Kinetics of acid leaching refining of an industrial Fe–Si alloy

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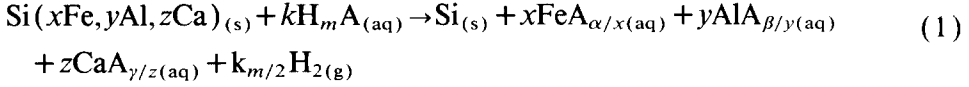
ABSTRACT

The effects of the three leaching parameters (concentration of HCl and FeCl₃ and stirring) on the purification of an industrial Fe–Si alloy, containing phases such as Fe–Al–Si–Ca (caalsifer) and FeSi₂, with a high Ca/Al ratio, were studied. The leaching residues, after analysis for particle size distribution, were characterized chemically, morphologically by scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) and structurally by X-ray diffraction. The experimental results conform with the cracking shrinking model, according to which a mechanism is proposed for the dissolution of the main impurities (Ca, Al and Fe). The leaching of these impurities was found to depend on the composition of the phases and nature of their distribution. For the proposed model, the leaching of the impurities are under chemical reaction control, which is in agreement with the microstructure observed by SEM/EDS.

INTRODUCTION

Indirect hydrometallurgy is one of the routes to purify metallurgical grade silicon (MG-Si) (Si > 98%) or iron–silicon alloys. The leaching systems used for purifying MG-Si in single or multiple steps generally comprise inorganic acids: HCl [1,2], H_2SO_4 [3], HF [3,4] and HNO_3 [3]. The results of these studies are very often contradictory as regards the relative efficiency of each acid [5–7] or the effect of particle size distribution [6,7]. For example, according to Juneja and Mukherjee [6] it was necessary to set free the phases carrying the impurities, by crushing the MG-Si to particle sizes under 150 μm, while Dietl [5] suggested 20 μm or less. The principal impurities of Fe–Si alloys are present in various intermetallic phases such as Al–Fe–Si, $FeSi_2$, Caalsifer, Ca–Si and $CaAl_2Si_{1.5}$ and tend to segregate to grain boundaries or to interstitial positions in polycrystalline silicon. The elimination of these impurities by acid leaching is generically expressed by:

$$Si(xFe, yAl, zCa)_{(s)} + kH_m A_{(aq)} \rightarrow Si_{(s)} + xFeA_{\alpha/x(aq)} + yAlA_{\beta/y(aq)}$$
$$+ zCaA_{\gamma/z(aq)} + k_{m/2}H_{2(g)} \tag{1}$$

In the present paper we report the results of a study on the kinetics of refining of an industrial Fe–Si alloy as a function of HCl and FeCl$_3$ concentrations with or without stirring.

SOLID–FLUID REACTION MODELS (NONCATALYTIC CASE)

There are several kinetic models proposed to describe noncatalytic solid–fluid reactions [8–15]. In searching for an appropriate model all relevant information was used, from reaction chemistry to a physical examination of the pellet. After analysing and testing experimental results we propose the cracking shrinking model [8], which can adequately describe and follow the behaviour of reacting Fe–Si alloy under the conditions used. Furthermore, the various parameters can be fitted directly throughout the experiment.

According to the cracking shrinking model [8], if we assume a solid particle, S, of radius, R, immersed in a fluid, A, of concentration C, the mechanism of attack can be viewed as follows:

(1) The fluid A attacks the surface of the particle, causing and/or accentuating microfissures. The attacking front moves steadily into the particle until the moment of disintegration, time t_c.

(2) The new particles, with grains of radius r ($r \ll R$), then react with the fluid according to the shrinking model [15], either by reaction or film diffusion control.

Conversion expressions for the cracking shrinking model

Let us develop the consequences of this model:

(1) The total time for conversion will be the time needed for cracking (disintegration), t_c, plus the time for each grain to be converted, t_g. Taking the composition at the cracking as the zero point:

$$t = t_c + t_g \tag{2}$$

(2) The conversion of each grain proceeds according to the shrinking model [12]. Then, for grain reaction control:

$$\frac{t - t_c}{\tau} = 1 - (1 - y)^{1/3} = 1 - \left(\frac{1 - X}{1 - X_i}\right)^{1/3} \tag{3}$$

where $\tau = \rho R / KC$.

While for grain film diffusion control and small particles we have: