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Investigations on Fiber Production Attempts from the Borosilicate and SMFMZS (SrO-MgO-Fe_2O_3-Mn_2O_3-ZrO_2-SiO_2) Glass Systems

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Abstract

The glass fiber production generally consists of various optimized processes. The glass formation tendency of melt and its crystallization behavior during drawing are significant process parameters. Furthermore, the resistance against to crystallization during glass melting generally plays a pivotal role on the stability of glass. Thus, this gains a tremendous importance on re-forming of an existing glass. In the present research, the glass fiber drawing attempts from a commercially available borosilicate glass and SMFMZS composition were investigated. Differentiate thermo-gravimetric analysis (DTA) data acquired from the borosilicate glass were firstly compared with those of SMFMZS glass composition to examine the appropriate crystallization behaviors of glass samples. Afterwards, both borosilicate and SMFMZS glass groups' long time heat treatment experiments were carried out for 24 hours using a specially designed thermal gradient furnace. As a result, X-ray diffraction (XRD) analysis findings indicated that there was no crystal formation in the borosilicate glass; whereas the SMZS system contains various crystal phases. Micro-structural observations through the combination of high resolution scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis determined that these crystal phases are rich in zirconium and/or magnesium-based (aluminium) silicates. Also, the former studies on the alkali resistance revealed that the SMFMZS glasses are more durable than borosilicate glass fibers. Therefore, the performed studies herein were focused on to improve the fiber drawing ability of the SMFMZS glasses.

Key words
Borosilicate; SMFMZS glass system; Characterization; Fiber production

Borosilikat ve SMFMZS (SrO-MgO-Fe_2O_3-Mn_2O_3-ZrO_2-SiO_2) Cam Sistemlerinden Fiber Üretim Denemeleri Üzerine İncelemeler

Özet

Cam fiber üretimi genellikle çeşitli süreçlerin en uygun hale getirilmesiyle gerçekleştirilmektedir. Eriyikten cam oluşum eğilimi ve çekim esnasında fiberin kristalleşmesi önemli süreç değişkenleridir. Ayrıca, ergime esnasında kristalleşmeye karşı gösterilen direnç camın kararlılığı üzerinde önemli rol oynamaktadır. Bu çalışmada, mevcut bir ticari borosilikat camı ve SMFMZS sistem bileşiminden cam fiber çekme denemeleri yapılmıştır. Borosilikat camından kaydedilen diferansiyel ısısal-ağırlık ölçümüne dayalı analiz (DTA) verileri öncelikle cam numunelerinin uygun kristalleşme davranışlarını incelemek için SMFMZS cam bileşimi ile karşılaştırılmışlardır. Sonrasında, borosilikat ve SMFMZS cam gruplarının uzun süreli ısıl işlem çalışmalarına özel olarak tasarlanmış bir ısıl gradyan fırını kullanılarak (24 saat) geçilmiştir. Sonuçta, X-ışını kırınım (XRD) analizi verileri borosilikat camı içerisinde herhangi bir kristalin gelişmediğini, buna karşın SMFMZS sistem camlarının çeşitli kristal fazları içerdiğini göstermiştir. Yüksek ayırma güçlü taramalı elektron mikroskobu (SEM) ve enerji saçınımılı X-ışını (EDX) analizi ile gerçekleştirilen mikroyapısal gözlemler söz konusu kristal fazların zirkonyum ve/veya magnezyumca zengin (alüminyum) silikatlar olduğunu belirlemiştir. Aynı zamanda, alkali dayanımı üzerine daha önce yapılan araştırmalar SMFMZS camlarının borosilikat cam fiberlerinden daha dayanıklı olduğunu göstermiştir. Dolayısıyla, burada SMFMZS cam sisteminden fiber çekme kabiliyetini iyileştirme üzerine odaklanılmıştır.

Anahtar kelimeler
Borosilikat; SMFMZS cam sistemi; Karakterizasyon; Fiber üretimi

1. Introduction

Glass fibers are currently considered as advanced materials in the heat and sound insulation applications. Additionally, the construction is crucial sector for fiber glass consumption that especially used for residential, commercial, industrial buildings and insulation. The glass fibers are also used as reinforcement components in cement, concrete and a variety of composites for many purposes [1].

