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Metal Recovery from Waste Bricks with Arc Plasma Treatment

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A process has been investigated for a new recycling technique of waste bricks with arc plasmas. In this process, the waste bricks containing sexivalent chromium could be detoxified and valuable metals could be separately recovered from the bricks by carbothermic reduction with adding iron. The bricks used in this study were magnesia-chromia bricks, which are used as fire bricks at the most corrosive part in the high temperature furnace such as cement kiln, steel making furnace. The carbothermic reduction of the waste bricks was made clear by the use of theoretical modeling, based on chemical equilibrium calculation. The detoxification of the waste bricks and the selective recovery of the valuable metals from the bricks were achieved by the carbothermic reduction with arc plasma treatment. Magnesium was recovered as oxide dust and chromium was recoverd as ferroalloy. The recovery ratios of magnesium and chromium were about 90% and 59%, respectively, at the laboratory scale experiments under atmospheric pressure.

Key words: Metal recovery, Arc plasmas, Carbothermic reduction, Magnesia-chromia bricks

1. INTRODUCTION

Recently there is a strong demand for a basic solution to waste treatment including resource recycling. Waste treatment of magnesia-chromia bricks produced in the ceramic industry will be focused, which is one of the main industry in Chubu area, Japan.

Since the bricks have high corrosion resistance against acidic and alkaline components, they are used as fire bricks at the most corrosive part in the high temperature furnace such as cement kiln, steel making furnace and so on. However toxic sexivalent chromium compounds are produced under oxidizing conditions. Sintering processes which reduces the sexivalent chromium compounds, have so far been developed [1][2]. But it was recently reported that the harmless residue was not possible to be reused as the raw material of the bricks, because the particle size of the bricks was too large to be effectively recycled [2].

In this study, a pyrometallurgical process with arc plasma has been investigated for a new recycling technique of waste magnesia-chromia bricks. This process can detoxify the waste bricks by changing sexivalent chromium into trivalent chromium and recover valuable materials such as magnesium, chromium, separately, from the bricks by carbothermic reduction with arc plasmas.

2. TREATMENT PROCESS

Figure 1 shows a schematic diagram of the present process. The waste magnesia-chromia bricks put into the

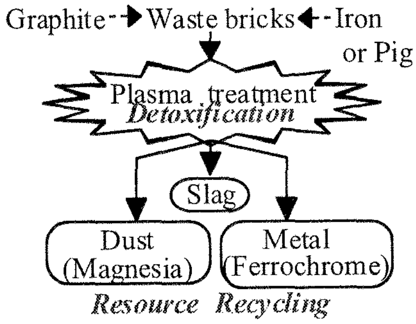

Fig.1 Material recovery process

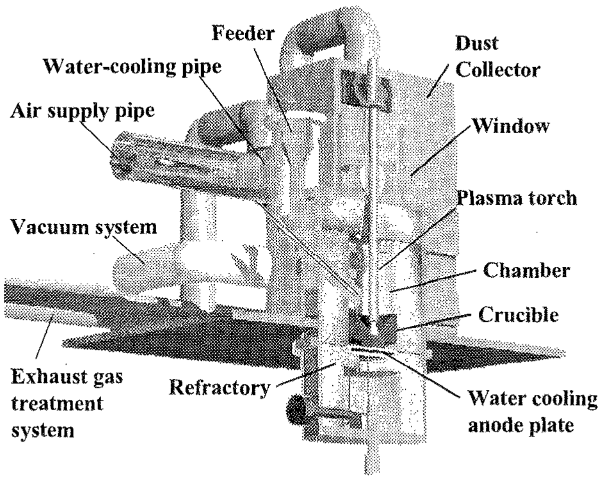

Fig.2 Experimental apparatus for small scale tests
[60 kW class plasma furnace]

