

Elimination and Neutralization of Boron in Ductile Irons

by

R. L. Naro – ASI International, Ltd., Cleveland, Ohio

J. F. Wallace and Yulong Zhu – Case Western Reserve University, Cleveland, Ohio

ABSTRACT

The presence of small amounts of boron in ductile iron is reported to have multiple and sometimes conflicting effects on the mechanical properties of ductile irons. The technical literature up until the early 1990's states that small amounts of boron is a powerful carbide stabilizing element. Boron levels as low as 0.001% (10 ppm's or parts per million) stabilize pearlite but larger amounts were found to form very stable carbides. Recent investigators have found just the opposite effects at very low boron levels in pearlitic ductile iron; reduced pearlite levels and Brinell hardness have been reported at levels between 0.0011 and 0.002% (11 to 20 ppm). The object of the present investigation was to evaluate the feasibility of removing boron from ductile iron melts by adding a mild fluxing agent that had the potential to react with boron but not harm a furnace refractory. The fluxing agent would form stable boron compounds that would subsequently be removed as a slag.

INTRODUCTION

Since the commercial introduction of ductile iron in the late 1940's, significant changes have taken place in the melting, metal holding and handling techniques of ductile iron. During the past decade, the general quality of metallic scrap units and other iron-unit feed stocks has steadily deteriorated. As a result, foundries have become increasingly concerned about trace element pickup as well as insoluble buildup in melting and metal handling vessels [1].

In the early 1970's, due to more complex requirements for deep drawing and more formable steels for the automotive and appliance industries, new steels were developed. The addition of 0.003% to 0.005% boron (30 to 50 ppms) to hot rolled steels provided vastly improved formability. Boron in very small amounts is also used to improve the hardenability of low carbon steel [2]. The recycling of these steels into the foundry scrap streams has been a recent concern to ductile iron producers. Several foundries have reported difficulty in meeting Brinell hardness properties in pearlitic ductile irons and have attributed these problems to boron contamination.

A direct consequence of all of the foregoing has been a renewed interest in the use of fluxes to control harmful trace elements [3]. A formal proposal was made to the Ductile Iron Society at the Annual DIS Meeting in Hilton Head, South Carolina on October 20, 2003 to investigate methods for the "Elimination and Neutralization of Boron in Ductile Irons".

EFFECTS OF BORON

Sources of boron contamination, in addition to steel scrap, may include boron pickup from refractory linings and silicon carbide charge materials. The technical literature relating to the effects of boron on the mechanical properties of ductile iron are somewhat conflicting. Very low levels of boron have been reported to act as carbide stabilizers and promote pearlite while recently others have reported just the opposite effect. Boron levels in the range of 0.0011% to 0.0020% (11 to 20 ppm's) reduce pearlite levels in pearlitic ductile irons and reduce Brinell hardness levels (BHN). Large quantities of pearlite stabilizing elements such as copper and tin are required to return to normal hardness and microstructures.

The 1991 Ductile Iron Society "Quality Control Manual" [4] categorizes boron as one of the most powerful carbide stabilizing elements in ductile iron. In strongly hypereutectic compositions, it has been observed that it causes inverse chill – in the center of gates, for instance. In the presence of about 0.002% boron, stable carbides will be observed. The maximum amount of boron that can be tolerated is 0.002% (20 ppm). Boron pick-up may come from boron-containing steels, from furnace linings or from boron-containing ferrosilicon.

A literature review published by the Watertown Arsenal [5] claimed that boron has an adverse effect on graphite form and mechanical properties in section sizes greater than 1 inch. An addition of 0.005% boron (50 ppm's) to nodular irons with section sizes between 0.5- to 1-inches had little effect on graphite form. However, in a 1.5-inch section, nodule count decreased from 85 to 59 nodules per square millimeter and spheroidal graphite percentage was reduced from 84% to 56%. In a 6-inch diameter nodular iron casting, 0.01% boron (100 ppm) reduced elongation from 12% to 7% and reduced tensile strength from 63,000 psi to 57,500 psi. Boron stabilizes pearlite and forms carbides in nodular iron. As little as 0.001% (10 ppm's) stabilizes pearlite but larger amounts may form carbides that cannot be removed by heat treatment.

Other technical references have also established the influence of larger amounts of boron on chilling tendency and carbide stabilization in ductile irons [6-8].

Recent technical bulletins in the Ductile Iron Society offer somewhat different findings. Lyle Jenkins reported that boron pickup could be responsible for reduced BHN hardness in pearlitic ductile iron and that increased levels of tin and copper were required for neutralization [9]. Typical boron levels in ductile iron are 0.0015% (15 ppm). Boron levels are not reduced during either cupola or induction melting. Jenkins pointed out the need to do further research to determine if boron can reduce toughness and fatigue strength and if its presence could improve nodule counts and segregation in heavy section castings.

