A study of the effects of bismuth and rare earths when used in inoculants for the treatment of ductile cast irons

Introduction

It is well known that small amounts of bismuth, when added to ductile cast irons, dramatically increase the nodule number. To avoid degeneration of the nodules back to the flake form it has been common practice to add rare earths, usually in the form of mischmetal or as an integral part of the nodularising alloy. This type of treatment has often been used in chunky section ductile iron castings to prevent exploded nodules and thus improve the mechanical properties of the iron.

The introduction of alloy-based inoculants containing bismuth and rare earths has only served to expand the application of such additions and one such application is in thin walled ferritic castings where chill can be markedly reduced.

A preliminary study by the authors into ferrosilicon based alloys containing bismuth and rare earths indicated two remarkable phenomena.

- Using a standard inoculating practice in ladle technology, magnesium losses of 5 - 10% were commonly found between the time immediately before inoculation and the solidified casting. When Bi/RE containing inoculants were used, this Mg loss increased to between 20 - 25%.
- The as-cast surface of castings treated with Bi/RE containing inoculants were found to be coated with a white powder and metallographically, the affected areas were associated with degenerate graphite shapes. This effect has only been noted in ferritic grades of ductile iron cast in green sand moulds.

The purpose of the present investigation was to investigate any connection between the levels of bismuth and/or rare earths in the inoculating material and the incidence of high magnesium losses and surface defects.

All the casting trials in this series were performed in the foundry of Josef Brechmann GmbH in Schola Holte - Stukenbrock, Germany as an integral part of a thesis written by Frank Brechmann, Dipl. Ing, from which this paper has been extracted. Support work for the project was conducted by Foseco GmbH, Borken, Germany and Foseco International Limited, Birmingham, England.

Experimental Procedure

The casting trials were carried out under industrial production conditions in the Brechmann foundry, thus allowing continual comparison with standard practice.

The slightly hyper-eutectic base metal had an analysis as in table 1.
Nodularisation processes changed the carbon and silicon values to 3.6% and 2.4%

Table 1. Chemical composition of the base melt.

Element	C	Si	Mn	P	S
Amount in weight %	≃ 4.0	≃ 1.6	<0.15	<0.03	<0.01

respectively giving a carbon equivalent of 4.3 - 4.5%. Magnesium treatment took place using a sandwich process and, dependant upon the test requirement, two types of magnesium ferrosilicon were used, FSM 1 (with 0.7% RE) and FSM II (RE free), table 2. The inoculating materials used are given in table 3.
A total of 73 melts were conducted and results are given in table 4.

Table 2. Chemical composition of the nodularising alloy.

Element	Content Weight (%)	Content Weight (%)
Si	46.0	45.5
Mg	5.9	5.3
RE	0.7	-
Al	<1.0	0.8
Ca	2.0	1.8
Fe	Rest	Rest

Table 3. Chemical composition of the inoculating material.

Ele-	Content (weight %)								
ment	IM 1	IM 2	IM 3	IM 4	IM 5	IM 6	IM 7	IM 8	IM 9
Si	65.0	66.4	75.0	75.0	76.0	73.4	74.7	74.6	74.7
Bi	-	-	1.49	1.6	-	1.33	1.47	1.4	1.44
RE	-	-	-	0.77	2.8	0.036	0.88	1.66	3.34
Al	1.5	4.2	1.54	1.51	0.94	1.61	1.63	1.58	1.6
Ca	1.3	1.2	1.61	1.64	0.78	1.75	1.72	1.75	1.76
Zr	5.0	1.72	-	-	-	<0.01	<0.01	0.01	0.03
Mn	3.5	-	-	-	-	0.02	0.04	0.04	0.07

Figure 1 shows the pattern plate for the ferritic valve housing chosen as the ideal test piece for the investigation. This casting is regularly produced in large numbers so that any irregularities which may occur would be recognised immediately. Five per cent pearlite maximum was allowed within the specification.
The tapping temperature was 1520°C and with the exception of melts 11 - 20, 61, 62, 66 and 70 - mould inoculation - the inoculation treatment was

Figure 1 Pattern plate of the test casting (valve body).

carried out in the metal stream during the transfer of the melt from the nodularising treatment ladle to the casting ladle. The measurement 'waiting before casting' in table 4 indicates the length of time that the inoculated metal was held in the ladle before pouring. An average t(waiting) of 180 seconds was chosen from observation of the foundry practice to give a time in the mid-pouring range but which would avoid any temperature problems for the chosen casting.

