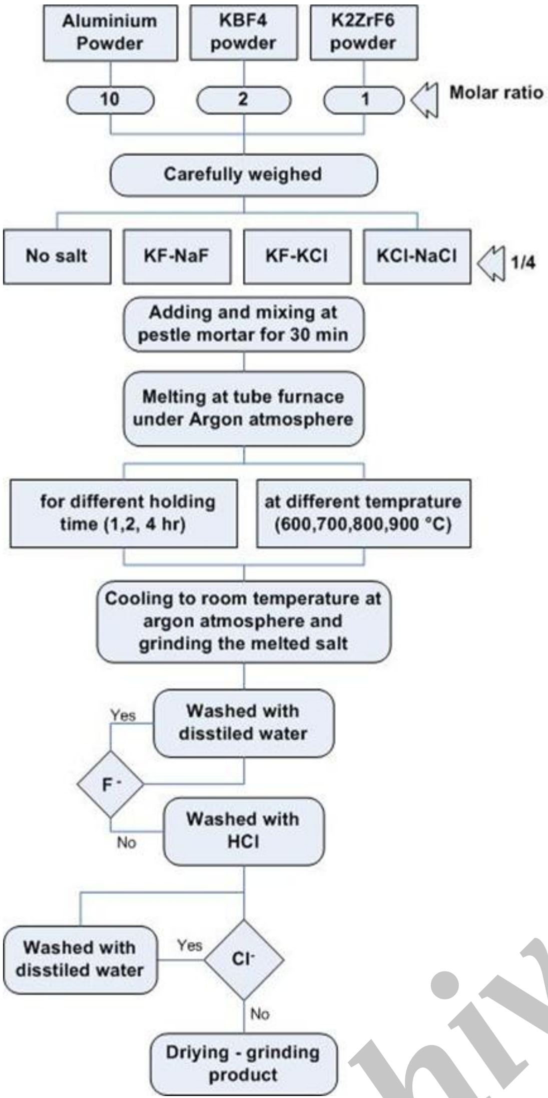

Fig. 1. The flowchart of the synthesis of the ZrB2 powders

3. Results and discussion

DSC/TG analysis was performed on the starting materials mixture to investigate the reactions sequence and the results were shown in Fig 1. The main reactions possibly involved in the synthesis process can be summarized as follows [15, 18]:

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \quad [1]$$

$$2K_2ZrF_6 + 13Al \rightarrow 3Al_3Zr + 2KAlF_4 + K_3AlF_6 \quad [2]$$

$$AlB_2 + Al_3Zr \rightarrow ZrB_2 + 4Al \quad [3]$$

As can be seen, two weak endothermic peaks on the DSC spectrum of the mixture at 180 and 230˚C (signal 1 and 2) can be attributed to the evaporation of the absorbed water with slight weight loss of the bath due to the removal of moisture. The medium endothermic peak around 290˚C is attributed to the phase transition of KBF4 from orthorhombic to cubic crystal structure in reasonable agreement with those reported in the literature [20]. The first exothermic peak (signal 4) appeared around 350˚C can be attributed to the reduction of KBF4 salt by aluminum (Eq. 1) [21]. Later, low intensity exothermic peaks around 460˚C (signal 5) can be assigned to the reaction of Al with K2ZrF6 to form Al3Zr (Eq. 2) [18]. The endothermic peak at 575˚C matches perfectly with the melting of the KAlF4 salt, which is not one of the ingredients of the mixture. The weight loss above 650˚C is attributed to the evaporation of spices such as AlF_3, BF3 etc. The small exothermic peak started from 700˚C is interpreted as the formation of the ZrB2 phase.

