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Vpliv različnih pokrivnih materialov za nodulacijo po »sandwich« metodi

Effect of Different Cover Materials for »Sandwich« Method

Povzetek

Glede na trenutno ekonomsko situacijo je vse večja potreba po finančno bolj učinkoviti proizvodnji duktilne litine. Članek prikazuje vpliv različnih kritnih materialov pri postopku krogličenja na delež končnega magnezija. Primerjava je bila narejena med jekleno kritno plastjo in kritno plastjo na osnovi ferosilija. Med preizkušanjem se je preučevala mikrostruktura, kemijska sestava in izdelala termična analiza.

Abstract

Based on the current economic situation, there is a need for more cost effective production of ductile iron. In this paper, the main objective was to research the influence of different cover materials in the process of spheroidization treatment on residual magnesium. The comparison was made between a steel cover and a ferrosilicon cover. During tests the samples were examined for metallographic analysis, chemistry and thermal analysis.

1 Uvod

Na obdelavo z magnezijem vplivajo številni različni parametri, ki so vsi zelo pomembni. Za obdelavo duktilne litine z magnezijem se uporabljajo različne vrste loncev in različni postopki. Prvi in najbolj preprost je postopek v odprtem loncu, pri katerem se predzlitina položi na dno lonca. Pri njem je izkoristek magnezija majhen. Drugi je postopek »sendvič«, ki predstavlja izboljšano tehniko. Lonec je izdelan tako, da ima na dnu žep za predzlitino. Da se zamakne začetek reakcije z magnezijem, se uporabljajo različni kritni materiali, navadno jeklo, ki se položijo na predzlitino. Naslednji postopek je postopek s potapljanjem, pri katerem se okrogli material potopi globoko v talino [1]. Postopek s pokritim vmesnim loncem izboljša izkoristek Mg, ker preprečuje dostop atmosferskega kisika v lonec in s tem v talino. Kadar krogličenje grafita v talini poteka v komori, ki je v kokili, se

1 Introduction

Magnesium treatment is influenced by many different parameters which all play an important part. For the magnesium treatment of ductile iron, there are different types of ladles and methods in use. First one and the simplest one is open ladle; here the master alloy is placed on the bottom of the ladle. This method has low recovery of Mg. The second method is sandwich which is an improved technique. The ladle design is different with the master alloy pocket on the bottom of the ladle. To delay the start of the Mg reaction, a cover material, usually steel, is put on top of the master alloy. Next is the plunging method where the spherical material is submerged deeply into the melt [1]. Tundish cover process improves Mg recoveries by disabling oxygen from atmosphere entering the ladle and thereby the melt. Where the spheroidization of the melt is done in a chamber placed in imenuje postopek v kokili. V zadnjih letih se je povečala uporaba procesa z jedrno žico, ki ima v jedru magnezij in se z dodajalno napravo vpihava v talino [2].

Drugi parametri, ki imajo vpliv na izkoristek magnezija so masa taline, masa in specifikacija FeSiMg, prebodna temperatura, delež O, S in oligoelementov, čas med obdelavo in začetkom ulivanja ter kritni material [3].

Namen modifikacije je kontrola mikrostrukture in lastnosti duktilne litine. To se doseže s čim manjšo podhladitvijo in povečanjem števila centrov za nukleacijo grafita med strjevanjem. Najpogostejši modifikatorji so danes na osnovi ferosilicija z majhnimi količinami elementov, kot so Ca, Al, Ba, Sr, Zr, Ce, Ti, Bi itn [4].

Oslabitev učinka modificiranja duktilne litine pomeni, da se s časom izgubi kroglasta oblika grafita [5]. Poslabšanje krogličavosti grafita je posledica predolgega časa držanja obdelane taline na temperaturi. Posledica je, da se grafit lahko pretvori v kompaktni ali celo luskasti grafit [6]. Mirnejša obdelava z Mg omogoča boljše razmere za nadaljnje modificiranje taline. Manjša reaktivnost pri obdelavi omogoča nastanek manjših in bolj razpršenih centrov nukleacije [7].

