

The crystallization of rutile from titaniferous slags

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SYNOPSIS

Factors affecting the precipitation of rutile from smelter slags were investigated, with particular reference to the effect of additions of phosphorus pentoxide to the slag. The phases were identified and the phase boundaries determined for slags having phosphorus pentoxide additions of 0 to 50 per cent. The liquidus temperatures of these slags were determined, and a pseudo-binary phase diagram was constructed.

Rutile crystallized as the primary phase from melts having a phosphorus pentoxide content of more than 15,5 per cent. Prismatic rutile crystals whose TiO₂ content was more than 97 per cent were grown from melts that had a phosphorus pentoxide addition of 30 per cent. However, the morphology of the precipitated rutile was such as to make subsequent separation impracticable.

SAMEVATTING

Faktore wat die presipitasie van rutiel uit smeltery'slak beïnvloed, is ondersoek met spesiale verwysing na die uitwerking van die byvoeging van fosforpentoksied by die slak. Die fases is geïdentifiseer en die fasegrense bepaal vir slakke met fosforpentoksiedbyvoegings van 0 tot 50 persent. Die liquidus-temperatuur van hierdie slakke is bepaal en 'n pseudo-binêre fase-diagram is saamgestel.

Rutiel het as die primêre fase gekristalliseer uit smeltings met 'n fosforpentoksiedinhoud van meer as 20 persent. Prismaatiese rutielkristalle met 'n TiO₂-inhoud van meer as 97 persent is gekweek van smeltings met 'n fosforpentoksiedbyvoeging van 30 persent. Die morfologie van die gepresipiteerde rutiel was egter van so 'n aard dat latere skeiding onuitvoerbaar was.

INTRODUCTION

The novel process successfully developed at Highveld Steel and Vanadium Corporation Limited for the processing of titaniferous magnetites of the Bushveld Igneous Complex can be summarized as follows. The ore, together with coal and a flux consisting of limestone, dolomite, and silica, is pre-reduced in rotary kilns and fed to electric smelting furnaces. The products from this smelting operation are pig iron, which contains the vanadium, and titaniferous slag, which contains the gangue from the ore. The vanadium-bearing pig iron is then partially blown with oxygen in a shaking ladle to produce a vanadium-rich slag and is converted to steel in a BOF unit.

The titaniferous slag associated with the production of the pig iron contains relatively high percentages of TiO₂ (30 to 35 per cent), and thus can be regarded as a potential source of TiO₂ provided that a suitable method can be found for its extraction. Previous studies¹ conducted on these titaniferous slags had indicated that the phase constitution of the slags was complex and

that the TiO₂ crystallized as CaO.TiO₂ in lime-rich slags, or as 4(MgO.2TiO₂).Al₂O₃.TiO₂ in magnesium-rich slags. Recovery of TiO₂ from such slags by physical means is not feasible. Subsequent testwork² showed that specific minimum additions of network-forming SiO₂ to these titaniferous slags altered the phase constitution to such an extent that TiO₂ in the form of rutile became the primary crystallizing phase, and that the remaining oxide could be quenched to form a glassy matrix. However, large additions of SiO₂ (about 35 per cent) were required, and the rutile crystals occurred as fibrous agglomerations of such small size that physical separation from the glassy matrix was not practicable.

Recent laboratory investigations by Elger and Stickney³ have indicated that, when phosphorus pentoxide is added to a titaniferous slag, TiO₂ separates as an independent crystalline phase, and this phase can be separated from the bulk of the slag by mineral-processing methods. When this process was applied by Oden, Summer, and Howe⁴ to slags from the Quebec Iron and Titanium Corporation that had a TiO₂ content of 72 per cent, it was found that rutile recoveries of more than 95 per cent at a purity of 75 to 80 per cent were obtainable. Although this work was done on a starting material of considerably higher TiO₂ content than that of Highveld slag, it was considered worth while to undertake a detailed

TABLE I
ANALYSIS OF SLAG

Component	Percentage	Component	Percentage
CaO	16,43	MgO	14,64
Al ₂ O ₃	13,04	TiO ₂	30,94
SiO ₂	20,23	V ₂ O ₅	0,73
Mn ₃ O ₄	0,72	Cr ₂ O ₃	0,18
FeO	3,76	C	0,45
		S	0,17

$$\text{Basicity ratio} = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} = 1,54$$