Magnesium loss was determined from the difference between:

- The spectrographic Mg values immediately before transfer from the treatment to the casting ladle.
- The ICP analytical determinations of the Mg content of the castings produced.

ICP methods were also used to determine the bismuth and rare earth contents in each casting. Evaluation of any surface defect was based on

Table 4. Melts investigated and results obtained.

Series	Melt No	Master Alloy	Amount (weight%)	Inoc-ulant	Amount (weight %)	Waiting time (seconds) before casting	%Magnesium in the treatment ladle	%Magnesium in the casting	%Bismuth in the casting	%Rare Earth Metals in the casting	Magnesium loss (%)
	1						0.038	0.035			7.89
	2						0.035	0.032			8.57
	3			-	-		0.030	0.029			3.33
	4						0.035	0.033			5.71
I	5	FSM 1	1.6			0	0.032	0.030	-	-	6.25
	6				0.5		0.034	0.032			5.88
	7				0.5		0.037	0.037			*0.00*
	8			IM 1	0.5		0.032	0.031			3.13
	9				0.5		0.036	0.033			8.33
	10				0.5		0.037	0.036			2.70
	11				0.14		0.040	0.038		0.0088	6.25
	12				0.14		0.042	0.038		0.0080	9.52
	13				0.14		0.046	0.044		0.0088	5.43
	14				0.14	180	0.042	0.038	not	0.0084	9.52
	15			IM 2	0.14		0.037	0.034	detec-	0.0080	8.11
	16				0.14	Mould	0.034	0.026	table	0.0068	*23.53*
	17				0.14	inocu-	0.047	0.042		0.0092	11.70
II	18	FSM 1	1.6		0.14	lation	0.042	0.039		0.0090	7.14
	19				0.14		0.046	0.040		0.0096	*13.04*
	20				0.14		0.043	0.037		0.0090	*13.95*
	21				0.4		0.043	0.039		0.0096	10.47
	22				0.4		0.047	0.037	not	0.0082	*21.28*
	23			IM 1	0.4	180	0.046	0.038	detec-	0.0086	*17.39*
	24				0.4		0.039	0.034	table	0.0082	12.82
	25				0.4		0.040	0.035		0.0100	12.50
	26				0.4		0.040	0.029	0.0025	0.0076	28.75
	27				0.4		0.031	0.023	0.0026	0.0076	25.81
	28			IM 3	0.4		0.040	0.031	0.0019	0.0080	22.50
	29				0.4		0.030	0.023	0.0020	0.0064	25.00
	30				0.4		0.036	0.029	0.0018	0.0072	*19.44*
III	31	FSM 1	1.6		0.4	180	0.040	0.032	0.0023	0.0106	20.00
	32			IM 4	0.4		0.039	0.031	0.0020	0.0096	20.51
	33				0.4		0.036	0.029	0.0021	0.0090	19.44
	34				0.4		0.035	0.031	not	0.0152	12.86
	35			IM 5	0.4		0.029	0.025	detec-	0.0128	13.79
	36				0.4		0.038	0.032	table	0.0152	15.79
	37				0.4		0.042	0.033	0.0018	0.0010	21.43
	38			IM 3	0.4		0.041	0.030	0.0021	0.0010	26.83
	39				0.4		0.039	0.028	0.0020	0.0010	28.21
	40				0.4		0.048	0.038	0.0014	0.0010	21.88
	41				0.4		0.042	0.034	0.0019	0.0030	19.05
IV	42	FSM 2	1.8	IM 4	0.4	180	0.041	0.031	0.0022	0.0032	*24.39*
	43				0.4		0.048	0.039	0.0019	0.0036	19.79
	44				0.4		0.036	0.030	0.0015	0.0030	18.06
	45				0.4		0.039	0.034	not	0.0086	12.82
	46			IM 5	0.4		0.037	0.031	detec-	0.0082	16.22
	47				0.4		0.042	0.035	table	0.0084	17.86
	48				0.4		0.039	0.034		0.0092	12.82

Table 4. Melts investigated and results obtained cont..

