

THERMODYNAMIC MODELING FOR THE ALLOY DESIGN OF HIGH SPEED STEELS AND HIGH CHROMIUM CAST IRONS

TERMODINAMIČNO MODELIRANJE NAČRTOVANJA SESTAVE HITROREZNIH JEKEL IN LITINE Z VELIKO VSEBNOSTJO KROMA

Massimo Pellizzari

Department of Materials Engineering and Industrial Technologies, via Mesiano 77, 38050 Trento – Italy
Massimo.Pellizzari@ing.unitn.it

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In recent years, Thermo-Calc was successfully used by the author for the development of as-cast High Speed Steels and High Chromium Irons. The correlation between solidification process and microstructure was studied in view of influence of alloying elements introduced to promote carbide precipitation. The solidification process occurs under non-equilibrium conditions, because of microsegregation phenomena connected with the solidification structure: the liquid between dendrites becomes progressively enriched in solute and its composition increasingly differs from that predicted by the equilibrium diagram. This behavior can be studied with good approximation by using the model proposed by Scheil and Gulliver. In this way it was possible to refine the phase constitution of High Speed Steels, even if kinetic-related phenomena still limit its correct prediction. Present results also show that microstructural tailoring is possible looking at the correlation existing between the fraction of liquid phase at eutectic MC carbides precipitation. The morphology of V-rich particles changes from a continuous *interdendritic* network to a *globular dissociated eutectic*, showing higher toughness. The composition of HiCrI should result as near as possible to the eutectic, to maximize eutectic carbide amount. Calculations allowed to define the parameter $T_L - T_{Ei}$ (T_L = liquidus temperature; T_{Ei} = eutectic start temperature) as representative of the material hypoeutecticity, and, on the basis of experimental results, a value of 20 °C was safely established in the development of the new composition.

Key words: thermodynamic modelling, solidification, high chromium alloy, high speed steel, phase composition, MC carbides

Zadnja leta je avtor uspešno uporabil Thermo-Calc za razvoj hitroreznih jekel (HSS) in veliko vsebnostjo litine kroma (HiCrI). Raziskana je bila korelacija med procesom strjevanja in mikrostrukturo z vidika legirnih elementov, ki so bili dodani za povečanje precipitacije karbidov. Proces strjevanja je neravnotežen zaradi povezanosti med strjevalno strukturo in mikrosegregacijo: talina med dendriti postopno postane obogatena s topljencem, njena sestava pa se naraščajoče razlikuje od tiste, ki jo napoveduje ravnotežni diagram. Tako vedenje je mogoče raziskati z zadostnim približkom, če uporabimo model, ki sta ga predlagala Scheil in Gulliver. Tako lahko izboljšamo fazno sestavo hitroreznih jekel, čeprav kinetični pojavi omejujejo natančno napoved. Prikazani rezultati dokazujejo, da je mogoče krogiti mikrostrukture z opazovanjem korelacije med deležem taline pri precipitaciji MC-karbidov. Morfologija zn, bogatih z V, se spremeni od povezane interdritske mreže v globularni disociirani evtektik in dobi večjo žilavost. Sestava litine z veliko vsebnostjo kroma (HiCrI) naj bo čim bližja evtektični, da se tako poveča delež evtektičnih karbidov. Z izračuni je bil določen parameter $T_L - T_{Ei}$ (T_L = likvidis temperatura; T_{Ei} = temperatura začetka evtektika), ki je merilo hipoevtektičnosti. Na podlagi eksperimentalnih rezultatov je bila opredeljena vrednost parametra 20 °C za razvoj novih sestav.

Ključne besede: termodinamično modeliranje, strjevanje, sestava faz, hitrorezno jeklo, litina z veliko vsebnostjo kroma, MC-karbidi

1 INTRODUCTION

The solidification and precipitation sequence play an important role on the microstructure and the final properties of high speed steels (HSS) and high chromium cast irons (HiCrI). The optimization of properties is related to the possibility to govern the phase precipitation, microsegregation and transformation temperature during solidification. This becomes crucial for spincast hot roll materials, that are not submitted to thermomechanical treatment after solidification. Hence, hardness, wear resistance and toughness (...) are largely dependent on the amount and type of primary and eutectic carbides, but also on the composition of the metallic matrix giving rise to secondary hardening during final treatment¹⁻³.

Different models have been applied to simulate the solidification behaviour of multicomponent systems like high speed steels⁴⁻⁷ and cast irons^{7,8} using thermodynamic methods. In general, the solidification does not follow the equilibrium and limitations regarding the diffusivity in the solid and, partially in the liquid phase, have to be taken into account^{9,10}. The Scheil-Gulliver model^{11,12}, considering the total lack of diffusion within the solid and the complete mixing in the liquid (produced by efficient stirring and diffusion), defines the upper limit for the solute segregation in the liquid and the minimum attainable solidus temperature. In the present work Thermo-Calc¹³ software was used to model the solidification process under both, thermodynamic equilibrium and under the conditions stated by the Scheil model.

2 THERMODYNAMIC MODELS AND DATABASE

The phases in the studied multicomponent systems are described by the sub-lattice model^{14,15}. The molar Gibbs free energy of a phase *m* in the system can be expressed as

$$G_m = G_m^{\text{ref}} - TS_m^{\text{id}} + G_m^{\text{ex}} + G_m^{\text{mg}}$$

where G_m^{ref} is the reference free energy, $-TS_m^{\text{id}}$ is the ideal mixing entropy, G_m^{ex} is the excess energy term and G_m^{mg} is the change in energy caused by magnetic ordering. The thermodynamic data used for the calculations are contained in the TCFE2000 database. Phases considered are reported in **Table 1**.

3 ALLOY DESIGN OF HIGH CHROMIUM IRON

The nominal chemical composition of standard HiCrI is reported in **Table 2**. The base-alloy contains mainly carbon and chromium, with only minor addition of secondary hardening alloying elements (Mo, V and W).

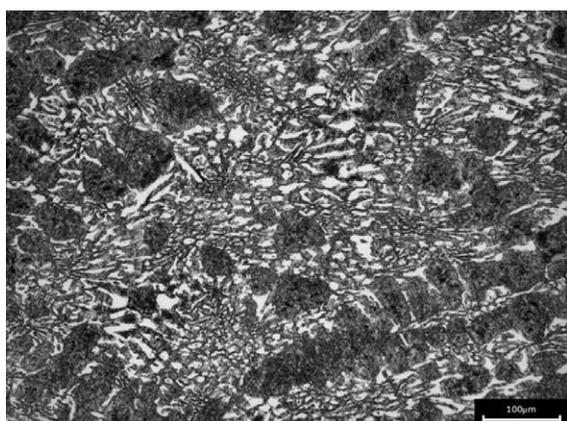


Figure 1: Microstructure of standard HiCrI

Slika 1: a) Mikrostruktura standardne HiCrI

Table 1: Model of the phases considered in the calculations

Tabela 1: Modeli faz, upoštevanih pri izračunih

Phase	N. sub.	N of sites Per sublatticee	Sublattice Species (Va = vacancies)
Liquid	1	1	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C, Va
FCC (austenite)	2	1 : 1	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C, Va
BCC (ferrite)	2	1 : 3	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C, Va
MC	2	1 : 1	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C, Va
M ₂ C	2	2 : 1	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C, Va
M ₃ C (cementite)	2	3 : 1	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C
M ₆ C	4	2 : 2 : 2 : 1	Fe : Mo, W: Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C
M ₇ C ₃	2	7 : 3	Fe, Si, Mn, Cr, Ni, Mo, V, Nb: C
M ₂₃ C ₆	3	20 : 3 : 6	Fe, Cr: Fe, Cr, Si, Mn, Cr, Ni, Mo, V, Nb: C

Table 2: Chemical composition of standard HiCrI

Tabela 2: Kemična sestava standardne HiCrI

C	Si	Mn	Cr	Ni	Mo	V	W
2.4–2.7	0.3–0.8	0.4–0.8	16–20	0.3–2.0	0.2–2.5	0.2–0.4	0.2–0.6

The hypo-eutectic nature of this alloy can be observed in the microstructure in **Figure 1**, displaying the material after quenching from 950 °C and double tempering. The result is also confirmed by the calculated isopleth in