Boron is the key constituent for glass making process [1]. When boron oxide is particularly added to glass fiber composition in 4-5 wt. %, the melting temperature of glass can easily be lowered. Thus, this event positively prevents the re-crystallization of glass with the increase of resulting glass' durability [1]. Borosilicate glasses exhibit the low crystallization tendency, small thermal expansion coefficient, high thermal shock resistance and relatively low density. As well-known by the glass technologists, the borosilicate glasses are very convenient materials for fiber withdrawal route at the commercial-scale [2].

The softening points of borosilicate glasses are usually higher than those of various glasses. Especially, the thermal expansion coefficient is about one third of soda-lime silica glass. As a result, the borosilicate glasses show excellent thermal shock resistance. Furthermore, this kind of glasses reveals better chemical resistance against to water and acidic environments, besides their electric insulation characters [2]. Thanks to these properties, they become promising candidates for glass fiber withdrawal.

To produce a glass fiber, the glass-batches are firstly heated up to fiber drawing temperature, and then glass fiber is withdrawn through the melt. Here, after vitrification of glass, a possibility on the crystal formation during cooling process can lead to cracking on the resulting glass fibers [3]. Prepared glass is heated to the fiber drawing temperature. Crystals formed after melting and vitrification of prepared glass may cause cracks and defects on the glass. Similarly, crystal formation at the heating process till to fiber drawing temperature leads to the same results [3]. Therefore, the precise determination of studied glass systems' crystallization behaviors is the first essential step for a successful fiber withdrawal.

In the present research, the glass fiber drawing attempts from a commercially available borosilicate glass and SMFMZS system compositions were comparatively carried out. DTA, XRD and micro-structural data on both resulting samples in borosilicate and SMFMZS systems prompt that how the appropriate glass fibers, bearing the process parameters in mind, can be produced.

2. Experimental Procedure

To draw fibers from borosilicate composition, a commercially well known borosilicate glass available in the market was used in the experiments. It was homogenously broke up to get ready for re-melting. Later, the borosilicate glass fibers were fabricated in Anadolu University, Department of Materials Science and Engineering, Glass and Glassy Materials Technologies Laboratory using a MSE brand and FP-100 model fiber production device at 1250^{o}C. Then, the produced glass fibers were annealed at 550^{o}C for 2 hours in MSE brand V-30 model furnace to remove the existing thermal stresses.

The obtained borosilicate glass fibers were afterwards coated by a polymeric material, which ensures to increase the strength of composite materials, to reduce the mobility of fibers and finally to give rise to an extra chemical resistance to the final product. This process was overall performed in Anadolu University, Department of Materials Science and Engineering, Polymer-Based Composite Materials Laboratory. At this stage, the stirred silane solution with 1 % ethanol addition was used to obtain the coating material.

To determine the chemical effects of performed coating process on the fibers, the chemical

resistance test was applied to both uncoated and silane coated borosilicate fibers during 4 weeks. The detailed description of chemical resistance test can also be found in our previous study [4]. Yurdakul et al. [4] concluded that SMFMZS glass group improved the fibers' characteristic in a positive way. Therefore, both SMFMZS and borosilicate glass groups in the fiber form were investigated together to reveal whether any kind of crystallization occurred or not. As a function of temperature and time, the thermal behavior of borosilicate glass fiber with 100 μm diameter was determined by using DTA and TG analyses. Similar experiments were also carried out for Fe11 glass belonging to SMFMZS system and possessing high alkali resistance.

To produce Fe11, Carbolite brand glass melting furnace was employed. Experimental procedure for Fe11 can be described with the conventional route; batch preparation, calcination and glass melting. Here, the prepared batch was firstly put in the platinum crucible, and then calcination was conducted to carbonate bearing compounds for the successful removal of CO_2. Finally, to melt the batches, homogeneously mixed batches were put into the furnace and the temperature was raised to 1550 °C and melt was hold for 6 hours 45 minutes. Also, the furnace was periodically controlled to prevent overflowing of melt.

The crystallization properties of Fe11 glass, previously mentioned as the modified composition of SMFMZS group, and borosilicate one were investigated. Glass samples were specially placed in MSE-GF-1300 model horizontal gradient furnace. The temperature was increased up to 1100 °C. Principally herein, the boat shape crucible that comprised of multiple cells including the several of samples was inserted into the gradient furnace, and it maked exposure to temperature under the define time. At the end of treatment, the samples were extracted from the boat, and their crystallization properties were examined by various characterization methods, i.e., XRD and SEM.

The flow chart of experimental procedure carried out in the present research can be summarized in Figure 1.

