NEW RECYCLING METHOD FOR GRINDING SLUDGE FROM THE PRODUCTION OF PERMANENT MAGNETS (ALNICO)

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Abstract

In the grinding process of steel products, considerable amounts of grinding dust are generated, polluted with coolant (oil, oil emulsions), and non-metallic material from abrasive (silicon carbide, aluminum oxide and others). Grinding sludge generated as a result of this mechanism is a valuable source of post-industrial waste containing, apart from iron, such alloying elements as: cobalt, nickel, copper, tungsten, molybdenum, and vanadium. Considering the metallurgical value of grinding sludge, a method for recovering these elements from the sludge has been developed. The article presents a recycling method in a three-stage technological process consisting of sludge de-oiling, sintering, and re-melting in an electrical furnace.

Keywords: Steel, grinding dust, new recycling method

1. INTRODUCTION

When grinding metal products in the machine and metallurgic industry, considerable amounts of fine-grained grinding sludge are generated, **Figure 1**. Apart from metals (iron and alloying elements), this sludge contains abrasive (silicon carbide and aluminum oxide), oil emulsions or oil used as coolant. Grinding sludge generated as a result of machining, containing these materials, is one of the sources of industrial waste, ranked as dangerous waste.

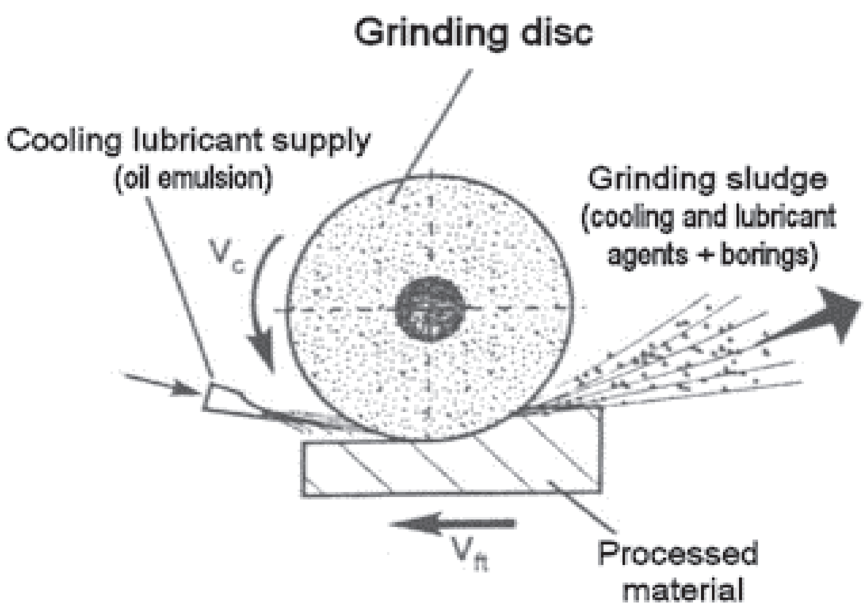

Figure 1 Formation of grinding sludge in the abrasive treatment process

Industrial waste contains substances that, after penetrating the environment, may cause adverse health effects to humans, animals, or plants, and, in most cases, hardly reversible or irreversible contamination of the environment and its resources [1].

Grinding sludge is a very valuable raw material for the iron metallurgy, due to its content of iron and alloy elements i.e. Cr, Ni, Co, Cu, W, Mo, V and others. Their processing is however extremely difficult due to contamination present there, or it is not very profitable due to energy-consuming processing methods. As a result, grinding sludge is deposited at a waste dump. The subject of the research conducted was to develop a new method for recovering alloy elements from grinding sludge, being competitive in the economic and ecological terms as compared to the methods applied to date. The new grinding waste processing method was developed based on the grinding sludge formed during the production of Al-Ni-Co type magnets

2. RESEARCH METHODOLOGY

2.1. Grinding sludge characteristic

The research material for developing the new recycling method was grinding sludge from Alnico 350, Alnico 400, Alnico 550, Alnico 650 alloys, consisting of 3 major component groups:

- the metalic part: 62 ÷ 70 %,
- abrasive from grinding discs: 23 ÷ 31 %,
- emulsion for magnet processing: 4 ÷ 5.5 %.

Table 1 presents chemical analyses of the grinding sludge supplied, whose have been performed in the chemical laboratories of the Ferrous Metallurgy Institute in Gliwice [2].

