

Mechanochemical Treatment of Mineral Raw Material

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(Received August 25, 2001)

Abstract

The application of self-propagating high-temperature synthesis (SHS) and mechanically stimulated self-propagating reactions (MSR) in the processes involved in the processing of geological materials is described. The outlooks of MSR are connected with the possibility to perform several processes simultaneously in a mechanochemical reactor: grinding and activation of the initial and final products, and the combustion of the thermite mixture of solids. Another rapidly developing direction is that connected with the use of geological materials (minerals, ores, concentrates and technogenic waste products) as one of the components of a thermite mixture, both for the treatment of mineral raw by means of SHS or MSR resulting in semi-products (metals and alloys, ceramics and glasses) and for express analysis of natural samples for ecological purposes. Some results of the investigations are considered.

INTRODUCTION

Self-propagating high-temperature synthesis (SHS) is widely used in various branches of science and technology [1, 2]. It is most widespread in metallurgy, chemistry, materials science, ore processing, ecology. It forms the basis of pyrotechnic (thermite) compositions. At present, various aspects of the traditional thermite processes are rather well investigated. Their advantages and shortcomings are due to rapid propagation, including the case when pressure with share in Bridgeman's anvils [3, 4] are athermally combined with very high temperature of the combustion front (up to 5000 K). As a result, the target products are formed as metal beads, sponges or agglomerates. As a rule,

their further investigation requires additional dispersing operations: melting with spraying, grinding, etc.

Mechanochemical methods are widely used, too [5–7]; their application area includes the treatment of mineral raw material [8, 9]. Within the recent years [10, 11], the investigations of mechanically stimulated self-propagating reactions (MSR or MASHS) are rapidly developing. Interest to these processes is explained by the possibility to perform several processes at the same time in one mechanochemical reactor: activation of the initial and final products, and chemical reaction of combustion itself. Because of this, replacement of SHS processes by MSR, whose rate can be governed in mechanochemical reactors by changing

the conditions of mechanical treatment from explosive or glowing regime to gradual progress, has broad outlooks.

The major advantages of thermite processes are connected with their small energy consumption (they proceed due to substantial thermal effect of the reaction) and universal character (they can be performed either under natural conditions in sites where ores and concentrates occur, or in special reactors under vacuum or any gas medium). In addition, there is the possibility to govern the rate of thermite process by changing the ratio of the material to be reduced and the reducing agent, or by adding oxidizers that increase the enthalpy of reaction, collectors (metal oxides) and fusing agents (neutral additives) that decrease heat evolution and possess other special properties, for example change the structure and chemical composition of primary minerals in ore or concentrate.

PROCESSING GEOLOGICAL MATERIALS WITH THE HELP OF SHS

It is known [12] that there are two methods to perform SHS processes (Fig. 1). Let us consider some features of processing geological materials both by means of combustion front quenching and by the quasi-adiabatic SHS.

As we understand, thermite technologies applied to geological materials can be divided into small- and large-scale processes. On the other hand, they can be classified by final products, which can be considered as a material ready for further use (metals, alloys and ceramics), or as a raw material for further processing (semi-products); by realization method (under natural conditions, in protective or active atmosphere, in special equipment, *etc.*); by final purpose (solution of ecological, analytical or economic problems). The economic aspect is solved, as a rule, by using the cheapest energy components in the thermite mixture.

