Journal of Ceramic Processing Research. Vol. 12, No. 1, pp. 34~37 (2011)

J O U R N A L O F
Ceramic Processing Research

Investigation of the percentage crystallization in glass ceramics using an image analyzer method

S. Mahdavi, V. Madahi, M. Samedani and H.R. Rezaie*
Dept. of Eng. Materials, Iran University of Science & Technology (IUST), Narmak,Tehran,Iran

Glass-ceramics are normally obtained by a controlled crystallization process of suitable glasses. Properties of glass-ceramics are affected by the amount of crystalline phases. In this paper, a new, fast, and simple method is investigated to measure the percentage crystallization in glass-ceramic samples. The most common method for measuring the percentage of crystalline phases is investigation of XRD patterns, but in this new method, image analysis (IA) is used for this purpose. Thus, SEM images of two cordierite-based glass-ceramics were investigated by image analyzer software and the variation in crystallization, which were obtained by two methods, were compared. A good correspondence between the results of the XRD patterns and SEM image analysis was achieved, and the difference between the results of these two methods was about 2%. Finally, it was shown that image analysis can be used to measure the percentage of crystalline phases in glass-ceramics with good accuracy.

Key words: Percentage crystallization, Image analysis, Cordierite based glass-ceramics.

Introduction

Cordierite base glass-ceramics (SiO_2-Al_2O_3-MgO) have been extensively studied because of many beneficial properties, such as elevated thermal and chemical stabilities, low dielectric constant (~5.0 at 1 MHz), low thermal expansion coefficient (~2×10^{-6}/ºC), low dielectric loss, and good infrared radiation performance. These ceramics are used in various industrial fields, in applications such as refractories, electrical, thermal or sound insulation, filters, membranes, heating elements, heat exchangers, microwave absorbents, electromagnetic waves absorbents, substrates, packaging, multichip modules (MCM), and in the microelectronics industry [1-11].

Glass-ceramics are normally obtained by a controlled crystallization process of suitable glasses. Internal or external nucleation is promoted to develop micro-heterogeneities from which crystallization can subsequently begin. As a result, the amorphous reservoir of the glass transforms into uniform microcrystalline ceramics. The composition of the crystalline phases and the crystallite sizes define the properties of the final material [12]. The most popular nucleating agents of glasses are TiO_2, ZrO_2, Cr_2O_3, Fe_2O_3 and P_2O_5 [13-15]. De Vekey and Majumdar found that depending on the concentration of nucleating agents in the glass, the crystallization mechanism changes. Thus, for glasses where the TiO_2 concentration is less than 7 wt%, crystallization starts from the surface but once this limit is exceeded, volume or bulk crystallization becomes the predominantmode [16]. In TiO_2 containing cordierite glasses, first a metastable β-cordierite solid solution is formed which at higher temperatures usually transforms to the stable α-cordierite [11].

Investigation of X-Ray diffraction (XRD) patterns is the most conventional method for measuring the percentage of crystalline (or amorphous) phase in glass-ceramics. This method is used especially to follow up the crystallization procedure with different heat treatment conditions. It is based on the comparison of XRD patterns of glass-ceramic samples with totally amorphous and crystallized specimens. Distances (intensities) of some points on the pattern, at some angles, from the base line are measured and then, usually using the method of Ohlberg and Strickler [19], the percentage of the crystalline phase is determined. However, for specimens with lower than 10% crystalline phase, the method is not effective and the probability of human errors is high [17, 18].

Another method used for measuring the amount of crystalline phases in glass-ceramics is analyzing SEM images with an image analyzer (IA). This method is also used to measure grain size, pore size distribution, fracture properties, and microstructural features [20-23]. Hattori and Nakao [24] examined the particles removed due to different stages of erosion using an image analyzer, and identified the particle size and also counted the particle number. A digital image is divided into as many as 256 gray levels, from zero (all black) to 255 (all white). In this method, SEM back scattered images are investigated with image analyzer software, and gray levels of different parts of the images are connected to different phases, they are then colored and the percentage of colored areas are measured [25].

