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TEM study of solid titanium oxides inclusions in steel melt at 1600°C

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Titanium can exist in three different oxidation states. Its oxides are numerous and in presence of iron and oxygen, iron-titanium oxide compounds can also form. Some of the oxides are non-stoichiometric, making the determination of the thermodynamic properties of titanium and its oxides in molten steel and in slag difficult. Therefore, for the assessment of titanium activity in molten steel using the electrochemical measurements of oxygen partial pressure, the identification of oxides in equilibrium with titanium is important.

This paper reports on an investigation of solid titanium oxide inclusions, which have been identified by combining different methods of analysis on quenched samples. These samples were taken from a Fe-Ti-melt at 1600°C, quenched in cold water then mounted and polished for optical microscopy. The oxide inclusions were analysed using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS). Both single crystal and polycrystalline diffraction patterns were used to identify the oxides by comparing the d spacings with those in the ICDD X-Ray Diffraction (XRD) database. XRD was used to analyse the oxide particles on the top of slow cooled samples.

It was found in the TEM study that the similarity of the diffraction patterns of the various phases meant that unique identification was difficult to achieve in some of the diffraction patterns. However, TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7 were identified in quenched samples, while TiO_2, FeO.TiO_2 and iron oxides were seen in slow cooled samples. It was also confirmed that the type of oxides is related to titanium content of the samples.

Keywords: Titanium, Titanium Oxides, Iron, TEM, XRD, thermodynamic.

Introduction

Titanium's great affinity for oxygen results in its use as one of the strongest deoxidizing agents in steel making. Therefore, it is desirable to establish its thermodynamic data with some accuracy to ensure good control of the deoxidation process. Thermodynamic assessment of deoxidation reactions is experimentally performed by using the electrochemical measurement of equilibrium oxygen partial pressure as well as the determination of oxide at this equilibrium.

However, titanium exists in different oxidation states, Ti^{2+}, Ti^{3+} and Ti^{4+}. The corresponding oxides are TiO, Ti_2O_3, Ti_3O_5, TiO_2 and a complex combination of oxides called Magneli phases, which correspond to the general formula Ti_nO_{2n-1} with $4 \leq n \leq 33$[1–3]. In the presence of iron and oxygen it can also form iron oxides-titanium oxides compounds such as FeO.TiO_2, FeO.Ti_2O_3 and 2 FeO.TiO_2[3,4]. The diversity of these oxides makes it difficult to determine the thermodynamic properties of titanium and its oxides in molten steel and slag. The stability of the titanium oxides is mainly influenced by the oxygen partial pressure, the titanium content of the steel, the temperature and the slag composition[1–15]. Thus, for the assessment of titanium activity in molten steel, not only must the oxygen partial pressure be measured, but also the titanium oxide in equilibrium with the melt must be identified.

Much research has been done to determine titanium and titanium oxides activities in the steel and slag[3–15]. However, there are disparities in the published results, as various deoxidation products have been assumed or considered. The identification of deoxidation products is not obvious even when using phase diagrams Ti-O or Ti-TiO_2[1–3]. Different phase diagrams show only little resemblance particularly in the composition range between TiO and TiO_2.

This work has been initiated to identify the oxides in equilibrium with titanium in molten steel. Quenched samples and floating oxides were examined using different methods of analysis such as X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). This information will be used to assess the titanium activity in steel at 1600ºC.

Background

The reaction between dissolved oxygen and titanium in iron melt could be generally represented as follows:

$$Ti + n/2\ O_2 = TiO_n \qquad [1]$$

Its reaction constant is:

$$K = \frac{a_{TiO_n}}{a_{Ti} \cdot P_{O_2}^{n/2}} \qquad [2]$$

Where a_{TiO_n} and a_{Ti} are the activities of TiO_n and Ti in the system respectively, P_{O_2} is the equilibrium oxygen partial pressure, and n is the atomic ratio of oxygen and titanium in titanium oxide. This ratio commonly varies between 1 and 2. The melting points of all titanium oxides are above 1600°C[1,2] and, thus, a solid titanium oxide is formed at this temperature. This separate phase forms a suspension or floats on the top of the melt. Therefore, its activity is unity. In such conditions, Equation [2] could be transformed in:

$$a_{Ti} = \frac{1}{K \cdot P_{O_2}^{n/2}} \qquad [3]$$

From Equation [3] the activity of titanium is depending on the reaction constant K, the oxygen partial pressure, and the factor n, which is directly related to the type of titanium oxide. According to this the type of titanium oxide that is in equilibrium with the melt cannot be neglected in the determination of titanium activity. It is known that titanium and oxygen combine in various forms. Iron oxides and titanium oxides can also form some other compounds. The oxygen partial pressure in equilibrium with the iron-titanium melt is very low ($<10^{-8}$ atm.)[5] and, therefore, a small change of the factor n in Equation [3] could considerably affect the titanium activity in the melt.

