

Thermal Treatment of Titania Slag under Oxidation-Reduction Conditions

T.A.I. Lasheen¹ and M.E.H. Shalabi^{2*}

¹Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt

²Central Metallurgical Research and Development Institute, Cairo, Egypt

Abstract

The present work provides a method for beneficiating of an Egyptian titanium slag by a thermal oxidation and reduction in a controlled gas atmosphere to obtain leachable slag suitable for use as a feed material in the production of TiO₂ by chlorination process. The mechanism of that process has been studied and the proposed reactions are presented. The effect of oxidation on the enrichment of titanium into rutile phase by blowing oxygen into the slag was studied at relatively high temperatures (900-1100°C) for different times (30-90 min). Heating of a fully divided slag under oxidizing conditions resulted in a major portion of iron in the ferric state Fe³⁺ and titanium species in Ti⁴⁺ state. The results demonstrate that through oxidation, the content of pseudobrookite and rutile phases increase. Reducing of the pre-oxidized slag was carried out using hydrogen gas at 800°C for different period of times to convert the major portion of iron in ferric state Fe³⁺ to ferrous state Fe²⁺. As a result of these treatments most of titania phases were converted into rutile. Thereafter, the reactive ore was treated with aqueous HCl acid then sodium hydroxide solutions to leach impurities to obtain a beneficiated product with an increased TiO₂ content.

Introduction

Rutile is appreciated by the manufacturers of TiO₂ pigment using chloride process. However, shortage of rutile forced these producers to develop of other feedstock's formed by upgrading low grade titanium ores such as ilmenite. Prior arts have evolved various processes for upgrading ilmenites to synthetic rutile by concentrating the TiO₂ content and removing iron as well as other impurities by mineral acid leaching processes [1-3]. Commercially ilmenites can be upgraded into titania slag by a smelting process conducted in electric arc furnaces. Slag produced in such a smelting operations will typically contain 70-85% TiO₂ compared to about 93-96% TiO₂ in rutile. It mainly consists of a pseudobrookite phase known as M₃O₅, M represents to Ti, Fe, Si, Mn, Cr, V and alkaline earths and silicate enriched glassy phase. Pseudobrookite phase can be described as solid solution of different titanates. It accommodates the main

oxidation states of Fe and Ti in its structure normally Fe²⁺, Fe³⁺, Ti³⁺ and Ti⁴⁺. This is more inert to leaching action of mineral acids because of its high pseudobrookite and its glass content. Also, the amount of impurities removed is not high enough to make the slag suitable as a feed stock for the chloride process. Most impurities cause difficulties which greatly complicate either the chlorination process itself or subsequent stages of condensation and purification and disposal of waste. So, none of various processes reported for upgrading of ilmenite are applied to beneficiate titania slag due to fundamental differences between ilmenite and slag material.

Several methods have been developed to recover TiO₂ from slag. Sulfatation and chlorination of impurities are proposed for removing of impurities in slag. It was reported that sulfation process to produce high-purity slag suitable for chlorination [4,5]. The slag is reacted with a SO₂ and air mixture at relatively high temperatures which selectively convertes the impurities to soluble sulfates. Some authors [6] investigated the recovery of titanium as rutile by sulphidization of solid titania slag at a relatively high temperature. The author stated that a mixture of hy-

*corresponding author. E-mail: shalabimeh@hotmail.com

drogen sulphide, sulfur, nitrogen and carbon was most efficient for removal of impurities. Synthetic rutile was recovered from slag by a method comprising contacting the slag with chlorine gas at a temperature between 400-900°C. The impurities are subsequently removed by water or dilute HCl solutions as in previous approaches [7].

A number of previously proposed processes for beneficiation titaniferous ore materials involve oxidizing the ore to convert its iron content entirely to the ferric state, reducing the oxidized material so as to convert its iron content, either wholly or in part, to metallic iron, and finally leaching the reduced product. It was reported that such slag particles undergoes oxidation-reduction roasting are more readily amenable to acid leaching [8,9]. It was stated that the reduction of the pseudobrookite enhances the leachability of the reduced material making it possible to obtain a beneficiated product having a high TiO₂ content [10]. It was mentioned that further reduction of slag having pseudobrookite phase yields anosovite phase, which is suitable for titanium recovery [11]. The conversion of iron values in titaniferous ore to the ferrite state may be achieved by oxidation, at temperatures below that at which sintering of particles occurs. Conversion of the oxidized product to the synthetic ore is extremely rapid and efficient when carried out by hydrogen at 800 to 900°C. Oxidation of Ti₂O₃ changes the phase balance in the slag [12]. For oxidation above 550°C, rutile and an anatase in some cases precipitates and the remaining pseudobrookite is enriched with iron; whereas the iron in the slag particles will render them more accessible to leaching. Even without oxidation, phases in the slag are predicted to change upon reheating, because M₃O₅ is unstable at temperatures below 1300°C, tending to transform to rutile and metallic iron through a disproportionation reaction [13]. However, this transformation appears to be quite slow, it occurs after it is triggered by slight oxidation of the slag.