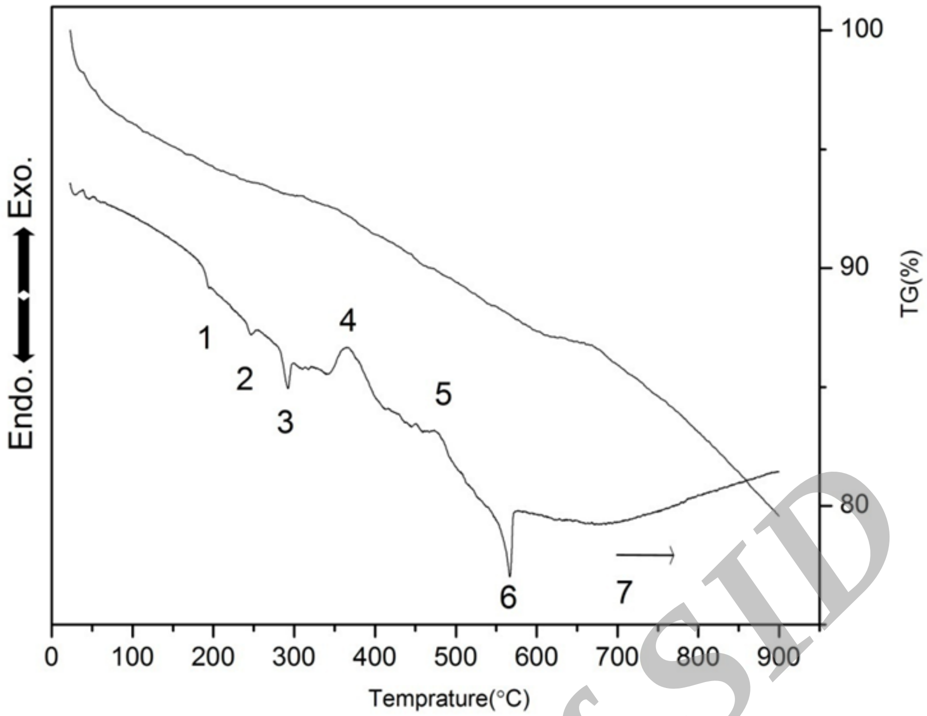

Fig. 2. DTA /TG curves of starting material mixture

The thermodynamic calculation shows this reaction (Eq. 3) is thermodynamically favorable (ΔG_700^°=-77.98 kJ/mol) but the peak intensity is rather low because of accompanying the ZrB2 formation reaction by severe evaporation of the salt. In addition, the low salt / Al ratio (1: 10) in the present batch results in a rather low - intensity peak in the DSC / TG pattern. Fig. 3 compares the XRD patterns of the powders synthesized by the molten salt reaction method at 700˚C in 2 hrs reaction time with different molten salt compositions. As can be seen, the dominant phase in the sample without excess molten salt is ZrB_2 with small amounts of Al3Zr. According to the above proposed reactions, the observed Al3Zr peaks show that the conversion of Al_3Zr to ZrB_2 (Eq. 3) has not completely developed. The absence of the AlB2 peaks can be attributed to the low amounts of AlB2 and its reaction with the salt at this temperature. Rui et al. reported same observation during synthesis of Al/ZrB_2 composite [18]. By using eutectic mixture of (KF-NaF), the intensity of the ZrB_2 peaks increased, whereas the intensity of the Al_3Zr peaks slightly reduced. It is probably due to the higher mobility of spices in the eutectic mixture as a result of lower viscosity and lower melting point of the salt mixture [22], the conversion of Al3Zr to ZrB_2 can take place further. Eutectic mixture of chlorofluoride salt (KF-KCl) has no significant effect in term of intensity and position on the ZrB_2 and Al_3Zr peaks in comparison with sample prepared without excess mixture of salt. However, the low amount of the ZrO_2 and B_2O_3 peaks can be seen. This result shows that the dominant peaks of the powder prepared by the eutectic mixture of chloride (KCl-NaCl) can be indexed as ZrO_2 and B_2O_3 with low amounts of ZrB_2. Assumedly, since melting point of eutectic mixture of KCl-NaCl was lower than 657˚C (Table 1), the reaction of chloride molten salt started at lower temperature led to the escape of Al from the melt in form of $AlCl_3$ (g). Due to the crucial role of Al in the formation of intermediate compounds such as Al_3Zr and AlB_2, which has been proposed by other authors [14, 15], the reaction that corresponded to formation of ZrB_2 cannot be completely proceeded. The formation of the ZrB_2 particles at 700˚C with different salts composition shows that KF-NaF is more effective than other compositions in ZrB_2

forming. It is because of the differences between the melting point of KCl-NaCl and KF-KCl, viscosity and the solubility of the product in these molten salts. Firstly, the melting point of different salts affected the reaction between Al and salt, at lower melting point, the molten salts and Al reacted earlier. Secondly, the diffusion of cations in the solvent depends not only on the temperature and size of the cations but also on the solvent viscosity.