Series	Melt No	Master Alloy	Amount (weight%)	Inoc-ulant	Amount (weight %)	Waiting time (seconds) before casting	Magnesium in the treatment ladle	Magnesium in the casting	Bismuth in the casting	Rare Earth Metals in the casting	Magnesium loss (%)
	49				0.4		0.038	0.040	0.0011	0.0014	*11.11*
	50			IM 6	0.4		0.037	0.030	0.0017	0.0012	18.92
	51				0.4		0.042	0.034	0.0020	0.0012	10.05
	52				0.4		0.032	0.033	0.0028	0.0038	*16.67*
	53			IM 7	0.4		0.034	0.027	0.0022	0.0038	20.59
V	54	FSM 2	1.8		0.4	180	0.032	0.026	0.0021	0.0034	20.31
	55				0.4		0.039	0.030	0.0018	0.0068	23.08
	56			IM 8	0.4		0.037	0.032	0.0020	0.0066	*13.51*
	57				0.4		0.041	0.033	0.0019	0.0066	20.73
	58				0.4		0.041	0.033	0.0020	0.0125	*20.73*
	59			IM 9	0.4		0.037	0.028	0.0027	0.0120	24.32
	60				0.4		0.041	0.030	0.0027	0.0115	26.83
	61	FSM 1	1.6	IM 2	0.14	m i	0.033	0.033	n t	0.0078	0.00
	62				0.2	m i	0.045	0.040	not	0.0014	11.11
	63			IM 1	0.4	45	0.049	0.042	detec-	0.0020	14.29
	64				0.4	90	0.052	0.038	table	0.0018	26.92
	65				0.4	180	0.048	0.032		0.0015	33.33
	66					m i	0.045	0.039	0.0003	0.0012	13.33
VI	67	FSM 2	1.8	IM 6	0.4	45	0.045	0.035	0.0015	0.0015	23.33
	68				0.4	90	0.040	0.030	0.0021	0.0011	26.25
	69				0.4	180	0.040	0.029	0.0019	0.0011	27.50
	70				0.2	m i	0.045	0.038	0.0005	0.0076	15.56
	71			IM 9	0.4	45	0.042	0.033	0.0014	0.0120	22.62
	72				0.4	90	0.044	0.031	0.0017	0.0100	*30.68*
	73				0.4	180	0.039	0.030	0.0023	0.0100	24.36

observations using both optical and scanning electron microscope techniques. It should be noted here that Test Series IV was deliberately designed to produce a surface defect.

Temperature determinations were made both in the treatment and casting ladles.

Assessment of microstructures and mechanical properties was made on several castings. However in this exercise these characteristics were only considered peripherally.

Test Results and Discussion

Apart from the results of the surface defect investigation, which for clarity is discussed separately, other results obtained are given in table 4, columns 8 -12.

From these results, the following understanding has been gained.

The Effect of Rare Earth Metals.

○ **Test Series I**

This pre-investigation series showed that, under the conditions prevailing in the Brechmann foundry, differences in Mg content could be detected.

○ **Test Series II**

In this series, the time ($t_{waiting}$ = 180 seconds) was defined for use in subsequent melts. A set of results particularly interesting in this series, melts 21 - 25, used inoculants containing no Bi or RE and yet showed very high levels of Mg loss (11.93% average). This was more than double the average loss for Series 1 - 5% at ($t_{waiting}$ = 0). i.e.

$t_{waiting}$	0 seconds	180 seconds
Mg loss	5%	11.93%

The only source of RE in these castings was from the nodulariser FSM 1.

○ **Test Series III and IV**

The average magnesium losses recorded have been summarised - see table 5. Note that anomalous results from table 4 have been eliminated from the calculations.

