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Razvoj duktilne litine za uporabo pri visokih temperaturah

Development of Ductile Cast Iron for High-Temperature Applications

Izvleček

Od novih vrst duktilne litine se zahteva, da izpolnjujejo zahteve po zmanjševanju velikosti motorjev z notranjim izgorevanjem in povečanju delovne temperature. Prispevek opisuje razvoj novih feritnih duktilnih litin, odpornih pri višjih temperaturah, njihove lastnosti, serijske uporabe in najnovejše dosežke pri razvoju materialov.

Zmanjševanje velikosti bencinskih in dizelskih motorjev z notranjim izgorevanjem prispeva k zmanjšanju emisij CO_2. Konstruiranje manjših motorjev z notranjim izgorevanjem s povečanimi močmi vodi do višjih temperatur izpušnih plinov. Pri osebnih vozilih te presegajo 850 °C pri bencinskih motorjih in celo 1050 °C pri bencinskih motorjih s turbopolnilniki. Toplotna izolacija ščiti okolico motorjev, a še bolj omejuje delovne razmere izoliranih vročih delov.

Feritne silicijeve in molibdenove duktilne litine so v Evropi standardizirane s standardom EN-16124. Vendar lastnosti teh materialov niso dovolj dobre, da bi se materiali uporabljali za najnovejše zmanjšane motorje z notranjim izgorevanjem. Na osnovi SiMo-duktilne litine so se razvili novi feritni materiali s ciljem povišati temperaturo pretvorbe ferit-avstenit, povečati trdnost pri visokih temperaturah in odpornost proti oksidaciji.

Ključne besede: siva litina s kroglastim grafitom, SiMo, temperaturna odpornost, izpušni kolektor, turbo polnilnik, feritno avstenitna transformacija

Abstract

New ductile iron grades are required to meet the challenges arising from engine downsizing and subsequent temperature increase. This paper describes the development of new ferritic, temperature resistant ductile iron grades, their properties, serial applications and newest achievements in material development.

Downsizing of gasoline and Diesel engines helps to reduce CO_2 emissions. Constructing smaller engines with increased power levels leads to higher exhaust gas temperatures. In passenger cars, these exceed 850°C in Diesel engines and even 1050 °C in turbocharged gasoline engines. Thermal insulation protects the engine's surroundings, but tightens the operating conditions of the insulated hot parts even further.

Ferritic silicon and molybdenum-alloyed ductile iron grades are standardized in Europe in EN- 16124. However, these materials' properties are not sufficient for being applied in the newest downsized engines. Based on SiMo ductile iron, new ferritic materials are developed with the aim to raise ferrite/austenite transition temperature, high temperature (HT) strength and scaling resistance.

Keywords: ductile iron, SiMo, temperature resistance, exhaust manifold, turbocharger, ferrite-austenite transformation

1 Uvod

Vsesplošna javna razprava o segrevanju ozračja in zahteve po drastičnem zmanjšanju emisij CO_2 sili proizvajalce avtomobilov, da čim prej razvijejo nove avtomobile z manjšo porabo bencina in zmanjšanimi emisijami. Povečanje specifične moči in povišanje tlakov v zmanjšanim motorjih z notranjim izgorevanjem vodi do povišanja temperatur izpušnih plinov. Te se pri dizelskih motorjih gibljejo med 850 °C in 900 °C. Pri bencinskih motorjih s turbopolnilniki pa se omenja celo vrednost 1050 °C [1]. Zamisel zmanjševanja velikosti motorjev vodi nadalje v povečanje prenosa energije glede na prostornino valja.

Ta dejanski razvoj motorjev z notranjim izgorevanjem vodi do občutnega povečanja toplotnih obremenitev sestavnih delov, ki so v stiku z izpušnimi plini, kot so izpušni sistemi ali turbopolnilniki. Standardni materiali so dosegli svoje meje, zato je treba priti do novih rešitev.

V splošnem so temperature sestavnih delov motorja 50 do 80 °C nižje od temperatur izpušnih plinov, toda na izpostavljenih mestih – tj. na tankostenskih delih, ki so z več strani v stiku z izpušnimi plini, ali na toplotno izoliranih delih se lahko njihova temperatura zelo približa temperaturam izpušnih plinov.

1 Introduction

The omnipresent public discussion about climate warming and the required drastic reduction of CO_2 emissions forces the car producers to develop new cars with lower gasoline consumption and reduced emissions as soon as possible. The raise of specific power and mean pressure of downsized engines leads to a raise of exhaust temperatures. These are in the region of 850 to 900 °C for Diesel engines. For turbocharged gasoline engines, a value of 1,050 °C is mentioned [1]. Furthermore, the downsizing concept leads to rising transferred energy amounts with respect to the cylinder volume.

These actual engine developments lead to a remarkable increase of thermal demands of components which are in contact with exhaust gas, such as exhaust manifolds or turbochargers. Conventional materials reach their limits, and new solutions have to be elaborated.

In general, the component temperatures remain 50 to 80 K below the exhaust gas temperature, but at exposed positions - e.g. thin walled areas in contact with exhaust gas from several sides, or areas with thermal insulation - the temperature of the material can reach values close to these of the exhaust gas.

1.1 Materiali za izpušne sisteme

Za te namene se uporabljajo v odvisnosti od temperatur izpušnih plinov različni materiali. Pri izpušnih sistemih tekmujejo med seboj konstrukcije iz varjene jeklene pločevine in ulitki, medtem ko so ohišja turbopolnilnikov v skoraj vseh primerih ulita. Za sestavne dele teh se do temperatur 820 °C uporabljajo feritna litina s 4 – 5 % silicija in 0,5 – 1,0 Mo, litina z vermikularnih grafitom

1.1 Materials for exhaust applications

Depending on exhaust temperatures, various materials are used for these applications. For exhaust manifolds, welded steel sheet constructions are in competition with castings, while turbocharger housings are cast in almost all cases. Ferritic cast iron with 4 to 5 % Si and 0.5 - 1.0 % Mo, compacted graphite cast iron (GJV) as well as spherodial graphite(GJS) is used

(GJV) kot tudi litina s kroglastim grafitom (GJS). Poleg standardnih SiMo-materialov se dobijo tudi različice z dodatkom 0,5 – 1,0 % Cr ali Ni (SiMoCr ali SiMoNi-litina), ki so bolj odporne proti oksidaciji [2]. Pri temperaturah izpušnih plinov do 950 °C se uporabljajo ali avstenitne duktilne litine kot GJSA-XNiSiCr35-5-2, znane tudi kot Ni-Resist D5S, ali feritna jekla, močno legirana s kromom. Pri temperaturah do 1000 °C lahko izpolnjujejo zahteve le močno legirana avstenitna jekla. Pri še višjih temperaturah pa se morajo uporabljati zlitine na osnovi niklja.

