Silico-Ferrites of Calcium and Aluminium (SFCAs) – complex cation substitutions, twinning, polysomatism and polytypism

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The heart of the steelmaking process is the blast furnace, where iron ore is reduced to metallic iron. Following the initial mechanical processing of the ore, two particle fractions can be distinguished: lump (31.5 to 6.3 mm) and fine (<6.3 mm) products [1]. However, the fine fraction (<6.3 mm) cannot be used directly in the blast furnace process. This is primarily due to the loss of particles in the top gas and the clogging of the gas permeability of the furnace [2]. Consequently, the fines are converted into larger pieces in an intermediate step by sintering [3]. In a series of complex high-temperature reactions at approximately 1300 °C, porous, semi-molten, centimeter-sized aggregates are formed containing ore particles (hematite and magnetite, 40 to 70% by volume). These aggregates are cemented by a matrix that comprises Ca-rich ferrites (20 to 50%), up to 10% of quenched melt (glass), and about 10% of calcium silicates such as larnite [4]. For the Ca-rich ferrites containing some silica and alumina, the acronym SFCA was coined. They represent complex solid solutions in the $CaO(+MgO)-Al_2O_3-Fe_2O_3(+FeO)-SiO_2$ system. Technologically, the SFCA phases act as the primary binder, maintaining the integrity of the sinters and enabling them to withstand the loading stress within the blast furnace.

From a structural perspective, the SFCAs belong to a polysomatic series that combines modules from the well-known spinel and pyroxene structures. Their general composition can be expressed as $A^{14+6n}O^{20+8n}$, where A represents one of the following elements: Ca, Al, Mg, Si, or Fe^{3+} or Fe^{2+}. To date, members with n = 0, 1, 2, and 1/2 have been identified (see [5-7] and references cited therein). The crystal structures of the series permit a number of cation substitution mechanisms, which can be summarized according to the following exchange reaction: $2(Fe^{3+}, Al^{3+}) = (Ca^{2+}, Fe^{2+}) + Si^{4+}$. Additionally, Mg^{2+} can be incorporated by replacing Fe^{2+} and/or Ca^{2+}. This contribution will present an overview of the different solid solutions, with a particular focus on polytypism and twinning, two phenomena that have been recently observed for the first time among the SFCAs and not yet studied in greater detail. The existence of different polytypes for a specific polysome introduces further complexity, which may have an impact on the quantification of the SFCAs in industrial sinters by powder X-ray diffraction. Moreover, the results of a theoretical study on the number of existing polytypes for a specific number of layers in the stacking sequence will be presented.

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