Utilizing Computational Materials Design in the Development of Iron-Based Alloys for Hardfacing

Robert Frykholm, Barbara Maroli, Karin Frisk
Höganäs AB, S-26383 Höganäs, Sweden

Abstract

Overlay welding using PTA or laser cladding is a technique commonly used to hardface components exposed to wear. State-of-the-art materials for these applications are nickel-based alloys with tungsten carbide particles embedded. Iron-based materials offer a cost effective alternative with lower environmental impact. The iron-based system offers different challenges compared to the nickel based system in terms of hard phase formation and stability upon processing. To be able to optimize composition and fulfill final application properties, microstructure evolution during processing needs to be understood and predicted. This paper focuses on computational materials design using thermodynamic calculations applied to multicomponent systems to optimize alloy compositions. Applying computational techniques allows investigation of a number of alloys, several orders of magnitude larger than what is possible experimentally. The method is used to generate large datasets, on which methods such as multivariate and statistical modeling can be applied to find composition regions fulfilling final application performance requirements. In this study, the method has been used specifically to optimize properties of PTA welded and laser cladded iron-based hard phase reinforced coatings for applications requiring resistance to abrasive and impact wear.

Introduction

Hardfacing by PTA welding and laser cladding is commonly used for coating of parts exposed to wear. With both methods, metallurgical bonding to the substrate is performed with limited dilution from the parent metal. Laser cladding typically has lower heat input and faster travel speed compared to PTA, which in turn results in lower dilution, reduced HAZ (heat-affected zone) and less distortion of the coated part. A drawback, in some cases, can be that the higher solidification rate of the laser cladding process increases the risk for crack and pore formation in the final clad. By proper choice of alloys and settings, this can, however, be reduced.

The most commonly used materials for hardfacing of parts exposed to severe abrasive wear are NiSiB alloy-mixes with tungsten carbides. These are relatively expensive materials, and for applications where both abrasive and impact wear resistance are required, iron based grades can instead be an interesting alternative. The iron based system offers high performance to cost ratio in combination with lower environmental impact. A hardfacing iron based overlay welded coating typically consists of a martensitic matrix with one or several hard phases dispersed. The abrasive and impact wear resistance of the coating depend on chemistry, shape, size, distribution and volume fraction of the hard phase as well as matrix microstructure. This in turn is affected by the cooling rate of the melt pool, which varies for different deposition methods and process parameters selected. Therefore, coatings with the same chemical composition can have different properties if deposited using different methods and/or different process parameters.

The chemistry of the clad can also vary depending on how the powder was applied. Different processes usually give different dilution from the substrate. Laser cladding can be performed with very low dilution, while PTA often results in higher dilution. A powder that should be possible to use in both processes must be able to tolerate higher levels of iron, assuming the substrate is a steel, without any significant changes in microstructure.

Also within a clad, properties can vary. In one clad, there can be different thermal history in different parts. To start with, the cooling rate will be different at the bottom and at the top of the clad. Heat transport is more effective in a metal substrate than in gas, resulting in higher cooling rate at the bottom. There is also an element of re-heating in overlap zones. Parts of the previous track will be re-melted when a new track is applied, and parts of it will undergo some form of heat treatment, with additional solid-state diffusion, which can have an effect on microstructure. Since parts are seldom heat treated after cladding, the as-received welded microstructure is usually the final structure.

The goal in alloy development for this type of applications is not only to achieve high performance, but also to achieve stable performance. The challenge is to find alloys as robust as possible. Alloys that can tolerate some dilution from the substrate and some variation in processing without any large variations in performance.

Iron based alloys used for hard facing are usually complex, consisting of several hard phase forming elements. Taking all factors into account, adding variations in processing, dilution etc., one realizes that the possible combinations and amount of experimental work needed to find new interesting alloys, and certify robustness of the alloys, becomes huge. Variation of single elements, or single process parameters can be performed experimentally to investigate the effect of that specific factor, but to understand and optimize a system, cross-effects from different factors also have to be considered. To fully explore
and optimize materials for hardfacing, the experimental work has to be complemented with other methods.