Boljše vrste materialov pogosto potrebujejo večje količine zlitinskih elementov. Predvsem nikelj, katerega cena je na borzah v bližnji preteklosti zelo nihala, se uporablja v velikih količinah. Z ekonomskega vidika je bolje razvijati manj legirane in zato cenejše materiale za uporabo pri povišanih temperaturah.

Glede na ta dejstva se je podjetje Georg Fischer pred več leti odločilo, da se bo osredotočilo na razvoj feritnih SiMo-materialov in s tem raztegnilo področje uporabe takšnih materialov tudi na višje temperature. Cilj tega razvoja je bil doseči lastnosti, ki bi bile blizu litini GJSA-XNiSiCr35-5-2, ki se uporablja predvsem za sestavne dele, ki vzdržijo najvišje temperature med 820 °C in 930 °C.

1.2 Zahteve za materiale za izpušne sisteme

Materiali za izpušne sisteme in ohišja za turbopolnilnike so izpostavljeni težkim toplotnim ter termomehanskim obremenitvam. Najpomembnejše lastnosti takšnih materialov so zato [3]:

- odpornost proti oksidaciji,
- natezna trdnost, predvsem pri povišanih temperaturah,
- temperaturna stabilnost mikrostrukture,

for component temperatures up to 820 °C. Along with standard SiMo materials, variants with additional Cr or Ni in the range of 0.5 to 1.0 % are available (SiMoCr and SiMoNi, respectively), which exhibit a better scaling resistance [2]. At higher exhaust temperatures up to 950 °C, either austenitic ductile iron grades, such as GJSA-XNiSiCr35-5-2, also known as Ni-Resist D5S, or highly Cr alloyed ferritic steels are used. At temperatures up to 1’000 °C, only highly alloyed austenitic steels are able to fulfil the requirements. At even higher temperatures, Ni-based alloys have to be used.

Superior grade materials often need a higher amount of alloying elements. Thus, material costs rise continuously with rising temperatures of the application. Especially nickel, which exhibited a volatile market price in the near past, is used in large amounts. From an economic point of view, it is advantageous to develop lower alloyed and therefore cheaper materials to be used at elevated temperatures.

Based on these facts, the company Georg Fischer decided to focus on the development of ferritic SiMo materials several years ago, and thus to extend the range of use of such a material to higher temperatures. The aim of this development was to attain properties close to GJSA-XNiSiCr35-5-2, which is predominantly used at maximum component temperatures between 820 °C and 930 °C.

1.2 Requirements for materials for exhaust applications

Materials for exhaust manifolds and turbocharger housings are exposed to heavy thermal and

thermo-mechanical loads. The most important properties of such materials are therefore [3]:

- toplotna utrujenost.

Toplotna utrujenost ali odpornost proti termomehanskemu utrujanju ni neodvisna lastnost materiala, ampak lastnost, ki je odvisna od številnih značilnosti materiala. Pri vsakem ciklu segrevanja sestavnega dela nastanejo temperaturni gradienti, ki povzročajo napetosti zaradi različnega toplotnega širjenja na različnih mestih in pri različnih temperaturah. Pri medsebojnem sestavljanju teh delov, npr. pri glavi motorja, je prosto toplotno širjenje omejeno, kar povzroča dodatne napetosti.

2 Zgodovina razvoja feritne duktilne litine za temperature nad 800 °C

Si-Mo duktilna litina je znana že več kot 30 let – leta 1980 je podjetje Georg Fischer delilo dokumentacijo o takšnih materialih [4]. V poznih osemdesetih letih so francoski znanstveniki veliko delali, da bi z dodajanjem aluminija izdelali duktilno litino, uporabno pri višjih temperaturah [5,6]. Zaradi ogromnih težav, ker ima tak material veliko nagnjenost k tvorbi oksidnih žlinder med litjem, razvoj ni dosegel uspehov na tržišču. Zato do sedaj še ni poznana nobena industrijska uporaba takega materiala. Konec devetdesetih let si je GF prizadeval nadaljevati delo Francozov in razvil patentirani material 'SiMo1000®' [7]. Leta 2008 je bilo možno z nadaljnjim

- Scaling resistance
- Tensile strength, especially at elevated temperatures
- Temperature stability of the microstructure
- Thermal fatigue

Thermal fatigue or the resistance against thermo-mechanical fatigue are not singular material properties, but depend on various material characteristics. With each heating cycle of the component, temperature gradients are created which induce tension due to different thermal elongation at different positions and temperatures respectively. By mounting this component to another, such as the cylinder head, free thermal expansion is restrained, causing additional stress.

2 History of the development of ferritic ductile iron for temperatures above 800 °C

Si-Mo-alloyed ductile iron is known since more than 30 years - e.g., in 1980, the company Georg Fischer distributed documentation about such materials [4]. In the late 80s, French scientists did a lot of work to find a ductile iron material applicable at higher temperatures, adding some Aluminium [5,6]. Due to massive problems caused by the very high tendency

Slika 1: Primer serijskega izpušnega sistema in ohišja turbopolnilnika, ki sta izdelana iz GJS SiMo1000®

Figure 1: Examples of a serial exhaust manifold and turbocharger housings made of GJS SiMo1000®.

razvojem tega materiala, predvsem postopka litja, začeti s serijsko proizvodnjo izpušnih sistemov in ohišij turbopolnilnikov za temperature izpušnih plinov blizu 900 °C [8]. Slika 1 prikazuje takšne dele, izdelane iz duktilne litine 'SiMo1000®', za uporabo pri visokih temperaturah.