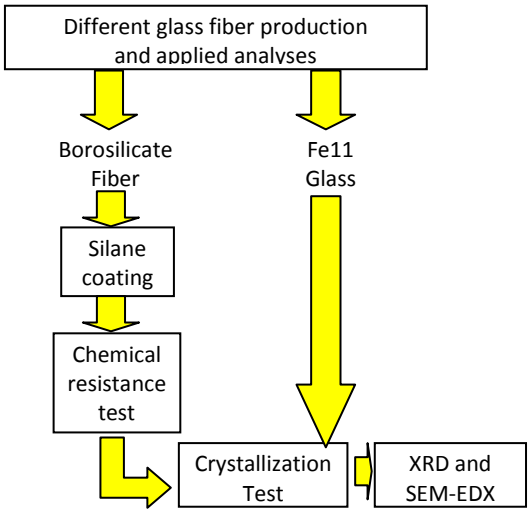

Figure 1. The flow chart of experiments performed in the study.

3. Results and Discussion

SEM image determining the morphological characteristics of borosilicate glass fibers, is presented in Figure 2. Here, the average diameter of lab-scale borosilicate glass fibers produced was determined as around 100 μm.

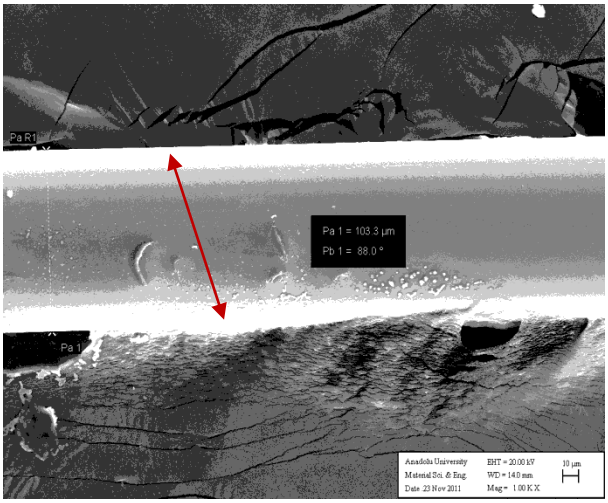

Figure 2. The SEM image indicating the borosilicate glass fiber with 100 μm diameter produced at lab-scale.

TG analysis data of the commercial borosilicate glass was given in Figure 3. When the dTG (mg/mm) graph examined, an explicit sharp peak corresponding to weight loss could be

approximately seen at 330 °C

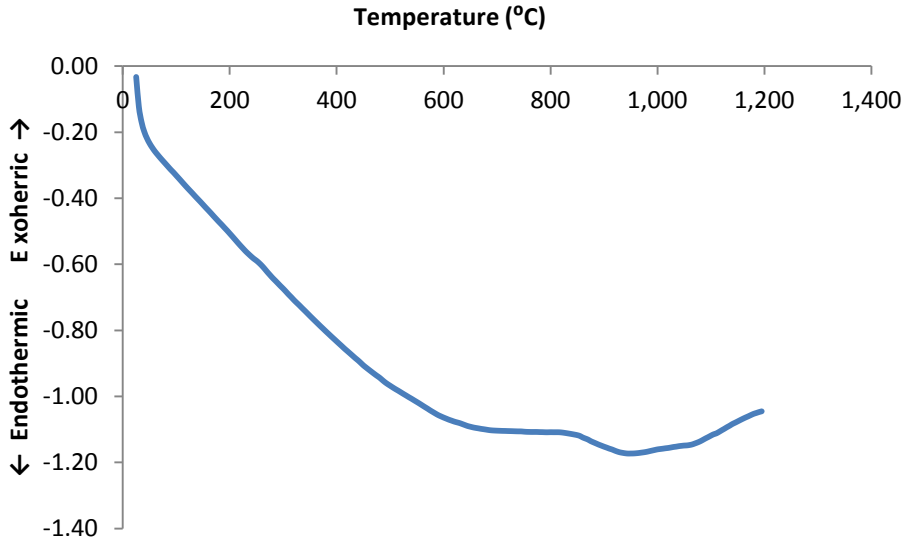

Figure 3. The dTG (mm/mm) graph for borosilicate glass.

The TG analysis result of Fe11 glass was demonstrated in Figure 4. In its case, the reaction was seen at 370 and 660 °C. If the peaks area of TG/DTA curves between Tg-glass transition and Ts-softening temperatures is quite high, the crystallization reaction tendency increases at the same proportion. Otherwise, as noticed in the case of SMFMZS system glass, when this area is small, crystallization does not occur. Such a characteristic of SMFMZS glass gives an advantage to it for possible and easy fiber drawal.

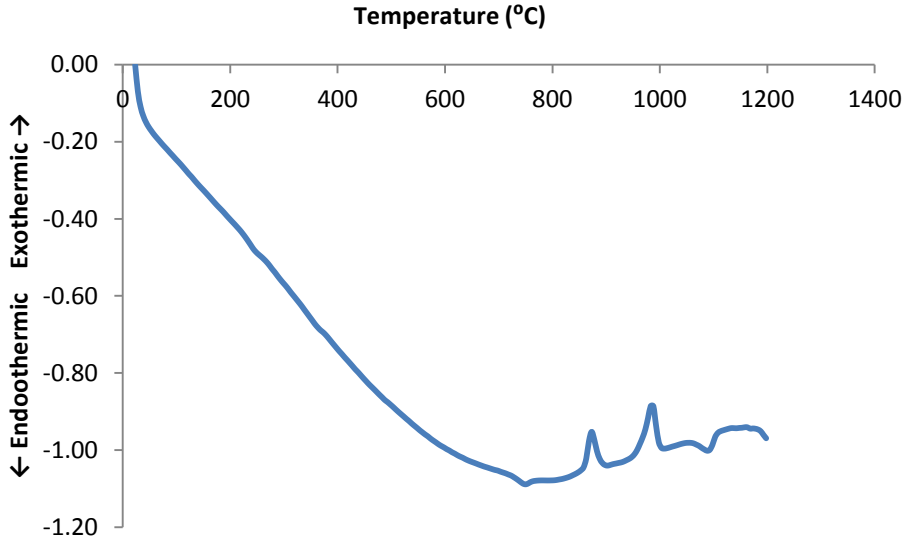

Figure 4. The temperature-dTG (mm/mm) graph for Fe11 glass.

The chemical resistance test results of borosilicate fibers during 4 weeks can be followed in Figure 5. When carefully examined, it is very clear that weight losses of silane coated and uncoated borosilicate fibers are close to each other. More preciously, the weight loss of silane-coated borosilicate glass was 52 %, whereas the as-received borosilicate one was 58 %. This may conclude that the coating process of borosilicate glass with a polymeric material, silane, gives a little bit improvement on the chemical resistance.

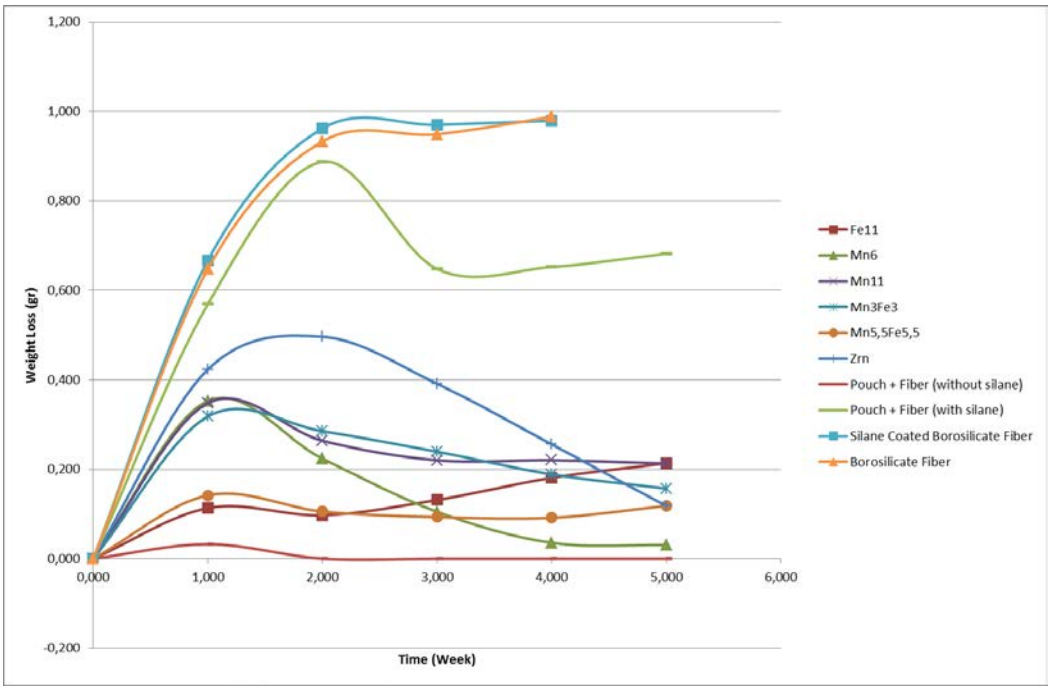

Figure 5. The chemical resistance test results of produced fibers with and without silane coating.