In this study, glasses with a specific compound were

*Corresponding author:
Tel : +98-9121025394
Fax: +98-9121025394
E-mail: hrezaie@iust.ac.ir

prepared and then heat treated differently. Cordierite based glass-ceramics with different crystalline phases were obtained. X-Ray Diffraction patterns and SEM images were prepared, and finally, the amounts of crystalline phases in different samples were investigated by these two methods and then the results were compared.

Experimental Procedures

The composition of the initial glass is shown in Table 1. Zedlitze kaolin, hamedan silica, MgO, and TiO_2 (as nucleation agents) were used to achieve a glass composition with 99% purity from an Iranian company, as raw materials. The batch compositions are shown in Table 2. Beside these materials, Pb_3O_4 (4.5 wt.%) was also added to the batch to reduce the melting temperature of glass and increase the amount of contrast between the amorphous and crystalline phases in SEM images. The mixture of the powders, with a total weight of 1kg, was charged in alumina crucibles. Then it was heated in a resistance furnace, with a heating rate of 10 K·minute^{-1} to 1450 °C for 2 hours. The prepared molten glass was poured into a steel mold which was preheated at 700 °C. Then this mold and glass were settled in an annealing furnace with a temperature of 700 °C. The resultant glass was cut into different pieces. Differential thermal analysis (DTA) (Shimadzu 50H) was performed for the powdered glass at 1250 °C with a heating rate of 10 K·minute^{-1}. According to the DTA curves the glass samples were settled in a resistance furnace, and the temperature risen up with a rate of 10 K·minute^{-1} for 1 hour at each temperature of 915, 1000, 1150 °C, 1240 °C and then were cooled in air. The resultant glass-ceramics were cut into two parts and one part of which was powdered. X-Ray diffraction (JEOL 8030) was used to identify the phase analysis of the powdered glass ceramic, the pure glass, and the initial mixture having the same composition as the parent glass. Other parts of the heat treated glass-ceramics were polished, gold coated, and then examined using a scanning electron microscope (SEM, Cambridge S360). Finally, after improving the quality of the SEM images with image analyzer software (Clemex Vision 3.5) and acquiring images with better contrast between the crystalline and glassy phases and sharper boundaries, these images were investigated with the same image analyzer software.

Table 1. Composition of the initial glass (in wt.%)

SiO_2	Al_2O_3	MgO	TiO_2
46.2	31.4	12.4	10

Table 2. Percentage of raw materials (in wt.%)

Zedlitze kaolin	Hamedan silica	MgO	TiO_2
70.9	7.6	12.3	9.2

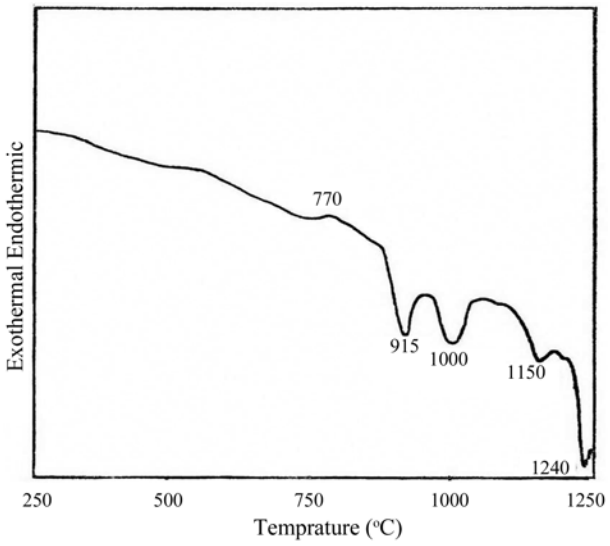

Fig. 1. DTA curve of the initial glass.