Ductile Iron Society technical bulletin "Hot Topics" by Gundlach discussed the consequences of boron pickup from refractory furnace linings [10]. It was reported that boron levels above 0.0005% (5 ppm) could influence the ability to develop fully pearlitic microstructures. It was also reported that when boron levels exceeded 0.0008% (8 ppm), copper content needed to be doubled to 0.47% before the original pearlitic microstructure was restored. Ferritic ductile irons having a microstructure of 20% pearlite (having a residual copper content of 0.20% and containing 0.0006% boron or 6 ppm), were unaffected by the addition of 0.0057% boron (57 ppm), thus indicating that boron isn't likely to promote ferritic structures in ductile irons. However, in one study of boron effects on reductions in Brinell hardness, rather extreme findings were noted. This foundry noticed significant reductions in Brinell hardness of pearlitic ductile iron after holding in pressure pour furnaces for several weeks. The foundry studied the metal chemistry and found that boron levels ranged from 0.0019% (19 ppm) to 0.0059% (59 ppm) during the problem period. As the boron content dropped below 0.0017% (17 ppm), the hardness returned to normal (200 - 210 BHN) without changes in the other chemical residuals. In addition, as the boron levels dropped below 0.0006%, the hardness increased to over 230 BHN.

At the higher carbon levels present in ductile irons, it is suspected that boron can exert considerable effects on the structure of pearlitic ductile iron by decreasing the hardenability factors for copper and other conventional hardening elements (tin). This subject was made apparent in a paper presented at a recent (June 2003) Ductile Iron Society meeting in a paper

written by Daniel A. Mayton [11]. This paper clearly shows the difficulties that can be obtained when boron is picked up in the melting process when extremely minute amounts of boron enter the cupola from various charge materials. Mayton reported that boron levels below 0.0012% (12 ppm's) do not result in any problems. Between 12 ppm and 100 ppm (0.01%), boron had a significant effect on reducing Brinell hardness levels. Above 0.01% boron (100 ppm), the effect of boron reverses and results in loss of elongation, increases carbides and reduces machinability. Mayton reported that the source of the boron contamination was from the silicon carbide used in their cupola charge. Mayton also reported in an informal survey of several foundries that boron pickup was not a universal problem, and many foundries reported that they had no boron related issues.

Following the DIS meeting of June 2003, Martin Gagne of Rio Tinto issued a report titled "Thermodynamic Evaluation of Boron Removal from Ductile Iron Melts" [12]. The report was initiated based on discussions pertaining to whether favorable thermodynamics conditions were possible between boron and mild proprietary fluxes containing the element sodium that were being successfully used by many ductile iron foundries that were experiencing insoluble buildup in channel furnaces and pressure pours [2].

Gagne theorized that based on thermodynamic calculations, injecting soda ash into molten iron could reduce boron levels from 20 ppm to 4 ppm. Gagne showed that at reasonable temperatures, such as 2530°F, the removal boron by treatment with $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ is possible from his thermodynamic model. Higher temperatures, such as 2850°F would generally not be very effective in removing boron. However, he reported that injection rates of 20 kg/ton (44 lbs) of soda ash would be necessary.

Theoretical considerations for boron removal by fluxing – Sodium based fluxes are known to have sufficient solubility for boron oxide. Figure 1 shows various reactions between Na_2O and B_2O_3 to form solutions of sodium oxide having multiple concentrations of B_2O_3 .

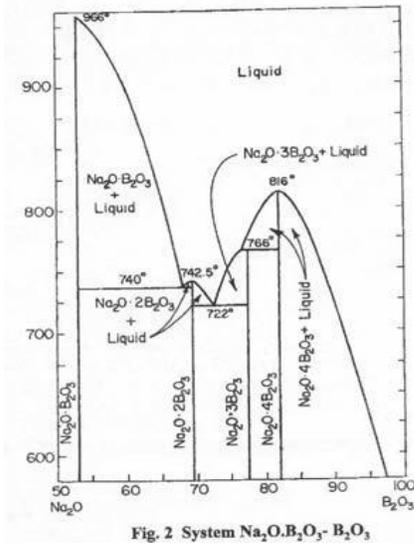


Figure 1: Section of the phase diagram for the system $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 - \text{B}_2\text{O}_3$

Figure 2 and 3 show that mixtures of B_2O_3 , Na_2O and SiO_2 can react together to form a glassy phase or slag that can be de-slagged and removed from the melt.

