Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 3161–3165

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Plasma assisted novel production process of glass-ceramic spheres in the quaternary system $CaO–SiO_2–Al_2O_3–MgO$

E.M. Saucedo *, Y.M. Perera, D. Robles

*Centro de Investigación en Química Aplicada (CIQA), Blvd. Ing. Enrique Reyna Hermosillo, No.140, C.P. 25253, Saltillo, Coahuila, Mexico*

Received 6 August 2011; received in revised form 6 December 2011; accepted 9 December 2011
Available online 16 December 2011

**Abstract**

In this work, a novel transformation process of industrial byproducts into spherical glass-ceramic materials in the quaternary system $CaO–SiO_2–Al_2O_3–MgO$ is presented. Byproducts used as precursor are blast furnace slags (BFS) generated by steelmaking industry located in northeastern Mexico. Several parameters for plasma projection process, such as Ar:He feeding flow and electric current were studied. Industrial Ar:He plasma projection equipment was used for vitrification and microstructural/morphological transformation of BFS. Precursor particles as well as produced glass-ceramic spheres were characterized by optical microscopy (OM), field emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XDS). In addition, density measurements from the generated powders were obtained using a Helium pycnometer.

These new materials have a highly amorphous structure, and their final properties, such as porosity, density and size can be controlled by process parameters and therefore they could be modified to obtain special features for specific applications.


*Keywords:* B. Porosity; D. Glass-ceramic spheres; Plasma processing

## 1. Introduction

Steel making industry have generated, beside steel products, enormous quantities of industrial wastes and/or byproducts such as iron oxide residues, and metallurgical slags, like blast furnace (BF) and blast oxygen furnace (B.O.F.) slags and others, which no have any outstanding potential applications. In recent years, investigations have been focused in recuperation and reuse of these kind of byproducts; for instance, cement industry uses industrial wastes such as volatile ashes, slags and certain domestic wastes to be incorporated as a second phase in cementing systems [1–7].

Chemical composition of blast furnace slags (BFS) basically depends on the iron ore nature. Four major components are calcium oxide (CaO), 32–48%; silicon oxide ($SiO_2$), 32–42% aluminum oxide ($Al_2O_3$), 7–16%; magnesium and iron oxide (MgO) between 1% and 1.5%, and sulfur between 1% and 2% in total content [4–7].

On the other hand, glass or glass-ceramics production from industrial wastes could be an alternative for reuse of these slags, considering the large quantities of industrial byproducts currently produced and the need of ceramic materials with specific properties for new and innovative industrial applications [1]. Basically, a glass-ceramic is a material that has been transformed into glass, and then is exposed to a controlled thermal process to achieve certain crystallization level inside of an amorphous matrix [1,2]. Formation of these phases will strongly depend on parameters such as cooling rate, precursor chemical composition, presence or absence of nucleating agents [2,3].

Development of glass-ceramics from blast furnace slags (BFS) by conventional melting involves a very expensive process, since the required melting furnace must be fabricated with refractive materials, inert to the slags chemical composition, such as silicon carbide or graphite [3]. However, BFS can be vitrified without be exposed to a melting process, in which case, their crystalline phases will gradually disappear, acquiring a high percentage of amorphous phase, while the crystalline structure remains in the matrix, producing glass-ceramic materials at low cost [4]. One of these methods is thermal spray plasma process, since it has special characteristics such as high temperatures,

* Corresponding author. Tel.: +52 844 438 98 30; fax: +52 844 438 98 39.
*E-mail address:* esaucedo@ciqa.mx (E.M. Saucedo).

0272-8842/$36.00 
doi:10.1016/j.ceramint.2011.12.019

high projection rates, high enthalpies inside the plasma, as well as high heating and cooling rates [8–14]. During this process, pulverized precursor is injected into the plasma plume, where it is softened, and acquires a spherical morphology. After that, obtained spheres will be recollected as powder.In this work, a new Ar:He plasma assisted process for BFS spheroidization is reported. Effect of plasma process parameters, such as electric current and gas feeding flow in final properties of glass-ceramics like microstructure, morphology and density are discussed.

