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Study of the Mechanochemical Reduction of Ilmenite Concentrate by Addition of Aluminum

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Mechanochemical reduction of ilmenite concentrate (FeTiO_3) with elemental aluminum powder was performed by high-energy milling in an industrial eccentric vibratory ball mill ESM 656-0.5 ks (Siebtechnik, Germany). The mechanochemically reduced ilmenite with various times of milling was characterized by X-ray diffraction analysis, which confirmed the presence of the Al_2O_3 and Fe_2Ti phases after 120 min of milling. Thermal analysis evidenced the completion of a mechanochemical reduction during milling. After 360 min of milling, the Fe_2Ti phase decomposed to α -(Fe,Ti) alloy, which was proven by ^{57}Fe Mössbauer spectroscopy. X-ray photoelectron spectroscopy detected the amorphous TiO phase in product after mechanochemical reduction, which is in accordance with thermodynamic prediction. Decreasing of specific surface area after 60 min of milling resulted from growing layers of the solid products of FeTiO_3 mechanochemical reduction.

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1. Introduction

The mineral ilmenite, FeTiO_3 , belongs to a group of titanium-containing minerals and its world's production reached 5.19 million metric tons in 2009 [1]. At present, FeTiO_3 is the most important source of titanium for the titanium industry. The preparation of metals and alloys by the reduction of their salts with metals has been described in pyrometallurgy [2]. The method is characterized by the fact that the reducing metal is converted by high temperature to a solid or a liquid product and not to a gas as in other reducing processes. The main parameters of these so-called metallothermic reactions are the contact surfaces of reacting particles and their area, where the solid-state reaction starts [3]. By applying mechanical activation, this parameter can be increased. It has been shown that the coefficient of the diffusivity of solids can be enhanced up to 3 orders [4, 5]. Both reactants and products are evenly dispersed through the reaction volume at a later stage of the redox reaction. The particles decrease to nanometer-sized crystallites and are brought into intimate contact, thereby greatly increasing the reacting areas. The high defect densities induced in the powder further increase the reaction rates by providing a short circuit diffusion path [6]. The mechanochemical reduction of FeTiO_3 with aluminum

and magnesium in a laboratory ball mill has been described by Welham [7, 8]. He demonstrated that the products of a mechanochemical reaction were nanocrystalline TiAl_3 , $\text{Fe}_3\text{Al}_{13}$, and Al_2O_3 after 100 h of milling.

In this paper, we followed a course of ilmenite mechanochemical reduction with elemental aluminum, in dependence on the milling time at ambient temperature in an industrial eccentric vibratory ball mill. We studied the physical, chemical, structural, and thermal changes of mechanochemically reduced ilmenite concentrate.

2. Experimental

2.1. Material

The investigations were carried out with ilmenite concentrate ($> 95\% \text{FeTiO}_3$, $< 5\% \text{SiO}_2$) of Russian origin (GMD, Mineral Trade Company). The chemical composition was as follows: 34.43% Fe, 30.02% Ti, 0.76% Si, 0.47% Mg, 0.42% Al, 0.34% Mn, 0.11% Zn, 0.09% Ca, 0.07% Cr, 0.06% Co, 0.03% Ba, 31.63% O and 1.57% insoluble rest.

2.2. Mechanical activation and mechanochemical reduction

Mechanical activation of FeTiO_3 was performed in an industrial eccentric vibratory ball mill ESM 656-0.5 ks (Siebtechnik, Germany) in air atmosphere and room temperature for 5–360 min with 100 g FeTiO_3 per charge. The mechanochemical reduction of FeTiO_3 with elemental aluminum Al (99.5%, Alfa Aesar, Germany) as a reductant was performed in the same mill in an argon

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atmosphere for 5–360 min with 100 g FeTiO_3 and Al mixture per charge. The other conditions were the following: 5 l steel satellite milling chamber, steel balls with a diameter of 30 mm with a total mass 17 kg, rotational speed of the eccentric 960 rpm. This type of mill is currently used in an animal food industry and was developed by Gock and Kurrer [9, 10]. The feed for mechanochemical reduction was the stoichiometric mixture of $\text{FeTiO}_3:\text{Al} = 0.49 \text{ mol}:0.96 \text{ mol}$ corresponding to the total mass 100 g of the precursors. According to the thermodynamic calculation using FactSage with FactPS database (no solution phases included) it was found that FeTiO_3 is thermodynamically unstable in the presence of Al, and the Al_2O_3 phase is already formed at ambient temperature. Subsequently, TiAl, TiO, and Fe_2Ti are stable phases up to 1057°C. With increasing temperature, TiAl phase decomposes and FeTi phase is developing. Between 1100°C and 1700°C, the following phases are in equilibrium: Al_2O_3 , TiO, Fe_2Ti , and FeTi.

