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Vpliv niklja in kobalta na mikrostrukturo duktilne litine, utrjene s trdno raztopino silicija

Influence of Nickel and Cobalt on the Microstructure of Silicon Solution- strengthened Ductile Iron

Izvleček

Zaradi ugodne kombinacije livnosti, mehanskih lastnosti, strojne obdelovalnosti in sorazmerno majhne cene se je proizvodnja železove litine s kroglastim grafitom, imenovana duktilna litina (DI), od leta 2009 do 2012 povečala v Nemčiji za 35 %, na 1,6 milijona ton letno. Izboljšane mehanske lastnosti bodo še izboljšale njen položaj materiala z dobrimi uporabnimi lastnostmi pri izpolnjevanju prihodnjih zahtev v tekmi z varjenimi konstrukcijami in izkovki. Mehanske lastnosti standardne duktilne litine v litem stanju so predvsem posledica razmerja med feritom in perlitom v mikrostrukturi, na kar vplivajo zlitinski elementi. Popolnoma feritna duktilna litina ima največjo duktilnost in najmanjšo trdnost. S povečanjem deleža perlita se povečuje natezna trdnost ob velikem zmanjšanju raztezka pri zlomu. V nasprotju s tem ima »druga generacija« duktilne litine z deležem silicija do 4,3 % popolnoma feritno osnovo, ki je raztopinsko utrjena s substitucijsko raztopljenim silicijem. Dobljene raztopinsko utrjene vrste litine, kot so EN-GJS- 450-18, EN-GJS-500-14 in EN-GJS-600-10, imajo izvrstno kombinacijo trdnosti, duktilnosti in zelo dobro strojno obdelovalnost zaradi popolnoma feritne osnove [Bjorkegren, L.E., K. Hamberg, Keith Millis Symposium on Ductile Cast Iron, 2003]. Poleg tega velik delež silicija dopušča prisotnost večjih količin karbidotvornih elementov, kot so vanadij, krom in titan [Löblich, final report of AIF Project 41EN, 2012]. Vendar je največja trdnost omejena na 600 MPa pri deležu silicija 4,3 %. Pri večjem deležu silicija se natezna trdnost in raztezek pri zlomu drastično zmanjšata zaradi predpostavljenega nastanka urejene silicijeve strukture dolgega reda. [Löblich, final report of AiF Project 41EN, 2012]. Podatki za učinek nadaljnjih elementov, ki omogočajo raztopinsko utrjevanje popolnoma feritne duktilne litine, se komaj kje najdejo v objavljeni literaturi. Da bi zapolnili to praznino pri raziskavah, smo v naši raziskavi feritno duktilno litino z masnima deležema silicija 3,8 % in 4,3 % legirali z 2 mas. % in 4 mas. % kobalta ter 1,5 mas. % in 3 mas. % niklja. Glede na popolnoma faktorsko zasnovo poskusov smo učinke kobalta in niklja ovrednotili s termično in mikrostrukturno analizo in poskusi natezne trdnosti. Poleg tega smo te rezultate statistično potrdili z analizo varianc. Ta prispevek prikazuje rezultate mikrostrukturnih analiz.

Abstract

Due to its favourable combination of castability, mechanical properties, machinability and a comparatively low price, the production volume of cast iron with spheroidal graphite, so called ductile iron (DI), increased in Germany between 2009 and 2012 by 35 % to 1.6 million tons per year. Improving the mechanical properties of DI will help to strengthen its position as a high-performance-material, to fulfill future requirements and to withstand the competition to welded constructions and forgings. The as-cast mechanical properties of conventional ductile irons are mainly adjusted by the ferrite and pearlite ratio of its microstructure, which is influenced by alloying. A fully ferritic ductile iron exhibits the highest ductility and lowest strength. By increasing the pearlite content the tensile strength is increased accompanied by a strong reduction of the elongation at fracture. In contrast to this, "Second Generation" DI with a silicon content of up to 4.3 % (mass fraction) exhibits a fully ferritic matrix, which is solution-strengthened by the substitutionally solved silicon. The resulting solution-strengthened grades like the EN-GJS-450-18, the EN-GJS-500-14 and the EN- GJS-600-10 offer superior combinations of strength, ductility and excellent machinability due to a fully ferritic matrix [Bjorkegren, L.E., K. Hamberg, Keith Millis Symposium on Ductile Cast Iron, 2003]. In addition a high silicon content leads to a higher tolerance against higher amounts of carbide-forming elements like e.g. vanadium, chrome and titanium [Löblich, final report of AIF Project 41EN, 2012]. However, the maximum strength is limited to 600 MPa at a silicon mass fraction of 4.3 %. At higher silicon contents the tensile strength as well as elongation at fracture are dramatically decreased due to the presumed formation of a silicon long range order [Löblich, final report of AiF Project 41EN, 2012]. The effect of additional solution strengthening elements on fully ferritic ductile iron is hardly addressed in literature. In order to close this current research gap, ferritic DI with a silicon content of 3.8 and 4.3 % Si were alloyed with 2 and 4 % Co and 1.5 and 3 % Ni in the present study. According to a full factorial experimental design, the effects of cobalt and nickel were evaluated with the aid of thermal and microstructural analysis and tensile tests. Further, these results were statistically proofed using analysis of variances. In this article the results of the microstructural analyses are presented.

1 Uvod

Zaradi dobre livnosti, duktilnosti, velike natezne trdnosti, korozijske in obrabne odpornosti, razmerja med uporabnostjo in ceno ter vsestranskosti je duktilna litina eden od najbolj uporabljenih litih materialov v svetu [1-4]. Npr. največ delov sodobnih vetrnih turbin, kot so pesta rotorja, cevni adapterji, glavni okvirji in osi, so narejeni iz duktilne litine [5]. Drugi primeri sedanje industrijske uporabe duktilne litine so varnostni deli avtomobilov, kot so členki krmila, okvirji kolutne zavore, naprave za skladiščenje in transport jedrskih odpadkov, cevi za svežo in odpadno vodo, črpalke in kroglasti ventili za delo v korozijskih medijih, strojni deli za poljedelstvo, rudarstvo, vojno industrijo in železnice [2,3,6].

Izvrstne lastnosti duktilne litine določa njena mikrostruktura, ki je v odvisnosti od

1 Introduction

Due to its good castability, ductility, high tensile strength, corrosion and wear resistance, performance to cost ratio and versatility ductile iron (DI) is one of the most used casting materials worldwide [1-4]. For example, most parts of modern wind turbine components, such as rotor hubs, tubular adapters, main frames and axles, are produced from DI [5]. Other examples of DI's actual applications are safety components of cars, such as steering knuckles and calipers, storing and transportation devices for nuclear waste, tubes for fresh and wastewater, pumps and globe valves operating with corrosive media, agricultural, mining, military, and railroad components [2, 3, 6].

DI's excellent properties are determined by its microstructure, which kemične sestave zlitine, hitrosti ohlajevanja, načina cepljenja med strjevanjem sestavljena iz jeklu podobne osnove (ferit, perlit, bainit, poboljšani bainit, martenzit ali kombinacija teh mikrostrukturnih sestavin) ter grafitnih kroglic v tej osnovi [1,2,5,7]. Perlitna osnova daje duktilni litini visoko trdnost, a je litina krhka, medtem ko je navadna feritna duktilna litina mehka in duktilna, a ima povprečno trdnost, medtem ko ima mešanica ferita in perlita ima vmesne lastnosti [5].

Poleg tega so mehanske lastnosti duktilne litine odvisne od števila, velikosti in oblike grafitnih kroglic. Med evtektičnim strjevanjem je najprej potrebno minimalno število kroglic v talini, da se zavre nastajanje karbidov in krčilnih razpok, ki bi poslabšale mehanske lastnosti; karbidi dodatno tudi poslabšajo strojno obdelovalnost ulitka.

