Preparation of High Purity Zinc Oxide from Zinc Metal Scrap

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Pyrometallurgical process is utilized to recover zinc in the form of high purity zinc oxide from a kind of zinc metal scrap containing 92.49 wt% zinc. The process uses tube-type furnace, where the reactor is divided into volatilization zone and oxidization zone by flowing nitrogen gas and air. In the process, zinc is firstly volatilized to vapor in inert atmosphere of nitrogen gas and carried forward to oxidization zone by nitrogen gas, then oxidized to zinc oxide in air atmosphere. The effect of temperature, air and nitrogen gas flow-rates, and reaction time on both purity and yield of the product is investigated in detail in this study. Subsequently, the characteristics of the products are examined by X-ray diffractometer and scanning electron microscope. The obtained results demonstrated that both the purity and the yield of the product have relationships with the operation parameters. The contents of the impurities grow with the rise of temperature, with the increase of nitrogen gas or air flow-rate, and also with the extension of reaction time. However, the yield decreases with the decrease of temperature, with the reduce of nitrogen gas flow-rate, with the rise of air flow-rate, and also with the diminishment of reaction time. In addition, very low air flow-rate resulted in the increase of metallic zinc in the product and the decrease of the yield of the product at the same time. Zinc oxide with purity of 99.97 wt% and yield of 94.45% in nano-grade dimension can be obtained in presence of 300 ml/min N_2 flow-rate and 800 ml/min air flow-rate for 12 minutes at 1253 K, whereas the impurity content of Al, Fe, Cu, Pb and Cd is 0.0072 wt%, 0.00060 wt%, 0.00096 wt%, 0.0048 wt% and 0.00031 wt%, respectively, which approaches the quality demands of the first-grade-zinc oxide in JIS (Japanese Industrial Standard) K 1410-1995.

Key Words : Zinc oxide; Zinc scrap; Pyrometallurgy; Preparation; Recycling

1. Introduction

Zinc is the fourth most widely used metal after iron, aluminum and copper. With new projects increasing total world capacity for both mine and zinc metal production, the zinc industry has experienced significant expansion in recent years. It is reported that the world consumption of refined zinc metal increased by about 7% in 1999 to 8.4 Mt, and the demand for zinc is expected to grow by an average of 3.4% to over 10 Mt by 2005, based on 1998 consumption. In the consumed zinc, most of it basically derived from zinc-containing ore such as sphalerite, the primary zinc; only a small part of it, e.g. not greater than one-third in 1990s' in the United States, is produced from scrap and residues, the secondary zinc. Fortunately, world zinc recycling has recently grown at three times the rate of primary zinc metal production. And it is estimated that more than 40 percent of world zinc consumption will be from recycled zinc by 2005.

The secondary zinc is principally associated with the carbon steelmaking dust and leaching residues of zinc plants. For example, approximately 0.5 million tons of electric arc furnace (EAF) dust are annually generated from steel production in Japan. Usually, the zinc content of residue from the leaching process or dust from the blast furnace (BF) or basic oxygen furnace (BOF) is less than 10 wt%, while the dusts generated from the EAF contain around 20 wt% zinc, which is rather higher than the grade of the primary zinc resources exploited. Since the pretreatment of the wastes required for landfilling are very expensive, several processes have been developed to recover zinc from the wastes, which are basically categorized as pyrometallurgical, hydrometallurgical, or their combinations. The Waelz kiln process is the most famous and typical pyrometallurgical method used for many years to recover zinc from EAF dusts[1]. Other similar processes include converter smelting, half shaft furnace, and electrothermic zinc process.[2,3] The main competitions for the Waelz process are the plasma smelting process[4,5], electric furnace process, flame cyclone process[6], and Inmetco direct reduction process[7]. Hydrometallurgical processes involve the direct

dissolution of the waste, solution purification, and precipitation or electrowinning to recover zinc values and ensure the non-hazardous disposable residues. Systems of leaching include sulfate, chloride, ammoniacal, alkaline, aqueous chlorine, and cyanide[7].