2.3. Characterization techniques

A specific surface area was measured by the low temperature nitrogen adsorption method using a NOVA Station A surface area analyzer (Quantachrome Instruments, USA). Differential thermal analysis (DTA) was performed using the STA 449 F3 Jupiter (Netzsch, Germany) under dynamic conditions in Ar (50 cm³/min) with a heating rate of 10°C/min. The phase composition identification was performed by X-ray diffractometry (XRD) with an X'Pert PW 3040 MPD diffractometer (Phillips, Germany) working in the 2 θ geometry with Cu K_α radiation. The Mössbauer measurements (MS) were performed with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A ⁵⁷Co/Rh source and a α -Fe standard were used. The experimentally obtained spectra were fitted with CONFIT2000 software [11]. The surface chemical analysis was carried out by X-ray photoelectron spectroscopy (XPS) with a SPECS XPS instrument equipped with PHOIBOS 100 SCD and non-monochromatic X-ray source. The spectra were acquired at a basic pressure of 2×10^{-8} mbar with Mg K_α excitation at 10 kV (150 W). The data were analyzed by SpecsLab2 CasaXPS software.

3. Results and discussion

It is generally known that mechanical activation results in a crystal lattice distortion of mineral and an increase in the specific surface area [5]. The specific surface area of mechanically activated FeTiO_3 has increased up to 60 min of milling and reached the value of 10 m²/g (Fig. 1). A further decrease in the specific surface area values over the milling time is caused by the recombination of the fine grains of FeTiO_3 . The specific surface area of mechanically reduced FeTiO_3/Al mixtures has only increased to 30 min of milling and reached the maximal value 3.6 m²/g, because during the first 30 min of milling, the Al particles become ductile and probably cold weld each other along with FeTiO_3 particles. The

plastic deformation makes particles hard and brittle and, therefore, the fracture mechanism activates together with a mechanochemical reduction of FeTiO_3 and the growing layers of solid products. It results in the gradual decrease of the specific surface area after 60 min of milling.

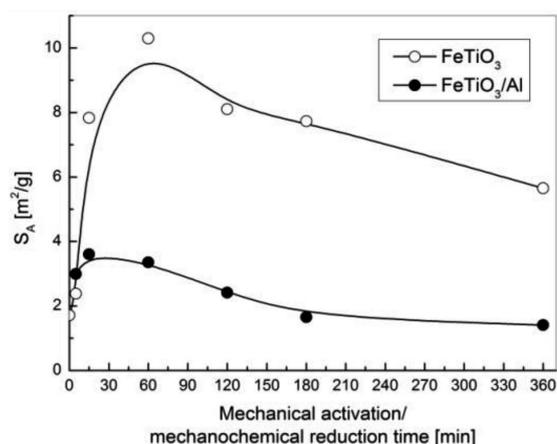


Fig. 1. Specific surface area of the mechanically activated FeTiO_3 and mechanochemically reduced FeTiO_3/Al mixture for various times of milling.

Expected chemical reaction (mechanochemical reduction) and structural changes in unmilled and milled FeTiO_3/Al powder mixtures have been monitored by DTA. The analyses of milled FeTiO_3/Al mixtures have shown that there were no mass changes (< 6.5%) up to 1200°C, confirming the solid-state nature of mechanochemical reduction. The DTA curves of the FeTiO_3/Al mixtures for various times of milling are shown in Fig. 2. The curve of the unmilled FeTiO_3/Al mixture shows an endotherm at 660°C for Al melting and an exotherm due to a reaction at 1015°C, which is in accordance with [7]. After 60 min of milling, Al is consumed below its melting point and two exotherm peaks appeared at a lower temperature (625°C, 775°C). The DTA curves for 120 min and 360 min of milling show no peaks, thus no thermal activity, which proves the completion of mechanochemical reduction during milling.

