Analysis on certain physical and resourceful properties of kish graphite containing materials

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As molten iron flows from furnaces during smelting (the temperature is about 1500°C; the carbon content is between 4.5%~6.0%), it comes into contact with its surroundings (such as air and fire-resistant elements), causing its temperature to drop to below liquids temperature; at this point, cementite (Fe_3C) releases graphite because it is oversaturated. Thanks to its scale-like structure, the released mineral is also known as kish graphite. By using the converter dust from a steel plant in Southern Taiwan, we studied the various physical properties of kish graphite and used a Scanning Electron Microscope (SEM) to observe the properties and structure of its surface.

The result of the sieve analysis indicates that kish graphite took up 5.65% of the composition of the converter dust; in contrast, the result of the elemental analysis shows that the carbon content of the converter dust was 27.99%. From these results, we assume that the low kish graphite content in the converter dust resulted from a drastic temperature drop during the smelting process, which caused a large amount of graphite to disperse into the atmosphere. In terms of the observations on kish graphite through SEM and the Energy Dispersive Spectrometer (EDS), the SEM analysis shows that kish graphite was characterized by a distinct foliated or layered structure and consisted of shattered and loosely distributed graphite. Meanwhile, the EDS analysis indicates that kish graphite was not only high in iron oxide, magnesium oxide, zinc oxide and carbon content, but also had a significant amount of impurities attached to its surface. We then assumed that we could remove the different kinds of oxides and minor elements on the surface of the kish graphite by applying liquid acid during the purification process, thus obtaining kish graphite of higher purity. Lastly, after analyzing the degree of weight loss of the converter dust under different temperatures using a thermogravimetric analyzer (TGA), we found that peaks of weight loss at its surface structure appeared between 150~200°C, 350~400°C, 600~700°C, and 700~900°C, with drastic weight reduction being observed under higher temperatures. Consequently, we can state that kish graphite produced from converter dust is characterized by the above-mentioned trends.

Keywords: Kish graphite, converter furnace dust, flotation, SEM analysis.

Introduction

Kish graphite forms due to the change in temperature during the smelting of iron or steel and is released as small flakes. The quality and quantity of kish graphite formed vary according to different processes from which it is produced. Kish graphite is a synthetic, flake-shaped graphite available at the multiton scale as a byproduct of steelmaking. This type of graphite forms on the surface of molten iron upon its cooling because of the oversaturation of iron with carbon, which typically occurs in cast iron making or blast furnace processes (usually from hypereutectic compositions)[1,2]. As formed, kish graphite normally encases impurities of various oxides (slag) and iron. Purification by levitation and HCl acid removes nearly all impurities, and 95–99% pure material remains.

Kish graphite is one of the most typical layered materials and has attracted much interest for novel and unusual physical properties by intercalation of atoms and molecules. The graphite intercalation compound (GIC) is considered as one of the candidates for the multi-functional materials. As a host material of GIC, it is important to elucidate the Fermi surface (FS) of kish graphite. According to the band-structure calculation[3,4], a hexagonal graphite has an electron pocket at the K point and a hole pocket at the H point. Although angle-

resolved photoemission spectroscopy (ARPES) studies on graphite have been done extensively so far[5,6], the electron/hole FS has not been directly observed since the size of the FSs are very small (k_F < 0.045 Å^{-1})[1,7] compared with the conventional momentum resolution ($\Delta k \sim 0.1$ Å^{-1}). Moreover, we should tune the incident photon energy to detect the K or H points. Owing to recent rapid development of high-resolution ARPES with synchrotron radiation ($\Delta E \sim 5$–10 meV, $\Delta k \sim 0.01$ Å^{-1}), one can access to the small FSs of kish graphite.

In this study, kish graphite with economic value was selected through flotation from the converter dust produced by iron smelting at a steel plant in Southern Taiwan. The structure and various physicochemical properties of the selected kish graphite were then analyzed, and its potential for becoming a resource was assessed.