Generally, the treatment of EAF dusts is conducted by the thermal process to generate non-hazardous disposable iron slag and zinc lead-bearing oxide fumes that continue with hydrometallurgical extraction for metal values. Since pyrometallurgical treatments involve thermal reduction and volatilization of zinc and produce a crude zinc oxide, a large quantity of energy is required for reduction[8]. The zinc leach residues are treated by both pyrometallurgical and hydrometallurgical processes[7] but are questionable economically. For BF/BOF dusts with low zinc content, the possibly treatment method is internally recycling by a sinter plant to form the same composition as EAF dust, and then treated as EAF dusts[9]. However, it is generally not economical to treat the residue or dust to recover zinc. Regardless of the type of waste, it is obvious that the cost will probably be a critical factor in process selection and technical activity in this challenging area will continue to expand in the future.

Aiming at high metallic zinc-bearing secondary resource, zinc recovery in the form of high purity zinc oxide from a kind of zinc metal scrap generated from zinc crocus is studied by means of pyrometallurgical process in this paper for the first time. By treatment of vaporization for separation zinc from the scrap combined with oxidation of zinc vapor, zinc oxide with purity of 99.97 wt% has been obtained in yield of 94.95% vs zinc in the scrap.

2. Experimental

The raw material sample of zinc metal scrap used in the study was taken from a certain metal corporation in Japan. The particle size is below 0.105 mm. The results of X-ray diffraction demonstrated that the components of the sample are mainly metallic zinc, metallic aluminum, and metallic iron. The primary chemical components are analyzed separately by total dissolution in aqua regia. The scrap is basically composed of about 92.49 wt% zinc, 4.41 wt% aluminum and 0.22 wt% iron. The other components account for less than 2.88 wt%, which consist of such elements as Cu, Pb, Cd, Na,, Mg, K,C, In and Bi.

Model IRH High Temperature Furnace, produced by Ishizuka Denki Seisakusho, which consisted of a horizontal alumina reactor tube with length of 700 mm and inside diameter of 20 mm, has
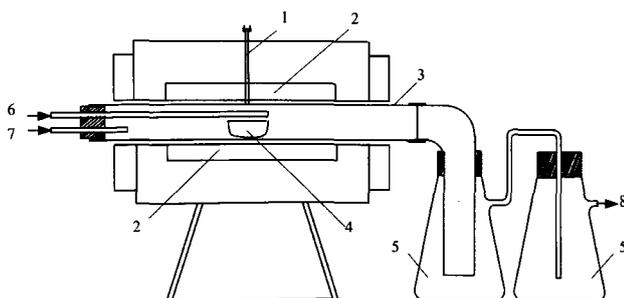
been used as experimental apparatus for separation and oxidation of zinc. Model DB1000 Temperature Controller, produced by Chino Corporation, is employed to control the temperature. The schematic apparatus is shown in Figure 1.

During experiment, a certain flow-rate of nitrogen gas is introduced to alumina reactor at given temperature of furnace, and ceramic boat with 5 grams of zinc scrap is placed in low temperature area. After it is preheated for 2 minutes, it is slowly pushed to reaction area. Simultaneously, a given flow-rate of air is introduced to the reactor for scheduled time to produce zinc oxide. Subsequently, flowing air and power of furnace are cut off, and nitrogen gas is kept untill the temperature of the reactor decreased to room temperature.

The zinc oxide carried by exhaust gas and the residue in the ceramic boat are collected and weighed. 1 gram of respective sample is taken out and dissolved by about 20 ml aqua regia at around 363 K. The obtained solution is diluted to 100 ml with deionized water and filtered with 5A quantitative filtrate paper. At the beginning of filtration, the several milliliters of filtrates are rejected, and the remains are sampled to determine the concentrations of metallic ions by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a SEIKO SPS 3000 spectrophotometer. Both content and yield of the product are calculated to investigate the impact of conditions such as temperature, nitrogen gas flow-rate, air flow-rate and reaction time. Since the principal impurities in the raw material are metallic aluminum and metallic iron, contents of aluminum and iron in zinc oxide product are basically concerned besides zinc content. Definition of yield is the ratio of zinc mass in the product to zinc mass in the raw material. The yield of zinc oxide product is calculated according to eq.(1) and the yield of residue is calculated according to eq.(2).

$$\text{Yield of product } (\%) = \frac{m_1 C_1}{mC} \times 100\% \qquad (1)$$

$$\text{Yield of residue } (\%) = \frac{m_2 C_2}{mC} \times 100\% \qquad (2)$$

Where m_1, m_2 and m presents the mass of the zinc oxide product, the mass of the residue and the mass of the given raw material, respectively; C_1, C_2 and C expresses the content of zinc in the zinc oxide product, the content of zinc in the residue and the content of zinc in the raw material, respectively, which is obtained by ICP.

