Powder Technology 270 (2015) 98–103

Contents lists available at ScienceDirect

Powder Technology

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

Multi-scale chemical characterization of a ground metallurgical-grade silicon powder

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ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form 11 August 2014
Accepted 14 August 2014
Available online 14 October 2014

Keywords:
Metallurgical-grade silicon powder
Grinding
Inductively coupled plasma
Energy dispersive X-ray spectroscopy
Atom probe tomography

ABSTRACT

A ground silicon powder was chemically characterized at multiple scales to quantify and localize the impurities of metallurgical-grade silicon. These impurities play a major role in the Rochow synthesis used to convert silicon into the primary monomer for silicone polymers. Characterizations were conducted before and after grinding to investigate the impact of the comminution step on the distribution of the impurities within the powder. At the macroscopic level, inductively coupled plasma showed that the concentration of the main impurities, Al, Ca, Fe and Ti, first increases with decreasing particle size but then drops drastically for the finest fractions (<30 μm). At the microscopic level, energy dispersive X-ray spectroscopy indicated that these impurities are concentrated in the grain boundary as intermetallic precipitates. At the atomic level, atom probe tomography on several particles, including micro-size fines, shows that there is no significant amount of metallic impurities inside the grains for both coarse and fine particles.

1. Introduction

The discovery of silicone polymers in the early 1940s was driven by military applications. After the publication of Eugene Rochow's paper [1] in 1945, silicones rapidly became prominent in many applications, including automobiles, cosmetics, medicine, agri-food and construction, due to their unique properties, such as electric insulation, water repellency and anti-adhesion. The so-called key to the silicone industry is the synthesis of dimethyldichlorosilane (DMDCS) [2], the common monomer from which polysiloxanes or silicones are obtained. The synthesis of DMDCS is a high-tonnage reaction and impacts all of the downward industrial operations at the silicone plant, thus making any optimization very valuable. DMDCS is produced by the chlorination of powdered silicon by gaseous methyl chlorine (MeCl) catalysed by copper and promoted by zinc and tin [3]:

$$2CH_3Cl(g) + Si(s) \xrightarrow{Cu(ZnSn)} (CH_3)_2SiCl_2(g).$$

The yield of DMDCS is as high as 90% [4] despite the apparent complexity of this gas–solid reaction catalysed by another solid and the risk of producing side products ($MeSiCl_3$, Me_3SiCl, etc.). On an industrial scale, the productivity is enhanced by conducting the reaction in fluidized bed reactors (FBRs), which promotes contact between gas and solid.

Metallurgical-grade silicon (MG-Si) is used as the silicon source in the reaction, for which it has to be comminuted down to an easy-to-fluidize powder. After making silicon ingots, the silicon producer usually crushes the ingots down to 10–100-mm lumps. Further grinding down to 10–500 μm is conducted by the silicone maker in industrial devices such as ball mills [5], after which the FBR is fed with a mix of silicon and catalysts and fluidized with MeCl. The first step is the formation of a catalytic active phase between copper and silicon [6,7] before the chlorination of silicon by MeCl [8]. However, catalysts and promoters are not the only components playing a major role in the reaction. It has been known for years that the impurities in MG-Si could inhibit or promote the various steps of the active-phase formation [4,9–15].

The most common impurities in MG-Si are aluminium, calcium, iron and titanium, referred to as alloying elements. Doping elements such as phosphorus and boron are also present. Aluminium is generally considered as an important, if not essential, activator [16]. However, aluminium catalyses both the formation and the decomposition of the active copper–silicon phase. The presence of calcium and iron is known to counter the effect, resulting in a decrease in the reactivity but enhancing the yield of DMDCS [17]. The effect of titanium has attracted less attention because it was shown that the Si_2FeTi phase was unreactive to MeCl [18], while phosphorus is said to reduce the incubation time of silicon [19].

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http://dx.doi.org/10.1016/j.powtec.2014.08.025

In the past, comprehensive studies have been carried out to determine the suitable proportions of impurities to better promote the reaction [20,21], and silicone makers should carefully monitor the level of impurities in the FBR to achieve the best activity and selectivity. To our best knowledge, the relative proportions of impurities over the whole particle size distribution (PSD) of the MG-Si powder have not been investigated. A high impurity content in the fine particles (<50 μm), as one would classically predict [22], implies a loss of impurities through elutriation over the bed [23], thus changing the optimized level of alloying elements coming from the silicon feed, among other effects. In general, it is now acknowledged that grinding is a non-neutral process and that its effects on silicon for the chemical industry should be considered. Moreover, the chemical nature of the particles is very likely to play a role in interparticle adhesion, which often causes problems in powder processing.

The present work aims to locate the impurities in industrially ground metallurgical-grade silicon powder over a wide size range and to investigate the effect of grinding on the distribution of the impurities in the powder. Efforts were focused on chemical characterizations of the particles on various scales, from macroscopic measurements to the atomic-scale measurements using atom probe tomography (APT) [24], taking advantage of background knowledge on silicon metallurgy [25].

