DUCTILE IRON SOCIETY

FALL NEWSLETTER

18 December, 2023 Issue #4

In this issue...

WWW.DUCTILE.ORG

UPCOMING EVENT

2024 Ductile Iron Production Seminar (DIPS)

$45 for Foundry Members!

Our aim is to keep the cost low for foundry members. The $45 covers the cost of dinner.

JANUARY 29TH-30TH

North East Indianapolis (Fishers)

Research Committee Meeting January 31st

The two-day seminar will focus on basic metallurgy & mechanical properties, melting practices & charge materials, treatment & inoculation methods, gating & risering basics, and more! Anyone from your company is invited to attend! Production personnel or members of any area of management can benefit from learning more about the science and controls beyond on the floor training.

REGISTER FOR DIPS

DIPS Sponsorship

DIPS is an opportunity for newer engineers and production employees to learn more about the basic metallurgy and properties of Ductile Iron in a classroom style setting.

It is vital that as a society we continue to invest in the training of incoming foundry personnel that is why this year we are making attendance for foundry members free! Whether you're a foundry member or an associate member consider sponsoring the Ductile Iron Production Seminar.

DIPS TENTATIVE SCHEDULE

MONDAY, JANUARY 29

12:00 PM	Registration Opens
12:30 PM	Basic Metallurgy & Mechanical Properties *with Kevin Pilon*
1:30 PM	Production Refractories *with Tim Hoyt*
2:15 PM	Break
2:30 PM	Melting Practices & Charge Materials *with Kevin Pilon*
3:45 PM	Break
4:00 PM	Treatment & Inoculation Methods *with Jeremy McLimans*
5:00 PM	Adjourn
6:00 PM	Dinner at Tre Mori

TUESDAY, JANUARY 30

8:00 AM	DI Gating & Risering Basics *with Josh Gammariello*
10:00 AM	Break
10:15 AM	Metal Filtration *with Jason Lachance*
10:45 AM	Heat Treating Ductile Iron *with Jeremy Lipshaw*
12:00 PM	Lunch
12:45 PM	Austempered Ductile Iron *with Jeremy Lipshaw*
1:30 PM	QC Procedures *with Brad Steinkamp*
2:15 PM	Casting Defects
3:00 PM	Adjourn

RESEARCH COMMITTEE DINNER

The Ductile Iron Society held its 7th Keith Millis Symposium at the Crowne Plaza Atlanta Perimeter at Ravinia in Atlanta, GA October 16-20. Thank you to everyone who made it to Atlanta and took time out of their week to join us! The meeting gave members and guests an opportunity to network, take part in professional development technical sessions, and participate in committee meetings all while having a great time. To kick off the Keith Millis Symposium, the Research Committee enjoyed dinner at Iron Hill Brewing Company on Monday, October 16 *(pictured above and below).*

COMMITTEE MEETINGS

Research Committee

During the meeting, the committee discussed changes to the Research Committee Guidelines. Subcommittees will play a more significant role in proposing projects, shifting away from universities initiating proposals. Suggestions were made to implement timelines for project submissions to facilitate voting processes.

PROJECT UPDATES

Project #62: Effect of Ceramic Sand on Cast Iron Mechanical Properties - Scott Giese

- Ductile Iron Portion Completed
- Target completion for full project: December 2023

Project #65 Refining Austenite Grains in DI Using Cerium and Titanium Additions – J. Qing, M. Xu, Georgia Southern University

- Findings revealed on Ce, Ti, and Al additions in grain refinement
- Correlating SDAS to amount of undercooling suggested
- Next step will be creating the final report

Project #66 Impact of Steel Tramp Elements of Ductile Cast Iron

- Correlations and confidence given for Boron levels with Mn, Cu, and Sn.
- Nearly complete with project – next steps would include looking at Curie temperature.
- A steering committee will be formed once the formal proposal has been submitted.

Project #67 Fracture Toughness

- Objectives: Fill in missing database information.
- Literature review in process.
- “Real” case studies are limited.

Project #68: Spectro Reference Materials - Lyle Herberling

- First molds were poured. “Hershey bars” both round and squares.
- Targeting January for next pour.

All three subcommittees reported on their top suggestions for research projects. Topics range from further research in heavy section castings, optimizing data design, utilizing a information database or AI to share tribal knowledge, Ductile Iron Opportunities in Electric Vehicles, and riserless design.

Member Services Committee

The Membership Committee welcomed Evercast (foundry) and Saint-Gobain (associate) as new members. The committee will be sending a survey to members in the new year to encourage the addition of multiple contacts under member’s DIS company profiles. As they look to the future the committee is compiling a list of Ductile Iron foundries in North America and aims to target these potential members for the 2024 Spring meeting. The committee is working to enhance the user experience of the website and exploring the possibility of a DIS app.

Marketing Committee

The discussion centered on creating a video transitioning from fabrication to casting. The video would aim to showcase benefits, overall advantages, and the end user standpoint. The committee’s goal is to complete the video within the next year and are looking for casting candidates. If you are interested in helping with this, please email **DIS@teamwi.com**.

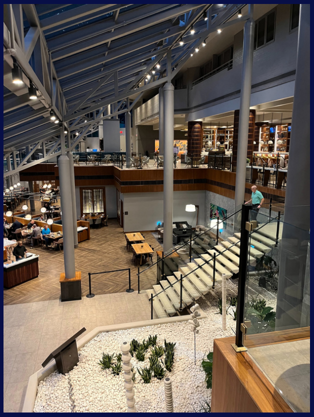
Other items the committee discussed included:

- Traveling seminar targeting OEMs and foundries to enhance membership and promote ductile iron.
- Increasing search engine optimization (SEO) for casting iron.
- Creating potential opportunities for education credits for classes and seminars.

NEW MEMBERS

EVERCAST
Foundry Member

SAINT-GOBAIN
Associate Member



Programs & Publications Committee

The 2024 Spring Meeting will focus on energy reduction and sustainability. For the 2024 Fall Meeting, the committee is actively working on determining a theme, with proposed topics including ladle maintenance, gating design, charge material, mold design, alloying and heat treatment, inoculation, quality control, simulation, and the transition from manual to autopour processes.

University Relations Committee

The committee began by reviewing its mission statement, aiming to expose a maximum number of young adults to ductile iron technology in areas such as design, manufacturing, career opportunities, applications, and research. The committee had three student attendees who emphasized the importance of inviting students to conferences and plant tours. High school outreach is an area that the committee would like to focus on in the future. Members of the committee attended the FEF College Industry Conference November 16 and 17, where DIS gave away the logo and sponsored t-shirts and four $3500 scholarships. The committee plans to sponsor students at the upcoming 2024 Ductile Iron Production Seminar.

KMS TECHNICAL SESSIONS

Keynote Address-Industry: "Thoughts & Insight on Ductile Iron and CGI for Ground Transportation Applications"
Andrew Halonen, Mayflower Consulting, LLC

Development of an Austempered Ductile Iron Unimog 3 Point Linkage Power Lift Arm
Arron Rimmer, ADI Treatments Ltd, West Bromwich, West Midlands U.K.

Advances and Considerations in the Prediction of Abnormal Graphite Formation in Ductile Iron
Konstantin Nikolov, MAGMA

Graphite Spheroids: The Place Where They Are Born
Ramón Suárez, Azterlan

Graphite Spheroids: The Way they Grow
Doru Stefanescu, The University of Alabama and The Ohio State University

The Effects of MgFeSi and Inoculant Selection on Microstructure and Mechanical Properties of Varying Section Size Ductile Iron Castings
Trevor Beach, Betz Industries

The Role of Mn, Cu and Sn in Spheroidal Graphite Irons: Pearlite Formation Mechanism
Leander Michels, Elkem Silicon Products and Andreas Bugten, Norwegian University of Science and Technology (NTNU)

Effects of Titanium and Cerium Addition on Grain Size and Mechanical Properties of Ductile Iron Castings
Jingjing Qing, Georgia Southern University

AI/ML Driven Metamodels for the Ductile Iron Foundry Process Engineers in an Industry 4.0 Environment
Jiten Shah, Product Development & Analysis (PDA) LLC

Keynote Address-Academia: "How to Build a Metalcasting Program from the Ground-up, Georgia Southern University Story"
Mingzhi Xu, Georgia Southern University

Improvement of High Temperature Performance of High Si SGI by Al Alloying and Optimizing Micro-Structural Dispersity
Simon N. Lekakh, Missouri University of Science and Technology

Comparison of Ba and Ca Additions on the Thermochemical Properties of Ductile Iron Slags, and Effects on MgFeSi Treatment Efficiency and Final Microstructure
Cathrine Hartung, Elkem Silicon Products

Impact of Quenching and Aluminum On B2 Superstructure Formation In Solid Solution Strengthened Ferritic Ductile Cast Iron
Betto David Joseph, Foundry Institute, RWTH Aachen University

Primary Austenite Morphology and Tensile Strength in CGI for Different C Contents, Cooling Conditions and Nodularity
Vasilios Fourlakidis, Department of Materials and Manufacturing - Jönköping University

Dendritic Austenite in Compacted and Spheroidal Graphite Iron
Björn Domeij, Department of Materials and Manufacturing - Jönköping University

CGI Global Update
Steve Dawson, SinterCast

GET TO KNOW THE DIS BOARD OF DIRECTORS

Lenny Basaj

Metallurgist, Metal Technologies, Inc.

Lenny is the **Vice President of the Ductile Iron Society**. He has a degree in Materials Science and Engineering from the University of Wisconsin – Milwaukee. He started as an engineering co-op prior to graduation, then worked as process engineer, quality engineer and metallurgist at several ductile and gray iron foundries. He is currently a Metallurgist at Metal Technologies, Inc. in Ravenna, MI. He is a member of the AFS Charge Materials Committee, and board member and past president of the Western Michigan Chapter AFS. He is also active with the Western Michigan Region of the Sports Car Club of America.