XRD patterns of unmilled and milled FeTiO_3/Al mixtures are shown in Fig. 3. It is clearly seen that after 60 min of milling there is no evidence of mechanochemical reduction because only broadened peaks for Al (JCPDS PDF 004-0787) and FeTiO_3 (JCPDS PDF 003-0793) are present. After 120 min of milling, new phases appeared: Al_2O_3 (JCPDS PDF 042-1468) and Fe_2Ti (JCPDS PDF 003-1040). This means that a mechanochemical reaction between Al and FeTiO_3 precursors was accomplished during milling. The missing TiO phase is probably amorphous, hence invisible. Longer 360 min milling has caused the Fe_2Ti phase to disappear and a new ambiguous Fe phase (JCPDS PDF 006-0696) was found. According to Guedea and co-authors, the milling of Fe_2Ti leads to its decomposition and formation of a material with a cubic (bcc) structure consistent with the solid solution of Ti in α -Fe [12].

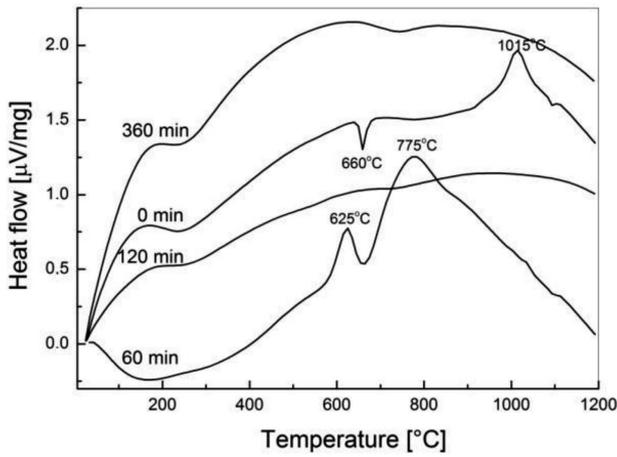


Fig. 2. DTA curves of FeTiO_3/Al mixtures for various times of milling.

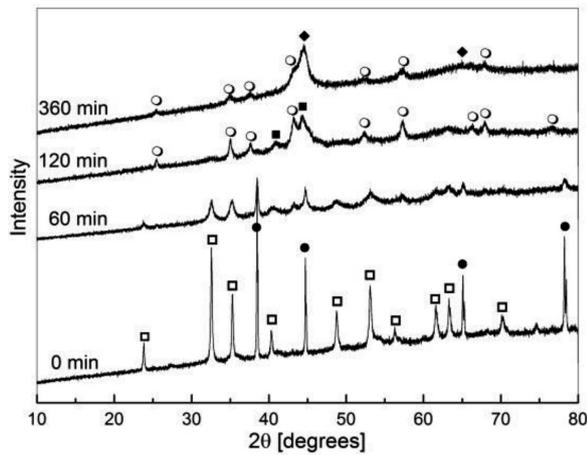


Fig. 3. X-ray diffraction patterns of FeTiO_3/Al mixtures for various times of mechanochemical reduction, □ FeTiO_3 , ● Al, ○ Al_2O_3 , ■ Fe_2Ti , ◆ Fe.

MS is a very sensitive and versatile technique that can be used to give information about the chemical, structural, magnetic and time-dependent properties of a material and is widely used to complement XRD analysis. The ^{57}Fe Mössbauer spectrum of unmilled FeTiO_3 , 0 min is fitted with two doublets model (Fig. 4). The results of fitting in Table evidently have shown the presence of Fe in oxidation states Fe^{3+} ($\delta = 0.35 \text{ mm/s}$, $\Delta = 0.47 \text{ mm/s}$) and Fe^{2+} ($\delta = 1.09 \text{ mm/s}$, $\Delta = 0.68 \text{ mm/s}$). The calculated parameters of doublets correspond to nonstoichiometric ilmenite $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3$ [13]. The relative weight of Fe^{3+} component (G) is 25%. In the milled FeTiO_3/Al mixtures, the components ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ is higher than this ratio in unmilled FeTiO_3 (Table). The MS spectrum of FeTiO_3/Al , 60 min consists of the same components as sample FeTiO_3 , 60 min. The ratio of the relative weights of doublets $\text{Fe}^{3+}/\text{Fe}^{2+}$ is calculated as 20/78 in the sample with Al, while in 60 min milled sample without Al it is 35/61. In the spectrum of FeTiO_3/Al , 120 min a new doublet component appeared with the parameters