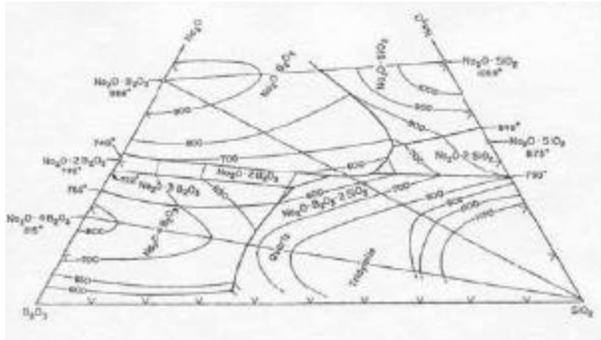


Figure 2: Section of the ternary phase diagram for the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$

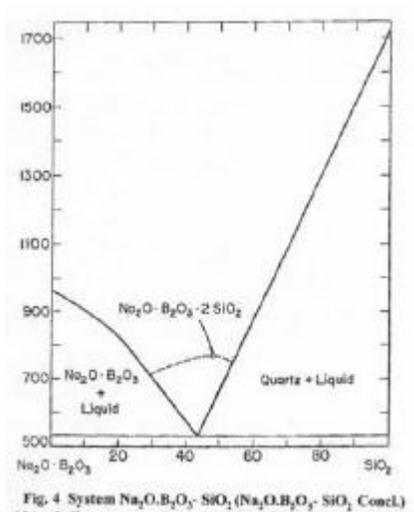


Figure 3: Section of the binary phase diagram for the system $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 - \text{SiO}_2$

For this investigation, it was assumed that boron would be oxidized by the presence of NaO_2 and other oxides such as SiO_2 in the melt. Even though boron will form carbides when present in the solid iron, its exposure in the melt to a sodium-based flux should produce sufficient oxidation for B_2O_3 to form and be subsequently eliminated by a fluxing action. It was anticipated that the reaction between sodium oxide and boron oxide should proceed to equilibrium and that the ensuing complex phase consisting of silica, boron oxide and sodium oxide would be removed from the melt as slag.

Fluxes based on sodium oxide along with minerals containing silica were added to experimental ductile iron heats when boron is present in the molten iron to determine the feasibility of boron removal. The sodium oxide or Na_2O would be added in the form of a proprietary pressed flux briquette.

MATERIALS AND PROCEDURES

Laboratory Studies – The original work that was proposed for this project involved a series of five heats. The procedure used in the investigation involved the addition of fluxes to the melt that have the capability of absorbing residual boron as the compound boron oxide. The first heat was to establish a basic composition that was agreed upon by Research Committee members.

The second heat would establish the effect of adding a sodium oxide based flux to the molten iron. The third and fourth heats would establish the influence of boron on the structure of the irons studied and the fifth heat will establish the joint effect of the boron plus suitable additions of a flux to remove it. The Citation Biscoe North Carolina foundry greatly assisted the authors by contributing valuable analytical support.

The ductile irons were prepared in a high frequency, 500-pound capacity induction furnace. The furnace was lined with a dry vibratable, 90% minimum magnesite refractory. The bonding agent in the magnesite refractory was a non-boric acid binder. The lining was used for several wash heats before this investigation began. All virgin charge materials were used for all of the experimental heats. Several members of the DIS were consulted for suggestions on target chemistries to produce pearlitic ductile iron. A description of the charge used, percentage of individual element charged and target chemistry is shown in Table 1.

Table 1: Charge Ingredients for Experimental Heats

Ingredients Charged	Weight in lbs. or (grams)	% Element Charged	Target
Desulco Carbon	0.65	0.144% Carbon	3.60 % C
Sorel Pig Iron (4.3% C)	345	3.70% Carbon	
75% FeSi 8 mesh x d	11.73	2.23% Silicon	2.13% Si **
Armco low carbon iron	40.02		
Electrolytic Manganese	426 grams	0.23% Mn	0.30% Mn
Copper wire	2.83	0.70% Cu	0.70% Cu
Ferroboron *	*204.3 grams to 325 lbs	*21 ppm when added	
Total Charge Weight	400.5		
Nodularizing additions to 90 pound ladles			
Nickel Mag Alloy No. 4	492 grams	0.07% Mg	0.045% Mg
65%FeSi with Mn & Ba	284 grams	0.50% Silicon	0.470%
** Total target silicon content was 2.60%, 2.13% base iron, 0.47% Si from ladle inoculant			

The charge materials shown in Table 1 were melted in approximately 30 minutes under moderate power conditions. Boron was added as a 17% boron containing ferroalloy, sized ¼ inch by down; ferroboron additions were made directly to the furnace. In one series of experiments (Heat No. 4), after the boron was added to the furnace, the metal was pigged. The pigs were allowed to air cool and were re-melted a few weeks later when they were then subjected to a second rigorous fluxing. It was felt that by having the flux in the charge from the onset of melting would allow longer reaction times. On other occasions, ferroboron was added to the furnace, test castings were poured, and then a modified sodium-based flux was added to the furnace and allowed to react for approximately 12 minutes at 2,750°F. The slag generated from the fluxing action was removed from the melt before pouring the castings.