The components of some zinc oxide products and residues in the boat are analyzed by a JEOL JDX-3500 X-ray Diffractometer with a monochromator under the following conditions: radiation, CuKα, 40kV, 30 mA; continuous scanning method; scanning speed, 0.3 deg per minute; scanning step, 0.02 deg; and angle range, 2~90 deg/2θ. The morphologies of some zinc oxide products are observed by a JSM-5900LV Scanning Electron Microscope at 15 kV of the accelerated voltage after loading on sheet copper and vaporization with gold, because of non-conductivity nature of zinc oxide.

3. Results and discussion

3.1 Effect of temperature

The formation of zinc oxide is greatly influenced by temperature because it depends on the volatilization of zinc scrap in the boat. Generally, saturated vapor pressure of a compound increases

1-Thermocouple, 2-Heater, 3-Alumina tube, 4-Boat,
5-Collecting vessel, 6-Air, 7- Nitrogen gas, 8-Exhaust gas

Figure 1 Experimental apparatus for preparation of zinc oxide

with the rise of temperature below boiling point. Among the waste zinc, the critical components are metallic zinc, aluminum and iron, whose boiling points are 1180 K, 2333 K and 3273 K, respectively. So, the lower the temperature is, the lower the saturated vapor pressure of aluminum or iron will be in gasifying area, and the lower the impurities will be in the zinc oxide product. On the other hand, the higher the temperature is, the higher the saturated vapor pressure of zinc will be in volatilizing zone, and the higher the yield of zinc oxide will be. That is to say, relatively high temperature which is around the boiling point of zinc will be advantageous to product yield, and relatively low temperature will be appropriate to improve the purity of zinc oxide.

The influence of temperature on purity and yield of zinc oxide in the condition of flow-rate of 200 ml/min nitrogen gas and 400 ml/min air for 15 minutes is shown in Figure 2 and Figure 3, respectively.

Figure 2 shows that the increase of temperature from 1013 K to 1213 K gives small impurities in zinc oxide in which aluminum is increased from 0.004 wt% to 0.011 wt% and iron is increased from 0.0003 wt% to 0.0013 wt%. In the temperature range from 1213 K to 1289 K, such impurities rise rapidly, as Al from 0.018 wt% to 0.047 wt% and Fe from 0.0013 wt% to 0.0053 wt%. However, the content of zinc is almost constant with temperature and keeps at around 81.32%.
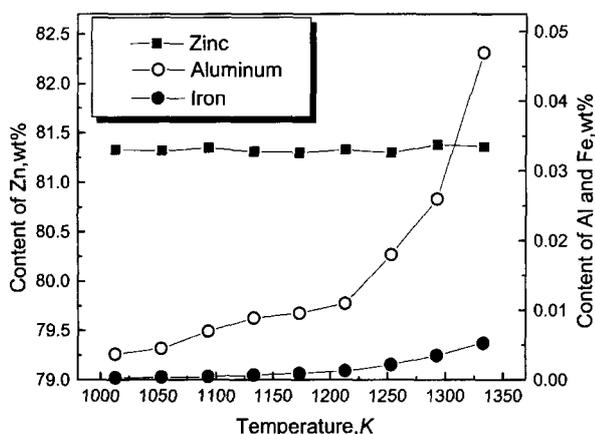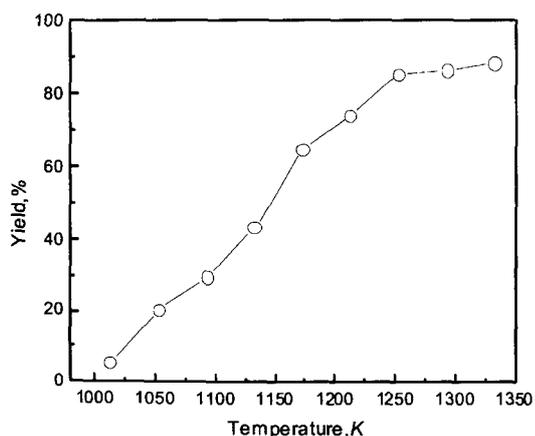
It is known that the theoretical content of Zn in zinc oxide and in zinc metal is 80.34 wt% and 100 wt%, respectively. It is easy to comprehend that the theoretical content of zinc in a mixture composed of zinc oxide and metallic zinc ranges between 80.34 wt% to 100 wt%, depending on the ratio of the two substances. That is to say, as long as the content of Zn in the generated zinc oxide is higher than 80.34 wt%, there exists metallic zinc in the product. Figure 4 shows the XRD pattern of the product of zinc oxide under 200 ml/min N_2 and 400 ml/min air at 1253 K for 15 min, which indicated metallic zinc is detected besides zinc oxide. It seems that the existence of metallic zinc in the product is resulted from incomplete oxidation of zinc vapor.