Materials and methods

The source of the samples:

Kish graphite forms mainly due to the change in temperature during the smelting of iron or steel; it is released as small flakes. The quality and quantity of kish graphite formed vary according to the different processes from which it is produced. The main source of kish graphite used in this study came from converter dust produced by an integrated steel mill of a large steel plant in Southern Taiwan, which was most likely to form kish graphite.

Sample collection and preconditioning:

We collected converter dust and mixed them thoroughly. After drying the sample in a thermostatic oven at 105°C for 48 h, the samples were placed in a freeze drier. To remove the moisture, we dried the samples were under –50°C and vacuum pressure of 5×10^{-4} torr for 12 h. Next, we put 0.5 kg of the dried sample into a ball mill and ground it for 30 min, after which the grain size was reduced to about 100 μm. We then used the ground grains for physical and chemical experiments.

Sieve analysis of the converter dust:

100 g of the aforementioned dried sample was analyzed using standard stainless-steel sieves. The analysis was divided into six phases: using sieves of 20 mesh, 60 mesh, 100 mesh, 270 mesh, 325 mesh, and a pan. The openings of the sieves were 0.840 mm, 0.250 mm, 0.149 mm, 0.053 mm, and 0.044 mm, respectively. After shaking the samples with a centrifuge and running them through the sieves, we measured the weight of the remaining grains on the sieves to predict the graphite content at different sampling points.

Elemental analysis of the converter dust:

This study applied a Germany-made Heraeus Vario III-NCSH to analyze the preconditioned converter dust. Major elements being analyzed included carbon, hydrogen, nitrogen, and sulfur. To measure and analyze element content, we used a vertical combustion tube to transfer the converter dust into a platinum container first, and then placed it in the sample tank, which was then transferred into, and burned in, a combustion tube of 1,150°C. By using an oxidizer (WO_3), the transient combustion temperature could reach 1,800°C. After the combustion, the sample underwent a reduction reaction with copper as the reducing agent; it was then checked using a thermal conductivity detector (TCD) for the content of different elements.

SEM and EDS analyses of kish graphite:

Scanning Electron Microscopes (SEMs) are widely applied for various purposes. When combined with an energy dispersive spectrometer (EDS), an SEM can be used for qualitative, quantitative, point, and line analyses, as well as mapping. An SEM was used in this experiment to observe the surface structure changes of the kish graphite. An EDS was used to observe the elemental distribution in the kish graphite structure and its properties.

Analyzing the converter dust using a thermogravimetric analyzer (TGA):

A thermogravimetric analyzer is mostly used to measure the pyrolysis temperature and composition of materials. This study used a dynamic TGA (Dynamic TGA 2950) to determine the weight loss of the sample under different temperatures. To analyze the sample, we placed 10–20 mg of dried sample in a platinum crucible and heated it at room temperature (about 25°C), with the air as the oxidizer. The temperature of the sample increased at a rate of 10°C per min until finally reaching the target temperature of 1000°C. After reaching the target temperature, the sample was analyzed for its weight reduction rate and induced degradation rate.

Potentiometric analysis of the pH value and oxidation-reduction potential of kish graphite:

An oxidation-reduction potential meter was used to mea-

sure the acidic functional groups contained in the kish graphite. A sample containing 0.3 g of kish graphite was added to a beaker holding 300 mL of deionized water, whose pH value was modified to 11 using 0.1 M NaOH. Titration was conducted by adding 0.2 mL of 0.1 M HNO$_3$ until the pH value dropped to around 3. A titration graph was produced presenting the changes in the potential of NaOH per unit volume and pH values, in which the maximal value represented the titration endpoint.