A crystallization study was applied to borosilicate glass fibers within the following heat treatment temperatures for 24 hours (Figure 6). It was determined that, if there was any crystal phase formation after removal of the samples from the gradient furnace thanks to SEM and XRD.

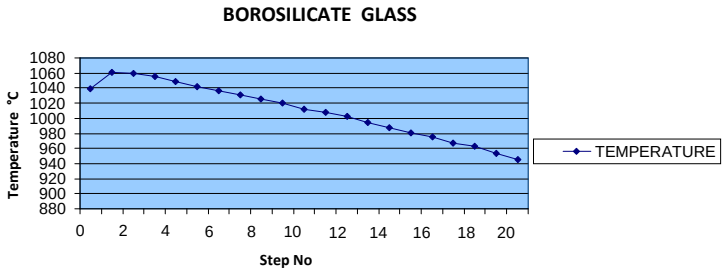

Figure 6. The data acquired from the gradient furnace for borosilicate glass.

XRD analysis results obtained from different heat treatment schedules (between step no 1 and 13) in the gradient furnace are given in Figure 7 (a and b). According to XRD results, there is no crystal phase formation detected for borosilicate glass fibers even after 24 hours heat treatment at different temperatures. This can be also confirmed by SEM images of related samples in Figure 8 (a and b). Only trace amount of thermal stresses, due to fast cooling of samples after completed heat-treatment, can be observed.

Fe11 glass of SMFMZS system having superior chemical resistance and not containing any alkali was also investigated in the gradient furnace to reveal its crystallisation characteristics and to make a decent comparison with the borosilicate glass (Figure 9).

To identify the crystal content of Fe11 glass after heat treatment in the gradient furnace, the micro-structural observations were performed with SEM analysis from the samples corresponding to temperature values of numbered-steps, respectively, with 1 and 13 of Fe11 glass (Figure 9). Thus, the acquired SEM images of samples heat

treated at step no 1 and step no 13 in gradient furnace experiment can be seen in Figure 10 (a-b). As a result, the Fe11 glass includes a variety of crystalline phases that leads to failure during fiber glass drawing.

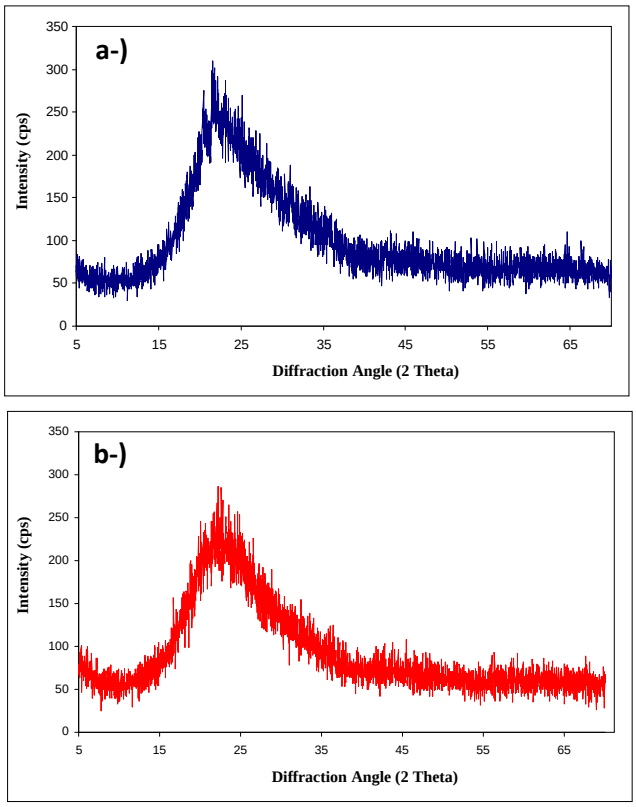

Figure 7 (a-b). The XRD analysis data obtained from the samples corresponding to temperature values of numbered-steps, respectively, with 1 and 13 of borosilicate glass in the gradient furnace.