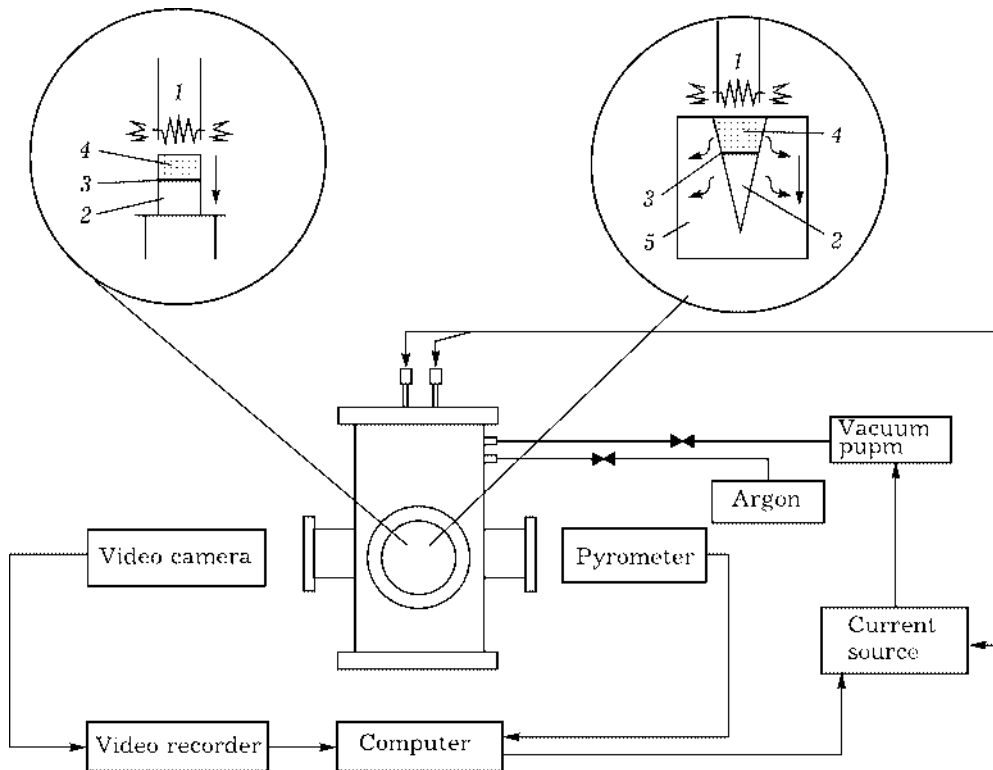


Fig. 1. A scheme of modern methods to perform SHS processes [12] : 1 - a device to initiate SHS; 2 - starting material; 3 - reaction front; 4 - final product; 5 - massive copper or duralumin block; a circle to the left is adiabatic SHS, a circle to the right is SHS with the quenching of combustion front.

ture: carbon, magnesium, aluminium and sulphur powders.

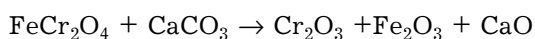
Large-scale SHS processes include obtaining and/or extraction of metals from minerals, ores, concentrates and technogenic raw materials that can be used in the production of construction materials, high-melting substances and rare metals. Let us consider specific examples of thermite processes investigated by us (references in parentheses are directly or indirectly related to the problem under consideration).

1. Pyrrhotine concentrate (see also [13]). Thermite mixture with the concentrate from the Norilsk SMP, containing ~85 % of metal sulphides based on pyrrhotine, in its optimal version had the following composition, % mass: concentrate, 80; Al, 12.5; Mg, 4; carbon, 3.5. The mixture was put into a sand pit or (under laboratory conditions) in a massive reactor made of duralumin. After thermite process was over, a bead of metal alloy was obtained (~45 % of the mass of mixture), surrounded by slag of Al and Mg oxides and sulphides. The composition of the bead was as follows, mass fraction, % mass: α -Fe - 88.1, Ni - 4.3, Cr - 0.74, Cu - 0.6, Ti - 0.45, Co - 0.2; r/T: Pd - 12.2, Pt - 1.7, Rh - 1.5.

2. Manganese ores (oxide and oxide-carbonate) [14, 15]. A sample of ore from the Tyn'in deposit, represented by rhodochrosite (30–45 %), quartz (25–40 %) and a clayish material, had the following composition, mass %: SiO₂, 37.2; Mn (calculated for the metal), 16.7; Al₂O₃ - 7.2, Fe₂O₃ - 5.5, FeO - 2.2, TiO₂ - 0.6, CaO - 2.9, MgO - 2.5, K₂O - 1.4, Na₂O - 0.6, P₂O₅ - 0.3, S - 0.9; losses for calcinations, 20. Direct thermite process with of the ore only with Al results in the bead (ferrosilicomanganese) with silicon content up to 15 %; it requires large consumption of relatively expensive Al powder. Because of this, the sample is washed with water to remove the clayish constituent; then the sample is kept at 300–600 °C for 3–1 h in order to dry and decompose rhodochrosite to manganese oxide. The resulting concentrate contains as much as 32.4 % Mn and is used to make thermite (% of the concentrate mass): Al (25–30); fusing agents: Na₂B₄O₇ (12–15) and CaF₂ (5–10). The bead contains, % mass: Mn - 78, Fe - 21, P - 0.05 (S is absent). It should be

noted that this method can be easily realized directly at the deposit of manganese ores.