The present study is aimed to remove of impurities contained in slag material to produce feed stock suitable for the conversion of rutile to titanium tetrachloride by chlorination. The present work involves heating a finely divided slag under oxidizing conditions to ensure that iron is in the ferric state and thereafter to reduce the iron to ferrous state. The reactive material is then treated with an aqueous HCl and NaOH solutions to leach the impurities before recovering finely divided solid material containing an increased proportion of TiO₂.

Experimental

Slag Characteristics

A sample of Egyptian slag was provided from the Nuclear Material Authority (NMA) project. This is generated from the metallurgical process of beach sand during which iron is removed from ilmenite ore by carbothermic reduction smelting in electric arc furnace. X-ray diffraction analyses of the studied slag material Fig. 1.1 indicate that titanium are distributed in more than one phase, pseudobrookite Fe₂TiO₅ [14,15], rutile TiO₂ and solid solution Fe₃Ti₃O₁₀ [16] which may formed at the end of smelting, pseudorutile Fe₂TiO₆ [16], brookite TiO₂ [15,17]. Metallic γ and α iron and quartz are also detected. The chemical compositions of slag sample are determined through wet chemical and atomic absorption analysis. All titanium constituents are expressed as TiO₂ and iron species as ferric iron. The slag, by chemical analysis, contained 72% TiO₂, 12.65% Fe₂O₃, 9.0% SiO₂, 0.6% MgO, 0.78% CaO, 1.63% MnO, 1.9% Al₂O₃, 0.32% Cr₂O₃ and 0.55% V₂O₅.

Oxidation-Reduction Roasting Experiments

Weighed slag samples – 200 mesh are charged into porcelain crucibles and heated in a tube furnace in an oxidizing atmosphere for a sufficient length of time at an oxygen pressure of 1 atmosphere (101000 Pa). After oxidation the material is reduced at temperature of 800°C by hydrogen for a definite period of time. X-ray diffraction analysis is used to follow up the change in phases after oxidation and oxidation-reduction processes, Table 1. Additional experiments are performed on reactive slag samples to leach impurities and excess silica using aqueous HCl and NaOH solutions.

Results and Discussion

Oxidation

A series of roasting experiments are performed at temperatures varied from 900 to 1100°C for different periods of time 30-90 minutes in anoxidizing atmosphere of oxygen to convert all of titanium oxides to titanium dioxide to allow growth of rutile crystals. When oxygen is blown in, the low valiance titanium ion could be oxidized into rutile which increases the activity of TiO₂, the reaction being as follows:

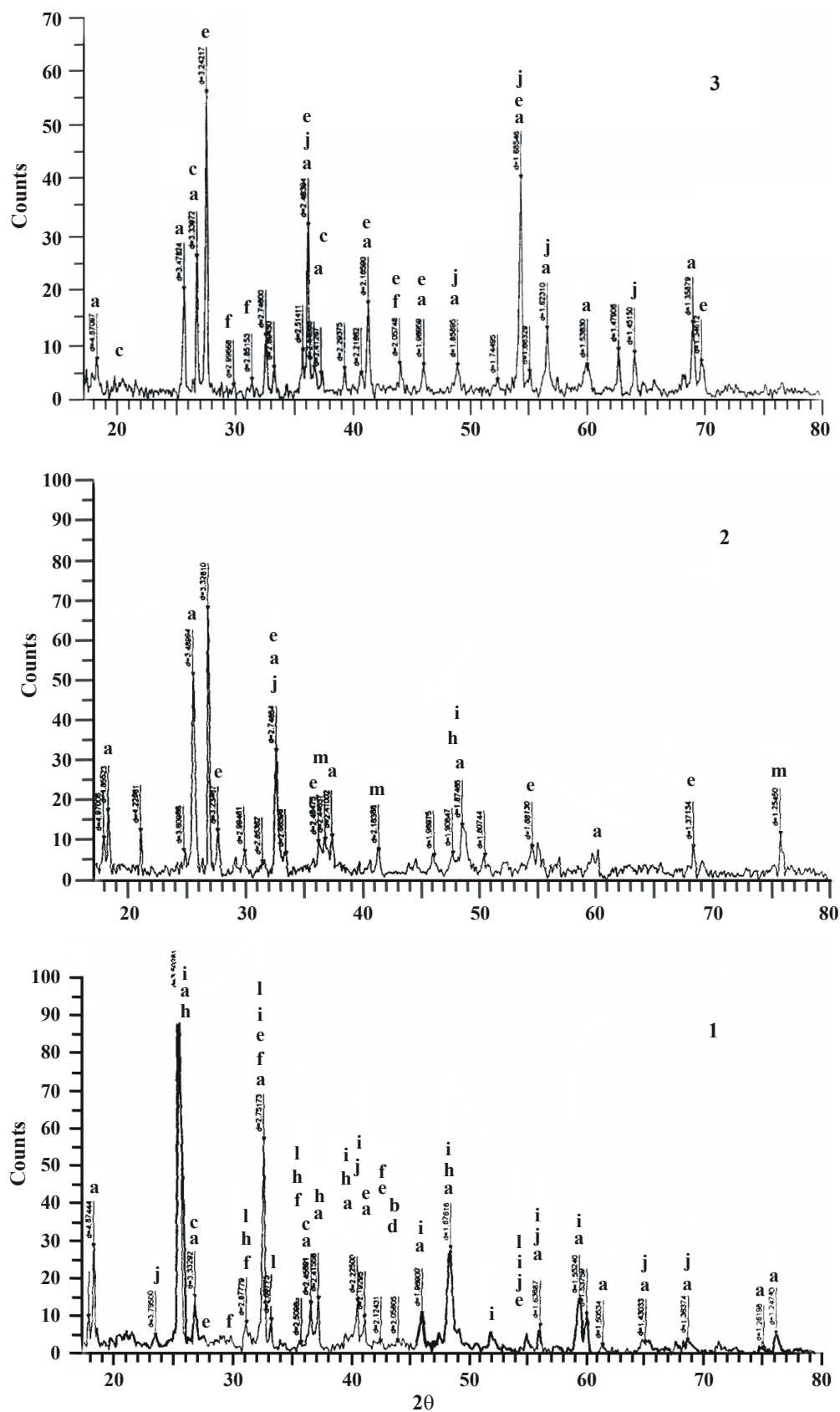
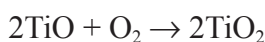


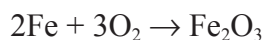
Fig. 1. X-ray diffraction patterns of slag sample (1), slag under direct reduction at 800°C (2) and direct oxidation at 1000°C (3). a – pseudobrookite, b – α -iron, c – quartz, d – γ -Fe, e – rutile, f – hematite, j – pseudorutile, h – brookite, i – solid solution $\text{Fe}_3\text{Ti}_3\text{O}_{10}$, l – β - Fe_2O_3 and m – FeO.

Table 1
Phases identified in slag, and treated samples using X-ray diffraction analysis

Symbol	Phase identified	Chemical formula	Slag	Oxid _{1000°C} 60 min	Red _{800°C} 30 min	Oxid _{1000°C} 1 h, Red _{800°C} 30 min	Oxid _{1050°C} 1 h, Red _{800°C} 30 min
A	Pseudobrookite	Fe ₂ TiO ₅	+	+	+	+	+
B	α-iron	α-Fe	+	–	–	–	–
C	Quartz	SiO ₂	+	+	+	+	+
D	γ-iron	γ-Fe	+	–	–	+	+
E	Rutile	TiO ₂	+	+	+	+	+
F	Hematite	Fe ₂ O ₃	+	+	–	–	–
J	Pseudorutile	Fe ₂ Ti ₃ O ₉	+	+	–	–	–
H	Brookite	TiO ₂	+	–	–	–	–
I	Solid solution	Fe ₃ Ti ₃ O ₁₀	+	–	–	–	–
K	Ilmenite	FeTiO ₃	–	–	–	+	+
L	β-hematite	β-Fe ₂ O ₃	+	–	–	–	–
M	Ferrous oxide	FeO	–	–	+	–	–