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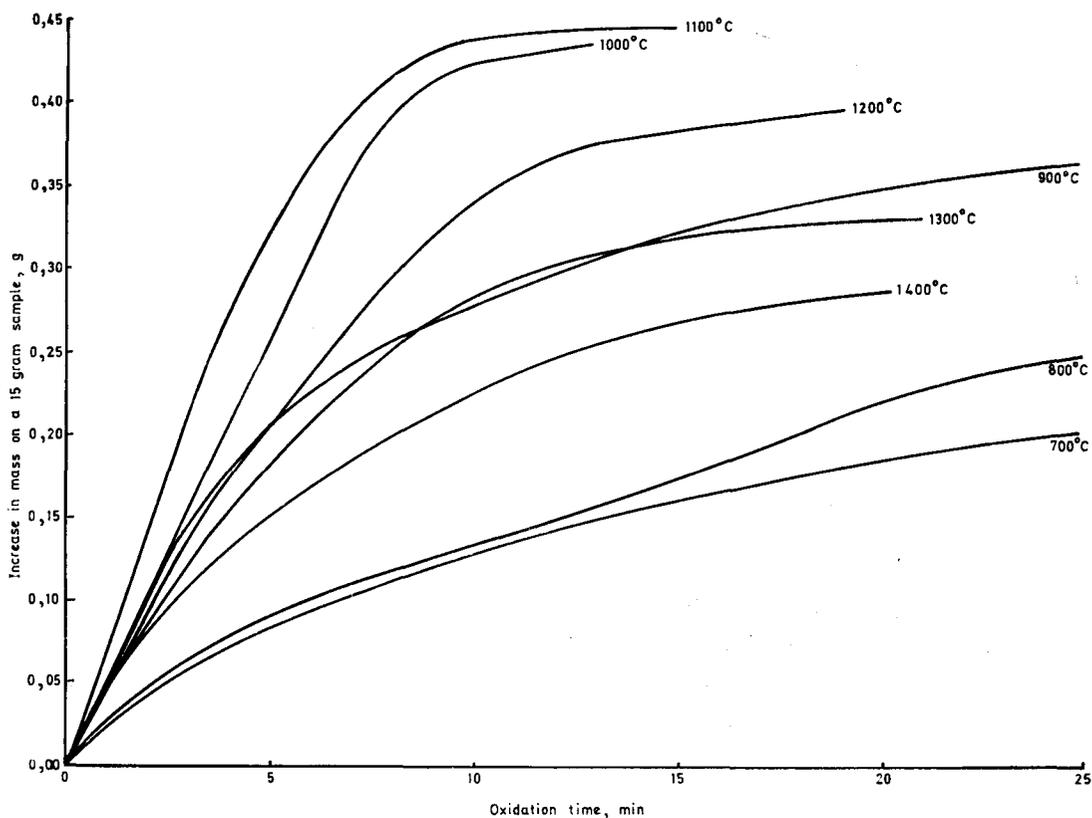


Fig. 1—Rate of oxidation of slag at various temperatures expressed as a function of time

investigation of the local slag on similar lines to those of Elger and Stickney.

OXIDATION OF TITANIFEROUS SLAG

Composite samples of slag from the electric smelting furnaces at the Highveld Steel and Vanadium Corporation Limited were mixed, riffled, and screened until a representative sample weighing several kilograms was obtained. The chemical analysis of this slag sample is given in Table I.

The phase diagram for titanium and oxygen shows that TiO_2 , TiO_3 , Ti_3O_4 , and TiO can each exist in defined stability regions. The reducing conditions in the smelting furnaces would be expected to produce lower, non-stoichiometric oxides of titanium in the slag. All the samples of slag tested were therefore oxidized to raise the titanium oxide to stoichiometric TiO_2 . The temperature at which the slag oxidized most readily was determined by measurement of the mass increase of particulate slag samples (between 106 and 150 μm) in an oxygen atmosphere at temperature intervals of

100°C between 700 and 1400°C. The results are presented graphically in Fig. 1.