2 Poskusi

Poskuse smo bili naredili v podjetju Livar d.d. v Ivančni Gorici. Prispevek obravnava vpliv različnih kritnih materialov in različnih vrst loncev na preostanek Mg v duktilni litini. Proces obdelave smo ovrednotili z izkoristkom Mg, ko je bila uporabljena predzlitina FeSiMg7 in postopek »sendvič«. Prva vrsta kritnega materiala je bilo odpadno jeklo z dodatkom FeSi 75 %, da se je doseglo želeni končni delež Si. Masni delež kritne plasti je bil 2 %. Drugi kritni material je bil FeSi 50 %, njegov masni delež je bil 0,8

the mould is called an in-mould process. In recent years, the use of the core wire process has increased, where filled wire is injected into the liquid iron with the feeding machine [2].

Other different parameters that have an effect on the recovery of Mg are weight of melt, weight and specification of FeSiMg, tapping temperature, content of S, O and trace elements, time between treatment and beginning of pouring and covering material [3].

The purpose of inoculation is to control the microstructure and the properties of ductile iron. This is achieved by minimizing the undercooling and increasing the number of graphite nucleation events during solidification. The most common inoculants today are based on ferrosilicon with smaller amounts of elements, such as Ca, Al, Ba, Sr, Zr, Ce, Ti, Bi, etc [4].

The meaning of fade effect in ductile irons is the loss of nodularity of graphite with time [5]. Deterioration of spheroidal graphite is the result of holding time of treated metal and the graphite can convert to compact or even flake graphite [6]. A calmer Mg treatment provides better conditions for subsequent inoculation. Lower reactivity of the treatment provides more small and dispersed nucleus sites [7].

2 Experimental

The experiments were carried out in Livar d.d in Ivančna Gorica. In this paper, the influence of different types of cover materials and different types of ladles on residual Mg in ductile iron has been dealt with. Evaluation of treatment process is based on Mg recovery where master alloy FeSiMg7 and »sandwich« method was used. First type of cover material was scrap steel and FeSi 75 adding combined of 2%.

Razpredelnica 1. Kemijska sestava kritne plasti z FeSi 50%

Table 1. Chemical composition of FeSi 50% cover

Si [%]	Ba [%]	Ca [%]	Al [%]	Fe [%]
54,4	2	0,5	0,7	ostanek / the rest

%. Kemično sestavo kritne plasti z FeSi 50 % kaže razpredelnica 1.

Poskuse smo delali več dni. Razdeljeni so bili na tri dele. Najprej se je uporabil lonec tipa 1 z kritnim materialom iz jekla. Ta kombinacija je bila označena kot obdelava A. V drugi skupini poskusov je bil uporabljen lonec tipa 2 in z kritnim materialom jekla (obdelava B). Tretji del poskusov je potekal tudi v loncu tipa 2, kritni material je bil FeSi 50 % (obdelava C).

Razlika med loncema je v legi žepa za predzlitino. Prvi lonec je imel žep na dnu v sredini, drugi na dnu ob strani. Druga razlike med loncema je bila v površini žepa. Žep v drugem loncu je imel za 25 % manjšo površino in ustrezno večjo višino, da sta bili prostornini obeh žepov enaki.

Pri poskusih smo zasledovali končni delež Mg, temperaturo litja, število kroglic, krogličavost, naredili smo termično analizo, zabeležili čas preboda lonca, začetka in konca litja. Termično analizo smo izdelali s sistemom ATAS (adaptive thermal analysis system). Za metalografsko analizo smo obruse pripravili z brušenjem na karborundnih brusnih papirjih 240, 320, 400, 600 in zaključnim poliranjem z 3μm glinico.