The lowest Mg losses were found using inoculant IM5 - containing only RE - regardless of the nodulariser used, values of 14.15% and 14.93% being found with FSM I and FSM II respectively.

The Bi and RE containing inoculants, IM 3 and IM 4, gave much greater Mg loss, 24.59% and 18.97% respectively. This clearly indicated that the high losses found with the Bi/RE containing inoculants were not caused by rare earths alone. Indeed, Mg losses of 20% plus were only found in the simultaneous or sole presence of bismuth.
More difficult to explain were the Mg losses of about 25% when the inoculant IM 3 (Bi, no RE) was used - Melts 26 - 30 - compared to the 19 - 20% loss with the IM 4 inoculant (Bi + RE) in melts 31 - 33, 41 - 44. This indicates that rare earths, in the presence of bismuth, reduced the high Mg loss.

Table 5. Average magnesium losses in Trial Series III and IV.

Inoculating material	Average Mg losses III (%)	Average Mg losses IV (%)
IM 3	25.52	24.59
IM 4	19.98	18.97
IM 5	14.15	14.93

Table 6. Bismuth yield of the melts from trial series III and IV which were inoculated with Bismuth and Rare Earth Metals.

Series	Melt No.	Inoculating Material	Rare Earth (Casting)	Bi yield %	Average Bi yield (%)
III (FSM 1)	26	IM 3	0.0076	41.95	36.24
	27		0.0076	43.62	
	28		0.0080	31.88	
	29		0.0064	33.56	
	30		0.0072	30.20	
	31	IM 4	0.0106	76.68	69.93
	32		0.0096	64.94	
	33		0.0090	68.18	
IV (FSM 2)	37	IM 3	0.0010	35.20	30.62
	38		0.0010	35.23	
	39		0.0010	33.56	
	40		0.0010	23.49	
	41	IM 4	0.0030	61.69	60.88
	42		0.0032	71.43	
	43		0.0036	61.69	
	44		0.0030	48.70	

If the use of FSM I - with RE - and FSM II - no RE - is compared, then the yield of Bi in the casting and the loss of Mg were increased in the case of the RE containing nodulariser. The contribution of the rare earths to the increase in magnesium loss was by indirect means via the increased yield in bismuth and did not contribute directly to this effect. The choice of nodulariser had little effect.

○ Test Series V

By increasing the rare earth content of the inoculants, IM6 through IM9, an increase in the loss of magnesium was noted, tables 3 and 4. However, insufficient data was available to form a firm trend. It appeared that increasing the rare earths had little effect on the degree of magnesium loss.

The Effects of Bismuth on Temperature

It is recognised that, for the foundryman, the relevant analysis is that of the casting, not necessarily the analysis of the material being added. With this in mind, figure 2 shows clearly a trend to increased magnesium loss with an increase in the retained bismuth level. The relationship between Mg loss and melt temperature was that which would be expected, the higher the temperature, the greater the Mg loss. In figure 2, the temperatures measured are those in the treatment ladle. Measurement in the casting ladle gave similar results with the temperatures approximately 100°C lower.

By connecting the upper boundaries of the columns in figure 2, the relationships became more apparent - see figure 3.

Theory

The boiling point of magnesium is 1104°C and that of bismuth is 1560°C. At the experimental temperature, under normal conditions, the liquid phases of both elements exist in equilibrium with their vapour phases. If several elements exist in such

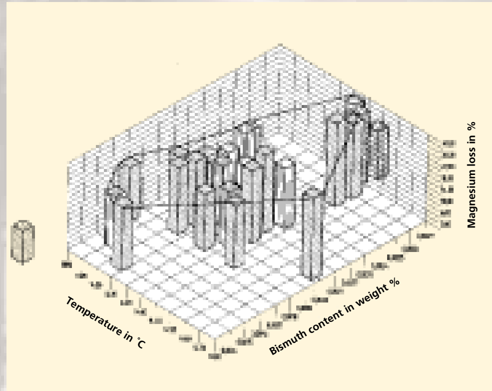

Figure 2. Representation of the individual results of test series III to V.

