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LADLE AND IN-MOLD MODIFICATION METHODS FOR OBTAINING CASTINGS FROM CAST IRONS WITH DIFFERENT GRAPHITE MORPHOLOGY

Introduction. *In the world practice of foundry, modification has reached the status of leading direction of research and applied work to improve the technological and service properties of structural cast irons.*

Problem Statement. *Modifying treatment of liquid iron provides for not only the creation of certain types of modifiers, but also for the development of such methods for introducing modifier into the melt, which are adaptable to the conditions of foundries and take into account the requirements for specific groups of castings.*

Purpose. *To develop a pilot technology for the modification of electric furnace melts of cast iron in unsealed ladle with removable bowl caver and casting molds using complex reagents in the form of pressed powder briquettes and lumpy fused master alloys for the production of castings with lamellar, vermicular and spherical graphite.*

Materials and Methods. *The following materials have been used in the research: gray cast iron, as an object of research for modifying treatment, magnesium-lanthanum-containing lumpy and briquetted powder modifiers, as well as nitrogen-containing lumpy and briquetted powder modifiers to produce cast iron with various forms of graphite, depending on the requirements for castings.*

Results. *A pilot technology for cast irons using pressed powder nitriding briquettes to increase twice the tensile strength of structural gray cast irons (from 200 MPa to 400 MPa) without alloying and heat treatment and a ladle process for modifying molten iron melts with lanthanum-containing modifiers have been developed. The prospects for the production of nitrated iron with vermicular graphite with a sulfur content of up to 0.1% wt. by re-melting the nitrogenous metal charge and fresh and rotary cast irons and therefore with the possible minimum additional introduction of nitrogen in the furnace or in the ladle or in the mold have been substantiated.*

Conclusions. *The pressed powder composite modifiers are recommended as the most effective ones for the mentioned modifying methods, depending on the requirements for castings.*

Keywords: ladles, intra-form modifying, magnesium-lanthanum- and nitrogen-containing complex modifiers.

According to the forty-sixth census of world foundry production [1], the global annual output of shaped castings of ferrous and non-ferrous alloys reaches 100 million metric tons, including 25 million ton CNG (cast iron with nodular graphite) and CVG (cast iron with vermicular graphite). 90% of total CNG and CVG tonnage (22.5 million tons worth about USD 40.5 billion) is manufactured using ladle modification methods, while the remaining 10% (2.5 million tons worth about USD 4.5 billion) is obtained

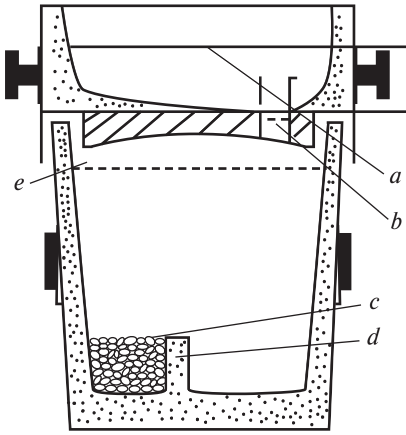

Fig. 1. Scheme of a tandish-cover ladle with a removable cap on the bowl [6–7]: *a* — the lid-bowl; *b* — pouring and exhaust hole; *c* — a spheroidizer or vermicularizer; *d* — fireproof partition; *e* — the upper level of filling the ladle with liquid iron; *h* — average height of the melt layer in the bowl

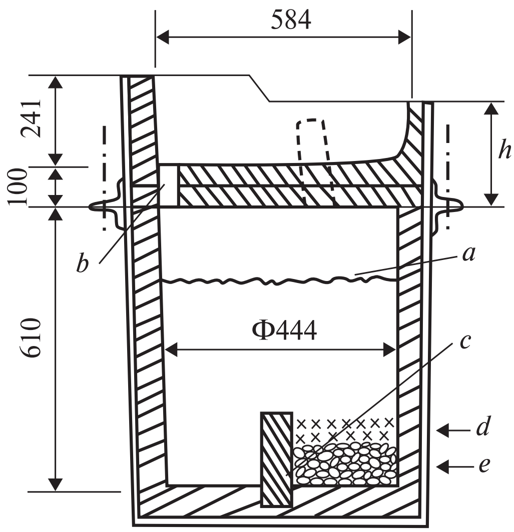

Fig. 2. Scheme of a tandish-cover ladle with a stationary cap of a bowl [7]: *a* — the upper level of the melt (mass — 455 kg); *b* — inlet/outlet port; *c* — fireproof partition; *d* — MgFeSi alloy; *e* — cover material; *h* — is the average height of the melt layer in the bowl

by in-mold methods for modifying treatment of liquid iron. The annual proceeds from sales of CNG and CVG castings amount to USD 45 billion, which makes it possible to assess the scale and significance of this large sector of world foundry production.

