PIXE ANALYSIS OF GRAPHITE PHASE IN NODULAR CAST IRON

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ABSTRACT

The graphite phase has been extracted from the nodular cast iron to measure the concentration of trace element in it. The impurity phase was removed from the extracted matter by dissolving it with HCl and HCl+ H_2O_2 to get the pure graphite phase. PIXE measurements were performed with thick targets of the pure graphite phase. Differences in the trace element concentrations between the graphite phase and the matrix have been observed. The effect of Ti and As in graphite phase on the nodularization rate and the mechanical properties have been studied.

Keywords: PIXE Graphite phase Nodular cast iron Trace elements

1 INTRODUCTION

The production of nodular cast iron is a kind of structural material and its application has been extending rapidly ever since it was developed in the 1950s.[1] The nodularization rate of graphite phase in nodular cast iron has a direct effect on the properties of the material. However, the nodularizing mechanism of graphite is still not clear, and little is known about the trace elements in the graphite phase, despite the efforts made so far to clarify the effect of the trace elements on the spheroidization of the graphite.[2,3]

In this paper, PIXE method[4] was used to analyze the trace elements in graphite phase. The anti- nodularizing elements Ti and As have been studied.

2 EXPERIMENTAL

Pig iron samples were taken from three places in China and various kinds of nodular cast irons were made by nodularizing. For some of the samples, certain amounts of Ti and As were added respectively to investigate the dependence of spheroidization of graphite phase on the elements. Mechanical properties and metallography of the samples were studied after the preparation.

The graphite phase was extracted from the nodular cast irons using "Speed" electrolytic technique.[5] A number of impurities, such as Fe_3C, VC, TiN, MnS, CaO, Al_2O_3 and TiC were found in the extracted materials. These impurities were removed by dissolving the extracted graphite in HCl and $HCl+H_2O_2$. Solubilities of the five main impurity compositions (Fe_3C, VC, TiN, MnS and CaO) in the solution were measured by ICP and the results are shown in Fig.1. The curves show that after about one hour, the main impurities had nearly been dissolved.

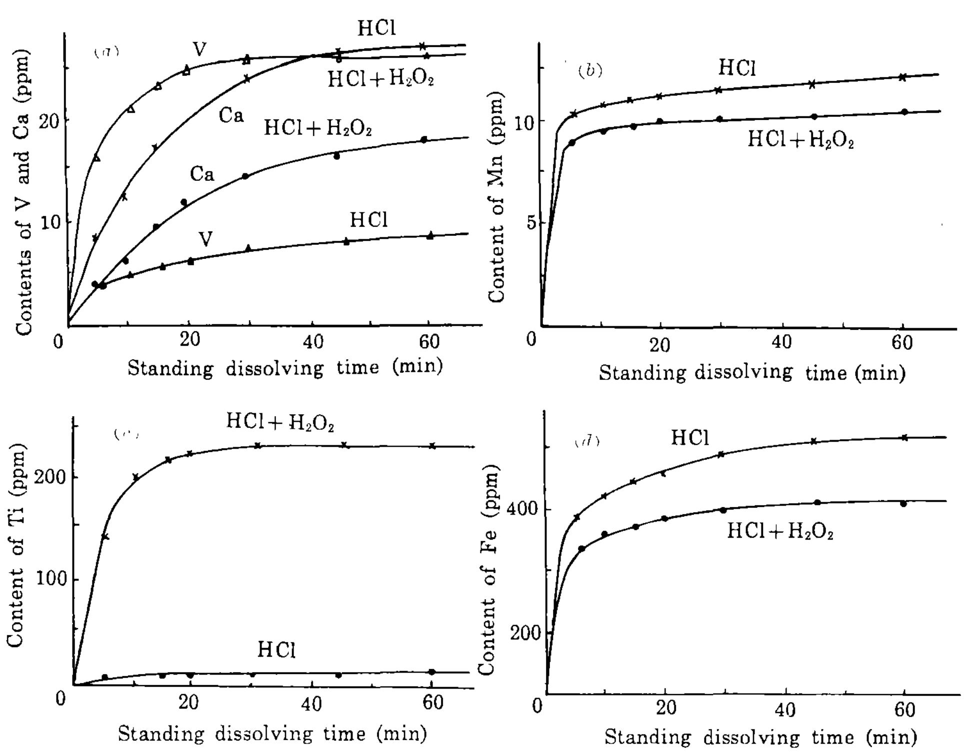

Fig.1 The solubilizing properties of VC and Cao (a), MnS (b), TiN (c) and Fe_3C (d)