3 Rezultati in razprava

Rezultati, prikazani v naslednjih razpredelnicah, predstavljajo povprečne vrednosti 10 vzorcev iste obdelave z Mg. Razpredelnica 2 prikazuje kemične analize preostalega Mg, izkoristek Mg, livno temperaturo, število kroglic in krogličavost.

FeSi 75% is added to achieve desired end content of Si. Second cover material was FeSi 50% cover in addition of 0.8%. Chemical composition of this material is presented in table 1.

The tests were carried out in several days. They were divided in three parts. First, ladle type 1 with cover material steel was used - this combination will be referred to as (A). Second trials were conducted with ladle type 2 also with steel cover material (B) and the third part of testing was done with ladle type 2 with FeSi 50% cover material (C).

The difference between the ladles is in position of the master alloy pocket. First ladle has a pocket positioned on the bottom in the center, second has the pocket positioned on the bottom side. The other difference between the two of them is the surface area of the pocket. Pocket in second ladle has 25% smaller surface and its height is in proportion so that the volumes of the two are equal.

During experiments we monitored final Mg, pouring temperature, nodule count, nodularity, thermal analysis, tapping time, start of pouring and finish of pouring. Thermal analysis was done with ATAS (adaptive thermal analysis system). For metallographic analysis, the samples were prepared on SiC grinding paper 240, 320, 400, 600 grid and then polished with Al_2O_3 3 μm.

3 Results and Discussion

The results in following tables present average values of 10 samples for each type

V loncu tipa 1 s kritnim jeklom (obdelava A) je bil odstotek izkoriščenega Mg podoben kot v loncu tipa 2 s kritnim jeklom (obdelava B), okoli 62–63 %, kljub 12 °C nižji temperaturi litja. Izkoristek Mg v loncu tipa 2 s kritnim materialom iz FeSi (obdelava C) je bil za 4 % večji kljub celo za 9 °C višji temperaturi litja, kar je bila posledica prisotnega Ca. Število kroglic in krogličavost sta bili najvišji v loncu tipa 2 s kritnim materialom FeSi zaradi mirnejše reakcije z Mg in prisotnosti Ba, ki je deloval kot modifikator. Manjše število kroglic in slabšo krogličavost pri obdelavi A povezujemo z burno reakcijo z magnezijem, kar je zmanjšalo število nukleacijskih centrov.

Želena je višja stopnja grafitizacije, ker to pomeni večje število kroglic. Razpredelnica 3 prikazuje rezultate termične analize, ki kaže, da je GRF 1 višji pri kritni plasti iz FeSi, kar ima za posledico večje število kroglic. To je potrdila tudi metalografska analiza.

Rekalescenca, ki nakazuje začetni čas rasti evtektika, je bila najnižja pri obdelavi C zaradi prisotnosti Ba v kritni plasti iz FeSi. Rezultati v razpredelnici 3 kažejo za 3 °C nižjo temperaturo evtektika, TElow, pri obdelavi A zaradi večjega dodatka predzlitine in nižje višine taline pred začetkom reakcije, zato

of Mg treatment process. Table 2 presents chemical analysis of residual Mg, recovery of Mg, pouring temperature, nodule count and nodularity.

Ladle type 1 with steel cover (A) has similar percentages of recovery Mg as the ladle type 2 with steel cover (B), around 62 - 63%, despite of 12 K lower pouring temperature. Recovery of Mg in ladle type 2 and with FeSi cover material (C) is higher by 4% despite even higher pouring temperature of 9 K due to content of Ca. Number of nodules and nodularity was highest in ladle type 2 and FeSi cover material due to calmer reaction with Mg and content of Ba which influences as inoculant. Reduced nodule count and nodularity was detected with process A linked to violent reaction with magnesium and with that the decrease of nucleus sites.

Higher graphitization factor is preferred which results in higher nodule count. Table 3 presents thermal analysis where we can see that GRF 1 is higher with FeSi cover which results in higher nodule count that is confirmed with metallographic analysis.

