APPLICATION OF THE LOW VACUUM SCANNING ELECTRON MICROSCOPE TO THE STUDY OF GLASS-CERAMIC SPHERICAL MATERIALS

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ABSTRACT

The use of a scanning electron microscope in low vacuum mode (or reduced pressure) permits to obtain secondary electron images of specimens that are non-conductive or specimens which have not been coated with a conductive material such as gold or carbon. This technique is advantageous for the observation of specimens like biological samples, moist samples, liquids, polymers and ceramics among others [1]. Unlike high vacuum mode (HighVac), the regime pressure of the low vacuum mode (LowVac) stands in the range of 10 to 130 Pa which assist to eliminate the effects of charge accumulation onto the surface and preserve fragile structures (biological samples) as well. The use of this mode of observation to the study of glass-ceramic spherical materials has been evaluated. Also this material was observed applying the HighVac mode in order to compare viewing conditions between both observation modes. The spherical material is obtained from crystalline blast furnace slags (BFS) generated by steelmaking industry [2]. The process involves a natural gas/oxygen thermal projection process and conversion of the BFS precursors into glass-ceramic spheres. The study and characterization of the new glass-ceramic spherical particles is required because their chemical properties depend on the morphology, finally these materials can be incorporated into specific cementing slurries formulation as lightweight aggregates and is expected that they will improve the thermal and acoustic isolation properties of the final concrete and/or cement systems. This study has demonstrated that the use of the LowVac mode is adequate to study the morphology of these structures over the HighVac mode, besides allowed to set operating parameters in order to obtain images with free-charge accumulation.

Keywords: Scanning electron microscopy, low-vacuum, glass-ceramic materials.

APLICACIÓN DEL MODO DE BAJO VACÍO EN MICROSCOPIA ELECTRONICA DE BARRIDO PARA EL ESTUDIO DE MATERIALES ESFÉRICOS VITRO-CERAMICOS

RESUMEN

El uso del microscopio electrónico de barrido en el modo de bajo vacío (o presión reducida) permite la generación de electrones secundarios y la obtención de imágenes de especímenes que no son conductores o por otro lado, especímenes que no han sido recubiertos con algún material conductor, como sería el caso de oro o carbón. Está técnica es ventajosa para la observación de especímenes como por ejemplo muestras biológicas, muestras húmedas, líquidos, polímeros y cerámicos entre otros [1]. A diferencia del modo de alto vacío (HighVac), el régimen de presión en el que opera el modo bajo vacío (LowVac) se encuentra en el rango de 10 a 1300 Pa, el cual ayuda a eliminar los efectos de acumulación de carga sobre la superficie así como también ayuda a preservar las estructuras frágiles en el caso de muestras biológicas. El objetivo de este trabajo fue evaluar el uso del modo de bajo vacío en el estudio de la morfología de esferas vitro-cerámicas. Así mismo, se utilizó el modo de alto vacío para comparar condiciones de obtención de imagen. El material esférico es obtenido a partir de escoria de alto horno (E.A.H.) generada por la industria acerera [2]. El proceso de transformación involucra un procedimiento de proyección térmica gas/oxígeno y la conversión de la escoria precursora en esferas vitro-cerámicas. El estudio y caracterización de las nuevas partículas esféricas vitro-cerámicas es requerido debido a que sus propiedades químicas permiten que sean incorporadas en formulaciones cementantes como agregados aligerantes y se espera que mejoren las propiedades térmicas y de aislamiento acústico de los sistemas concreto y/o cemento. El estudio ha demostrado que el uso del modo de bajo vacío es adecuado para el estudio de la morfología de estas estructuras sobre el modo de alto vacío, además permite ajustar parámetros de operación y así obtener imágenes libres de acumulación de carga.

Palabras clave: Microscopio electrónico de barrido, bajo vacío, materiales vitro-cerámicos.