The treatment ladle was preheated prior to tapping. Because of the very precise laboratory conditions required, along with making 75-pound taps, the nodulizing alloy selected was NiMag Alloy No. 4. This alloy contains 4.5% magnesium, 65% nickel and 30% iron and has a density of 7.35 grams/cc so that it can be simply tossed into a treatment ladle where it will sink immediately and release magnesium vapor for nodulizing. Because of NiMag No. 4's high density compared to molten base iron (6.65 grams/cc), magnesium recoveries are very high and consistent, and the nodulizing reaction is extremely calm, with negligible flare and violence. A rapid-dissolving barium and manganese bearing ferrosilicon, sized 20 by 70 mesh was used as a

ladle inoculant. The inoculant was placed in the bottom of the open treatment ladle. Base iron was poured to a to a predetermined level in the treatment ladle, and the amount was further verified by weighing. The ladle was then stirred to insure complete dissolution of the nodulizing alloy and inoculant. Samples of treated ductile iron were taken from each treatment ladle and spoon poured into a chill mold. The remaining iron was then poured into green sand mold using two configurations of tensile test castings. The test castings were allowed to cool to room temperature before shakeout. The tensile bars were pulled and tensile strength, yield strength and elongation were measured. Brinell hardness measurements were made on sections of the 7/8 inch diameter tensile bar ends. Metallographic evaluations were also conducted on the tensile bars.

Several foundries co-operated with the authors and were utilized to measure carbon, silicon, copper, magnesium, manganese and nickel levels as well as assist in hardness measurements. Participating foundries that volunteered to do the analytical work did so to reduce costs to the DIS and they are recognized in the acknowledgements in this paper. The Citation Biscoe North Carolina plant participated in all of the assays and provided what was later found to be excellent and the most consistent boron analysis.

In-Plant Studies – During the course of the tests, one foundry that was experiencing elevated boron levels, above 0.0012% (12 ppm), elected to run fluxing trials. For the flux trials, a 9-ton, medium-frequency coreless induction furnace, lined with a Silica Dri Vibe refractory was used.

At this foundry, boron levels typically run between 0.0010% to 0.0013% (10 to 13 ppm's) mainly due to the steel scrap and jump to levels between 0.0017% to 0.002% (17 to 20 ppm's) during refractory relines and sintering. Pressed sodium oxide flux briquettes or tablets were used for the fluxing experiments and added at levels ranging from 1 lbs per ton to 4 lbs per ton in various experiments. It should be noted that normal recommended addition rates from the flux producer are 0.5 to 2.0 lbs per ton of metal melted.

RESULTS AND DISCUSSION

Laboratory Studies - A first heat was made to access various charge and recovery variables. The aim chemistry is shown in Table 2. These target chemistry levels were selected based on private conversations with various Ductile Iron Society Research Committee members.

Table 2: Target Chemistry Levels for Boron Studies

Element	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% B
Desired	3.60%	2.60%	0.30%	0.70%	0.009%	0.010%	0.8%	0.0450%	As needed

Results of the first heat made in late April 2004 using spectrographic analysis from the Citation Biscoe plant are shown in Tables 3 below:

Table 3: Citation Biscoe – Heat No. 1

Element	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% B
Actual	n.a.	2.49%	0.30%	0.61%	0.009%	0.010%	1.15%	0.087%	0.0006%

Results of the second heat poured in late May 2004 are shown in Table 4. These results were reported at the DIS Research Committee meeting in June 2004. For Heat No. 2, boron levels were increased by adding 60 ppm to determine effect. In addition, 0.30% sodium-based flux for boron neutralization was studied.

Table 4: Citation Biscoe Chemistry Results – Heat No. 2

Heat Tap #’s	Notes	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% Boron
2 – 1		3.40%	2.22%	0.35%	N.A	0.017%	0.020%	1.23%	0.085%	0.0009%
2 – 2	1	3.44%	2.57%	0.34%	N.A	0.031%	0.015%	1.81%	0.106%	0.0060%
2 – 3	2	3.33%	2.52%	0.34%	N.A	0.025%	0.014%	1.53%	0.085%	0.0055%
2 – 4	3	3.30%	2.34%	0.34%	N.A	0.022%	0.013%	1.12%	0.064%	0.0050%

Notes: 1) 0.006% boron (60 ppm) as ferroboron added to furnace
 2) 0.30% flux added to furnace
 3) Additional 0.30% flux added to furnace

A DIS associate member also volunteered to analyze for boron. A summary comparison of boron results from Citation Biscoe and the associate member is shown in Table 5.