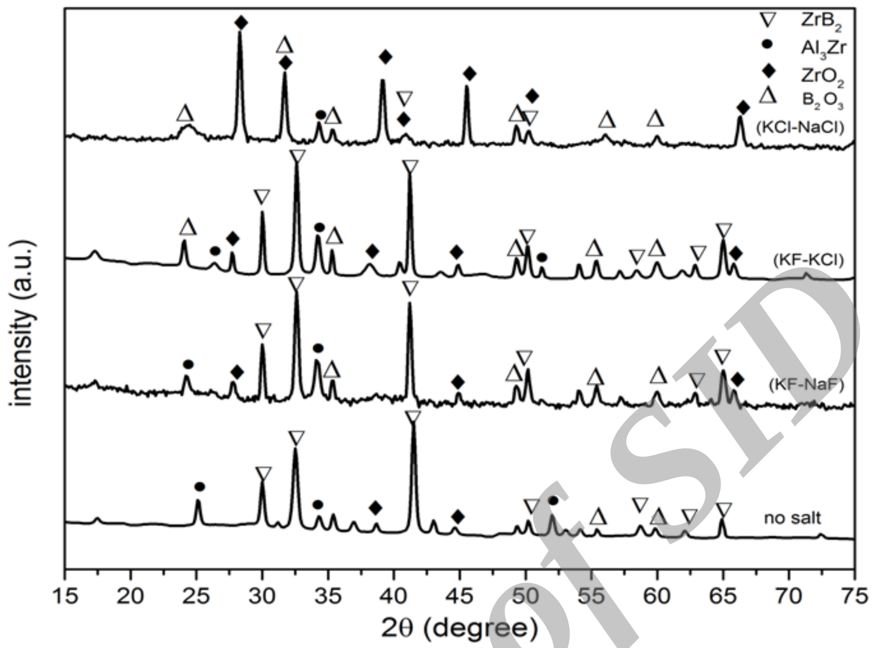

Fig. 3. The XRD patterns of the samples with different salt composition heat treated at 700 °C for 2 hrs reaction time

Table 1. Compositions and characteristics of used eutectic molten salts [23]

Molten salts system	Mixed (mol %)	Eutectic point (˚ C)	Density (g/cm^2)
NaF-KF	40-60	719	1.34
KCl-KF	55-45	605	1.67
KCl-NaCl	50-50	657	1.56

In this work, the viscosity of the molten mixtures was observed as follows: KF-NaF < NaCl-KCl< KF-KCl at 700˚C [24]. As a result, due to the lower viscosity of the solvent, the cations diffuse quickly in KF-NaF and lead to complete reaction and form ZrB_2 with higher particle size. In the KBF_4-K_2ZrF_6 system, relatively weak B—F—B bonds are formed. By Introducing F- ions into the mixture via the addition of KF-NaF, the B—F—B bridges break off, and it leads to the lowering of the viscosity and the negative deviation from the ideal behavior in the system [22]. With introducing Cl- ions into the mixture, the exchange of fluoride atoms in the union for the chloride ones takes place. Consequently, the less stability of the B—Cl—B bridges and the lower concentration of the B—F—B ones lead to the positive deviation of the viscosity [25]. Table 2 shows the amount of the samples

