

SELF-PROPAGATING REACTIONS OF BURNING OF THE THERMITE COMPOSITIONS (MT, SHS, MSR) WITH USE OF MINERAL RAW MATERIAL

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It is known [1,2] that there are two ways of realization of the thermite processes – metallothermia and self-propagating high-temperature synthesis (SHS). Let's consider some features of processing of geological materials both by methods MT and SHS in natural and laboratory conditions and mechanically stimulated reactions of burning (MSR) of the thermite compositions in mechanochemical reactors [3-review].

The thermite technologies are subdivided into two classes – much and low-tonnage. On the other hand, the thermite technologies can be classified by a final product, which can be considered as ready for use or as raw material for further pyrometallurgical processing. Classification is possible by a way of realization also – in natural conditions, in a protective atmosphere, in the special equipment etc. And, at last, if applied and somewhat theoretical aspects of the thermite processes are studied sufficiently, their analytical, economic and ecological opportunities aren't practically touched on. Economic aspect, as a rule, is solved using as reducing agents in a thermite batch the cheapest power additives – powdered C, Mg, Al and S.

MT and SHS processes of obtaining and/or extraction of metals from minerals, ores, concentrates and technogenic raw material belong to multitonage manufactures. They can be used in manufacturing constructional, refractory and precious metals. Let's consider concrete examples of developed thermite technologies:

- *Pyrrhotite concentrate and sulphide ores.* The thermite batch with concentrate from Norilsk GMK containing ~85% sulphides (most of all FeS₂) in optimum established variant had composition (in wt.%): a concentrate – 80%, aluminium – 12.5, magnesium – 4, carbon – 3.5. The stirred batch is filled up in natural conditions to a sandy pit, or in laboratory conditions to the massive duralumin reactor. After completing of the thermite process a regulus of the metal alloy in the amount of 45% in relation to the weight of the starting mixture is formed. It is covered with slag of Al₂O₃, MgO, Al₂S₃, MgS and has the composition (in wt.%): α-Fe – 88.1, Ni – 4.3, Cr – 0.74, Cu – 0.6, Ti – 0.45, Co – 0.2 and (in gram/tonne) Pd – 12.2, Pt – 1.7, Rh – 1.5.

- *Manganese ores (oxide and oxide-carbonate).* By way of example one can consider Tyniyan deposit's ore. It includes: rhodochrosite (30-45%), quartz (25-40) and clay material and has the following composition: (in wt.%) SiO₂ – 37.2, Mn (in recalculation on 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, the percentage of loss after annealing – 20. The direct thermite process of the ore only with aluminium give a metallic regulus – ferrosilicamanganese with silicon content up to 15% and requires a lot of relatively expansive aluminium powder. Therefore sample (the crude ore) is preliminarily subjected to water cleaning in order to remove clay and other natural impurities, then it is maintained at the temperature 300-600°C for 3-4 hours with the purpose of drying and decomposition of rhodochrosite up to manganese oxide. The received concentrate contains already 32.4% Mn and it's used for preparation of the thermite in % to 1 kg of a concentrator: Al, 25-30; Na₂B₄O₇ as a flux, 12-15; CaF₂, 5-10. The regulus contains (in wt.%): Mn – 78, Fe – 21, P – 0.5, S – isn't present. Let's note that thus way can be easily realized directly on a place of development.

- *Chromite ores.* In our experiments chromite concentrates obtained from ores: a) stratiform deposits (Aganozerskoe, Karelia) where chromitium is connected with pyroxenes (diopside) and initial content Cr₂O₃ in ore is 25-35% b) alpinotype chromite ores (Ri-Ray-Is, Polar Ural) where chromium is connected with olivine and initial content Cr₂O₃ in ore is ~ 30% were used. A main object is to produce ferrochromium. The concentrate (fraction <0.1 mm) with a limestone in the ratio of 3:1 - 5:1 is subjected to thermal treatment at the temperature 900-1000°C for 6-8 hours for producing of the sinter of oxides FeCr₂O₄ + CaCO₃ → Cr₂O₃ + Fe₂O₃ + CaO that serve as natural collector and flux (CaO). In the thermite batch the following weight composition: 4 (sinter): 1 (Al): 0.1 (Cr₂O₃). The regulus contains Cr ~ 80%, Fe ~ 8% and a number of other non-ferrous, rare and the precious metals (for example up to 3%).