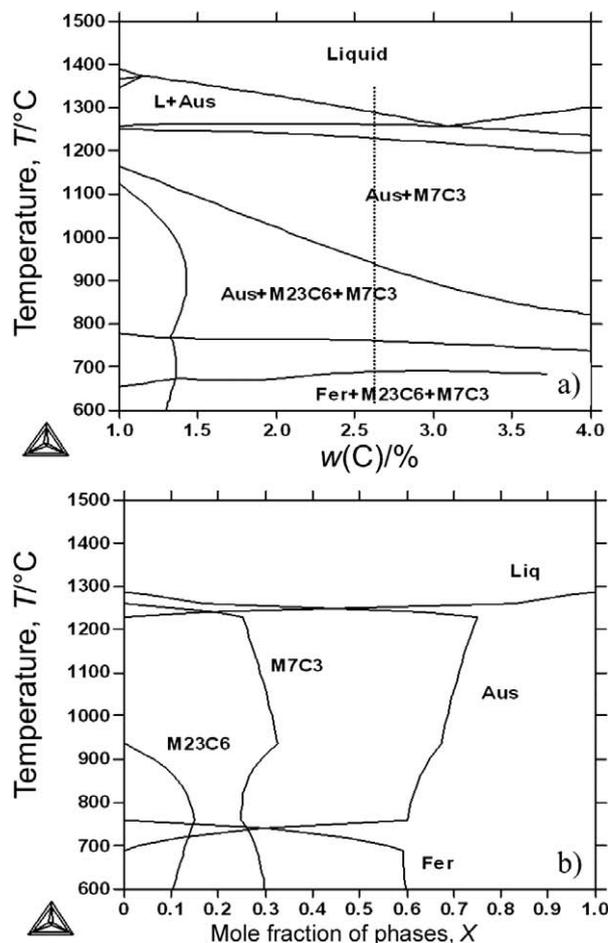


Figure 2: a) Isopleth of standard HiCrI and b) mole fraction of phases vs temperature microstructure

Slika 2: a) Isopleth standardne HiCrI; b) molski delež faz v odvisnosti od temperature

Figure 2a. Microstructure after heat treatment comprises tempered martensite dendrites and a eutectic consisting of an interpenetrating network of M_7C_3 carbides and tempered martensite.

The volume percentage of eutectic carbides assessed with Image Analysis is $28.0 \pm 4 \%$. This agrees well with that predicted by Thermo-Calc, using TCFE2000 database: the carbide volume percentage, as calculated by the lever rule at $950 \text{ }^\circ\text{C}$, is of 32% (**Figure 2b**). The discrepancy can be explained in view of the lower kinetics of carbides precipitation in the solid state than in the liquid phase. This is confirmed by **Figure 2b** showing that the fraction of M_7C_3 at solidus is much lower (25%) than at $950 \text{ }^\circ\text{C}$.

The solidification of the melt starts with the precipitation of primary austenite at $1287 \text{ }^\circ\text{C}$ ($T_L = \text{liquidus}$), while, the eutectic reaction starts at $1260 \text{ }^\circ\text{C}$ (T_{Ei}) and ends at $1228 \text{ }^\circ\text{C}$ ($T_{Ei} = T_s = \text{solidus}$). Looking to a novel cast iron with higher wear resistance, the composition of the modified HCrI should results as near as possible to the eutectic to maximize eutectic carbide amount. However, in designing the new composition, containing higher percentages of alloying elements than in the stan-

dard grade, attention was paid on avoiding hypereutectic solidification which may occur in internal sections of the shell ¹⁶, due to segregation. Large pro-eutectic carbides are known to worsen wear resistance and toughness, as well.

Therefore, the new composition was tailored to be slightly hypoeutectic. Since alloying elements influence eutectic carbon, Thermo-Calc was used to simulate solidification of alloys with different compositions, using standard products to validate the theoretical predictions. The content in Cr and Mo was modified. The width of the solidification range of the base alloy by varying content in Cr and Mo is reported in **Figures 3a and 3b**, respectively. While the increasing Cr causes a general reduction of solidification range, Mo plays the opposite effect ¹⁷. **Table 3** resumes the influence of an increasing content of both alloying on the solidification of standard HiCr. The parameter $T_L - T_{Ei}$ ($T_L = \text{liquidus temperature}$; $T_{Ei} = \text{eutectic start temperature}$) was taken as representative of the material hypoeutecticity and, on the basis of the experimental results, a value of $20 \text{ }^\circ\text{C}$ was safely established in the development of the new composition. Data in **Figure 3** show that the parameter $T_L - T_{Ei}$ is more sensitive to an increase in Cr than in Mo. Thus, in a material with 20% Cr proeutectic carbides may easily