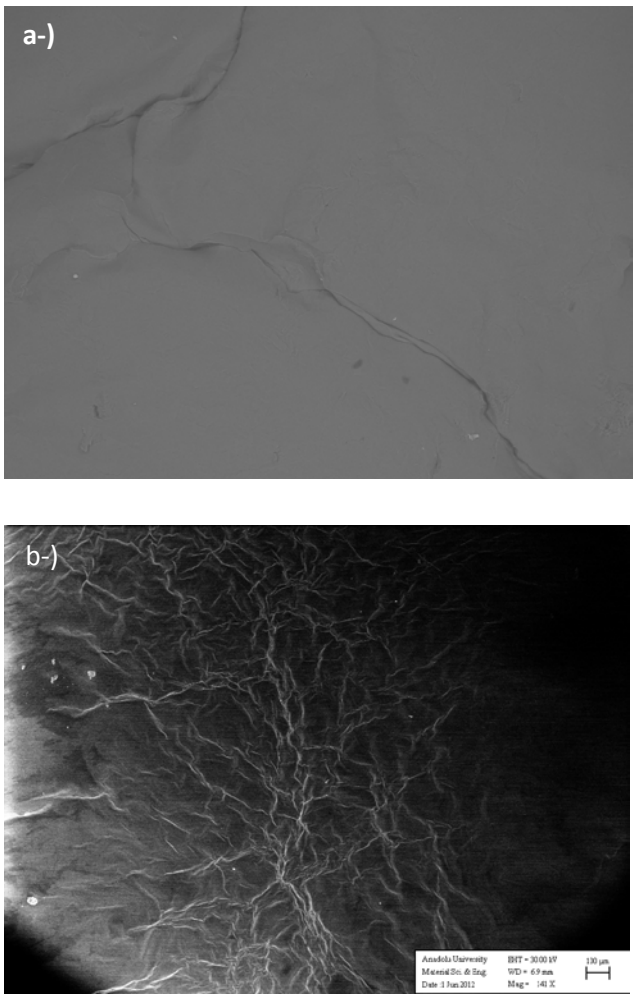

Figure 8 (a-b). The SEM images taken from the samples corresponding to temperature values of numbered-steps, respectively, with 1 and 13 of the borosilicate glass in the gradient furnace.

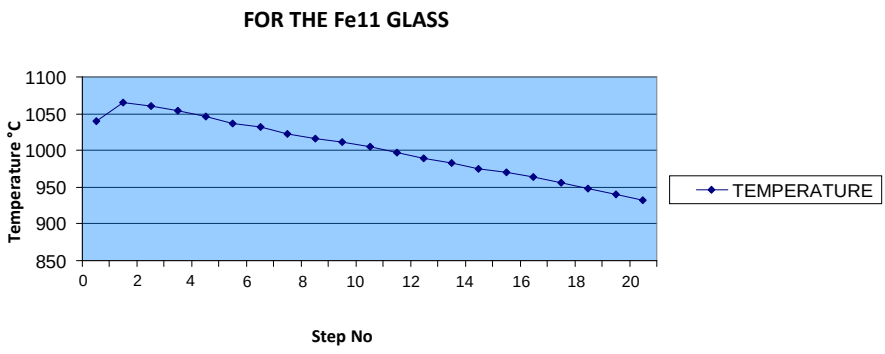

Figure 9. The data acquired from the gradient furnace for Fe11 glass.