On the contrary, from the results shown in Figure 3, as the temperature rises, the yield of product is going up with a large scale such as from 5.49% to 85.31% when the temperature is raised from 1013 K to 1253 K. On the other hand, when the temperature goes up from 1253 K to 1333 K the yield is slowly up such as from 85.31% to 88.11%. The reason why the yield of zinc oxide grows in different speed in different temperature range is possibly that the vaporization of zinc is the process of the decisive ratio in the preparation of zinc oxide. That is to say, the effect of temperature on the yield of product is mainly dependent on the vaporization of zinc that is obedient to Clausius-Clapeyron equation.

Under temperature of 1253 K, a good result such as relatively low impurity and higher yield is realized. The contents of Zn, Al, and Fe in the product of zinc oxide are 81.30 wt%, 0.018 wt%, and 0.0022 wt%, respectively, and the yield of product is 85.31%.

3.2 Effect of air flow-rate

Air flow-rate has great influences on the purity and yield of zinc oxide. Figure 5 and Figure 6 show the results of the influence of air flow-rate on purity and yield of zinc oxide, respectively, in presence of 200 ml/min of flow-rate of nitrogen gas at 1253 K for 15 minutes.

For product purity, air flow-rate has little influence on such impurities as Al_2O_3 and Fe_2O_3 because the contents of Al and Fe are ranging between 0.014 wt% to 0.020 wt% and 0.0017 wt% to 0.0022 wt%, respectively. Nevertheless, air flow-rate affects on the content of Zn. As the air flow-rate increases from 200 ml/min to 2000 ml/min, content of Zn reduces rapidly from 82.38 wt% to 80.33 wt% in flow-rate range of 200~600 ml/min, and remains at

Figure 2   Effect of temperature on purity of zinc oxide in presence of 200 ml/min N_2 flowrate and 400 ml/min air flowrate for 15 min

Figure 3   Effect of temperature on yield of zinc oxide in presence of 200 ml/min N_2 flowrate and 400 ml/min air flowrate for 15 min
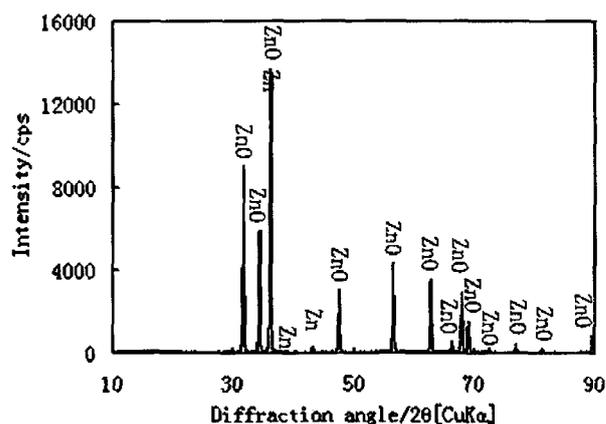
Figure 4   XRD pattern of product in presence of 200 ml/min N_2 flowrate and 400 ml/min air flowrate at 1253 K for 15 min

around 80.33 wt% in flow-rate range of 600~1200 ml/min, and then increases rather slowly from 80.33 wt% to 80.69 wt% in flow-rate range of 1200~2000 ml/min. It is remarkable that the product of zinc oxide contains metallic zinc when air flow-rate is less than 500 ml/min or more than 1500 ml/min.

As for the yield of the product, it increases quite slowly from 85.04% to 91.69% with the increase of flow-rate of air from 200 ml/min to 800 ml/min, and then decreases fast from 91.69% to 59.13% with raising flow-rate of air from 800 ml/min to 2000 ml/min.