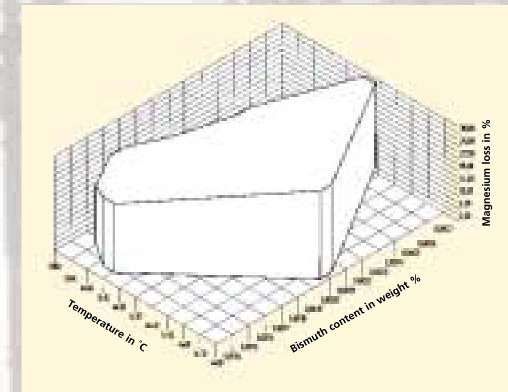

Figure 3. Representation of the whole picture in a smoothed form.

Table 7. Assessment schedule for the quantitative formation of surface defects.

Inoculating method		Inoculating material without Bi and Rare Earths	Inoculating material only with Bi and	Inoculating material with Bi and Rare Earths
Mould inoculation		+	---	----
Ladle inoculation with a waiting time of	45 s	+	--(-)	---
	90 s	+	--	--(-)
	180 s	+	-	--

KEY
\+ no, - very few, -- few, --- many, ---- very many defects

a system, then their vapour pressures are cumulative.
As the vapour above a liquid is constantly enriched with the component which has the greater vapour pressure - the lower boiling point - then this element will be the first to reduce in content from the liquid. In the case of Mg and Bi, the magnesium, which is already above its boiling point, will have the higher vapour pressure. As bismuth will have a relatively low vapour pressure at these temperatures it will contribute to the increased expulsion of magnesium. The effect of rare earths will be negligible as they boil only at about 3470°C.

The effect of temperature is now clear. At higher temperatures the tendency for Mg to vaporise is greater and more Mg escapes from the melt. The combination of a high Bi content and high temperature is the most detrimental.

Surface Defects

Many of the castings treated with Bi or Bi/RE containing inoculants showed unusual white surface blemishes. These can be associated with the adhesion of moulding sand. Was the defect associated with Bi or Bi/RE alone or was there a connection with some element from the moulding medium?

The surface blemish was at its worst in castings from Melt No. 70. These were inoculated with IM9, Bi and RE. A reduction in the RE content of the inoculant and/or a longer twaiting resulted in a less destructive defect. From figures 4 - 6 it can be seen that the amount of surface defect was proportional to the amount of degenerate graphite under the casting surface. Although rare earths do not appear to be responsible for an increase in Mg loss, they promote an increase in surface defects in the presence of bismuth, although bismuth alone will produce the noted defect.

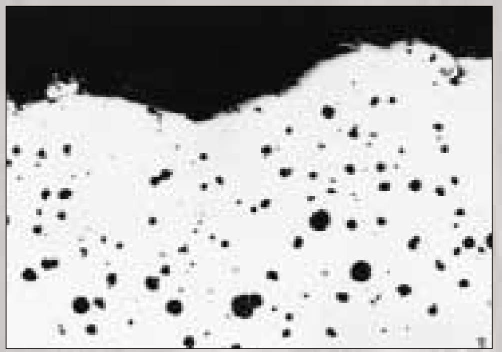

Figure 4. Light microscope photo micrograph of the defect free edge zone of sample 61 (master alloy FSM 1, mould inoculation with IM 2).

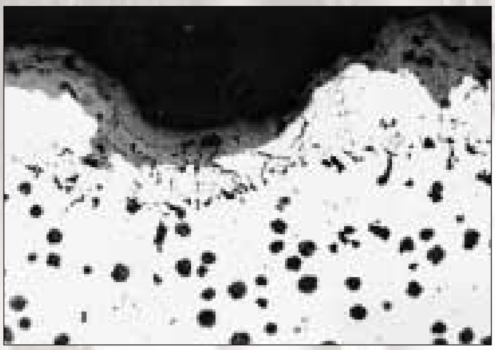

Figure 5. Light microscope photo micrograph of the edge zone of sample 69 with surface defects (master alloy FSM 2, ladle inoculation with IM 6, waiting time 180 seconds).