The most effective ladle method, as the practice has shown, is a method called tandish-cover in the USA and known under this name in many countries. The method involves the use of unsealed ladles with a removable or fixed lid-bowl and a refractory partition in the bottom of the ladle.

The first versions of tandish-cover ladles were developed in the USA in the late 1970s [2–5]. They enabled on the whole to solve the actual problem of economy, simplicity, and safety of the modification process, to significantly reduce the pyroeffect and smoke evolution, to increase the assimilability of magnesium and other modifier elements up to 70–80% by installing a bowl on the ladle of a removable or stationary casting lid.

The purpose of this publication is to present data on modern designs and experience in the operation of unsealed ladle with a lid-bowl, and also to substantiate the choice of modifiers for the production of castings from CNG and CVG using the ladle and the in-mold methods.

UNSEALED LADLES WITH LID, A BOWL FOR MODIFYING TREATMENT OF LIQUID CAST IRON

This highly efficient and relatively simple method involves the use of a removable or fixed lid-refill lid and a pouring outlet. The cast iron melt is poured through the lid that is a bowl into the ladle, in the reagent chamber of which there is a magnesium-containing modifier (Figs. 1, 2).

Figs. 3–6 show several other effective designs for ladle tandish covers, to release the cast iron from the ladle through the hole in the same bowl. In comparison with the known ladle methods "pour-over" and "sandwich", this method has the following advantages: a higher and reproducible assimilation of magnesium (60–80%); the absence of pyroeffect and a sharp decrease in smoke evolution; reduced losses of carbon and temperature of liquid iron; a less violent reaction; a more efficient ladle design; and a smaller amount of slag formed during the modifying treatment.

The thickness of steel cover is set taking into account the weight of refractory lining and liquid iron in the sprue bowl. The skirt is a reflector and the bowl is made of a thinner steel sheet. No special refractories for the lid are required. When calculating the diameter of casting-outlet opening it is assumed that the molten iron must remain in the bowl until the reaction between the modifier and the cast iron melt ceases.

The calculation is based on the well-known Ozanna formula for cast iron [5]:

$$F_0 = \frac{G}{\tau_з \, \mu 0{,}31 \sqrt{h_ч}},$$

where F_0 is the area of the cup opening, cm^2; $\tau_з$ is duration of filling, s; μ is the dimensionless flow coefficient when the metal flows out of the cup opening (approximately $\mu = 0.85$); 0.31 is coefficient with the dimension of kg / (cm$^{2.5}$ · s); $h_ч$ is the average metallostatic head (average height of the melt layer in the bowl), cm; *G* is the mass of the metal poured into the ladle, kg.

When the mass of iron is less than 1 ton, *h* should be within 10—15 cm, and the height of bowl's cavity should be 2—3 times larger. In ladles with a fixed cover for insertion of the magnesium modifier into the ladle cavity and relief of excess pressure, a special hole is provided in the

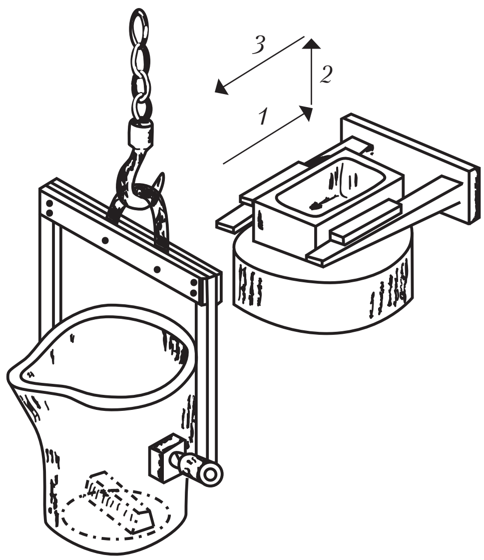

Fig. 3. Scheme of a tandish-cover ladle with removable-sliding lid-bowl. Arrows *1*, *2* and *3* indicate the direction of movement of the lid-bowl [7]