It is obvious that very high or low air flow-rate does not work on either purity or yield of the product. In order to achieve the high purity zinc oxide with high yield, the air flow-rate should be controlled in range of 600~1000 ml/min.

The possible reasons why the content of zinc varies presented in Figure 5 under different air flow-rate are as follows. In the low flow-rate range of air, the amounts of oxygen gas are not enough to oxidize zinc comparing to the amounts of volatilized zinc vapor, and there exists metallic zinc in the product. On the contrary, in the high flow-rate range of air, although the amount of oxygen gas is enough to react completely with zinc, high flow-rate of gas results in short time of zinc vapor in reacting area. That is to say, zinc vapor is carried out of reacting zone by exhaust gas before it

is completely reacted.

3.3 Effect of flow-rate of nitrogen gas

The flow-rate of nitrogen gas also has great influence on purity or yield of zinc oxide product; Figure 7 and Figure 8 show the results of the effect of flow-rate of nitrogen gas on purity and yield of zinc oxide, respectively, in presence of 800 ml/min of air flow-rate at 1253 K for 15 minutes.

There are evidences that flow-rate of nitrogen gas hardly influences on the contents of such impurities as aluminum oxide and iron oxide, since the contents of Al and Fe in the product of zinc oxide remain at around 0.016 wt% and 0.0018 wt% in flow-rate range of 100 ml/min to 1000 ml/min, respectively.

However, content of Zn in the product of zinc oxide alters with the variety of flow-rate of nitrogen gas. In 100~400 ml/min of low flow-rate range, it has little effect on content of Zn, which keeps around 80.31 wt%. With the increase of N_2 flow-rate from 400 ml/min to 1000 ml/min, the content of Zn rises gradually. It exceeds 80.34 wt% when the flow-rate of nitrogen gas reaches 600 ml/min, which demonstrates that the product contains a certain amount of metallic zinc. The reasons why high flow-rate of nitrogen gas results in high impurity of metallic zinc in the product are that the formed zinc vapor, which is not completely oxidized
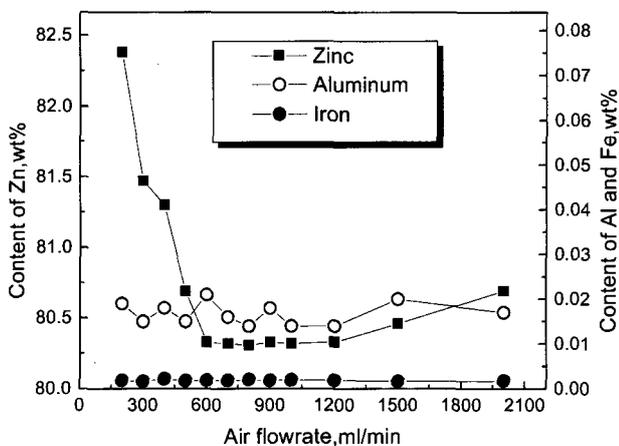
Figure 5 Effect of air flowrate on purity of zinc oxide under 200 ml/min N_2 flowrate at 1253 K for 15 min
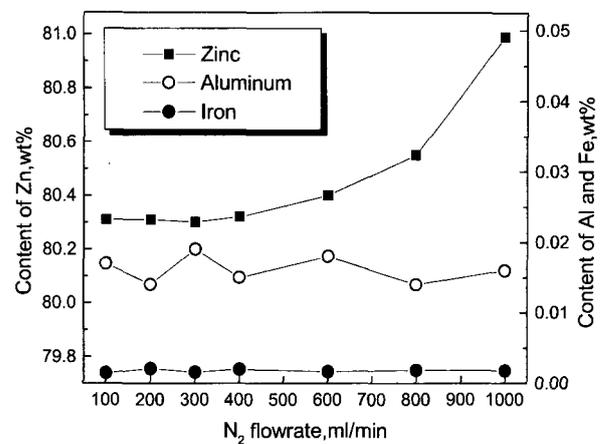
Figure 7 Effect of N_2 flowrate on purity of zinc oxide in presence of 800 ml/min air flowrate at 1253 K for 15 min
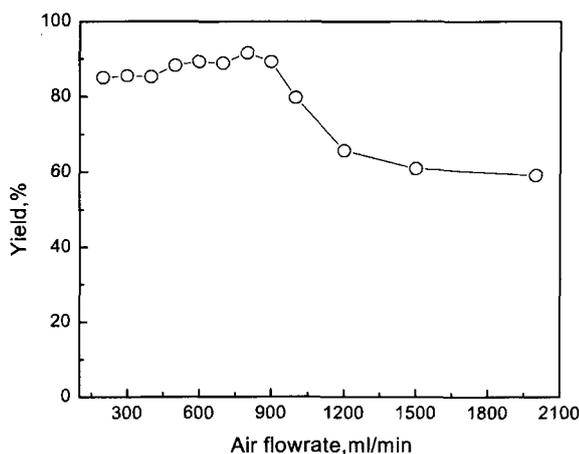
Figure 6 Effect of air flowrate on yield of zinc oxide under 200 ml/min N_2 flowrate at 1253 K for 15 min
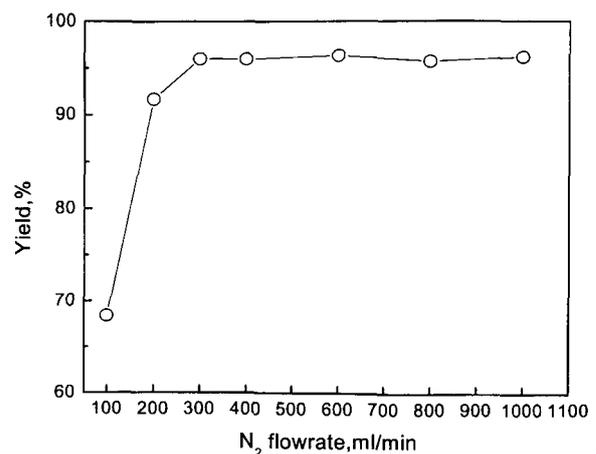
Figure 8 Effect of N_2 flowrate on yield of zinc oxide in presence of 800 ml/min air flowrate at 1253 K for 15 min

