Refractory Materials from Waste

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The recycling of refractory materials in the chemical, metallurgical and glass industry has only had minor relevance until now because of the high performance required from these materials (stability against corrosion, inert when coming into contact with the glass melt, etc.). Refractory lifetimes are limited because of corrosion at higher temperatures. The best furnace lifetimes has been achieved with chromium oxide and chromium oxide corund refractories. Waste from the production and use of refractory material is generated in three main forms: as residues from cutting and grinding, as refractories which have limited or no contact with glass melts, and as refractories with infiltration of sublimation residues or condensates. The waste material is classified as hazardous waste due to its chromium content. In this study, arc furnace technology was used for thermal treatment of the waste materials to enable recycling of refractory materials.

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1. Introduction

Refractories are ceramic materials used in processes where there are severe service conditions, such as high temperatures, aggressive liquids or gases, or mechanical stress. These processes are found in the metal, cement, ceramic, and glass industries. Although most waste materials are now statistically surveyed (*i.e.*, European waste catalogue, EWC, code 100206, spent refractories), little is known about the quantity arising of various waste refractories. Refractories containing chromium cause the most problems due to the risk of mobilizing toxic hexavalent chromium ions where under certain process conditions, trivalent chromium (Cr_2O_3) can be oxidized to hexavalent Cr (CrO_4^{2-}). *e.g.* contact with alkali metal or alkaline earth metal oxides at elevated temperatures. However, chromium-containing refractories are the most suited to processes with high temperatures and highly corrosive environments.

Chromium-containing refractory wastes are currently treated using physical processes, *i.e.*, crushing, sieving and flotation to remove components that could interfere with its reuse as raw materials for new refractories. Therefore, these materials are used in applications with lower operational criteria.¹⁾ Chemical reduction of the waste together with chromium ores was also successfully tested and produced chromium metal.²⁾

Treatment of spent refractories also conveniently includes the treatment of residues from furnace and refractory construction and installation, *i.e.*, sludge from sawing, grinding, and polishing. In Germany, the production of this sludge alone amounts to approx. 500 tons per year according to co-operating companies.

2. Ecomaterials with a Green Environmental Profile

The world's chromium production is 13.7 million ton/year. The ore-TMR (total materials requirement) is 8.9 thus 121.4 million ton/year ore must be processed,³⁾ therefore it is advantageous to recycle chromium-containing materials and products is to keep the TMR as low as possible. Because

chromium-containing wastes are regarded as hazardous materials requiring either special treatment or safe disposal, products containing chromium cannot therefore be considered free of hazardous substances. However, until now no alternative to refractory chromium oxide, with its high resistivity against corrosion, has been found. If production waste and chromium-containing refractories can be recycled, natural resources could be saved and the generation of hazardous waste considerably reduced. Waste incorporated in manufactured materials avoids disposal in landfills or other sites, so the products are regarded as ecomaterials.⁴⁾ Refractories manufactured from materials derived from recycling are thus good examples of an ecomaterial. The category, ecomaterials with a green environmental profile, is applicable to this type of material.⁵⁾

Chromium oxide in waste refractories is recycled by the formation of mixed Cr_2O_3 and Al_2O_3 crystals (escolait-corund). The Cr_2O_3 -rich waste and clay is melted in an arc furnace and the resulting product can be used as a raw material for new refractories with high resistivity against corrosion. It can be reasoned that the mixed crystals will show at least equal, if not better, refractory properties than the conventional, two-phase $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ refractory mixtures.

3. Experimental Section

The pilot plant used for the experiments consists of a closed 300 kW AC arc furnace equipped with three graphite electrodes with a melting capacity of approx. 100 kg/h. The material is fed continuously via a manual or mechanical feed system into the furnace and smelted by the arc plasma at temperatures exceeding 2100°C. The graphite electrodes are consumed during the operation and so are continuously advanced. This results in a reducing atmosphere in the furnace preventing the oxidation of Cr-III to Cr-VI. Gaseous compounds released during the thermochemical treatment are extracted from the melt by the off-gas system, organic materials decompose in the high temperatures and any CO resulting from the graphite electrodes is oxidized in the afterburner of the off-gas system. The gases leaving the afterburner are quenched immediately to temperatures below

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Fig. 1 Free enthalpy, ΔG , of Cr_2O_3 , Al_2O_3 , and CO as a function of temperature.¹²⁾

200°C. The furnace is described in detail elsewhere.^{6,7)}

The reducing environment can be used to remove heavy metals from the mixtures fed to the furnace. For example, when used for the treatment of ash from municipal solid waste incineration (MSWI), heavy metal compounds are reduced to their elemental form and are either evaporated off through the off-gas system (as in the case of lead and zinc) or sink down to form a layer of metallic alloy (*e.g.*, copper).^{6,8–11)} Reduction to the elemental form is not desirable when recycling spent refractories and chromium-containing sludge, however, at elevated temperatures, the reduction of Cr_2O_3 and even of SiO_2 (to SiO , which is a stronger reducing agent than CO) is possible as can be seen from the thermodynamic data displayed in Fig. 1. [where the values of ΔG are plotted against the temperature¹²⁾]. Reduction of the oxides by CO is thermodynamically possible at temperatures higher than the temperature of intersection of the lines. The formation of carbides has not been taken into consideration here. It is therefore necessary to choose reaction conditions carefully to avoid reduction of chromium to its elemental form. Oxidation of Cr-III to Cr-VI is irrelevant when air or oxygen is introduced due to the thermal decomposition of chromates to Cr_2O_3 and O_2 at high temperatures.

