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Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Impact of surface impurity on phase transitions in amorphous micro silica



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ARTICLE INFO

Article history: Received 2 March 2016 Received in revised form 17 May 2016 Accepted 26 July 2016 Available online xxxx

Keywords: Amorphous micro silica Impurity Phase transition Crystallization

ABSTRACT

In this work we study three types of spherically shaped micron and submicron sized amorphous micro silica (MS) as common raw material for production of porous calcium silicate products used for insulation, which are selected on basis of chemical composition and production method. Two of them have silica content of 96% (from silicon production) and one has that of 92% (from ferro-silicon production). In order to achieve high quality calcium silicate products, which strongly depends on the characteristics of the raw MS, it is crucial to study the chemical and physical properties of the raw MS obtained from different sources. We find that the surface impurities of raw MS lower its crystallization temperature determined from differential scanning calorimetry (DSC). The thermodynamic origin of this correlation is discussed. From the surface crystallization behaviour of raw silica, it is inferred that impurities are located at the surface of the MS, and this is further verified by acid treatment of raw MS. The acid treatment leads to an increase in crystallization temperature by 50 °C. The DSC proves to be an effective tool for the calcium silicate industry to detect and monitor the chemical fluctuation of raw MS.

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1. Introduction

Micro silica (MS) is a kind of amorphous (non-crystalline) material, which has a large range of applications, e.g., as raw materials in porous calcium silicate production, and as additives in concrete and ceramics [1–5]. MS was firstly collected from electric arc furnaces from silicon production to prevent pollution, and lately has been of great interest for several industries, particularly a lot of research in MS as additive in cement and in the colloidal behaviour of MS have been performed [3, 6–9]. However, the research in MS as raw material for production of calcium silicate is still limited.

Porous calcium silicate is an excellent insulation material, especially for high temperature applications. In its production, MS is dispersed in water and then reacts with quicklime (CaO), leading to formation of amorphous calcium silicate gel. After reaction, fibres are added to the slurry, and the slurry is pressed into boards with desired dimensions, and autoclaved at 180–230 °C to enhance the hydrothermal reaction. During this process, the amorphous gel crystallizes to become tobermorite and/or xonotlite [10]. It is known that the impurities and characteristics from various sources of silica have a strong impact on the performances and properties of the final products [4,11–13]. To understand the mechanism of such impact and hence to improve their properties, it is crucial to determine the morphology and chemical

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impurity of the raw MS from different sources and/or produced using different methods.

MS is a by-product from the production of silicon and silicon alloys (e.g. ferro silicon, calcium silicon etc.), in which high-purity quartz is reduced to silicon at temperatures up to 2000 °C. In the silicon furnace, an intermediate reaction involves formation of SiO (silicon monoxide) that escapes together with CO (carbon monoxide). The gaseous SiO/CO escapes and is oxidised to SiO₂ and CO₂ by oxygen at the top of the furnace. The resulted SiO₂ fume consist of amorphous and spherical SiO₂ particles which subsequently are collected in filter bags [8,14,15], with a purity of up to 98 wt% SiO₂, but the SiO₂ content is normally lower. The MS derived from the silicon production is usually purer than that from the production of silicon alloys. The purity and other characteristics depend on the processing conditions for the same method [8]. Small amounts of Fe, Mg, alkali oxides, as well as carbon and sulphur, are often present in raw MS.

Despite the amorphous nature of MS, traces of crystalline silica can be present in the raw MS, e.g. cristobalite, tridymite and quartz [1,16– 18] upon heating even though SiO₂ is a very stable glass former [19, 20]. This is due to surface nucleation [21,22]. The devitrification of silica is strongly catalysed by traces of impurities, especially alkali metal oxides (Na₂O) [25,26]. The impurities lower the energy barrier of crystallization by breaking up the network structure [17]. The phase transition temperature depends on the type and amount of impurities, as well as the degree of crystallinity already present on the surface of the MS particles. The amorphous MS crystallizes to cristobalite and

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tridymite, the formation of tridymite is, however, only possible with the presence of alkali [17,23,24]. Amorphous silica is chemically simple, but its structure, dynamics and properties are rather complicated and fascinating [27].

In this work we study the chemical and physical characteristics of three types of MS from different sources. Ferro silicon accounts for the major part of industrial silicon production [28], and hence a great amount of MS by-product originates from the Ferro silicon production. Therefore, one MS from this production method is chosen for the object of characterizations, with a silica content of 92 wt%. The MS materials from different production sites and with similar chemical composition exhibit different quality, therefore two MS of grade 95–96 are also chosen for characterization. The chemical impurities of the three types of MS are determined using X-ray fluorescents (XRF), the particle size distribution is measured using light scattering (LS) and the zeta potential is determined. Morphology of the MS particles is investigated using scanning electron microscopy (SEM). The phase transitions in MS are detected using differential scanning calorimetry (DSC), while the crystal types are identified using X-ray diffraction (XRD).

2. Experimental

Three types of MS were selected on basis of their chemical composition and production method, two with grade of 95–96 (from silicon production) and one with a lower grade of 92 (from ferro-silicon production). These silica contents are based on data sheets from the manufacturers. We measured the chemical compositions of the MS samples using X-ray fluorescence (Epsilon 3x, PANalytical). Approximately 0.40 g of dry MS was mixed with 6.0 g of lithium borates (Li₂B₄O₇ and LiBO, Claisse), and the mixture was melted at 1100 °C. Loss on ignition (LOI) was determined for each type of MS.

The particle size distribution was determined using a particle size analyser (Microtrac S3000, PA), based on the Mie theory and a refractive index of 1.47 for SiO₂. Prior to size distribution analysis, the MS was ultra-sonicated (GS 3, GeneralSonic) for 1 h in deionized water. The distribution widths, D_{10} , D_{50} and D_{90} , of the particles were determined.

