The metallurgy of tin smelting in a submerged-arc furnace

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SYNOPSIS
The control of tin smelting demands a knowledge of slag characteristics and of the equilibrium reaction that governs the process. These factors are explained by reference to the tin-smelting operation at Iscor, Vanderbijlpark.

In the primary cycle, it is important to obtain the highest possible FeO content in the slag. In the secondary cycle, a primary slag high in FeO gives a hardhead (iron-tin alloy) high in iron, which is essential if a high ratio of FeO to SnO is to be obtained in the secondary slag. This determines the economy of the smelting operation: the iron that is introduced into the system from the ore concentrate must go out in the secondary slag. Additions of lime are necessary in the secondary cycle but must be limited if the volume of slag is to be kept low.

SAMEVATTING
Die beheervan tinsmelting vereis 'n kennis van slakiekseis en van die ewewigreaksie wat die proses beheer. Hierdie faktoere word verduidelik met betrekking tot die tinsmeltbewerking by Yskor, Vanderbijlpark.

At the Iscor (Vanderbijlpark) works, tin is smelted from a cassiterite concentrate in a submerged-arc furnace with a power input of 350 kVA, the electrodes being amplitund controlled. The sidewall of the furnace is lined with fireclay bricks and the hearth with carbon blocks. The waste gas, which is sucked off round the perimeter of the furnace, is collected in a bag filter. The layout of the plant is shown in Fig. 1.

The Process

The tin-smelting operation is divided into two cycles as shown in the flow diagram of Fig. 2.

The Primary Cycle
Tin is smelted from the cassiterite concentrate by the reducing action of coal char, and iron is smelted from the hardhead (iron–tin alloy) produced in the secondary cycle of the previous campaign. The reduction is strictly controlled to produce the best slag for smelting in the secondary cycle. In the primary slag, the activity of SnO is higher than that of FeO, but the ratio of FeO to SnO can be increased by an increase of the reducing agent. However, over-reduction leads to an increase in the iron content of the tin. The control criterion is the formation of a reasonable amount (5 to 10 per cent) of hardhead in the ladle on cooling.

After tapping, which is done every 1,5 hours, the ladle is deslagged and the tin is allowed to cool in the ladle until most of the dissolved iron has crystallized out as hardhead, which is then scooped off. Further refining is done in a heated kettle at a temperature just above the melting-point of tin: air is bubbled through until the iron content has been reduced to 0,1 per cent.

In the secondary cycle, FeO and SnO act as fluxes in the primary slag and lend a basic character to it. This requires a certain minimum amount of iron in the hardhead. The relationship between the SnO and the FeO in the primary slag is shown in Fig. 3, which indicates the ideal operating range with 30 to 40 per cent FeO.

The Secondary Cycle

The slag arising from the primary cycle is smelted in the secondary cycle with coal char as the reducing agent and burnt lime as the flux. The FeO and SnO, which acted as fluxes in the primary slag, are now reduced to fairly low levels.

After tapping, which is done every 2 hours, the slag is decanted and scooped off, the liquid hardhead being granulated in a strong stream of water. This hardhead is used again during the primary cycle of the following campaign.

Despite the lime that was added, which must be limited to keep the volume of slag low, the slag acquires an acid character. A considerable portion of the tin that is lost in the secondary slag is in the form of trapped metal droplets, and the viscosity of the slag is important in limiting losses. In practice, the last slag that is scooped off is returned to the furnace so that such losses are minimized.

The secondary slag, which has a tin content of 2 to 3 per cent, is sold for its (Nb, Ta)2O5 content, which depends on the source of the concentrate and the percentage concentration; these determining the volume of the slag. Fig. 4 shows the slag as a function of the tin in the concentrate.

When the concentrate is leaner, it is important to increase the ratio of iron to tin so that the most economical ratio of FeO to SnO can be attained in the secondary slag. Fig. 5 shows the relationship between the FeO and the SnO in the secondary slag from a typical

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Fig. 1—Layout of the tin-smelting plant at Iscor, Vanderbijlpark
Fig. 2—Flow diagram for the tin smelter at Iscor, Vanderbijlpark

Fig. 3—The relationship between SnO and FeO in the primary slag

Fig. 4—The secondary slag as a function of the tin in the concentrate
Fig. 5—The relationship between FeO and SnO in the secondary slag

Fig. 6—Composition of secondary slags in the ternary system CaO-FeO-SiO

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The importance of controlling the ratio of FeO to SnO in the primary cycle becomes clear when the aim is to achieve a high ratio of iron to tin in the hard-head.

In the ternary phase diagram of the system CaO-FeO-SiO₂ (Fig. 6), typical compositions of the secondary slag are indicated around the 1300°C liquidus line. The ratio of CaO to SiO₂ plays an important role in determining the activity of the FeO and SnO in the slag.

The secondary cycle can be represented by the equilibrium reaction between the Fe and the Sn in the metal and the FeO and SnO in the slag:

$$\text{Fe} + \text{SnO} \rightleftharpoons \text{FeO} + \text{Sn}$$

$$\text{FeO}/\text{SnO} = K(\text{Fe}/\text{Sn})$$

The value of the equilibrium constant $K$ is dependent on the ratio of CaO to SiO₂ in the slag, as shown in Fig. 7.

By linear regression analysis, the following relationship was obtained from actual production data, giving a correlation coefficient of 0.68:

$$K = 25.7(\text{CaO}/\text{SiO}_2) - 4.34$$

The ratio of FeO to SnO in the secondary slag is thus dependent on both the ratio of iron to tin in the hard-head and the ratio of CaO to SiO₂ in the slag.

**Conclusion**

For efficient tin smelting, it is necessary to maintain a high ratio of FeO to SnO in the secondary slag and so ensure that iron is not accumulated in the system. The best solution is to achieve a high ratio of FeO to SnO in the primary slag. This will ensure a high ratio of iron to tin in the hardhead of the secondary cycle, which in turn will give a high ratio of FeO to SnO in the secondary slag.