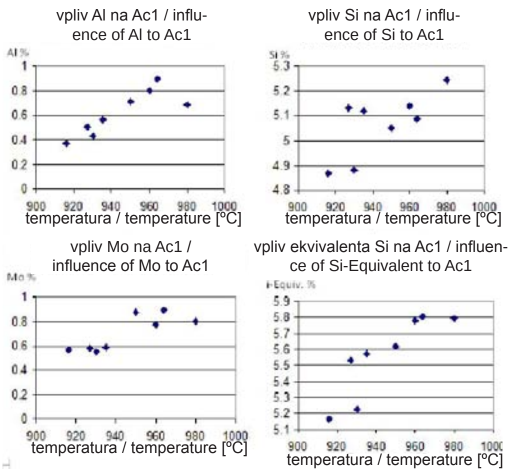
Razvoj materiala se ni zaključil s serijsko proizvodnjo. Prispevek ponuja izvleček razprave o najnovejših aktivnostih in metodah, kako izboljšati visokotemperaturne lastnosti feritne duktilne litine.

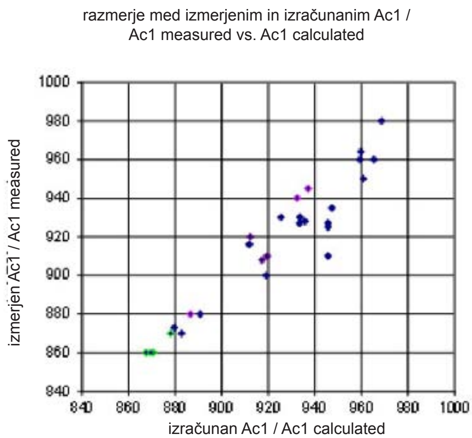
3 Zadnji razvoj SiMo-materialov v GF

Uliti so bili vzorci z različnimi deleži Si, Al, Ni in Mo. Dilatometrsko so se ugotavljale temperature pretvorbe ferit-avstenit v teh materialih in ocenjevali vplivi zlitinskih elementov na temperaturo pretvorbe. Pokazalo se je, da molibden, silicij in aluminij povišajo temperaturo transformacije [9]. Kombinacija silicija in aluminija s silicijevim ekvivalentom (Si_{ekv} = % Si + 0.8 · % Al)

of this material to build oxide slags during the pouring process, the development was not successfully introduced on the market. No industrial application of this material is known as yet. At the end of the 90s, GF pursued the French work and developed the patented material 'SiMo1000®' [7]. In 2008, with further development of this material and especially the casting process, it was possible to go into serial production of exhaust manifolds and turbocharger housings for exhaust temperatures close to 900 °C [8]. Fig. 1 shows such parts, produced with SiMo1000® ductile iron for HT applications.

Material development has not ended with the start of serial production. In this paper, the most recent activities are summarised, and methods to improve high temperature properties of ferritic ductile iron are discussed.





Slika 2 (levo) in **slika 3** (desno): Vpliv različnih zlitinskih elementov na temperaturo pretvorbe ferit-avstenit in korelacija med izračunanimi in izmerjenimi vrednostmi

Figure 2 (left) and **3** (right): Influence of different alloying elements on the ferrite/austenite transformation temperature, and correlation between calculated and measured values daje mnogo boljšo korelacijo s temperaturo pretvorbe kot posamezna elementa (slika 2).

Z večkratno regresijsko analizo se je razvil obrazec za napovedovanje temperature pretvorbe. Primerjavo izračunanih in izmerjenih temperatur pretvorbe kaže slika 3.

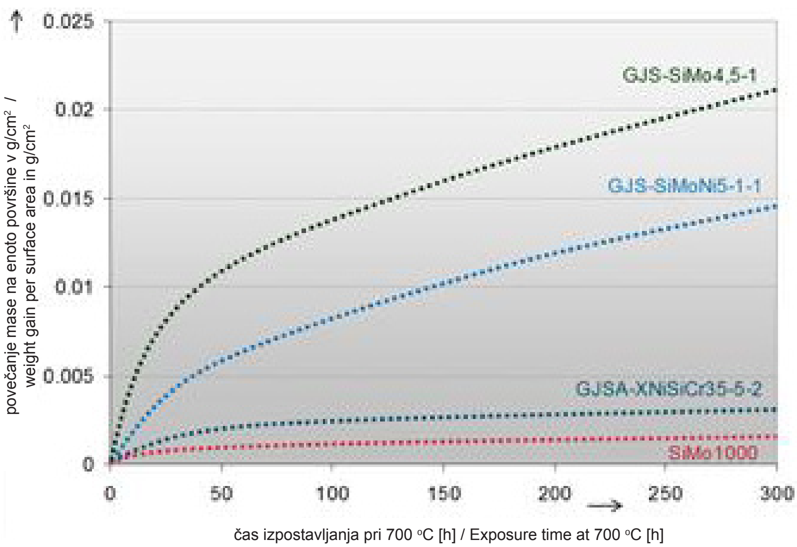
Vendar je temperatura pretvorb ferit-avstenit, ki je višja od temperature izpušnih plinov, le eden od kriterijev. Glede uporabnosti materiala je treba upoštevati še trdnost, obnašanje pri lezenju ter oksidacijo pri povišanih temperaturah. Obnašanje pri oksidaciji se preskuša empirično z različnimi kemičnimi sestavami ter merjenji razmerij prirastek mase-izguba mase in debeline oksidne plasti pri povišanih temperaturah. Slika 4 kaže tvorbo oksidne plasti na različnih materialih. V primerjavi s klasičnimi materiali ima SiMo1000® mnogo boljšo odpornost proti oksidaciji pri visokih temperaturah [2].

3 Recent SiMo materials development at GF

Samples with variations in Si, Al, Ni and Mo content were cast. Their ferrite/austenite transformation temperatures were measured by dilatometry, and the influence of the alloying elements on the transformation temperature was evaluated. Molybdenum, Silicon and Aluminium were shown to increase the transformation temperature [9]. The combination of Silicon and Aluminium by a Si-equivalent (Si-eq. = % Si + 0.8 • % Al) results in a much better correlation to the transformation temperature than with the two elements separately (Fig. 2).

Using multiple regression analysis, a formula to predict transformation temperatures was developed. A comparison of calculated and measured transformation temperatures is shown in Fig. 3.