3. Chromite ores [16–18]. Chromite concentrates of the following ores were used in experiments: a) from stratiform deposits (Aganzero, Karelia); in this ore, chromium is connected with pyroxenes (diopside), the initial Cr₂O₅ content of the ore being 25–26 %; b) from the Alpine type deposits (Ri-Rai-Iz, Polar Urals), in which chromium is connected with olivine at the initial content of Cr₂O₅ in the ore ~30 %. The main goal was to obtain ferrochromium. The concentrate (fraction with the particle size less than 0.1 mm) with limestone at a ratio of 3 : 1–5 : 1 is kept at a temperature of ~1000 °C for 6–8 h to obtain a cake of oxides:



which serve as natural collectors and a fusing agent (CaO) in the thermite mixture of the following composition (by mass): 4 (cake): 1 (Al) : 0.1 (CrO₃). The bead contains ~80 % Cr, ~8 % Fe, and a series of other nonferrous, rare and precious metals (for example, gold up to 3 %).

4. Columbite, pyrochlorocolumbite and loparite-mossite ores (see also [19, 20]). Technical-grade sodium niobate and niobium concentrates from the mentioned ores were used; the concentrates were subjected to alkaline fusing at a temperature of 450–600 °C in order to obtain the niobate of an alkaline metal. Niobates were washed from water-soluble impurities, dried, crushed, and used to prepare thermite mixtures of the following composition, % mass: 50–70 (niobate), 27–45 (Al), 3–5 (Mg). The niobium content of the resulting bead was 75–97 % at the content of hazardous impurities (P, S, etc.) less than 0.01. The proposed method with some variations (carbon is also used) can be applied in processing tantalite-columbite (Nb, 7%; Ta, 12 %) and tantalite (Ta, 35 %) concentrates.

5. Utilization of the residues from industrial works (see also [21–24]). As an example, let us consider processing of the wastes of a plane-building plant. When manufacturing details, enormous amount of chips is formed during lathe and milling treatment of large aluminium parts. On the other hand, residues containing valuable metal components are formed during the treatment of plane parts in solu-

tion-melt and electrolysis works. Thermite process involving residues and chips allowed one to bring almost all the nonferrous and rare metals in the bead; the resulting ecologically safe slag based on Al_2O_3 can be used in construction.

Let us consider small-scale thermite processes investigated by us.

1. Obtaining precious jewels (see also [25, 26]). A necessary condition for obtaining diamonds is high pressure and temperature. Because of this, we used either appropriate standard autoclaves or specially manufactured explosion chambers made of heat-proof alloys of EI652 and 12Kh18N10T grades. Among a wide choice of possible thermite compositions, we shall mention only two examples, % mass: a) 52 g of mixture Mg (20), Al (50), Zr (0.1), Ce (0.9), graphite (4), Cr_2O_3 (10), NiO (10), Fe_3O_4 (2), MnO_2 (3) is placed into a chamber made of 12Kh18N10T steel, ignition of thermite is initiated, the resulting bead (15 g) is dissolved in Aqua Regia (several hundred diamond crystals were detected on the filter; their size varied from 10 to 500 nm, with total mass of 0.45 carats; b) 100 g of a mixture containing diamonds (0.1–1 mm fraction) (9), Mg (17), Al (30), Ce (5), Zr (1), SnO_2 (6), Cr_2O_3 (10), Co_3O_4 (2), MoO_3 (5), NiO (5), Fe_3O_4 (10) is placed in EI652 autoclave (diamonds grown up to the size of 10–100 nm at a ratio of 1 : 1 to the number of initial crystals were detected on the filter).

2. Obtaining precious metals from schlichs and residues. In case of high (>3–5 %) content of precious metals (for example, in schlichs and semi-products), thermite recovery becomes profitable; it allows obtaining high-grade metals. We investigated the wastes of photographic labs (silver-containing multicomponent solutions). It is very easy to obtain silver from these solutions. Thermite process slime + Mg and/or Al allows obtaining rather pure silver.

3. Thermite analytical procedures (see also [27, 28]). Preparation of anodic alloys is used to recover precious metals from various materials (ores, concentrates, semi-products). This method can also be used for more precise analytical determination of precious metals in samples both under the field and laboratory conditions. We shall describe the results for only one system among the variety of the investi-

gated ones. A sample composed of pyrite and chalcopyrite was added to a mixture of the following composition, % mass: sample, 60; magnesium, 27; copper oxide, 3; iron oxide, 2; fluoride, 8. The bead contained precious metals recovered by electrolysis; their content was 3.5 g/t, calculated for the content in the sample. A standard analytical procedure gave 2.95 g/t.