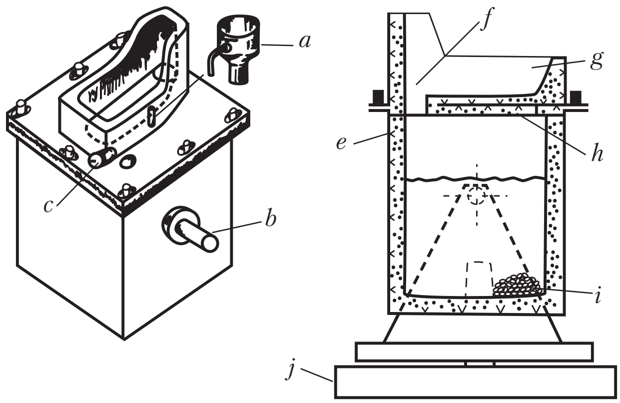

Fig. 4. Scheme of a tandish-cover ladle with a semi-stationary lid-cup [7]: *a* — funnel for loading the modifier into the ladle; *b* — a gear transmission; *c* — steel cork; *e* — filling hole; *f* — pouring bowl; *g* — a passage sealed with a clay mass; *h* — modifier of MgSiFe; *i* — sensor for measuring gravity

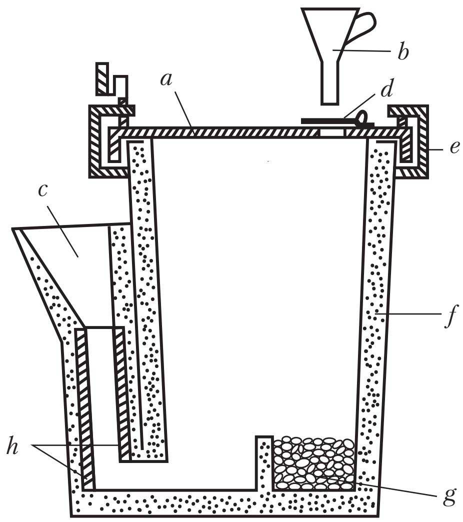

Fig. 5. Teak type ladle tandish cover with one port for liquid cast iron [7]: *a* — cast-iron ladle cover; *b* — funnel for loading the modifier into the ladle; *c* — pouring bowl; *d* — cover; *e* — device for fixing the ladle cover; *f* — fireproof packing; *g* — spheroidizing modifier; *h* — refractory tube

ladle. To create a reagent and a metal receiving chamber in the ladle cavity, a refractory separation partition should be used. The use of partition and a cover material with appropriate fluxes reduces the intensity of build-up in the ladles. It is desirable to use a circular ring of fibrous ceramic insulators between the lid and the ladle lining, which acts as a cushion and seals the junction area.

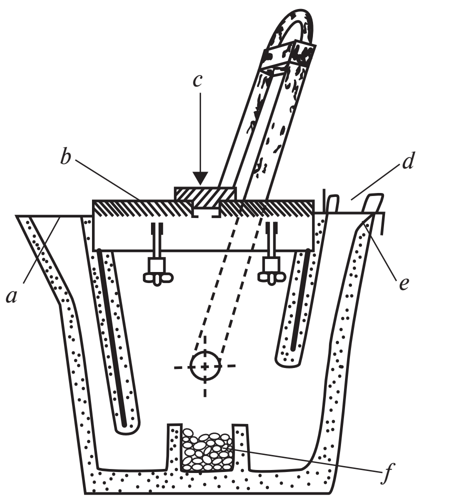

Fig. 6. Teapot type ladle tandish cover with two ports for liquid cast iron [7]: *a* — outlet port; *b* — ladle cover with an edge grip of the ladle shell; *c* — cork (plug) used when filling the ladle with a modifier; *d* — filling port; *e* — reflecting plate; *f* — a spheroidizer (vermicularizer)