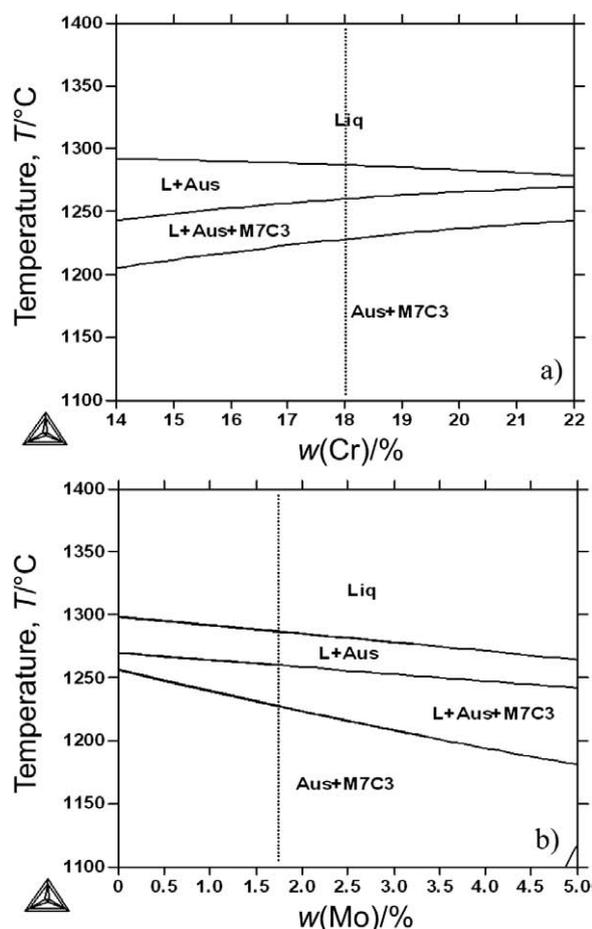


Figure 3: Influence of a) Cr and b) Mo, on the solidification range of standard HiCrI

Slika 3: Vpliv a) Cr in b) Mo na strjevalni interval standardne HiCrI

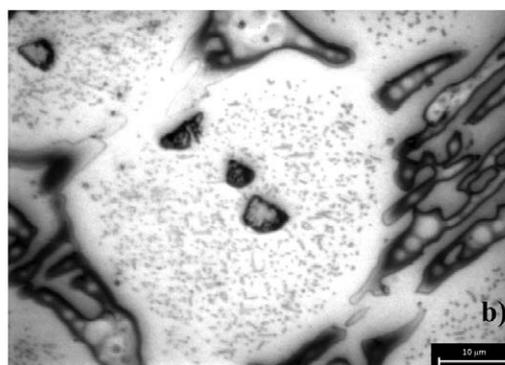
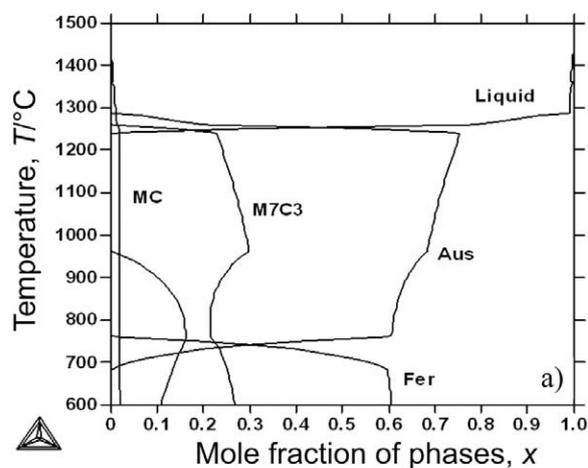


Figure 4: a) Mole fraction of solid phases vs. temperature b) proeutectic (Nb,V)C carbide within the metallic matrix

Slika 4: a) Molski delež faz v odvisnosti od temperature, b) proevtektični (Nb,V)C-karbid v kovinski matici

form at solidification, while no proeutectic carbides could be found up to high Mo content.