Svetlana Dodik-Pelja

Business Development Manager, HA International

Svetlana is **a member of the Board of Directors**. She holds a Metallurgical Engineering Diploma from the University of Sarajevo, BiH, a Bachelor of Science in Industrial Engineering from the University of Sarajevo, Six Sigma Black Belt Certification from Motorola University, and has received Excellence in Lean Training from the Lean Enterprise Institute. Professionally, Svetlana invested 7 years as a Process Engineer at Mittal Zenica. Following that, she lent her expertise to TB Woods Foundry for an impressive 18 years, serving both as a Process Engineer and Technical Director. Currently, she plays a pivotal role as the Business Development Manager for Feeding Systems at HA International, a position she's held for the past 6 years. A recognized figure in the metallurgy domain, Svetlana has been a speaker at renowned industrial conferences like the Cast Expo, Metalcasting Congress, and AFS regional events. Furthermore, her leadership skills are evident as she actively serves on the DIS Board of Directors and chairs the Service Member Committee. A cause close to her heart is the Women in Metalcasting Group, where she strives to amplify the voices and roles of women in the industry. On a personal note, sports, especially volleyball, and skiing, are Svetlana's refuge from her demanding professional life. Friday evenings, she looks forward to unwinding at happy hour with her husband and friends.

Thermal Analysis of Ductile Iron - A New Way to Predict the Mechanical Properties
Johannes Schüssler, RWTH Aachen University

How Well Controlled is Your Foundry Process?
Rebecca Ward, Impact NDT, LLC

XRD-Analysis of the Correlation of Stacking Fault Formation and the TRIP-effect in ADI
Felix Stieler, TU Clausthal

Prediction of Cross-Section-Dependent ADI Microstructures by Experimental Heat Treatment Simulation
Patrick Lachart, TU Clausthal

Inoculation effects on Mass Effect in Ferritic Spheroidal Graphite Iron Castings with Heavy Section
Satoshi Yamamoto, Daiwa Heavy Industry Co., Ltd, Hiroshima, Japan

Shrinkage Investigation of Ductile Iron Castings
Anhua Yu, Ward Manufacturing LLC

Ductile Iron Fade Sampling Campaign
James Cree, Grede-New Castle

Molten and Semi-Solid Gravity Die Casting in Ductile Iron Castings
Haruki Itofuji, I2C Technology Institute

High Modulus Ductile Iron Alloy Design and Characterization
Shane Anderson, Materials Technology

Thank you to all our speakers for taking the time to present!

SAVE THE DATES

2024 Spring Meeting

JUNE 3RD-6TH
Hilton Garden Inn, Cedar Falls, Iowa
Keep your eyes out for details and registration!

TOUR HOSTED BY JOHN DEERE

2024 Fall Meeting

OCTOBER 2024
Lancaster, PA
Stay tuned for more details and registration!

KMS PAPER HIGHLIGHT

Comparison of Ba and Ca Addition to the Thermochemical Properties of Ductile Iron Slags and Effect on MgFeSi Treatment Efficiency and Final Microstructure

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ABSTRACT

To produce ductile iron, it is necessary to perform a Mg-treatment on the melt, a process often called nodularisation. Typically, this is achieved using a MgFeSi-alloy, added to a treatment ladle before tapping. A common by-product of this process is slags, mainly Si-oxides, with other active elements in the alloy, such as Mg, Ca, and Al. The composition of the MgFeSi alloy can be customized to fit the process and improve the quality of the spheroidal graphite iron produced. In the present work, the effect of Ba-containing cover material as an inoculation support and as a slag conditioner is investigated. The effect of holding time is also investigated in order to verify the fade resistance of the property of Barium-containing inoculants. Thermochemical (CALPHAD) evaluation of the slag shows that Ba decreases the liquid fraction and the transition range for the slag, which provides a higher ability to clean the melt.

KEYWORDS

Ductile irons, Slag, Ba, Ca CALPHAD

INTRODUCTION

Production of ductile iron has been linked to magnesium and a Mg-treatment since its invention in 1949 [1, 2]. To produce ductile iron, it is necessary to perform a Mg-treatment process called nodularisation. The Mg-treatment aims to tie up O and S and change the growth mechanism of graphite during solidification from flake to spheroidal or nodular graphite [3, 4]. Magnesium can be added using different alloys, but MgFeSi-alloys were early recognized as an excellent material to introduce Mg into cast iron [5, 6]. Magnesium is soluble in silicon and forms phases that are released more slowly and controlled into the iron when dissolved [6]. Combining magnesium with MgFeSi, an alloy with a higher density than magnesium, can be obtained, which can be crushed and handled without special precautions. The MgFeSi-alloy is commonly added to the treatment ladle before tapping and can be placed either on the bottom or in a specially designed-pocket before liquid iron is added to the melt. The amount of alloy added depends on the size of the treatment, base iron S-level, and time from treatment to pouring. Ideally, as little as possible magnesium should be used to reduce the risk for slag inclusions and shrinkage in the final casting, but depending on the initial S and O-level and the required residual Mg-level needed to produce ductile iron is recommended to be in the range of 0.030 to 0.060 wt% [7]. However, to achieve this residual Mg-level, a higher amount of magnesium will normally have to be added as magnesium is lost during the Mg-treatment to flare, fume, and slag, as seen from the formula below [1, 3].

$$Mg_{add} = \frac{0.75 \times S_{initial} + Mg_{residual}}{Mg_{yield}}$$

The magnesium added will either stay in the iron and be measured as Mg-residual or react with S and O to form slag, fume, and microparticles[8, 9]. The amount of magnesium assumed lost to tying up S can be found by comparing the S-level of the base iron and the final iron after Mg-treatment.

A common way to measure the efficiency of the Mg-treatment is then to calculate the Mg-yield or Mg-recovery by using the formula below [7]:

$$Mg\text{-recovery} = \frac{0.75 \times (\%S_{base\ iron} - \%S_{residual}) + Mg_{residual}}{\%Mg_{added}}$$

Slag is a common by-product of the Mg-treatment process, while the fume and flare are measures for the reactivity of the MgFeSi-alloy. A high amount of flares, fume, and slag are typical signs of an inefficient Mg-treatment. While control of the base iron S-level will help limit the amount of slag generated and reduce the amount of Mg lost to slag. It is recommended to keep base iron S below 0.02 wt% and ideally in the range of 0.012 to 0.015 wt% [3]. Improvements and changes to both ladle, treatment, and treatment alloy can be made to improve the efficiency of the Mg-treatment and reduce the loss of Mg to fume and flare.

One common way to improve the efficiency of the Mg-treatment is to use a cover on top of the MgFeSi-alloy or a cover on the treatment ladle [6]. The purpose of the cover on the MgFeSi-alloy is to allow for more liquid iron to be added to the ladle before the reaction with MgFeSi alloy starts. The higher amount of iron in the ladle will provide a higher ferro-static pressure on MgFeSi-alloy, which should help reduce the flotation of the MgFeSi alloy to the surface where it can react and lead to excessive loss of magnesium to fume and flare. Another effect of the cover is locally reduced temperature before the liquid iron meets the MgFeSi-alloy. A lower temperature is beneficial for improving the Mg-recovery.

Many materials have been used as cover materials, like shell sand, steel, ductile iron machining chips, reclaimed metal spill, copper (in the case of pearlitic grades), cast iron disks from leftover metal, and FeSi [11]. The type of cover material used varies depending on availability and preference.

When a cover or lid is added to the treatment ladle, the treatment process is referred to as tundish treatment and is one of the most widely used methods for ductile iron production [7]. This treatment process gained industrial acceptance in the 1980s, although it was known from the late 1960s [3]. The cover on top of the ladle can be fixed or removable. It usually consists of a basin with a hole to lead the liquid iron into the ladle. In the case of a fixed cover, there may also be a hole for adding the MgFeSi-alloy, which is typically sealed during treatment.

The purpose of the tundish cover or lid overlaps partially with the alloy cover. Providing a more thermally efficient treatment can take place at a lower temperature, which will give a higher Mg-recovery. The cover also helps reduce air contact during the ladle's tapping and filling. In contrast, the hole in the tundish cover helps to fill the ladle more controlled and avoid premature reaction with the MgFeSi-alloy in the pocket.

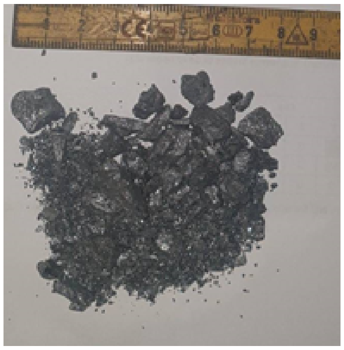
For foundries working with tundish cover/lid ladles, using cover materials can be considered unnecessary as it is believed that the benefit from additional cover material will have a limited effect on the Mg-recovery.

The present study investigated the effect of two common cover materials, steel, and FeSi, on the Mg-treatment efficiency and final iron quality. Both cover materials were used in a tundish treatment process in a ladle with a pocket. The FeSi cover material had a controlled level of Ba to provide inoculation support in addition to helping condition the slag in the treatment ladle. Ba-containing inoculants are often referred to as fade resistant. Thermochemical (CALPHAD) evaluation was done on the slag removed from the treatment ladle to determine if the slags generated with the two cover materials were different in behaviour due to the introduction of Ba. The inoculation was also done with a Ba-containing, and the holding time effect was evaluated.

DESIGN OF EXPERIMENTS

The experimental work aimed to study the effect of two common types of cover materials used in producing ductile iron, a steel, and a specialized Ba,Ca-FeSi alloy, on the Mg-recovery and slag properties of treated iron and the final quality of ductile iron. The experimental work was executed in the pilot-test facility at Elkem Technology in Kristiansand, Norway, and the trial description can be seen in **Table 1**.