Results and discussion

The result of sieve analysis:

100 g of converter dust sample was dried and sifted through stainless-steel meshes for sieve analysis. The results are shown in Table 1. The findings indicate that the weight of the remaining dust on the 20 mesh, 60 mesh, 100 mesh, 270 mesh, 325 mesh sieves, and the pan was 0.1327 g, 2.3326 g, 3.2675 g, 8.9690 g, 3.4900 g, and 81.5842 g, respectively. Also, the sample recovery rates fell between 98% and 105% because smaller or lighter grains were dispersed or accumulated when being shaken during the sifting process, resulting in discrepancies[8]. Besides, since the samples were obtained from dust collectors, the size of the dust was smaller than normal, and smaller than the kish graphite as well. Those with sizes smaller than 0.053 mm were identified as slags; their shapes were irregular. Moreover, through the sieve analysis results, the percentage of kish graphite in different converter dust was estimated to be approximately 5.65%.

The result of elemental analysis:

Elemental analysis of the converter dust was conducted to study its elements, including carbon (C), hydrogen (H), nitrogen (N), and sulfur (S); the results are shown in Table 2.

The carbon content of the converter dust was 27.99%, which is relatively low compared with the kish graphite content, which stood at 5.65%. A speculated cause of this phenomenon is that an intense decline in temperature during the steelmaking process at this steel plant caused a great amount of kish graphite to be released and dispersed into the atmosphere. Dispersed kish graphite was then collected via dust collectors and retained in the ashes, thus making the final kish graphite content lower than the carbon content observed.

The results of SEM and EDS analyses:

Fig. 1 shows the surface structure of the kish graphite through an SEM, while Fig. 2 demonstrates the mapping of kish graphite by applying an SEM and an EDS. The result of the SEM analysis indicates that kish graphite was characterized by notable foliated or layered structures, most of which
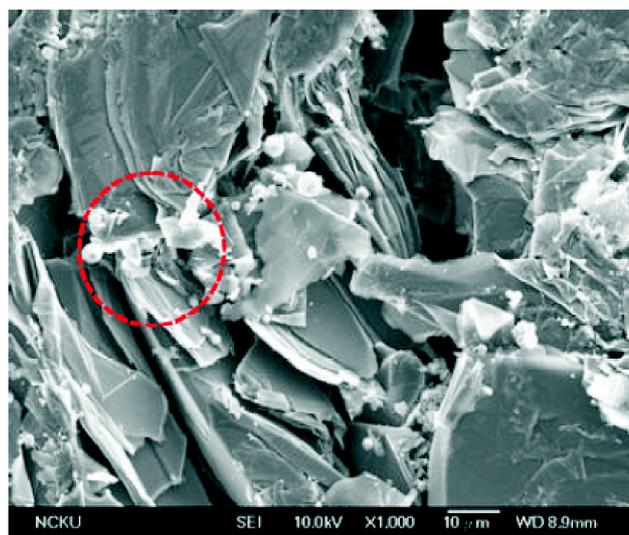
Fig. 1. Mapping of kish graphite's structure using an SEM.

Table 1. Results of the sieve analysis

Drying time (h)	Temp. (℃)	Original weight (g)	Opening size	Sieve analysis						
				>20 mesh >0.840 mm	60 mesh 0.250 mm	100 mesh 0.149 mm	270 mesh 0.053 mm	325 mesh 0.044 mm	Pan < 0.044 mm	Total weight
48	105	100	–	0.1327 g	2.3326 g	3.2675 g	8.9690 g	3.4900 g	81.5842 g	99.7760 g

Table 2. Results of the elemental analysis

Type of sample	Type of element (%)			
Converter dust	N	C	S	H
	0.22	27.99	0.37	1.74