A powerful tool in alloy development is thermodynamic modeling using the CALPHAD approach. With this method, structures can be simulated using different types of calculations. It is a time and cost effective way to screen large composition and process windows in order to find interesting candidates for further evaluation. The method presently applied for the calculations is the use of Thermo-Calc software [1], controlled through a Python language based interface. The use of an interface makes it possible to process large data sets automatically, and allows large degree of freedom when it comes to set up the calculations. Thermodynamic calculations have long been used at Höganäs AB in alloy development, but previously in a manual mode. With manual input, the calculation process was not as time effective, and the amount of calculations possible to perform within a development project was somewhat limited. With the Python interface, several parameters can systematically be varied, and large data sets can be calculated. Input for the calculations is generated in matrix form as a .csv file, where limits and steps of the parameters of interest, such as chemistry, temperatures etc., are set. Calculation times are kept down by applying parallel computing, and with current setup, millions of calculations can be performed per day. Both input data and calculation results are stored in a data warehouse for easy access for further evaluation.

The simplest case for prediction of microstructure is to perform equilibrium calculations. With the high cooling rates in the welding process, one could argue that the material is far from equilibrium. Still, this is a relevant first approximation. The calculations show which phases are expected to form, and for which temperatures precipitation and transformation becomes possible. Additionally, it is possible to see if hard phases precipitates as primary phases or not. This is important information, since primary phases and eutectic phases have different morphology. Due to primary phases formation in the liquid, they have the possibility to grow, and compared to eutectic hard phases become relatively large.

A second calculation type used is the Scheil-Gulliver solidification. This calculation is performed with the assumption that no diffusion occurs in the solid phases, and that the liquid phase, at all temperatures, is homogeneous. This calculation result will deviate from equilibrium as temperature is decreased. This somewhat affects the amount and composition of different phases present.

In reality, even at high cooling rates, some diffusion will occur. This is theoretically treated by using a diffusion module in the software. However, with high cooling rates, the time step in a diffusion calculation needs to be kept very small, and this, combined with multi-component and multi-phase systems, makes the calculation rather time consuming. One calculation can take several hours, or even days. Consequently, this makes diffusion calculations less practical to use for large input matrixes over wide composition ranges. It is more a tool to study specific phenomena in the cladding process, e.g. the effect of reheating when a second track is applied in the cladding process.

![Figure 1: Comparison between equilibrium calculation (grey), and Scheil solidification (black) for Rockit 706.](image)

The setup allows for calculations in several steps, where parts of a result set can be used automatically as input in new calculations, and different types of calculations can be combined. This is a powerful tool for simulating a cladding process, or to study in detail certain phenomena during cladding.

The output from calculations is phase fractions, compositions and distributions. The calculation results are quantitative, not qualitative. It is up to the materials scientist to interpret the results and set conditions that needs to be fulfilled, or to apply further modelling to obtain actual mechanical properties and performance. Criteria that can be set are e.g. type and amount of hard phases, formation of primary hard phases, FCC-BCC transformation, and composition of matrix. For stable performance, martensite transformation should be ensured.
within the whole process window, ferrite and retained austenite should be avoided. If corrosion resistance is important, the chromium level of the matrix should be kept sufficiently high.

With large volumes of calculations, there will also be large volumes of results to analyze. The result matrix will be n-dimensional, and with $n > 3$, visualization by traditional methods becomes difficult. The simplest approach is to sort and filter, one dimension at a time, based on fulfillment of the criteria set. With this method, candidates for new alloys can be identified and further evaluated. However, in a complex system, there will be many cross effects which cannot intuitively be comprehended. In order to understand the combined effect of all factors, more advanced methods are necessary. Currently, different statistical and mathematical methods are evaluated for more effective interpretation of the results.