However, a ferrite/austenite transformation temperature, which is higher than the exhaust gas temperature is only one criterion. For the applicability of a material, strength, creeping behaviour and scaling at elevated temperature have to be



Slika 4: Tvorba oksidne plasti na različnih visokotemperaturnih materialih v mirujočem zraku pri 700 °C

Figure 4: Scaling of different high temperature materials in unmoved air at 700 °C

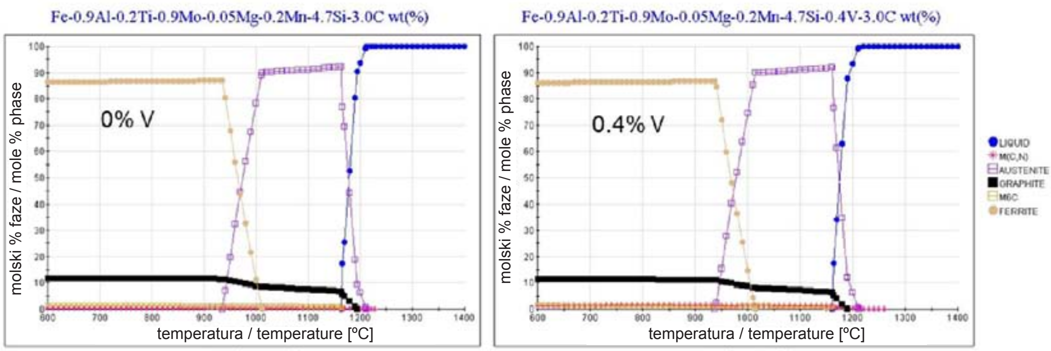
3.1 S simulacijo podprti razvoj materiala

Danes se simulacijska orodja uporabljajo za napovedovanje temperatur pretvorbe, izločanja in tvorbe faz za izboljšanje trdnosti in odpornosti proti lezenju pri visokih temperaturah. Sliki 5 in 6 kažeta primerjavo simulacijskih rezultatov pri uporabi programske opreme JMatPro [10]. Narejena je bila simulacija pri dveh kemičnih sestavah z različnima deležema vanadija, enkrat brez vanadija, drugič z 0,4 mas. % V [11]. Dodatek vanadija naj bi pripeljal do izločanja karbidov vrste VC iz trdne raztopine [12]. Simulacija je pokazala, da je temperatura pretvorbe ferit-avstenit pri 935 ^{o}C, če ni prisotnega vanadija, in 938 ^{o}C, kadar je prisotnega 0,4 mas. % V. Dodatek 0,4 % V povzroči povečanje M(C,N) z 0,42 % na 1,2 % in zmanjšanje z 2,21 % M_6C na 0,86 % M(C,N). M(C,N) je sestavljen iz VC, medtem ko M_6C vsebuje iz Mo_6C in Fe_6C [12]. Poskus je pokazal, da se je povečala celotna količina karbidov v mikrostrukturi, kot je bilo napovedano s simulacijo (sliki 7 in 8).

considered. The scaling behaviour is tested empirically by varying chemical composition and measuring weight gain/loss and oxide layer thickness at elevated temperatures. Fig. 4 shows the scaling of different materials: Compared to conventional materials, SiMo1000® exhibits a much better resistance to high temperature oxidation [2].

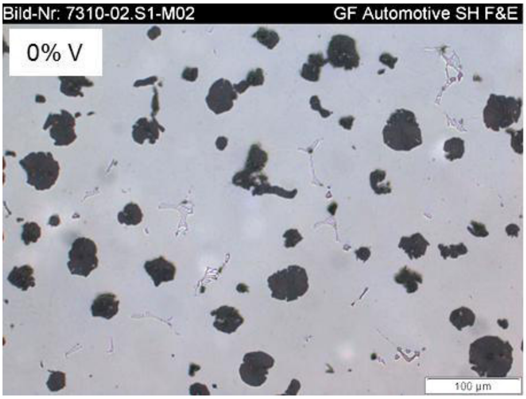
3.1 Simulation assisted material development

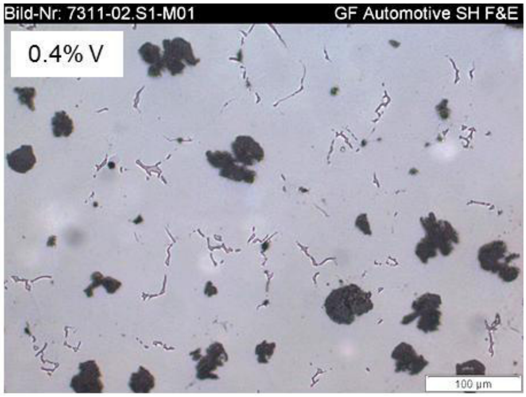
Nowadays, simulation tools are used to predict transition temperatures, precipitations and phases to improve high temperature strength and creep resistance. Fig. 5 and 6 show a comparison of simulation results using the software JMatPro [10]. Two chemical compositions with variations in the Vanadium content were simulated, one without V, the other one with 0.4 V (mass fraction, %) [11]. The addition of V should lead to carbide formation from solid solution with VC stoichiometry [12]. The simulation shows a ferrite/austenite transformation temperature of 935 °C without V and 938 °C with 0.4 % V. The addition of 0.4 % V leads



Slika 5 (levo) in **slika 6** (desno): Simulacija dveh sestav z različnima deležema vanadija z JMatPro: slika 5 brez V, slika 6 z 0.4 % V

Figure 5 (left) and **6** (right): JMatPro simulation of two compositions with variations in the Vanadium content: Fig. 5 without, Fig. 6 with 0.4 % V





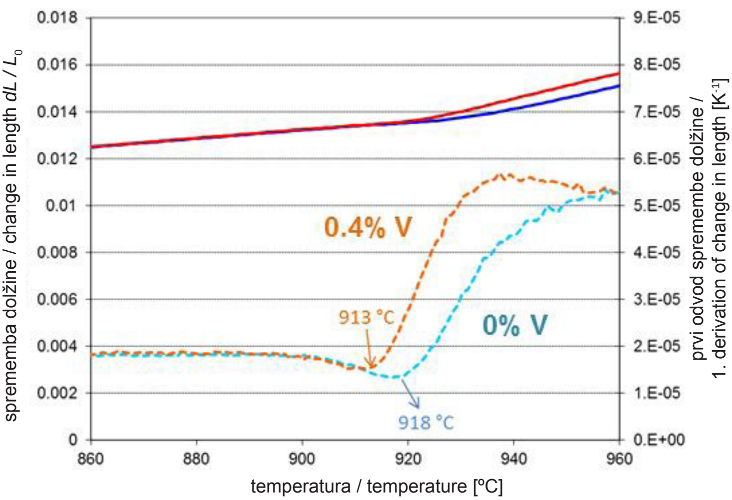
Slika 7 (levo) in **slika 8** (desno): Mikroposnetka različic brez V (levo) in z 0.4 % V (desno)