Zeta potential of the MS particles was determined using Zetasizer Nano (Malvern) for each of the three MS. Prior to zeta potential measurement the MS was ultra-sonicated for 1 h in deionized water. The pH was monitored and regulated with HCl to be pH = 7.0 ± 0.6 . The MS suspension was transferred to a folded capillary cell (DTS1070, Malvern), three measurements were performed on the same sample to calculate the average Zeta potential.

The surface morphology of the MS was determined using scanning electron microscope (SEM) in a Zeiss 1540 XB. The SEM images were obtained on Au coated as-received MS at 10 kV.

The phase transition behaviour was measured using differential scanning calorimetry (DSC) in argon atmosphere (STA Jupiter 449C, Netzsch). Both a baseline (blank) and a reference sample (sapphire) were measured. Approx. 25 mg of the as-received MS was transferred to an alumina crucible. The sample was heated to 1250 °C at 20 K/min, and subsequently downscanned at 20 K/min to 300 °C. All the samples were subjected to the second upscan and downscan at 20 K/min. Duplicate measurements were performed on each sample to ensure the reproducibility of the results.

The crystallites present in the as-received MS were determined by X-ray diffraction (XRD) (Empyrean, PANalytical). The voltage and working current were 45 kV and 40 mA, respectively, with a 2 θ scan range of 5° to 70° and an interval of 0.013°. The measurements were performed twice on each sample. The identification of phases in the samples were performed by comparing peak positions with diffraction patterns in the Joint Committee on Powder Diffraction Standards (JCPDS) data files using the HighScore software (PANalytical). To determine the crystal phase at T_{exo} , found from the DSC analysis, the three types of MS are heated to their individual T_{exo} , and the temperature is

Table 1

Chemical composition and loss on ignition (LOI) of the three types of MS, determined using X-ray fluorescence. The chemical composition is given in weight percentage.

MS type	Na ₂ O	MgO	Al_2O_3	SiO ₂	K ₂ 0	CaO	Fe_2O_3	LOI
MS1	0.04	0.32	0.17	95.94	0.49	0.32	0.08	1.94
MS2	0.00	0.25	0.11	96.13	0.47	0.05	0.06	2.17
MS3	0.53	1.17	0.01	92.08	0.82	0.16	0.73	3.08

held for 3 h. After cooling, the crystal structure was determined using XRD, with same settings as for the as-received MS.

MS3 was the MS with the highest impurity content (Table 1). To remove impurities from the MS surface, MS3 was treated with 50% (volume fraction) H_2SO_4 (Sigma Aldrich) at 95 °C for 1 h. The mixture was repeatedly filtered and rinsed with water and then the treated MS3 (MS3T) was dried. Afterwards the dried MS3T was analysed using DSC and XRD.

3. Results

3.1. Chemical composition and size distribution

The chemical compositions of the three types of MS are listed in Table 1. It is seen that MS1 and MS2 has an SiO₂ content of 95.9% and 96.1%, respectively, whereas the MS3 has a lower SiO₂ content of 92.1%. The impurity content in MS3 is higher than that in MS1 and MS2, especially the content of Fe₂O₃, MgO, Na₂O and K₂O are significantly higher.

The particle size distribution of the MS is listed in Table 2. Striking differences in size distribution of the three types of MS are observed, i.e., MS1 has the narrowest size distribution and MS2 has the widest. At D_{10} MS2 particles (0.38 µm) are slightly smaller than MS3 particles (0.4 µm), but larger than MS1. However, at D_{50} and D_{90} MS3 particles (5.03 and 16.76 µm, respectively) are smaller than MS2 particles (7.83 and 32.41 µm, respectively).

Zeta potential (ξ) of the three types of MS and the pH of the MS suspension are listed in Table 2. The zeta potential of MS1 and MS2 are both approx. -29.5 mV, whereas MS3 is slightly lower, however, the difference in zeta potential among the MS is not significant.

In Fig. 1 the SEM images of the three types of MS are presented. From these images it can be seen that the MS is composed of spherical particles in the range from approx. 500 nm down to 50 nm. The smallest particles are attached to the surface of the larger particles. MS1 and MS3 generally have smaller particles than MS2, however, no great difference is observed among the three types of MS.

3.2. Phase transitions in raw MS

Fig. 2 shows the first DSC upscan curves for the MS1, MS2 and MS3 samples. It is seen that each of the sample exhibits a distinct exothermic response, which is attributed to the typical formation of cristobalite. The peak temperatures are different among the three samples (see Table 2). These temperatures are regarded as the characteristic temperature for crystallization, *T_{cryst}*. As illustrated in Fig. 3, when the samples are

Table 2

Mean particle size (D), zeta potential (ξ), pH, crystallization temperature (T_{cryst}), phase transition temperature (T_{phase}) for MS.

MS	Mean (µm)	Mean particle size (µm)		Zeta potential	pН	Characteristic values from DSC	
	D ₁₀	D ₅₀	D ₉₀	ξ (mV)		T_{cryst} (°C)	T_{phase} (°C)
MS1	0.17	0.63	13.94	$-29.5(\pm 0.50)$	7.4	1106 (±0.3)	227 (±0.6)
MS2	0.38	7.83	32.41	$-29.4(\pm 0.36)$	6.8	1183 (±0.2)	249 (±1.4)
MS3	0.40	5.03	16.76	$-28.8 (\pm 0.87)$	7.6 ^a	$1102(\pm 1.5)$	$240(\pm 1.5)$

^a pH regulated with HCl.

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