Po objavljeni literaturi [8] je število kroglic manjše od 60 na mm^2 nezadostno za preprečitev nastanka krčilnih razpok in/ali karbidov. Največje število kroglic še ni določeno, ker je lahko močno odvisno od kemične sestave litine in debeline stene ulitka [8]. Vendar število kroglic ne vpliva le na nastanek krčilnih razpok, ampak tudi na delež ferita oz. perlita v osnovi, kar tudi vpliva na mehanske lastnosti [7-9]. Čim večje je število kroglic, tem večji je delež ferita, ker termodinamično stabilna faza nastaja z difuzijo ogljika iz avstenita v prisotni grafit med evtektoidno reakcijo. Čim manjša je difuzija ogljika v grafit zaradi velikega števila kroglic, tem večja je možnost nastanka ferita. Poleg vpliva na samo mikrostrukturo število kroglic neposredno vpliva tudi na mehanske lastnosti duktilne litine. Večje število kroglic namreč omogoča večjo trajno nihajno trdnost in mejo vzdržljivosti [10].

Večje število kroglic ima za posledico tudi manjšo povprečno velikost teh kroglic, ker sta ta dva grafitna parametra obratno sorazmerna [3]. Neodvisno od

consists, depending on the alloy’s chemical composition, cooling rate and inoculation condition during solidification, of a steel-like matrix (ferrite, pearlite, bainite, ausferrite, martensite, or a mixture of these), and embedded graphite nodules [1, 2, 5, 7]. A pearlitic matrix leads to high strength but comparatively brittle DI, conventional ferritic DI is normally soft and ductile but shows an average tensile strength; a mixture of ferrite and pearlite leads to intermediate mechanical properties [5].

Besides the influence of the matrix, the DI’s mechanical properties are influenced by the number, size and shape of the present graphite nodules. First, during eutectic solidification a minimum number of graphite nodules is required in the melt to suppress the formation of carbides and microshrinkage, which lead to decreased mechanical properties; carbides additionally decrease the casting’s machinability. According to [8] a nodule count smaller than 60 noduls/mm^2 is insufficient to avoid microshrinkage and/or microcarbides. A suggested maximum nodule count is not yet established since it may depend strongly on the DI’s chemical composition and the casting’s wall thickness [8]. In addition to the carbide and microshrinkage formation the number of nodules influences the ferrite/pearlite content of the matrix also affecting the mechanical properties [7-9]. The higher the number of nodules the higher is the amount of ferrite, since this thermodynamically stable phase is formed by diffusion of carbon from austenite to the present graphite during the eutectoid reaction. The smaller the carbon’s diffusion way to the graphite due to a high number of nodules, the higher is the possibility of the formation of ferrite. Besides the influence on the microstructure itself the number of nodules directly influences the mechanical properties of DI. For example, a higher mikrostrukture osnove se življenjska doba zaradi utrujenosti pri kotalnem stiku (RCF - rolling contact fatigue) in duktilnost močno povečata z zmanjšanjem števila kroglic [11]. Poleg tega je večje število kroglic povezano z manjšim mikroizcejanjem zlitinskih elementov, kar vpliva na nastajanje krhkih delov in karbidov v mikrostrukturi.

Manjše kroglice so tudi bolj želene, ker imajo bolj kroglasto obliko. Ta oblika vpliva na napetost tečenja, natezno trdnost, raztezek pri zlomu in žilavost pri zlomu [4, 12-15]. Predvsem velika žilavost duktilne litine in dobra odpornost proti napredovanju razpok sta predvsem posledica nenavadnih oblik grafitnih sestavin [13]. Med nateznim obremenjevanjem malo nad napetostjo tečenja se kroglice navadno ločijo od osnove. Z večanjem obremenitve se praznine, ki vsebujejo grafitne kroglice, večajo in združujejo. Ko je dosežen določen prostorninski delež, postane to trganje nestabilno, kar vodi do zloma strojnega dela. Čim več praznin odstopa od okrogle oblike, tem hitrejše je njihovo večanje, kar je povezano z zmanjšanjem duktilnosti kot pri majhnem številu kroglic [12]. Vpliv perlita na učinek grafitnih kroglic se lahko zanemari, dokler njihov delež ne preseže 10 % [5,16].

V preteklih letih so postale nove popolnoma feritne duktilne litine, ki so bile cenovno ugodne in dobro raztopinsko utrjene s silicijem v območju 3 do 4,3 mas. % Si, vse bolj priljubljene [17]. Mehanske lastnosti kot tudi toplotna odpornost in odpornost proti vremenskim vplivom teh s silicijem raztopinsko utrjenih vrst feritnih duktilnih litin (SSF DI - solution strengthened ductile iron) so enake ali celo boljše od lastnosti standardnih duktilnih litin. Prenos litin SSF DI v proizvodnjo je pomenil prihranek stroškov do 10 %, ker so se zmanjšali stroški strojne obdelave litin zaradi mehke feritne osnove in večjih dopustnih toleranc pri konstrukcijah kot

nodule count leads to a higher fatigue strength and endurance limit [10].

A high number of nodules lead to a smaller average nodule size, since both graphite parameters behave inversely proportional [3]. Independent of the matrix structure the RCF life and ductility are strongly increased with a decreased nodule size [11]. Furthermore, a higher amount of small nodules is accompanied by a smaller alloying elements' microsegregation, which influences the formation of brittle parts and carbides in the microstructure.

Besides this, smaller nodules are favoured since these exhibit a more spherical shape. This shape influences the yield strength, tensile strength, elongation at fracture and fracture toughness [4, 12-15]. In particular the DI's high toughness and good crack propagation resistance are mainly due to the peculiar graphite elements shape [13]. During tensile loading slightly above the yield stress the nodules normally debond from the matrix. With increasing load the voids, containing the graphite nodules, grow and coalesce. After a certain volume fraction is reached this tearing becomes unstable leading to the component's failure. The more the voids deviate from the spherical shape, the faster is the growth of the void, which is in line with the reduction in ductility for low nodularity [12]. The influence of pearlite on the effect of the graphite nodules can be neglected if its ratio does not exceed 10 % [5, 16].

In the past years, new full ferritic DI grades were getting more and more popular, which are cost-efficient and effectively solution strengthened by a silicon content in a range of 3 to 4.3 % [17]. The mechanical properties as well as thermal and weather-resistance of these silicon solid solution strengthened full ferritic DI grades (SSF DI) are equal to better than these properties of the conventional DI grades. Transferring posledica višje napetosti tečenja in raztezka pri prelomu. Leta 2012 so bile litine SSF DI (EN-GJS-450-18, EN-GJS-500-14 in EN-GJS-600-10) standardizirane v standardu DIN EN 1563, kar je omogočilo prikazati njihovo mnogo boljšo duktilnost ob enaki trdnosti, kot jo imajo feritno-perlitne litine. Za njihovo izdelavo se priporočajo predvsem deleži silicija 3,2 mas. %, 3,8 mas. % in 4,3 mas. [17-22].

Vendar so zaradi velikega deleža silicija največja trdnost in udarna žilavost litin SSF DI kot tudi livne lastnosti omejene [8,20,23-27]. Dodatno je pri zlitini EN- GJS-600-10, izdelani kot raztopinsko utrjeni s trdno raztopino silicija, predviden delež silicija 4,3 %. Ker delež silicija 4,4 mas. % vodi do dramatičnega zmanjšanja tako natezne trdnosti kot duktilnosti [23], je procesno okno za izdelavo zlitine EN-GJS-600-10 zelo majhno. Najmanjši raztros deleža silicija v talini, npr. zaradi raztrosa deleža silicija v cepivu ali cepivu za litino s kroglastim grafitom kot posledica nenatančnih meritev, lahko pripelje do popolne porušitve ulitka.