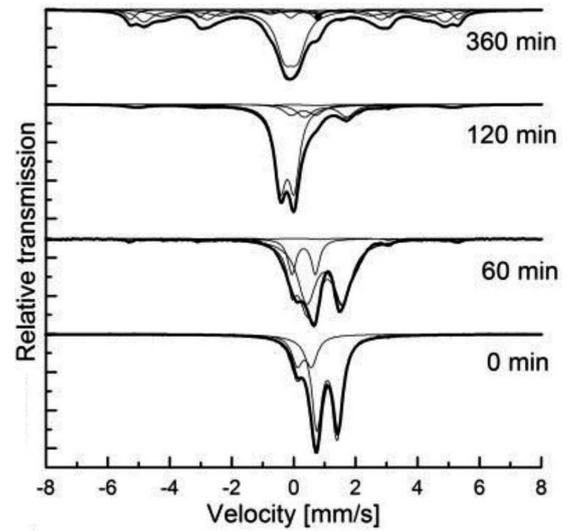


Fig. 4. ^{57}Fe Mössbauer spectra of unmilled FeTiO_3 and FeTiO_3/Al mixtures for various times of mechanochemical reduction.

TABLE

Calculated Mössbauer parameters of investigated samples: isomer shift (δ), quadrupole splitting (Δ), effective internal magnetic field (B), line widths (Γ_{exp}), and relative weight (G) of the partial components in the spectra

Sample, milling time	Components	δ [$\frac{\text{mm}}{\text{s}}$]	Δ [$\frac{\text{mm}}{\text{s}}$]	B [T]	Γ_{exp} [$\frac{\text{mm}}{\text{s}}$]	G [%]
FeTiO_3 , 0 min	Db1- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{3+}$	0.35	0.47	-	0.43	25
	Db2- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{2+}$	1.09	0.68	-	0.40	75
FeTiO_3 , 60 min	Sx- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.00	0.00	32.8	0.31	4
	Db1- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{3+}$	0.36	0.75	-	0.40	35
	Db2- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{2+}$	1.02	1.10	-	0.71	61
FeTiO_3/Al , 60 min	Sx- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.00	0.00	32.9	0.30	2
	Db1- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{3+}$	0.32	0.76	-	0.32	20
	Db2- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{2+}$	1.00	1.16	-	0.72	78
	Sx- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.00	0.02	31.7	0.88	9
FeTiO_3/Al , 120 min	Db1- $\text{Fe}_2\text{Ti-Fe}^0$	-0.21	0.44	-	0.44	65
	Db2- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{3+}$	0.32	0.81	-	0.56	11
	Db3- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{2+}$	1.03	1.37	-	0.59	15
	Sx1- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.02	0.00	32.9	0.37	11
FeTiO_3/Al , 360 min	Sx2- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.02	0.01	30.1	0.62	24
	Sx3- $\alpha\text{-(Fe,Ti)-Fe}^0$	0.04	-0.02	26.3	0.94	20
	Db1- $\text{Fe}_2\text{Ti-Fe}^0$	-0.09	0.42	-	0.66	39
	Db2- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{3+}$	0.32	0.85	-	0.40	5
	Db3- $\text{Fe}_{1+x}\text{Ti}_{1-x}\text{O}_3\text{-Fe}^{2+}$	1.00	1.16	-	0.36	1

$\delta = -0.21 \text{ mm/s}$ and $\Delta = 0.44 \text{ mm/s}$, corresponding to Fe in the Laves phase Fe_2Ti [12]. The MS spectrum of FeTiO_3/Al , 360 min is consisting of 50% magnetically ordered phase. This is in accordance with a previous investigation of the decomposition of the Laves phase Fe_2Ti into $\alpha\text{-(Fe,Ti)}$ alloys during milling [12] and confirm the rightness of X-ray diffraction pattern identification.