As would be expected, the rate of oxidation increases rapidly with increasing temperature. However, from 1200°C the rate of oxidation decreases, which can be attributed to the fact that the solidus temperature of the slag is between 1000 and 1200°C. At temperatures above the solidus temperature, incipient fusion of the slag particles takes place and the available surface for oxidation is decreased. It is expected that complete oxidation will occur at these temperatures, and that the rate will again increase with temperature above the liquidus temperature of the slag. On a plant scale, submerged injection of the oxidizing gas may be advantageous.

Calculation of the stoichiometry of the oxide of titanium in the slag as produced on the plant indicates that the titanium is present as $TiO_{1.487}$, which approximates Ti_2O_3 .

CRYSTALLIZATION OF TITANIFEROUS SLAG

In this section of the work, the purpose was to identify the phases

that crystallize from the oxidized titaniferous slag melt when various amounts of phosphorus pentoxide are added, and subsequently to define the conditions under which primary precipitation of rutile would occur.

The oxidized slag, in 10 g amounts, together with various selected masses of P_2O_5 , were placed in a crucible made of Pt-5% Au alloy. The sample was then raised rapidly into the hot zone of a molybdenum-wound furnace at 1440°C, at which temperature the slag melted almost immediately. This technique had been shown to minimize losses of P_2O_5 by volatilization. Previous tests had indicated that 1440°C was above the liquidus temperature of the slag when it was mixed with 0 to 50 per cent P_2O_5 .

A period of time was allowed for the system to attain a constant temperature before the cooling process was initiated. Each sample was cooled to a predetermined temperature at the rate of 21°C per minute before being quenched with water, and the quenched slag samples were subjected to microscopic examina-