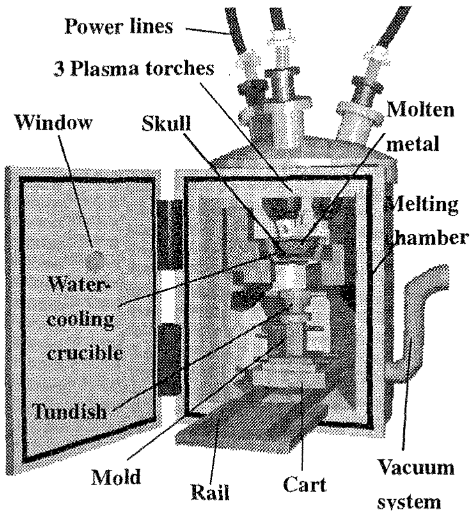

Fig.3 Experimental apparatus for large scale tests
[240 kW class PSC furnace]

graphite crucible with the reductant of graphite lumps and iron. Pig iron can be also used. When they are heated up to 2000 K with arc plasmas, the reduction reaction occurred and the valuable metals might be recovered as follows: magnesium vapor was produced and transferred into gas phase by carbothermic reduction. The magnesium vapor is reoxidized again and recovered as oxide. Metallic magnesium vapor can be also recovered by quenching of magnesium vapor in the some way of the magnesium recovery method from calcined dolomite [3]. On the other hand, chromium is dissolved into the molten iron and recovered as ferroalloy. The removed magnesium oxide can be recycled for the ceramic industry and the ferrochrome can be used as a raw material for stainless steel production.

3. EXPERIMENTAL

3.1 Sample preparation

The chemical composition of the waste magnesia-chromia brick sample employed in this study and the result of the elution test for sexivalent chromium are shown in Table I . As the results, sexivalent chromium was eluted 410 mg./l under the clean experiment conditions of the elution test. The bricks were crushed into powder of which size was under 100 mesh in order to increase the reaction surface area. Additive materials were graphite powder under 400 mesh and small pieces of iron under 2 - 5 mm. In some experiments, pig iron was used instead of pure iron. The purity of graphite and iron were higher than 99% and 99.99%, respectively. The carbon content of pig iron was 4 mass%. The graphite content of samples was 30 mass% in each experiment. The amount of graphite was more than that determined by stoichiometric calculation with brick composition.

3.2 Experimental apparatus for small scale tests

Figure 2 shows a schematic diagram of the experimental apparatus. The plasma furnace consists of a chamber with a D.C. transferred type torch and a graphite crucible on a water cooled anode plate, a dust collector and a scrubber for exhaust gas treatment. Generating power of the furnace is 60 kW, with argon (1.7 x 10^{-4} m^3/s) as plasma gas during the plasma operation. The masses of the bricks with 30 mass% graphite and iron were changed 1.0 kg - 2.5 kg and 0.25 kg -1.0 kg. The sample was heated in the graphite crucible at 2000 K - 2100 K and 101.3 kPa. The treatment temperature was measured by the radiation thermometer and the thermocouple. The treated samples were quantitatively analyzed by inductively coupled plasma spectrometry (ICP), atomic absorption spectrometry (AAS) and X-ray diffraction (XRD). An elution test was also carried out to ascertain the detoxification of the treated samples.

Table I . Chemical composition of waste magnesia-chrome bricks
(mass%) (mg/l)

MgO	Cr_2O_3	Fe_2O_3	Al_2O_3	K_2O	CaO	SiO_2	Na_2O	Cl	S	Cr^{6+}
67.5	11.9	5.30	5.00	4.50	1.90	1.60	0.50	1.30	0.40	410