Table 5: Summary of Boron Results for Heat No. 2

Heat Tap #’s	Biscoe	Associate Member*
2 – 1	0.0009%	0.0012%
2 – 2	0.0060%	0.0069%
2 – 3	0.0055%	0.0069%
2 – 4	0.0050%	0.0067%

*Note: Samples sent to an outside laboratory

There was significant scatter in the boron results between Citation Biscoe and the co-operating associates outside lab. At this time, it was also observed that the sulfur levels increased to unacceptable levels. Use of a calcined pet coke, pour quality steel scrap rather than Armco iron, and possibly questionable calcium bearing 75% FeSi were all possible contributors. The microstructures contained considerable carbides.

While some reduction in boron was noted in the above heats, the DIS research committee felt that the boron levels were too high and requested a change to 20 ppm. Further, it was recommended that the boron contaminated furnace metal be pigged and melted down simultaneous with a second flux addition to more clearly duplicate conditions that arise in actual foundry charging and to provide the flux more time to “refine”.

Heat No. 3 was poured during the second week of August 2004. The spectrographic results are shown in Table 6, along with complete chemistries of the pig iron and steel scrap used (Table 11)

Table 6: Citation Biscoe Chemistry Results – Heat No. 3

Heat Tap #’s	Notes	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% Boron
Armco Iron		0.01%	0.01%	0.14%	0.04%	0.011%	0.014%	0.02%	0.000%	<0.0001%
Sorel Pig		4.43%	0.15%	0.01%	0.02%	0.002%	0.007%	0.07%	0.000%	<0.0001%
3 – Furnace	1	3.66%	2.46%	0.24%	0.74%	0.010%	0.011%	0.06%	0.000%	0.00030%
3–1	2	3.58%	2.79%	0.29%	0.70%	0.010%	0.011%	0.77%	0.049%	0.00050%
3–2	3	3.60%	2.81%	0.29%	0.70%	0.010%	0.011%	0.81%	0.048%	0.00250%

Notes: 1) Base Furnace Iron before Nodulizing
 2) Nodulized with 0.055% Mg as NiMag No. 4, inoculated with 0.38% silicon in the ladle
 3) Same as 2, except 0.0022% (22 ppm) boron, as ferroboron added to furnace.

A summary of all of the boron assays, including the newly submitted results from the DIS associate member company are shown in Table 7.

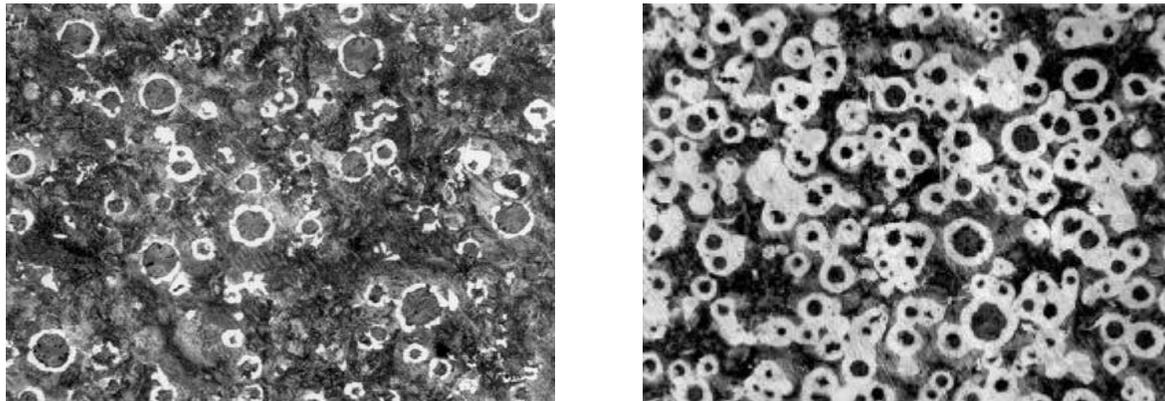
Table 7: Summary of Boron Results for Heat No. 3

Heat Tap #'s	Biscoe	Associate Member*
Armco Iron	<0.0001%	0.0007%
Sorel Pig	<0.0001%	0.0017%
3 – Furnace	0.00030%	0.0015%
3-1	0.00050%	0.0011%
3-2	0.00250%	0.0019 to 0.0041%

*Note – sent to an outside laboratory

Boron recoveries for Heat No. 3 were close to 100% based on spectrographic analysis from Citation Biscoe (with reported boron levels of 0.0025% or 25 ppm's). The associate member's lab experienced problems in assaying the samples and had them sent to an outside lab. The outside laboratory reported boron levels considerably higher than the levels reported by Citation Biscoe. The marked differences between Biscoe and the associate member's outside laboratory is unclear but does illustrate the difficulty in accurately determining boron levels.

The microstructures obtained from test coupons are shown in Figure 4 and the physical properties taken from the test bars from Heat No. 3 is shown in Table 8.



a. Base Iron – 5 ppm Boron (100x)

b. 25 ppm Boron (100x)

Figure 4: Microstructures obtained from test castings with and without boron additions.