Za dodatno optimiranje lastnosti izvrstnih novih duktilnih litin in zagotavljanja njihove široke uporabe, je uporaba elementov za raztopinsko utrjevanje perspektivna. Kaže, da imata kobalt in nikelj prednosti, da se z dodatnim raztopinskim utrjevanjem izdelajo litine z večjimi nateznimi trdnostmi ob dobri duktilnosti ali da se določena količina silicija nadomesti, pri čemer se ohranijo enake izvrstne lastnosti materiala, a se poveča procesna zanesljivost.

Nikelj ima dobro topnost v feritu in omogoča dobro utrjevanje s trdno raztopino glede na atomsko razmerje z železom [28]. Ker nikelj pospešuje grafitizacijo med evtektičnim strjevanjem, ne bo imel škodljivega učinka na evtektično strjevanje in na nastajanje grafitnih kroglic [2].

Kobalt ima podoben atomski polmer kot železo, zato se na prvi pogled zdi, da

SSF DI into the production scale resulted in a cost safety of up to 10 % due to decreased machining costs, related to the soft ferritic matrix, and construction tolerances, related to a higher yield strength and elongation at fracture of SSF DI. In 2012 the SSF DI grades EN-GJS-450-18, EN-GJS-500-14 and EN-GJS-600-10 were implemented in the DIN EN 1563, which exhibit a much higher ductility at the same strength than the conventional ferritic/pearlitic grades. For their realization, a silicon content of 3.2 %, 3.8 % and 4.3 % is suggested, in particular [17-22].

However, due to the high silicon content the SSF DI's maximum and impact strength as well as casting properties are limited [8, 20, 23-27]. In addition, the EN-GJS-600-10, realized by a silicon solid solution strengthening, envisages a silicon content of 4.3 %. Since a silicon content of 4.4 % leads to a dramatically decrease of both, the tensile strength and ductility [23], the process window for the production of an EN-GJS-600-10 can be defined as very small. A minimal scatter of the silicon content in melt, e.g. by a scatter of the silicon content in the nodularizer, in the inoculation agent or due to an imprecise measuring, can lead to a complete failure of the casting.

To further optimize the properties of the outstanding new ferritic DI grades and to ensure their widespread application the use of other solid solution strengthening elements is promising. Nickel and cobalt seem to be advantageous for further solid solution hardening to realize higher tensile strength grades with good ductility or to substitute some amounts of silicon with the same excellent material properties at the same time with an increased process safety.

Nickel exhibits a high solubility in ferrite and achieves a high solid solution strengthening per atom ratio [28]. Since ni dovolj dobro sredstvo za utrjevanje s trdno raztopino [28]. Vendar ga njegova navidezno neomejena topnost [28] in grafitizacijski učinek med evtektično in evtektoidno reakcijo delata zanimivega za optimizacijo litine SSF DI.

Vpliv niklja in kobalta na mehanske in mikrostrukturne lastnosti, predvsem na grafitno fazo, je najbolj poznan pri standardnih popolnoma feritnih duktilnih litinah. Z dodatkom 1 mas. % Ni se temperatura prehoda iz duktilnega v krhko stanje poviša za 10 oC, s tem pa se izboljša udarna trdnost materiala pri nizkih temperaturah [29]. Majhne količine niklja premaknejo pri železovi litini krivuljo v diagramu čas - transformacija k višjim časom, kar pripelje do povečanja natezne trdnosti zaradi raztopinskega utrjevanja ferita [2, 30]. Med strjevanjem nikelj zmanjša stabilnost evtektičnega karbida [2], poveča število grafitnih kroglic, zmanjša velikost kroglic in udrobni feritna zrna [31,32].

V literaturi obstajajo različne trditve o vplivu kobalta na krogličavost grafita. Poroča se, da dodatek kobalta zmanjša [2] krogličavost, kot da jo tudi poveča [33,34]. Z dodatkom kobalta se število kroglic povečuje in njihova velikost zmanjšuje. Zaradi raztopinskega utrjevanja ferita celo pri dodatku 2 mas. % Co, se napetost tečenja in natezna napetost povečata ob sočasnem zmernem zmanjšanju raztezka ob zlomu [2, 33,35]. Pri 6 do 9 mas. % Co se dosežejo največja napetost tečenja, raztezek in udarna žilavost ter občutno poveča hitrost grafitizacije [34,35]. Višji deleži silicija povečajo udrobnilni učinek kobalta na grafitne kroglice [34]. Do 0,55 mas. % ni vpliva kobalta [35]. Kar se tiče udarne žilavosti feritne duktilne litine, kobalt povečuje temperaturo prehoda iz duktilnega v krhko stanje in zmanjšuje udarno žilavost [33,34].

nickel supports the graphitization during the eutectic solidification it will not be harmful regarding the eutectic solidification and nodule formation [2].

Cobalt exhibits a similar atom radius compared to iron thus making it at first glance an insufficient solid solution hardener [28]. However, its quasi unlimited solubility [28] and graphitizing effect during the eutectic and eutectoid reaction makes it an attractive element for the optimization of SSF DI.

The influence of nickel and cobalt on the mechanical and microstructural properties, in particular the graphite phase, of conventional fully ferritic DI is mostly known. With 1% Ni, the ductile to brittle transition temperature is increased by 10 K and the material's impact toughness at low temperature is improved [29]. Small nickel amounts move the curve of the cast iron's time transformation diagram to higher time intervals and lead to an increased tensile strength due to solid solution strengthening of the ferrite [2, 30]. During solidification, nickel decreases the eutectic carbide stability [2], increases the nodule count, decreases the nodules' size and refines the ferrite grains [31, 32].

According to the cobalt's influence on the graphite nodularity there are different statements in literature. Besides a decrease of nodularity [2] also an increase of the nodularity by a cobalt addition is reported [33, 34]. With the addition of cobalt the nodule count is increased and the nodule size is decreased. Due to a solid solution strengthening of the ferrite, even at an addition of 2% Co, the yield and tensile strength are increased accompanied with a moderate decrease of the elongation at fracture [2, 33, 35]. 6 to 9% Co achieve the maximum yield strength, elongation and impact value and a marked increase in the graphitization rate [34, 35]. Higher silicon contents increase the nodule refining

Kljub temu, da sta nikelj in kobalt obetavna elementa za nadaljnje povečanje raztopinskega utrjevanja ali za zamenjavo silicija v litini SSF DI, je njun vpliv na mikrostrukturo popolnoma feritne, raztopinsko utrjene duktilne litine neznan. Da bi zapolnili to sedanjo raziskovalno praznino, smo v tekoči raziskavi dve duktilni litini, EN-GJS-500-14 in EN-GJS-600-10, ločeno legirali z nikljem in kobaltom po popolni faktorski zasnovi poskusov. Ulili smo klinaste vzorce vrste II in IV glede na standard DIN EN 1564 ter s svetlobnim mikroskopom preiskali učinke niklja in kobalta na mikrostrukturo duktilne litine.

2 Metode in materiali

2.1 Zasnova poskusov

V naši sedanji raziskavi smo litini, ki je imela sestavo blizu evtektične, EN-GJS- 500-14 (3,8 mas. % Si) in EN-GJS-600-10 (4,4 mas. % Si), legirali v prvi seriji poskusov z dvema različnima količinama kobalta in v drugi seriji poskusov z dvema različnima količinama niklja glede na popolno faktorsko zasnovo poskusov. Da bi se pokazalo lastnosti določene osnovne GLS-litine, sta obe seriji vsebovali tudi parameter, ko ni bilo dodanih zlitinskih elementov. Da bi izključili sistematično napako spremenljivk, so bile zasnove poskusov poljubno razporejene (razpredelnici 1 in 2). Za statistično ovrednotenje merjenih rezultatov je bila vsaka postavitev parametra ponovljena trikrat, kar je v celoti zahtevalo 36 talin.

