Synthesis of sintered glass-ceramics in air and argon obtained from industrial waste revealed by hot stage microscopy

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I. Introduction

Many industrial streams in the metallurgy provide large amounts of waste raw materials, e.g., in the form of slag, containing the necessary composition allowing its entire recycling with the introduction of just minor modifications. In this way new glass-ceramic materials can be obtained. The used technology includes melting and subsequent sinter-crystallization treatment [1, 2] usually carried out in atmospheric environment. The used raw material contains iron oxides, which is a valuable property. These oxides are known to act as foamers at certain known conditions, i.e. they can initiate the formation of new foam materials.

The existing dependence of the linear heating rate on the sintering behavior during the formation of new glass-ceramic materials can be considered as the motivation of present investigation. From the point of view of the kinetics, the process of sintering can be satisfactory approximated with viscous flow. Among the many well established physical models of viscous flow used toward the determination of activation energies, e.g. the Cheng method can be (and is currently being used here) successfully applied in the present particular case of sintering of glass-ceramic materials.

Recent implementation of innovative synthesis in air and argon or in a mixed air/argon environment used by the authors, has led to increase of the degree of sintering and to a stronger kinetic effect when carrying out a stage of the synthesis of sintered glass-ceramics in argon instead of air.

Up to now, the authors have performed calculations of activation energies in the framework of the Cheng kinetic model assuming constant degree of transformation [3].

II. Materials and methods

For the purposes of current experimentation with sintered glass-ceramic materials, slag from the iron and steel company Helwan, Cairo Governorate, Egypt was used for the synthesis of the samples under investigation.

The slag was enriched in silica by mixing 70 wt.% slag and 30 wt.% industrial sand. The parent batch of 150 g was brought to melting in corundum crucibles using an electric furnace. After an exposure for 2 hours at a temperature of 1450 °C, the resulting homogenous melt was quenched in water. Thus obtained glass frit was crushed, grinded in a planetary mill FRITSCH (Germany) and sieved below 75 μm with a digitally programmed sieving machine CISA (Spain).

The sintering was performed by a thermal-optical measuring and imaging system with a HSM-1400 MISURA (Italy). This instrument combines two methods: high-precision, high-resolution contactless optical dilatometry (ODLT) and hot-stage microscopy (HSM). This arrangement is an established laboratory technique in recent years, since it turns out to be reliable and fast and is used already by many research groups worldwide as well [2, 4].

For the aims of thermal synthesis and kinetic analysis, all measurements of glass-ceramic samples were carried out by means of HSM. Most of the measurements were performed with holding times of 30 minutes at a temperature of 950 °C in air or in mixed air/argon environment.

All XRD spectra for determination of the structure were recorded with a Panalytical Empyrean (USA) spectrometer. SEM imaging was realized with a JEOL 6390 (Japan) device.

III. Results and discussion

As already noted, the innovative point of current research is, besides the use of the applied method of sinter-crystallization toward the production of sintered glass-ceramic materials, the use of a controlled environment (air and inert atmosphere) during the synthesis of sintered glass-ceramics.

The effect of the environment on sintering has been unambiguously determined as it is shown in Figure 1: the onset of the sintering process in argon is shifted to lower temperatures. It starts earlier, and the degree of structural densification is considerably higher than the one in air. As it is evident from EPR measurements the ratio of Fe^{2+}/Fe^{3+} is strongly drawn to the right. This is a prerequisite for viscosity decrease due to a predominant presence of Fe^{3+} (it doesn't contribute to the sintered material's crystal lattice) in the parent glass.

The effect of the rate of heating on the sintering behavior of newly obtained glass-ceramic materials has been and is currently being subject of detailed investigation by the authors. The most important feature is, besides the kinetic shift in temperature, the influence of the linear heating rate on the degree of sintering.

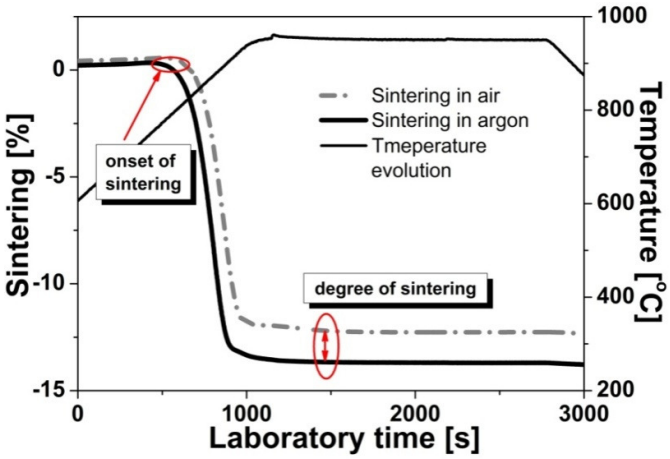

Figure 1. HSM sintering curves of glass-ceramics in different environments

Variations of the heating rate from 2 to 30 degrees per minute lead to approx. 10 % variations in the degree of sintering.

XRD spectroscopic investigations reveal that the new sintered material is built mainly of pyroxene crystal phases. It has also been found that the crystallinity in argon is higher than that in air.

SEM imaging reveals despite the good overall sintering in both atmospheres, a better granular sintering in argon that that in air. Presence of surface porosity with a concave morphology has been discovered as well.

Applying the Cheng method toward the determination of activation energies of sintering, the authors have determined as initially anticipated, the presence of a linear dependence of the parameters governing the kinetics of sintering. As a result of the performed analysis, reasonable energetic values in the range of 900 kJ mol-1 (energy of sintering) have been determined.

IV. Conclusions

In presented investigation the authors have shown the possibilities for carrying out successful synthesis and kinetic investigations of the process of sintering, depending on the firing programs and the applied atmosphere of well-sintered glass-ceramics. It was shown that synthesis in a mixed air/argon environment leads to the production of materials with higher degree of sintering.

If properly engineered, the practice and experience show that a glassy-crystalline material with high density can be obtained, which can be considered as more than a satisfactory result.

One can thus further summarize that utilizing the HSM technique for the sake of synthesis of well-sintered glass-ceramic materials and for the exact tuning of an appropriate thermal treatment is the right approach. HSM turns out to be a good and precise tool for measuring the kinetics of sintering of glass-ceramic materials as well.

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