The microstructure of the base iron, which had a residual boron content of 5 ppm (0.0005%), consisted of 90% pearlite and 10% ferrite. The addition of 25 ppm boron produced a significant reduction in pearlite content; pearlite levels were reduced from 90% to 40% with an accompanying increase in ferrite. Carbides were totally absent from the microstructures.

Table 8: Effects of Boron on Microstructure and Properties – Heat No. 3

Heat Tap #'s	Microstructure	Yield (ksi)	UTS (ksi)	Elongation	Brinell Fdry A & D	
					A	D
3 – 1	90% Pearlite	69.5	103.4	2.6%	241	280
3 – 2 (25 ppm B)	40% Pearlite	63.75	95.7	4.75%	217	222

The apparent modest increase in boron content (20 ppm) reduced pearlite levels to 40%, reduced ultimate tensile and yield strengths by 8.4 ksi and 5.75 ksi respectively, and increased elongation

by 2.15%. Although there was considerable scatter in Brinell hardness levels in the base sample (tap 3–1), the increase in residual boron level from 5 ppm to 25 ppm reduced pearlite levels by 50% and Brinell hardness values were likewise reduced.

Approximately 225 lbs of base iron containing 25 ppm boron from Heat no. 3 was pigged and then re-melted a few weeks later (Heat no. 4). This procedure was done so that during the remelting of the pigs, the flux would have additional contact with the charge as it became molten. During re-melting, the equivalent of 3.5 lbs per ton (0.175%) of a sodium-based flux was added. From start of melting to tapping the first ladle took approximately 25 minutes. Thus, the flux was in contact with the molten metal for approximately 20 minutes. A second addition of flux was then added to the remaining metal in the furnace (0.175%) and the metal stirred for approximately 10 more minutes. An adjustment to carbon (0.10%) was made to compensate for alloy loss. These results are shown in Table 9.

Table 9: Citation Biscoe Chemistry Results – Heat No. 4

Heat Tap #s	Notes	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% Boron
4–1	1,2	3.50%	2.68%	0.26%	0.68%	0.009%	0.011%	0.67%	0.032%	0.00200%
4–2	3	3.47%	2.67%	0.26%	0.67%	0.009%	0.011%	0.79%	0.047%	0.00200%

- Notes: 1) Base boron levels initially assayed at 0.0025% (25ppm)
 2) 0.175% flux added to furnace during melt down,
 3) An additional 0.175% flux was added to the remaining metal

Citation Biscoe reported that boron levels were reduced from 25 ppm to 20 ppm by the first flux treatment for Heat no. 3. Remelting the pigged metal and the subsequent addition of 0.175% flux had little to no effect on boron reduction. Microstructural evaluation and physical properties taken from the test bars from Heat No. 4 is shown in Table 10:

Table 10: Combined Effects of Boron on Microstructure and Physical Properties

Heat No.	Microstructure	Yield (ksi)	UTS (ksi)	Elongation	Brinell Fdry A & D **	
					A	D
3 – 1	90% Pearlite	69.50	103.4	2.60%	241	280
3 – 2 (25 ppm)	40% Pearlite	63.75	95.70	4.75%	217	222
4 – 1	40% Pearlite	63.50	89.94	3.50%	179	208
4 – 2	40% Pearlite	64.00	90.84	3.57%	214	211
** Brinell Hardness measurements were all run on 0.875 in. diameter tensile bars						

The addition of boron to Heat no. 3 resulted in significant reductions in pearlite levels. Without boron additions, the microstructure of the base casting (3–1) was 90% pearlite and with a Brinell hardness average of 260 (based on averages from Foundry A and D). After boron treatment, the hardness was reduced to 220 and while the pearlite content was likewise reduced to 40%. After fluxing (4–1), the hardness was further reduced to an average of 194 from 220 even though there was no difference in pearlite content. Further additions of flux (4–2) had no effect on pearlite levels but some increase in hardness was noted. The mechanical properties were directly affected by increase amounts of ferrite in the microstructure.

Because the magnitude of the boron reductions was less than hoped for, additional work was under taken. After reviewing available thermodynamic data, it was concluded that an addition of 25% by weight of sodium fluoride might assist in the removal of boron. The mechanism for boron removal would be the reaction between boron and fluorine to form boron fluoride, which will enter the slag whereupon it would be removed. However, there was some concern over

adding fluoride compounds to the moderately potent sodium-based flux, since fluorides are known to be very aggressive toward refractories.

Heat No. 5 was made in January 2005 to determine whether the fluoride modifications would assist in boron removal. Table 11 shows the results of these tests.