Največji delež kobalta je bil nastavljen na 4 mas. %, ker literatura [34] navaja zmanjšanje napetosti tečenja pri tem deležu kobalta. Srednji delež kobalta je bil nastavljen na 2 mas. %, ko se pojavi prvi učinek raztopinskega utrjevanja pri klasični feritni duktilni litini.

effect of cobalt [34]. Up to 0.55 %, there is no influence of cobalt [35]. Concerning the impact toughness of ferritic ductile iron cobalt increases the ductile to brittle transformation temperature and decreases the impact toughness [33, 34].

However, although nickel and cobalt are promising elements for further solid solution strengthening or substitution of silicon in SSF DI, their influence on microstructure of fully ferritic solution strengthened DI is unknown. To close this current research gap, in the present study two ductile iron grades, EN-GJS-500-14 and EN-GJS-600-10, have been separately alloyed with nickel and cobalt according to a full factorial design, Y-shaped edges type II and IV have been casted, according to DIN EN 1564, and the nickel and cobalt's effects on the DI microstructure have been examined by means of light microscopy.

2 Methods and Materials

2.1 Design of experiments

In the present work near-eutectic EN-GJS-500-14 (3.8% Si) and EN-GJS-600-10 (4.3% Si) were alloyed in the first test set with two different amounts of cobalt and in the second set with two different amounts of nickel according to a full factorial design. To show the properties of the particular basis GJS grade both sets contained a parameter setting without additional alloying elements. To exclude a systematic influence of disturbance variable the designs were randomized (table 1 and 2). For a statistical evaluation of the measured results each parameter setting was repeated three times leading to overall number of 36 melts.

The maximum cobalt content was set at 4% because [34] reports a decrease of the yield strength at this cobalt amount. The

Največji delež niklja je bil nastavljen na koncentracijo niklja, pri kateri nastaja največji delež perlita 5 % glede na standard DIN EN 1563. V svojih patentih družba Siempelkamp Giesserei GmbH (Krefeld, Nemčija) omejuje delež niklja na 2,5 mas.% pri največjem deležu silicija 4 do 4,5 mas. % [36, 37]. Glede na to, je bil največji delež niklja nastavljen na 3 mas. % in srednji delež niklja na 1,5 mas. %.

2.2 Eksperimentalni postopek

Za ovrednotenje vpliva ohlajevalne hitrosti na učinek kobalta in niklja v litini SSF DI smo uporabili klinaste klinaste vzorce vrste II (debelina stene 25 mm) in vrste IV (debelina stene 75 mm) (slika 1), ki so bili simetrično razporejeni na okroglem modelu, da bi dosegli enakomerno zapolnjevanje forme in enakomerne razmere ohlajevanja. Forma je bila narejena iz kremenovega peska F 32 (Quarzwerke GmbH, Nemčija) in smole 7830 ter aktivatorja 7674 (oboje

mean cobalt content was set to 2%, which provides first solution strengthening effects in conventional ferritic DI.

The maximum nickel content is determined by the nickel content that generates a maximum perlite amount of 5 %, like it is advised in DIN EN 1563. In their patents the Siempelkamp

Giesserei GmbH (Krefeld, Germany) limits the nickel content at 2.5 % at a maximum silicon content of 4 to 4.5 % [36, 37]. Due to this, the maximum nickel content was set at 3% and the mean nickel content at 1.5 %.

2.2 Experimental procedure

To evaluate the influence of the cooling rate on the effect of cobalt and nickel on SSF DI, Y-wedges of the type II (25 mm wall thickness) and IV (75 mm wall thickness) were used (figure 1), symmetrically arranged on a circular pattern to realize uniform mould filling and cooling conditions.

Razpredelnica 1. Načrt poskusov prve serije

Table 1. Experimental design of the first set

test run	Co [%]	Si [%]
1	0	3.8
2	4	4.3
3	4	3.8
4	0	4.3
5	4	3.8
6	2	3.8
7	2	3.8
8	4	4.3
9	4	4.3
10	2	4.3
11	2	4.3
12	4	3.8
13	0	4.3
14	0	4.3
15	0	3.8
16	2	4.3
17	2	3.8
18	0	3.8

Razpredelnica 2. Načrt poskusov druge serije

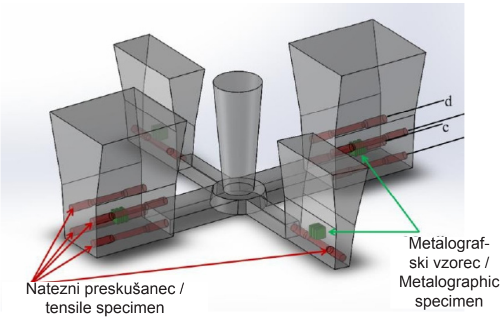
Table 2. Experimental design of the second set

test run	Ni [%]	Si [%]
1	0	3.8
2	3	4.3
3	3	3.8
4	0	4.3
5	3	3.8
6	1.5	3.8
7	1.5	3.8
8	3	4.3
9	3	4.3
10	1.5	4.3
11	1.5	4.3
12	3	3.8
13	0	4.3
14	0	4.3
15	0	3.8
16	1.5	4.3
17	1.5	3.8
18	0	3.8

iz HÜTTENES-ALBERTUS Chemische Werke GmbH, Germany).

Slika 1. Uporabljeni model in mesta vzorčenja

Figure 1. Used pattern and sampling positions



Napajalniki duktilne litine GJS-400-15, ki jih je dobavila družba Georg Fischer GmbH (Mettmann, Nemčija), malolegirana jeklena lomnina (Albert Hoffmann GmbH, Eschweiler, Nemčija), zelo čisti katodni kobalt in nikljevi peleti (FESIL SALES GmbH, Duisburg, Nemčija) so bili staljeni v grafitnem loncu (Aug. Gundlach KG, Großalmerode, Nemčija) v srednjefrekvenčni indukcijski peči. Talina (kemična sestava v razpredelnici 2) je bila pregreta na 1500 oC in zadrževana pri tej temperaturi 10 min, nato je bila posneta žlindra. Po obdelavi s cepivom ELMAG za litino s kroglastim grafitom (Elkem GmbH, Düsseldorf, Nemčija) s potopnim zvoncem pri temperaturi približno 1450 oC, posnetju žlindre in cepljenju taline z 0,3 mas. % SMW605 (ASK termične analize izbranih talin. Kemično sestavo talin smo ugotavljali na ulitih spektrometrskih vzorcih (premer 40 mm, CCD, debelina 5 mm; ulito v bakreno kokilo) z

Chemicals Metallurgy GmbH, Unterneukirchen, Nemčija), se je talina ulila pri približno 1350 oC v pripravljeno formo, v kateri je bil pesek vezan s smolo. Z napravo QuiK Cups (HERAEUS

The moulds were produced using silica sand F32 (Quarzwerke GmbH, Germany) and the resin 7830 and activator 7674 (both from HÜTTENES-ALBERTUS Chemische Werke GmbH, Germany).