Figure 7 (left) and **8** (right): Micrographs of the two variants without V (left) and with 0.4 % V (right)

Vendar simulacija ne more vedno nadomestiti poskusa: glede na simulacijo naj bi bila temperatura pretvorbe ferit-avstenit pri litini z 0,4 % V 938 °C v primerjavi z 935 °C pri litini brez V. Dilatometrsko meritev prikazuje slika 9. 0,4 % V zniža temperaturo pretvorbe za 5 °C, namesto da bi se povišala za 3 °C. Vendar sta obe spremembi temperature, pri simulaciji in poskusu, nepomembni.

Večji delež karbidov pri vanadijevi duktilni litini SiMo1000® pomeni povečanje to a raise of 0.42 % M(C, N) to 1.2 % and a drop of 2.21 % M6C to 0.86 %. M(C,N) consists of VC, whereas M6C consists of Mo6C and Fe6C [12]. The experiment results in an increased total amount of carbides in the microstructure, as predicted by the simulation (Fig. 7 and 8).

However, not every simulation result can be reproduced by experiment: According to the simulation, the variant with 0.4 % V should exhibit a ferrite/austenite transformation temperature of 938 °C, compared to 935 °C



Slika 9: Dilatometrska meritev, ki nakazuje temperaturo pretvorbe ferit-avstenit

Figure 9: Dilatometer measurement indicating the ferrite/austenite transformation temperature

natezne trdnosti pri 800 °C za 20 % (z 52 MPa na 63 MPa). Delež karbidov, ki je manjši od 1 %, tako učinkovito poveča visokotemperaturno trdnost (slika 10).

Ena od omejitev simulacijskih metod je pomanjkanje podatkov o nekaterih zanimivih elementih, npr. o Co, ki utrjuje trdno raztopino. Tega do sedaj uporabljana programska oprema ne upošteva, bo pa to vključeno v podatkovno bazo programske opreme v prihodnje.

4 Nove duktilne litine za uporabo pri visokih temperaturah: materiali in metode

Obstaja manj načinov, kako povečati trdnost pri temperaturah >0.4·T_m kot pri sobni temperaturi. Nasprotno, Hall-Petchov mehanizem za drobnozrnato strukturo ni samo neuporaben, po njem ima udrobnitev mikrostrukture celo nasproten učinek na odpornost proti lezenju. Utrjevanje z dislokacijami zmanjšuje podaljšek pri lezenju in lahko pripelje celo do rekristalizacije. Utrjevanje s trdno raztopino je uspešna metoda, ki pa ima omejitve. Edina zanesljiva metoda za izboljšanje visokotemperaturnih mehanskih lastnosti pri T_m je utrjevanje z

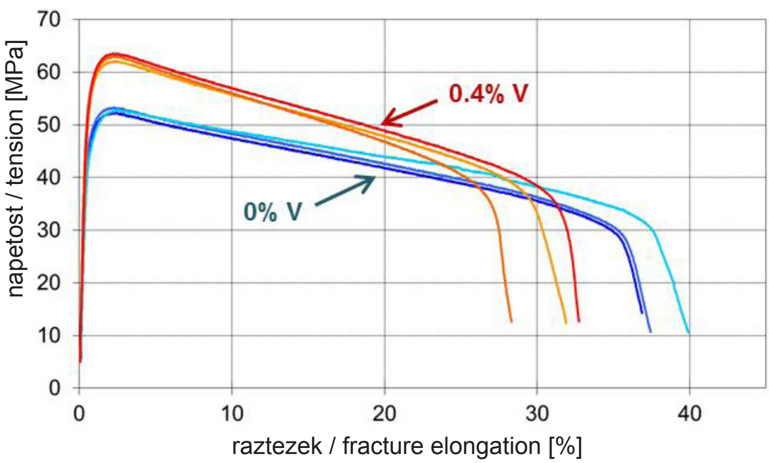
without V. The dilatometer measurement is shown in Fig. 9. 0.4 % V reduces the ferrite/austenite transformation temperature by 5 K instead of increasing it by 3 K. However, both temperature changes - in simulation and experiment - are insignificant.

The higher carbide content of V-alloyed SiMo1000® ductile iron leads to an increase of tensile strength of 20 % at 800 °C (from 52 MPa to 63 MPa). A carbide content of less than 1 % thus effectively increases high temperature strength (Fig. 10).

One limitation of simulation methods is the lack of data on some elements of interest, e.g. the solid solution strengthening element Co. So far, it has not found consideration by the software used, but might be included in the software's database in the future.

4 New ferritic ductile iron grades for high temperature applilcations: materials and methods

There are less ways to improve strength at temperatures >0.4•Tm than at ambient conditions. On the contrary, the Hall-Petch mechanism of a fine grained structure is not only inoperative, but grain refinement has adverse effects on



Slika 10: Rezultat nateznih preskusov pri 800 °C: občutno višja natezna trdnost pri 0,4 % V (merjeno na ÖGI (avstrijski livarski inštitut)), www.ogi.at, s hitrostjo 0,3 mm/min, po ISO 6892-2:2011)

Figure 10: Result of tensile tests at 800 °C: significantly higher tensile strength with 0.4 % V (measured at ÖGI, www.ogi.at, with a speed of 0.3 mm/min, according to ISO 6892-2:2011)

delci [13]. Dodatno se lahko s povišanjem T_m potisne visokotemperaturne lastnosti na višjo raven.

Z upoštevanjem teh osnov so bile izdelane štiri sestave z različnimi deleži Si, Al, Co in V, da bi se izboljšala uporabnost SiMo duktilne litine pri visokih temperaturah. Temperature pretvorbe ferit-avstenit so bil merjene z vakuumsko tesnim dilatometrom z vodoravnim pritiskanjem vrste Netsch DIL402C pri hitrosti segrevanja in ohlajevanja 4 K/min. Visokotemperaturni natezni preskusi so bili narejeni v osrednjem laboratoriju GF z walter+bai statičnim preskuševalnim strojem. Uporabljeni so bili preskušanci po DIN 50125 oblike B z 10 mm premera, segrevani v uporovni peči in obremenjevani s hitrostjo 0,2 mm/min po ISO 6892-2:2011.