When performing calculations using the CALPHAD approach, it is important to bear in mind that the model databases used as input data for the calculations are based on experimental results. When new alloys are developed, the compositions might be outside the specifications for available databases. Then, the thermodynamic description of the phases present might not be accurate enough to deliver reliable results. Experimental work to verify phases and phase compositions is essential to improve available databases and ensure reliable predictions.

A new material developed at Höganäs is Rockit® 706. The aim was to develop an alloy for extreme wear applications with hard carbides dispersed in a martensitic matrix. By combining vanadium, chromium and a high carbon content, the material was optimized both regarding performance and cost sensitivity. V forms hard cubic carbides (MC-type) [2], which are beneficial for wear properties. This has been shown for A11 steel, which has a relatively high V-content [3]. By lowering V and keeping high C-content, a eutectic Cr-rich structure is introduced. This structure helps to maintain hardness and wear performance, but with a lower V-content, cost is reduced.

For laser cladding settings resulting in very high cooling rate, there can be problems with cracking. To cover these processes, a version of the material with lower C-content is also available, Rockit 606. At very high cooling rates, this material offers good weldability combined with high hardness.

**Experimental**

Höganäs AB steel powders Rockit® 706, Rockit® 606, and A11, with chemical composition reported in Table 1 were investigated. Sieve cut used was 53 to 150 µm to fit the requirements of the powder feeders used.

For thermodynamic calculations, the database TCFE9 was used [2].

PTA welding was performed using a commercial unit from Commersald (300J). EN S235JR mild structural steel was used as substrate material. The tracks were deposited using a welding current of 130 A, a feed rate of 30 g/min and welding speed of 10 cm/min. Argon admixed with 5% hydrogen was used as shielding gas. Welding parameters were selected to achieve clads with good bonding to the substrate and dilution < 15% in one layer.

| Table 1: Main alloying of investigated powder grades. |
|----------------|---|---|---|---|---|
|                | C  | V  | Cr | Si | Fe  |
| Rockit® 706    | 2.6| 6.0| 5.0| 1.0| Bal.|
| Rockit® 606    | 2.0| 6.0| 5.0| 1.0| Bal.|
| A11            | 2.45| 9.75| 5.25| 1  | Bal.|

For laser cladding, a Laserline LDF 7000-40 fiber-mated direct diode laser was used. Deposition was performed using both circular and rectangular laser beams having different spot sizes. EN S235JR mild steel substrates were used for the experiments. The aim was to produce clads with sufficient bonding to the substrate, dilution below 5% and minimize the risk for crack and pore formation.

The overlays were sectioned perpendicular to the coating direction, moulded in Bakelite, ground and polished using standard procedures for metallographic sample preparation. The samples were etched in Vilella (100 ml 95% ethyl alcohol, 1 g picric acid, 4 ml concentrated HCl) to reveal the matrix microstructure. Etched cross-section specimens were examined using a light optical microscope (LOM) and unetched specimens using a scanning electron microscope equipped with an EDS detector. Rockwell hardness HRC was measured using Wolpert Universal hardness tester. The coatings were ground, seven hardness indents were performed on the flat surface and the average was calculated.

Low stress abrasive wear testing was performed according to ASTM G65 standard, procedure A [3], by using a commercial multiplex sand/wheel abrasion tribometer (Phoenix tribology TE 65). A schematic of the testing is illustrated in Fig. 2. Five sample replicas per material were tested.