MSR in application to geomaterials are only at a stage of scientific researches. Therefore we studied MSR of mentioned above materials using small samples in weight and they as well as a number of other MT and SHS processes can be referred to low-tonnage thermite technologies. It's especially perspective the application of MSR to hard opening minerals and concentrates for direct obtaining from them functional materials [3]. Let's consider a number of such thermite processes:

- *MSR of zircon, one of the most hard-wearing minerals.* Samples of stoichiometric batch of zircon (Bashgumbez) with powder of boron (sample B), magnesium (M) and aluminium (A) in amount of 5 g were subjected to processing in a ball water-cooled centrifugal mill AGO-2 for 90 minutes. The milled powders were analyzed by X-Ray diffraction (XRD) and differential thermal analysis (DTA). It was established that samples B and A were completely amorphous, and in XRD of the sample M there were reflexes, which it was difficult to correlate with the certain substances. DTA (10°C/min, 900°C, argon) in the samples A and M showed absence of melting effects of Al and Mg, and XRD of the sample B after DTA showed presence of reflexes of only initial zircon. The sample A after DTA has remained amorphous, and the appeared weak reflexes were very wide for their correlation with any substances. MSR is unambiguously established only for the sample M ($\text{ZrSiO}_4 + 4\text{Mg} = 4\text{MgO} + \text{ZrSi}$): XRD after DTA has shown presence of reflexes magnesium oxide (MgO) and zirconium silicide (ZrSi). MSR of zircon with boron there is no place;

- *The obtaining of gemstones.* A necessary condition of the obtaining of them (for example diamonds) is a creation of high pressure and temperature. Therefore appropriate standard autoclaves or specially made explosive chambers from heatproof alloys of the marks ЭИ 652 and 12X18H10T were used. From a wide range of possible thermite compositions two examples are given (in wt.%): a) 52 g of a mixture of composition Mg – 20, Al – 50, iron oxide – 2, manganese oxide – 3, Zr – 0.1, Ce – 0.9, graphite – 4 is loaded into the chamber from steel 12X18H10T, ignition of the thermite is initiated, the formed regulus (15g) is dissolved in nitrohydrochloric acid and on the filter several hundreds crystals of diamond with the sizes 10-50 µm in amount of 0.45 carat are revealed; b) 100 g of the mixture of diamond (fraction 0.1-1 µm) – 9, Mg – 17, Al – 30, Ce – 5, Zr – 1, oxides Sn – 6, Cr – 10, Co – 2, Mo – 5, Ni – 5, Fe – 10 is placed into the autoclave. On the filter one can see grown to sizes 10-100 µm crystals of diamond in ratio of 1:1 to initial amount of the primary crystals.

- *The obtaining of precious metals from heavy concentrates and slimes.* In case of large (>3-5%) content of precious metals (for example in heavy concentrates and middlings) the thermite process of their extraction becomes profitable and allows receiving metals of the high order. It has been studied waste products from photographer's studio – multicomponent solutions containing silver. The obtaining of slime from these solutions is easily feasible. The thermite process a slime + Mg and/or Al allows receiving silver of enough high purity.

- *Thermite analytics.* The item concerns a way of the obtaining of anodic alloys for extraction of precious metals from various materials (ores, concentrates, middlings) and can also be used for their exacter analytical determination in samples both in field and laboratory conditions. From a set of the investigated systems results of only one are given. A sample consisting of pyrite and chalcopyrite is mixed with the batch of the following composition (in wt.%) – the sample – 60, Mg – 27, CuO – 3, Fe₂O₃ – 3, CaF₂ – 8. The obtained amount of precious metals in the regulus in recalculation on the content in the sample was 3.5 g/t. It was determined 2.95 g/t by a standard method.

The opportunities and prospects of the application of the thermite processes for processing and analysis geological and technogenic materials are shown. Advantages of the thermite technologies consist in their small power consumption, simplicity, without waste products and ecological cleanliness.

References

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