Table 1 Al-Ni-Co grinding sludge chemical composition

Sample no.	Chemical composition (wt.%)							
	C	Mn	Si	Cr	Ni	Co	Cu	Al
1	2.8	0.06	n.m.	n.m.	12.5	20.0	2.1	14.0
2	2.0	0.10	0.44	0.07	14.0	19.0	2.8	7.0
3	2.8	n.m.	0.59	0.04	9,6	13.2	1.9	21.4

n.m. - not measured

In further processing of grinding sludge, the oil fraction content in the sludge is important. From the data obtained from the manufacturer of the magnets, it seemed that the grinding sludge which was acquired for processing contained micro-emulsion oil for metal machining. It is a semisynthetic oil concentrate that contains mineral oil (20 ± 2 %), corrosion inhibitors (8 %), water condensate (25 emulsifiers ± 2 %), and emulsifiers (the rest). The oil did not contain biocides or other components harmful to health, including sodium nitrite, chlorine, and hardly biodegradable emulsifiers. The tests performed revealed that the content of oil substances in the grinding sludge samples varies around 0.64 4 ÷ 1.65 %

The sieve analysis revealed that the sludge was substantially fine-grained. Almost 94 % of grains were below 0.125 mm. In the batch obtained, approx. 83 % of the sludge mass are magnetic fractions, being fines of the alloy intended for magnets. The remaining approx. 17 % are non-magnetic fractions containing, first of all, corundum abrasive from grinding discs.

Alloy elements from sludge generated during the production of Al-Ni-Co type magnets were recovered on the basis of a four-stage test cycle presented in **Figure 2** [2, 10].

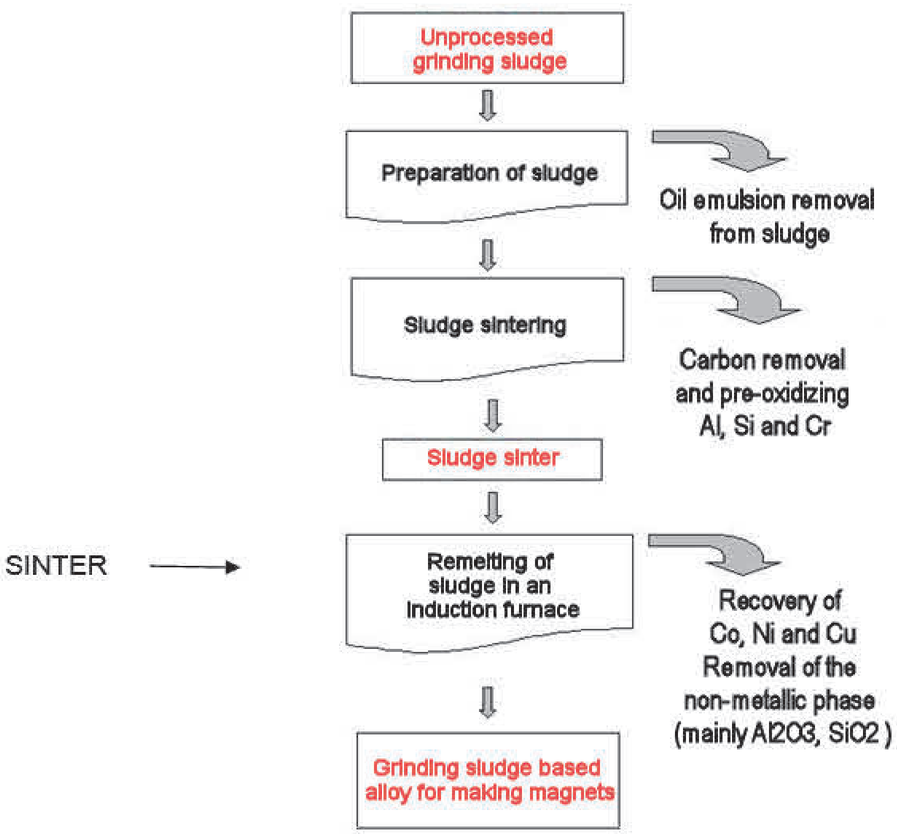

Figure 2 Diagram of the tests performed [2]

2.2. STAGE 1 - Removing oil contaminants

To remove the oil contaminants, the mechanical wet cleaning method was applied [3, 4]. When selecting agents for deoiling of grinding sludge, the principle was to use environment-friendly agents for washing, degreasing, or industrial cleaning, free of halogenated and aromatic hydrocarbons, freons, and detergents and emulsifying compounds.

For grinding sludge deoiling, 21 preparations recommended by an expert company involved in cleaning agent sales and consulting were tested [5-7].