Some related specific directions of SHS investigation should also be mentioned: investigation of the effect of preliminary mechanical treatment of the components of thermite mixture of SHS [7, 12, 29, 30]; examination of the role of slag formed in thermite process, and its possible applications as ceramics, abrasive materials, *etc.* [9, 31]; utilization of radioactive wastes [32, 33]; power engineering, ecology, *etc.* [34].

MSR WITH GEOLOGICAL MATERIALS

Systematic investigation of MSR with geological materials as components of thermite mixture started recently; a generalization is presented in [9]. Our experiments on MSR with mineral raw material were performed in AGO-2 planetary-centrifugal ball mill (steel, 0.253 g mass, radius $R = 0.2$ cm, with variation of the number of balls ($N = 100$ –424) and surface ($S_b = 0.251N \text{ cm}^2$) of ball load) with two drums (steel, cylinder, height $h = 4.6$ cm, radius $l_2 = 3.1$ cm, volume $V = 140 \text{ cm}^3$, surface $S_v = 150 \text{ cm}^2$), water cooling (water flow rate $\sim 60 \text{ cm}^3/\text{min}$, rotation frequency $\omega_1 = 12 \text{ s}^{-1}$, opposite number of drums rotation $\omega_2 = 29 \text{ s}^{-1}$) with the following characteristics [35]: geometric factor, $m = l_1/l_2 = 1.7$; kinematic factor $k = \omega_2/\omega_1 = -2.4$; $\cos \varphi = -(1 + k)/m = 0.82$; rate of ball collisions with drum wall, $W = 2\pi\omega_1 l_2 [(k + 1)^2 + m^2 - 2m(k - 1)\cos \varphi + (m + 1)^2]^{0.5} = 11 \text{ m/s}$. A weighed portion of material to be treated was 5 g, treatment time 90 min. Products of mechanical activation were investigated by standard procedures involving thermal analysis (DTA, $10 \text{ }^\circ\text{C}/\text{min}$ to 900 – $1000 \text{ }^\circ\text{C}$ in argon) and XPA. The most important results not reported in [9] are listed below.

1. Induction period of the ignition of MSR (see also [9–11]). Experimentally, the moment of MSR ignition ($t = \tau^*$) is detected as a sharp

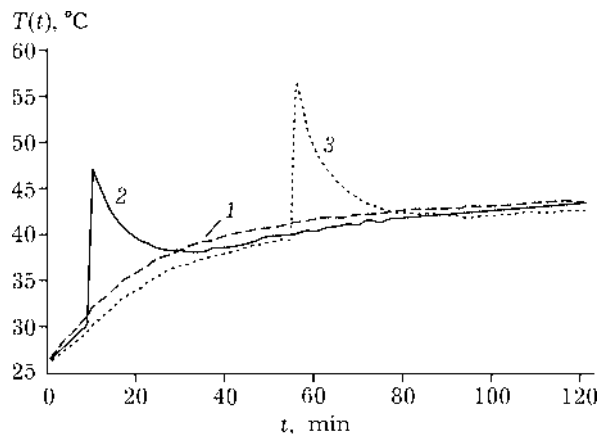
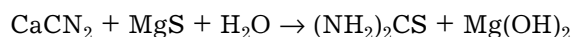


Fig. 2. Change of the temperature of external wall of the ampoule of SPEX 8000 mill during MSR $<3\text{Fe}_3\text{O}_4 + y\text{Al}$ [37]: $y = 2$ (1), 8 (2), 16 (3).

change of temperature T at an arbitrary point of the wall of mechanochemical reactor with time t of mechanical treatment [36]. A typical $T(t)$ dependence for aluminothermal treatment of magnetite in a SPEX 8000 mill on the composition of thermite mixture [37] is shown in Fig. 2; some regularities of the change of induction period τ^* depending on the conditions of mechanical treatment and properties of thermite mixture are listed in Table 1. It should be noted [11] that τ^* is a well reproducible parameter for constant conditions of mechanical treatment.

Not all thermite compositions react burning in a mill. For example, for MSR of magnetite $\text{Fe}_3\text{O}_4 + y\text{Al}$, deviation from stoichiometry ($y = 8$) causes an increase of τ^* ; for $16 < y \leq 2$, combustion does not occur at all (see Fig. 2). MSR of hematite $\text{Fe}_2\text{O}_3 + 2\text{Al}$ occurs in the gradual regime; complete transformation is achieved after mechanical treatment in SPEX 8000 mill for ~ 10 h [12], while in KhK871 planetary mill it takes less than 1 h [9]. One of the criteria of MSR ignition, in addition to temperature, can be the data of XPA of the product of mechanical activation. Combustion is accompanied by crystallization of final products; their further treatment, as a rule, results only in broadening of XPA lines. Reflections of the final products of combustion for the MSR $\text{Fe}_{1-x}\text{S} + \text{Mg} \rightarrow \text{Fe} + \text{MgS}$ are shown in Fig. 3; MgO lines are due to the mass fractions of metal oxides $\sim 15\%$ in our samples of pyrrhotine concentrate, see above). It should be noted that both SHS and MSR of pyrrho-

