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Non-Waste Processing of Ilmenite and Titanomagnetite Concentrates

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Abstract

Fundamental potential of single-stage processing of ilmenite concentrate to synthetic rutile of commercial quality has been shown experimentally and by thermodynamic computations. The method has its origins in selective chloridation of iron and impurity of magnesium, chrome, manganese, sulphur, and vanadium by chlorine with no use of any reducer. Possibility to extract vanadium without reduction smelting and without loss of titanium and other target ingredients of the concentrate was revealed for high-titanium titanomagnetite concentrate. The other target ingredients can be later isolated by the reduction chlorination. It has been found that the great bulk of iron and vanadium can be extracted from titanium concentrates for 10 min at a temperature of 1373 K and under atmospheric pressure.

Keywords: titanium, rutile, ilmenite, titanomagnetite, vanadium, titanium dioxide, chlorine metallurgy

Conventional technology of processing ilmenite concentrate (IC) and vanadium-containing titanomagnetite concentrate (TMC) to yield titanium and vanadium respectively involves reduction smelting at its first stage to withdraw the major quantity of iron from IC and to withdraw vanadium and iron from TMC into steelmaking iron. Titanium scorias that remain after electric arc melting of IC are characterized by relatively low content of titanium (~85 % TiO_2) and by high content of iron, which hinders production of pure titanium chloride from them [1]. Reduction smelting of TMC with initially low titanium content (3–4 % TiO_2) to yield vanadic pig iron is accompanied by the formation of blast-furnace slag that contains 10–12 % TiO_2. This slag goes to a dump or to a slag-melting furnace to produce titanium-containing rich alloys, while the pig iron is fed into a converter for smelting vanadic scoria from it. Several hydrometallurgical treatments are used to produce commercial vanadium pentoxide from vanadic scoria. Losses of vanadium in the process amount to 55–60 %. By virtue of the fact that high-titanium TMC cannot be processed under this schematic diagram because of a high viscosity of the slag, they are subject to melting to yield vanadic pig-iron in electric furnaces adding dolomite and quartz to fluidity the scoria that goes to dump after melting in this case [2].

We suggested to process IC and TMC by way of selective chloridation that is reduced at the first stage to chlorination of these concentrates by chlorine with no use of reducer. Thermodynamic computations for IC (Fig. 1) demonstrate that with almost 10-fold excess of chlorine over the stoichiometry, it is possible to achieve practically full extraction of iron in the form of gas mixture of its chlorides at $T > 1060$ K. At $T > 1200$ K, titanium chlorination begins. These features are evidenced for TMC, too. Aluminium that is inherent in it starts to chlorinate at $T > 1400$ K, and vanadium, according to computations, even at $T > 660$ K completely transforms to the gas phase in the form of $VOCl_3$ (b. p. = 400 K). However, as it was implied in our experiments, vanadium was not distilled

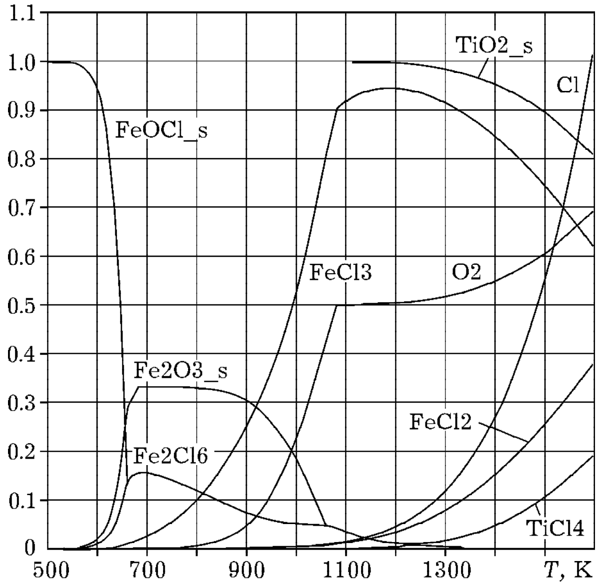

Fig. 1. Calculated molarities of reaction products of $FeTiO_3 + 10Cl_2 + Ar$ ($P = 0.1$ MPa). "s" – solid ingredients, the remaining ones – gas.

off at the given temperature. It appears that it is related to intradiffusive restraints that have an influence on infiltration of chlorine in depth of the mineral. Vanadium is present in the mineral in small proportion, replaces iron, and consequently, it can be distilled off only together with it. Temperature and time profile of vanadium sublimation in this case should coincide with these dependences for iron.