Table 2. The sample weight loss during 700˚C for 2 h in argon atmosphere

Composition	Weight loss %
No salt	5 %
KF-NaF	6 %
KF-KCl	9 %
KCl-NaCl	17%

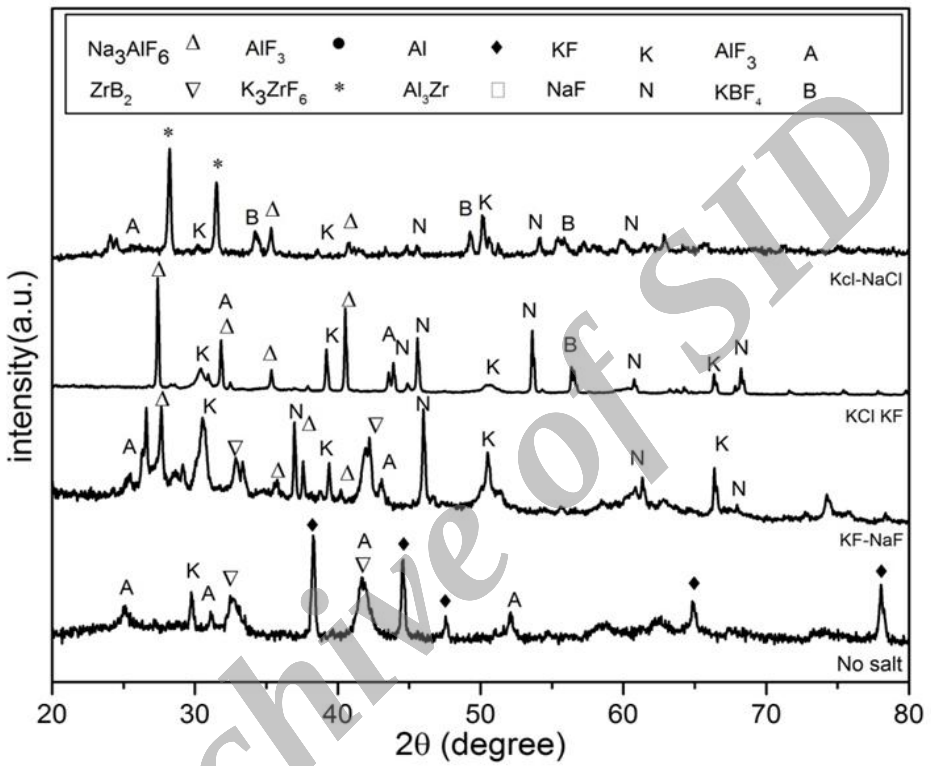

Fig. 4. The XRD patterns of the unwashed as prepared samples with different salt composition heat treated at 700˚C for 2 hrs reaction time

weight loss after heating at 700 ˚C for 2 h. It can be inferred that the sample with eutectic mixture of chloride has higher weight loss compared to others. As can be seen, there is no Al peak in the X-ray diffraction pattern of the sample with eutectic mixture of fluorides salt (KF, NaF), but the relatively high intensity of Na_3AlF_6 peaks indicates that the remained AlF3 reacts with NaF (Eq.4) and forms Na_3AlF_6. This reaction is thermodynamically favorable at this temperature.

$$AlF3 + 3NaF \rightarrow Na_3AlF_6$$
$$\Delta G^{\circ}_{700} = -104.09 \quad kJ/mol \qquad [4]$$

The X-ray diffraction pattern of the sample prepared by the mixture of chlorofluoride salt shows no Al Peak. Presumably, the reaction with chloride salt led to the escape of Al as $AlCl_3$ (g) at the temperature lower than the synthesis temperature. The XRD result of the sample with eutectic mixture of chloride salt shows K_3ZrF_5 and KBF_4 peaks and no evidence of Al. These results confirmed that the reaction of Al with salt at lower temperature leads to escape Al before contribution in the reaction with fluoride salt. Furthermore, K_2ZrF_6 has an allotropic transformation to K_3ZrF_5 at 592˚C.

