Thermochimica Acta, 103 (1986) 169—174
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

SOME RESULTS OF INVESTIGATIONS INTO RELATIONSHIP BETWEEN A FEW ELEMENTS OF NODULAR GRAPHITE CAST IRON AND NODULAR GRAPHITE

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ABSTRACT

An investigation of the fractured surfaces of pins, having a diameter of 1.5 mm, obtained during the production of commercial nodular cast irons of Meehanite types is reported. The investigation was performed using a scanning electron microscope, with a Kevex system for energy dispersive analysis and scanning Auger microprobe, where the principal attention was given to SAM. Point analysis, Auger images and Auger line scans were performed on the fractured surfaces and also approx. 200 Å and 1 µm under the surface. The nodule/metal and intercrystalline interfaces in the investigated iron were free of foreign elements.

INTRODUCTION

The mechanism by which modifying elements, such as magnesium and cerium change the shape of the graphite phase in cast iron from flake graphite to nodular graphite is not understood(ref.1 to ref.6). Several of the proposed models involve the effect of surface active elements, present as impurities in cast iron, on the morphology of the graphite phase. Recently (ref.7 and ref.8) it was shown, that sulphur and oxygen, being always present in commercial alloys adsorb at the graphite/melt interface, effectively "stabilizing" the growth ledges and spirals of the graphite basal planes, and preventing spherulitic growth. The purpose of modifiers is then to getter these impurities. A review of the previous work does indicate that the reasonable modification theories all depend on subtle changes in the chemistry, either the graphite/metal phase boundaries or the intercrystalline graphite boundaries for the change in graphite morphology(ref.9 to ref.15). Unfortunately conventional analysis techniques such as microprobe(ref.1), autoradiography (ref.15) or sessile drop measurements(ref.6) are not sensitive enough or lack the necessary elemental sensitivity to succes-

0040-6031/86/$03.50

sfully detect the limited chemical variations responsible for the effect.

The purpose of this study was to analyze the chemical composition of the nuclei and interfacial chemistry of fast cooled samples of nodular graphite iron. The fast cooled samples of nodular graphite were obtained during the production of nodular graphite iron as a controlling tool aimed at the performance of chemical analysis of carbon and sulphur.

In our study besides chemical analysis methods, metallography, SAM and SEM together with Kevex energy analysis were used for the investigation of pin samples obtained in the production of nodular cast iron. This resulted in a clearer picture of the mechanism of crystallisation of these alloys, which is very important for practical applications.

METHODS

Materials

Samples used to perform chemical analyses during the control process in the production of nodular cast iron were investigated. One of the usual processes to produce the Meehanite types of nodular graphite irons is the Osmose process, basically consisting of the following operations :

[a]preheating of the teapot ladle fitted with an oxygen diffuser

[b]desulphurization and carburization carried out during tapping, the carbide and graphite being added via a dispensing funnel into the vortex of the whirlspout. Agitation with nitrogen is made during tapping and desulphurization is complete in 2 minutes after the desired weighed amount of metal has been collected

[c]following desulphurization, agitation is decreased slightly and a nodulariser is added via a second funnel. Nitrogen flow is stopped immediately when the reaction of the nodulariser with the melt has finished.

Desulphurizing, e.g. with calcium carbide, is dependent upon time, temperature, contact and other factors. The nodularizing process cannot be controlled properly unless the sulphur content can be mantained at a low and constant figure after desulphurization. During this investigation two types of Meehanite nodular irons, being produced in a foundry in Rijeka, were examined : spheroidal pearlitic-ferritic and spheroidal ferritic, SPF and SF.

The chemical composition of one of the investigated pins was 3,80 % C , 0,003 % S and 2,75 % Si and the production procedure was aimed to obtain SF Meehanite cast iron.

Method of analysis

The samples, fractured surfaces of the pins, were first investigated in a SEM manufactured by Cambridge Scientific Instruments Comp., in conjunction with a Kevex X - ray energy spectrometry system. The SEM was used to provide high resolution micrographs necessary for interpretation of the fracture mode of the fractured surfaces investigated. The energy spectrometry system was used to obtain the chemical composition of the areas being investigated in the SEM.

In order to determine the chemistry of cast iron phase boundaries, the technique chosen must have both surface sensitivity and sufficient spatial resolution to probe the phase boundary areas. Auger electron spectroscopy has been used successfully in studying embrittlement and grain boundary segregation(ref.16 to ref. 18). Assuming that nodular iron phase boundaries could be obtained as free surfaces through fracture, having in mind that graphite nodules often separate cleanly from the metal, we have chosen pins for investigation. In this way the number of nodules was smaller and also the area fraction of phase boundary fracture contained on this surface is relatively small ; hence the method of analysis chosen must have sufficient spatial resolution to analyse only these areas, i.e. the nodules. The scanning Auger microprobe, SAM, PHI Model 545 A is such an instrument and can be used to obtain Auger images, Auger line scans and Auger point analyses of a surface. The instrument used in this investigation manufactured by Physical Electronics Industries, Inc., Eden Prairie, Minnesota. The Instrument has an exciting electron beam with a minimum diameter of 3 micron and can be rastred over the surface of the probe.