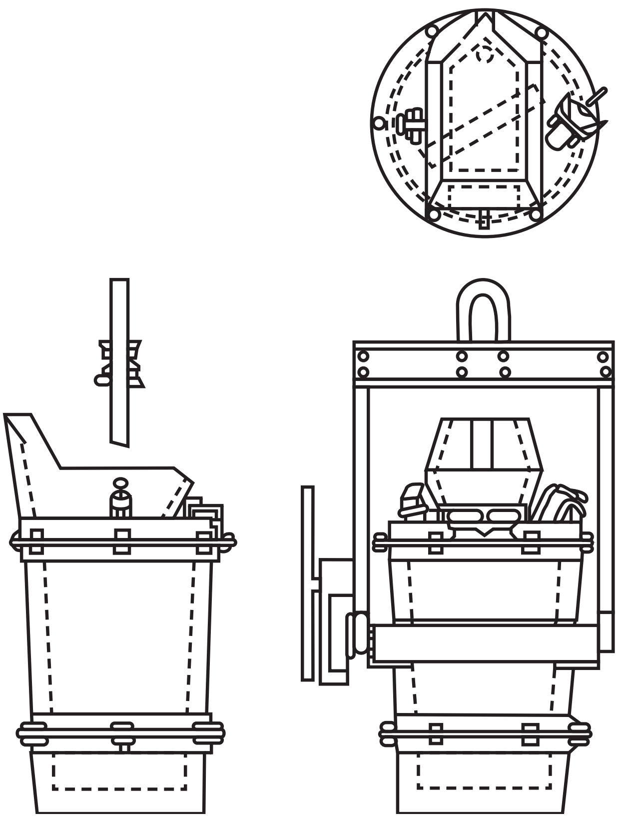

Fig. 7. Scheme of the "De Tait Cover" ladle for spheroidizing graphite for processing molten iron [2]

The variant of the tandish-cover method with the use of multi-position carousel tables enables to provide a high performance of spheroidizing treatment.

Specialized firms in the USA have mastered the production of several types of tandish-cover ladles and supply them to foundries that manufacture CNG castings. American Foundation Funds have developed a series of 10 models of DE Tait-cover ladles with a nominal capacity of 0.45 to 4.5 tons (Fig. 7). The ladle consists of three bolted parts: a "Tait-cover" cover, a body, and a detachable bottom. The joints of the assembled units are sealed with refractory paste. The lid fixed to the upper part of the ladle body, is not removed until the next repair or replacement of the lining. It consists of a receiving-pouring bowl with a grooved toe and a hole for the outlet-metal inlet; tubes for loading a portion of shredded spheroidizer provided with a quick-acting and tightly fitted weighted cap-latch; self-sealing vent to relieve excess gas pressure and to insert a burner to preheat the ladle, and a window with a quick-release door for slag discharge.

The ladle body is equipped with a gear mechanism for turning the ladle and with an upper suspension frame. The removable bottom is divided by a vertical partition into a reagent- and a metal-receiving chamber. When the ladle is filled with cast iron, the bowl must be filled to, at least, half its height, which prevents aspiration of air into the ladle.

Accurate weight control of the cast iron is required to avoid overfilling the ladle and filling the vent hole and the tube. The rate at which the metal leaves the ladle depends on the diameter of the hole in the bowl. The ladles are delivered without refractories, but are balanced for a certain thickness of the liner. The delivery set also includes special metal plates with models for lining the slag window, the main body, and the bottom. These models have a rigid structure, so the lining mass for all ladle assemblies, with the exception of the bowl, can be compacted by tamping, pouring or vibrating (the mass for the bowl