Previous research on titanium activity and titanium oxides stability has lead to different values of activity as different titanium oxides were considered to be in equilibrium with titanium[1–15]. Evans and Sloman[4] investigated the titanium oxides solid inclusions using XRD and optic microscopy. Oxides ranging from TiO to TiO_2 and even iron-oxide-titanium-oxide spinel and magnetite were seen in that study. It was found that the type of oxide depended on the titanium content of the melt. Iron-oxide-titanium-oxide spinel is formed at low titanium contents (0.04 mass per cent) and Ti_2O_3 at titanium contents over 0.2mass per cent. Kojima *et al.*[6] investigated the equilibrium between Fe-Ti-melt and oxygen at 1600°C using the Debye-Hull-Scherrer technique to identify solid inclusions and concluded that the deoxidation product of the reaction between titanium and dissolved oxygen might be Ti_3O_5 when the titanium content is under 0.4 mass per cent and Ti_2O_3 when it is between 0.4 and 2 mass per cent. However, this method of extracting the particles from the solid steel included attack by a strongly oxidizing solution of iodine in ethanol. According to Janke and Fischer[7], the deoxidation product is Ti_3O_5 for titanium content between 0.001 and 0.1 mass per cent and Ti_2O_3 when the titanium content is between 0.1 and 2.1 mass per cent. Ghosh and Murthy[8] used numerical computer-oriented models of curve fitting to carry out experimental data from earlier works[6,7]. Their conclusion confirmed the limit between Ti_3O_5 and Ti_2O_3 to be 0.4 mass per cent. Whereas, at titanium contents lower than 0.4 mass per cent, the experimental results do not match the numerical model.

Kojima *et al.*[6] as well as Janke and Fischer[7] obtained different values of interactions parameters as they assumed that different oxides were in equilibrium with the titanium in the melt.

Smellie and Bell[9] investigated titanium deoxidation reactions in liquid iron in Ti_3O_5 crucible blowing a mixture of H_2 and H_2O into the Fe-Ti melt at 1625 and 1700°C. They showed that the equilibrium product is Ti_3O_5 for titanium content from 0.001 to 0.18 mass per cent and Ti_2O_3 for contents from 0.75 to 1.35 mass per cent.

In general, previous researchers show that the stability of the different types of titanium oxide is related to, among other parameters, the titanium content of the melt. However, it is clear that the oxide phase boundaries as a function of titanium content is still controversial.

Experimental

In the experiments, an alumina crucible containing approximately 400 grams of electrolytic iron and a small amount of grade A titanium was loaded into the hot zone of the alumina reaction tube of a furnace heated with lanthanum-chromite elements. After the Fe-Ti was charged, the reaction tube was sealed and evacuated. The reaction tube was then filled with 99.999 volume per cent purity argon that was dehydrated with silica deoxidized with magnesium turnings at 550°C, and a continuous flow of argon was maintained. The furnace was then slowly heated to 1600°C at a rate of 100°C per hour and held for 6 hours at this temperature. Half an hour after the furnace reached the working temperature, a metal sample was aspirated with a silica tube (6 mm OD and 4 mm ID) and quenched in cold water. Titanium additions were made to increase the titanium content of the melt. A metal sample was then taken 10 minutes after each addition and quenched in cold water. The titanium content of the samples was determined using inductive coupled plasma (ICP) at UIS Analytical Services Laboratories. When titanium was added to the melt, a fraction of the titanium oxide formed, floated to the surface of the melt. After the samples have been taken to represent different titanium contents, the melt was slowly cooled down under argon, its surface remained clean and a sample of oxide adhering on the top could be mechanically removed and analysed by XRD to identify the oxide particles. A Siemens D-501 diffractometer with a rotating sample holder was used for this purpose.