The methodology of the preliminary tests consisted in mixing 100 g of a grinding sludge sample with 200 ml of a solution containing a cleaning agent by means of a laboratory robot. Multi-option tests of deoiling in solutions containing different concentrations of the cleaning agent were conducted. The level of oil removal from the sludge was examined after 1, 3 and 5 minutes of mixing with the cleaning preparations. Then, the cleaning agent was decanted, the sludge dried, and the amount of oil contaminants in the deoiled sample was measured. On the basis of the tests completed, the most efficient and economically feasible preparation for grinding sludge deoiling was selected. For sintering, approx. 1,500 kg of grinding sludge was deoiled each time, no deterioration of this preparation's cleaning properties in the bath was observed. The bath with a concentration of the agent in water of 5 g/l provided deoiling by 62 %. The test (mixing) time was 15 minutes, and the cost of the 80 litre bath - 2.7 euro.

2.3. STAGE 2 - Grinding sludge sintering

In the second stage of the tests, the deoiled sludge was sintered on an experimental sintering pan in various charge configurations. The purpose was to remove carbon and to pre-oxidize Al, Si, Cr, and to bring the sludge to the balled form in order to make dosage to the electrical furnace possible.

This type of sludge has never been subjected to sintering before, and there were no criteria for selecting the most suitable process parameters. It was planned that to obtain the correct process parameters, this waste will be sintered in 3 options:

1) Sludge sintering with added fly ash.
2) Sludge sintering without fly ash.
3) Sludge sintering with various amounts of iron ore.

The sintering mix was prepared in a balling disc, and Alnico grinding sludge was test-sintered on a laboratory sintering pan. During sintering the sludge with fly ash (option 1), the test was aborted in emergency due to a high temperature of waste gas > 800 °C, which could have caused burnout of the grate and damage the sintering pan. This test revealed that the share of fuel (fly ash) in the mix is unnecessary. In option2, the tests were performed without fly ash in the sintering mix. In this version, the sintering process was stable, the flue gas temperature was within 360÷450 ˚C, and the sintering time was from 11'15''÷14'50''. It has been assumed that a large amount of the non-metallic fraction in the sludge will result in the formation of large amounts of slag in the electrical furnace, which may hinder the process of sinter melting in the metal bath. To avoid this problem, it was decided to prepare option 3, in which 5 %, 10 %, 20 % and 30 % of iron ore was added to the sintering mix. For all mixes, the sintering process proceeded in the same way as in option 2.Altogether, from the deoiled grinding sludge, a batch of approx. 2500 kg of sinter was produced (**Figure 3**) with different content of iron ore. The chemical composition of the sinters produced is presented in **Table 2**, and an analysis of the waste gas from sintering in **Table 3**.

Table 2 The chemical composition of the sinters made of Alnico grinding sludge

Sinter composition	Chemical composition (wt.%)										
	C	Mn	Si	P	S	Cr	**Ni**	**Co**	**Cu**	Al	Fe
with fly ash 0 % of iron ore	0.10	n.m.	1.26	n.m.	n.m.	0	**6.62**	**11.24**	**1.32**	20.59	n.o
with 5 % of iron ore	0.014	0.045	1.23	0.012	0.025	0.031	**7.78**	**12.48**	**1.52**	14.67	24.02
with 10 % of iron ore	0.014	0.043	1.00	0.015	0.023	0.023	**8.10**	**12.04**	**1.46**	14.12	24.41
with 20 % of iron ore	0.016	0.039	1.69	0.019	0.016	0.017	**7.82**	**11.67**	**1.31**	13.30	26.80
with 30 % of iron ore	0.016	0.038	1.40	0.020	0.027	0.016	**7.65**	**11.52**	**1.32**	10.08	28.78

Figure 3 Sample sinter from grinding sludge

The chemical analyses of the sinters present a very favourable level of the so-called undesirable elements in the magnet alloys, in particular C, S, P and Cr. The low and very low level of these elements obtained in the sintering process certainly made it possible to use the Al-Ni-Co sinters as a charge for an induction furnace, without having to use additional refining treatments. Minor loss of valuable elements such as: Co, Ni and Cu did not decrease the value of sludge processing with the method applied.