Table 11: Foundry B Chemistry Results – Citation Biscoe Heat No. 5

Heat Tap #	Note	% C	% Si	% Mn	% Cu	% S	% P	% Ni	% Mg	% Boron
5 –1		3.58%	2.62%	0.30%	0.64%	0.007%	0.005%	0.66%	0.028%	0.00022%
5 –2		3.67%	2.67%	0.31%	0.64%	0.007%	0.005%	0.74%	0.028%	0.00204%
5 –3	1	3.72%	2.64%	0.31%	0.64%	0.005%	0.005%	0.69%	0.033%	0.00199%
5 –4	2	3.67%	2.65%	0.32%	0.63%	0.004%	0.004%	0.80%	0.036%	0.00186%

Notes: 1) Base boron levels initially assayed at 0.0021 (21ppm)
 2) 0.175% flux plus sodium fluoride added to furnace during melt down – 12 minutes of refining.
 3) An additional 0.175% flux plus sodium fluoride was added to the remaining metal – 12 minutes of refining

For boron analysis, Citation Biscoe was used exclusively for analyzing Heat No. 5. The Biscoe lab reported that boron levels were reduced from 20.4 ppm to 19.9 ppm, a disappointing 0.5 ppm reduction from the first modified flux treatment. The subsequent addition of 0.175% flux, modified with sodium fluoride, again had little effect on boron reduction. Boron levels dropped to 18.6 ppm, a 1.8 ppm reduction. Since this heat was not pigged after the ferroboration addition, it is possible that the marginal results were due to reduced exposure time and temperature that the flux had with the melt.

In Gagne’s [12] thermodynamic approach for boron removal, he noted that lower temperatures would be more effective for boron removal, although the times needed for removal were not detailed. Hence, there was less refining time for the modified flux and the temperature was higher during the refining period as opposed to Heat No. 4, in which the flux was in contact with the melt during the melt down stage. Further, during the refining stage in Heat No. 4, the times and temperatures during melt down would be more favorable for boron removal, based on Gagne’s study. Thus, based on the results of Heat no. 5, additions of sodium fluoride showed no improvement in the ability to combine with boron to form boron fluoride.

Microstructural evaluation and physical properties taken from the test bars from Heat No. 4 is shown in Table 12.

Table 12: Combined Effects of Boron on Microstructure and Physical Properties

Heat Tap #	Microstructure	Yield (ksi)	UTS (ksi)	Elongation	Brinell Foundry A	
					0.875” Dia	1.75” Dia
5 –1 (2.2 ppm)	90% Pearlite	66.27	88.99	4.25%	207	229
5 –2 (20.4 ppm)	90% Pearlite	70.58	92.14	3.50%	241	248
5 –3 (19.9 ppm)	90% Pearlite	70.58	92.14	3.50%	212	241
5 –4 (18.6 ppm)	90% Pearlite	73.93	99.52	3.80%	241	241

Unlike the previous heats, the addition of boron to Heat no. 5 produced entirely different results. While the chemistry of Heats no. 3 and 5 are almost identical, the addition of boron had very different effects on pearlite levels. The microstructures remained constant with 90% pearlite and boron had no effect on microstructure or Brinell hardness values. It should be noted that other researchers have reported similar findings of boron increasing hardness. The microstructure of the base casting (5–1) with 2.2 ppm boron was 90% pearlite with a Brinell hardness average of

218 (based on averages from 0.875 and 1.75 in. diameter bars). Addition of boron to the base heat resulted in increased tensile strength, increased yield strength and generally increased Brinell hardness values in both the 0.875-inch rounds and 1.75 inch round bars. Boron additions generally resulted in a nominal 10% increase in Brinell hardness. The reasons for why Heat no. 5 behaved in a totally different manner than Heats no. 3 and 4 is not known at this time, although all of the test coupons have been retained.

In-Plant Studies – Boron levels at this foundry typically run between 10 to 13 ppm mainly because of the quality of the steel scrap used in ductile iron production. During refractory installations, boron levels will climb to 17 ppm to 20 ppm during the sinter and heat up phase. At times, boron levels will increase to 30 ppm.

During the first trial, 2.0 pounds per ton were added to the molten heal before back charging. This procedure reduced the boron level from 19 ppm to 11 ppm. The foundry continued to make flux additions to the heal, back-charged and continued melting for 45 minutes until the heat was up to temperature and ready for tapping. Melting time was 45 minutes and tapping temperature was 2,750°F.

Although boron levels were appreciably reduced, the target boron level of 8 to 10 ppm was never achieved by fluxing. The fact that boron levels were reduced almost 50% during furnace relines and the longer fluxing times utilized in a production environment, strongly indicates that thermodynamic equilibrium conditions were not achieved in the laboratory trials.