To check the thermodynamic computations we executed, an experiment has been conducted in a quartz pipe-still heater with controllable temperature and the gas stream. IC from Volnogorsk State Mining and Metallurgical Integrated Plant (Ukraine) that is the main titanium supplier for the Russian titanium industry and high-titanium TMC from Medvedevskoye deposit (Urals Mountains) were used. Decrease of total mass of concentrate powders with the coarseness of −140 μm and variation in their elemental chemical composition was registered as a function of the temperature and chlorination time. Assay was conducted using a X-ray fluorescence spectrometer Bruker-AXS S4 Pioneer. It is found that titanium concentrates practically cannot be chlorinated at a temperature <873 K. Appreciable chlorination rate is evidenced at $T > 900$ K and it grows with a rise in the temperature, which is supported by kinetics of IC and TMC chloridation for $T = 1073$ and 1373 K, respectively (Fig. 2). After chlorination over the course of 30 min at a temperature of 1373 K, the registered mass of the residue was equal to 67.4 % for IC and 13.5 % for TMC, from initial mass. Elemental analysis of the residues has suggested (Table 1) that iron is distilled away from IC at the rate of 98.6 %, and at the rate of 99.4 % from TMC. Titanium can be partially (<7 %) chlorinated (Fig. 3, *a*); magnesium, manganese, chrome, vanadium, and sulphur chlorides are distilled away. Vanadium can be isolated from the received gas mixture as a separate product by consecutive fractional condensation and by known methods of decontamination of chlorides [1]. One of variants to recover chlorine in the process is oxidizing of iron chlorides in a current of oxygen to yield pigment iron oxide. Alternative variant involves $FeCl_3$ transformation into metal powder in the current of hydrogen and its withdrawal from the stream by magnetic field, and Deacon process is applied to withdraw chlorine from the formed HCl.

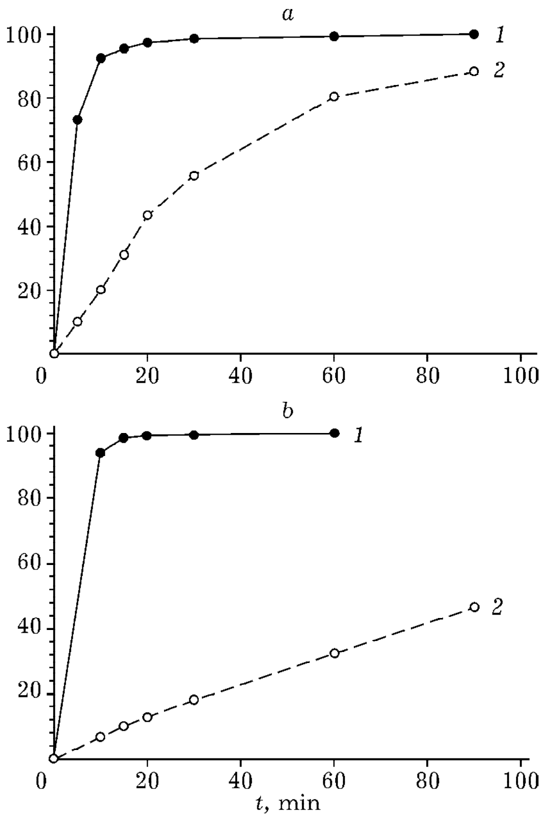

Fig. 2. Kinetics (in terms of a decrease in the mass of powder) of chloridation for IC (*a*) and TMC (*b*). $P = 0.1$ MPa; T, K: 1373 (*1*), 1073 (*2*).