with oxygen gas. That is similar situation in the case of high flow-rate of air is used.

Moreover, it scarcely influences on the yield of product when the flow-rate of nitrogen gas is over 200 ml/min, and the yield is ranging around 96%. Nevertheless, the yield decreases promptly when the flow-rate of nitrogen gas is less than 200 ml/min.

Figure 9 is the XRD pattern of the residue in the boat under 100 ml/min N_2 flow-rate and 800 ml/min air flow-rate at 1253 K for 15 min. The results demonstrated that both metallic zinc and zinc oxide are found in the residue under the above conditions. So, the reason why the product yields decreased in presence of low N_2 flow-rate can be understood. That is, in low flow-rate of nitrogen gas, a small quantity of air diffuse to the boat where the test sample of the zinc scrap is placed and results in oxidation of some zinc in the boat. On account of the oxidation reaction taking place in the boat, the generating zinc oxides cover on the surface of zinc particles and prevent zinc from volatilizing, which lead to low yield of zinc oxide.

In order to get product with high purity and high yield, the flow-rate of nitrogen gas should be controlled around 300 ml/min. Under this condition, the content of Zn, Al, and Fe in the zinc oxide product is 80.30 wt%, 0.019 wt%, and 0.0016 wt%, respectively, and the yield of product is 96.01%.

3.4 Effect of reaction time

The purity of product and their yield as a function of time are shown in Figure 10 and Figure 11, respectively, in the condition of 300 ml/min flow-rate of N_2 and 800 ml/min flow-rate of air at 1253 K. Those figures show that prolongation of the reaction time caused the high impurities in the product and high yield of the product.

On one hand, the contents of the impurities increase slowly with extension of the time within 12 minutes and increase promptly after that time. The contents of Al and Fe in the product are 0.0015 wt% and 0.00019 wt% at time of 2 minutes, respectively, and increases by 0.0054 wt% and 0.00036 wt% at time of 10 minutes, respectively. Whereas, it is 0.0072 wt% and 0.00060 wt% at time of 12 minutes, respectively, and increases by 0.034 wt% and 0.0014 wt% at time of 20 minutes, respectively. Obviously, within the same time of 8 minutes, the content of Al and Fe after 12 minutes accordingly increases approximately 6.9 times and 4.7

times versus that before 12 minutes.