Samples extracted from the titanium containing iron melt at 1600ºC and quenched in cold water were also examined to identify titanium oxides solid inclusions. These samples were mounted and polished for optical microscopy and TEM. Subsequently the samples were lightly etched in 5 volume per cent nital, and sputter coated with amorphous carbon layer of ± 20 nm thick. This was scored and etched off the sample with 10 volume per cent nital. The films were rinsed in distilled water and caught on copper grids. The oxide particles extracted in this manner were analysed in a Philips CM200 TEM. Both single crystal and polycrystalline diffraction patterns were used to identify the oxides by comparing the d spacings with those in the International Centre for Diffraction Data (ICDD) database[16,17]. The crystal diffraction patterns were used to identify the oxides by comparing the d spacings with those in the XRD database. Diffraction calibration was performed with an aluminium metal standard. Further zone axis simulation was used to separate the phases found by diffraction[18].

Results and discussion

The results of TEM analysis are summarized in Table I, with the corresponding predictions from literature. The particles and diffraction patterns of various particles at different titanium contents are shown in Figures 1–5. XRD analysis on slow cooled samples are given in Table II and Figure 6.

From the results, the progression of titanium oxide from Ti^{+4} to Ti^{2+}, corresponding to increasing titanium content is confirmed. This progression also corresponds to a reduction

Table I
Summary of Ti content in mass per cent and corresponding crystal structure of the oxide

Sample no.	Figure	Mass % Ti	Oxide type	References
FeTi 1	1	0.001	Ti_4O_7	this work, 10
			$FeO.TiO_2$, TiO_2	4
FeTi 3	2	0.015	Ti_3O_5	this work, 6,7,8 and 9
			$FeO.TiO_2$, TiO_2	4
FeTi 10	3	0.164	Ti_2O_2	this work, 4
			Ti_3O_5	6, 7, 8, 9 and 10
FeTi 6	4	1.23	TiO	this work
			Ti_2O_3	4, 6, 7, 8, 9 and 10
FeTi 8	5	1.38	TiO	this work
			Ti_2O_3	4, 6, 7, 8, 9 and 10

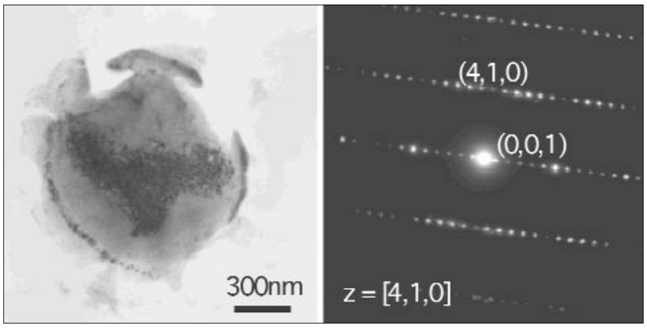

Figure 1. Transmission electron micrograph and diffraction pattern of Monoclinic Ti_4O_7 (ICDD77-1391) particle from melt containing 0.001 mass per cent Ti.

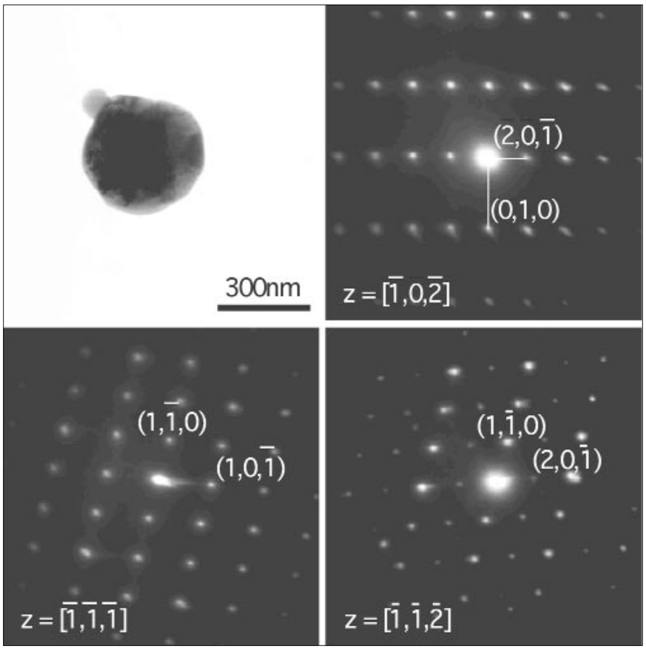

Figure 2. Transmission electron micrograph and diffraction patterns of monoclinic γ-Ti_3O_5 (ICDD 40-0806) particle from melt containing 0.015 mass per cent Ti