Table 3: Influence of Mo and Cr on the solidification range of standard HiCrI

Tabela 3: Vpliv Mo in Cr na strjevalni interval standardne HiCrI

	Standard HiCrI	Standard HiCrI 3% Mo	Standard HiCrI 20% Cr
T_L	1295 °C	↓	↓
T_{Ei}	1260 °C	↓	↑
T_{Ef}	1230 °C	↓	↑
$\Delta T_E = T_{Ei} - T_{Ef}$	30 °C	↑	↓
$T_L - T_{Ei}$	35 °C	↑	↓

An improved high Mo HCrI grade was thus designed on the base of the above results to obtain a value of $T_L - T_{Ei}$ greater than 20, after proper modification of the C content of the standard composition. A further development was the introduction of a stronger carbide former than Mo, like V and Nb. Depending on the content of these two elements, pro-eutectic precipitation of MC carbides is possible (Figure 4a) directly from the liquid

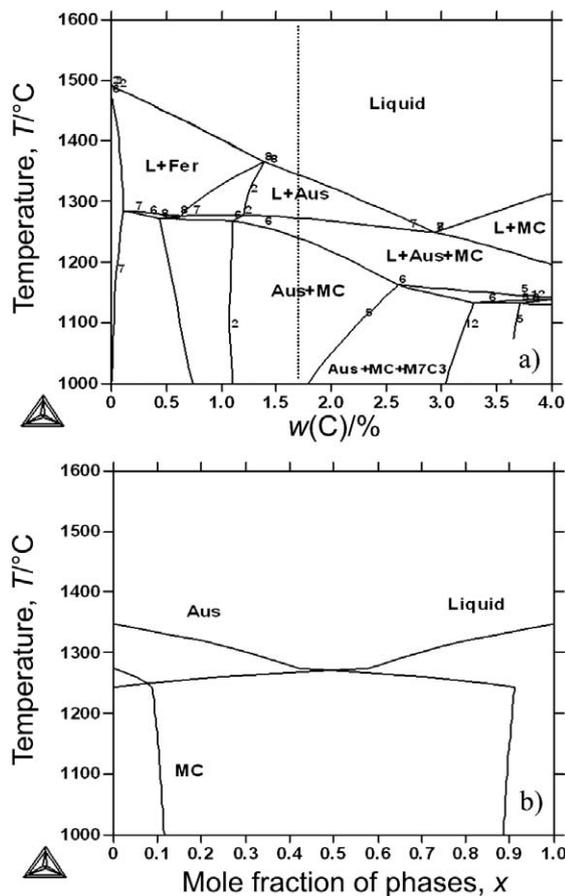


Figure 5: a) Isotherm of the studied HSS (dotted line represent the composition of the studied HSS). b) Diagram reporting the mole fraction of phases vs temperature.

Slika 5: a) Izoplete raziskanega HSS (črtkane črte pomenijo raziskani HSS); b) diagram, ki ponazarja molski delež faz v odvisnosti od temperature

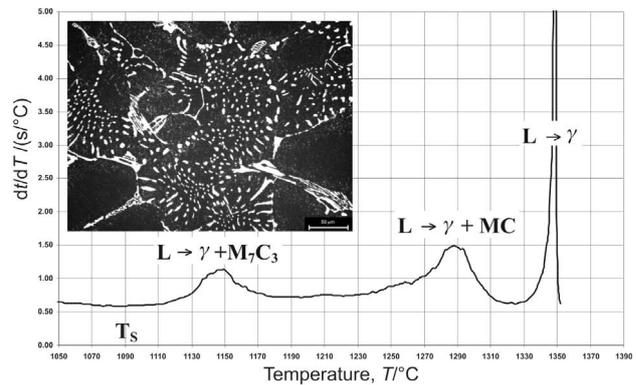


Figure 6: DTA showing the reactions occurring on solidification of HSS. In the frame the microstructure showing the presence of MC and M7C3 eutectic carbides

Slika 6: DTA, ki prikazuje reakcije med strjevanjem HSS. V okvirju je mikrostruktura, kjer so prikazani eutektični karbidi MC in M7C3

at much higher temperature than eutectic M7C3 carbides. Under this conditions, MC carbides are located in the interior of dendrites (Figure 4b), causing a substantial strengthening of the metallic matrix, without any embrittlement produced by interdendritic precipitation.

4 ALLOY DESIGN OF HIGH SPEED STEEL

The nominal composition of the base high speed steel in reported in Table 4.

Table 4: Nominal composition of the base HSS

Tabela 4: Nominalna sestava osnovnega HSS

C	Si	Mn	Cr	Ni	Mo	V
1.65-1.70	0.8-0.9	0.85-0.90	5.400	0.500	2.900	4.600

The related pseudo binary phase diagram calculated with Thermo-Calc is displayed in Figure 5a and the mole fraction of phases provided by equilibrium are shown in Figure 5b.