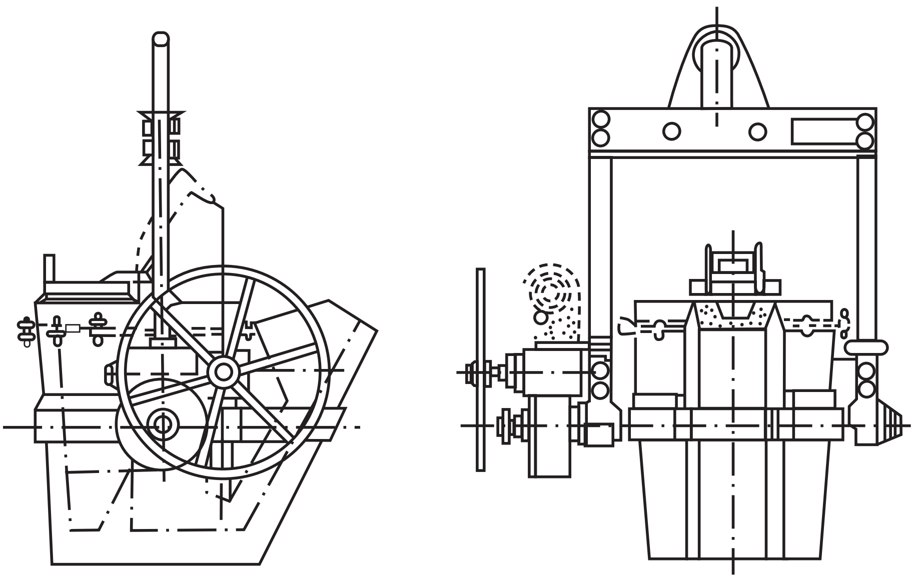

Fig. 8. Diagram of a teapot of the "mod-tandish" type for spheroidizing graphite for processing molten iron [2]

is sealed only with the packing). The modifier is loaded through a removable funnel with a diameter of 90 or 115 mm. On average, assimilation of magnesium in a ladle of the “DE Tait-cover” type makes up 60—70%, depending on the magnesium content in the modifier and on other factors. The experience of the operation of these ladles has been considered in [3—4].

Alco Stendad Corporation (USA) produces 13 models of tee-tandish teapots with a nominal capacity of 0.23—4.6 tons (Fig. 8). Pouring and casting of cast iron are made through the ladle's toe, and the the modifier is loaded into the reagent pocket through a window equipped with a hinged lid. An automatic system for loading portions of spheroidizer into a ladlet has been developed. As compared with the methods of pour-over and tandish cover (in the De Tait-Cover ladles), the spheroidizing treatment of cast iron in such ladles provides a saving of about USD 16 per each ton of pig iron due to a reduction in the consumption of magnesium ligature and inoculator ferrosilicon.

There has been a positive experience in the production of cupola-melt CGS by treatment with magnesium-containing ligatures in large unsealed tandish ladles equipped with a removable lidcup [1]. The Institute of Casting Problems of the NAS of Ukraine has developed and tested this technology at the iron foundry of the Novo-Kramatorsk Machine-Building Plant, using 10- and 20-ton ladles. The assimilation of magnesium from Mg-REM-Si-Fe master alloy (6—7% Mg, 0.6% REM) is, at least, 60%. Filling of a 10-ton ladle with cast iron through a hole 100 mm in diameter lasts about 3 minutes. The tandish-cover method provides sufficiently high properties of cast iron in the cast state ($\sigma_в$ = 530—680 MPa, σ = 330—420MPa, δ = 3—8%), at a moderate hardness (197—229HB).

COMPLEX MODIFIERS FOR SPHEROIDIZATION AND VERMICULARIZATION OF GRAPHITE IN CAST IRON BY THE LADLE AND INTRA-MOLD MODIFICATION METHODS

In the composition of complex modifiers, regardless of the method of their production and the method of modification (in ladles or inside molds), it is recommended to introduce magnesium and lanthanum together without any other rare-earth metals (especially, cerium) in all cases where it is required to obtain castings from cast iron with increased ductility.

The combination of magnesium and lanthanum into the composition of complex modifiers for cast iron is not accidental. Magnesium is known to be the most economical and affordable graphite spheroid in cast iron. Lanthanum is the most powerful plasticizer of cast irons, regardless of graphite morphology. It does not form carbides, due to which it provides a high level of plasticity, resistance to mechanical and thermal shocks in a wide range of temperatures, an increase in the specific number of spheroids (2—3 times, more than 800 spheroids/mm^2) [8] and in the degree of graphite spheroidization. An exceptionally valuable technological property of lanthanum is the ability to prevent the formation of gas-shrinkage macrodefects and microporosity in castings and to improve the quality of the cast surface.