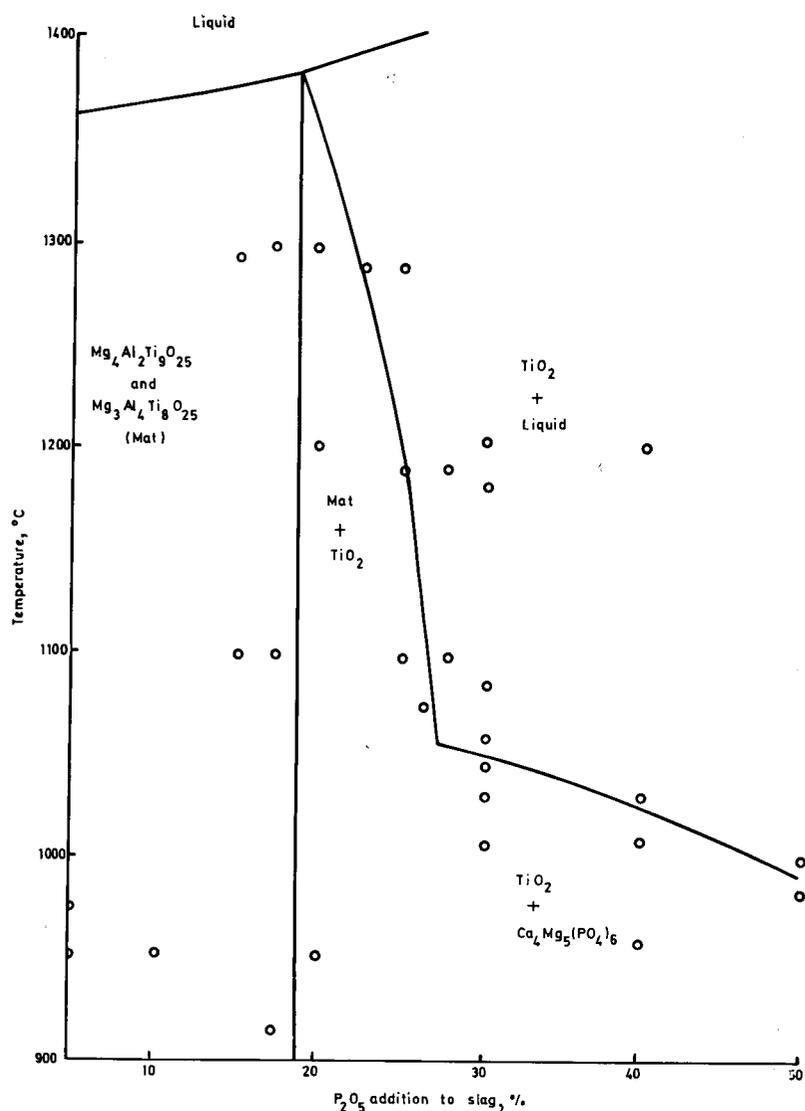


Fig. 2—Pseudo-binary phase diagram for the system slag—P₂O₅, based on the P₂O₅ addition to the slag

tion, X-ray diffraction studies, and electron-microprobe analysis.

LIQUIDUS DETERMINATIONS

Three common methods are available for the determination of liquidus temperatures of oxide slags: differential thermal analysis, hot-stage microscopy, and the classical quench technique. Of these, the differential thermal analysis and classical quench methods would have been suitable because of the high crystallization potentials of these particular slags. Hot-stage microscopy would not have been suitable owing to the high opacity of the slags.

An indirect means of determining the liquidus temperature of a slag

involves measurement of the electrical conductivity of the slag at selected intervals through the temperature range in which the liquidus temperature of the slag lies. A graph is then plotted of $\log_{10}R$ (resistance) versus the inverse of temperature, and an inflection is obtained at the liquidus temperature. As the necessary equipment was readily available, this method was adopted.

Platinum crucibles were used in this investigation. Successive additions of the appropriate mixture of P₂O₅ and oxidized slag were melted down by being heated in a box furnace held at 1500°C until the full charge of 170 g had been added to the crucible. Each sample was

placed on the crucible support stand, raised slowly into position in the hot zone of the molybdenum-wound furnace, and allowed to remain in this position in air for approximately half-an-hour.

After the slag had attained equilibrium, the electrodes were carefully lowered to a depth of 10 mm below the surface of the slag, the depth of immersion being checked by a vernier arrangement. Resistances were measured by the use of a modified Wheatstone bridge, at selected temperature intervals, both above and below the slag liquidus temperature.

THE PSEUDO-BINARY PHASE DIAGRAM

The liquidus temperatures and the composition and temperature of formation of the crystalline phases having been determined, it was possible to construct a section of the pseudo-binary phase diagram (Fig. 2).

The diagram shows that, when slags containing 22 per cent P₂O₅ (i.e., 30 per cent addition of P₂O₅) are cooled, the rutile crystallizes as a primary phase, the next crystalline phase to form being Ca₄Mg₅(PO₄)₆. Samples of slag having a P₂O₅ addition of 30 per cent were quenched from 1200, 1150, 1100, 1080, and 1060°C, and the resulting crystals and glass-phase matrix were analysed by electron microprobe for titanium, iron, manganese, calcium, and chromium. The object was to determine the purity of the rutile crystals and the amount of titanium remaining in the glass phase at various temperatures. It should be pointed out that, after crystallization of the rutile, the slags were sufficiently viscous to permit further cooling without crystallization of the compound Ca₄Mg₅(PO₄)₆. The results of the electron-microprobe analysis, after corrections had been applied for atomic number, fluorescence, and absorption, are given in Table II.

DISCUSSION

When a high-titania slag of the type used by Elger and Stickney but having no additions of P₂O₅ is cooled, rutile would crystallize as the primary phase (if the slag had been fully oxidized), but the purity

TABLE II

ELECTRON-MICROPROBE ANALYSIS OF CRYSTALS AND MATRICES FROM THE SLAG CONTAINING 22 PER CENT P_2O_5

	A2 Crystals	A2 Matrix	B2 Crystals	B2 Matrix	C2 Crystals	C2 Matrix	D2 Crystals	D2 Matrix	E2 Crystals	E2 Matrix
TiO ₂	97,17	9,14	96,72	5,82	97,57	4,33	97,26	5,59	96,77	4,16
Cr ₂ O ₃	0,77	0,00	0,63	0,05	0,60	0,03	0,59	0,04	0,65	0,06
CaO	0,33	14,19	0,38	14,88	0,46	14,66	0,50	15,26	0,43	15,23
Fe ₂ O ₃	0,94	2,91	1,14	2,84	0,93	2,93	2,57	2,53	1,17	2,59
Total	99,23	26,95*	98,94	24,23*	99,58	22,61*	101,00	24,12*	99,06	23,07*

*The totals for the matrix do not approximate 100 per cent because P_2O_5 and SiO_2 were not determined.

of the rutile concentrate, which may be obtained by physical separation techniques, is adversely affected by adhering slag.