The solidification starts with the formation of primary dendrites of austenite at 1348 °C. The fraction increases up to 0.42 at 1273 °C, as the eutectic reaction, i.e., $L \rightarrow Aus + MC$ carbides starts. The amount of eutectic phases then increases by decreasing the temperature down to the calculated solidus temperature (1243 °C). At this point, the provided molar fraction of MC carbides is 8.8 %. In equilibrium, no other eutectic reactions are predicted.

Thermal analysis highlights that solidification starts at 1355 °C, in good agreement with the calculated value (Figure 6). The first eutectic reaction, i. e., $L \rightarrow Aus + MC$, starts at about 1320 °C and shows the fastest kinetic at about 1280 °C in correspondence of the DTA peak. A second eutectic reaction, i. e., $L \rightarrow Aus + M7C3$, starts at about 1180 °C and shows the maximum rate at 1160 °C. Solidification ends at about 1090 °C, i. e., at a much lower temperature than that provided by equilibrium

Table 5: Computer simulation of the solidification sequence in HSS (Thermo-Calc), using the Scheil Gulliver model

Tabela 5: Računalniška simulacija sekvenc strjevanja HSS (Thermo-Calc) po modelu Scheil Gulliver

Temperatures, $T/^\circ\text{C}$				Volume Pct of Eutectic Carbides, $\varphi/\%$			
T_L	T_{MC}	T_{M7}	T_S	MC	M_7C_3	M_2C	TOT
1348	1273	1175	1087	8.0	2.0	trace	10.0

Table 6: Computer simulation of the solidification sequence in HSS (Thermo-Calc), using the Scheil Gulliver model

Tabela 6: Računalniška simulacija sekvenc strjevanja HSS (Thermo-Calc) po modelu Scheil-Gulliver

DTA Temperatures, $T/^\circ\text{C}$				Volume Pct of Eutectic Carbides, $\varphi/\%$			
T_L	T_{MC}	T_{M7}	T_S	MC	M_7C_3	M_2C	TOT
1355	1320	1180	1110	7.0	2.8	trace	10.0

calculations (1243 °C). Discrepancies between calculations and DTA can be explained in view of the micro-segregation to which liquid is exposed during solidification, caused mainly by the limited diffusion of solute atoms in solid phase. The result of simulation using the Scheil-Gulliver model in Thermo-Calc better reflects the experimental one. In **Figure 7**, the comparison between calculated molar fractions and experimental data indicate a quite good agreement. Now, beneath the eutectic reaction allowing the precipitation of MC carbides, a second reaction involving the precipitation of M_7C_3 is provided, as well. The fractions of carbides assessed with image analysis and calculations are very close, such as the solidus temperatures. As expected, in view of the maximum possible segregation of the liquid provided by the Scheil model, the calculated solidus underestimates the experimental value.

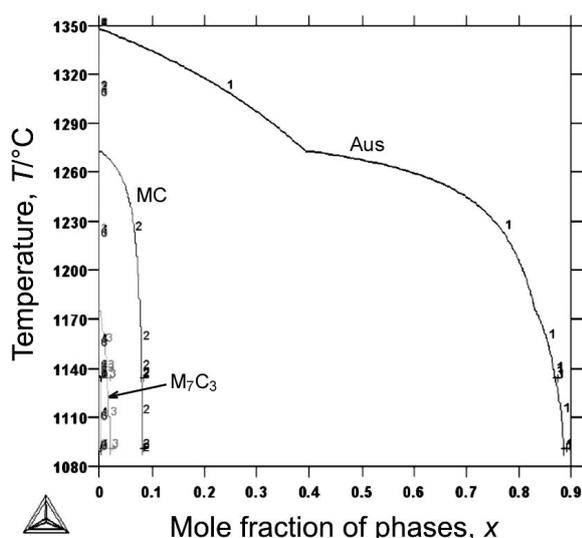


Figure 7: Molar fraction of solid phases provided by Thermo-Calc simulation using the Scheil Gulliver model

Slika 7: Molski delež faz, določen na podlagi Thermo-Calc simulacije po Scheil Gulliver modelu