tine concentrate with magnesium or calcium (MSR proceeds with combustion, too) are practically important because they allow one not only to recover all metal components into the bead or in the magnetic $\alpha\text{-Fe}$ phase but also to obtain sulphides necessary for the production of thiocarbamide (which is also used to recover precious metals) by cyanamide method:



2. MSR of complex minerals and ores. Above we considered MSR treatment of some simple minerals, including the combustion regime. Of practical interest is MSR of difficultly processable complex minerals, such as ilmenite (FeTiO_3), zircon (ZrSiO_4), chromite (FeCr_2O_4) and manganese ores. For example, there is a problem to recover oxygen at the future basis on the moon, because its transportation is very expensive. The moon rocks are composed of ilmenite; because of this, the authors of [38] investigated MSR in the system ilmenite – carbon under vacuum (we investigated MSR of the Aldan ilmenite with the addition of Al, Mg and S). The treatment of zircon by means of MSR with Mg and Ca was investigated in [39]; in [39, 40] also with the oxides and hydroxides of alkaline earths (we investigated MSR of zircon also with aluminium and boron; treatment of chromite and manganese ore was studied by MSR in thermite mixture of the same composition as that for SHS experiments, for comparison).

Common features of all these studies were as follows. MSR proceed in glowing or gradual more, leading finally to complete amorphization of thermite mixture (in [38–46], this was achieved after hundreds hours of mechanical treatment in a multi-purpose vertical mill [47] made of 316S steel with 4–5 single-inch balls made of 420C steel, equipped with magnetic drives, at the ball to sample mass ratio of

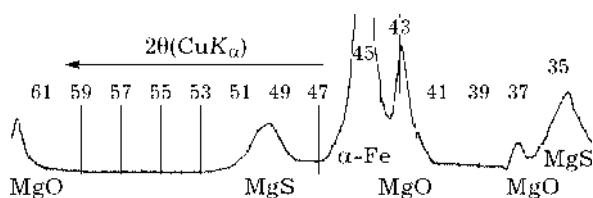


Fig. 3. XPA spectrum of a mixture of 3.56 g of pyrrhotine concentrate with 1.51 g of magnesium powder after mechanical treatment in AGO-2 mill ($N = 200$).

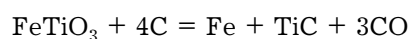
TABLE 1

Induction period of the ignition of MSR (τ^*) of minerals (cuprite, tenorite, bunsenite, zincite and magnetite) with titanium, zirconium, hafnium, and aluminium in a SPEX8000 mill, depending on the conditions of mechanical treatment

Reaction (<i>ND</i> = 15S, <i>m</i> = 3 g)	τ^* , s	Major (and minor) phases in the final product	Reaction	Conditions		M = Ti		M = Zr		M = Hf	
				<i>ND</i>	<i>m</i> , g	$-\Delta_r H^\circ$, kJ/mol	τ^* , s	$-\Delta_r H^\circ$, kJ/mol	τ^* , s	$-\Delta_r H^\circ$, kJ/mol	τ^* , s
$3\text{Fe}_3\text{O}_4 + y\text{Al}$											
<i>y</i> = 2	No combustion	$\text{Fe}_3\text{O}_4(\text{Al})$	$2\text{CuO} + \text{M} =$ $2\text{Cu} + \text{MO}_2$	3L	3	620	60	778	15	794	50
<i>y</i> = 6	3180	$\alpha\text{-Fe}$, FeAl_2O_4	$2\text{Cu}_2\text{O} + \text{M} =$	3L	3	598	1730	754	60	772	1980
			$4\text{Cu} + \text{MO}_2$	10S	3		5860		400		4800
<i>y</i> = 8	540±60	$\alpha\text{-Fe}$, $\alpha\text{-Al}_2\text{O}_3$ ($\gamma\text{-Al}_2\text{O}_3$, FeAl_2O_4)	$2\text{NiO} + \text{M} =$ $2\text{Ni} + \text{MO}_2$	3L	3	464	570	622	90	638	470
<i>y</i> = 11	840	$\alpha\text{-FeAl}_{0.333}\text{O}_4$, $\alpha\text{-Al}_2\text{O}_3$	$2\text{ZnO} + \text{M} =$ $2\text{Zn} + \text{MO}_2$	3L	3	244	5860	400	3160	416	4500
<i>y</i> = 16	3360	$\alpha\text{-FeAl}_{0.890}\text{O}_4$, $\alpha\text{-Al}_2\text{O}_3$	$\text{Fe}_3\text{O}_4 + \text{M} =$	3L	3	195	570	273	50	282	130
			$3\text{Fe} + \text{MO}_2$	6L	6		1190		110		320