TABLE 1

Elemental composition of ilmenite (IC) and titanomagnetite (TMC) concentrate before and after chloridation at 1373 K over the course of 30 min (P = 0.1 MPa), mass %

Compound	IC	TMC
MgO	0.37/–	1.19/–
Al_2O_3	2.37/3.78	2.1/8.28
SiO_2	2.85/4.22	3.5/12.8
SO_3	0.069/–	0.38/–
CaO	0.15/–	0.985/3.7
TiO_2	63.56/90.4	10.2/71.93
V_2O_5	0.34/–	0.83/–
Cr_2O_3	1.46/–	0.345/–
MnO	0.88/–	0.2/–
Fe_2O_3	25.22/0.26	79.18/0.43
CuO	0.16/0.1	0.19/0.11
ZnO	0.142/0.073	0.198/0.071
ZrO_2	0.117/0.175	–/0.108
Nb_2O_5	0.1/0.133	–/–

Note. The first value – before chloridation, the second value – after it.

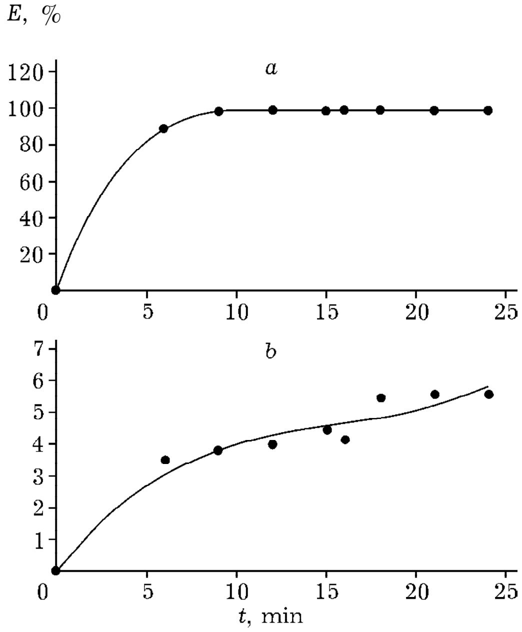

Fig. 3. Kinetics (according to elemental analysis data) of chloridation of iron (*a*) and titanium (*b*) for ilmenite concentrate: *a* – dE/dt = 25.603 at t = 0, T = 1373 K, P = 0.1 MPa; *b* – dE/dt = 0.7164 at t = 0, dE/dt = 0.1149 at t = 15 min, T = 1373 K, P = 0.1 MPa.

The residue of iron distillation that was produced in our experiment from IC through one stage surpasses titanium scoria in its content of titanium and impurities and it is close to synthetic rutile that can be obtained in practice from IC through many-stage pyrometallurgical and hydrometallurgical treatment. It is slightly less than pigment titanium dioxide in its whiteness, which is associated with its residual content of chromophore impurity of iron oxide (0.26 %).

Pigment titanium oxide that was received by combustion in oxygen or by steam conversion of rectified titanium tetrachloride has no this impurity [1]. As opposed to IC, a residue of TMC chlorination is characterized by a high content of SiO_2 (see Table 1) and it may be exposed to chloridation of titanium and aluminium oxides, now in the presence of a reducer (to take an example, CO), to yield marketable chlorides that are free from impurities of silicon [3].

Kinetic curves of sublimation of iron and titanium from IC at T = 1373 K have been plotted (see Fig. 3) according to elemental analysis data. Macrokinetic chlorination rate was determined from tilt of the experimental curve. The speed of titanium sublimation at an early stage ($t < 5$ min) is 35.7 times less than the speed of iron sublimation, and it becomes even less upon the elimination of a great bulk of iron ($t > 10$ min). Our experiments with model mixtures have confirmed this effect: sublimation of titanium dioxide by chlorine at the given temperature runs slowly, but the speed of sublimation shows a sharp rise upon addition of iron oxide. The same action of iron was previously registered in the reduction chlorination of titanium scoria in salt melts [1]. The difference in the chlorination speeds for iron and titanium is testimony to a good selectivity of iron extraction from titanium concentrates. Consequently, it becomes possible, first, to obtain synthetic rutile from Volnogorsk IC for its further use as a constituent of fusion mixture in processes of coating of welding electrodes, bypassing the traditional stage of smelting of titanium slags and steel-making iron; second, to conduct practically full component-wise extraction of vanadium, titanium, aluminium, and iron from TMC without high-temperature (>1400 K) pirometallurgical and hydrometallurgical treatments.

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