The recalescence which indicates the initial time of growth of eutectic is lowest in treatment type C because of presence of Ba in FeSi cover. Results from table 3 show

Razpredelnica 2. Povprečne vrednosti izkoristka Mg, temperature litja, število kroglic in krogličavost

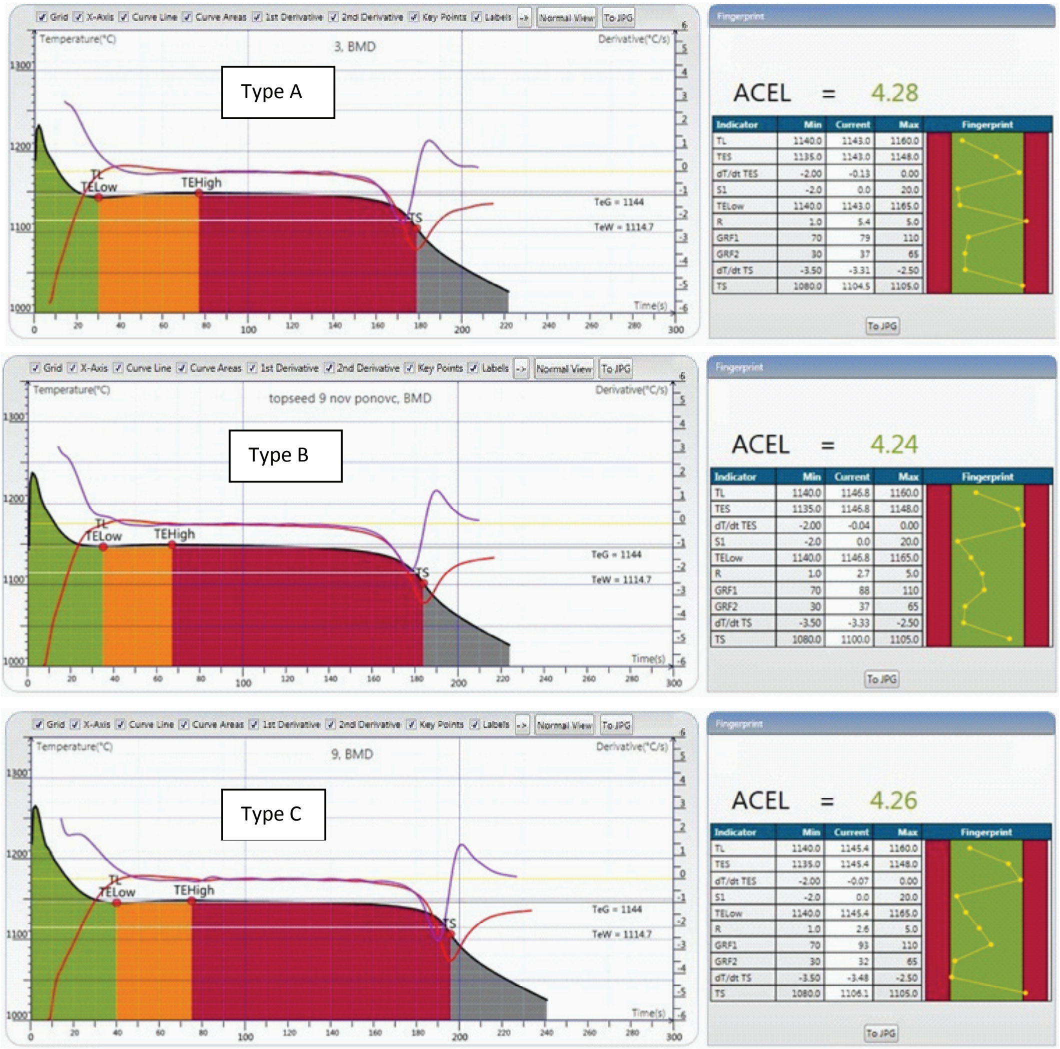
Table 2. Average values of recovery of Mg, pouring temperature, nodule count and nodularity