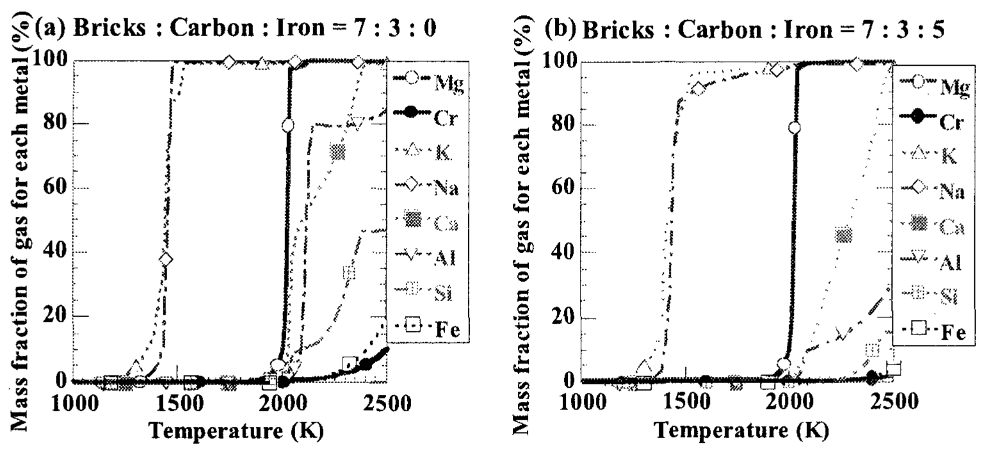

Fig.4 Relationship between mass fraction of gas and temperature by chemical equilibrium calculation
(a) 70 mass% bricks - 30 mass% carbon (b) 47 mass% bricks - 20 mass% carbon - 33 mass% iron

3.3 Experimental apparatus for large scale tests

Figure 3 shows a schematic diagram of the experimental apparatus. The plasma furnace consists of a chamber with 3 plasma torches and a water cooled crucible, a bag filter and a exhaust gas cooling system. Power supply is 240 kW, with argon (1.3 x 10^{-3} m^3/s) as plasma gas. The masses of the bricks with 30 mass% graphite and iron (or pig iron) were 3.0 kg and 17.0 kg, respectively. The experimental pressure was 101.3 kPa in all experiments. The analysis of treated samples was same as the small scale test.

4. RESULTS AND DISCUSSION

4.1 Thermodynamical analyses

Process modeling is important to predict the behavior of each component. Therefore, the chemical equilibrium calculation software, Chemsage (ver.3.13, GTT Co. Ltd.) reported by Eriksson and Hack [4] was used to predict the complex reactions on the carbothermic reduction of magnesia-chromia bricks. In the present study, calculation by Chemsage was made under the pressure of 101.3 kPa. Calculations were carried out for two conditions of the initial composition as follows.

(a) Mixture of 30 mass% carbon and 70 mass% bricks
(b) Mixture of 20 mass% carbon and 47 mass% bricks and 33 mass% iron

The carbon ratio of sample (a) was 30 mass%, whose ratio was more than that determined by stoichiometric calculation with brick composition. In the sample (b) added iron, the carbon ratio to the bricks except iron was the same as the sample (a).

Figure 4 shows the relationship between mass fraction of gas for each element produced by carbothermic reduction of bricks and temperature. According to the calculation, magnesium starts to vaporize at 2000 K in the sample (a). Calcium and aluminum also vaporize at the same temperature. Calcium seems to vaporize as calcium gas or calcium chloride gas, and aluminum vaporizes as aluminum suboxides. On the other hand, only magnesium vaporizes at about 2000 K in the sample (b). The vaporization temperatures of calcium and aluminum are shifted to much higher temperature because aluminum may be dissolved in molten iron and calcium may exist as calcium oxide. Potassium and sodium may be removed at lower temperature of about 1500 K, magnesium can be recovered selectively as its vapor at 2000 K by the addition of iron.

Chromium seems to exist in the metal as $(Fe,Cr)_7C_3$ when the partial pressure of CO is relative high (Pco_2 / $Pco < 10^{-2.7}$) in the above temperature range by Katayama et al. [5].

4.2 Plasma treatment

The mixture of iron, graphite and waste bricks was separated into each phases of metal, slag and dust by plasma treatment. The experimental apparatus were shown in Figs. 2 and 3.