2. Experimental

Standard MG-Si lumps and ground powder were analysed by laser diffraction using a MasterSizer 2000, and the results are presented in Fig. 1(a). The particle size distribution (PSD) has been determined by laser diffraction with a MasterSizer 2000. Powders containing particles larger than 100 μm were analysed as sampled using the Scirocco 2000 accessory to the MasterSizer 2000, which assists dry dispersion. Powders without such large particles were first dispersed in pure ethanol and then analysed in water using the Hydro 2000 accessory to achieve a wet dispersion. This requires far smaller sample quantities and provides a better resolution in the small particle range, due to the decrease in interparticle forces. In this paper, particles from 500 μm to 50 μm will be referred to as coarse particles, particles from approximately 10 μm to 50 μm as fines and particles below 10 μm as superfines.

A cylindrical glass fluidization column, 1 m in height and 75 mm in inner diameter, with a perforated plate distributor was utilized to classify the fine particles by fluidizing a ground powder with nitrogen at a gas speed of 0.05–0.15 m/s. An external glass cyclone separator guaranteed most of the gas-fines separation, and the remaining fines were removed from the gaseous cyclone overflow using a filter. Such fluidization devices have been defined as a batch unsteady-state elutriation bed in [26].

A Varian Vista Pro inductively coupled plasma (ICP) with optical emission spectroscopy instrument was used to determine the chemical composition of a sample with a ppm detection limit. A known mass of silicon powder was dissolved in a nitric/fluorhydric acid mix; silicon and HF were then removed, while the other impurities remained in the HNO_3 phase. This liquid was fed into a nebulizer to be excited by the plasma torch. The optical emission wavelengths recorded were compared with a standard sample for each analysed element to determine their concentration in HNO_3 and then calculate their concentration in the silicon powder sample.

The scanning electron microscope (SEM) used in this study was a Tescan VEGA TS 5136 XM upgraded with an energy-dispersive X-ray spectrometer (EDX) that determines the elemental surface chemistry with a sensitivity of approximately 0.1%.

The chemical composition of the coarse and ultrafine particles was determined at the atomic level using atom probe tomography (APT). Powder measurements by APT are difficult, especially for small particles. Methods similar to those described by Miller [27] and Larde [28] were applied for 100-μm and 20-μm particles, respectively. Superfines ranging from 1 to 4 μm were successfully sampled while attached to coarse particles and then stuck on top of the support needle before annular milling to obtain a sharp tip (see details in Section 3.3). Several tips were also sampled inside coarse particles. Pulsed picosecond-laser evaporation was performed with an Imago LEAP 3000X HR APT instrument. The analyses were carried out at a specimen temperature of 80 K, pulse repetition rate of 100 kHz, energy input of 0.8 nJ per pulse, evaporation rate of 0.02 ions per pulse and vacuum greater than 10^{-11} mbar.

3. Results

The size distribution of the silicon powder obtained after grinding is shown in Fig. 1(c). The median diameter is labelled d50, and d10 and d90 are the particle diameters under which 10 and 90% of the distribution are included, respectively. The median diameter cannot fully describe this asymmetric distribution because two powders may have the same d50 for very different d10, which accounts for the fines content.

The morphology of the particles is highlighted in Fig. 1(b). The particles exhibit sharp edges, a low sphericity and typical patterns of brittle

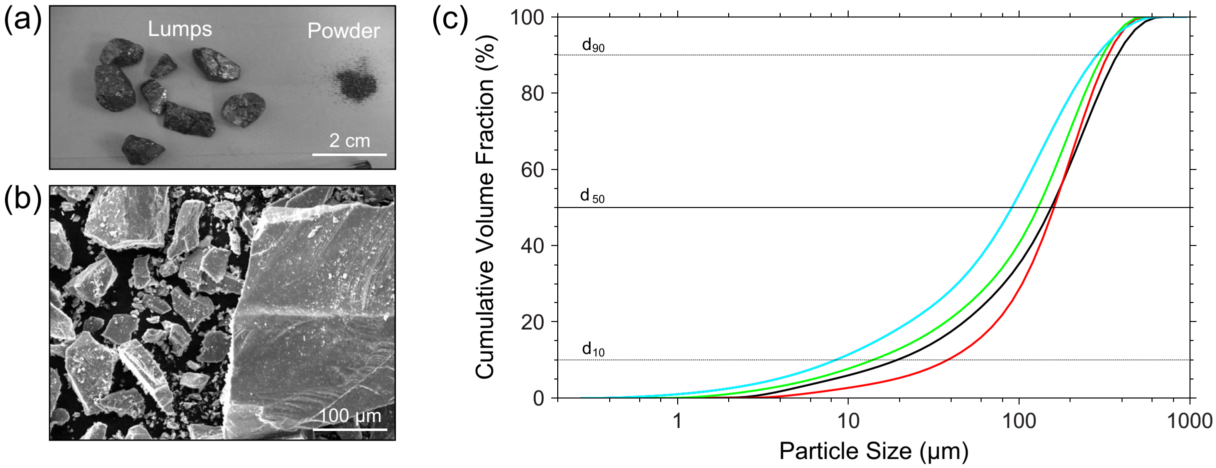

Fig. 1. Photograph of silicon lumps and powder as sampled (a), SEM image of the ground silicon powder (b) and typical wide PSDs for the mill product (c). Many fines and superfines are produced, the latter being attached to the coarse particles.