consisted of shattered and loosely distributed graphite. Converter slags are byproducts formed under high temperature during smelting, and their temperature declined drastically during the cooling process, causing the crystalline graphite to fracture[6]. Concerning the result of the EDS analysis, Fig.
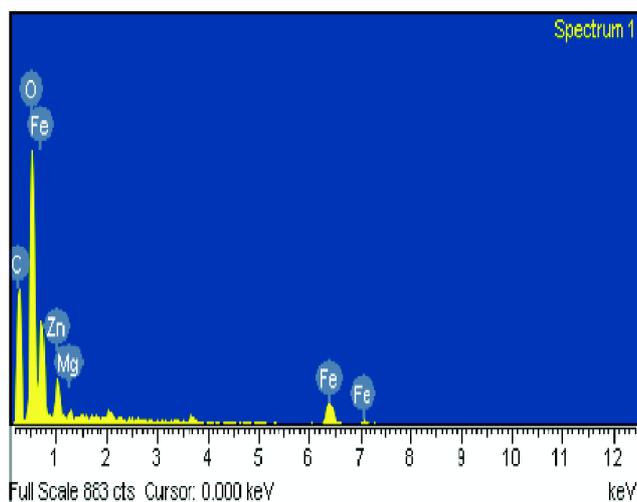
Fig. 2. Result of the EDS analysis of kish graphite.

2 indicates that kish graphite was high in iron oxide, magnesium oxide, zinc oxide, and carbon content, and a significant amount of impurities was attached to its surface. Besides, the oxides mentioned above were merely attached to the surface of the converter dust, not combined with the graphite, suggesting that liquid acid can be used to remove various oxides and minor elements during purification processes, thus obtaining kish graphite of higher purification[7].

The result of TGA analysis:

A TGA was adopted for analyzing the rate of weight loss of the converter dust under different temperatures; the re-

sults are shown in Fig. 3. The aforementioned results indicate that the kish graphite content of the converter dust was relatively low (about 5.65%) and that its surface attracted a large number of impurities. However, since the materials added during the smelting process differ from those during the desulfurization process, different properties and trends can be observed through the TGA. For instance, peaks of weight loss occurring at the surface structure of the converter dust were observed when temperatures rose to 150~200°C, 350~400°C, 600~700°C, and 700~900°C; changes in weight were also more notable under high temperatures[4,9]. From the results obtained through a TGA, we can say that kish graphite produced from converter dust is characterized by the abovementioned trends.

The result of pH value and oxidation-reduction potential curve analysis:

Fig. 4 shows the titration curves of pH value and oxidation-reduction potential (ORP). The end points were hard to recognize, and the trend appeared to be precipitous. Also, a higher amount of alkali (or more NaOH) had to be used during the titration because the crossing points of the pH value curve and the titration curve were far apart, and the impurities on the surface of the converter dust also impacted the titration. This result suggests that disassociation was relatively unremarkable during titration because the kish graphite content of the converter dust was low, and several acidic functional groups on the surface were hampering the pro-
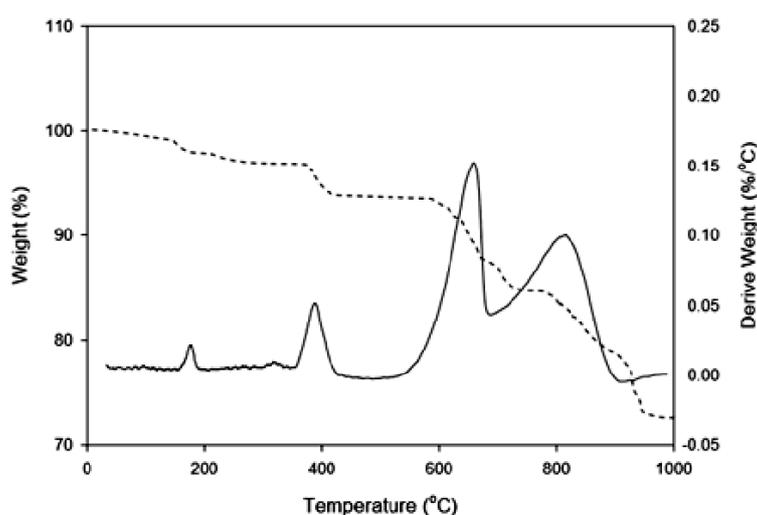
Fig. 3. Result of the differential thermal analysis of the converter dust.
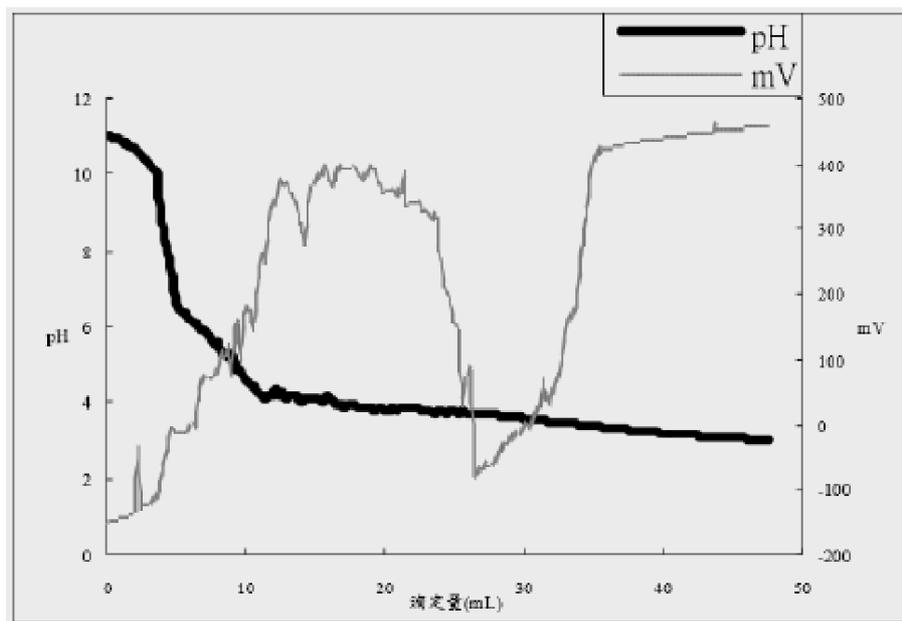
Fig. 4. Result of the titration curve of the converter dust.