INTRODUCTION

A requirement of a scanning electron microscope (SEM) is that the electron-optic column and the specimen chamber should be under high vacuum (HighVac) 10^{-3} Pa or lower. This means that specimens with potential interest that are non-conductive, such as the so called "soft matter" like biological samples (tissue, cells, bacteria, etc.), moist samples, liquids, colloids, polymers, ceramics, etc. [1], cannot be observed in their natural state by SEM. Either the samples are non-compatible with the vacuum in the chamber, or it would contaminate the system. HighVac mode is conventionally used for observing conductive specimens and if they are not, they have to be coated with a conductive layer, gold or carbon most commonly, to dissipate the surface charge and make possible the formation of an image. The use of SEM in LowVac mode or reduced pressure permits the observation of non-conductive and uncoated specimens. This is accomplished by introducing a micro atmosphere of water vapor (most commonly) into the SEM specimen chamber, water molecules are ionized when enter into the beam path and thus generates positive and negative charges that promote neutralization of negative charge accumulated onto the surface. Ionization cascade effect occurs during scanning and amplifies the signal with the topographical information of the specimen making possible to obtain an image. Surface charging issues experienced in HighVac are eliminated in LowVac [3] by adjusting important parameters like energy of the primary beam, gas pressure, gas chemistry, working distance among other parameters [4], allowing a wide range of imaging capabilities for samples that are not suitable for HighVac mode. On the other hand, specimens that require conditions near atmospheric pressure in order to preserve their natural state are adequate for the environmental scanning electron microscopy (ESEM®) mode. Due to their names, it is common to confuse and distinguish LowVac mode and ESEM mode only as pressure regimes. "Low Vacuum" name is appropriate when the gas performs an electronic role, such as charge stabilization or signal amplification. Moreover, "environmental" name is given when the gas primarily performs a thermodynamic role, such as preventing evaporation of liquids or initiating chemical reactions [4].

In this work, the LowVac and HightVac modes were evaluated to study the morphology of glass-ceramic spherical materials in order to establish the optimal conditions parameters to obtain a quality image. Due to the fact that the sample does no need a moisturized environment, ESEM® mode was discarded. These spheres are obtained from crystalline blast furnace slags (BFS) generated by steelmaking industry [2]. The development of new materials generated from industrial by-products is a global need, moreover if these materials help to preserve the environment; it would have higher impact not only at environmental level but also at industrial and social areas. The study and characterization of the new glass-ceramic spherical particles is required because their chemical properties allow that these materials can be incorporated into specific cementing slurries formulation as lightweight aggregates and it is expected that will improve the thermal and acoustic isolation properties of the final concrete and/or cement systems. Also hopefully in a few years the BFS could have a proper use instead of being an industrial by-product without low potential applications.

MATERIALS AND METHODS

Materials

Blast furnace slags (BFS) were obtained from "Altos Hornos de México", steelmaking industry from Monclova, Coahuila, México. Flame precursors were ultra-high purity oxygen gas (UHP) and natural gas from commercial installation.

Experimental

The conversion process of the BFS into glass-ceramic spherical particles is described as follows (Fig. 1). Step 1: Injection of BFS particles with size lower than< 38 µm into the plume of oxygen/gas natural flame; step 2: softening and/or melting of the precursor particles and beginning of the formation of large spheres by particle aggregation inside the turbulent flow of the flame; step 3: formation of spherical particles and nucleation of small gas bubbles inside the spheres; step 4: formation of the multi-bubble systems through coalescence of small inner bubbles; step 5: bubble migration from the inside the spheres to the surface [2].

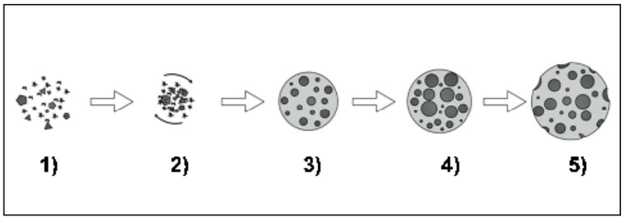

Fig 1. Scheme of blast furnace slags (BFS) transformation into glass-ceramic material.

The study of the morphology is a fundamental task in the BFS conversion process; there are certain parameters, such as oxygen-natural gas rate, flow rates, precursor feeding distance, etc., that must be adjusted in order to get the needed morphology and thus the desired properties. Comparing methods of observation has the purpose of obtaining the better image that will help to decide if the process is leading to the desire morphology.