Table 1 Description of the trial and samples.

	Melt 1	Melt 2
Nodulariser	1.30 wt% low RE MgFeSi	
Cover	Steel 0.73 wt%	Ba,Ca-FeSi 0.45 wt%
		
Inoculation	None 0.20 wt% BaCa-FeSi Inoculant	None 0.20 wt% BaCa-FeSi Inoculant
Holding	1 min 10 min	1 min 10 min
Samples	Steel – None 1 Steel - None 10 Steel – Inoculated 1 Steel - Inoculated 10	BaCa-FeSi – None 1 BaCa-FeSi - None 10 BaCa-FeSi – Inoculated 1 BaCa-FeSi – Inoculated 10

Chemical composition of the alloys used in the trial can be seen in **Table 2.**

Table 2 Composition of alloys used.

Element	Fe %	Si %	Mg %	Ca %	Al %	Ba %	Ce %
Nodulariser		47.1	6.0	1.8	0.5		0.1
Steel cover	>99	<0.5	-	-	-	-	-
BaCa-FeSi Cover	rest	47.1	-	1.4	1.5	2.6	-
BaCa-FeSi Inoculant	rest	73.1	-	1.4	1.5	2.6	-

The steel cover comprises small plates or sheets, while the Ba,Ca-FeSi consists of granules from 0 to 10 mm.

From **Table 1**, two melts of 280 kg were prepared with the target composition (%C 3.70, %Si = 1.47, %S 0.012, %P = 0.030.) from premade base iron and recarburiser.
The melts were tapped out at 1500°C (2732°F) into a tundish ladle where 1.30 wt% MgFeSi (6.0% Mg, 1.8% Ca, 0.65% Al) was added to the bottom of the pocket and covered with 0.73 wt% steel cover or 0.45 wt% Ba,Ca-FeSi cover. The wt% amounts differed to maintain the same cover height before final inoculation with 0.20 wt% Ba,Ca-FeSi. Steel has a much higher density than the FeSi cover. A rare earth-free MgFeSi was used for the study only to have the effect of Mg to consider and any effect of the cover material on this.

After completion of the treatment, the tundish lid was removed to allow for observation of the slag on the surface and de-slagging. The treated iron was then divided into four 32-kg capacity pouring ladles made from alumina at 30-second intervals. The inoculant was added to the bottom of the pouring ladles, and the iron was held for 1 or 10 minutes before casting. For the uninoculated pouring ladles addition of Si was made to compensate for the missing Si-input gained from the inoculation and to have the same final iron composition. The target final iron composition can be seen in **Table 3**.

Table 3: Target final-iron composition.

Element:	%C	%Si*	%S	%Mg	%P	%Mn	%Cu
Target:	3.60 ±0.10	2.20 ±0.15	0.008 ±0.005	0.035 – 0.040	0.030 ±0.005	Max. 0.20	Max. 0.05

Samples for chemical composition are collected with an immersion dip sampler from the furnace, treatment ladle, and pouring ladles. While cooling curves were collected with cylindrical cups at the furnace before tapping, from treatment ladle after de-slagging, and from pouring ladles in connection with pouring. The cylindrical thermal analysis cups were further used for microstructure analysis.

From the treatment ladle, the slag generation was documented with video recording of the ladle surface prior to de-slagging. The slag was collected without slag coagulant and collected for later evaluation and chemical analysis.

Chemical analysis was determined with a combination of optical emission spectrometer and combustion technique for cast iron, while the chemical analysis of the slag was determined using energy dispersive spectrometry (EDX).

Thermal analysis measurements were made by pouring liquid iron into sand crucibles with 36 × 36 × 40 mm dimensions containing a type-k thermocouple in its geometrical center. Each cup was connected to a data logger that measures temperature with a frequency of 10 Hz.

Microstructure quantification was carried out with a Leica DM6 M optical microscope equipped with an automatic stage controller at a magnification of 100x. The digital camera provided an image resolution of 0.49 µm/pixel, and an image size of 2736 x 1824 pixels. The images were taken within an area of 10 x 10 mm covering a total image area of 15.6 mm2 to give repeatable and reproducible results. The image analysis is based on ASTM E2567 using ImageJ and Excel as tools. The microstructure was examined in both polished (1µm finish) and etched (Nital) condition.

RESULTS

The first section of the results focuses on the effect of the different cover materials on the performance of the MgFeSi treatment process.

Mg-recovery

The purpose of cover material is to protect the MgFeSi and delay the reaction by allowing a larger amount of iron to fill the ladle and cover the MgFeSi with a certain height before the reaction starts. In this case the amount as in height covering the MgFeSi in the pocket of the tundish treatment ladle was the same for the two cover materials.
Tapping temperature for melt 1 was 1495°C (2723°F) while it was 1501°C (2734°F) for melt 2. After treatment and de-slagging the temperature was measured to 1425°C (2597°F) for the treatment with steel cover and 1422°C (2592°F) for the treatment with Ba,Ca-FeSi cover showing that the different cover amounts did not result in a different temperature profile for the two melts.

A typical way to measure the effect of the Mg-treatment process is to calculate the Mg-yield, the Mg retained in the iron, and the amount Mg bonded to S. **Eq. (2)** showed the formula for calculating the Mg recovery, which requires information from both the base iron composition and treated iron composition.

In **Table 4** the target and actual base iron composition for the two melts is presented and show that similar composition was achieved for both melts. For melt 2 the base iron Si-level is lower to make up for the Si-contribution coming from the Ba,Ca-FeSi cover addition

Table 4: Target vs actual base iron composition for the two melts prepared.

Element:	%C	%Si*	%S	%P	%Mn	%Cu
Target:	3.70 ±0.10	1.47 ±0.15	0.015 ±0.005	0.030 ±0.005	Max. 0.20	Max. 0.05
Melt 1	3.71	1.47	0.018	0.035	0.18	0.041
Melt 2	3.74	1.31	0.021	0.034	0.19	0.039

In **Table 5** the target, and the actual composition of the iron after treatment with MgFeSi and cover can be seen. Compared to the target, higher C-level, Si-level and residual Mg-level is observed with for the treatment with Ba,Ca-FeSi-cover

Table 5: Target vs actual iron composition for the two melts after treatment with MgFeSi and cover.

Element:	%C	%Si*	%S	%Mg	%P	%Mn	%Cu
Target:	3.60 ±0.10	2.05 ±0.15	0.010 ±0.005	> 0.050	0.030 ±0.005	Max. 0.20	Max. 0.05
Melt 1 – Steel cover	3.59	2.10	0.014	0.057	0.034	0.19	0.04
Melt 2 – Ba,Ca-FeSi cover	3.76	2.18	0.014	0.063	0.033	0.20	0.04

For the two treatment the same MgFeSi alloy with 6% Mg and addition rate of 1.3 wt% was used which gives an addition of 0.078 wt% Mg.

When using the **Eq. (2)** above the a Mg-recovery of 90% is achieved with the Ba,Ca-FeSi cover and a Mg-recovery of 77% is achieved with the steel cover as can be seen from Fig. 1.

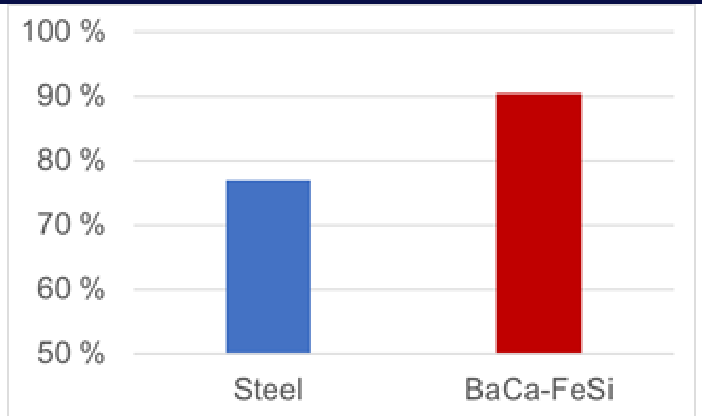


Fig. 1. Mg-recovery achieved for the two cover materials.

As stated previously, purpose of the addition of Mg is to tie up S and O from the melt and change the growth mechanism of graphite from flake to spheroidal. The Mg added is then either retained in the iron, lost to slags or lost to fume and flares. Although there are other elements in the MgFeSi that can react with S and O it is assumed that Mg will do the main job as the compounds with Mg are more thermodynamically stable.

The Mg-recovery formula **(Eq. (2))** only considers the Mg-retained in the iron and the Mg assumed lost to MgS-slag, but Mg also has the important job of tying up O. Oxygen level is however not normally reported for cast iron as it is difficult to measure and greatly depend on the temperature. However the Mg-recovery can be broken down into the individual parts as seen in **Fig. 2**, where **Fig. 2(a)** shows the share of the Mg retained in the iron where it is present as dissolved and as micro particles important for later graphite nucleation, **Fig. 2(b)** shows the fraction of the Mg used to desulfurize the iron, while **Fig. 2(c)** is then the Mg which has been lost to reaction with O in the form of fume, flare or slag.

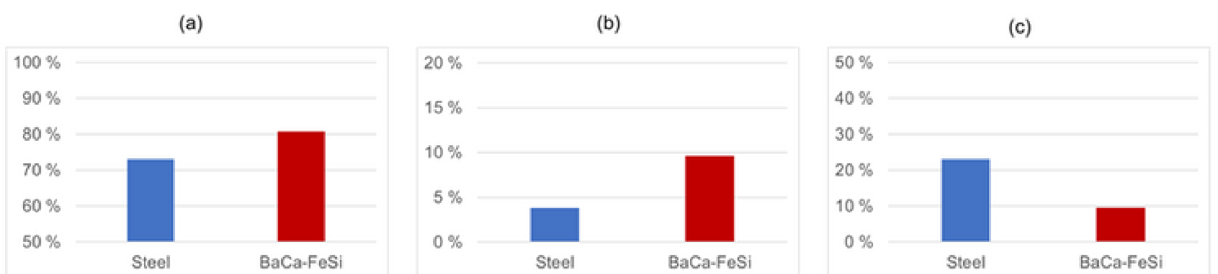


Fig. 2. (a) Mg retained in the iron (final Mg-level), (b) Mg lost to S-removal, (c) Mg lost to O slag, fume and flare.