poskusi in kritni material / Type of ladle and cover material	končni Mg (mas. [%]) / Final Mg (mass fraction [%])	izkoristek Mg / Recovery of Mg [%]	T litja / T pouring [°C]	Število kroglic [število/mm^2] / nodule count [number/mm^2]	nodularnost / nodularity [%]
Povprečje poskusov A / Average type A	0,037	62	1361	230	89
Povprečje poskusov B / Average type B	0,036	63	1373	306	94
Povprečje poskusov C / Average type C	0,037	67	1382	335	96

Razpredelnica 3. Termična analiza: TElow, rekalescenca in GRF 1

Table 3. Thermal analysis: TElow, Recalescence and GRF 1

Vrsta obdelave in kritnega materiala / Type of ladle and cover material	TElow [°C]	R [°C]	GRF_1
Povprečje, vrsta A / Average type A	1141	4,7	71,1
Povprečje, vrsta B /Average type B	1144	4,3	79,6
Povprečje, vrsta C /Average type C	1144	2,6	85,9



Slika 1. Krivulje termične analize za vse tri vrste obdelav

Figure 1. Experimental thermal curves of all three types of treatments

je bila reakcija burnejša. Višja podhladitev pomeni časovno zamaknjen začetek evtektične reakcije in večji delež izločenega avstenita. Pri prvem tipu lonca s kritnim jeklom je bil GRF1 najnižji in pri drugem tipu lonca s kritno plastjo FeSi najvišji, kar ima za posledico število kroglic. Pri obdelavi (A) je bilo povprečno 230 kroglic/mm^2 in pri obdelavi C 335 kroglic/mm^2. Rezultate termične analize kaže slika 1 za vse tri vrste obdelav.

Razpredelnica 4 kaže povprečne izmerjene čase trajanja izpuščanja taline v lonec, začetek in konec litja v kokile. Časi izpuščanja taline so bili pri poskusih A daljši zaradi zgodnejšega začetka reakcije in burnejše reakcije z magnezijem, kar je imelo za posledico manj preostalega magnezija, čeprav je bil čas litja najkrajši. Višina taline naj bo čim višja ob začetku poteka reakcije z Mg. Kljub hitrejšemu izpuščanju taline pri obdelavi B, ko je po litju začela potekati reakcija po vsem loncu, je bil izkoristek Mg manjši kot pri obdelavi C, pri kateri je bila reakcija mirnejša zaradi prisotnosti Ca v kritni plasti iz FeSi.

4 Sklepi

- Izkoristek Mg v povezavi s temperaturo litja je bil pri obdelavi:
    - o obdelava A: Tlitja = 1361°C 62%,

lower eutectic temperature TElow of 3K in treatment type A as a result of more addition of master alloy and lower height of the melt before the start of the reaction therefore more violent reaction. Higher undercooling means delayed eutectic start and with that more austenite precipitation. First type of ladle with steel cover has the lowest GRF 1 and the second type of ladle with FeSi cover has the highest which results in nodule count, type A has average 230 nod/mm^2 and type C has 335 nod/mm^2. The results of thermal analysis are presented in Fig.1. of all three type of treatments done at this experiment.

In table 4 we can see average measured times of tapping of the melt into the ladle, start of pouring into the moulds and the finish times of pouring. Tapping time of experiment type A is longer due to an earlier start of the reaction and violent reaction of magnesium which results in lower residual magnesium although the pouring time was the shortest. Height of the melt is better to be as high as possible at the beginning of start of reaction with Mg. In spite of faster tapping time done with treatment type B where the reaction started after pouring all of the melt into the treatment ladle, the recovery of magnesium is lower than with treatment type C where the reaction was calmer because of content of Ca in FeSi cover material.