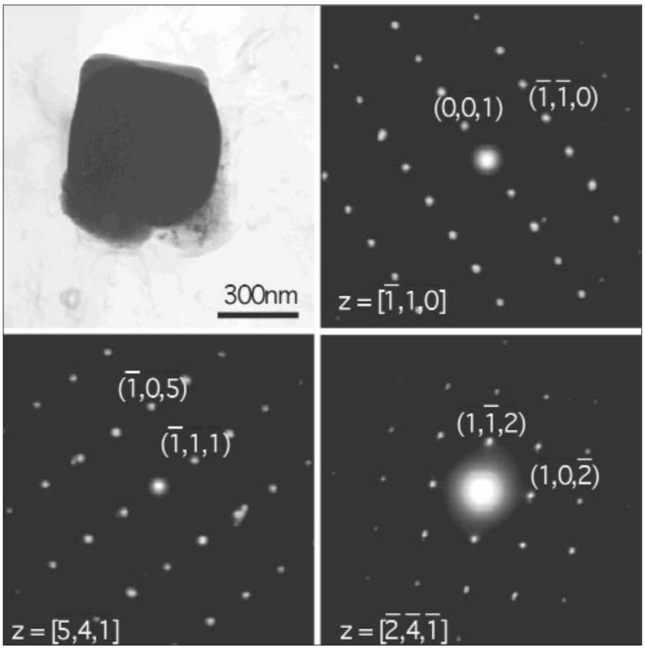

Figure 3. Transmission electron micrograph and diffraction patterns of rhombohedral Ti_2O_3 (ICDD 10-0063) particle from melt containing 0.164 mass per cent Ti

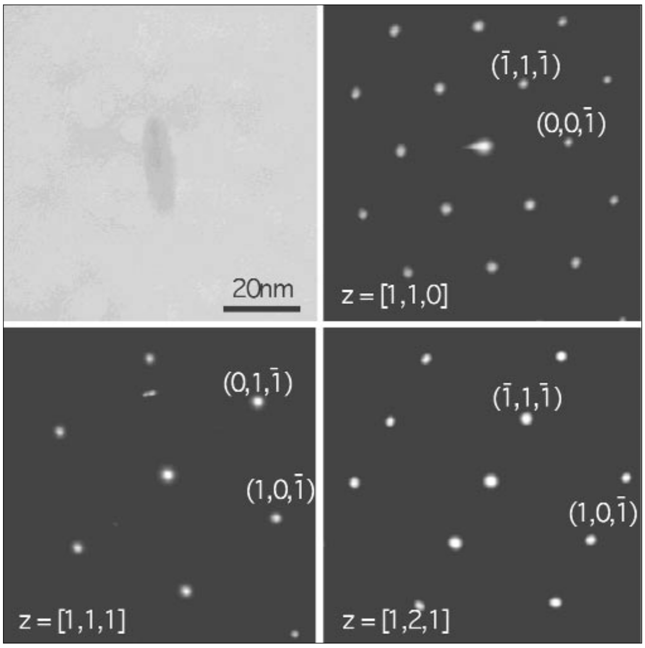

Figure 4. Transmission electron micrograph and diffraction patterns of cubic TiO (ICDD 77-2170) particle from melt containing 1.23 mass per cent Ti

in the oxygen content of the melt. Titanium contents covered in this work vary between 0.001 and 1.38 mass per cent. According to previously published data[8], these contents correspond to oxygen contents in the iron melt between 10 parts per million and 0.1 mass per cent.

The existence of Ti_4O_7 at very low titanium content (0.001 mass per cent Ti) as seen in reference[10] has been confirmed in this work.

In comparison to previously published results, for given titanium content, the oxidation state of titanium is lower