Note. *N* is number of balls, *D* is diameter, equal to 1.27 cm (L) and 0.635 cm (S).

50(30) : 1. Reflections of final MSR products appear either after thermal annealing or during DTA. Other conditions being kept constant, as a rule, temperature of the synthesis of final products from activated samples is lower by hundreds of degrees while the reaction rate is several times higher than for non-activated samples (see [38] the example involving MSR



followed by the recovery of oxygen in the reaction $\text{CO} + \text{H}_2 = \text{C} + \text{H}_2\text{O}$).

MSR of zircon (Bashgumbez deposit), a mineral that cannot be treated by SHS process, was investigated with boron powder (B sample) at $N = 300$, magnesium (M) at $N = 424$ and aluminium (Al) at $N = 401$. It is stated that B and A samples were fully amorphous (the same effect was obtained in [39] by treatment for 340 h, and in [40] for 225–200 h); XPA of the sample M (final product was obtained as granules with a size up to 2 mm) revealed only the broadened lines of the initial zircon. DTA of the A and M samples showed the absence of effects in Al and Mg melting (M sample has two strong exothermal peaks at 390 and 580 °C); XPA of the B sample after DTA exhibited only the presence of reflections of initial zircon. Sample A remained amorphous after DTA (it was demonstrated in [41] that the crystallization of amorphized zircon occurs only at temperature above 1200 °C); the appearing very weak reflections were too broad to relate them to any phases. The gradual MSR has been unambiguously stated only for the M sample ($\text{ZrSiO}_4 + 4\text{Mg} = 4\text{MgO} + \text{ZrSi}$); XPA after DTA demonstrates the presence of reflections related to magnesium oxide and zirconium silicide (ZrSi) (compare with the results of [46]). MSR does not proceed in the system composed of zircon and boron. Similarly difficult is crystallization of the final products in the systems with ilmenite at $N = 100$ (nevertheless, DTA of activated samples up to 1000 °C involves the disappearance of the conserved reflections of initial ilmenite phase; only one clearly expressed reflection of the magnetic phase based on $\alpha\text{-Fe}$ appears). At this background, MSR in the systems with chromite concentrate at $N = 250$ and manganese ore annealed at 500 °C (in order to decompose rhodochrosite) at $N = 150$

can be revealed both in XPA data (manganese, ferrochromium lines) and by the presence of substantial fraction of magnetic phases directly in the products of mechanical activation.

So, it can be stated that the MSR differs from SHS by at least two features: a) the formation of crystallized fine metal phase (for example, after the dissolution of the product of MSR with pyrrhotine in water, metal particles detected in precipitate have a size of 100 to less than 1 micrometer); b) the presence of almost fully amorphized slag phase (except for MSR of pyrrhotine concentrate (see Fig. 3), oxide slag is completely amorphous in MSR of other minerals).

3. MSR of minerals with gases. The reaction $\text{FeTiO}_3 + \text{H}_2 = \text{Fe} + \text{TiO}_2 + \text{H}_2\text{O}$ can also be used at the future basis on the moon to recover O_2 [38, 40]. The effect of a 400 h long preliminary mechanical activation (in vacuum) of the shore ilmenite with mass fraction of rutile 8 % on its reduction at temperature up to 1200 °C in argon flow (100 ml/min) containing 5 % H_2 is investigated in [42]. It is demonstrated that in comparison with the initial sample (4.6 % to 1000 °C) activated samples react with exceeding theoretically expected mass loss (10.5 %, due to the reduction of TiO_2 into Ti_3O_5 and TiO) within time shorter by several orders of magnitude.