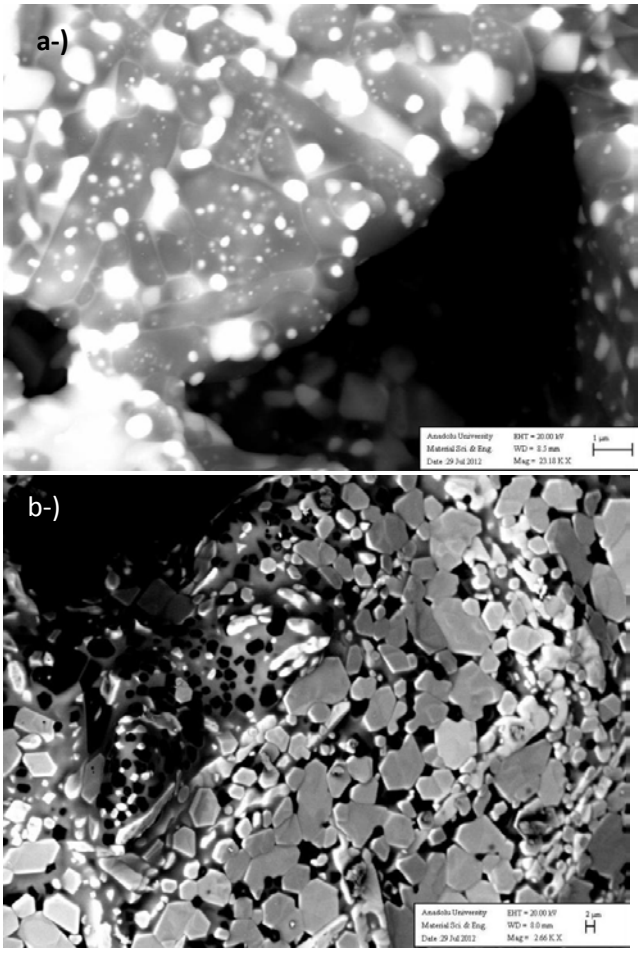

Figure 10. The SEM images of samples **a-)** at step no 1, **b-)** at step no 13.

As shown in the previous SEM images of heat treated Fe11 samples at different temperatures, there are many phases with different crystal shapes. Obtained results on these heat treated samples can be revealed the reason of having difficulties during the fiber drawing process of Fe11 glass. Detailed SEM and EDX analyses were carried out on the sample taken from the part of the platinum rod used for fiber drawing process. The obtained microstructures are given in Figs 11 (a to d) and 12 (a to d). These microstructures from the glassy part on the tip of the platinum rod revealed that there are mixtures of crystal phases with different shapes (needle-like, pentagon and hexagon) in this part. EDX analyses for these phases revealed Mg- and Zr-aluminosilicate based crystal formation.

In the present research, we report a study on the examinations of fiber production attempts from the borosilicate and SMFMZS system glasses. Drawing fiber from the commercially available borosilicate glass was successfully performed. The detailed XRD and SEM analyses revealed that no crystalline phase was observed in it.

Furthermore, the borosilicate fibers including alkali elements exhibit the limited chemical durability when compared to a silane, polymeric material, coated one. So, we concluded that the use of a polymeric material on the coating of borosilicate fibers improves the chemical resistance of glass for further applications.

4. Conclusion

We have tried another fiber drawing attempt from the Fe11 glass composition. However, the results clearly presented that this compound is not convenient for fiber drawing due to intense crystal phase formations evolved nearly all the bulk glass. Here, we can say that the formed crystals which are Mg- and Zr-aluminosilicates through the bulk Fe11 glass severely disrupted the fluidity of glass melt, causing discontinuity in fiber drawing. Therefore, it was decided that the composition of Fe11 must be tailored in terms of suitable viscosity which will not allow undesired crystallization for a successful fiber drawal.