The X-ray diffraction patterns presented in Fig. 1.3 proved that oxidation of slag at 1000°C for 1 h was sufficient to yield a product consisting substantially wholly of pseudobrookite, pseudorutile and rutile [15]. Pseudorutile is decomposed directly to pseudobrookite and rutile when the sample is brought directly to reaction temperature. Hematite and quartz are also identified [18]. The proposed oxidation reactions as a result of oxidation by oxygen can be represented by the following equations:



It was concluded that the temperature of the ore material should not exceed 1000°C to avoid excessive sintering of the ore material [20]. Increasing oxidation temperatures > 1000°C increases the size of rutile crystal formed. However, increasing oxidation temperatures > 1300°C decreases the conversion of pseudobrookite to rutile and increases the amount of glass phase present in the oxidized slag. This result is quite undesirable. At lower temperatures, and relatively short times the oxide material will be usually found

to contain some hematite in addition to pseudobrookite and rutile [19,20]. At temperatures more than or equal 800°C the rate of oxidation and phase transformation become sufficiently great to be attractive, however the rutile crystals formed thereof have extremely small particle size making their beneficiation unfeasible.

During oxidation the iron present in the slag tends to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe²⁺ state to convert to the Fe³⁺. A fast diffusion of iron and titanium cations occurs within the pseudobrookite phase resulting in the formation of large number of small pores and channels in each grain of slag. This in turn increased porosity and radically changed the crystal structure which facilitated the subsequent reduction and leaching steps. Also, during oxidation, the glassy silicate phase of the slag is decomposed which facilitates leaching out the CaO impurity which was mainly present in the glassy silicate phase [8,10,21].

Direct Reduction

The reduction products as a result of direct reduction of slag by hydrogen are shown through XRD in Fig. 1.2. As can be seen, reduction encourages the formation of pseudobrookite phase in addition to pseudorutile and ferrous oxide phases at the expense of other phases. The amount of other phases in the

sample had considerably diminished. The figure also reveals that direct reduction of slag occurs in one stage, as $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$. The results depicted in Table 2 demonstrate that the efficiency of removal of major impurities is low. Leaching of iron species was incomplete 46%.

Table 2

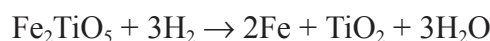
Leaching efficiency of soluble iron and titanium constituents at different thermal conditions

Thermal condition, °C	Time, min		Leaching efficiency, %	
	Oxide	Red	Fe	Ti
Oxidation ₁₀₀₀	60	–	68.5	0.30
Oxidation ₉₀₀	60	–	57.8	0.25
Red ₈₀₀	–	30	46.0	0.35
Oxid ₁₀₀₀ , Red ₈₀₀	60	30	81.6	0.76
Oxid ₁₀₀₀ , Red ₈₀₀	60	60	82.5	0.70
Oxid ₁₀₀₀ , Red ₈₀₀	60	90	80.5	0.70
Oxid ₁₀₅₀ , Red ₈₀₀	60	30	85.0	0.72
Oxid ₁₁₀₀ , Red ₈₀₀	60	30	84.6	0.65

Reduction of Pre-oxidized Samples

The oxidized samples were reduced by hydrogen gas at temperature of 800°C to convert major portion of iron in Fe^{2+} state. Temperatures in excess of 1000°C lead to increasing difficulties in preventing excessive reduction. It must be emphasized that the desirable crystallinity and porosity will be lost if the temperature at high with no reduction occurring. The residence time of the material at the reduction temperature varied from 30 to 90 minutes.

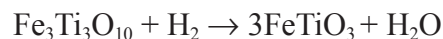
Results of X-ray patterns presented in Fig. 2 indicate that 30 minutes was enough for complete reduction of iron oxide in the pre-oxidized samples. The conversion of oxidized product to synthetic ore was efficient and rapid. The use of excessive amounts of hydrogen may lead to the formation of metallic iron in the titaniferous material. The following reactions are proposed for the reduction of pre-oxidized slag:



Finally divided hematite and rutile can reform ilmenite:



$\text{Fe}_3\text{Ti}_3\text{O}_{10}$ is an undesirable solid ferric-ferrous solution whose composition can be designated $\text{Fe}_2\text{TiO}_5 \cdot \text{FeTi}_2\text{O}_5$. By reduction, it forms ilmenite:



Ilmenite is reformed by a recombination-reduction reaction involving rutile [22]:



An increase in the amount of metallic iron and rutile will correspond to further reduction of ilmenite in the sample:



Some authors [9] proved that the reduction of the oxidized slag takes place in two stages. In the initial stage, the ferric state Fe^{3+} iron oxide contained in the pseudobrookite phase is reconverted to ferrous state Fe^{2+} iron oxide. The pseudobrookite phase is already freed of Ti^{3+} constituents which were oxidized during the oxidation step and removed from the pseudobrookite phase as rutile. In a second stage, a solid state reaction results in radical changes in the crystal structure of the slag. It is related to porosity and crystallinity of the obtained product. It occurred when pseudobrookite phase has just disappeared.