The oxidative treatment of ilmenite by mechanical processing for 120 h at the initial pressure of O_2 in drums 200 kPa is investigated in [43]. It is demonstrated that the MSR $6\text{FeTiO}_3 + 3\text{O}_2 = 2\text{FeTi}_3\text{O}_9 + \text{Fe}_2\text{O}_3$ takes place within the first 30 h of treatment; further activation is unimportant. Even more substantial results are obtained in [44] by grinding for 1 h in pure oxygen atmosphere ($\text{MSR Cu}_3\text{AsS}_4 + \text{O}_2 \rightarrow \text{CuSO}_4/\text{CuS} + \text{S}/\text{SO}_2 + \text{As}_2\text{O}_3$ take place, depending on initial O_2 pressure, time of mechanical activation, and temperature (up to 100 °C) in the mill drum, in comparison with grinding for 50 h in argon or air, no changes being detected in the latter cases. This is a full solution of the problem of enargite treatment, as well as other similar geological materials [9].

However, the most promising processes for the treatment of raw materials and for direct preparation of functional materials are MSR in the atmosphere of N_2 . For example, in [46], at the sequential grinding of zircon in vacuum and in pure nitrogen for up to 500 h, it is

stated that $\text{MSR } 3\text{ZrSiO}_4 + 8\text{Al} + \text{N}_2 = 4\text{Al}_2\text{O}_3 + 2\text{ZrN} + \text{ZrSi}_2 + \text{FeSi}$ (from impurities) proceeds. Similar results for other minerals are presented in [9, 47].

An interesting method of treating silicate materials (diopside $\text{CaMgSi}_2\text{O}_6$, enstatite $\text{Mg}_2\text{Si}_2\text{O}_6$, wollastonite CaSiO_3 , akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$) by MSR with CO_2 in a mechanical mortar, AL-1000 and AGO-2 activators is described in [48]. MSR leads to carbonization of silicates (mass fraction of CO_2 being up to 15 %) as carbonate-containing silicate glasses, while their acid treatment leads to complete leaching of Ca and Mg. Some other problems concerning MSR and geological materials are considered in detail in [6–12, 49].

CONCLUSIONS

The possibilities of applying mechanothermite processes (SHS and MSR) to the processing and analysis of geological and technogenic materials are demonstrated. Their advantages involve low energy consumption, simplicity, waste-free character and ecological safety.

The investigation has been supported by the Program of Fundamental Research «Universities of Russia» (Grant No. UR.06.01.001), RFBR (Grants No. 01–05–65048 and No. 01–03–32834) and Integration Grant of SB RAS.