An elution test of sexivalent chromium was carried out for all phases after plasma treatment. As the results, the elution concentration of sexivalent chromium was under 0.025 mg/l in each phase. This value is satisfied with the environmental standard of soil in Japan (< 0.05 mg/l). Therefore the detoxification of the waste bricks was achieved with plasma treatment.

Table II shows the recovery ratio of magnesium and chromium calculated from the chemical compositions of metal and slag solidified in the crucible after plasma treatment at small scale test. Most of magnesium could be recovered as dust. While chromium was not only recovered in the metal but also in the dust.

According to the result of the experiments used pure iron as iron resource and pig iron at large scale tests, the vaporization of chromium seemed to be suppressed by the coexistence of iron.

The comparison of recovery ratio of chromium in the metal between with pure iron and with pig iron at large scale test was shown in Fig.5. Chromium recovery was improved by using pig iron. This result could be explained as follows.

In the case of pure iron, the solid-solid reactions between the chromium oxide in the bricks and graphite occurred and most chromium vaporized before contacting with molten iron.

On the other hand, in the case of using pig iron, chromia was reduced by not only graphite but also carbon in molten pig iron and chromium was easy to dissolve in the metal.

Katayama.,et al.[4] investigated the carbothermic reduction of synthetic chromites and found that the reduction behavior of chromium with iron was different from that without iron.

When iron was not added to the mixture, chromium carbide, Cr_3C_2 was produced, which was hard to be dissolved into iron. As increasing temperature, Cr_7C_3 was produced and the vaporization of chromium started.

When iron was added to the mixture, chromium carbide, Cr_3C_2 was not produced. $(Cr,Fe)_7C_3$ was produced at first and the production rate was rapid compared with the rate without iron. Since $(Cr,Fe)_7C_3$ could be dissolved into molten iron, the vaporization ratio of chromium became small. This is agree with the results of the chemical equilibrium calculation as shown in Fig.4.

Another reason was that metal pool of pig iron was easy to be formed compared with pure iron because of the low melting point.

Therefore, the reduction of the bricks under coexistence of molten iron would be considered to be effective for the improvement of chromium recovery.

5. CONCLUSION

The results were summarized as follows.

Table II . Metal recovery ratio

$$\left(=\frac{\text{Amount of recovery after plasma treatment}}{\text{Initial amount in the waste bricks}}\right)$$

Recovery element	Metal recovery (mass%)	Recovery phase
Mg	89 - 99	Dust
Cr	33 - 59	Metal

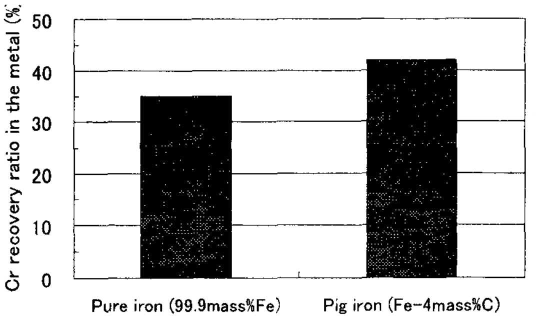

Fig.5 Distribution ratio of chromium at large scale test

(1) Detoxification of the waste magnesia-chromia bricks was achieved by carbothermic reduction of toxic sexivalent chromium oxide from the bricks. The waste bricks could be successfully treated with arc plasmas.

(2) The carbothermic reduction of the waste bricks was made clear by the use of theoretical modeling, based on chemical equilibrium calculation. It was ascertained that most of magnesium vaporized separately at about 2100 K by addition of iron.

(3) The process was developed by which the valuable metals could be separately recovered from the waste bricks. It was found that the metals could be recovered efficiently by addition of iron. Recovery ratios of magnesium and chromium were 99 % and 59 %.

(4) It was found that the usage of pig iron was more effective for the improvement of chromium recovery. Chromia in the bricks was reduced by not only graphite but also carbon in molten pig iron, reduced chromium might be easy to dissolve in the metal.

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