Results and Discussion

The DTA curve of the initial glass is shown in Fig. 1. It can be seen that critical temperatures for nucleation and growth of crystalline phases are 915, 1000, 1150, and 1240 °C. Thus these temperatures were selected for heat treatment of the initial glass.

XRD patterns of the two glass-ceramic samples, the initial glass, and initial powder having the same composition as the parent glass, are shown in Fig. 2. In this figure, XRD patterns of the initial glass and initial powder mixture are taken to be fully-amorphous and fully-crystallized samples, respectively. Distances between XRD peaks of the samples and the horizontal axis were measured at various 2θs. The Ohlberg & Strickler equation [19] was used for comparison of these distances and to obtain the volume fraction of crystallization in glass-ceramic samples, from eq(1) below:

$$X_c = \frac{(I_g - I_x)}{(I_g - I_b)} \times 100 \quad (1)$$

In this equation, I_g, I_x and I_b are the XRD intensity scattered by the parent glass, the partially crystallized glass and a mechanical mixture of oxide powders having the same composition as the parent glass, respectively.

The percentage crystallization in two glass-ceramic samples is shown in Table 3. By using this method, the average amounts of crystallization in these samples are 58% and 77.5%, respectively.

SEM images of two glass-ceramic samples are shown in Fig. 3. In these images, dark areas are crystalline phases, and because of the lead dissolved in the glassy phase, light regions are the glassy phase. This difference in contrast leads to better separation of crystalline and glassy phases by an image analyzer. Some of the SEM images after analyzing by the image analyzer software are shown in Fig. 4. In these images dark regions show crystalline phases which are separated by the image analyzer from the contrast between crystalline and glassy phases. Some percentages