**Figure 2: Schematic of abrasive wear testing according to ASTM G65 standard, procedure A**
Results and discussion

Both calculations and experimental work were conducted to find a suitable candidate alloy for high wear applications. Aim was set for a structure containing hard carbides, a eutectic interdendritic structure, and a martensitic matrix. The system found to be suitable was a vanadium and chromium alloyed steel with high carbon content. To fine tune the composition and to validate the predictions, different alloying levels were experimentally evaluated. To visualize correlation between experiments and calculations, and effect of alloying, Fig. 3 shows two examples from the development work: Rockit 706 and a low alloy version with composition Fe-5.7Cr-2V-1.5C. At low V and C, the structure consists of martensitic dendrites and interdendritic eutectic. No MC-type carbides are detected. When V and C is increased, MC carbides are found in the structure. These carbides can be seen as bright particles in the martensitic matrix. They are also present in the bright eutectic structure, but there it is very difficult to separate the phases. The presence of these hard carbides is beneficial for wear properties and therefore desired for the intended application.

Equilibrium calculations for the compositions are presented in Fig. 4. As can be seen, there is a significant difference in amount of MC-type carbides, while the amount of M7C3 is similar in both materials. This matches the experiments, where the amount of M7C3 containing eutectic is similar for both alloys, while MC is only detected in Rockit 706.

To better understand the microstructure of Rockit 706, a SEM study with EDX mapping was performed. Figure 5 shows a SEM micrograph of the material. In this image, the MC-type carbides, appearing as black, become much more visible than in the LOM micrograph. The size of the carbides is a few micrometers. Spot analysis with EDX was performed in different parts of the structure, and the results are found in Table 2. It was verified that the carbides are vanadium carbides, and that the eutectic structure is enriched in chromium due to the presence of M7C3 carbides. There is an iron signal for the vanadium carbides, but this contribution comes from the matrix. 

![Figure 3: Comparison between Fe-5.7Cr-2V-1.5C (top) and Rockit 706 (bottom).](image)

![Figure 4: Equilibrium calculation comparison between Rockit 706 (black) and Fe-5.7Cr-2V-1.5C (grey).](image)
Table 2: EDX analysis of different parts of the microstructure

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<tr>
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<th>V</th>
<th>Cr</th>
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<tr>
<td></td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>Eutectic</td>
<td>5.1</td>
<td>7.5</td>
</tr>
<tr>
<td>MC</td>
<td>54</td>
<td>4.9</td>
</tr>
<tr>
<td>Matrix</td>
<td>1.6</td>
<td>3.1</td>
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</table>

Figure 6 shows the result from elemental mapping. This overview shows how the elements are distributed in the coating. Iron seems to be found in all phases, except in the vanadium carbides, which contain mainly vanadium and carbon, but also some chromium. Actually, there is some iron present also in the VC, but due to how contrast is set in the maps, the VC appears free from iron. Chromium is found to be concentrated to the eutectic structure and the carbides, but is to some extent also present in the matrix. Besides in the MC-carbides, vanadium is also found in the eutectic structure.

The structure indicates the importance of working with different types of calculations to understand a system and predict the structure. Figure 1 showed a comparison between equilibrium and Scheil calculation. In the equilibrium result, vanadium carbide was the only carbide predicted to form during solidification. $M_7C_3$ were predicted to form first in solid state. From Fig. 3, it is, however, clear that there is a eutectic structure comprising chromium carbides, which is also predicted in the Scheil calculation.

Mechanical performance was evaluated for PTA clads of Rockit 706. The results were compared with performance of A11 steel. This is a material with a similar microstructure. The difference is that A11 is designed to have a structure consisting of a martensitic matrix reinforced with vanadium carbides. There is no or very low presence of other hard phases. Equilibrium calculation and microstructure of A11 can be found in Fig. 7.

As mentioned earlier, heat treatment is not standard procedure for overlay welding hardfacing, but sometimes it is performed to restore or alter the substrate material microstructure. For the application where Rockit 706 is used, two different heat treatments performed by industry were identified and tested. One was a quenching operation, where the specimens were held at 900°C for 1 hour and then quenched in oil, the other was a high temperature tempering at 700°C for 2 hours, after which the specimens were cooled in air. Hardness and wear resistance of PTA coatings of Rockit 706 and A11 were investigated, and results are reported in Fig. 8. As can be seen, Rockit 706 performs very well, as welded hardness is around 65 HRC and wear loss is 14 mm$^3$. Both hardness and wear are better than for A11. The quench operation has no significant effect on the coating hardness, but seems to somewhat improve wear resistance for both materials. The tempering process has larger influence on performance. Hardness is decreased and wear is increased. The results, however, show a much higher stability of Rockit 706 compared to A11, regarding both hardness and wear.
Figure 7: A11, Scheil calculation and LOM micrograph showing VC in a martensitic matrix.