The dominant phases that occurred as a result of oxidation-reduction processes were rutile, iron, ilmenite, pseudobrookite and quartz. Maximum leaching of main gangue impurities Fe occurred at 1050°C oxidation temperature for 1 h and reduction at 800°C for 30 minutes.

Acid Leaching of Treated Slag Samples

The treated slag is then contacted with aqueous 30% w/wt HCl while boiling in a vessel connected with a condenser to leach out impurities [3]. Iron and titanium values are determined in the leach liquor under these conditions. The leaching efficiencies are summarized in the following Table 2. An alkaline leaching step is added to remove excess silica. It leads to a product having the following composition, 93.5% TiO_2 , 1.9% Fe_2O_3 , 0.4% Al_2O_3 , 0.6% CaO , 0.4% MgO , 0.19% MnO , 0.1% Cr_2O_3 , 0.25% V_2O_5 and 2.5% SiO_2 after washing and calcination.

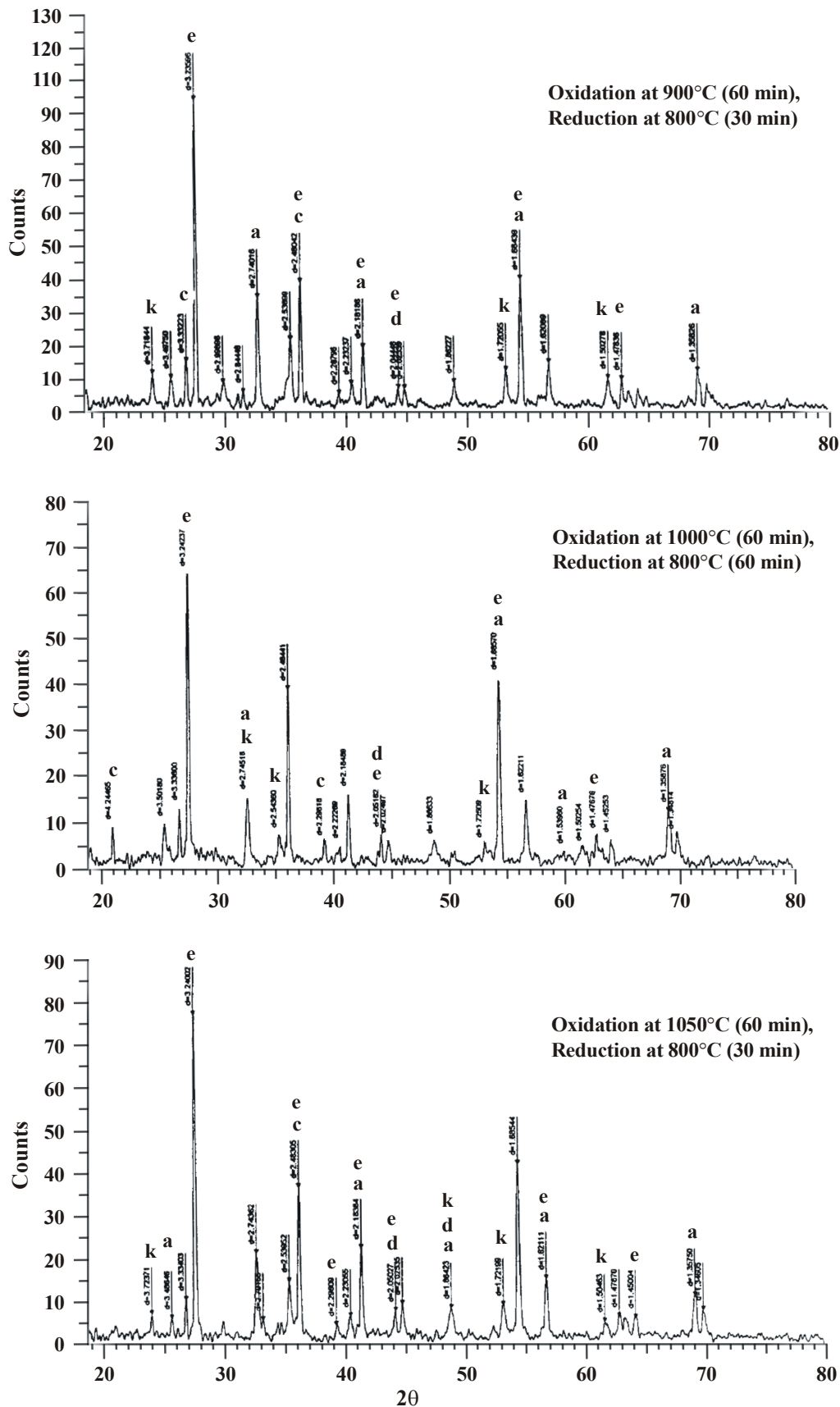


Fig. 2. X-ray diffraction patterns of roasted slag products at different conditions: a – pseudobrookite, c – quartz, d – γ -Fe, e – rutile, k – ilmenite.

Conclusions

Thermal treatment of titania slag under oxidation-reduction appears to be useful for treatment of slag containing appreciable quantities of impurities. Oxidation of slag results in a major pseudobrookite, pseudorutile, rutile, hematite and quartz phases. Reduction of pre-oxidized samples provides more reactive materials that could be leached with HCl solution. The pseudobrookite concentration progressively decreases, whereas ilmenite is being reformed. However, pseudorutile phase disappears. It decomposed into ilmenite and rutile phase as proposed in the reaction sequences. Further reduction of ilmenite in the sample leads to increasing in the amount of metallic iron and rutile. The reaction sequence at studied temperatures is essentially the same leading to a mixture of rutile, ilmenite, iron and quartz. Some pseudobrookite is observed and it is believed to have been stabilized by dissolved impurities such as Mn or Mg. The heat treatment presented in this study produces phase are much more readily leached for removal of the iron content and significant amount of impurities such as Cr, V, Mn. Under experimental conditions the titanium component can be remarkably enriched into rutile phase of at least 93% TiO₂.