Nucleation potential

From **Fig. 2**. it can then be seen that with Ba,Ca-FeSi cover more Mg is retained and more S is removed while less Mg is lost to oxygen. This indicates that the Ba,Ca-FeSi cover alloy has additional effects beyond the covering part, but also supports the MgFeSi treatment. From the treated iron a sample for microstructure evaluation as well as thermal analysis was collected and in **Fig. 3** the microstructure can be seen and shows that with the Ba,Ca-FeSi cover a carbide free microstructure is produced without inoculation with Ba,Ca-FeSi cover, while a carbidic structure is seen with the steel cover.

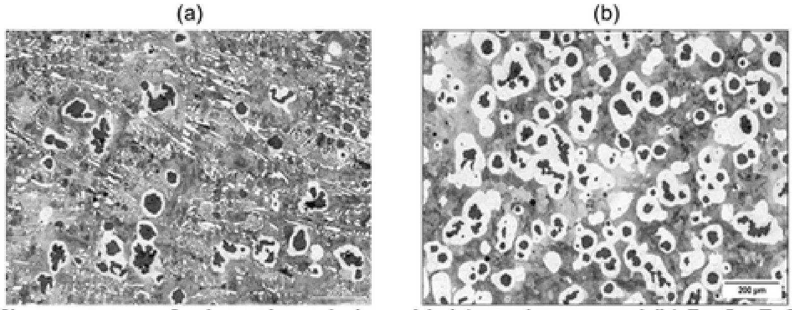


Fig. 3. Microstructure of prior to inoculation with (a) steel cover and (b) Ba,Ca-FeSi cover.

The details from the microstructure evaluations are presented in **Fig. 4**.

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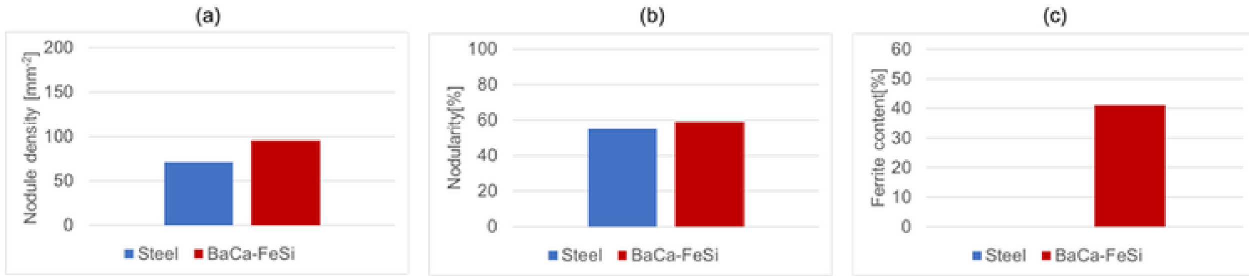

Fig. 4. Microstructure parameters of the samples. (a) Nodule count density, (b) nodularity, and (c) ferrite content. Note that due to the presence of cementite, the matrix fraction of the steel cover is not shown.

The microstructure achieved with only MgFeSi treatment shows a nodule density of less than 100 mm-2 for both cover materials and nodularity of less than 60%, but for the Ba,Ca-FeSi cover a carbide free structure with 40% ferrite was produced, suggesting that the Ba,Ca-FeSi cover supports the MgFeSi-treatment with providing improved graphite nucleation potential. This is supported by the thermal analysis presented in **Fig. 5**, which shows a lower eutectic temperature (LET) of 1127.5°C (2061.5°F) with steel cover and 1140.2 °C (2084.4°F) with Ba,Ca-FeSi cover.

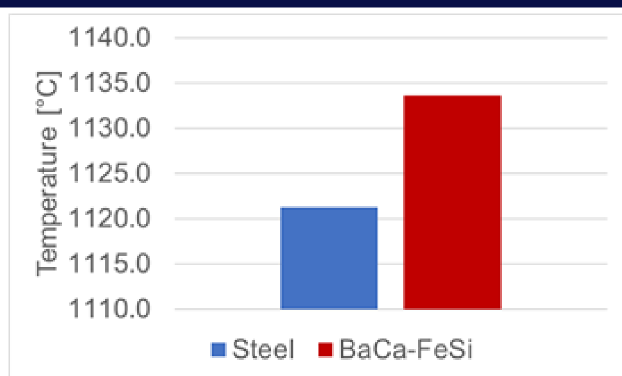

Fig. 5. Lower eutectic temperature (LET) or maximum undercooling for the two cover materials.

Slag generation

In addition to the Mg-recovery, the slag generation is of interest when evaluating the performance of the MgFeSi treatment process. After treatment, the ladle tundish lid was removed, and slag was collected.

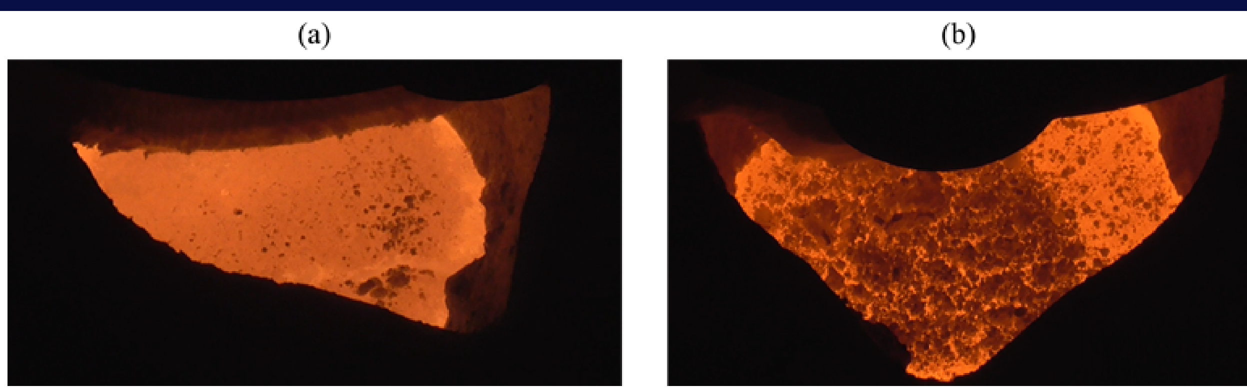

Fig. 6. Slag observed on the melt surface with (a) steel cover and (b) Ba,Ca-FeSi cover after treatment.

Fig. 6 shows the amount of slag on the surface of the treatment ladle. From the image, it is apparent that there is more slag with the Ba,Ca-FeSi cover than with the steel cover. However, the chemical analysis shows that the Ba,Ca-FeSi cover has less Mg lost than with the steel cover. When collecting slag, entrapped metal is often present [12] and separating both phases can be challenging. **Fig. 6(a)** shows a slag layer generated after the MgFeSi treatment with steel cover. This slag was mixed with the metal, and it was difficult to separate both phases. While for the Ba,Ca-FeSi cover the slag was dry and floating on top of the melt, and far easier to separate. **Fig. 7** and **Fig. 8** show slags collected with the two different cover materials.

Fig. 7(a) shows the slag sample collected from the surface of the ladle shown in **Fig. 6(a)**. The slag phase is seen covering the surface of the metal. **Fig. 7(b-d)** shows the cross section, and the area where the slag was evaluated. However, the nature of the slag generated from the Ba,Ca-FeSi cover treatment is different. As seen in **Fig. 8**, this slag is brittle and can be completely separated from the attached metal. **Fig. 8(a)** shows the pieces of the slag. But in order to evaluate the slags in the same condition as the steel cover, the surface of the melt shown in **Fig. 6(b)** was scooped and a slag area closer the metal was measured, as seen in **Fig. 8(b-d**).

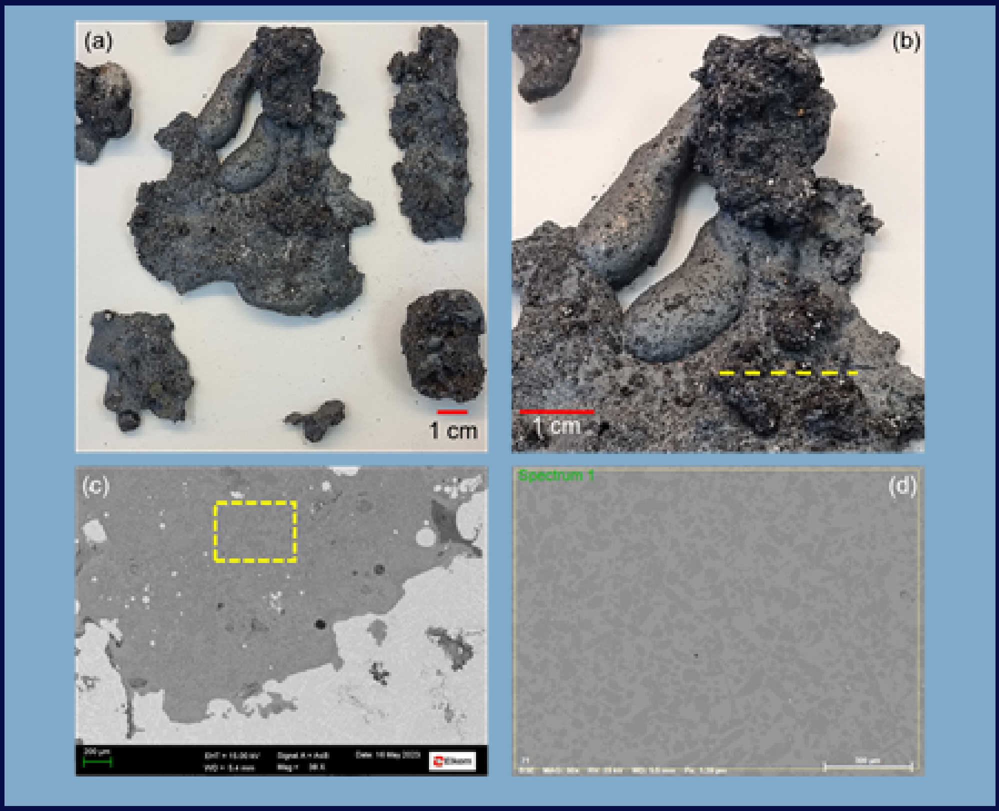

Fig. 7. (a) Metal/slag collected from the surface of the melt with steel cover. (b) showing the location (dashed line) where a cross-section evaluation with SEM was made. (c) shows the area where the composition was obtained with EDX.