The advantage of Auger electron spectroscopy is the ability of performing the analysis of very small volumes. This is very important factor in analysis of phases whose magnitude is of the order of .1 um, the method adopted is sensitive for elements with low atomic numbers. The surfaces of the samples, which were ground and polished before the specimens were mounted in the UHV chamber of the spectrometer were etched by sputtering with Ar ions under the pressure of 6;6 $\cdot 10^{-3}$ Pa. Ar was injected at pressures lower than

$1{;}33 \cdot 10^{-7}$ Pa.

With ion sputter etching the layer of oxides and impurities on the surface of the pin samples was removed, thus enabling us to observe the metal matrix, graphite nodules and oxide inclusions of the investigated nodular iron. First analysis was performed approximately 200 Å under the surface and then deeper, about 1 µm under the surface. The diameter of the primary electron beam was estimated to be smaller then 5 µm. Point analysis, Auger images and Auger line scans were performed on metal matrix, graphite and oxide inclusions.

RESULTS

From the results which were obtained during this investigation only some results of AES spectrometry are shown here.

In this connection it is still interesting to mention the results which were obtained on behalf of the energy dispersive analysis. The results of EDA showed iron peaks on the surface of graphite nodules and smaller peaks of silicon.

In Table 1 are the results of chemical analysis of a pin and in Table 2 are the results of a qualitative estimation of the composition of the phases first being analysed 200 Å under the surface and then 1 µm under the surface of the pin, having the chemical analysis as shown in Table 1.

From the results shown in Table 2, the following qualitative estimated composition of metal matrix, graphite and oxide inclusion can be given.

Besides iron in the metal matrix we found carbon and some oxygen. In the investigated sample we found at the depth of 200 Å traces of sulphur, being not more present at the depth of 1 µm under the surface.

On graphite nodules in the investigated sample larger concentrations of carbon were found. On the graphite nodules at 200 Å under the surface, smaller concentrations of iron and oxygen, and also traces of sulphur were found. Sulphur again disappeared at a depth of 1 µm under the surface.

During the investigation of oxide type inclusions we found besides iron, oxygen and carbon, also silicon and magnesium. At 200 Å under the surface nitrogen and potassium were found too. At both depths traces of sulphur were found.

During the in - depth etching procedure, in order to construct elemental concentration at the 1 µm level under the surface, the

TABLE 1

Chemical composition of the pin investigated by AES spectroscopy

	Fe %	C %	O %	S %	N %	Na %	Mg %	Si %
pin		4,06		0,014				2,79

TABLE 2

Qualitative composition for metal matrix graphite and oxide inclusions in Sample pin with the chemical analysis

	Element							
	Fe	C	O	S	N	Na	Mg	Si
200 Å under the surface								
metal matrix	o	o	o	o	o			
graphite	o	o	o	o				
oxide inclusion	o	o	o	o	o	o	o	o
1 µm under the surface								
metal matrix	o	o	o					
graphite	o	o	o					
oxide inclusion	o	o	o	o			o	o

concentration of alkaline elements was markedly lowered, or alkaline elements were removed. As a cause of the nature of ion sputtering and specimen surface chemistry, there exist a number of factors which can contribute to possible artifacts in depth profiling. Alkaline elements could have sufficiently mobility even at room temperature to migrate readily under the influence of electric fields produced by electron or ion beam upon the surface of some specimen. This can contribute to the possibility of lowering concentration of sodium and potassium and can be contemplated as one of the weak parts of the AES method, but it must be pointed out that we did not observe greater changes in the concentration of both elements during bombardment of oxide inclusion only on behalf of the primary electron beam.

CONCLUSION

The following are the main findings of this SAM study of the pins of nodular cast iron. In the metal matrix carbon was detected with Auger spectrometry, a result which is consistent with the result of metallographic structure investigations of the pins, where cementite was the main constituent. The origin of iron signal on graphite nodules was confusing, since all nodules showed it, indicating that it probably was not due to scattering from the surrounding metal. Secondary images from the SEM did not indicate the cause but in the backscattered mode, the SEM images clearly showed specks of a different phase. The strong atomic weight contrast obtained in the backscattered electrons mode can resolve these particles, which are not visible in the secondary electron images. They have the same contrast as the metal matrix and are apparently metal inclusions that become trapped in the nodules during solidification. During the in-depth ion etching procedure the concentration of alkaline elements was markedly lowered and possible cause for such behavior are discussed.

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