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

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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 \( T_L - T_E \) (\( T_L \) = liquidus temperature; \( T_E \) = 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

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 treatment 1-3.

Different models have been applied to simulate the solidification behaviour of multicomponent systems like high speed steels 4-7 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-Calc 13 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

\[
G_m = G_m^{\text{ref}} - T S_m^{\text{id}} + G_m^{\text{ex}} + G_m^{\text{mg}}
\]

where \(G_m^{\text{ref}}\) is the reference free energy, \(-T S_m^{\text{id}}\) is the ideal mixing entropy, \(G_m^{\text{ex}}\) is the excess energy term and \(G_m^{\text{mg}}\) 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).

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 1: Microstructure of standard HiCrI](image)

![Figure 2: a) Isopleth of standard HiCrI and b) mole fraction of phases vs temperature microstructure](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>N. sub.</th>
<th>N of sites Per sublatticee</th>
<th>Sublattice Species (Va = vacancies)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1</td>
<td>1</td>
<td>Fe , Si , Mn , Cr , Ni , Mo , V , Nb : C , Va</td>
</tr>
<tr>
<td>FCC (austenite)</td>
<td>2</td>
<td>1 : 1</td>
<td>Fe , Si , Mn , Cr , Ni , Mo , V , Nb : C , Va</td>
</tr>
<tr>
<td>BCC (ferrite)</td>
<td>2</td>
<td>1 : 3</td>
<td>Fe , Si , Mn , Cr , Ni , Mo , V , Nb : C , Va</td>
</tr>
<tr>
<td>M23C6</td>
<td>2</td>
<td>3 : 1</td>
<td>Fe , Si , Mn , Cr , Ni , Mo , V , Nb : C , Va</td>
</tr>
<tr>
<td>M23C6</td>
<td>3</td>
<td>3 : 3 : 6</td>
<td>Fe , Cr , Fe , Cr , Si , Mn , Cr , Ni , Mo , V , Nb : C , Va</td>
</tr>
</tbody>
</table>

**Table 1:** Model of the phases considered in the calculations

**Table 2:** Chemical composition of standard HiCrI

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4–2.7</td>
<td>0.3–0.8</td>
<td>0.4–0.8</td>
<td>16–20</td>
<td>0.3–2.0</td>
<td>0.2–2.5</td>
<td>0.2–0.4</td>
<td>0.2–0.6</td>
</tr>
</tbody>
</table>
Figure 2a. Microstructure after heat treatment comprises tempered martensite dendrites and a eutectic consisting of an interpenetrating network of M7C3 carbides and tempered martensite.

The volume percentage of eutectic carbides assessed with Image Analysis is 28.0 ± 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 °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 M7C3 at solidus is much lower (25 %) than at 950 °C.

The solidification of the melt starts with the precipitation of primary austenite at 1287 °C (\(T_L\) = liquidus), while, the eutectic reaction starts at 1260 °C (\(T_{Ei}\)) and ends at 1228 °C (\(T_{Es} = T_S\) = 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 standard grade, attention was paid on avoiding hypereutectic solidification which may occur in internal sections of the shell, 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.

Table 3 resumes the influence of an increasing content of both alloying on the solidification of standard HiCr. The parameter \(T_L - T_{Ei}\) (\(T_L\) = liquidus temperature; \(T_{Ei}\) = eutectic start temperature) was taken as representative of the material hypoeutecticity and, on the basis of the experimental results, a value of 20 °C was safely established in the development of the new composition. Data in Figure 3 show that the parameter \(T_L - T_{Ei}\) more sensitive to an increase in Cr than in Mo. Thus, in a material with 20 % Cr proeutectic carbides may easily
form at solidification, while no proeutectic carbides could be find up to high Mo content.

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

<table>
<thead>
<tr>
<th></th>
<th>Standard HiCr</th>
<th>Standard HiCr 3% Mo</th>
<th>Standard HiCr 20% Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_L$</td>
<td>1295 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_E$</td>
<td>1260 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_E$</td>
<td>1230 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta T_E = T_E - T_E$</td>
<td>30 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_L - T_E$</td>
<td>35 °C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An improved high Mo HiCrI grade was thus designed on the base of the above results to obtain a value of $T_L - T_E$ 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 at much higher temperature than eutectic $\text{M}_7\text{C}_3$ 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 is reported in **Table 4**.

**Table 4: Nominal composition of the base HSS**

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65-1.70</td>
<td>0.8-0.9</td>
<td>0.85-0.90</td>
<td>5.400</td>
<td>0.500</td>
<td>2.900</td>
<td>4.600</td>
</tr>
</tbody>
</table>

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., $L \rightarrow \text{Aus} + \text{MC}$ 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., $L \rightarrow \text{Aus} + \text{MC}$, 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., $L \rightarrow \text{Aus} + \text{M}_7\text{C}_3$, 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.
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 model 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 M7C3 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.

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

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

<table>
<thead>
<tr>
<th>Temperatures, °C</th>
<th>Volume Pct of Eutectic Carbides, %</th>
<th>TCP</th>
<th>TMC</th>
<th>M7C3</th>
<th>TOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL 1348</td>
<td>1273</td>
<td>1175</td>
<td>1087</td>
<td>8.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>DTA Temperatures, °C</th>
<th>Volume Pct of Eutectic Carbides, %</th>
<th>TCP</th>
<th>TMC</th>
<th>M7C3</th>
<th>TOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL 1355</td>
<td>1320</td>
<td>1180</td>
<td>1110</td>
<td>7.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

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

Slika 7: Molski delež faz, določeni 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: Morfološka izgleda karbidov MC kot funkcija vsebnosti V in Nb

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

Slika 9: Naraščajoče deleži disociacije evtektičnih karbidov pri rasti razmerja vsebnosti V/Cr (z zgoraj na dol)
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 M7C3 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 + M7C3 (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.

6 REFERENCES

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