Industrial refractories are produced from corundum and chromium oxide mixtures which have very high melting points as shown in the phase diagram¹³⁾ in Fig. 2. The Cr_2O_3 content in refractories for high-end applications is around 90%. Spent refractory material may contain considerably more unfavourable components after use in melting furnaces, *e.g.*, melting residues. The residual constituents are listed in Table 1.

4. Results

The waste refractories were crushed, milled, and subsequently mixed with clay (Al_2O_3) for experimental investiga-

Fig. 2 Phase diagram of Cr_2O_3 – Al_2O_3 .¹³⁾

Fig. 3 X-ray pattern of chromium-corundum mixed crystals with Cr_2O_3 concentrations from 10 to 60%. Three peak positions are indicated to show the general shift in peak positions observed.

tion. The mixing ratio of $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ was varied from 0.66 to 9. The various mixtures were heated in an arc furnace and the resulting melt decanted. The escholaite-corundum phase is formed by solidification. The formation of the chromium-corundum mixed crystals is confirmed by the X-ray patterns shown in Fig. 3. The general shift in the 2θ angle of the peaks in the XRD pattern is indicated by vertical lines at three peak positions. The replacement of chromium on Al-lattice sites results in slight deformation of the corundum-structure implied by decreasing intensities and increasing full width-half maximum (FWHM) in the XRD patterns (see Fig. 3) with higher amounts of chromium. Due to low amounts and partial amorphous state (vitreous phase), other phases are not detectable by powder diffraction but can be observed by microscopic methods. These phases arise from the thermochemical treatment (*i.e.* reduction) and from residual matter in the waste material (glassy attachments) and are found in all

Table 1 Average composition of dried sludge from refractory grinding.

	Component									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	CaO	MgO	Na_2O	K_2O	Cr_2O_3
Concentration (% by weight)	2.1	7.4	0.49	2.9	1.9	0.11	0.04	0.08	0.02	85.0

Fig. 4 Microsection of the melt product with 50% Cr_2O_3 under a light-optical microscope (pilot installation). 1-matrix (chromium corund), 2-matrix (chromium corund, slightly higher amount of Cr_2O_3), 3-metallic phase (Cr-Fe), 4-phosphorous-rich phase, 5-glass phase.

Fig. 5 Microsection of the melt product with 50% Cr_2O_3 under a light-optical microscope (industrial installation). 1-matrix (chromium corund), 2-matrix (chromium corund, slightly higher amount of Cr_2O_3), 3-metallic phase (Cr-Fe), 4-phosphorous-rich phase, 5-glass phase, 6-pore.

products.

Figure 4 shows a microsection of the melt product with 50% chromium in the mixed crystals which is representative of all products resulting from waste. The predominant phase is chromium-corund. As can be seen in Fig. 4, the main phase consists of crystals with more (brighter matrix) and less (darker matrix) chromium. The Cr/Al ratio between this two types of mixed crystals varies by less than 5%. A glassy phase appears (around 3% by volume) in the gussets between the esclaite-corundum crystals consisting of SiO_2 (55–60%), Al_2O_3 (20–25%), Cr_2O_3 (2–7%) and CaO (7–11%). A phosphorus-rich phase (less than 2% by volume) adjacent to the glassy phase can also be seen. This phase is composed mainly from a mixture of CrP and TiO_2 . The CrP results from the reaction between Cr_2O_3 and phosphates in the waste. Droplets of an intermetallic phase (less than 1.5% by volume) consisting mainly of Cr with small additions of Fe was also detected. This phase results from an undesired reduction of Cr_2O_3 in the arc furnace and could lead to problems in the manufacture of new refractories. Separation of the metallic phases based on their densities did not take place during the melting process. However, by changing the operational parameters (*e.g.* distance between electrodes and the surface of the melt) and by the use of additives (*e.g.* Fe_2O_3 as oxidizing agent), the reduction potential can be decreased to such an extent that the formation of the metal phase is almost completely prevented. Initial tests for corrosivity with melting products in glass melts showed equal or better results than conventional refractories of comparable compositions.

The experiments described above were all performed in a pilot plant. Results from a pilot scale are often not directly transferable to the technical scale. Therefore, large scale melt tests with 10000 kg were performed at the facilities of our industrial partner. As can be seen in Fig. 5, the structure and chemical composition of melt products compare well to those produced in the experimental study (Fig. 4). However, depending on various industrial melt processes (open furnace, block melting), there are some differences in the

amounts of impurities: for instance, in zonal smelting, a common method for purification of high-quality single crystals, the later solidifying glassy and phosphorus-rich phases will partially accumulate at the top of the melting block. This results in lower amounts of these phases in large areas of the products. The upper part of the block layer with higher concentrations of impurities can be eliminated manually. In any case, the amount of the metallic phase is significantly lower than in the pilot plant products due to the open furnace and thereby lower reducing operation conditions.

5. Conclusion

Thermochemical treatment in an AC arc furnace is an ideally suited process for handling hazardous and problematic waste since the process enables material separation. Various applications have already been tested successfully: treatment of MSWI residues (ash and slags), treatment of residues from the iron and steel industry and treatment of inorganic waste such as chromium-containing refractories. The operating conditions of the arc furnace can be adapted in such a way that the waste material input can be transformed into usable products and raw materials. Although there is a high energy demand for the operation of the electric arc furnace, the consumption is justified if useable products are generated. Refractories are designed for high temperature applications and can therefore only be produced in a high-temperature process. The technical feasibility of recycling spent chromium oxide refractories was demonstrated on both pilot and technical scales. It is thought desirable to adapt the process in industrial applications so that ecomaterials can be used as refractory materials in the near future.

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