Scanning electron microscopy

Spherical material was examined using a FEI QUANTA 200 3D, which is capable of both low high and environmental vacuum operations. The electron gun, column and specimen chamber were all maintained at approximately 10^{-4} Pa under HighVac condition, which, in LowVac mode, was set up in the specimen chamber in a range of pressure between 30 and 60 Pa, depending on viewing conditions.

High vacuum

For HighVac imaging two different samples were prepared: a) sample without coating and b) sample with sputter-coating of Au-Pd deposited with a Denton Vacuum DESK II evaporator; both samples were attached to an aluminum holder with double sided carbon tape and viewed at an accelerating voltage of 10 and 30kV.

Low Vacuum

Glass-ceramic spheres were analyzed using LowVac mode in order to follow the slags conversion process. The parameters evaluated in order to obtain a good quality image in this case were: energy of the primary beam 10 and 30 kV, chamber pressure interval of 30 to 60 Pa and a working distance 7 and 20 mm. Low vacuum is accomplished by allowing a small pressure of water vapor into the specimen chamber. Gas molecules are ionized when enter into the beam path by the electrons emitted from the primary beam. The resultant ions assist to neutralize charge accumulation onto the surface (Fig. 2).

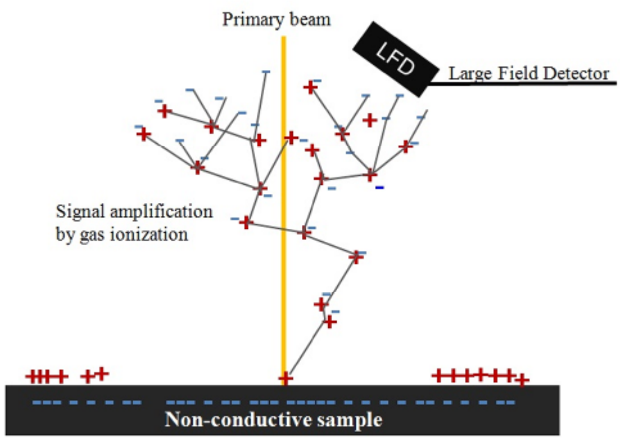

Fig. 2. Scheme of charge neutralization process and signal amplification by gas ionization effect.

The sample was attached to an aluminum holder by using double sided carbon tape. Considering that is a non-conductive sample then is suitable for low vacuum technique, no previous treatment is needed.

RESULTS AND DISCUSSION

The importance of the morphology of these new glass-ceramic spherical porous particles stands in their properties; since depending on their composition, density and morphology, is possible to incorporate them into conventional cementing slurries. Therefore these new spherical particles can be used as a new lightweight material for "light mortars" due to their multi-bubble inner structure. On the other hand, variables such as energy of the primary beam, working distance and chamber pressure were evaluated to achieve images with no charge accumulation regardless the spherical shape of the particles, it is well known that the edge effect in SEM is charge accumulation. Below a series of images acquired as a function of microscope operating variables are shown.

Effect of the energy of the primary beam

"Charged-induced" secondary electron contrast is well known in conventional (high vacuum) microscopy of specimens such as insulators. However, in high vacuum SEM, the usefulness of this imaging mode is limited by difficulties in the control of charging artifacts that can lead to image degradation [5] and if the beam energy is too high it could cause a permanent damage to the surface sample. The use of a conductive coating yield an option as a removal of charge accumulation above the sample surface, but there are specimens, like the spheres studied in this work that are preferred to be evaluated without any surface modification. Images were acquired using acceleration voltages of 30 and 10 kV (Fig. 3a and 3b respectively) for spheres without any conductive layer. In both cases charge accumulation was noticeable and a decrease of the beam energy only caused a slight change in the acquired image. Considering that having insulating materials and high vacuum mode means the necessary use of a conductive layer, the spheres were coated with a gold-palladium layer. It might be expected that charge accumulation problems disappear, instead of that, images with charge artifacts and low contrast were obtained with both energies as well (Fig. 3c and 3d). Charge-induced contrast is present in both images, even with the coating layer; as was already mentioned, shape is a factor that can induce edge effect, in this case spherical shape and micron-size contributes to enhance this effect. After all, neither option is useful for these spherical particles.