Figure 8: Hardness and wear resistance for Rockit 706 and A11, as welded and after heat treatments.

In Fig. 9, elemental mapping of V and Cr in Rockit 706 for the three conditions is found. The images show that the MC carbides remain stable, while there is a change in the matrix and eutectic structure, especially when annealed. For the 900°C treatment, there is an indication on increase of chromium in the MC-carbides, while for the 700°C treatment Cr is more evenly distributed in the structure. An important difference between the two treatments is that 900°C is above the austenite transformation temperature, while 700°C is below. The 700°C treatment will therefore have a softening effect on the martensite. Since martensite is the main structure in A11, this treatment has large effect on performance, while in Rockit 706, there is still, besides vanadium carbides, a eutectic structure to ensure performance.

High carbon content can sometimes be a problem in laser cladding processes with very high solidification rate, such as when small circular spots are used. There might in that case be a risk for porosity or cracks in the clads. To ensure high performance of the material in a wide range of cladding processes, trials were performed with laser cladding and different carbon levels.

Due to relatively high carbon content in relation to vanadium in Rockit 706, there is a possibility to decrease carbon, without significantly altering the solidified structure. Figure 10 shows a calculation with two different carbon contents, 2.6 and 2 wt.%, corresponding to the two materials Rockit 706 and Rockit 606. Vanadium is a strong carbide former, and most of the vanadium will go into the MC carbides. 2wt.% carbon is sufficient to maintain the amount of this phase. The figure shows very little decrease in MC carbides with 2% carbon. The decrease in M7C3 is more pronounced. Figure 11 shows microstructure after laser cladding.

When laser cladding is performed with Rockit 606, it shows good weldability and clads without porosity can be achieved, as seen in Fig. 12. Performance is close to Rockit 706. Hardness is on the same level, and wear loss is slightly higher. Table 3 shows a comparison between the two materials. Hardness for Rockit 606 in PTA is also included. A drop in hardness is
detected for PTA, and it is beneficial to maintain the high carbon content for PTA to ensure hardness.

**Figure 9:** Vanadium and chromium EDX maps, as welded (top), quenched (middle), tempered (bottom).

**Figure 10:** Comparison between 2.0 wt.% C (grey) and 2.6 wt.% C (black).

**Figure 11:** LOM micrograph of laser cladded Rockit 606.

**Figure 12:** Pore and crack free clad of Rockit 606 deposited using circular 6.3 mm laser spot.

**Table 3:** Hardness and wear of Rockit 706 and Rockit 606 coatings.

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<th>ASTM G65 A (mm³)</th>
<th>Hardness (HRC)</th>
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<tr>
<td>Rockit 706 (PTA)</td>
<td>14</td>
<td>65</td>
</tr>
<tr>
<td>Rockit 606 (LC)</td>
<td>24</td>
<td>65 (62 HRC, PTA)</td>
</tr>
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</table>
Conclusions

By combining thermodynamic calculations and experimental work, two Fe-based alloys optimized for PTA welding and laser cladding were developed.

Rockit 706 is a material for extreme wear applications, showing a hardness of 65 HRC and a wear loss of 14 mm$^3$ according to ASTM G65.

Rockit 706 shows high stability regarding hardness and wear performance with heat treatments.

Rockit 606 is a lower C-level alternative optimized for laser cladding with small spot size, showing hardness of 65 HRC and 24 mm$^3$ wear loss.

References