Table 1

The Physical Properties of Lanthanum and Magnesium [9]

Property, unit of measure	Element	
	Lanthanum	Magnesium
Density at 20 °C, g/cm^3	6.174	1.74
Melting point, °C	920	651
Boiling point, °C	3469	1103
Latent heat of fusion, kcal/g *	17.3	0.0822
Latent heat of evaporation, kcal/g *	690	1337
The specific heat at 20 °C, kcal/g * deg	0.048	0.250

Note: * – 1 kcal = 4.184 kJ.

Table 2

The Technical and Economic Indicators of Complex Modifiers in the Form of Fused Fractionated Ligatures and Pressed Powder Briquettes

Index, Unit	Type of modifier	
	Fractionated fused master alloy	Powder briquette modifier
Electricity consumption, kW/h	1500 ± 200	140 ± 20
Assimilation of magnesium in the manufacture of a modifier, %	70 ± 10	100
Scatter about of magnesium content in one brand, % by mass.	2 ± 1	0.1
Waste of modifier at crushing, %	30 ± 10	0
Relative consumption of the modifier, %	100	75 ± 5

A comparison of the physical properties of lanthanum and magnesium (Table 1) shows that, as compared with magnesium, lanthanum is potentially much safer and more technologically efficient in modifying the treatment of molten iron, retains the melt modifying effect for a longer time, has a higher and stable assimilation.

There is one more important qualitative advantage of lanthanum: in the case of lanthanum, the limiting solubility in liquid CNG is unlimited, while in the case of magnesium, it is very low [10—11].

Let's compare the main technical and economic indices of the two most dissimilar types of complex modifiers, namely, the fractionated fused ligatures and the pressed powder briquettes (Table 2).

The production of 1 ton fractionated master alloys obtained by conventional technology provides a ferrosilicon compound with magnesium (with magnesium losses reaching 30%), ligature casting, crushing and sieving by fractions (yield of 75—80%, the rest is waste in the form of pulverized fractions that are not used for modification due to the instability of their assimilation). At the same time, the variation in magnesium content in the ligature of the same brand reaches 1—2% for magnesium, which is 20—25% of the magnesium content in the ligature. The production of 1 ton briquetted modifiers by the powder metallurgy technology provides for the operation of mixing the original powder components and the briquetting operation. At the same time, energy consumption for the production of a ton briquetted powder modifier as compared with the production of a ton cast fractionated ligature requires 8—10 times less electricity. The loss of magnesium in the production of briquetted modifiers is no more than 0.1%, the magnesium content in the same brand is, at most, 0.1%, which enables to reduce the consumption of ligature for modifying cast iron 1.3—1.4 times due to the stability of its composition.

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One of the most important advantages of powdered briquetted modifiers is the possibility of introducing into their composition components that cannot be introduced in the cast ligatures including, the use of dusty wastes of ferroalloy production, serial powder materials, fluxes, inoculators, nitriding or carbide stabilizing constituents, and ultrafine powders of refractory compounds (carbides, nitrides, carbonitrides, etc.). The principal feature of the powder briquetted modifiers obtained by the developed technology, in contrast to the known ones, is the absence of any binders that pollute the modifiable alloy in their composition.

The technology of powder metallurgy enables to vary the shape (Fig. 9), dimensions, mass, and chemical composition of briquettes within a wide range, flexibly adapting them to the conditions of a particular foundry production (for example, ultradispersed compounds — inoculators, nitrides, borides of refractory compounds, etc.).

The results are not in favor of ligatures due to the use of the melting process.

Theoretical and technological foundations of industrial production of powder briquette modifiers have been developed jointly by two institutes of the NAS of Ukraine: the Institute of Problems of Materials Science and the Physico-Technological Institute of Metals and Alloys [12—14].

The lanthanum-containing modifiers ensure equiaxial crystallization of CNG with an increased number of uniformly distributed centers of SG crystallization [15]. In this case, the thickness of the columnar crystallization zone is greatly reduced, leaving more free channels to compensate for the shrinkage processes. Thus, as 0.15% wt. is added to the jet of cast iron and the inoculator contains successively 0%, 1.2%, and 2.4% wt. lanthanum, the thickness of the solid-hard crust of the cylindrical casting at the time when 50% of the cast iron melt mass is solidified amounts to 6 mm, 2 mm, and 0.5 mm, respectively, i.e. decreased 12 times [14]. A semi-solid cast zone contains more solids, which reduces the amount of liquid phase to compensate for the re-