In a variable pressure SEM, the artifacts caused by the beam can be reduced or eliminated by introducing a gas into the specimen chamber. Nowadays there are several types of gases that these microscopes can manage, but has been proved that water vapor is advantageous since is non-reactive, explosive or flammable and generates good images with good contrast [6]. Fig. 3e and 3f shows LowVac images of the spheres acquired changing the energy of the primary beam (30 and 10 kV). With 30 kV the charge-induced contrast is not controllable since the more energy, the more negative charges above the surface and keeping constant variables such as pressure, brightness and contrast this effect was not able to be fixed. Most likely increasing the pressure chamber this would have been corrected. Lowering the beam energy to 10 kV an image free-charge accumulation is obtained. At low pressure, when the ion generation is low, the contrast becomes more pronounced [5].

No damage was observed in the sample (morphology change), the material is not a soft material that could be easily damaged from stress of dehydration [7], hence there is no significant reason to continue a comparison between LowVac and HighVac mode. Further explanation and discussion will be only based on LowVac mode parameters.

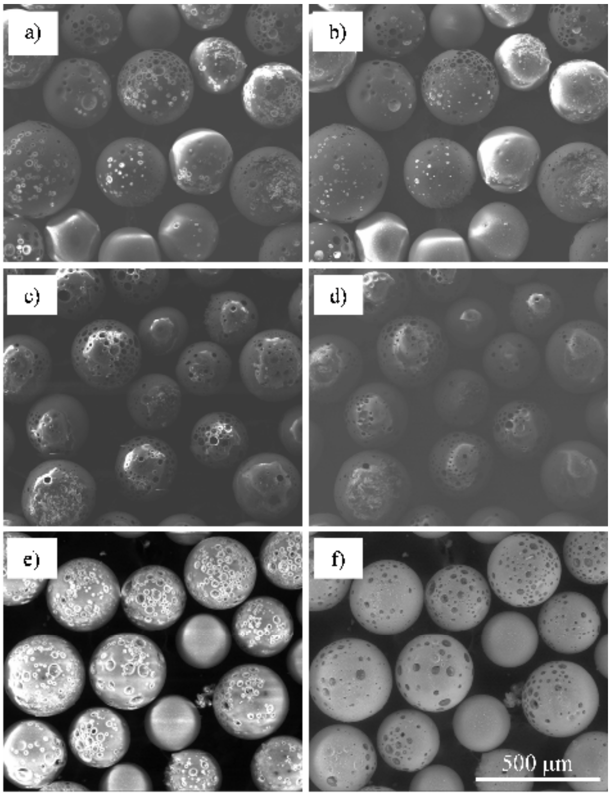

Fig. 3. SEM images of a glass sphere acquired as a function of primary electron beam energy: HighVac on uncoated sample a) 30 kV and b) 10kV; HighVac on coated sample c) 30kV and d) 10 kV; and LowVac e) 30 kV and f) 10 kV. Contrast, brightness and focusing of each image were kept constant.

Effect of working distance

The working distance is the distance measure from the specimen to the detector ("gap" distance). Under many conditions, increasing the working distance can apparently increase the signal; however, it also results in a longer beam path length [8]. In LowVac mode the smaller the path length the better resolution, otherwise if the path length is too large it would be more dispersion of the beam before it reaches the sample, that means the working distance should be small in order to preserve a less disperse beam. It this work working distances of 7.5 and 20mm (Fig. 4a and 4b respectively) were evaluated. For a 7.5mm a detailed image was obtained, no charge presence and the contrast seem to be adequate for the measurement of the micro pores. Pressure was kept constant at 40 Pa, which apparently is the optimum point between pressure and brightness/contrast. At working distance of 20mm there is more gas in the beam path length, which could lead to several processes that affect imaging: scattering of the primary beam due to the presence of gas molecules is one of them, this fact contributes to a general rise in the signal background level and, in terms of imaging, there is a reduction in the desired secondary electron level, as we can observe in the image obtained at 20mm, it is poorly contrasted, the features in the spheres are not as clear as the 7.5mm image.