Table 3 The chemical composition of the sinters made of Alnico grinding sludge

Waste gas composition	O_2 (wt.%)	CO_2 (wt.%)	CO (wt.%)	NO (ppm)	NO_2 (ppm)	NO_x (ppm)	SO_2 (ppm)
	11.73÷12.09	0.97÷0.98	1.30÷1.48	14÷21	0	14÷21	68÷82

2.4. STAGE 3 - Remelting the sinters in an induction furnace

In the third stage, the sinter produced was melted down in an electrical induction furnace in order to obtain a full quality charge for the making of permanent Al -Ni-Co type magnets. The heats from the Al-Ni-Co sinters were made at a magnet manufacturer's facility in the induction furnace with the crucible capacity of 110 kg [8]. As part of the tests, two test melts were conducted with different content of sinters and iron ore in the charge. The first melt took place in a crucible with acidic refractory lining and the second one with alkaline refractory lining. The charge of the first melt was Armco iron and Al-Ni-Co sinters without any addition of iron ore. The second melt contained also a charge of Armco iron and sinter pieces with iron ore being added in increasing percentage amounts of the ore in the sinter: 5%, 10%, 20% and 30%. In the two melts, billets of Armco iron were melted in the first place, then after obtaining the assumed temperature, portions of Al-Ni-Co sinter pieces were loaded. Melt 1 made in a crucible with acidic refractory lining did not meet the expectations, in spite of the fact that the first portion of the Al-Ni-Co sinters was melted in the metal bath without problems. However, the increasing amount of dense and sticky slag on the surface of the metal bath caused difficulties in dispensing subsequent sinters and prolonged melting. The type of the lining and the final phase of the furnace campaign caused the need to interrupt the experiment due to the risk of damaging the crucible lining and of a metal leakage. The second test (melt 2) of remelting Al-Ni-Co sinters was prepared in a crucible with alkaline refractory lining, at the beginning of the induction furnace campaign. The sinters were melted in the same way as in the first melt, i.e. under the same temperature conditions of the metal bath and after melting the Armco iron. During melting subsequent sinter portions, no adverse impact of slag on the lining of the furnace or sudden reactions causing disturbance in the metal bath were noticed. After melting the last portion of the Al-Ni-Co sinters, and after reaching the discharge temperature in the metal bath, the metal was poured from the induction furnace into a ladle and casted into casting forms. **Table 4** presents chemical analysis of the casts from test casting.

Table 4 The chemical composition of the alloys with sinter

Melt number	Chemical composition (wt.%)										
	C	Mn	Si	**P**	**S**	**Cr**	**Ni**	**Co**	**Cu**	Al	O
I	**0.010**	0.008	0.25	**0.014**	**0.020**	**0.016**	**4.55**	**7.05**	**1.12**	0.016	-
II	**0.013**	<0.01	<0.05	**0.008**	**0.016**	**0.004**	**4.60**	**7.10**	**0.91**	0.020	0.148

2.5. STAGE 4 - Making magnets with the use of alloy from grinding sludge recycling

In the final fourth stage, the obtained alloy from sinter melting was used as one of the components in the charge for the making of Alnico 400 type magnets (**Table 5**). The magnet manufacturer made 8 experimental castings in an induction furnace.

Table 5 The chemical composition of Alnico 400 magnet [9]

Chemical composition (wt.%)										
C	Mn	Si	P	S	Ni	Co	Ti	Cu	Al	Fe
max 0.03	max 0.05	max 0.15	max 0.03	max 0.1	14.0 15.0	24.0 25.0	max 0.3	2.8 3.5	7.5 8.5	the rest

The charge for the experimental castings was: circulating scrap, iron alloys, Armco iron, clean metals (Ni, Co, Al, Cu), and an alloy from grinding sludge recycling, whose share in the charge was from 10 % to 20 %. The permanent magnets made from the experimental castings have met all the requirements of the standards binding for this class (**Figure 4**).

Figure 4 The Alnico 400 magnets after removing from the moulding flasks

3. CONCLUSIONS

The new grinding sludge recycling method developed under the research made it possible to obtain a valuable material for re-use in the production of permanent magnets. The four-stage process of grinding sludge processing conducted on a laboratory and half-industrial scale demonstrated that it is possible to effectively remove oil from grinding sludge. Alternative tests of sintering deoiled grinding sludge revealed that carbon contained in sludge can serve the role of fuel in the sintering process. Undesirable components such as Mn, P, S are reduced below the value required for this type of alloys. The sintering process makes it possible to recover from sludge highly valuable elements, i.e. Co, Ni and Cu. To obtain a full quality charge for the making of permanent Al -Ni-Co type magnets, the sinters produced should be melted in steel-making processes. On the half-industrial scale, it is possible to process them further in an induction furnace, while on the industrial scale, it will be more beneficial to apply an arc furnace.

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