On the other hand, the yield grows quickly with the extension of the time within 12 minutes and increases very slowly after that time. The yield of zinc oxide product is 26.40% at time of 2 minutes, and reaches 85.13% at time of 10 minutes, which raises 58.73%. Nevertheless, it is 94.95% at time of 12 minutes, and reaches 97.99% at time of 20 minutes, which only increases 3.04%. Apparently, within the same time of 8 minutes, the rise of product yield before 12 minutes is approximately 28 times high as that after 12 minutes.

Considered from both zinc oxide purity and product yield, the time should be controlled around 12 minutes. Under this condition, the content of Zn, Al, and Fe in the zinc oxide product is 80.32 wt%, 0.0072 wt%, and 0.00060 wt%, respectively, and the yield of product is 94.95%.

3.5 Characteristics of the product under optimal conditions

From the above discussions, the optimal conditions for preparation of zinc oxide from zinc scrap are: 1253 K of temperature, 300 ml/min of nitrogen gas flow-rate, 800 ml/min of air flow-rate and 12 minutes of reaction time. In order to observe the characteristics of the product, several measurements are carried out.

The XRD pattern of the product generated from the optimal
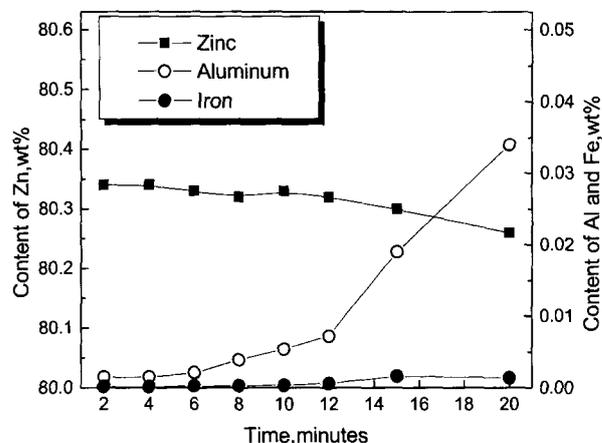
Figure 10   Purity of zinc oxide as a function of reaction time under 300 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K
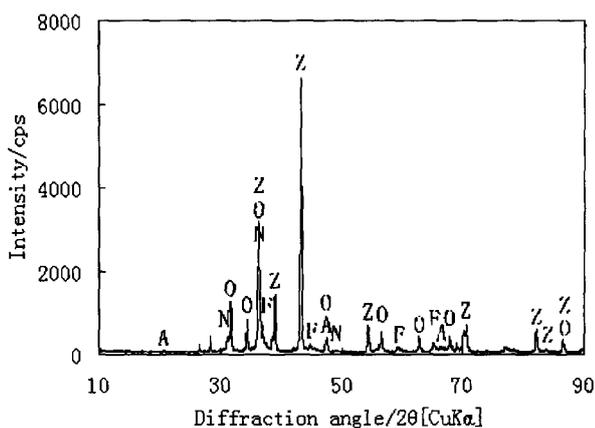
Figure 9   XRD pattern of the residue in the boat under 100 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K for 15 min (A=Al_2O_3, Z=Zn, F=Fe_3O_4, O=ZnO, N=$ZnAl_2O_4$)
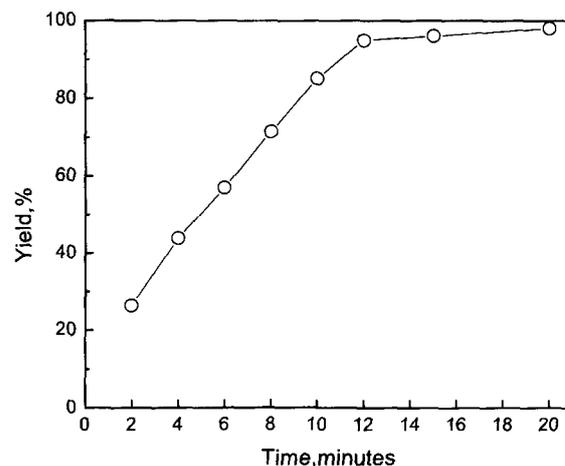
Figure 11   Yield of zinc oxide as a function of reaction time under 300 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K

Table 1   Quality demands of zinc oxide in JIS K 1410-1995 and corresponding index of the product under 300 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K for 12 min

Items	Purity ZnO wt%	Pb wt%	Cd wt%	Al wt%	Fe wt%	Cu wt%
1	≥99.5	≤0.005	≤0.002	-	-	-
2	99.97	0.0048	0.00031	0.0072	0.00060	0.00096

1-Demands of grade one in JIS K 1410-1995, 2-Content in this experiment

conditions is demonstrated in Figure 12, where zinc oxide is the only detected component from the product in presence of the sensitivity of the utilized X-ray diffractometer.