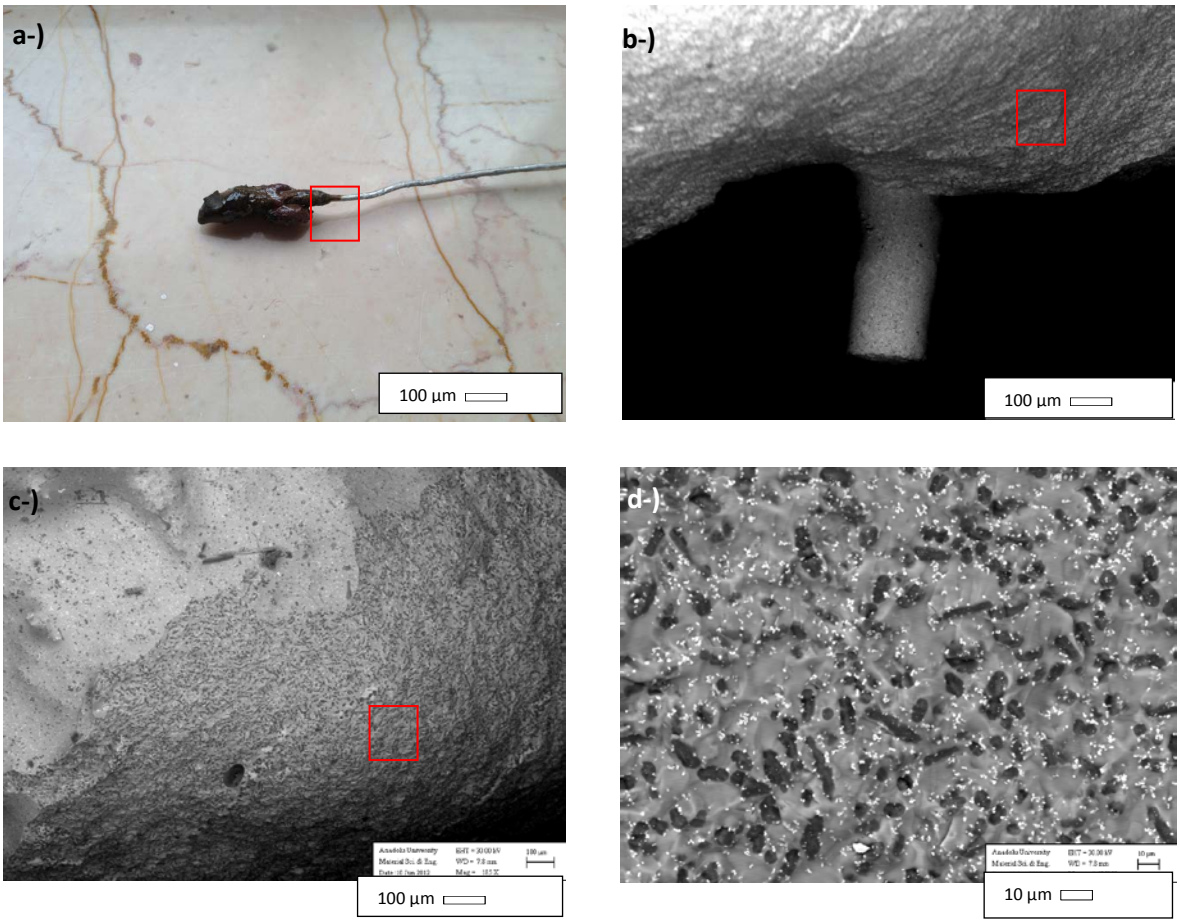

Figure 11. (a) The digital photograph of Fe11 glass stuck edge of the platinum rod after fiber drawing process, **(b-d)** SEM images of regions marked with red lines in previous one, respectively.

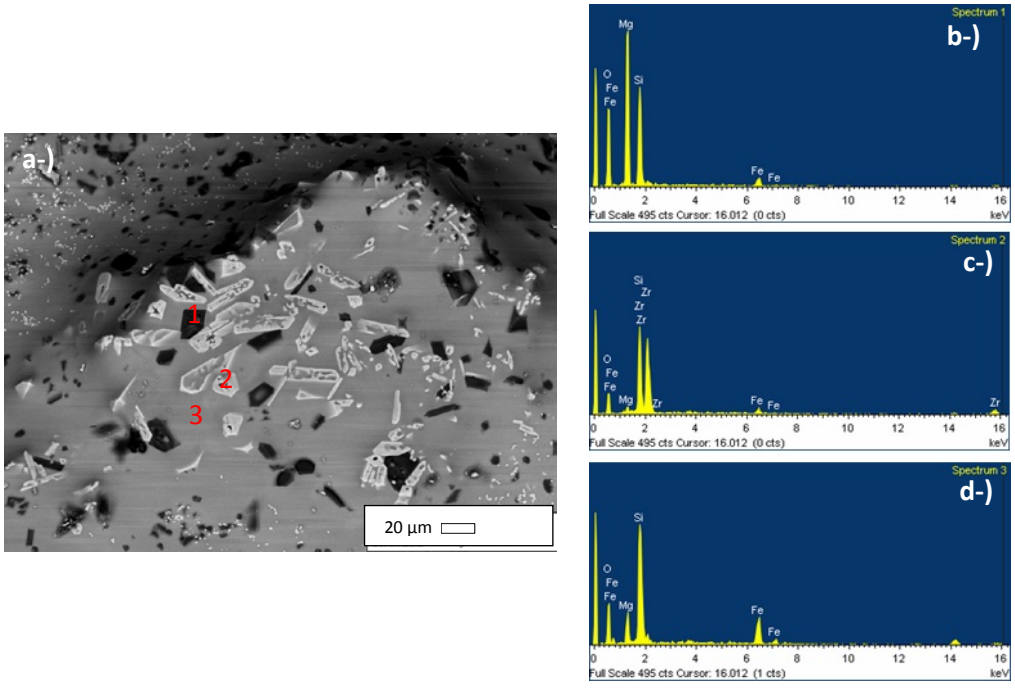

Figure 12. (a) The SEM image of Fe11 glass stuck edge of the platinum rod after fiber glass drawing process, **(b-d)**

EDX analysis results obtained from the areas shown as 1, 2 and 3 in Figure 12 (a), respectively

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