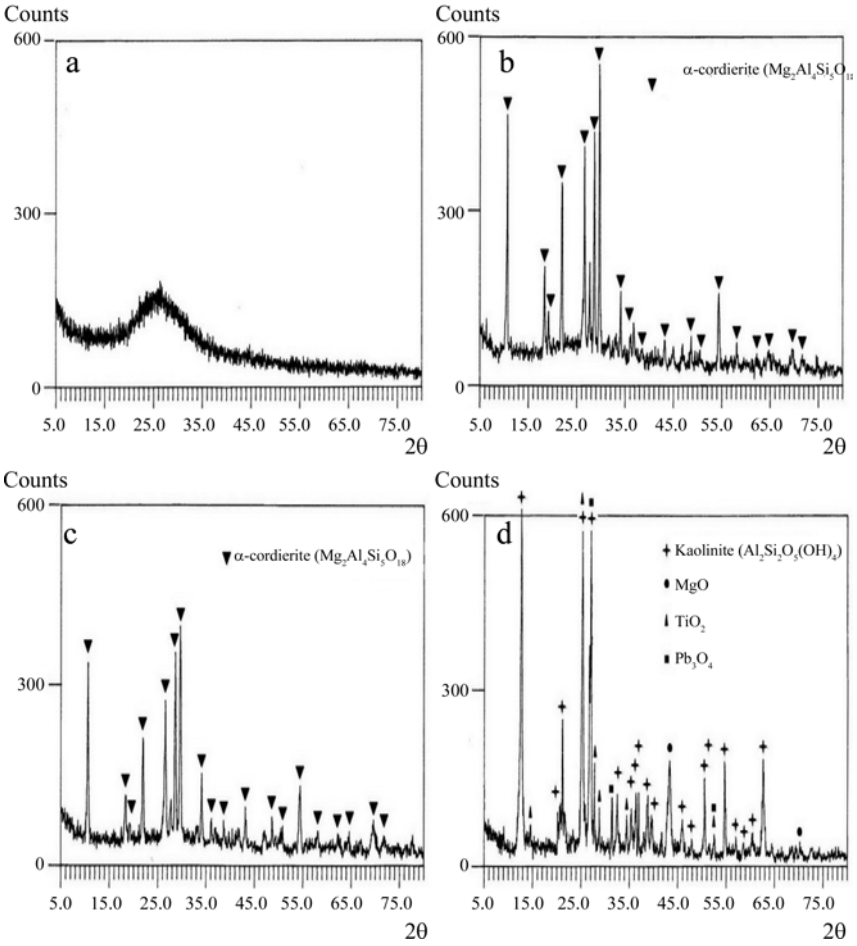

Fig. 2. XRD patterns of: (a) the initial glass (fully-amorphous sample), (b) sample 1, (c) sample 2, and (c) powder mixture with the same composition as the parent glass (fully-crystallized sample).

Table 3. Percentages crystallization at various 2θs for two samples

	9°	20°	24°	29°	31°	53°
Sample 1(%)	60.5	59.0	70.8	56.9	58.5	59.3
Sample 2(%)	79.8	77.6	88.4	72.2	78.2	79.6

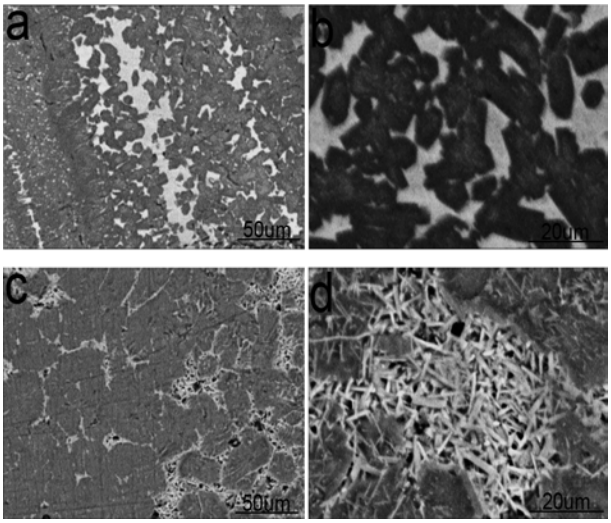

Fig. 3. SEM images of sample 1 (a, b), and sample 2 (c, d), at two magnifications.

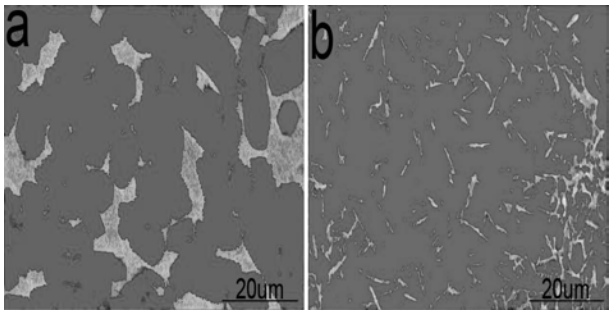

Fig. 4. Two SEM images of (a) sample 1, (b) sample 2, after analyzing by the image analyzer software.

of crystalline phases for two glass-ceramic samples, which were obtained from different SEM images with different magnifications, are shown in Table 4. Using this method, the mean percentage of crystalline phases obtained for samples 1 and 2 were 54.1% and 75.7%, respectively.

It can be seen from the results that there is no significant difference between the percentage of crystalline phases which were obtained from XRD patterns and analysis of SEM images by the image analyzer. There are only about 2 and 4% difference between the results of sample 1 and 2,

Table 4. Some percentages of crystalline phases which were obtained by an image analyzer

Sample 1	57.2	56.7	55.2	53.8	51.1	51.7	53.2	49.6
Sample 2	80.3	76.1	77.7	74.5	74.1	70.3	78.3	69.8

respectively. It should be considered that XRD results are related to the bulk of the samples, but SEM image analysis results are related to a small section of the surface of the samples. So it would be better to get several SEM images from the depth of the sample to get better results to analyze by the image analyzer. When the samples are homogenous, coincidence between the results of the two methods should be better.