EN-GJS-400-15 DI feeder, provided by Georg Fischer GmbH (Mettmann, Germany), low alloyed steel scrap (Albert Hoffmann GmbH, Eschweiler, Germany), high purity FeSi75, high purity cathode cobalt, and nickel pellets (FESIL SALES GmbH, Duisburg, Germany) were melted in a graphite crucible (Aug. Gundlach KG, Großalmerode, Germany) using a 50 kg medium frequency induction furnace. The melt (chemical composition see Table 2) was superheated to 1500 °C, held at this temperature for 10 min and slagged off. After the nodularization treatment using ELMAG (Elkem GmbH, Düsseldorf, Germany) in a plunger at a melt temperature of approx. 1450 °C, slagging off and inoculating the melt with 0.3 wt.% SMW605 (ASK Chemicals Metallurgy GmbH, Unterneukirchen, Germany) the melt was cast at approx. 1350 °C in the prepared resin-bonded mould. From selected melts thermo analyses curves were recorded with the aid of QuiK Cups (HERAEUS ELECTRONITE GmbH & Co. KG, Hagen, Germany). The chemical composition of the melts was determined with the aid of cast spectrometer specimens (40 mm diameter, 5 mm thickness; cast in a copper die) using the spark emission spectrometer SPECTRO LAB Jr.CCD (SPECTRO Analytical Instruments GmbH, Kleve, Germany). In addition selected specimens were analyzed by means of wet chemical analyses. The basic chemical composition was as follows mass fractions: 0.02-0.38% P; 0.01-0.03% S; 0.12-0.24% Mn; 0.86-0.12% Cu; 0.03-0.05% Mg; 0.03-0.05% Cr; 0.00-0.01% Al.

ELECTRONITE GmbH & Co. KG, Hagen, Nemčija) smo izdelali krivulje iskrnim emisijskim spektrometrom SPECTRO LAB Jr. ((SPECTRO Analytical Instruments GmbH, Kleve, Nemčija).

Dodatno smo izbrane vzorce analizirali z mokro kemično analizo. Osnovna kemična sestava je bila: 0,02-0,38 mas. % P, 0,01-0,03 mas. % S, 0,12-0,24 mas. % Mn, 0,86-0,12 mas. % Cu, 0,03-0,05 mas. % Mg, 0,03-0,05 mas. Cr, 0,00-0,01 mas. % Al.

2.3 Analize vzorcev

Za pripravo tankih metalografskih obrusov so bili vzorci izrezani iz Y-klinov (slika 1) z vodno hlajeno cirkularno žago in vloženi v mešanico araldita in utrjevala Ren HY 956 (oboje firme Huntsman GmbH & Co. KG, Bergkamen, Nemčija). Vzorci so bili potem brušeni na papirjih 180 do 1000 ter polirani z različnimi polirnimi sredstvi zrnavosti 9,3 in 0,25 µm. Tanki obrusi so bili jedkani z nitalom, da bi se odkrilo perlitno razmerje. Mikrostrukture vzorcev smo preiskali pri različnih povečavah s svetlobnim mikroskopom Axio Imager A1 m (LM from Carl Zeiss Microscopy GmbH, Jena, Nemčija). Pri vsaki povečavi je bilo narejenih vsaj 5 slik. Z računalniško opremo Axiovision KS 400 3.0 (Carl Zeiss Microscopy GmbH, Jena, Nemčija) za analizo slik so bile obdelane svetlobnomikroskopske slike nejedkanih mikrostruktur pri povečavi 100 x, da bi se dobila količina, število, velikost, sferičnost (enačba 1 [38]) in krogličavost grafitnih krogel (enačba 2 [39]).

$$\text{F (sferičnost)} = \frac{4 \cdot \pi \text{ (površina delca)}}{\text{(premer delca}^2\text{)}}$$

(> 0.7 = “kroglasta tvorba”) (1)

$$\text{N (krogličavost)} = \frac{\text{število kroglastih tvorb}}{\text{število vseh grafitnih delcev}} \quad (2)$$

2.3 Specimen Analyses

For the preparation of the metallographic thin sections, samples were cut from the Y wedges (figure 1) using a water-cooled circular saw and were embedded in Araldite combined with the hardener Ren HY 956 (both from Huntsman GmbH & Co. KG, Bergkamen, Germany). The sections were then ground using abrasive paper (180 to 1000 grades) and polished with various polishing agents (9, 3 and 0.25 µm grain). The thin sections were etched with Nital to reveal the pearlite ratio. The microstructures of the specimens were examined at different magnifications using an Axio Imager A1 m light microscope (LM from Carl Zeiss Microscopy GmbH, Jena, Germany). Per magnification a minimum of 5 pictures was taken. With the aid of the image analyses software Axiovision KS 400 3.0 (Carl Zeiss Microscopy GmbH, Jena, Germany) the LM pictures of the unetched microstructures in 100x magnification were analyzed to reveal the amount, number, size, sphericity (eq. 1 [38]), and nodularity of the graphite nodules (eq. 2 [39]).

$$\text{F (sphericity)} = \frac{4 \cdot \pi \text{ (particle's area)}}{\text{(particle's circumference}^2\text{)}}$$

(> 0.7 = “spherulites”) (1)

$$\text{N (nodularity)} = \frac{\text{number of spherulites}}{\text{numb. of all detected graphite particles}} \quad (2)$$

The detected graphite particles were classified according to their size into particles class 1 (5 to 100 µm²), particles class 2 (101 to 600 µm²), and particles class 3 (> 601 µm²).

All measurements were evaluated by using analyses of means (ANOM) and analyses of variance (ANOVA), and were modelled by linear regression [40].

Zaznane grafitne delce smo razvrstili glede na velikost delcev v razred 1 (5 do 100 µm²), razred 2 (101 to 600 µm²) in razred 3 (> 601 µm²).

Vse meritve so bile ovrednotene z analitičnimi sredstvi (ANOM), narejene so bile analize varianc (ANOVA) ter izdelana regresijska odvisnost [40].

3 Rezultati

Sliki 2 in 3 kažeta mikrostrukture poliranih in z HNO3 jedkanih vzorcev. V vseh vzorcih je bila mikrostruktura sestavljena iz grafita v kovinski osnovi brez cementita.

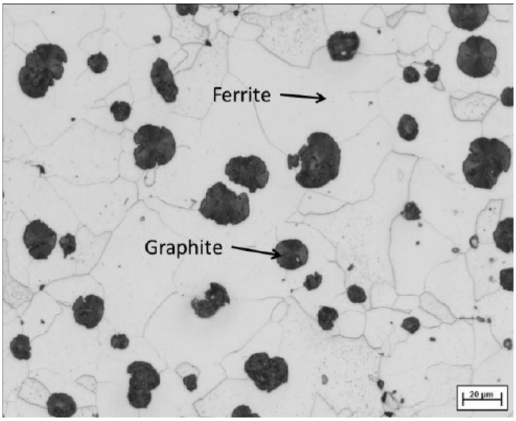
Reprezentativno izbrana mikrostruktura vseh vzorcev, legiranih s kobaltom (serija 1), prikazana na sliki 2 (legirana z 3,8 mas. % silicija in 4 mas. % kobalta), kaže popolnoma feritno osnovo. Rezultati svetlobno mikroskopske preiskave kovinske osnove so prikazani na sliki 4. Dodatek 1,5 mas. % niklja litini SSF DI vodi do nastanka perlita v kovinski osnovi v deležu do 2 5 %

3 Results

Figures 2 and 3 show the microstructures of polished and HNO3 etched specimen. All specimens show a microstructure that consists of graphite in a metallic matrix without the formation of cementite. Representatively selected for all cobalt alloyed specimens (set 1), the microstructure in figure 2 (alloyed with 3.8 % Si and 4 % Co) shows a fully ferritic matrix.