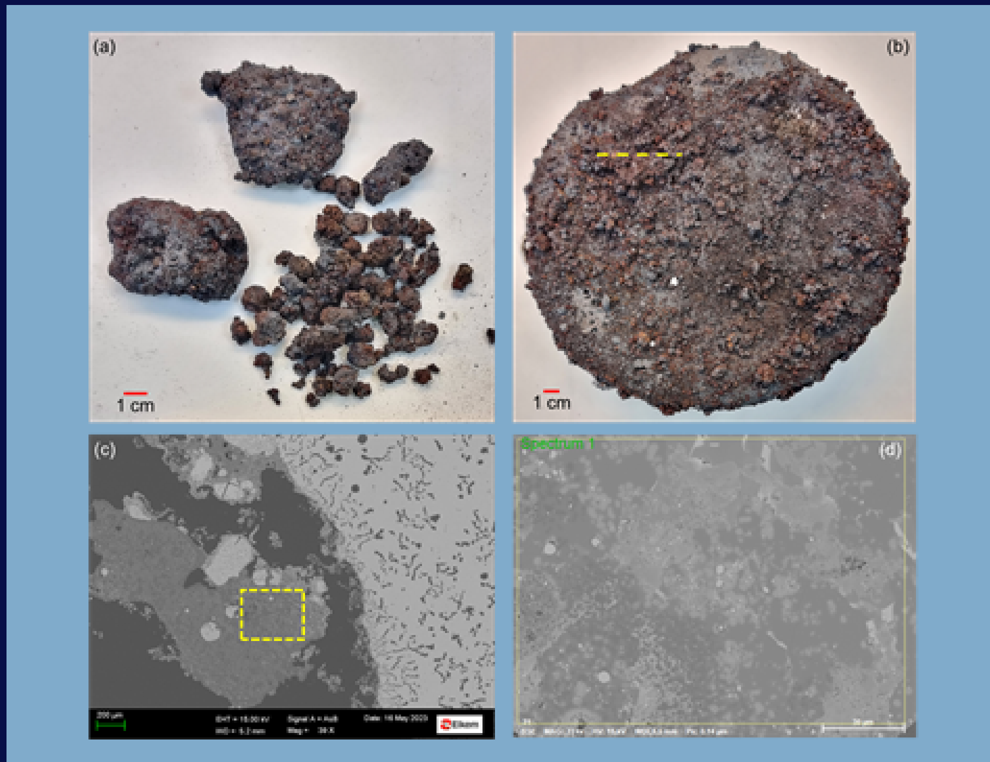

Fig. 8. (a) slag collected from the surface of the melt with Ba,Ca-FeSi cover. (b) showing the location (dashed line) where a cross-section evaluation with SEM was made. (c) shows the area where the composition was obtained with EDX.

The EDX results from the images **Fig. 7(d)** and **Fig. 8(d)** is shown in **Fig. 9(a)**. The composition of the slag was used as input for thermodynamic calculations [10] and the liquid fractions of each slag are shown in **Fig. 9(b)**.

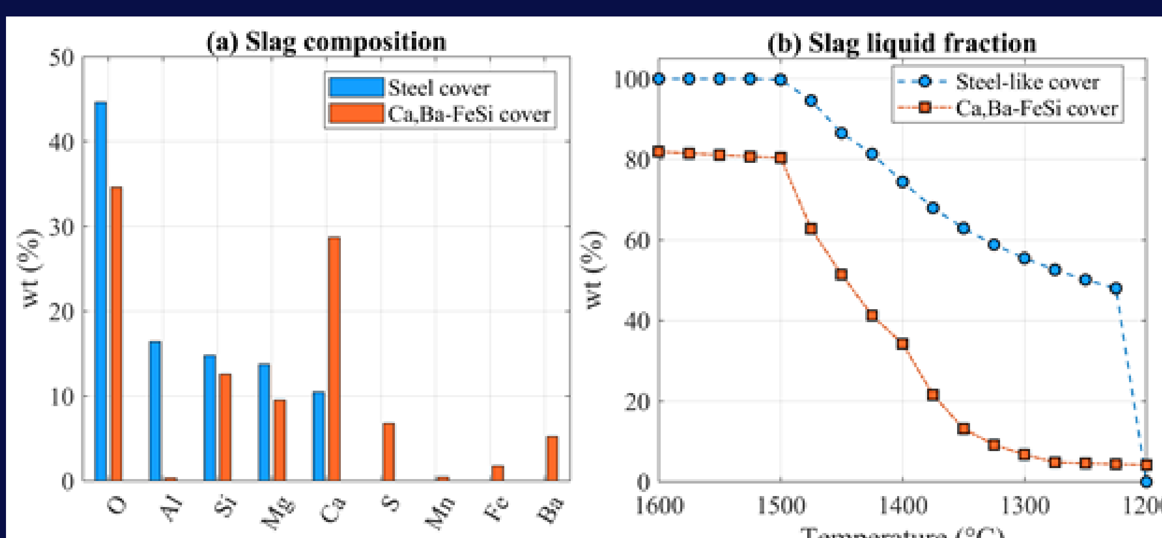

Fig. 9. (a) Composition of the slag. (b) Liquid fraction of the slags computed using thermodynamics.

Slags generated with the MgFeSi with steel cover and Ba,Ca-FeSi-cover are markedly different. The former has higher Al, and Mg content, while the latter contains more Ca, S and Ba. These differences are evident when computing the liquid fraction using CALPHAD, as seen in **Fig. 9(b)**. The slag from the steel cover is 100% liquid until the temperature reaches 1500°C (2732°F). Similar behavior is observed for the Ba,Ca-FeSi slag, which is 80% liquid until 1500°C (2732°F). However, the liquid fraction substantially decreases with decreasing temperature. This explains the behavior seen in **Fig. 6**. Furthermore, a more liquid slag is likely to be attached on the metal during the sample collection, making the separation process challenging.

Effect of cover material on final iron quality

It is standard practice to inoculate the iron when making ductile iron and as can be seen from the samples from treated iron only cover is not sufficient to make acceptable ductile iron.

In the second part of the evaluation of the results the purpose was to evaluate if the cover has effect also on the final casting quality in addition to the the performance of the MgFeSi treatment process.

From the treatment ladle the iron is transferred to pouring ladles where inoculation with 0.20 wt% of a Ba,Ca-FeSi inoculant or only the Si-units equivalent to the inoculation addition are added prior to pouring the final casting. Addition of Si-units is done to maintain the same final Si-level for both the inoculated and uninoculated samples.

Effect of cover material on composition and Mg-recovery of final iron

In **Table 6** and **Table 7** the chemical composition of both the uninoculated and inoculated samples from the two melts are presented together. For melt 1 where the steel cover was used lower C was observed for both the uninoculated and inoculated samples although the base iron C-level was the same as for the two melts. This was also observed right after the treatment and de-slagging. Further it can be seen that Si-level was also lower for the samples with steel cover, but that the difference in Si is within the uncertainty of the analysis. S-levels are observed to be similar for all samples, while for residual Mg-level the difference observed from treatment is maintained with higher residual Mg-level observed for the samples with Ba,Ca-FeSi cover than with steel. Further it can also be seen that higher residual Mg-level is achieved for all inoculated samples compared to uninoculated, suggesting that inoculation with Ba-containing inoculant helps prevent fading of Mg. For the elements like P, Mn and Cu no difference is observed between the melts and all elements are on target.

Table 6. Target final-iron composition – No inoculation.

Element:	%C	%Si	%S	%Mg	%P	%Mn	%Cu
Target:	3.60 ±0.10	2.20 ±0.15	0.010 ±0.005	> 0.040	0.030 ±0.005	Max. 0.20	Max. 0.05
Steel - None 1	3.59	2.18	0.009	0.048	0.033	0.19	0.04
Steel - None 10	3.59	2.24	0.010	0.044	0.034	0.19	0.04
BaCa-FeSi – None 1	3.73	2.31	0.010	0.050	0.033	0.20	0.04
BaCa-FeSi – None 10	3.64	2.27	0.013	0.052	0.033	0.20	0.04

Table 7. Target final-iron composition – 0.20 wt% BaCa-FeSi.

Element:	%C	%Si	%S	%Mg	%P	%Mn	%Cu
Target:	3.60 ±0.10	2.20 ±0.15	0.010 ±0.005	> 0.040	0.030 ±0.005	Max. 0.20	Max. 0.05
Steel – Inoculated 1	3.60	2.25	0.008	0.049	0.033	0.19	0.04
Steel - Inoculated 10	3.55	2.24	0.009	0.046	0.034	0.19	0.04
BaCa-FeSi - Inoculated 1	3.67	2.29	0.010	0.053	0.033	0.20	0.04
BaCa-FeSi - Inoculated 10	3.71	2.31	0.010	0.053	0.033	0.20	0.04

In **Fig. 10** below the residual Mg-level for the different conditions evaluated are presented.