It is clear from the results that there is good agreement between the results of SEM image analysis and XRD patterns investigation, so this method can be used instead of the XRD method. Furthermore, this method is faster than XRD and there is no need to grind the samples.

Conclusion

The following conclusions can be drawn from this study:

Image analysis is an efficient tool for measuring the percentage crystallization in glass-ceramics. Results of image analysis are in good agreements with those of XRD pattern investigations, and there is only about 2% difference between the results.

Results of SEM image analysis are only related to a small part of the samples, and to achieve more reliable results, more images should be investigated.

Measurement of crystalline phases by an image analyzer is faster and more reliable than by XRD, because there is no need for extra stages such as grinding of bulk samples and manual measurements.

References

1. S. Wang and K. Liang, Journal of Non-Crystalline Solids 354 (2008) 1522-1525.
2. K.H. Zum Gahr and P. Neumann, Wear 203-204 (1997) 107-118.
3. C. Ghitulica, E. Andronescu, O. Nicola, A. Dicea and M. Birsan, Journal of the European Ceramic Society 27 (2007) 711-713.
4. E. Ozel and S. Kurama, Journal of Materials Processing Technology 198 (2008) 68-72.
5. G. Chen, Journal of Alloys and Compounds 455 (2008) 298-302.
6. S. Mei, J. Yang, X. Xu, S. Quaresma, S. Agathopoulos, J.M.F. Ferreira, Journal of the European Ceramic Society 26 (2006) 67-71.
7. H. Shao, K. Liang, F. Zhou, G. Wang and F. Peng, Journal of Non-Crystalline Solids 337 (2004) 157-160.
8. S. Mei, J. Yang and J.M.F. Ferreira, International Journal of Inorganic Materials 3 (2001) 1249-1252.
9. S. Mei, J. Yang and J.M.F Ferreira, Journal of the European Ceramic Society 21 (2001) 185-193.
10. Y.S. Cho, D.T. Hoelzer, W.A. Schulze and V.R.W. Amarakoon, Acta Mater. 46 (1998) 6421-6430.
11. V.K. Marghussian, U. Balazadegan and B. Eftekhari-yekta, Journal of the European Ceramic Society 29 (2009) 39-46.
12. D.U. Tulyaganov, M.J. Ribeiro and J.A. Labrincha, Ceramic International 28 (2002) 515-520.
13. X. Guo, H. Yang, Han and F. Song, Thermochimica Acta 444 (2006) 201-205.
14. M. Rezvani, B. Eftekhari-yekta, M. Solati-Hashjin and V.K. Marghussian, Ceramics International 31 (2005) 75-80.
15. O.A. Al-Harbi, Ceramics International 35 (2009) 1121-1128.
16. F.J. Torres and J. Alacro, Journal of the European Ceramic Society, 23 (2003) 817-826.
17. M. Rodrigues, G.T. Niitsu, E.D. Zanotto, M.O. Prado and V. Fokin, Non-Crystalline Solids, 353 (2007) 2237-2243.
18. V.K. Marghussian, Iran University of Science and Technology (2002).
19. S.M. Ohlberg and D.W. Strickler, Journal of American Ceramic Society 45 (1962) 170-172.
20. K. Mannesson, M. Elfwing, A. Kusoffsky, S. Norgren and J. Agren, International Journal of Refractory Metals & Hard Materials 26 (2008) 449-455.
21. P. Varela, J.M. Aguilera and S. Fiszman, LWT 41 (2008) 10-17.
22. R. Ziel, A. Haus and A. Tulke, Journal of Membrane Science 323 (2008) 241-246.
23. K.Y. Kang, J.G. Roemer and D. Ghosh, Powder Technology 108 (2000) 130-136.
24. S. Hattori and E. Nakao, Wear 249 (2002) 839-845.
25. E. Richard, American Ceramic Society (2002).