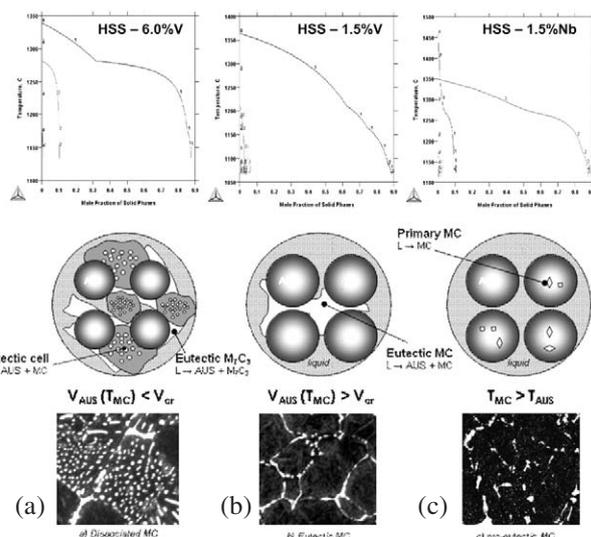


Figure 8: Morphology of MC carbides as a function of the content in V and Nb

Slika 8: Morfologija karbidov MC kot funkcija vsebnosti V in Nb

Hence, it can be stated that solidification proceeds under non equilibrium conditions, is caused principally by the limited diffusion in the solid phase.

This allows the author to use the Scheil-Gulliver model in the alloy design of such steel grade. Interdendritic eutectic carbides reduce toughness of HSS, since they constitute an almost continuous brittle network in

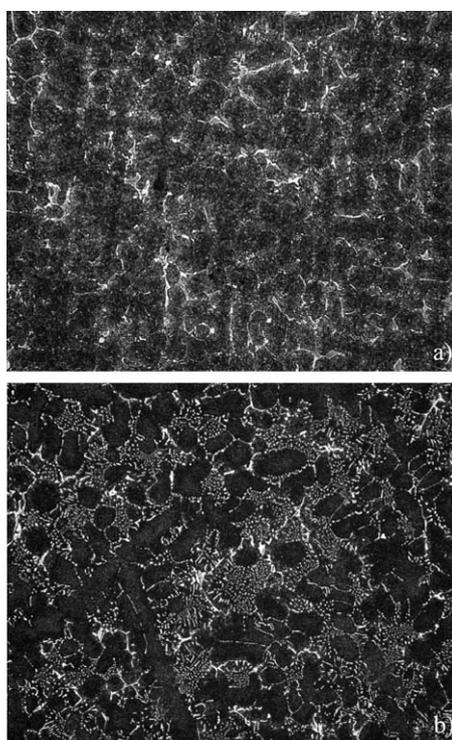


Figure 9: Increasing fraction of dissociated eutectic carbides by increasing V/Cr content (from up to down)

Slika 9: Naraščajoči delež disociacije evtektičnih karbidov pri rasti razmerja vsebnosti V/Cr (z zgoraj na dol)

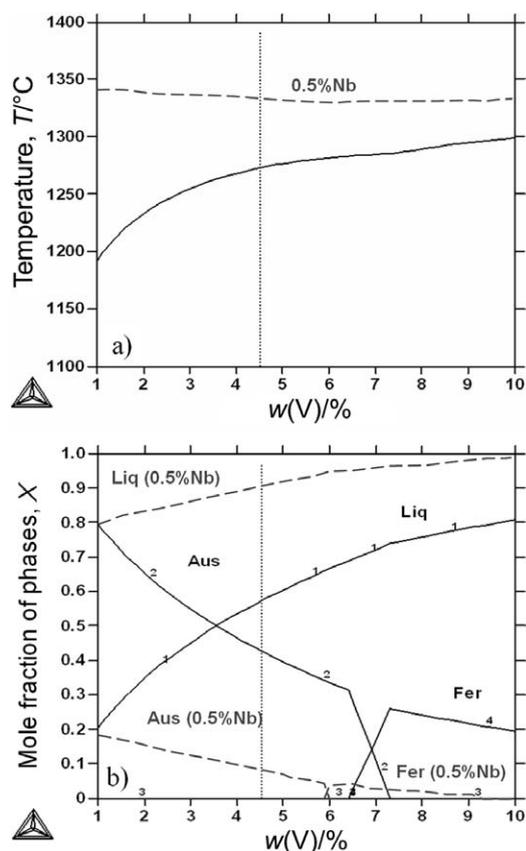


Figure 10: a) Eutectic MC start temperature and b) Mole fraction of phases as a function of V content at eutectic MC start

Slika 10: a) začetna temperatura MC-evtetika in b) molski delež faz v odvisnosti od vsebnosti V pri začetku MC-evtetika

the microstructure. Moreover, crack usually nucleates either at the carbide-matrix interface or inside the carbide particle, because the different elastic properties of the two constituents rise local stresses. Depending on the chemical composition, MC carbides tend to precipitate with different morphology.