4.1 Sestava taline

Element Co je znan, da stabilizira ferit in v trdni raztopini poviša mehanske lastnosti ferita. Dodatek Co SiMo-litini bi lahko bil način, kako povišati temperaturo pretvorbe ferit-avstenit in s tem visokotemperaturno trdnost. Na žalost naša simulacijska orodja niso imela v programu kobalta. Da bi se ugotovil vpliv Co, se je njegov učinek na temperaturo pretvorbe in s tem na visokotemperaturno trdnost ugotavljal s poskusi. Izdelana talina 1 je imela sestavo: 2.5 % C, 5.2 % Si, 0.25 % Mn, 0.21 % Cu, 0.6 % Al, 1.8 % Co. Sestava taline 2 je bila: 2.5 % C, 5.2 % Si, 0.24 % Mn, 0.21 % Cu, 0.4 % Al, 4.0 % Co.

S ciljanjem na temperaturo pretvorbe ferit-avstenit nad 1000 oC se je delež aluminija in silicija povečal glede na prejšnje sestave ter na serijsko proizvodnjo. Tako sta bili izdelani dve dodatni talini. Talina 3 je imela sestavo: 2.5 % C, 5.3 % Si, 0.27 % Mn, 0.2 % Cu, 1.96 % Al, 0.15 % Cr, 0.42 % V, 1.8 % Co. in talina 4 sestavo: 2.5 % C,

creep resistance. Dislocation hardening reduces creep elongation and may even lead to recrystallization. Strengthening by solid solution is a variable method with restrictions. The only secure method to increase high temperature mechanical properties at constant Tm is via particle strengthening [13]. Furthermore, one can try to increase Tm to push HT properties to higher levels.

With these basic principles at hand, four compositions with variations in Si, Al, Co and V contents were produced with the aim to enhance HT-performance of ferritic SiMo ductile iron. Ferrite/austenite transformation temperatures were measured using a Netzsch DIL402C vacuum- tight, horizontal pushrod dilatometer with heating/cooling rates of 4 K/min. HT tensile tests were performed at GF central lab with a 600 kN walter+bai static universal testing machine on DIN 50125 Form B specimens with 10 mm diameter using a resistive furnace and testing rate of 0.2 mm/min, according to ISO 6892-2:2011.

4.1 Melt compositions

The element Cobalt is known as a ferrite stabilizer and increases the mechanical properties of ferrite by solid solution. Adding Co to a SiMo iron could thus be a means to raise ferrite/austenite transformation temperature and thus high temperature strength. Unfortunately, our simulation tools have no Co implemented. To characterize the influence of Co, its effect on transformation temperature and high temperature strength was measured empirically. Melt No. 1 was prepared with the following composition: 2.5 % C, 5.2 % Si, 0.25 % Mn, 0.21 % Cu, 0.6 % Al, 1.8 % Co. The composition of melt No. 2 was: 2.5 % C, 5.2 % Si, 0.24 % Mn, 0.21 % Cu, 0.4 % Al, 4.0 % Co.

5.5 % Si, 0.27 % Mn, 0.2 % Cu, 2.91 % Al, 0.15 % Cr, 0.40 % V, 1.7 % Co.

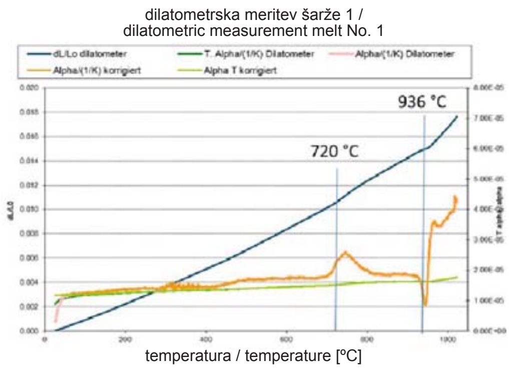
5 Rezultati: temperature pretvorbe ferit-avstenit in mehanske lastnosti pri visokih temperaturah

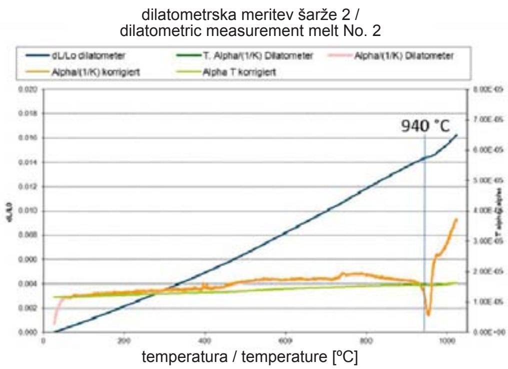
Pozitiven učinek vanadija na visokotemperaturne lastnosti s tvorbo karbidov po strjevanju je bil prikazan že prej. Njegov vpliv na temperaturo pretvorbe ferit-avstenit je nepomemben [11]. Z zgoraj omenjenim empiričnim obrazcem sta bili izračunani temperaturi pretvorbe ferit-avstenit okoli 930 °C in 920 °C za talino 1 oz. talino 2 (10 % nižja zaradi vpliva Al) – brez upoštevanja Co v izračunu. Razlika med izračunano in izmerjeno temperature pretvorbe se je povečala s plus 6 na plus 10 °C s povečanjem deleža Co z 1,8 % na 4,0 %. Očitno ima Co le manjši učinek na povišanje merjene temperature pretvorbe (sliki 11 in 12). Čeprav tvori trdno raztopino, Co nima občutnega vpliva na visokotemperaturno trdnost (slika 13). Natezni trdnosti taline 1 z

Aiming at ferrite/austenite transformation temperature above 1000 °C, the silicon and aluminium contents were increased compared to previous compositions and to serial production. Two further melts were thus prepared: Melt No. 3 with the following composition: 2.5 % C, 5.3 % Si, 0.27 % Mn, 0.2 % Cu, 1.96 % Al, 0.15 % Cr, 0.42 % V, 1.8 % Co. And melt No. 4 with: 2.5 % C, 5.5 % Si, 0.27 % Mn, 0.2 % Cu, 2.91 % Al, 0.15 % Cr, 0.40 % V, 1.7 % Co.