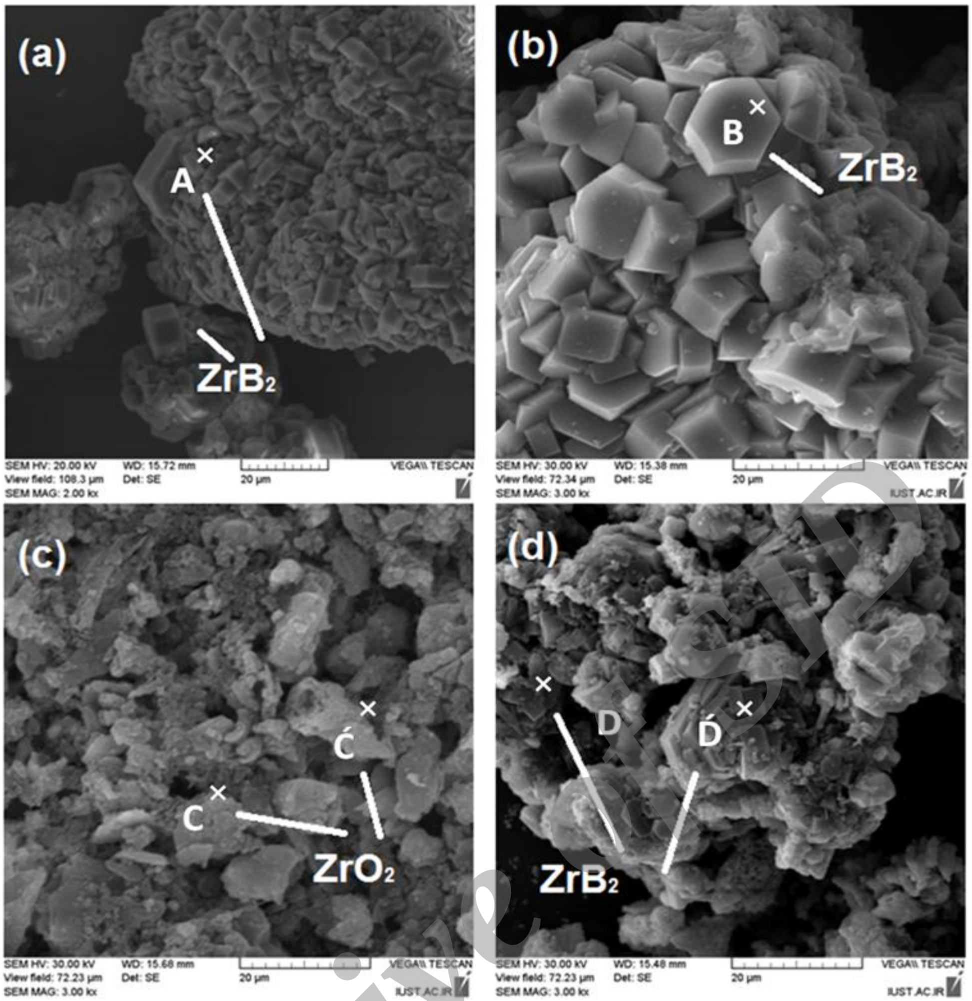

Fig. 5. Microstructure of sample prepared at 700˚C with 2 hrs holding time with different molten salt composition (a) no excess salt (b) KF-NaF **(c)** KCl-KF **(d)** KCl-NaCl

Table 3. EDAX elemental analysis of the selected point in illustrated in Fig.3

Point	Al%	Zr%	O%
A	2.2	96.3	1.5
B	1.6	97.7	0.7
C	3.2	95.3	1.5
C´	33.3	45.1	21.6
D	2.7	62.2	35.1
D´	3.2	34.6	62.2

Presumably, during the washing process, the reaction of KBF_4 and K_3ZrF_5 with water leads to the formation of ZrO_2 and B_2O_3, moreover, the lower amount of B_2O_3 can be attributed to the solubility of B_2O_3 in hot distilled water.

Fig. 5 shows the microstructure of prepared powder with different molten salts composition. EDAX elemental analysis was done on selected point (Zr, Al and O in consideration with the B could not be detected by EDS) for establishing phases and the results shown in Table 3. The sample without additional molten salt has free grown hexagonal plate like particles. As can be seen in Fig.5 (b), the sample prepared by the eutectic mixture of KF-NaF consists of hexagonal prism like ZrB_2 particle with larger average particles size than the samples prepared without additional molten salt. Elemental analysis on thetwo point A and B shows high percentage of Zr and low amount of Al and O was assumedly detected because of glass lamb under the powders. larger particles size is a result of increasing the salt activity and ion mobility [19] which leads to the preferring of growth on nucleation.