To overcome this difficulty, Elger and Stickney made additions of P_2O_5 to produce a glassy-phase matrix that would be soluble in phosphoric acid, thus permitting acid scrubbing of the rutile crystals after they had been separated from the bulk of the slag. In the present work, the addition of P_2O_5 to a slag having a relatively low TiO₂ content serves two purposes. The first and more important aim was to change the crystallization conditions so that rutile would be present as a primary phase; the second, to produce a

glassy matrix soluble in acid.

To achieve maximum crystallization of rutile, an addition of 30 per cent P_2O_5 is required. Therefore, the object of obtaining rutile as a primary crystallizing phase can be achieved, but the P_2O_5 required is excessive. To decrease the quantity of P_2O_5 required, it may be possible to add both SiO_2 and P_2O_5 in such proportions as to promote crystallization of rutile and to obtain the glassy matrix amenable to acid scrubbing. Elger and Stickney indicate that 10 per cent additions of P_2O_5 to slags containing about 70 per cent TiO₂ are sufficient to permit scrubbing of the remaining slag from the rutile crystals.

By the addition of 30 per cent by weight of P_2O_5 to Highveld slags, rutile will crystallize in an acceptable degree of purity. As shown in Fig. 3, however, the morphology of the rutile crystals is unsuitable for the application of processes of physical separation. Fairly extensive laboratory tests were carried out in an attempt to separate the rutile from the slag, but effective separation proved impossible.

As will be evident by comparing Figs. 3 and 4, there are very marked differences in the morphology of the crystals of rutile obtained during the investigation by Elger and Stickney and those obtained in the work reported here. The photomicro-

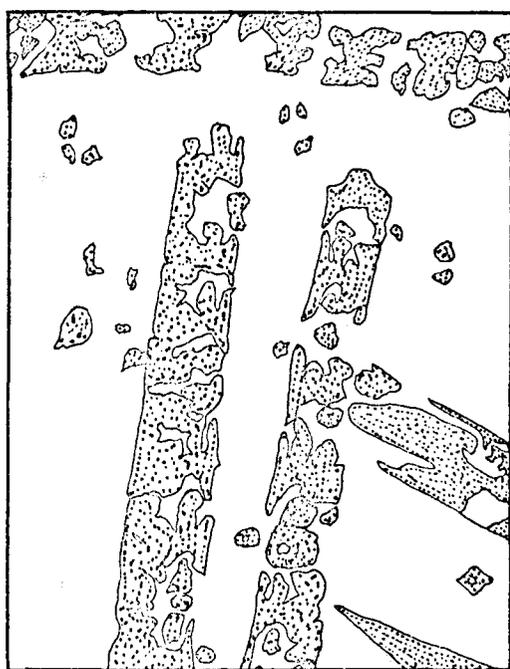


Fig. 3—Diagram showing the rutile crystals obtained in this investigation (x184)