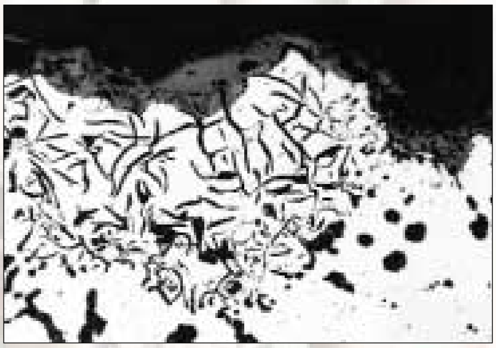

Figure 6. Light microscope photo micrograph of the edge zone of sample 70 with very pronounced surface defects (master alloy FSM 2, mould inoculation with IM 9).

Thus it seems probable that a relationship exists between the surface defect and the high Mg losses caused by bismuth.

Investigations using a scanning electron microscope

Examination of the casting surface by the SEM was undertaken on specimens which had not been shotblasted. As such, any residuals resulting from the chemical and thermodynamic processes in the mould during and after casting were present.

Depending on the inoculating material and the time $t_{waiting}$, there were clear differences in the chemical compositions of the residues between defect and defect-free surfaces.
In defect-free castings, only Fe, O and Si were detected see figure 7.

On slightly - figure 8 - and strongly - figure 9 - defective surfaces the presence of distinct peaks of Mg and Al could be detected - magnesium aluminium silicate. Clearly, the Mg originates from the melt and may well be present as MgO. Aluminium originates from either the melt or from the bentonite in the green sand, from montmorillonite Al_2O_3, $4SiO_2 \cdot H_2O+nH_2O$, and may well be present also as the oxide.

If figures 8 and 9 are compared, then in the case of inoculation with Bi and RE, Mg and Al occur in greater amounts than after treatment with inoculants containing only Bi. This indicated that rare earths participate in the formation of the surface defect.

From this investigation, the following causes for the formation of the surface defect may be understood. The castings containing the defect were inoculated with materials containing bismuth and thus high Mg losses occurred. Analysis of results using the SEM confirmed the association between Mg loss and the severity of the surface defects. Notably, with increased time between inoculation and casting (increased $t_{waiting}$), the poured castings showed less surface defects, indicating that the Mg vaporising processes had proceeded mainly in the ladle and not in the mould.

The reasons behind the effects of rare earths are less apparent. Whilst RE did not contribute to the loss of Mg, they have been shown to contribute to the severity of the surface defect. In the case of the moulding sand adhering to specimen 70, inoculated in the mould with a high RE containing material and the highest Al peaks associated with this sample, a reaction between RE and probably the bentonite is indicated. If the Al peaks were present in the other samples it could be argued that they had originated from the melt. Notably, the phenomenon of surface defects has been noted only in green sand castings, not for example, in cold-set resin, and this tends to support an association between RE and the moulding medium.

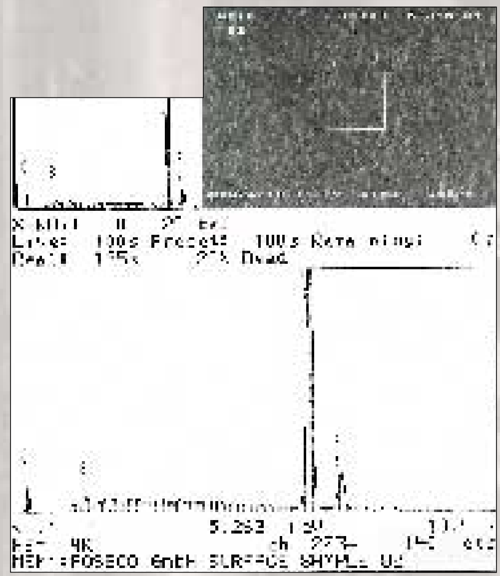

Figure 7. SEM analysis of the cast surface before shot blasting of casting 65 (no defects) (master alloy FSM 2, ladle inoculation with IM 1, waiting time 180 seconds).

