

the practical separation of slag and the ultimate purity of the poured silicon. For instance, a high CaO content will lead to a low viscosity slag, which will sink to the bottom of the ladle, while CaF will increase the viscosity. Sufficiently different properties in density and viscosity of both the slag and the molten silicon are required to achieve a good separation. Many studies and practical on-site developments have been devoted to this step of the process [13].

Carbon is present in crude liquid silicon mainly as dissolved C and suspended SiC particles. The fraction of SiC increases as the temperature is lowered; SiC particles are then efficiently captured by the slag phase and thus are removed from liquid silicon during the ladle treatment and the subsequent pouring. SiC is removed simply by mechanical separation, precipitated particles sticking to the walls of the ladle and the other devices containing the liquid silicon [14]. Dissolved carbon in the range of 80 to 100 ppm(w) in best cases will finally remain in the purified alloy of metallurgical silicon.

The use of these refining principles to prepare solar grade silicon will be further discussed later in the present chapter.

5.3.3 Casting and Crushing

The refined melt is poured from the ladle into a cast iron mold or onto a bed of silicon fines. The casting should preferably be removed from the mold while bleeding, that is, not fully solidified. After solidification in standard industrial conditions, metallurgical grade silicon is multicrystalline. The individual Si grains vary in size typically from 1 mm close to the iron mold wall to up to more than 100 mm in the centre section if cast on a bed of silicon fines [10]. The impurities are generally located at the Si grain boundaries as silicides and intermetallic compounds, but may also be incorporated in the Si grains if solidification has been sufficiently rapid [15]. Oxides and carbides are found as inclusions located at the grain boundaries and to a lesser degree inside the Si grains.

To be used in customers' processes, solidified silicon needs to be further crushed down to small lumps up to 100 mm. This is performed in jaw crushers and roll crushers, since at room temperature metallurgical grade silicon is hard and brittle. This operation generally generates significant amount of fines, which are undesirable because they may be contaminated by impurities and are difficult to handle during further transport and handling. Therefore, fines are removed after the primary crushing. The dominant fracture mode was found by Forwald *et al.* [7, 16] to be transgranular. For chemical applications, silicon lumps need to be further reduced to small powder particles of a few tens to a few hundreds of micrometers. This is carried out in industrial equipment such as ball mills.

Alternative methods based on rapid cooling have recently been developed to increase the homogeneity of the solidified structure of silicon through an even distribution of the impurities and intermetallic phases. Granulation in water, resulting in small granules of a few millimeters and thus avoiding casting and subsequent coarse crushing, has become a standard practice for several producers [17–19]. In an earlier attempt to avoid casting, crushing and milling, gas atomisation was tested by producers and users, but was not further industrialised for economical reasons [20, 21].