Razpredelnica 4. Trajanje izpuščanja taline, začetek in konec litja

Table 4. Tapping time, Start of pouring, Finish time

Obdelava in kritni material / Type of ladle and cover material	Trajanje izpuščanja taline / Tapping time [min/s]	Začetek litja / Start of pouring [min/s]	Konec litja / Finish of pouring [min/s]
Povprečje, obdelava A / Average type A	1:14	3:41	6:00
Povprečje, obdelava B / Average type B	0:50	4:34	7:23
Povprečje, obdelava C / Average type C	0:56	4:16	7:28

  - o obdelava B: Tlitja = 1373°C 63%
  - o obdelava C: Tlitja = 1382°C 67%.
- Pri drugem tipu konstrukcije lonca sta manjša površina žepa in večja višina kritne plasti povzročila zakasnitev reakcije z Mg.
- Izkoristek Mg 67 % je bil najvišji pri obdelavi C zaradi Ca v kritni plasti iz FeSi, čeprav je bila takrat temperatura izpuščene taline najvišja. Boljši izkoristek Mg smo tudi opazili pri obdelavi B zaradi naknadne reakcije po izpustu taline, kar je bila posledica večje višine taline nad reakcijsko komoro.
- Število kroglic 230 kroglic/mm^2 je bilo najmanjše pri obdelavi A zaradi vpliva burne reakcije z Mg. Najvišjo vrednost 335 kroglic/mm^2 smo ugotovili pri metalografski analizi taline po obdelavi C, kjer je bil kritni material FeSi, kar je potrdila še termična analiza, pri kateri je imel GRF 1 najvišjo vrednost 85,9 zaradi Ba, ki je vplival kot modifikator. To je povzročilo višjo krogličavost in manjše kroglice.
- Višji TElow, ki je bil 1144 °C, smo opazili pri obdelavah B in C, kar je imelo za posledico zmanjšano nevarnost za makro krčenje.

4 Conclusions

- Recovery of Mg in conjunction with pouring temperature was with treatment:
  - o type A Tpouring = 1361°C 62%,
  - o type B Tpouring = 1373°C 63%
  - o type C Tpouring = 1382°C 67%.
- At second design of ladle smaller surface of the pocket and higher height of the cover material delays the reaction with Mg.
- Yield of Mg 67% is highest with treatment type C as a result of content of Ca in FeSi cover although the highest tapping temperature. Better recovery of Mg is also seen with treatment type B due to subsequent reaction after tapping of the melt which is the result of higher melt height above reaction chamber.
- Nodule count 230 nod/mm^2 is lowest in treatment type A as influence of violent reaction with Mg. Highest nodule 335 nod/mm^2 count was observed at metallographic analysis with treatment type C with FeSi cover material which was confirmed with thermo analysis where factor GRF 1 was the highest at 85,9 due to content of Ba which influences as inoculant. That results in higher nodularity and smaller nodules.
- Higher TElow 1144°C was observed with treatments type B and C which results in decreasing the risk of macro shrinkage.

5 Viri / References

[1] Ghosh, S.,2008, Production aspects of spheroidal graphite iron, CAFP Special Metal casting and Forming Processes, pp. 38-51
[2] Skaland, T., Ductile iron production – A comparison of alternative treatment methods, Elkem ASA, Norway
[3] Cobanne, Pierre-Marie,July 2008, The Efficiency of your Magnesium Treatment Varies: Check the following points!, Rio Tinto Iron & Titanium,
[4] R., Elliott, Cast Iron Technology, 1988, London, UK Betterworths
[5] Goldrich, George M., 1992, Ductile Iron Handbook,pp 233
[6] Huerta, E., Popovski, V., 2005, A Study of Hold Time, Fade Effects and Microstructure in Ductile Iron, Proceedings of the AFS Cast Iron Inoculation Conference, Illinois , pp 43-55
[7] Skaland, T., 1992,"Fading of Inoculant in Cast Iron", Casting Congress, Czechoslovakia