5 Results: Ferrite/austenite transformation temperatures and mechanical properties at high temperatures

The positive effect of vanadium on HT properties via the formation of carbides after solidification was shown above. Its influence on ferrite/austenite transformation temperature is insignificant [11]. Using the empirical formula mentioned above, the calculated ferrite/austenite transformation temperature was around 930 °C and 920 °C for melt No. 1 and melt No. 2, respectively





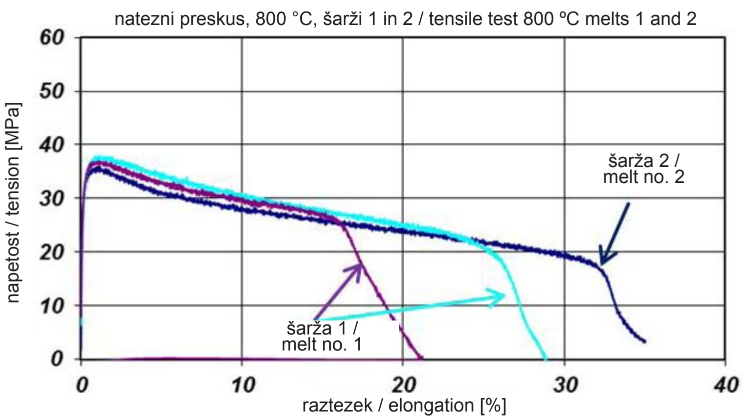
Slika 11 (levo) in **slika 12** (desno): Dilatometrske meritve nakazujejo temperaturo transformacije ferit-avstenit vzorca iz taline z 1,8 % Co in taline 2 z 4,0 % Co. Prva konica pri vzorcu 1 pri 720 °C je verjetno posledica raztapljanja preostalega perlita

Figure 11 (left) and **12** (right): Dilatometer measurements indicating the ferrite/austenite- transformation temperature of melt No. 1 with 1.8 % Co, and melt No. 2 with 4.0 % Co. The first peak of melt 1 at 720 °C is probably due to solution of remaining pearlite

1,8 % in taline 2 z 4,0 % Co sta bili 36 MPa oz. 38 MPa.

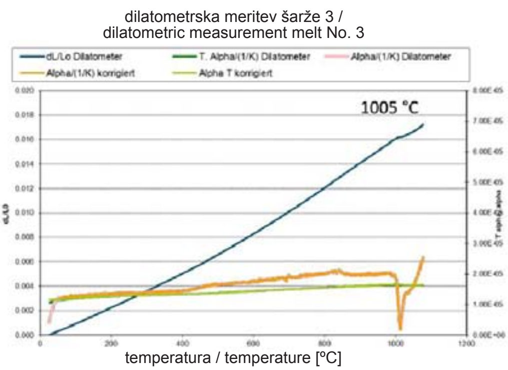
Empirični obrazec je dal vrednosti za temperaturi pretvorbe ferit-avstenit 988 °C in 1040 °C za šarži 3 in 4 (predvsem zaradi vpliva Al) – zopet brez upoštevanja kobalta. Dilatometrske meritve so potrdile, da je vpliv kobalta na temperaturo pretvorbe zanemarljiv, pokazal pa se je občuten vpliv silicija in aluminija. Z 5,5 % Si in 2,9 % Al je možno doseči temperature pretvorbe precej nad 1000 °C (sliki 14 in 15). Natezne trdnosti pri 800 °C so se povečale s povišanjem

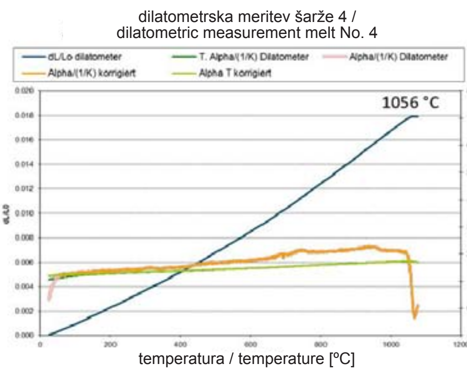
(10 % lower due to the influence of Al) - without considering cobalt in the calculation. The difference between calculated and measured transformation temperature is increased from plus 6 to plus 10 K by raising the cobalt content from 1.8 to 4.0 %. Apparently, Co has a minor raising effect on the measured transformation temperature (Fig. 11 and 12). Although it forms a solid solution, Co does not have a significant effect on HT strength (Fig. 13). The tensile strength of melt No. 1 with 1.8 % Co and



Slika 13: Natezni preskusi vzorcev iz talin 1 in 2 pri 800 °C

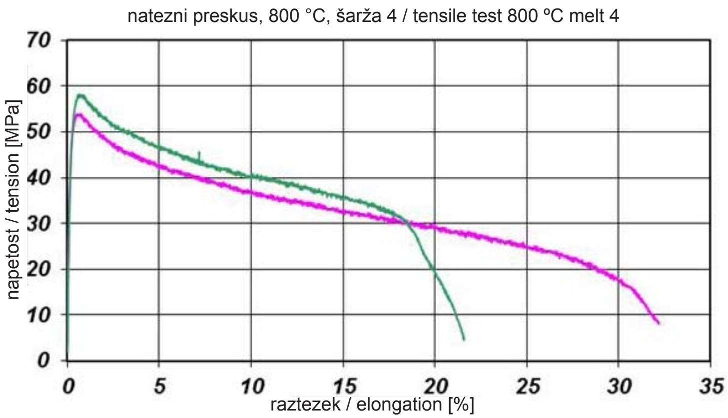
Figure 13: Tensile tests of melts No. 1 and 2 at 800 °C





Slika 14 (levo) in **slika 15** (desno): Dilatometrske meritve nakazujejo temperaturo pretvorbe ferit-avstenit za vzorec iz taline 3 z 5,3 % Si in 1,96 % Al ter taline 4 z 5,5 % Si in 2,91 % Al

Fig. 14 (left) and **15** (right): Dilatometer measurements indicating the ferrite/austenite transformation temperature of melt No. 3 with 5.3 % Si and 1.96 % Al, and melt No. 4 with 5.5 % Si and 2.91 % Al



Slika 16: Natezni preskusi vzorcev iz šarže4 z 5,5 % Si in 2,91 % Al pri 800 °C

Figure 16: Tensile tests of melt No. 4 with 5.5 % Si and 2.9 % Al at 800 °C

temperature pretvorbe in trdnosti trdne raztopine zaradi povečanja deleža tako Si kot Al, kar se vidi na sliki 16. Natezni trdnosti sta bili 54 MPa in 58 MPa. Za šaržo 3 manjkajo vrednosti preskusa strojne obdelave.