REFERENCES

- 1 A. G. Merzhanov, *Protsessy goreniiya i sintez materialov*, ISMAN, Chernogolovka, 1998.
- 2 *Khimiya sinteza szhiganiyem*, in M. Koidzumi (Ed.), Mir, Moscow, 1998.
- 3 P. V. Brijmen, *Noveyshiye raboty v oblasti davleniy, Isd-vo inostr. lit.*, Moscow, 1948.
- 4 N. S. Enikolopyan, A. A. Mkhitarian, A. S. Karagezyan, *DAN SSSR*, 294 (1987) 912.
- 5 V. V. Boldyrev, N. Z. Lyakhov, Y. T. Pavlyukhin *et al.*, in M. E. Vol'pin (Ed.), *Sov. Sci. Rev. Series, Sect. B: Chemistry*, Vol. 14, Part 3, Harwood Acad. Publ., Amsterdam, 1989, pp. 105–161.
- 6 P. Yu. Butyagin, in M. E. Vol'pin (Ed.), *Chemistry Reviews*, Vol. 23, Part 2, Harwood Acad. Publ., Amsterdam, 1998, pp. 89–165.
- 7 T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, *Uspekhi khimii*, 70 (2001) 52.
- 8 V. G. Kulebakin, V. I. Terekhova, V. I. Molchanov, A. M. Zhizhaev, *Aktivatsiya vskrytiya mineral'nogo syr'ya*, Nauka, Novosibirsk, 1999.
- 9 F. Kh. Urakaev, V. S. Shevchenko, A. P. Chupakhin *et al.*, *FTPRPI*, 6 (2001) 78.
- 10 F. Bernard, E. Gaffet, *Int. J. of SHS*, 10 (2001) 109.
- 11 F. Kh. Urakaev, L. Takacs, V. Soika *et al.*, *Khimiya v interesakh ustoychivogo razvitiya*, 10 (2002) 255.
- 12 G. Cao, G. Concas, A. Corrias *et al.*, *Zeitschrift für Naturforschung (A)*, 52 (1997) 539.
- 13 V. I. Volkov, V. G. Dyachenko, *Tsv. metalli*, 2 (1995) 40, 51.
- 14 M. I. Gasis, *Marganets, Metallurgiya*, Moscow, 1992.
- 15 T. G. Gabdullin, Ph. D. Thesis, Moscow, 1992.
- 16 G. P. Yugov, I. N. Chernega, Pat. 2103401 RF, 1998.
- 17 A. V. Simonyan, V. I. Ponomarev, V. I. Yukhvid, *Int. J. of SHS*, 8 (1999) 81.
- 18 P. Zivanovich, R. Curcich, G. Djurkovich *et al.*, *Ibid.*, 10 (2001) 91.
- 19 K. Kobayashi, T. Fujinuma, Pat. 0509447 Eur., 1992.
- 20 O. I. Ripinen, O. N. Tolstykh, Pat. 2074114 RF, 1998.
- 21 M. Sittig, *Izvlacheniy metallov i neorganicheskikh soyedineniy iz otkhodov: Spravochnik, Metallurgiya*, Moscow, 1985.
- 22 G. P. Shveykin, V. A. Perelyaev, *Izv. RAN. Ser. khim.*, 2 (1997) 233.
- 23 Y. Miyamoto, S. Kanehira, K. Hirota, O. Yamaguchi, *Int. J. of SHS*, 9 (2000) 357.
- 24 G. Cao, S. Doppiu, M. Monagheddu *et al.*, *Ind. Eng. Chem. Research*, 38 (1999) 3218.
- 25 O. I. Ripinen, O. N. Tolstykh, Pat. 2118390 RF, 1997.
- 26 E. A. Levashov, I. P. Borovinskaya, A. S. Rogachev *et al.*, *Int. J. of SHS*, 7 (1998) 103.
- 27 O. I. Ripinen, O. N. Tolstykh, Pat. 2081926 RF, 1997.
- 28 O. I. Ripinen, O. N. Tolstykh, Pat. 2002836 RF, 1993.
- 29 T. V. Barinova, I. P. Borovinskaya, V. I. Ratnikov *et al.*, *Int. J. of SHS*, 10 (2001) 77.
- 30 A. N. Avramchik, O. K. Lepakova, Yu. S. Naiborodenko *et al.*, *Ibid.*, 10 (2001) 83.
- 31 Yu. S. Naiborodenko, E. G. Sergeeva, A. A. Zhigalin, *Ibid.*, 7 (1998) 501.
- 32 N. N. Mofa, G. I. Ksandopulo, T. A. Ketegenov *et al.*, *Ibid.*, 7 (1998) 451.
- 33 O. G. Terehova, O. A. Shkoda, Yu. M. Maksimov *et al.*, *Ibid.*, 8 (1999) 299.
- 34 *Kontseptsiya goreniiya i vzryva kak oblasti nauchno-tekhnicheskogo progressa: Sb. mater., Territoriya, Chernogolovka*, 2001.
- 35 F. Kh. Urakaev, V. V. Boldyrev, *Neorgan. materialy*, 35 (1999) 248.
- 36 L. Takacs, *J. Solid State Chem.*, 125 (1996) 75.
- 37 L. Takacs, *Mater. Lett.*, 13 (1992) 119.
- 38 N. J. Welham, *J. Mater. Sci.*, 36 (2001) 2343.
- 39 T. Puclin, W. A. Kaczmarek, B. W. Ninham, *Mater. Chem. Phys.*, 40 (1995) 73 and 105.
- 40 N. J. Welham, *Metallurgical and Mater. Trans. (B)*, 29 (1998) 603.
- 41 T. Puclin, W. A. Kaczmarek, *Colloid Surface (A)*, 130 (1997) 365.
- 42 N. J. Welham, *J. Mater. Sci. Lett.*, 20 (2001) 1849.
- 43 Y. Chen, *J. Alloys Compounds*, 266 (1998) 150.
- 44 N. J. Welham, *Hydrometallurgy*, 62 (2001) 165.
- 45 T. Puclin, W. A. Kaczmarek, *J. Mater. Sci. Lett.*, 15 (1996) 1799.
- 46 T. Puclin, W. A. Kaczmarek, *J. Alloys Compounds*, 266 (1998) 283.
- 47 A. Calka, A. P. Radlinski, *Mater. Sci. Eng. (A)*, 134 (1991) 1350.
- 48 A. M. Kalinkin, A. A. Politov, V. V. Boldyrev *et al.*, *Neorgan. materialy*, 38 (2002) 215.
- 49 F. Kh. Urakaev, L. Takacs, V. S. Shevchenko *et al.*, *Zhurn. fiz. khimii*, 76 (2002) 1052.