Fig. 9. Powdered briquette-modifiers of various purposes for ladle and intramodal ways of production of CNG and CVG

sulting shrinkage. Lanthanum generates compounds that increase the intensity of nucleation in the liquid phase of the crystallizing CNG. For the CNGs obtained by treatment with magnesium-lanthanum-containing modifiers, the so-called bimodal or asymmetric distribution of SG inclusions is typical, with the number of small globules predominating in comparison with the number of large ones. Probably small globules are formed at the late stage of the SG formation; at the final stage of the crystallization cycle, when the late increase in the number of SG inclusions prevents further shrinkage [18].

We give some data on the composition and efficiency of industrial use of Mg-La containing modifiers. Foundry enterprises increase the use of magnesium-lanthanum-containing modifiers, in which cerium and other rare-earth metals are completely replaced by lanthanum. In particular, 100—150 ton FSMg5La modifier (5.2—6.0 Mg, 0.3—0.45 La, 0.4—0.6 Ca, 43—49 Si, 0.8—1.2 Al, the rest is Fe) [18] is produced at the Chelyabinsk Research Institute of Metallurgy. NIIM serially produces modifiers of two more brands [16]:

FeSiMg7La (5.8—6.4 Mg; 0.35—0.55 La; 0.4—0.6 Ca; 43—49 Si; 0.8—1.2 Al; the rest is Fe);

FeSiMg10La (5.5—6.2 Mg; 0.35—0.6 La; 0.8—1.2 Ca; 43—49 Si; 0.5—1.0 Al; the rest is Fe).

Other modifier grades are also produced in the form of ligatures containing Mg and La, using the mixture as purified from harmful impurities (As, Sb, Pb, Bi, Ti, S, P) as possible. By rapid quenching of the melt, self-shedding of casted modifiers is prevented during their storage and transportation.

According to consumers of *Lamet* spheroidizing modifier manufactured by *Elkem ASA*, Norway (5.0—6.0 Mg, 0.25—0.4 La, 0.4—0.6 Ca, 44—48 Si, 0.8—1.2 Al, the rest is Fe), the *Lamet* modifier has made it possible to significantly improve the cleanliness of the surface of cast crankshaft from the CNG and significantly reduced the laboriousness of the castings machining due to a reduction in the size of graphite globules [18]. Having replaced the FSMG5 master alloy (4.5—6.5 Mg, 0.7—1.2 rare-earth metal, 0.2—1.0 Ca, 45—55 Si, ≤1.2 Al) by *Lamet* master alloy, one foundry company decreased the average number of products with shrinkage defects from 18.92% to 1.27%, i.e. almost fifteen times. The cost of good casting has decreased by 14.2%, on average. The annual economic effect only due to reducing the cost of casting is estimated at EUR 2.2 million with the use of intra-mold modified 50 thousand tons of liquid iron [18].

So, the use of unsealed ladles with a lid-cup for the modification of cast iron melts in the production of castings from CNG and CVG, together with the use of magnesium-lanthanum-containing complex modifiers, with the complete elimination of other REMs, especially cerium, from them enables to significantly improve the technical and economic indices of the casting process.

The pressed powder briquettes are recommended as the most effective spheroidizers and vermicularizers for both the ladle and the in-mold production methods for CNG and CVG, which, in contrast to ligatures, are based not on the melting of the batch, but on the pressing of a mixture of powder components making up their composition. In comparison with the fractionated ligatures, the production of a ton powder briquette modifier requires 8—10 times less electricity, increases the assimilation of magnesium in the same brand by one order, eliminates dust formation and losses due to abandonment of crushing. The powder briquettes are easily adaptable to changing requirements and conditions of foundries.

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КОВШОВІ ТА ВНУТРІШНЬОФОРМОВІ СПОСОБИ МОДИФІКУВАННЯ ДЛЯ ОТРИМАННЯ ВИЛИВКІВ ІЗ ЧАВУНІВ З РІЗНОЮ МОРФОЛОГІЄЮ ГРАФІТУ

Вступ. У світовій практиці ливарного виробництва модифікування досягло статусу провідного напряму науково-дослідних та прикладних робіт з поліпшення технологічних і службових властивостей конструкційних чавунів.

