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EXTRACTION OF RARE-EARTH METALS FROM WASTES MAGNETIC ALLOYS AND WARES FROM THEM

Report 1. Wastes of alloys of the system «samarium-cobalt» and exhaust storage batteries

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There is carried out review, including the description of waste magnetic alloys samarium-cobalt and of spent nickel metal hydride batteries as a secondary raw materials, containing rare-earth metals, and also technologies intended for attraction of rare earth metals and their cleaning from impurities of oxygen and carbon.

Keywords: alloys Sm-Co, nickel metal hydride battery waste, leaching, chemical precipitation, ion exchange, extraction, electrolysis, chlorination, smelting and cleaning from impurities

The last decades demonstrate the considerable increase of production and consumption of rare-earth products. It is explained by that rare-earth metal (REM) possess unique properties, due to what they in a great deal formative development of science intensive technologies.

Ordinary hydrochemical technology of processing of wastes *Sm-Co* alloys includes degradation of wastes and dissolution of them shallow in *HCl* or HNO_3. From solution a samarium is extracted by extraction. The coefficient of segregation for samaria and cobalt is great, therefore for their complete division five stages are enough. Then a samarium is converted in the form of carbonate or oxalate and from them Sm_2O_3 get by tempering. Processing of wastes by this way foresees the making of samaria oxide a cleanness 99,5 %.

Muriatic solution of salts for samaria and cobalt in work [1] run through cation-exchange resin and then aluate cobalt, copper and other metals with help 2n *HCl*. The got eluate runes through anion-exchange resin and process by solution of *NaOH* for deposition of hydrate of cobalt. From cation-exchange resin aluates a samarium and add to solution *NaOH* for deposition of $Sm(OH)_3$. By tempering of both hydrogates at a temperature ~ 1000 °C get the oxides of cobalt and samaria.

Scrap, containing REM and cobalt, dissolve in *HCl* with convert of valuable of all components in the form of chlorides. Cobalt solutions expose to electrolyze and in form oxalates deposition from mother solution by addition of oxalic acid. After dry sediment expose to thermal decomposition at a temperature 1000 °C, getting the oxides of REM.

In the patent of France [2] for dissection of wastes it is suggested to use a nitric acid. From reextract REM deposition as hydroxides or oxalates at tempering further

to the oxides of 99 % cleanness. Extraction of REM is ≥ 95 %.

Similar technology for the regeneration of samaria and cobalt from wastes as powders, shaving or slipping of bars and containing 10-50 % REM and 30-80 % cobalt, offered in a patent [3]. The degregating wastes process by (6-15)*N* solution of HNO_3 at a temperature 15-100 °C. By tempering oxides of REM get sediments with cleanness ~ 99 %. From aquatic solution of cobalt nitrate after extraction of REM deposition of cobalt in composition oxalate. By tempering it got Co_2O_3 cleanness higher 98 %. Extraction of REM and cobalt from wastes on this method exceeds 95 %.

There is worked out and applied in industry technology for utilization of marriage and wastes *Sm-Co* of magnets by their melting and use of remelt in a quantity 12.5-25.0 mass. % from composition of alloy as additions to the cast alloy of $SmCo_5$ for making of material KC37 [4].

There is method of renewal for the oxidized wastes *Sm-Co* magnets by a calcium for joint extraction of samaria and cobalt is perspective.

Processing of the mixed wastes of magnetic alloys (*Sm-Co* and *Nd-Fe-B*) is carried out on hydro- and pyrometallurgical technologies. So, in USA patent [5] processing of mixed scrap of their alloys is offered on a chart «lixiviating-floatation», allowing selective to extract a neodymium and samarium.

Technological chart of processing of the mixed wastes of magnetic alloys of systems *Sm-Co* and *Nd-Fe-B*, in basis of which there is liquid extraction, includes in itself: oxidizing burning at a temperature 700 °C during 8 hours; hydrochloride-acid lixiviating; extraction of EHPNA with extraction in the organic phase of iron; extraction of samaria by mixture of EHPNA-OPO; extraction of neodymium by EHPNA; extraction of copper by VA9; extraction of cobalt by EHPNA. Reestract in all cases it is carried out by muriatic acid [6].

New process of recirculation of samaria and neodymium from scrap of permanent magnets, containing ~ 30 % samaria or neodymium and 50-60 % cobalt or iron, presented in work [7]. A method includes dissolution of scrap in *HCl* or HNO_3, making of sulfates, deposition of iron as jarosite, factious crystallization and electroreduction of Samaria, neodymium and cobalt from sulfate medium.

Chloric method of extraction of REM from dried up slimes of intermetallic connections of Sm_2Co_{17}, $Nd_2Fe_{14}B$ and $LaNi_5$ with the use of chemical transport reactions is considered in work [8]. As chlorinating and transporting agents used a chlorine and Al_2C_{l6}, the chlorides of REM were transported in composition the complexes of $RAlnCl_3$+3*n* (where *R* - REM) and $MA_{l2}C_{l6}$ (where *M* – *Ni*, *Co*). The chlorides sediments of REM concentrated in a hot area furnaces (800-900 °C), and chlorides of nickel and cobalt - in more cold (500.700 (C). Extraction of metals made, %: *Ni* and *Co* > 99, *Sm* > 89.

Original technology of processing «wet» scrap and wastes of magnetic materials considered in the patent of Japan [9]. Wastes dehydrate, dry out and mix up with metallic calcium or with hydrolith calcium in a quantity 1.5-2.5 time greater stoichiometric correlation, necessary for fastening of oxygen and carbon in wastes. The got material is polishing powder, having a middle size of grain of 1-2 mcm and containing oxidized REM.

Optimal mode of lixiviating for scrap of negative plastins of exhaust nickel-hydrogen batteries (concentration of H_2SO_4 2 moth/l, temperature 60 °C, duration 2 hours) offered in work [10].

The process of selection of ions Ni^{2+}, Co^{2+} and REM, from nickel-manganess batteries is presented in work [11]. Lixiviating of scrap was conducted by *HCl* of concentration 12 moth/l, chloride solution was purged from tracks of ions of Fe^{3+} and Zn^{2+}. Then ions Co^{2+} extracted on 93.6 % by two-phase treatment the extracting of Alamine 336. Remaining in raffinate more than 98 % REM extracted by extraction PC88A or deposition of oxalates at pH = 0.5. A nickel as ions Ni^{2+} was deposited on 99 % in form oxalate at pH = 2.

Conclusion. Wastes of magnetic *Sm-Co* alloys and exhaust nickel-metalhydride storage batteries are by valuable secondary raw material, containing rare-earth metals. For extraction and cleaning of REM hydro- and pyrometallurgical technologies are used, namely: lixiviating bi mineral acid, chemical deposition, ionic exchange, liquid extraction, electrolysis, high-temperature chlorinating mineral acids, cleaning from oxygen and carbon by a calcium, melting with addition of titanium or zirconium.

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