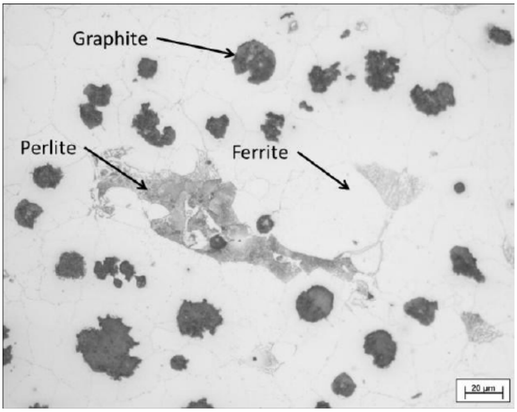
The results of the LM investigation of the metallic matrix are shown in figure 4. The addition of 1.5 % Ni to SSF DI leads to a perlite content of up to 2 % in the matrix; alloying with 3 % Ni results in a microstructure with up to 15 % perlite.

Alloying with cobalt causes no statistically proved effect on the graphite nodule count (figure 5 and table 3). With increasing nickel content a tendency of increasing nodule count can be observed (figure 6). However, this cannot be statistically confirmed, because the Tukey-Test classifies the results of all Co-levels as



Slika 2 Mikrostruktura vzorca s 3,8 mas. % Si in 4 mas. % Co v svetlobnem mikroskopu, polirano, jedkano z HNO3, povečava 500x

Figure 2. Light optical microstructure with 3.8% Si and 4% Co, polished, HNO3-etched 500x



Slika 3 Mikrostruktura vzorca s 4,3 mas. % Si in 3 mas. % Ni v svetlobnem mikroskopu, polirano, jedkano z HNO3, povečava 500x

Figure 3. Light optical microstructure with 4.3 wt.% Si and 3% Ni, polished, HNO3-etched, 500x

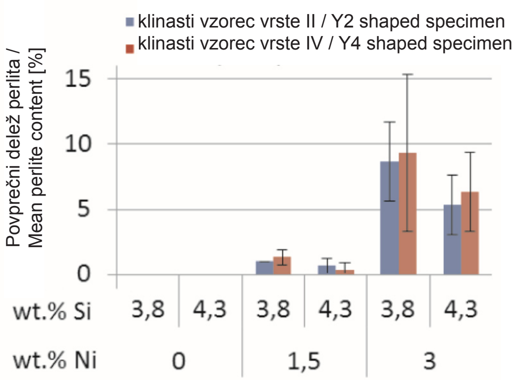
Legiranje s 3 mas. % niklja ima za posledico mikrostrukturo z do 15 % perlita.

Legiranje s kobaltom ni povzročilo nobenega statistično dokazanega učinka na število grafitnih kroglic (slika 5 in razpredelnica 3). S povečevanjem deleža niklja se je opazila tendenca povečanja števila kroglic (slika 6). Vendar tega ni bilo mogoče statistično potrditi, ker Tukeyev preskus razvršča rezultate vseh ravni kobalta, ker sta vrednosti »A« in p večji od kritične vrednosti 0,05 (razpredelnica 4). V obeh serijah vodi povečan delež silicija do povečanega števila grafitnih delcev. Manjša ohlajevalna hitrost v debelejših vzorcih Y4 ima za posledico manjše število kroglic.

Dodatek kobalta kot tudi dodatek niklja vodi do povečane krogličavosti (sliki 7 in 8). V prvi seriji smo opazili učinek zmanjšanja krogličavosti zaradi velikega deleža silicija pri 0 in 2 mas. % kobalta. Ko se poveča delež kobalta na 4 mas. %, pa silicij ne vpliva več na krogličavost grafitnih delcev. Rezultati druge serije niso pokazali statistično ovrednotenega vpliva deleža silicija na število grafitnih delcev. Na drugi strani je vpliv povečanega deleža niklja na

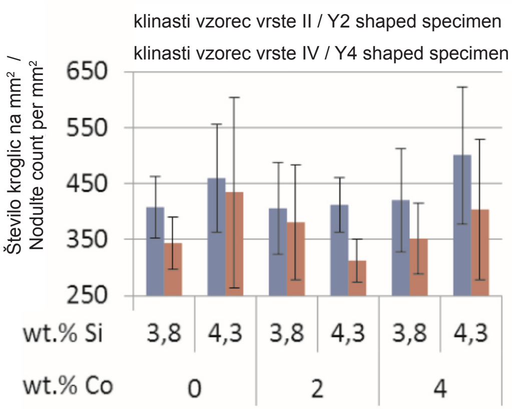
"A" and the p value is bigger than the critical value of 0.05 (table 4). In both sets, a higher content of silicon leads to an increased number of graphite particles. The slower cooling rates in the thicker Y4 shaped specimens result in lower nodule counts.

The addition of cobalt as well as the addition of nickel leads to an increasing nodularity (figures 7 and 8). For the first set



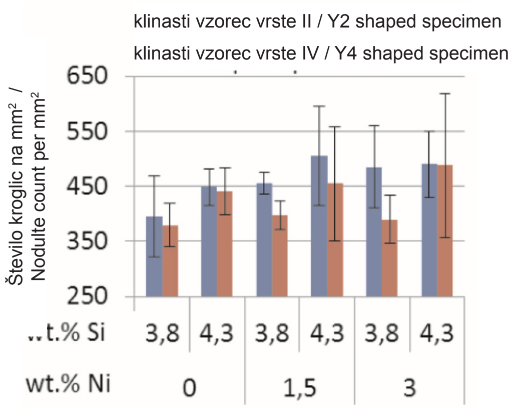
Slika 4. Vpliv silicija in niklja na mikrostrukturni delež perlita

Figure 4. Effect of silicon and nickel on the microstructure's perlite content



Slika 5 U činek silicija in kobalta na število kroglic na mm^2

Figure 5. Effect of silicon and cobalt on the nodule count per mm



Slika 6. Učinek silicija in niklja na število kroglic na mm^2

Figure 6. Effect of silicon and nickel on the nodule count per mm

Razpredelnica 3 Rezultati ANOVA-meritev števila kroglic, serija 1 (interval zaupanja 95 %). Različne črke v isti vrsti in p-vrednosti manjše kot 0,05 kažejo na statistično pomemben vpliv določene spremenljivke, ukazuje. N = število merjenih vrednosti, S = standardna deviacija

Table 3. Results of the ANOVA of the nodule count measurements, set 1 (confidence interval of 95 %). Different letters in the same line and p values smaller than 0.05 indicate a statistically significant influence of the particular command variable. N = number of measuring values, S = standard deviation

		Povprečno število kroglic na mm² / Mean nodule count per mm²	N	S	Grupiranje po Tukeyevi metodi / Grouping per Tukey-method		p-vrednost / p-value
Si [mas.%]	3.8	385.4	103	80.2	A		0.016
	4.3	422.1	76	121.7		B	
Co [mas.%]	0	404.1	59	103.5	A		0.121
	2	380.6	60	84.0	A		
	4	418.2	60	112.4	A		
Oblika vzorca / Specimen shape	Y2	431.4	90	90.0	A		0.000
	Y4	370.4	89	103.2		B	

Razpredelnica 4. Rezultati ANOVA-meritev števila kroglic, serija 2 (interval zaupanja 95 %)

Table 4. Results of the ANOVA of the nodule count measurements, set 2 (confidence interval of 95 %)

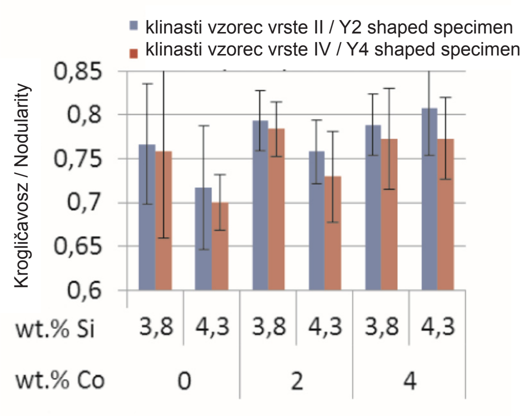
		Povprečno število kroglic na mm² / Mean nodule count per mm²	N	S	Grupiranje po Tukeyevi metodi / Grouping per Tukey-method		p-vrednost / p-value
Si [mas.%]	3.8	417.3	103	61.8	A		0.002
	4.3	471.0	76	81.6		B	
Ni [mas.%]	0	415.9	59	54.4	A		0.077
	1.5	453.3	60	76.1	A		
	3	462.8	60	89.0	A		
Oblika vzorca / Specimen shape	Y2	462.8	90	68.6	A		0.034
	Y4	424.8	89	79.5		B	

boljšo krogličavost statistično pomemben, kot kažejo rezultati ANOVA (razpredelnici 5 in 6).