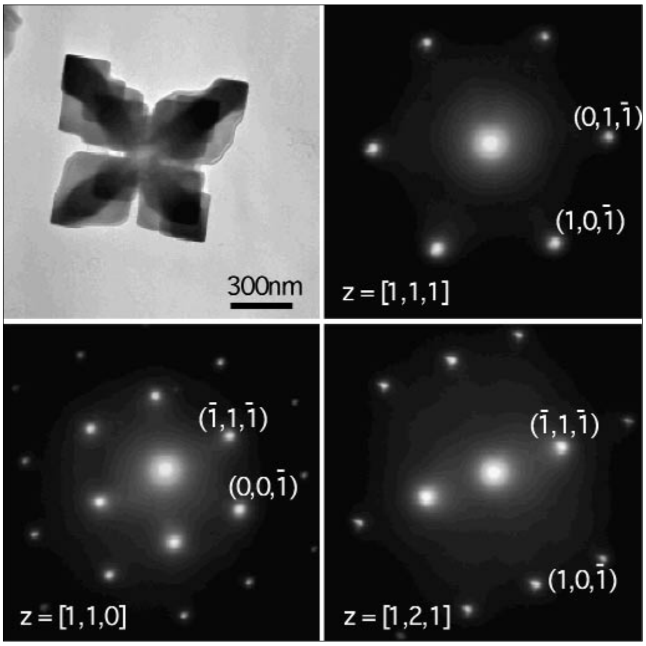

Figure 5. Transmission electron micrograph and diffraction patterns of cubic TiO (ICDD 77-2170) particle from melt containing 1.38 mass per cent Ti

than that has been reported[1,2,4,6–10]. In the authors' opinion, these differences are from one or two of the following reasons. Firstly, slow cooling of samples increases the oxidation state at a given titanium level. In Table II and Figure 6 the oxides formed on slow cooling are similar to those found in literature[4,9]. At lower titanium contents (sample FeTi 3b), the oxide products are similar to those found in Evans and Sloman[4], namely TiO_2, $FeO.TiO_2$ and iron oxides, while on fast cooling the Ti_3O_5 is seen, what is also reported by Kojima *et al.*[6] and Janke *et al.*[7] At higher titanium contents (sample FeTi 8b) TiO is seen in this work as compared with Ti_2O_3 in the previous work[4,6–9]. This is corroborated by Evans and Sloman[4], who observed TiO in combination with Ti_2O_3 at relative low titanium content (0.12 mass per cent). The slow cooling of the same melt gives TiO_2 as shown by the XRD analysis in Table II and Figure 6. From these observations it can be concluded that transformation occurs during slow cooling, possibly due to presence of small amount of oxygen in the argon. Secondly, the fact that different types of titanium oxides are seen in different work could also be related to method used to isolate the particles. The use of oxidizing extraction agents, such as iodine in ethanol[6], is suspected to change the oxidation state of the titanium.

Conclusion

This work shows that the oxidation states of the titanium in the oxide at a given titanium content at 1600°C are generally lower than that reported previously[4,6–9]. To retain the high temperature oxide structure, quenching the samples is essential. Extraction of the particles must not be done in strongly oxidizing mediums, as this also seems to affect the oxidation state.

Determining the deoxidation products, especially the titanium oxide, is important to assess the activity of titanium in steel correctly. Although it has been confirmed that the titanium oxide in equilibrium with a Fe-Ti-melt depends on, among other things, the titanium content, the stability limits of different titanium oxides need to be experimentally determined. Therefore, it would be desirable to obtain more data to delineate the phase boundaries of the oxides in equilibrium with Fe-Ti-melts containing less than 1.4 mass per cent titanium. Although this result is a qualitative indication of the titanium oxide present at various titanium levels, a great deal more investigation is required.

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Table II
Results of XRD analysis of oxides on the top of slow cooled samples

Sample	Mass % Ti	Oxide type	References
FeTi 3b	0.015	Ti_2O_3	4
		TiO_2	this work, 4
		$FeO.TiO_2$	this work, 4
		2 $FeO.TiO_2$	4
		$Fe_2O_3.TiO_2$	this work
		Fe_2O_3 and Fe_3O_4	this work, 4
FeTi 8b	1.38	TiO_2	this work

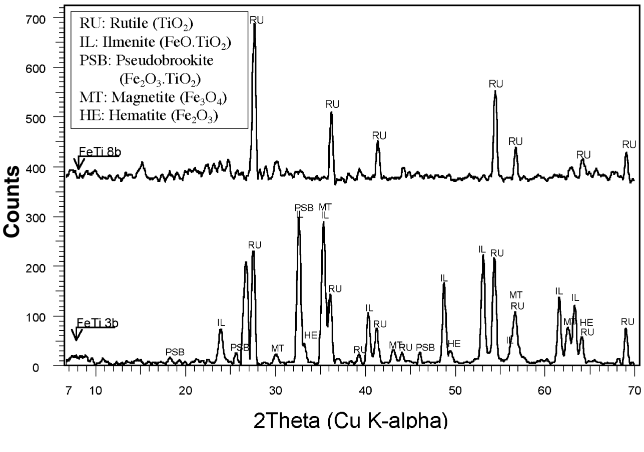

Figure 6. XRD analysis of slow cooled samples (FeTi 3b and FeTi 8b)

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