cess[1,7]. More extract and time are needed if extracting kish graphite from converter dust through ion exchange is desired.

Conclusion

The major object of this study was the converter dust from a steel plant in Southern Taiwan. The results of a sieve analysis indicate that the kish graphite content of the converter dust was only 5.65%. The low kish graphite content suggests that a large amount of kish graphite was released and dispersed into the atmosphere due to the precipitous drop in the surface temperature of the converter dust, which occurred during the smelting process. SEM and EDS analyses also confirm that the surface of kish graphite attracted various impurities containing metal oxides; these complex compounds can subsequently affect the purification of converter dust. The kish graphite produced from the converter dust under a drastic decline in temperature at this steel plant can be recycled and used. The percentage of kish graphite acquired after sorting was not high because this study adopted flotation as the approach. We suggest that future researchers use different sorting methods to increase the recovery rate.

References

1. R. Frost, "The recovery of kish graphite from secondary sources", MRes Thesis, University of Birmingham, Birmingham, 2015.

2. M. Inagaki and F. Kang, "Materials Science and Engineering of carbon: Fundamentals", Butterworth-Heinemann, Oxford, 2014, **2**, pp. 17-217.

3. J. C. Charlier, J. P. Michenaud, X. Gonze and J. P. Vigneron, *Phys. Rev.*, 1991, **B44**, 13237.

4. M. S. Wu, B. Xu, L. Q. Chen and C. Y. Ouyang, *Electrochim. Acta*, 2016, **195**, 158.

5. C. Heske, R. Treusch, F. J. Himpsel, S. Kakar, L. J. Terminello, H. J. Weyer and E. L. Shirley, *Phys. Rev.*, 1999, **B59**, 4680.

6. S. Wang, K. V. Kravchyk, F. Krumeich, M. V. Kovalenko, *Appl. Mater. Interf.*, 2017, **9**, 28478.

7. M. L. Agiorgousis, Y.-Y. Sun and S. Zhang, *ACS Energy Lett.*, 2017, **2**, 689.

8. B. Moradi and G. G. Botte, *J. Appl. Electrochem.*, 2016, **46**, 123.

9. G. H. Chen, D. J. Wu, G. Weng and C. L. Wu, *Carbon*, 2003, **41**, 579.