6 Razprava

Pričakovano utrjanje pri visokih temperaturah z dodajanjem kobalta se ni zgodilo, čeprav ima trdna raztopina utrjevalni učinek pri sobni temperaturi. Drugi elementi, ki tudi utrjujejo trdno raztopino železa pri sobni temperaturi (npr. Si), pa pripeljejo do velike trdnosti pri povišanih temperaturah. To lahko razložijo razlike med atomskimi polmeri, ki so 30 pm med Fe in Si, 15 pm med Fe in Al ter samo 5 pm med Fe in Co. Zato je popačenje mreže, ki jo povzroči Si, večje in s tem tudi očitno bolj učinkovito pri visokih temperaturah. Z drugimi besedami, energija napake zloga se mogoče s kobaltom ne zmanjša dovolj, da bi vplivala na visokotemperaturne lastnosti.

Poleg tega Si in Al povišata temperaturo transformacije ferit-avstenit. Zato ni možno kvantificirati očitnega povečanja visokotemperaturne trdnosti samo s trdno raztopino. S spreminjanjem deleža teh elementov se predvidoma dobi povezan

melt No. 2 with 4.0 % Co is 36 MPa and 38 MPa, respectively.

The empirical formula yields ferrite/ austenite transformation temperatures of 988 °C and 1’040 °C for melts No. 3 and No. 4, respectively (mainly due to the influence of Al) - again without considering cobalt. Dilatometer measurements confirm that the influence of cobalt on the transformation temperature is negligible, but that there is a significant influence of silicon and aluminium. With 5.5 % Si and 2.9 % Al, it is possible to attain transformation temperatures well above 1000 °C (Fig. 14 and 15). Tensile strengths at 800 °C were increased by raising the transformation temperature and solid solution strength with increasing both the Si and Al contents, as depicted in Fig. 16. The tensile strength is 54 and 58 MPa. No values of melt No. 3 are available due to machining issues.

6 Discussion

The anticipated strengthening by the addition of cobalt did not happen at high temperatures, although it does have solid solution strengthening effects at ambient temperatures. Other elements however, which also strengthen the solid solution of učinek utrjanja s trdno raztopino in spreminjanja temperature pretvorbe ferit-avstenit. Majhno povečanje temperature solidus, ko se zlitini dodajo ti elementi, ima verjetno samo manjšo vlogo pri visokotemperaturnih mehanskih lastnostih preiskovanih materialov.

7 Sklepi

Povezani učinki utrjanja z delci in s trdno raztopino ter povišana temperatura pretvorbe ferit-avstenit omogočajo najboljše visokotemperaturne mehanske lastnosti. S pozitivnim učinkom Si, Al in Mo na odpornost proti oksidaciji se bo bodoči razvoj materialov osredotočil na optimizacijo sestav, predstavljenih tukaj, in iskanju drugih načinov, da se izrabi preje omenjene mehanizme utrjanja (npr. z dodajanjem karbidotvornih in/ali nitridotvornih elementov, kot sta Cr ali Ti).

Kobalt tvori v feritu trdno raztopino. Vendar dodajanje tega elementa ne izboljša visokotemperaturnih lastnosti materialov. Ob upoštevanju teh rezultatov je pomen kobalta kot zlitinskega elementa zanemarljiv tako s tehnološkega kot trgovskega vidika.

Duktilne litine s povečanimi deleži Si, Al, Cr, V, Ti, N imajo velik potencial pri izdelavi novih duktilnih litin v ulitem stanju ob le zmerno povečanih stroških za zlitinske elemente glede na klasično SiMo-litino, a s temperaturami pretvorbe ferit-avstenit nad 1000 ^{o}C in visokotemperaturno trdnostjo, ki je primerljiva z dražjimi avstenitnimi duktilnimi litinami. Ta novi material predstavlja potencial za uporabo pri izdelavi izpušnih sistemov in ohišij turopolnilnikov obremenjenih bencinskih motorjev z notranjim izgorevanjem.

iron at room temperature (e.g. silicon) do lead to higher strength at elevated temperatures. This can be explained by the differences of atomic radii, which are 30 pm between Fe and Si, 15 pm between Fe and Al, but only 5 pm between Fe and Co. Therefore, lattice distortions provoked by Si are more severe and apparently much more effective at high temperatures. In other words, the stacking fault energy might not be reduced enough by the element cobalt in order to affect HT properties.

However, Si and Al also increase the ferrite/austenite transformation temperature. It is therefore not possible to quantify the apparent increase of high temperature strength via solid solution only. When varying these elements, a combined effect of solid solution strengthening and changes in ferrite/austenite transformation temperature is thus assumed. The slight increase of solidus temperature when adding these elements to the alloy is believed to play only a minor role for the examined materials' HT mechanical properties.

7 Conclusions

The combined effects of particle hardening, solid solution strengthening and increased ferrite/austenite transformation temperature yield the best HT mechanical properties. With the positive effect of Si, Al and Mo on scaling resistance, future material development will focus on optimisation of the compositions presented here, and finding other ways to employ the aforementioned strengthening mechanisms (e.g. adding elements to provoke carbide and/or nitride formation, such as Cr or Ti).

Cobalt forms a solid solution in ferrite. However, the addition of this element does not increase the material's HT properties. Considering these results, the importance

Zahvale

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of Co as an alloying element is negligible both from technological and commercial points of view.

Ductile iron materials with increased Si-, Al-, Cr-, V-, Ti-, N-contents show a big potential for a new as cast ductile iron with moderately higher element costs compared to conventional SiMo, but with a ferrite/austenite transformation temperature above 1000 °C and high temperature strength similar to the much more expensive austenitic ductile iron. This new material provides a potential for being used for exhaust manifolds and turbocharger housings of charged gasoline engines.

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