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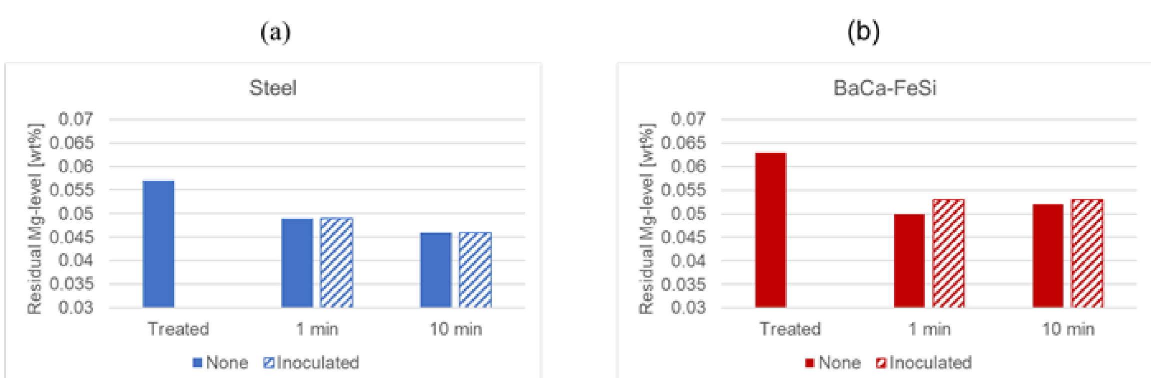

Fig. 10. Comparison of residual Mg-level for (a) steel and (b) Ba,Ca-FeSi cover

With the Ba,Ca-FeSi cover a higher residual Mg-level is retained after treatment than with the steel cover. Some Mg is lost when the metal is transferred from the large treatment ladle to the smaller pouring ladles for both cover materials, but for Ba,Ca-FeSi cover there is no additional loss after 10 min holding while for the steel cover the residual Mg-level continues to drop. For both cover materials inoculation helps reduce the Mg-loss but in combination with Ba,Ca-FeSi cover inoculation helps maintain the residual Mg-level above 0.050 wt% even after 10 min holding.

Effect of cover material on cooling curves of final iron

In **Fig. 11** below the cooling curves for the uninoculated and inoculated samples can be seen.

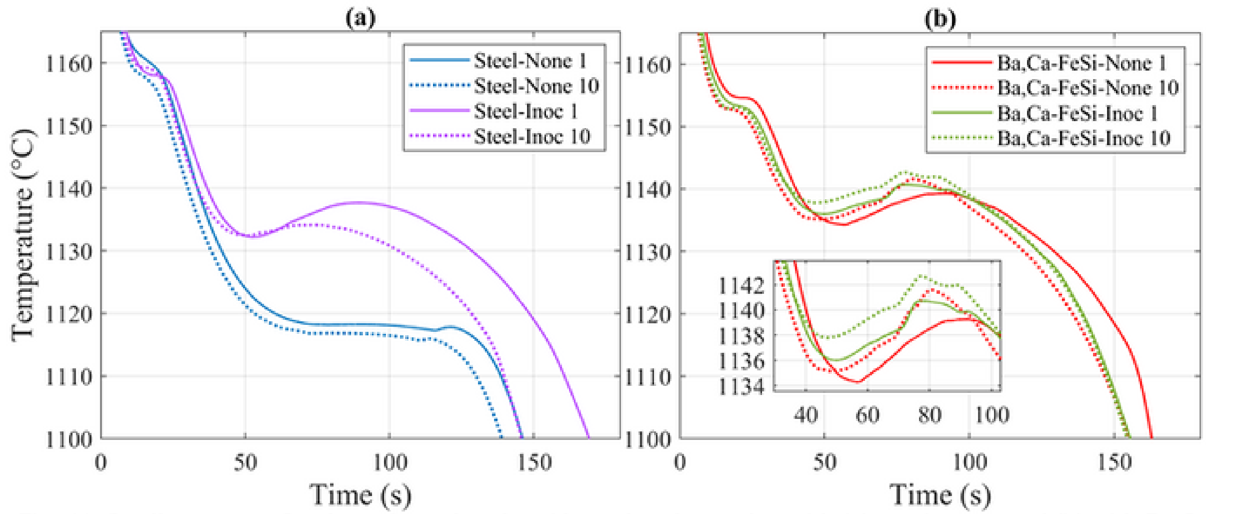

Fig. 11. Cooling curves for the uninoculated and inoculated samples with (a) steel cover and (b) with Ba,Ca-FeSi cover.

The cooling curves are very different with Ba,Ca-FeSi cover than with steel cover. For Ba,Ca-FeSi, all the cooling curves, both inoculated and inoculated are, showing lower eutectic temperature (LET) values around 1135°C (2075°F), while for the steel cover, a lower eutectic temperature (LET) of below 1120°C (2048°F) for the uninoculated samples and around 1135°C (2075°F) for the inoculated was observed. For the steel cover, the inoculation makes a huge improvement in cooling curves, while for the Ba,Ca-FeSi cover, the inoculation only improves the lower eutectic temperature (LET) with 2-3°C (35-37°F).

The lower eutectic temperature (LET) values can be seen in detail in **Fig.12** below.

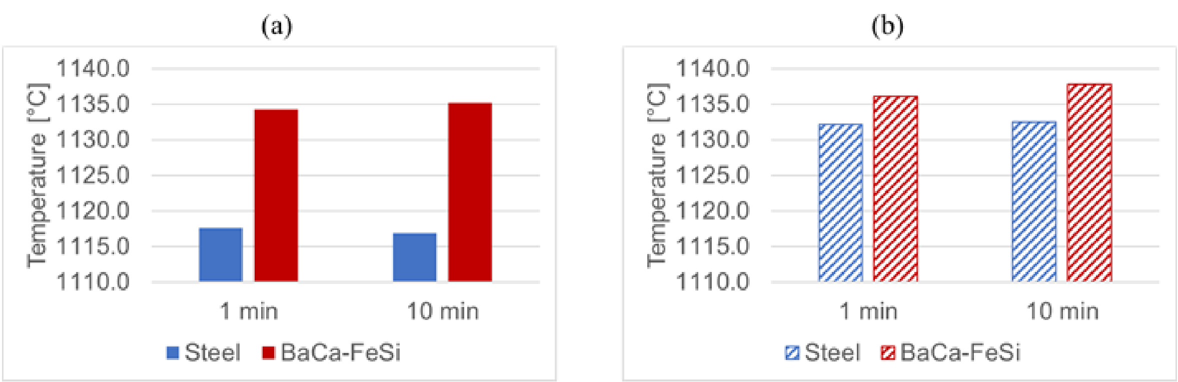

Fig. 12. Lower eutectic temperature (LET) for (a) uninoculated, (b) inoculated conditions.

As can be seen from the lower eutectic temperatures, a better nucleation condition is achieved with the Ba,Ca-FeSi cover with and without inoculation compared to the steel cover. Still, it can also be seen that the inoculation improves the nucleation condition of iron with the steel cover to almost the same level as with only the Ba,Ca-FeSi cover. An interesting observation is also that inoculation maintains lower eutectic temperature values after 10 min holding for both steel and Ba,Ca-FeSi cover. Similar observations have been reported [9].

Effect of cover material on the microstructure of final iron

In this study, the microstructure was studied in the same samples as the cooling curves were recorded. The microstructure from the uninoculated condition is presented before the inoculated condition and compared to the inoculated after 1-minute and 10-minute holding times.

In **Fig. 13**, the etched microstructure from the uninoculated condition is shown.

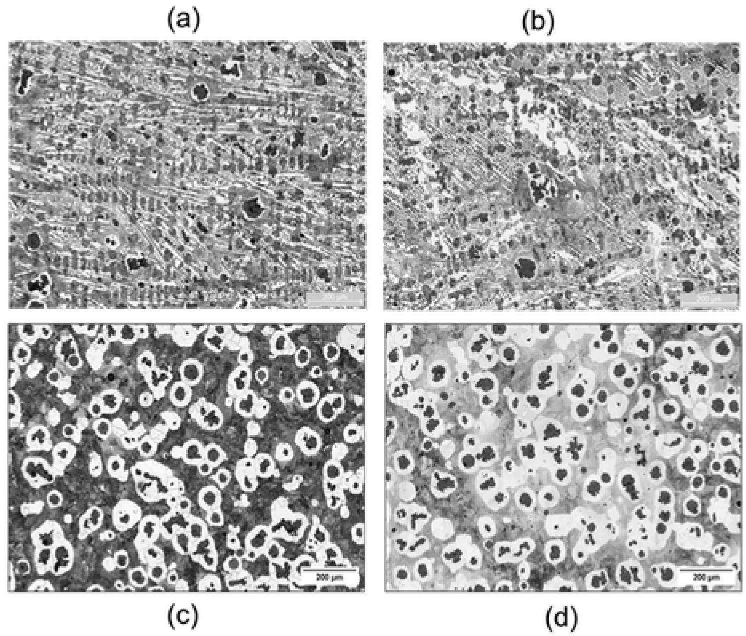

Fig. 13. Microstructure of Steel cover with (a) 1 min holding time and (b) 10 min holding time, compared to Ba,Ca-FeSi cover with (c) 1 min holding time and (d) 10 min holding time for uninoculated condition.

From **Fig. 11**, the cooling curve with only steel cover showed a LET value below 1120°C with no recalescence, and the microstructure observed, seen in **Fig.13(a-b)**, is carbidic. While for Ba,Ca-FeSi, the TElow values are approximately 1135°C, and the structure is carbide free for both 1 min and 10 min holding times.