In view of the difficulties of preparing thin graphite targets and possible loss of low melting point elements such as S and As, thick targets were prepared for PIXE analysis. The graphite powder was mixed with about 10% of boric acid in target weight, it was pressed into a disc of 10 mm in diameter and about 2 mm in thickness: The PIXE measurement was conducted on the Van de Graff at the Institute of High Energy Physics. The proton beam energy was 2.4 MeV, with a beam spot of 0.13 cm^2 and beam current of 9—11 nA. An Ortec Si (Li) detector with active diameter 10 mm and resolution 174 eV at 5.9 keV was used. An absorber of 37 μm Al foil with 1 mm hole was placed in front of the detector to reduce low energy radiation. X-ray spectra were analyzed by the AXIL code on a PDP-11/23 computer.

Ultrapure graphite standards were applied to calibrate the PIXE system. X-rays of several elements were counted at different points to determine the homogeneity of the elemental distributions. The fluctuations were less than 15%. Typical PIXE spectra of a nodular graphite sample is shown in Fig.2.

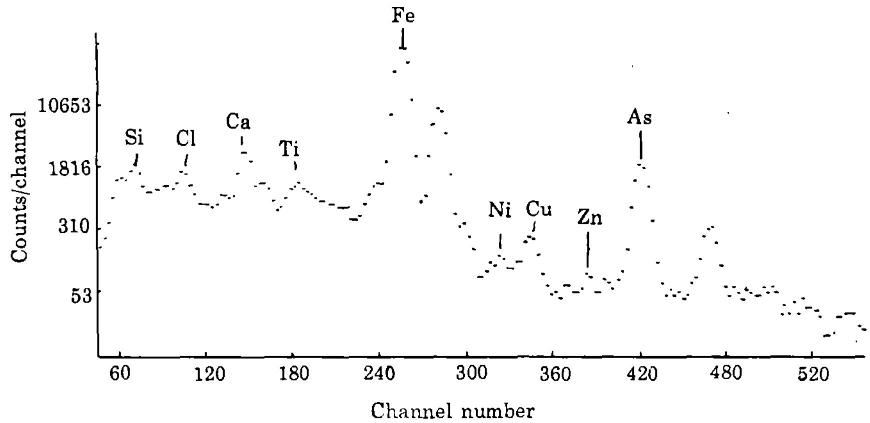

Fig.2 Typical PIXE spectra of a nodular graphite sample

3 RESULTS AND DISCUSSION

The concentrations of Si, P, Cl, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As in graphite phase were measured. The contents of some elements in the solution removing the impurities were also measured. These experimental results are shown in the following figures and tables.

As shown in Fig.2, PIXE analysis technique can be applied to give out the clear PIXE spectrum of thick target made of graphite phase and to measure the trace elements in graphite phase. It showed that many trace elements exist obviously in the graphite phase. Therefore, we have a presentment of complexity on the chemical composition in it.

The curves of solubilities given by Fig.1 show the contents of five main impurity elements have nearly reached the stable condition for about one hour. According to that, these impurity phases have almost been dissolved. It is in agreement with the result obtained by X-ray refraction. Besides the five main impurity elements, Cr, Cu, Mg and As were observed in the solution. Although the contents of the elements were very low, it indicated that the chemical compounds of the elements have been removed too On the other hand, it is possible to dissolve some of these elements down from the surface of graphite phase as the impurity phase was removed away using the acid-dissolution. However, the curves showed that the variation of chemical composition in the solution was generally ppm below when dissolving has lasted a certain time. If the acid had corroded into the inner of graphite phase, the variation of chemical composition would have gradually increased with dissolving time throughout the acid-solubilizing process. Whether the acid was able to corrode into the graphite has been checked by soaking the pure graphite balls in acid again and measuring the contents of certain elements in the solution at regular intervals. The variation of concentrations of seven elements is shown in Table 1. After having soaked for 2 h, the variation for most of them was almost below 2 ppm, except the variation with 11 ppm on Fe. We dissolved the impurities with acid within two hours, so that acid-corroding on graphite phase was very small and have not obviously effect on the measuring results of graphite phase by PIXE analysis. In the light of the discussion and the results as above, it can be seen that the method of removing impurity is efficacious. However, there is a problem yet. Cores exist in some graphite balls. It is a question to be worth considering and studying. The various impurity cores such as CaO, MgO, SiO_2 and TiN had already been found by the scientists. They are more difficult to be separated away from the graphite phase. How to get the influence in the measuring over are to be resolved in future.