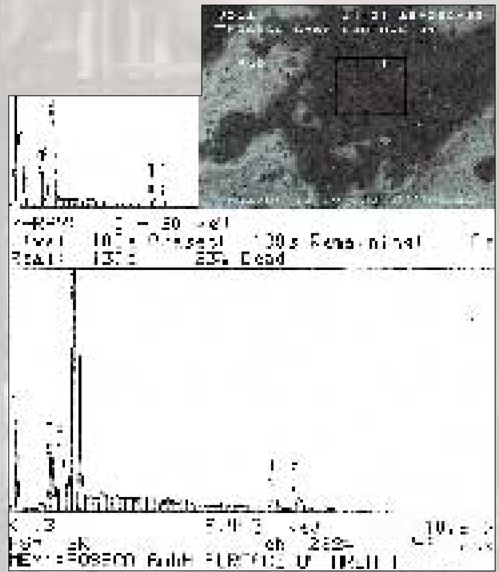

Figure 8. SEM analysis of the cast surface before shot blasting of casting 70 (very many surface defects) (master alloy FSM 2, ladle inoculation with IM 1, waiting time 180 seconds).

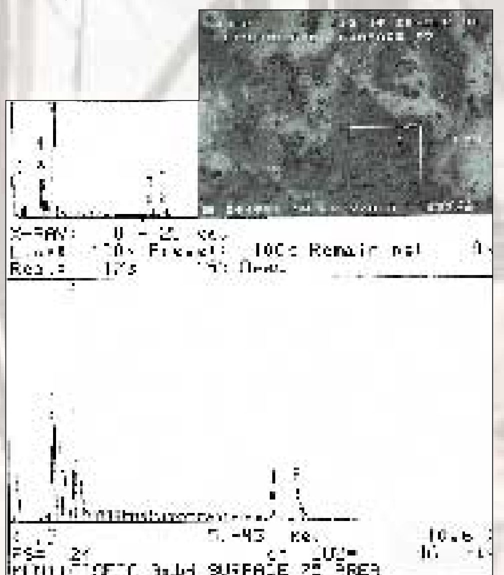

Figure 9. SEM analysis of the cast surface before shot blasting of casting 70 (very many surface defects) (master alloy FSM 2, mould inoculation with IM 9).

Graphite formation and mechanical properties

An increase in nodule number due to the presence of bismuth, as indicated in the literature, was confirmed. However the reduction in nodule size was not easily quantified.

With the exception of two valve housings, all the micro-sections contained Type IV graphite. These results do not concur with the literature in that it is claimed that RE should be present to prevent conversion to Type III or even Type I graphite. It is suspected that some traces of RE were present in this test series, as a result of recirculating returns.

Determined values for tensile strength have shown that castings inoculated with bismuth or Bi/RE containing materials lie in the upper regions of the spread normally obtained in the foundry with conventional inoculants. However some values of 0.2% proof stress were about 20 N/mm² above the normal spread of values. Elongation values were not affected by the change in inoculant.

Summary

This series of trials has shown that, using inoculants containing bismuth or Bi/RE an increase in nodule number can be obtained. Further consequences of these inoculations have been noted:

- Magnesium losses of up to 25% occur. This loss is over twice that found under conventional conditions.
- The addition of inoculating materials containing only bismuth, and in particular those with a combination of bismuth and rare earths, allow the formation of surface defects in the production of ferritic ductile iron. These are characterised in that they can appear anywhere on the casting surface, but more usually on the upper surfaces of the mould. These indentations contain magnesium silicates and magnesium aluminium silicates and the defect is accompanied by degeneration of graphite form at the casting surface. This degeneration is particularly severe in zones which contains Mg/Al – silicate slags.

The casting defect described has only been noted in ferritic grades of ductile produced in green sand moulds.

This paper has been abstracted from the thesis produced by F. Brechmann and the full document is held in the library of the Institute for Ferrous Metallurgy and Foundry Practice at the Technical University of Clausthal, Germany.