By high C and V concentration VC homogeneously precipitates in eutectic cells to form a *dissociated eutectic* (Figure 8a). A relative high amount of fine and globular particles precipitate together with eutectic austenite, so that they are expected to be less detrimental for toughness than interdendritic carbides. The criteria to obtain this kind of microstructure is that the eutectic reaction is started with a high fraction of residual liquid phase. This allows eutectic cells to develop fully. Figure 8a shows the fraction of solid phases in the base HSS added with 6 % V. Two effects have to be underlined. The MC start temperature is increased with respect to the base material (1281 °C vs 1273 °C) and the corresponding fraction of liquid phase is higher (0.69 vs 0.58), as well. Indeed, Figure 8b shows the opposite result for the steel with V content decreased to 1.5 %. The MC start temperature drops to 1210 °C and the corresponding fraction of liquid phase to 0.38. Experimental results (Figure 9) confirm that the increasing content in V

facilitates the formation of a microstructure with a high fraction of dissociated eutectic.

It is interesting to point out that Thermo-Calc allows the easy calculation of the MC start temperature (Figure 10a) and of the fraction of liquid phase (Figure 10b) by varying the content in V. Continuous lines in Figure 10b highlight the increasing fraction of liquid phase at MC precipitation start as the content in V increases. Correspondingly, the fraction of solid, i.e. austenite up to 7.2 % V and ferrite above 6.5 %, decreases.

With the aid of data in Figure 10 a critical value for the fraction of austenite, for the formation of dissociated MC carbides could be determined. Increasing the V content above this value, the amount of eutectic cells progressively increases. A limiting factor is represented by the segregation of VC carbides during centrifugal casting of bimetallic rolls. Because of the lower density of these particles the liquid phase, MC carbides tend to segregate at the shell-core interface. This phenomenon is responsible for poor bonding and must be controlled to preserve roll quality. Hence, as proposed previously, Nb can be added, allowing the formation of composite Nb-V MC carbides with higher density. Nb is an MC former stronger than V. The addition of a small amount of this element dramatically increases the precipitation temperature of MC carbides (Figure 10). In Figure 10a and 10b dashed lines are referred to the standard alloy with 0.5 % Nb. As MC precipitate in the 1 % V – 0.5 % Nb alloyed high speed steel the fraction of liquid is about 0.8, i.e. much higher than that observed in the base material (0.2). As the content in V is close to the mass fraction 10 %, the fraction of liquid at MC precipitation start becomes almost 1, indicating the ultimate condition before the occurrence of proeutectic precipitation of MC carbides. This circumstance is verified by the higher amount of Nb, as confirmed by Figure 8c, showing the fraction of solid phases in the base HSS with addition of 1.5 % Nb. NbC particles now precipitate directly from the liquid at a much higher temperature than Nb-free or low-Nb grades promoting the heterogeneous nucleation of austenite dendrites. From this point of view, a refinement of the solidification structure can be obtained with properly selecting/handling Niobium. A basic form of inoculation can be realized.

Finally, in order to drive solidification transformations towards dissociate eutectic and to minimize the amount of interdendritic carbides, the chemical composition must be designed with a prevailing amount of V and a limited amount of Cr, Mo and W. As an example, if the amount in Cr is increased keeping V constant, the temperature of Cr-rich M_7C_3 eutectic carbides is increased, as their total fraction with respect to VC. The possibility of eutectic cells development is hindered by the concurrent precipitation of solid Aus + M_7C_3 (Figure 9). Moreover, carbon content has to be designed to both sustain the precipitation of carbides and harden tempered martensite.

5 CONCLUSIONS

The present paper briefly resumes the authors knowledge in the field of alloy design of high Speed Steels and High Chromium Irons by means of thermodynamic modelling. The basic criteria for the development of new alloys were illustrated in view of the eutectic reactions occurring during solidification. The influence of type and amount of different alloying elements on the solidification sequence was analysed and correlated to the microstructure. The results confirm the possibility to successfully employ computer modelling in the alloy design of high alloyed steels and cast irons.

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