Morphology of the prepared powder with eutectic mixture of KF-KCl in Fig. 5 (c) shows irregular growth agglomerated ZrB2 particles with small amount of impurity. Elemental analysis in Table 3, points C and C´ shows that point C has Zr and low amount of Al and O similar to points A and B but point C´ shows relatively high Al and O content which can be attributed to the existence of B_2O_3 and ZrO_2 or Al_3Zr phase in this area. Assumedly, the reaction of Al with chlorides salt at higher temperature and removing the Al from the melt led to the limitation of growth and unaccomplished reaction. ZrO_2 agglomerated particles as a product of the reaction of remained salt with water can be seen in the sample prepared with eutectic KCl-NaCl mixture (Fig. 3 (d)). Points D and D´ from Table 3 show the high amount of O and Zr is in agreement with the XRD result of this sample. Higher amount of O in D´ probably shows that this point consists of the B_2O_3 phase due to the higher oxygen content in comparison with ZrO_2. Morphology and agglomeration of the ZrO_2 particles show that ZrO_2 has produced at lower temperature because of low crystallinity and low particle size. The B_2O_3 amount is also lower than ZrO_2 due to the solubility of this compound in water.

According to the solubility of the reactants in molten salts, the process of molten salt synthesis has been described in two mechanisms: template formation mechanism (or interracial reaction controlled mechanism), and the other is the dissolution–precipitation mechanism (or diffusion controlled mechanism).

The product obtained in the former will retain the similar size and morphology of the insoluble or less soluble raw reactant; whereas in the later, the size and morphology of the product will be different from the raw reactants. Fig.6 shows the microstructure of the starting materials K_2ZrF_6 and KBF_4 used as the sources of Zr and B, respectively. As can be seen in Fig.5 (a), the morphologies of the synthesized ZrB_2 crystals are not similar to their respective K_2ZrF_6 or KBF_4 starting materials (Fig. 6(a) and (b)), the dissolution–precipitation mechanism may play a predominant role in the current molten salt synthesis of ZrB_2.

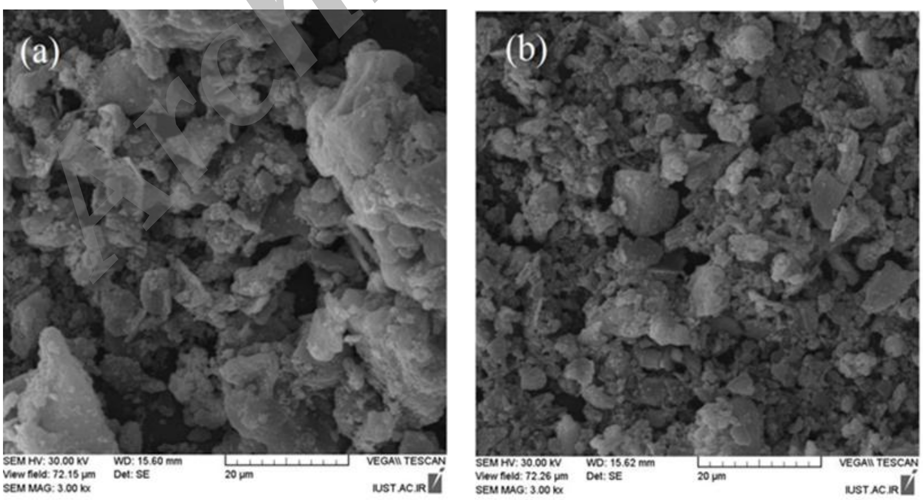

Fig. 6. Microstructure of the starting material **(a)** K_2ZrF_6 **(b)** KBF_4 were used as source of Zr and B respectively

4. Conclusion

In this study, the effect of different molten salt compositions on the synthesis of the ZrB_2 compound was examined. ZrB_2 powders were successfully synthesized through the mixing of reaction salts of KBF_4 and K_2ZrF_6 with Al with halide molten salt except eutectic mixture of NaCl-KCl. Based on the present results, aluminothermic reduction of salt at molten salt medium was responsible for the synthesis mechanism. The ZrB_2 particles with using eutectic mixture of NaF-KF have higher particles size and purity in comparison with no using of additional molten salt and chlorofluoride salt. Because of no similarity between raw material and products, the dissolution–precipitation mechanism may play a predominant role in the current molten salt synthesis of ZrB_2.

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