Table 1

The check of acid— corroding graphite by ICP ppm

Sample	Fe	Ca	Ti	V	Mn	Mg	Al
1h	18	4.8	3	1.5	-	1.7	2.9
3h	7	3.5	-	-	-	2.0	1.3

The concentrations of trace elements in graphite phase of various kinds of nodular cast iron are shown in Table 2. Most of them are very low except Fe.

Table 2

The contents of elements in graphite phase of nodular cast iron ppm

Sample	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As
BC	69	51	3.1	5.0	31	1780	<1.0	3.8	7.4	2.4
	±13	±14	±0.9	±1.3	±7	±322		±0.8	±1.6	±1.4
BJC	32	48	7.0	<1.0	49	2320	3.0	3.3	4.1	3.3
	±6	±13	±4.7		±12	±417	±0.7	±0.9	±1.0	±0.9
BXC	41	69	9.2	2.6	60	2610	5.1	5.4	6.0	2.3
	±8	±19	±2.0	±0.8	±11	±470	±1.1	±1.4	±1.4	±0.9

Titanium is one of the anti-nodularizing elements. In order to study its anti-nodularizing characteristic, the different amount Ti were added in nodular cast iron by sintering it. The concentrations of Ti in graphite phase and matrix are listed in Table 3. The concentration of Ti in graphite phase is 51 ppm and 340 ppm in the matrix in sample BC. Most of the graphites in sample BC have got spheroidizing. The spheroidizing percentage is 86.4. After having added the amount of Ti to 3600 ppm in sample BCTi-2, a part of Ti intruded into the graphite phase while sintering the nodular cast iron. The graphite phases which was originally spherical became grotesque in shape. The nodularizing rate decreased evidently from 86.4% to 32%. Its mechanical properties got worse as well. Because the Ti was added in the nodular cast iron the part of it formed TiC. Probably the TiC can increase the tensile strength, in fact it did not. Therefore decreasing nodularizing rate would cause not only the tensile strength being decreased but also the elongation being cut down.

Table 3

The effect of Ti on nodularizing rate and mechanical properties of nodular cast iron

Sample	Content of Ti in matrix (ppm)	Content of Ti in graphite (ppm)	Nodularizing rate (%)	Tensile strength (N/mm^2)	Elongation (%)
BC	340	51 ± 14	86.4	480	22.4
BCTi-1	780	30 ± 5	84	490	20
BCTi-2	3600	110 ± 11	32	285	4

Arsenic is another one of anti-nodularizing elements. It was added to certain concentration for the same purpose in the same way as above. The contents of As in both the matrix and the graphite phase are shown in Table 4. It is very low in sample BC. The concentration of As in the graphite phase of specimen BCAs-1 changed slightly as it was being increased to 260 ppm in matrix. Most of the graphite phase remained the spherical yet. An abrupt change of As in the graphite phase of sample BCAs-2 took place as the concentration of it in the matrix was added to 1800 ppm. The nodularizing rate got worse. The mechanical property of nodular cast iron does not completely depend on the nodularizing rate, however, it affects the elongation obviously.

Table 4

The effect of As on nodularizing rate and mechanical properties of nodular cast iron

Sample	Content of As in matrix (ppm)	Content of As in graphite phase (ppm)	Nodularizing rate (%)	Tensile strength (N/mm^2)	Elongation (%)
BC	62	2.4 ± 1.4	86.4	480	22.4
BCAs-1	260	4.6 ± 3.6	90	519	16
BCAs-2	1800	150 ± 29	81	595	0.6

4 SUMMARY

a. Our separation technique of electrolysis and thick target analysis for graphite phase are feasible.

b. The anti-nodularizing characteristics of As and Ti are correlated with the concentrations in graphite phase. They mainly exist in the matrix as a form of impurity phase for good products. The contents of anti-nodularizing elements in graphite phase are far less than those in the matrix. A small amount change of the anti-nodularizing elements in graphite phase is able to affect the nodularization and the mechanical properties.

c. As a result, we deduced that the concentration of trace elements in graphite phase might act as a characteristic of the graphite nodularization.

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