SUMMARY

1. Laboratory evaluations of sodium-based flux additions to experimental heats intentionally contaminated with boron showed slight reductions in boron levels, indicating that there was some reaction between the flux and boron.
2. Significant deviations in boron levels were found on the same samples analyzed by two of the participating foundries, illustrating the difficulty in measuring low levels of boron.
3. The effect of boron on the microstructure of pearlitic ductile iron produced mixed results. In the first series of experiments, the addition of boron reduced Brinell hardness and reduced pearlite levels from 90% to 40% with an accompanying increase in ferrite content. A second series of experiments provided exactly the opposite effect; pearlite levels remained the same with identical boron additions, microstructures remained constant at 90% pearlite and Brinell hardness values increased 10%. The exact cause of these results is not known at the present time and further examination of the test coupons needs to be done.
4. Boron was found to have varying effects on the structure of pearlitic ductile irons when present in amounts of 20 parts per million. The addition of 20 ppm boron reduced Brinell hardness, reduced pearlite levels from 90% to 40% with an accompanying increase in ferrite content. This same addition rate was also found to have no effect on reducing pearlite levels and Brinell hardness values actually increased 10%. Although both pearlitic ductile iron heats had virtually identical chemistries, the exact nature and mechanism of boron's dual behavior is not known at the present time.
5. Actual foundry experiments to reduce boron levels stemming from boron containing steel scrap in a 10-ton medium frequency induction furnace were more successful. It was reported

that boron levels were reduced from 17 ppm to 20 ppm before fluxing to 11 ppm after flux refining for 45 minutes during melt down.

6. In the laboratory trials, flux refining to remove boron was limited to intervals of 12 minutes and 24 minutes at 2,700°F. While boron levels were reduced somewhat, the results seem to indicate that the reaction of sodium with boron did not go to completion.

7. Although boron levels were reduced in laboratory experiments, the length of time for the flux refining period and the elevated temperatures employed (2,750°F) may not have been either long enough or at too high of a temperature for greater boron reductions. In order to better define these parameters, additional research is recommended.

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ADDENDUM

This research program was initiated based on the DIS Research Report written by Martin Gagne' of Rio Tinto titled "Thermodynamic Evaluation of Boron Removal from Ductile Iron Melts, and it published in the Ductile Iron News, Vol. 2, No. 2, August 2003. It suggested that reactions between boron and sodium were possible, hence, it was likely that sodium compounds could theoretically reduce boron in ductile iron melts.

The objective of the current DIS study was to determine whether it was feasible to reduce boron by fluxing with a commercially available sodium based flux in the laboratory as well as at an operating foundry. The actual melting, melt refining and pouring of test castings was done at CWRU. To reduce costs, co-operating foundries analyzed metal samples for boron and conducted BHN testing, while metallographic work was done at CWRU.

SUMMARY

1. There were many changes and discrepancies in the testing procedure and metal analysis that make drawing a conclusion from this research report difficult. Generally it is reported that Boron levels have shown some decrease when Ductile Iron melts are fluxed with a sodium based flux during testing in a lab environment and a plant case study, but specific concentrations should be taken with caution.
2. No slag analysis was performed so the reaction product was not verified.
3. Laboratory evaluations of Flux additions to experimental heats intentionally contaminated with boron showed slight reductions in boron levels, indicating that there was some reaction between the flux and boron.
4. Significant deviations in boron levels were found on the same samples analyzed by up to 3 various sources, illustrating the difficulty in measuring low levels of boron.
5. The effect of boron on the microstructure of pearlitic ductile iron produced mixed results. In the first series of experiments, the addition boron reduced Brinell hardness and reduced pearlite levels from 90% to 40% with an accompanying increase in ferrite content. A second series of experiments provided exactly the opposite effect; pearlite levels remained the same, microstructures remained at 90% pearlite and Brinell Hardness values increased 10%. Although both pearlitic ductile iron heats had virtually identical chemistries, the exact nature and mechanism of boron's dual behavior is not known at the present time and further examination of the test coupons needs to be done.
6. Actual foundry experiments to reduce boron levels stemming from boron containing steel scrap in a 10 ton medium frequency induction furnace were more successful. It was reported that boron levels were reduced from 17 to 20 ppm before fluxing to 11 ppm after flux refining for 45 minutes during melt down.
7. In the laboratory, flux refining to remove boron was limited to intervals of 12 minutes and 24 minutes at 2,700°F. Boron levels were slightly reduced indicating that the reaction of sodium with boron might not have gone to completion.
8. Although boron levels were reduced in laboratory experiments, the length of time for the flux refining period and the elevated temperatures employed (2,750°F) may not have been either long enough or at too high of a temperature for greater boron reductions. In order to better define these parameters, additional research is recommended.
9. In the trials at Citation Biscoe: The fact that boron levels were reduced almost 50% during furnace relines at Citation Biscoe and the longer fluxing times utilized in a production environment, strongly indicates that thermodynamic equilibrium conditions were probably not achieved in the laboratory trials. All hardness coupons, spectrographic samples have been retained. Retained samples of the pig iron used in all heats have also been retained.