References

- Ogasawara T., Veloso de Araujo, R.V., Hydrometallurgy, 56:203 (2000).
- Jayasekera S., Marinovich Y., Avraamides J. and Bailey S.I., Hydrometallurgy, 39:183 (1995).
- Lasheen T.A.I., Hydrometallurgy, 76:123 (2005).
- Elger G.W., Stadler R.A. and Sankar P.E., 1977. US Patent No. 54120694, USA.
- Elger G.W., Write J.B., Tress J.E., Bell H.E. and Jordan R.R., USBM, Report No. R19003, 1986.
- Borowiec K. Scandinavian journal of metallurgy, 20:198 (1991).
- Gueguin M., 1995. US Patent No. 5,389,355.
- Borowiec K., Grau A.E., Gueguin M. and Turgeon J.F., 1998. US Patent, No. 5,830,420.
- Van Dyk J.P., Vegter N.M., Visser C.P., De lange T., Winter J.D., Walpole E.A. and Nell J., 2004. US Patent, No. 6,803,024 B1.
- Sinha H.N., Hills S. and Waugh, 1977. D.MB. US Patent No. 3,597,189.
- Sahu K.K., Alex T.C., Mishra D. and Agrawal A., Waste Manage Res. 24:74 (2006).
- Pistorius C.P. and Motlhamme T., Minerals Engineering, 19:232 (2006).
- Eriksson G., Pelton A.D., Wermann E., and Ender A., Berchte der Bunsen-Gesellschaft fur physikalische Chemie, 11:1839 (1996).
- Pauling L.Z., Kristallogr., Kristllgeom Kristallphys., Kristall. Chem., 73 (1930).
- Calculated from, ICSD Using Powd-12++ (1997).
- Jones D.G., The Institution of Mining and Metallurgy, 186 (1973).
- Meagher E. P and Larger G.A., Can Mineral, 17:77 (1979).
- Novosadova, *et al.*, Ukr. Chim. Zh. (Russ. Ed), No. 52:704 (1986).
- Robinson M., Clamp F., Aberdeen D., Mobbs D.B. and Pearse R.V., 1975. US Patent No. 3,875,286.
- Robinson I., Engineering News. Mining, 25 September (1992).
- Sinha H.N. 1979. Solubility of titanium minerals. In P reprints international Conference on "Advances in chemical metallurgy" Bhabha Atomic research center, Bombay, India, 1979, 2, paper 35.
- Haggerty S. E and Lindsley D.H., Rep. Dir. Geophys Lab. Camegie Inst, 68:247 (1968-69).

Received 13 February 2007.