The nodule density and nodularity in **Fig.14** show that both are low regardless of cover material used. Although carbide-free, it would not be an acceptable final structure with only the BaCa-FeSi cover.

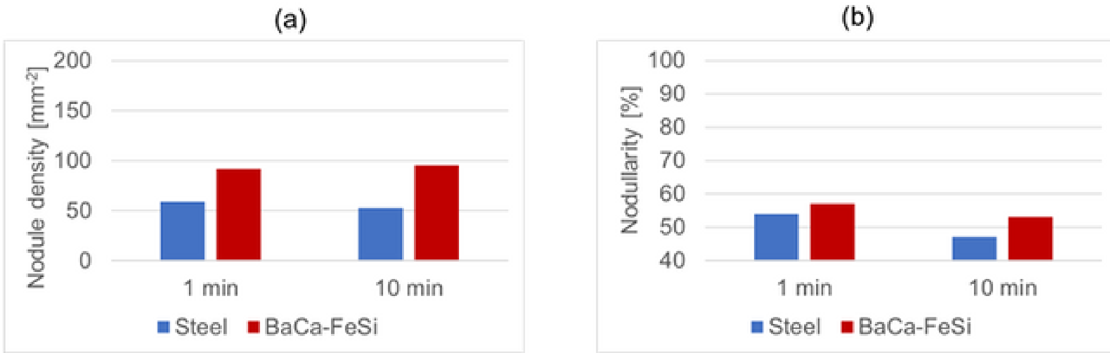

Fig. 14. Comparison of (a) nodule density and (b) nodularity with 1 and 10 min holding with steel and Ba,Ca-FeSi cover in uninoculated condition.

Fig. 15 shows the microstructure after 1 min holding for uninoculated and inoculated conditions and the two cover materials.

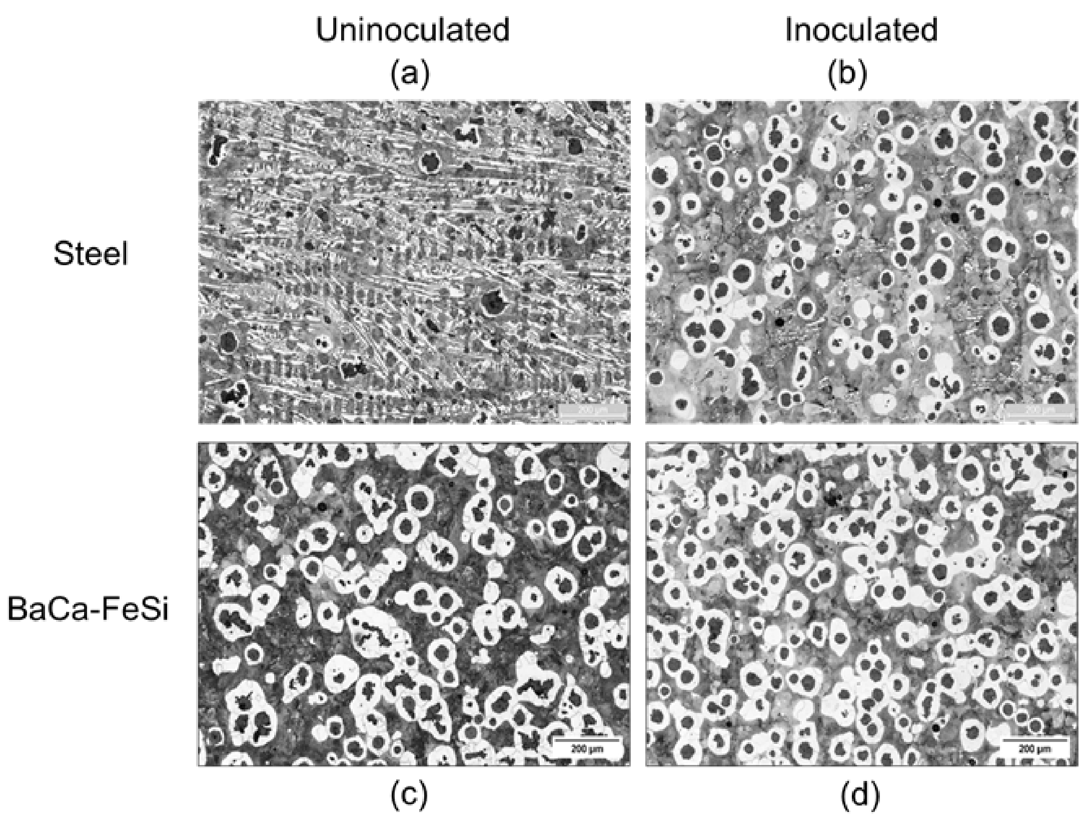

Fig. 15. Microstructure after 1 min holding with steel cover (a) without inoculation and (b) with inoculation, compared to Ba,Ca-FeSi cover (c) without inoculation and (d) with inoculation.

When comparing the samples after 1 min holding, improvement is seen with inoculation for both steel cover and Ba,Ca-FeSi cover, as seen in **Fig 16** below.

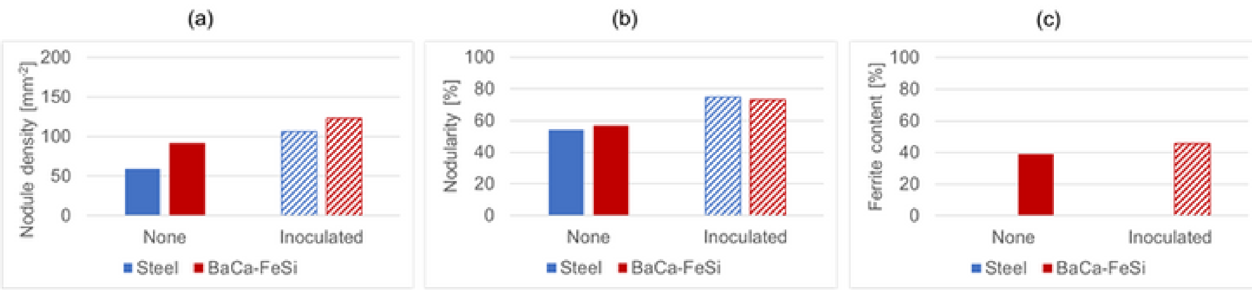

Fig. 16. Comparison of (a) nodule density and (b) nodularity with and (c) ferrite content with steel and Ba,Ca-FeSi cover for the uninoculated and inoculated condition after 1-minute holding.

For the steel cover, inoculation increases the nodules density from ~ 60 mm-2 to above 100 mm-2, while nodularity increases from below 60% to close to 80%. However, the inoculation was not sufficient to eliminate the carbides. The ferrite content is shown because the carbides have the same white appearance in the etched structure. For Ba,Ca-FeSi cover inoculation also improves the nodules density increases from below 100 mm-2 to above 120 mm-2 and nodularity from below 60% to close to 80%. A minor increase is also seen for the ferrite content from ~ 40% to ~45%.

Fig. 17 shows the microstructure after 10 min holding for uninoculated and inoculated conditions and the two cover materials.

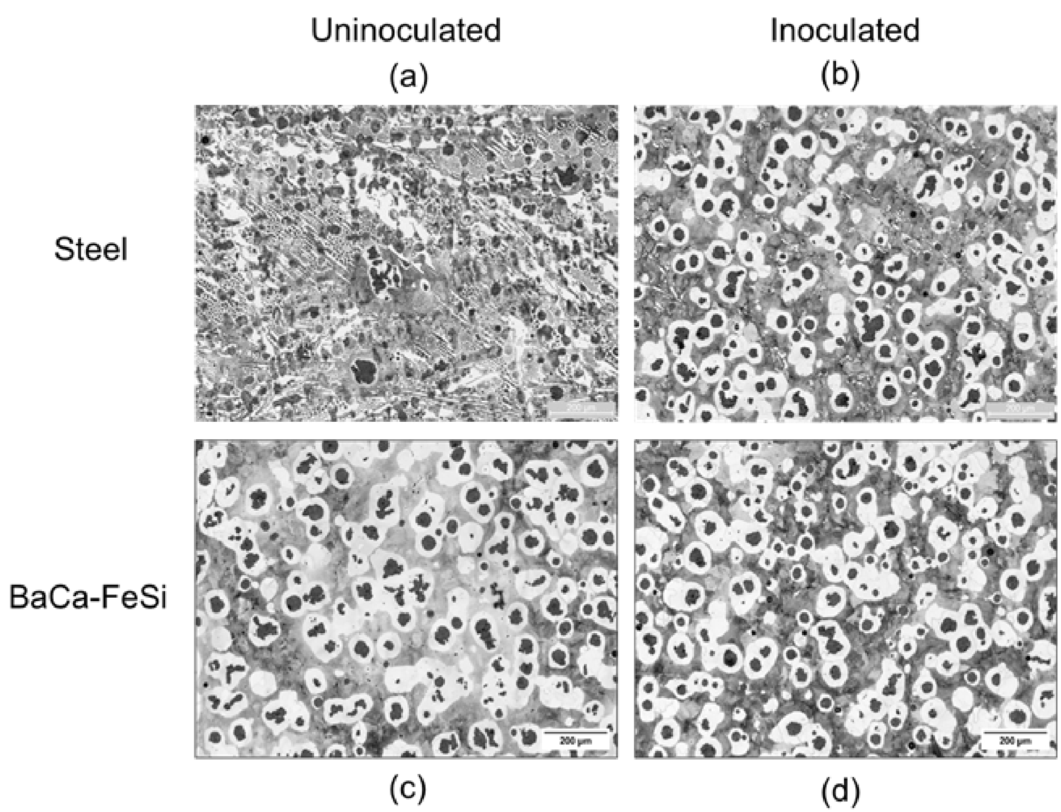

Fig. 17. Microstructure after 10 min holding with steel cover (a) without inoculation and (b) with inoculation, compared to Ba,Ca-FeSi cover (c) without inoculation and (d) with inoculation.