X-ray photoelectron spectroscopy (XPS) is being used as a surface analytical tool to determine the surface chemical structures. The XPS survey spectra

have demonstrated changes that are caused by a mechanochemical reduction in the surface stoichiometry of the products. The detailed spectral lines of Ti 2p and Fe 2p are shown in Fig. 5a and b. The binding energy

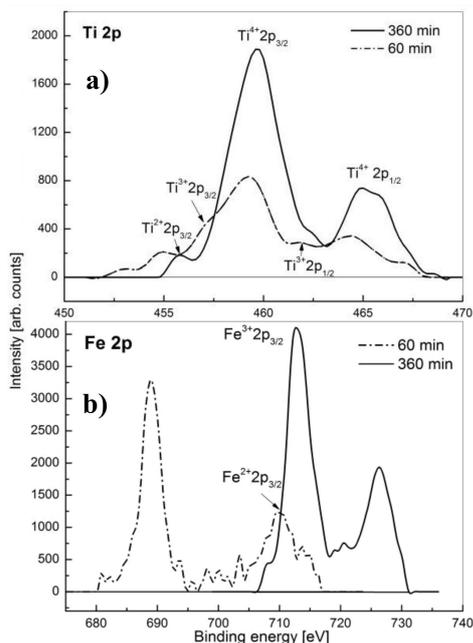
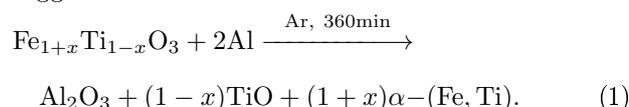


Fig. 5. (a) Ti 2p XPS spectrum of FeTiO₃/Al mixtures for 60 and 360 min of milling. (b) Fe 2p XPS spectrum of FeTiO₃/Al mixtures for 60 and 360 min of milling.

(BE) values 459.5 eV and 465.2 eV of the Ti 2p_{3/2} and Ti 2p_{1/2} lines correspond to Ti⁴⁺ doublet [14, 15]. In addition, minor contributions from Ti²⁺ (BE (Ti 2p_{3/2}) = 456 eV) and Ti³⁺ (BE (Ti 2p_{3/2}) = 457.4 eV and BE (Ti 2p_{1/2}) = 463.1 eV) have appeared in the spectrum after mechanochemical reduction FeTiO₃ with Al. This confirms the creation of the amorphous TiO phase according to thermodynamic prediction. The spectral lines of the Fe 2p of FeTiO₃/Al mixture after 60 min and 360 min of milling in Fig. 5b are in a different binding energy scale. According to MS data, Fe²⁺ ions in FeTiO₃/Al mixture after 60 min of milling are more present as Fe³⁺ ions and, therefore, the Fe²⁺ peak (BE (Fe 2p_{3/2}) = 709.5 eV) has been clearly identified in the XPS spectrum. This peak is attributed to FeO [16]. The Fe 2p spectrum after 360 min of milling is similar to the spectrum of Fe₂O₃ (BE (Fe 2p_{3/2}) = 711.1 eV), which was prepared as a thin film grown on iron metal [16]. This evidences that α-Fe as a product of mechanochemical reduction of ilmenite has oxidized in the surface layer. On the basis of our results the following formula for mechanochemical reduction of nonstoichiometric ilmenite by addition of aluminum can be suggested:



4. Conclusion

Mechanochemical reduction of nonstoichiometric FeTiO₃ with Al has been achieved after 120 min of milling by ambient temperature in the industrial eccentric vibratory ball mill. The product phases found from the thermodynamic calculations by 1100 °C–1700 °C (Al₂O₃, TiO, Fe₂Ti, and FeTi) have already appeared after 360 min of mechanochemical reduction. The reaction mechanism of the mechanochemical reduction can probably be described with reaction (1). However, the more detailed study would be desirable, which is not the scope of this study. Such mechanochemical processing of ilmenite concentrate decreases the temperature and subsequently the time of thermal reduction of FeTiO₃, which could be used in the titanium industry.

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