## 2. Experimental procedure

### 2.1. Slags pretreatment and transformation process

Prior to transformation process, BFS were treated according to a mineralogical process, which consist of sampling, drying, crushing, grinding and sieving. Obtained particles were classified by size in three ranges: 74–105, 400–841 μm and 1.7–2 mm. After that, slags were transformed by Ar:He Plasma projection, using Plasma thermo spray equipment Plasmadyne (Praxair) SG-100. UHP Argon and Helium gases were used to generate the plasma flame. Two Ar:He (rate 1:1)gases feeding flows were used: 2 and 6 L/min. Electric current was varied as follows: 700, 1000 and 1500 A. Is important to notice that only precursor whit particle sizes between 74 and 105 μm was treated, because due to the small inlet of the plasma gun nozzle, only the smallest particles were able to pass through it.

### 2.2. Optical microscopy

After the Plasma projection treatment, all the samples were observed using an optical microscope Olympus BX60. Images were taken at 50× and 200× with reflected light and bright field.

### 2.3. Phase identification

X-ray diffraction patterns of precursor BFS and glass-ceramic spheres were obtained to determine the phase transformation carried out during the projection process under different process parameters. Samples were characterized at room temperature using a Siemens diffractometer. Diffraction parameters were $2\theta$ ranging from 5° to 60° with a step size of 0.01° ($2\theta$). Cu-Kα (λ = 1.5418 Å) radiation was used in all experiments at 35 kW and 25 mA.

### 2.4. Particle size and morphology

Particle morphologies and sizes from the particulate slags and vitro-ceramics spheres were evaluated using a field emission scanning electron microscope (FE-SEM) JEOL 7401-F, operating at low voltage (2 kV), and 8 mm as work distance.

### 2.5. Real density

In order to determine BSF and spheres density, a volumetric helium pycnometer *Quantachrome Instruments* was used. Ultra high purity helium gas was used at 3 psi. Tests were carried out according to standard ASTM D5965.

## 3. Results and discussions

### 3.1. Optical microscopy

Optical microscopy observation was used to evaluate the grade of transformation of BFS into glass-ceramic spheres (Fig. 1). It was observed that at low feeding flow (2 L/min) more quantity of glass-ceramic spheres are generated. In order to establish the spheroidization efficiency, stereological measurements on images obtained at 50× were done. Spheres generated under the following parameters: gas feeding flow of 2 and 6 L/min, using the same Ar:He rate of 1:1 were evaluated. Fig. 2 shows a comparative graph generated from these measurements. It can be observed that the highest spheroidization percentage corresponds to 2 L/min and 1000 A; while at 700 A shows the lowest transformation percentage for both evaluated systems. As far as the gases feeding flow is increased to 6 L/min, residence time is not enough to completely carry out all the steps of vitrification and spheroidization process. About electric current, there is more quantity of spherical particles produced as far as the electric current is higher since plasma energy is increased, and the precursor particles can quickly reach high enough temperatures to be transformed into glass-ceramic micro-spheres inside the plume. From these results, the feeding flow of 2 L/min (Ar:He = 1:1) and electric current of 1000 A were selected for this work.

Moreover, bubbles inside the particles were observed (Fig. 3). These bubbles are generated during processing by gases release, and spheres obtained at 1000 A are more porous that the ones obtained at 700 and 1500 A. Presence of bubbles has a direct effect on glass-ceramics density. Since gases

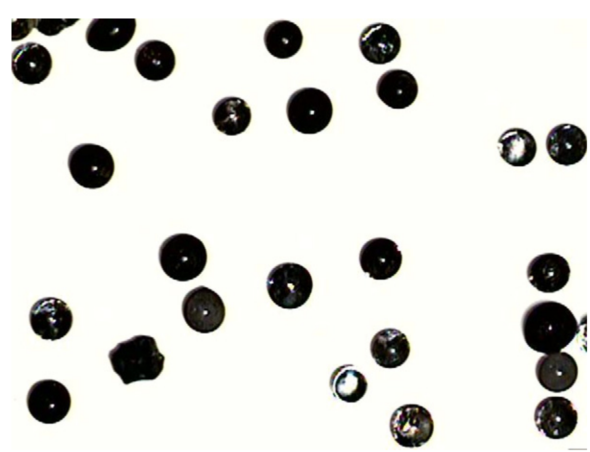

Fig. 1. Morphology of microspheres obtained at gases feeding flow of 2 L/min (1:1Ar:He rate) and 1000 A.