Проблематика. Модифікуюча обробка рідких чавунів передбачає створення не тільки певних типів модифікаторів, а й розробку таких способів введення модифікатора в розплав, які адаптовані до умов ливарних цехів, а також враховують вимоги до конкретних груп виливків.

Мета. Розробка дослідної технології модифікування електропічних розплавів чавуну в негерметизованих поворотних ківшах і ливарних формах з використанням комплексних реагентів у вигляді пресованих порошкових брикетів і кускових плавлених лігатур для отримання виливків з пластинчастим, вермикулярним і кулястим графітом.

Матеріали й методи. Сірий чавун як об'єкт дослідження модифікуючої обробки, магній-лантанвміщуючі кускові та брикетовані порошкові модифікатори, а також азотовмісні кускові й брикетовані порошкові модифікатори для отримання чавунів з різною формою графіту залежно від вимог до виливків.

Результати. Розроблено дослідну ківшову технологію азотування чавунів з використанням пресованих порошкових азотвміщуючих брикетів, що дозволяє підвищити тимчасову розривну міцність сірих конструкційних чавунів вдвічі — з 200 МПа до 400 МПа, без легування й термічної обробки, а також розроблено ковшовий процес модифікування розплавів чавунів магній-лантанвміщуючими модифікаторами. Обґрунтовано перспективність виробництва азотованого чавуну з вермикулярним графітом з вмістом сірки до 0,1 % мас. шляхом переплавлення азотної металошихти, а також свіжих і поворотних чавунів, з мінімальним додатковим введенням азоту в піч, ківш чи ливарну форму.

Висновки. Пресовані порошкові модифікатори рекомендовано до використання як найбільш ефективні для вказаних способів модифікування залежно від вимог до виливків.

Ключові слова: ківшове, внутрішньоформове модифікування, магній-лантанвмісні та азотвмісні комплексні модифікатори.

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КОВШОВЫЕ И ВНУТРИФОРМОВЫЕ СПОСОБЫ МОДИФИЦИРОВАНИЯ ДЛЯ ПОЛУЧЕНИЯ ОТЛИВОК ИЗ ЧУГУНОВ С РАЗЛИЧНОЙ МОРФОЛОГИЕЙ ГРАФИТА

Введение. В мировой практике литейного производства модифицирование достигло статуса ведущего направления научно-исследовательских и прикладных работ по улучшению технологических и служебных свойств конструкционных чугунов.

Проблематика. Модифицирующая обработка жидких чугунов предусматривает создание не только определенных типов модификаторов, но и разработку таких способов ввода модификатора в расплав, которые адаптированы к условиям литейных цехов, а также учитывают требования к конкретным группам отливок.

Цель. Разработка опытной технологии модифицирования электропечных расплавов чугуна в негерметизированных поворотных ковшах и литейных формах с использованием комплексных реагентов в виде прессованных порошковых брикетов и кусковых плавленых лигатур для получения отливок с пластинчатым, вермикулярным и шаровидным графитом.

Материалы и методы. Серый чугун, как объект исследования модифицирующей обработки, магний-лантансодержащие кусковые и брикетированные порошковые модификаторы, а также азотсодержащие кусковые и брикетированные порошковые модификаторы для получения чугунов с различной формой графита, в зависимости от предъявляемых требований к отливкам.

Результаты. Разработана опытная ковшовая технология азотирования чугунов с использованием прессованных порошковых азотирующих брикетов, позволяющая повысить временную разрывную прочность серых конструкционных чугунов вдвое — с 200 МПа до 400 МПа, без легирования и термической обработки, а также разработан ковшовый процесс модифицирования расплавов чугунов лантансодержащими модификаторами. Обоснована перспективность производства азотированного чугуна с вермикулярным графитом с содержанием серы до 0.1 % масс. путем переплава азотистой металлошихты, а также свежих и возвратных чугунов, что минимизирует дополнительное введение азота в печь, ковш или литейную форму.

Выводы. Прессованные порошковые модификаторы рекомендованы к использованию как наиболее эффективные для указанных способов модифицирования в зависимости от требований к отливкам.

Ключевые слова: ковшовое, внутриформовое модифицирование, магний-лантансодержащие и азотсодержащие комплексные модификаторы.