4 Razprava

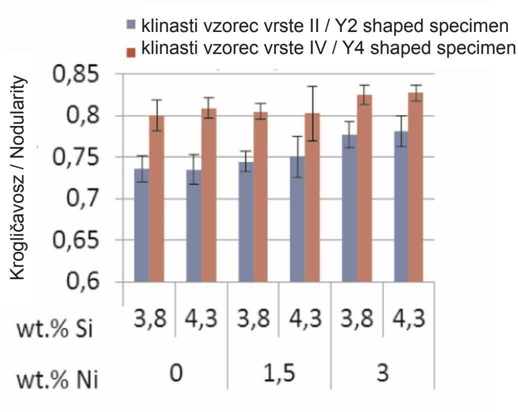
V tej predstavljeni študiji smo spreminjali ohlajevalno hitrost z izdelavo različnih oblik vzorcev z določenimi toplotnimi moduli. Lahko se vidi, da povečana ohlajevalna hitrost vodi do povečanega števila kroglic

a nodularity decreasing effect of the higher silicon content can be found at 0 and 2 % Co. When the cobalt content is increased to 4 %, silicon shows no effect on the nodularity of the graphite particles. The results of the second set reveal no statistically validated influence of the silicon content on the nodule count. The effect of improved nodularity by increasing the nickel content to 3 % on the other hand is statistically significant, as the results of the ANOVA show (table 5 and 6).



Slika 7. Vpliv silicija in kobalta na krogličavost grafita

Figure 7. Effect of silicon and cobalt on the nodularity



Slika 8. Vpliv silicija in niklja na krogličavost grafita

Figure 8. Effect of silicon and nickel on the nodularity

Razpredelnica 5. Rezultati ANOVA-meritev krogličavosti, serija 1 (interval zaupanja 95 %)

Table 5. Results of the ANOVA of the nodularity measurements, set 1 (confidence interval of 95 %)

		Povprečna krogličavost / Mean nodularity	N	S	Grupiranje po Tukeyevi metodi / Grouping per Tukey-method	p-vrednost / p-value
Si [mas.%]	3.8	0.777	103	0.05	A	0.002
	4.3	0.750	76	0.068	B	
Co [mas.%]	0	0.741	59	0.072	A	0.000
	2	0.771	60	0.046	B	
	4	0.785	60	0.05	B	
Oblika vzorca / Specimen shape	Y2	0.775	90	0.058	A	0.042
	Y4	0.757	89	0.061	B	

Razpredelnica 6. Rezultati ANOVA-meritev krogličavosti, serija 2 (interval zaupanja 95 %)

Table 6. Results of the ANOVA of the nodularity measurements, set 2 (confidence interval of 95 %)

		Povprečna krogličavost / Mean nodularity	N	S	Grupiranje po Tukeyevi metodi / Grouping per Tukey-method	p-vrednost / p-value
Si [mas.%]	3.8	0.77	36	0.07	A	0.985
	4.3	0.73	36	0.08	A	
Ni [mas.%]	0	0.7	24	0.08	A	0.001
	2	0.71	24	0.07	A	
	4	0.77	24	0.05	B	
Oblika vzorca / Specimen shape	Y2	0.67	36	0.06	A	0
	Y4	0.78	36	0.04	B	

v obeh serijah (sliki 5 in 6). Pričakovana odstopanja v seriji 2 kažejo na povečanje deleža kroglic z zmanjšanjem ohlajevalne hitrosti. Za ta pojav nismo našli razlage. Dobro je znano, da povečana ohlajevalna hitrost prispeva k povečanju števila kroglic, krogličavosti in sferičnosti. To občutno povečanje števila kroglic povzroči večja podhladitev, ki se pojavi med strjevanjem tanjših prerezov, kar naknadno aktivira večje število podlag za heterogeno nukleacijo grafita [7].

Z mikrostrukturno analizo se ni našlo nobenih omejitev za nadaljnje raztopinsko utrjevanje litine SSF DI s kobaltom. Osnove vzorcev, legiranih s kobaltom (serija 1), so bile pri vseh uporabljenih deležih kobalta iz 100 % ferita. Ti rezultati potrjujejo pričakovanja, ker je dobro znano, da kobalt pospešuje nastajanje ferita. Zato ni omejitev za raztopinsko utrjevanje do 4 mas. % Co in predvidoma niti pri večjih deležih kobalta ni moteno nastajanje ferita. Ker legiranje s silicijem vodi do zmanjšanja deleža krogličavosti, legiranje s kobaltom izboljša obliko grafitnih kroglic. Ti učinki so v skladu z opazovanji standardnih vrst duktilne litine [33, 34]. Zaradi povečanja krogličavosti in s tem zmanjšanja zareznega učinka grafitnih delcev se lahko pričakuje boljše razmerje med natezno trdnostjo in duktilnostjo.2 E. Modl [34] je opazil, da se poveča število grafitnih delcev z 140 na 340 na mm , če se standardna duktilna litina legira z do 6 mas. % kobalta. Povečanja števila kroglic in s tem udrobnjenja mikrostrukture pri legiranju s kobaltom nismo opazili v naši sedanji raziskavi. Ena od možnih razlag je, da prisoten delež silicija vodi do večjega 2osnovnega števila kroglic tako, da so vzorci že brez kobalta imeli 404 kroglice na mm . Nadalje, povprečno število kroglic 370 do 431 delcev na mm^2 v vzorcih legiranih s kobaltom je očitno preseglo minimalno število 60 delcev na mm , tako da je bil

4 Discussion

In present study the cooling rate has been varied by the production of different specimen shapes with defined thermal modules. It can be shown, that an increase in cooling rate leads to an increased nodule count in both sets (figures 5 and 6). Contrasting expectations, set 2 shows an increased nodularity with a decreasing cooling rate. For this phenomenon no explanation was found. It is well known that the increase of the cooling rate contributes to a raise in nodule count, nodularity and sphericity. This noticeable raise in nodule count is caused by higher undercooling that takes place during solidification of thinner sections, which subsequently activates a large number of substrates for heterogeneous nucleation of graphite [7].

Via microstructural analysis, no limitation for a further solid solution hardening of SSF DI by alloying with cobalt can be found. The matrixes of the cobalt alloyed specimens (Set 1) consist of a 100 % ferrite for all investigated cobalt contents. These results meet the expectations, since it is well known that cobalt promotes the formation of ferrite. Therefore, no restrictions for a solid solution hardening by alloying with up to 4% Co and presumably even higher contents of cobalt are given due to no interference with the formation of ferrite. While alloying with silicon leads to a decrease in nodularity, alloying SSF DI with cobalt improves the shape of the graphite nodules. These effects are in accordance with observations made in conventional ductile iron grades [33, 34]. Due to the increasing nodularity and the respective decreased notching effect of graphite particles, an enhanced ratio of tensile strength to ductility can be expected. E. Modl [34] observed an increase from 140 to 340 graphite particles per mm^2 by alloying a conventional DI with up to 6% Co. An izključen nastanek mikroporoznosti kot posledica tega.