Inoculation provides improved microstructure with both cover materials after 10 min holding, as shown in **Fig. 18** below.

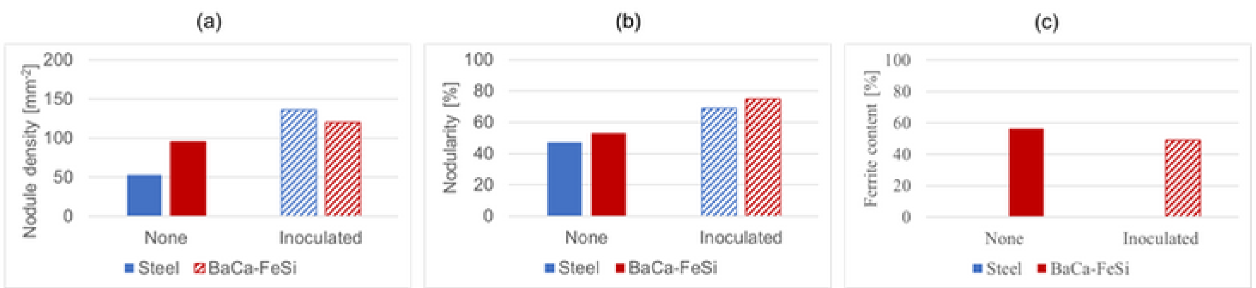

Fig. 18. Comparison of (a) nodule density and (b) nodularity with and (c) ferrite content with steel and Ba,Ca-FeSi cover for uninoculated and inoculated conditions after 10-minute holding.

For steel cover, inoculation increases the nodules density from around 50 mm-2 to close to 140 mm-2, and nodularity increases from below 50 to around 70%. In contrast, for 1 min holding, inoculation was not sufficient to eliminate the carbides.

For Ba,Ca-FeSi cover inoculation also improves nodule density from ~100 mm-2 to ~120 mm-2 and nodularity below 60% to ~80%. For 10 min holding, a decrease in ferrite content with inoculation is seen from close to 60% to around 50%.

DISCUSSION OF RESULTS

The purpose of the cover material is to protect the MgFeSi alloy and delay the reaction.

Mg-recovery

Fig. 1 shows that a Mg-recovery of 77% is achieved with a steel cover, which is a high recovery for a tundish treatment process. However, with the Ba,Ca-FeSi cover, a 13% higher recovery is achieved with 90%.

Table 8 shows the main differences between the two MgFeSi treatments.

Table 8. Mg-recovery in detail.

	Mg retained in the iron	Mg lost to removal of S	Mg lost to O as slag, fume or flare
Steel cover	73%	4%	23%
Ba,Ca-FeSi cover	81%	10%	9%

With the Ba,Ca-FeSi cover more Mg is retained in the iron and bonding with S, and less is lost to O as slag, fume, or flare. This indicates that the Ba,Ca-FeSi provides a better cover as less Mg is lost from the treatment. The effect is achieved although Ba,Ca-FeSi has a lower density, and the addition is around 30% lower.

Nucleation potential

A clear difference is seen between the two cover materials regarding the nucleation potential. While **Fig. 3** shows that a carbide-free structure is achieved directly after treatment with Ba,Ca-FeSi, the same is not observed with a steel cover. This positive effect from Ba,Ca-FeSi on the nucleation potential is confirmed by the ~15 °C (59°F) higher lower eutectic temperature (LET) seen in **Fig. 5**.

Slag generation

Slag is a common by-product of the Mg-treatment, especially if the base iron S-level is higher than recommended. In this case, the base iron S-level was on the high side with around 0.020 wt%, as seen in **Table 4**, which increases the risk for slag generation. Slag was observed with both cover materials, but the amount and behaviour observed were different. More slag could be observed on the surface of the treatment ladle after treatment with Ba,Ca-FeSi cover, as seen in **Fig. 6(b)**, but the slag was easier to remove as it was dry and floating on the top than with the steel cover. The slag generated with a steel cover was difficult to remove, explained by the thermodynamic evaluation in **Fig. 9(b)**, showing this slag to be more liquid at higher temperatures than the Ba,Ca-FeSi cover slag.

The Ba,Ca-FeSi cover may generate more slag, but it does so without losing Mg to slag, fume, and flare. By covering with Ba,Ca-FeSi, a zone of high Si is probably generated when it dissolves, increasing the solubility of Mg locally. In addition, the Ba,Ca-FeSi cover contains elements like Ba and Ca which will help remove S and O and leave Mg to stay in the iron. As a result, the slag with Ba,Ca-FeSi cover contains more Ca in addition to S and Ba.

The steel cover comes without Si, Ca, and Ba to help dissolve and protect Mg. As a result, more Mg is lost to O, and less can react with S to form slag, resulting in lower Mg-recovery.

EFFECT OF COVER MATERIAL ON FINAL IRON QUALITY

The residual Mg retained in the iron after Mg-treatment reacts with oxygen from the air until the melt solidifies. After the treatment, the melt is, in this case, transferred to pouring ladles with or without inoculation before casting, and it is expected to have an additional loss of Mg. Therefore, a high initial residual Mg-level provides greater safety against Mg-fading and insufficient Mg-level in the final casting.

Mg-recovery

As expected, the residual Mg-level is lower with both cover materials in the final casting, as seen from **Table 6** and **Table 7**. Compared to after treatment, the Mg-recovery is 15 to 20% lower in the final casting, with the loss being lower for the steel cover after 1 min. For both cover materials, it can also be observed that inoculation Ba-containing inoculant decreases the

Mg-fading. The higher recovery seen for inoculated conditions results from the elements like Ba, Ca, and Al that can also react with oxygen instead of the Mg.

After 10 minutes of holding, a higher Mg-recovery is observed in **Fig 10(b)** with Ba,Ca-FeSi cover than with the steel cover in **Fig 10(a)**. In fact, with the Ba,Ca-FeSi cover, there is no Mg-fading observed compared to the results after 1 minute of holding, while with the steel cover, the Mg-fading continues.

The temperature in the pouring ladles at the time of pouring is in the range of 1320°C (2408°F) after 10-minute holding and 1360°C (2480°F) after 1-minute holding. **Fig. 9(b)** shows that the slag with a steel cover is still predominantly liquid at these temperatures, while the Ba,Ca-FeSi is predominantly solid. For the steel cover, the slag is poorly separated from the iron and will probably require more time to be rejected [11], while with the Ba,Ca-FeSi cover, the slag is solid, leading to a faster rejection. As a result, a higher Mg loss is seen with Ba,Ca-FeSi cover after 1-minute holding than with steel cover.

Nucleation potential

Compared to steel cover, the Ba,Ca-FeSi cover provides a higher lower eutectic temperature (LET) both with and without inoculation, as can be seen from **Fig. 12**, confirming that the Ba,Ca-FeSi cover provides inoculation support. This is also clear when looking at the microstructure for uninoculated in **Fig. 13** and inoculated conditions in **Fig. 15** and **Fig. 17**, where carbide-free structures are seen with Ba,Ca-FeSi cover with and without inoculation regardless of holding time, while for steel cover carbides can be seen in the structure even with inoculation.

Although the structure is carbide free with only Ba,Ca-FeSi cover, inoculation is needed to make the structure acceptable in terms of nodule density and nodularity. Inoculation improves the structure with a steel cover but has not been sufficient to provide a carbide-free structure in this case, as seen in **Fig. 15** and **Fig. 17**.

Fade resistance

In this study, Ba was introduced both as part of the cover material and as inoculation. Ba-containing inoculants are often referred to as fade resistant. Looking at the Mg-recovery in **Fig. 10**, the Ba,Ca-FeSi cover also helps reduced Mg-fading. This is also observed from the cooling curves where the lower eutectic temperature (LET) without inoculation in **Fig. 12(a)** after 10-minute holding is maintained with Ba,Ca-FeSi cover while it decreases slightly for steel cover.

A similar observation can be made for the structure in **Fig. 14**, where nodule density is maintained after 10 minutes of holding with a minor decline in nodularity for Ba,Ca-FeSi cover, while both nodule density and nodularity are lower after 10-minute holding with steel cover. This confirms that Ba introduced as part of the cover also provides fade resistance. Previous work has demonstrated the ability of Ba to reduce fading in terms of microparticles and thermal analysis [9]. However, that study was done based on Ba added as part of the inoculation. In this context a future study will focus on the fundamentals behind the ability of Ba to increase fade resistance when added as cover and in slower cooling rate condition.

Fig. 16 and **Fig. 18** show that with Ba-inoculation, nodule density and nodularity are maintained after 10-minute holding with both steel and Ba,Ca-FeSi cover confirms the statement that Ba-containing inoculants are fade resistant. This is further confirmed by **Fig 12 (b)**, showing that the lower eutectic temperature (LET) is unchanged for steel cover while an increase is seen with Ba,Ca-FeSi cover.

CONCLUSION

The use of Ba, Ca-containing cover material provides higher Mg-recovery, inoculation support, and better resistance to fade, in addition to a slag that is easier to remove from the treatment ladle after treatment. Although a higher amount of slag is generated with the Ba,Ca-containing cover material, less Mg is lost to reaction with oxygen as the cover material provides a better dissolution of Mg into the iron. At the same time, it provides additional elements (Si, Ba, Ca, and Al) that can react with S and O. The effect of the Ba, Ca-containing cover material is also maintained in the final iron. However, the Ba, Ca-containing cover material cannot replace inoculation but will provide inoculation support allowing for less subsequent inoculation and a longer retained inoculation effect.

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