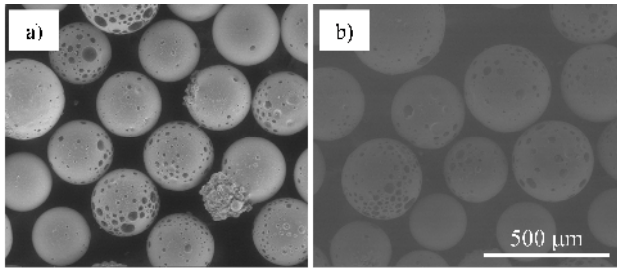

Fig. 4. Glass-ceramic spheres images were obtained at different working distance: a) 7.5mm and b) 20mm. The brightness of each image was optimized.

Effect of pressure chamber

The introduction of a low pressure (P) gaseous atmosphere into a SEM chamber has been observed to reduce charging artifacts dramatically [5], since influences physical processes which affect imaging signal, for example: gas cascade amplification. It was established that pressure reduction significantly improves the visibility of structures. Figure 5 show a series of images of glass-ceramic spheres obtained as a function of P. The micrographs illustrate the sensitivity of image contrast to pressure, no matter if the specimen is an insulator on a conductive substrate. As P is elevated from 15 to 20Pa (Fig. 5a and 5b) the small charge decreases slightly, small P alterations cause significant changes in the gas cascade amplification. When P is increased from 20 to 50 Pa (Fig. c) no more charge at the surface is seen. At 80 Pa a brighter-low contrast image was acquired; it has been seen that at very high P, the amount of gas causes a significant increase in the cascade amplification, when this occurs the optimum point, where contrast/brightness and pressure are balanced and generates the maximum contrast, is exceeded and only brightness prevails [6]. Pressure reduction clearly improves the visibility of structures.

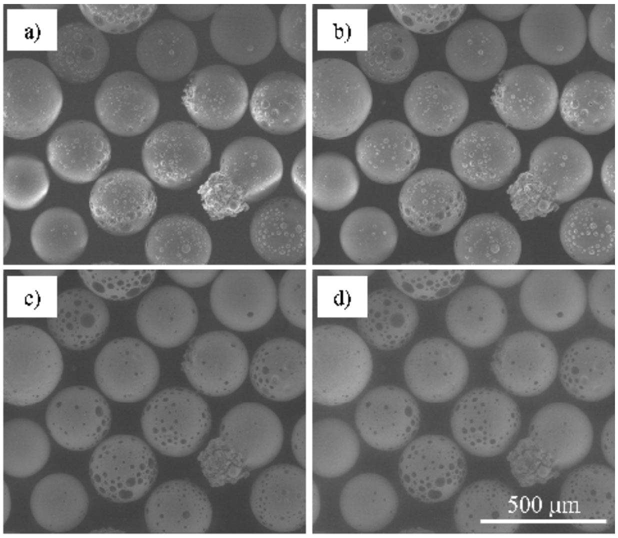

Fig. 5. LowVac images of glass-ceramic spheres acquired as a function of gas pressure, P: a) P = 15 Pa, b) P = 20 Pa, c) 50 Pa and d) 80 Pa. The brightness was optimized while other parameters than P were kept constant during image acquisition.

CONCLUSIONS

Secondary electron images in LowVac and HighVac mode were obtained to follow the conversion of BFS into spherical porous micron-size structures, to achieve this two modes of observation were evaluated, HighVac and LowVac, aside to compare viewing conditions. LowVac mode has demonstrated to be adequate in the characterization of this kind of samples and enables to observe details in the morphology of the spheres that allow us set up the variables during conversion process. Variables such as energy of the primary beam, working distance and chamber pressure were evaluated in order to optimize imaging. For this work, optimal operating parameters were established in order to acquire images with no artifacts, it was observed that the energy of the primary beam must be around 10 kV, set up a pressure chamber in a range of 40 - 50 Pa and a working distance around 7mm. All these variables in conjunction permits to obtained the better image.

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