Zaradi velikega učinka raztopinskega utrjevanja [28] in s tem optimizacijskega potenciala za litino SSF DI je obetavno legiranje z nikljem. Največja količina niklja je povezana z učinkom nastajanja perlita, ki ga nikelj povzroča med evtektoidno reakcijo transformacije. Glede na strojno obdelovalnost in ohranitev izvrstnega razmerja med trdnostjo in duktilnostjo po DIN EN 1563, delež perlita v litini SSF DI ne sme preseči 5 %. V naši študiji je delež perlita presegel to mejo pri zlitinah, ki so bile legirane s 3 mas. % Ni. Rezultati potrjujejo največji delež 2,5 mas. %, ki je naveden v patentih firme Siempelkamp Giesserei GmbH [36, 37]. Zaradi učinka nastajanja ferita je vzorec, legiran z 4,3 mas. % silicija, pokazal manj perlita v mikrostrukturi kot vzorec, legiran s 3,8 mas. %. Pri vrednotenju deleža perlita je treba upoštevati elemente, ki povzročajo nastajanje perlita. Glede na kemično sestavo napajalnikov (EN-GJS-400-15), ki so se uporabljali kot surovina, in glede na sestavo jeklenih odpadkov smo privzeli, da se dopušča delež okoli 0,2 mas. % mangana in okoli 0,1 mas. % bakra. Ker baker pospešuje nastajanje perlita približno 13-krat bolj kot nikelj, se opažen delež nastanka perlita razume kot prekrivanje učinkov teh elementov. V nasprotju z učinkom silicija vodi dodatek niklja k povečani krogličavosti v litini SSF DI. To je v nasprotju z opažanji C.H.Hsuja in sodelavcev [2] za standardno feritno duktilno litino. Kar se tiče legiranja s kobaltom, se zato lahko pričakuje, da bo nadaljnje raztopinsko utrjevanje z dodajanjem niklja imelo za posledico izboljšano razmerje med trdnostjo in duktilnostjo. Opažena tendenca po večjem številu kroglic zaradi dodajanja niklja se ni mogla statistično potrditi za litino SSF DI s Tukeyevin preskusom in p-vrednostjo v intervalu zaupanja 95 %. Ta

increase in nodule count and respectively a grain refining effect of cobalt cannot be seen for the cobalt contents used in the present study. One possible explanation is that the present silicon content leads to a higher base nodule count, so that specimens without cobalt already showed a nodule count of 404 nodules per mm^2. Furthermore, the mean nodule count of cobalt alloyed specimen of 370 to 431 particles per mm clearly exceeds the minimum amount of 60 particles per mm so that microporosity as an outcome of this can be excluded. Due its high solid solution hardening effect [28] and the resulting optimization potential for SSF DI grades, it is promising to alloy with nickel. The maximum amount of nickel is a result of the pearlite forming effect, which nickel reveals during the eutectoid phase transformation.

For reasons such as machinability and conserving the excellent ratio of strength to ductility, according to DIN EN 1563, the perlite content of SSF DI grades should not exceed 5 %. In the present study, the pearlite content exceeds this amount for alloys with the addition of 3% Ni. These results confirm the maximum amount of 2.5 %, that is given by the patents of Siempelkamp Giesserei GmbH [36, 37]. Due it ferrite forming effect, specimen alloyed with 4.3% Si exhibit less pearlite in the microstructure than specimen alloyed with 3.8%. When evaluating the pearlite content, the amount of other pearlite forming elements needs to be considered. Due to the chemical composition of the risers (EN-GJS-400-15) that have been used as raw material and due to the composition of the steel scrap an amount of about 0.2% Mn and about 0.1 % Cu were adapted. Since copper promotes the formation of pearlite approximately 13 times stronger than nickel, the observed pearlite forming can be understood as an overlaid effect of those elements. In contrast to the effect of silicon, tendenca bi vodila do manjših kroglic, ki naj bi bile bolj okrogle kot večje kroglice in to bi lahko bila možna razlaga za opaženo povečanje krogličavosti. Število kroglic, ki smo ga dosegli v seriji 2 s povprečno 416 - 471 kroglic na mm^2, je precej nad potrebnim minimumom, da se izogne mikroporoznosti.

5 Sklepi

Namen naše raziskave je bil ugotoviti vpliv kobalta in niklja na mikrostrukturo litine SSF DI. Rezultati preiskovanih zlitin, legiranih z do 4 mas. % kobalta in do 3 mas. % niklja omogočajo naslednje sklepe:

1. Dodatek do 4 mas. % kobalta ni škodljiv za nastajanje ferita. Ta dodatek ne vpliva negativno na število kroglic in z dodajanjem kobalta se povečuje krogličavost.
2. Dodajanje niklja je omejeno zaradi neizogibnega nastanka več kot 5 % perlita, kar se zgodi že pri 3 mas. % niklja. Dodajanje niklja nima vpliva na število kroglic, povečuje pa njihovo krogličavost.

Glede na omejitve zaradi nastajanja perlita pri legiranju z nikljem se lahko pokaže, da sta kobalt in nikelj z vidika mikrostrukture primerna za nadaljnje raztopinsko utrjevanje litin SSF DI. V nadaljnjih preiskavah se bo analizirala interakcija med kobaltom in nikljem. Zaradi močnega vpliva kobalta na tvorbo ferita lahko to omogoči večje dopustne deleže niklja, kar bo vodilo do nadaljnjega raztopinskega utrjevanja ferita. Učinek obeh serij legiranja na mehanske lastnosti litine SSF DI bo predstavljen v prihodnjih prispevkih.

a nickel addition leads to an increased nodularity in SSF DI. This disagrees with the observations made by C.H. Hsu et al. [2] for conventional ferritic DI. As for alloying with cobalt it can therefore be expected, that a further solid solution strengthening by the addition of nickel results in an improved ratio of strength to ductility. The observed tendency for a higher nodule count with the addition of nickel cannot be statistically confirmed for SSF DI by the use of the Tukey-test and p-value at a confidence interval of 95 %. This tendency would lead to smaller nodules that tend to be more spherical than larger nodules, which could be a possible explanation for the observed increase in nodularity. The nodule count achieved in set 2 with an average of 416-471 nodules per mm^2 is well above the necessary minimum of 60 nodules per mm^2 to avoid microporosity.

5 Conclusions

The purpose of the present study was to analyse the microstructural influence of cobalt and nickel on SSF DI. The results of the investigated alloying with up to 4% Co and up to 3% Ni can be concluded as follows:

1. The addition of up to 4% Co is not harmful to the formation of ferrite. The nodule count is not negatively influenced and the nodularity increases with the addition of cobalt.
2. The addition of nickel is limited to the intolerable formation of more than 5 % pearlite, which occurred at 3 % Ni. Besides this, the addition of nickel results in an unaffected nodule count and an improved nodularity.

With respect to the restrictions regarding the pearlite formation by alloying with nickel, it can be shown that cobalt and nickel

6 Zahvale

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are, from a microstructural point of view, suitable for a further solution strengthening of SSF DI. In further studies, the interaction of nickel and cobalt will be investigated. Due to its strong ferritization effect cobalt maybe leads to a higher tolerable nickel content thus leading to a further solid solution strengthening of ferrite. The effect of both alloying series on the mechanical properties of SSF DI will be presented in future publications.

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