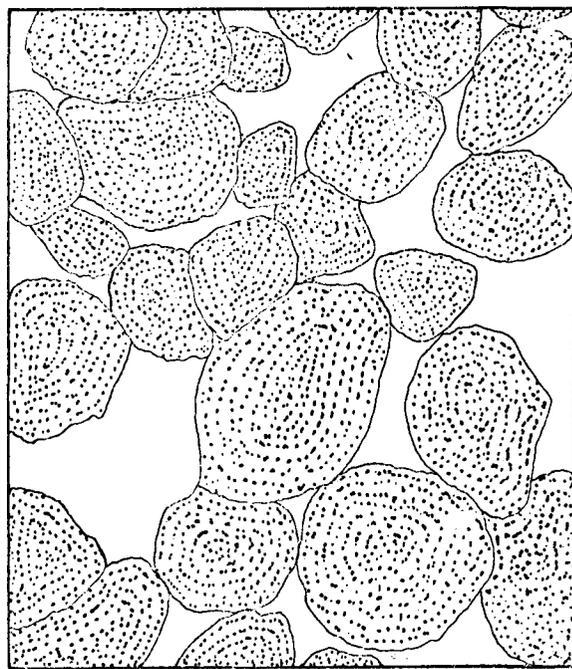


Fig. 4—Diagram showing the rutile crystals obtained by Elger and Stickney³ (x 172)

graphs published by Elger and Stickney show that the crystals of rutile obtained were subhedral in shape, with relatively poorly defined crystal faces, and had an axial ratio of approximately one. As is obvious from Fig. 3, the crystals of rutile produced during the present investigation have a decidedly skeletal structure indicating an incomplete growth pattern.

The differences in crystal habit of the rutile in the two slags can possibly be attributed to two import-

ant factors, namely viscosity of the slag and concentration of TiO_2 in the slag.

ACKNOWLEDGEMENTS

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NIM reports

The following reports are available free of charge from the National Institute for Metallurgy, Private Bag 7, Auckland Park 2006.

Report no. 1725

The determination of silica in fluor spar by 14MeV neutron-activation analysis.

Silica has been determined down to a content of 0,3 per cent, with a coefficient of variation of 11 per cent. The coefficient of variation for a sample of 100 per cent silica, which was used for calibration purposes, was 0,70 per cent. This high level of precision was attained with a new sample-packing

procedure, and the use of analogue stabilizers in the detection system.

Iron, magnesium, and aluminium give rise to small interferences in the determination, and corrections for these interferences have been determined. Phosphorus is a major source of interference since it readily produces the same radio-isotope as does silicon; a correction must therefore be made, based on the phosphorus content.

Results obtained on standard samples of fluor spar agree well with the recommended values, the precision of determination being 1 per cent relative for concentrations greater than 10 per cent.

Report no. 1732

A mineralogical examination of eight nickel-bearing rocks from the Grasvally Chromite Mine.

The nickel contents of four samples of serpentinite, three samples of chromitite, and one sample of pyroxenite are given. In all but one of the samples, only negligible amounts of nickel are present as sulphides. The chromitite horizon from the lowest level has a nickel content of 0,2 per cent in the form of heazlewoodite. Because this horizon is already exploited for chromite, it may prove possible to extract this nickel profitably.

New refining processes

During the past four years, the National Institute for Metallurgy (NIM) has been engaged in the development of new processes for the refining of the platinum-group metals. One aspect of this work, after successful laboratory tests, has now been proven so thoroughly on a pilot plant that a commercial company is actively interested in erecting a full-scale plant using the NIM process. The company, Lonrho, has supplied feed material for the pilot plant, which is situated at its existing platinum refinery in Brakpan, near Johannesburg, and it is hoped that the proposed plant will be in operation in 1976. It would be an extension to the existing plant, which produces platinum, palladium, and gold from concentrates having

a platinum-group-metal content of between 20 and 50 per cent. The remaining platinum-group metals, namely rhodium, ruthenium, iridium, and osmium, are not produced currently as pure metals, and the proposed plant will process crude concentrates containing these metals to produce metals with a purity exceeding 99,95 per cent.

Before expressing its wish to use the NIM process, Lonrho made a detailed comparison with existing processes originally developed overseas; it is believed that the capital and operating costs of the NIM process will be significantly lower than those of the conventional process. Two other advantages of the NIM process are that hold-up

times for the valuable metals are considerably reduced, and higher recoveries are achieved.

The process employs entirely new technology, and depends upon solvent-extraction and ion-exchange processes for most of the separation steps. It should greatly enhance NIM's already well-established international reputation in these areas, especially in view of the fact that new solvents, which will be manufactured in South Africa, are being used.

NIM has also developed new processes for the refining of platinum, palladium, and gold, and is confident that, in the not too distant future, platinum refiners will also be using these new processes.