Figure 13 shows the SEM photograph of the product resulting from the optimal conditions. It can be seen that the zinc oxide product is in homogeneous, loosen, and fibrous. It is very interesting to note that the average diameter of the threads is below 0.1 μ m which approaches nano-grade dimensions.

Table 1 shows the index of the product under the optimal conditions. According to the quality standard of zinc oxide in JIS K 1410-1995 the impurities in the product all reaches the demands of the first grade product in the Standard, and the content of zinc oxide is higher than the demand of the Standard.
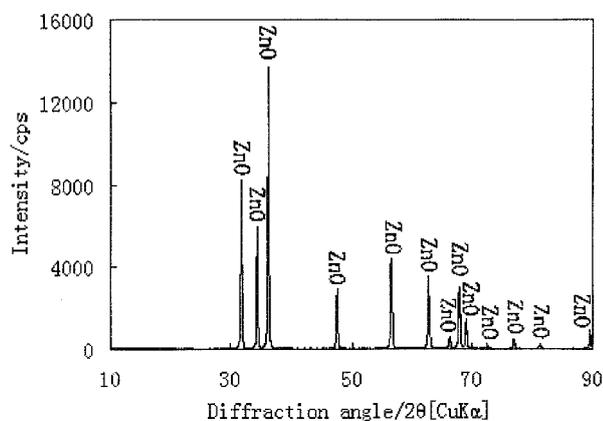
Figure 12   XRD pattern of the product in presence of 300 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K for 12 min
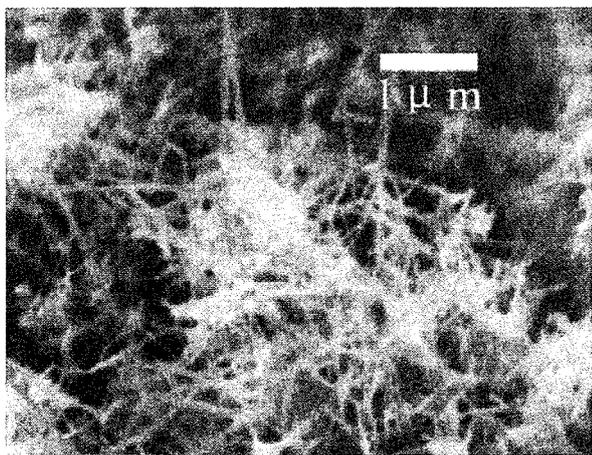
Figure 13   Scanning electron microphotograph of the product under 300 ml/min N_2 flowrate and 800 ml/min air flowrate at 1253 K for 12 min

4.   Conclusions

(1)   Zinc metal scrap can be recovered in the form of high purity zinc oxide by means of pyrometallurgical treatment as volatilization and oxidization.

(2)   The optimal conditions for preparation of high purity zinc oxide from zinc metal scrap are as follows: 300 ml/min of N_2 flow-rate and 800 ml/min of air flow-rate at 1253 K for 12min.

(3)   In the product generated under the optimal conditions, the purity of the product is 99.97 ZnO wt%, and the impurity of Al, Fe, Cu, Pb and Cd is 0.0072 wt%, 0.00060 wt%, 0.00096 wt% 0.0048 wt% and 0.00031 wt%, respectively, which approaches the quality demands of the first grade product in JIS K 1410-1995, and the yield of zinc oxide reaches 94.45%.

(4)   Temperature, N_2 flow-rate, air flow-rate and time influence either the purity or yield of the zinc oxide product. Raising temperature or prolonging time, both the impurities in the product and the yield of the product increase. Very low or high air flow-rate results in both the increase of the content of metallic zinc in the product and the decrease of the yield of the product. Very low N_2 flow-rate leads to the decrease in the yield of the product, and very high N_2 flow-rate results in the increase of metallic zinc in the product.

(5)   The high purity zinc oxide product obtained under the optimal conditions appeared in homogeneous fibre with an average diameter below 0.1 μ m, which is possible to be applied in nanomaterial production field.

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