ALLOY DESIGN FOR ULTRA–HIGH TEMPERATURE STEAM TURBINE APPLICATIONS:
PHASE–FIELD SIMULATION OF THE REMELTING PROCESS

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Abstract

A multiphase–field model coupled to thermodynamic databases is presented which is able to handle multicomponent and multiphase structural evolution on microscopic scale. Databases assessed according to the CALPHAD approach are connected online to the phasefield code using the thermodynamic software package Thermo–Calc and a fortran interface. Multi–binary extrapolation is used to make simulations of realistic systems viable. A unit cell approach is used to apply this model to the remelting process, which locally is simulated as a directional solidification under high thermal gradients.

The model is applied to remelting of the three Ni–base superalloys IN706, IN617 and Waspaloy, respectively, which are used as a starting point for the development of new alloys for ultra–high temperature steam turbine applications. From the results secondary phase formation, incipient melting as well as homogenisation times and temperatures can be predicted. Additionally an alloy–specific freckle criterion is calculated from the simulation results, which allows the estimation of the freckle risk under typical remelting conditions.

Keywords: phase–field, simulation, thermodynamic coupling, superalloys, alloy development

Introduction

In the design process of new alloys for steam turbine applications, the remelting process, being the first step in the lifecycle, is of special importance. The production of high quality ingots from Ni–based superalloys by vacuum arc (VAR) or electroslag remelting (ESR) is not in all cases as straightforward as e.g. for IN706, where even large ingot sizes are obtained in industrial practice. One typical problem is the formation of freckles, which arise from liquid density inversion in the mushy zone. This effect is a direct consequence of the microscopic segregation process and can completely prohibit the use of a specific alloy as it is the case for large Waspaloy ingots. Further problems can be caused by precipitation of brittle phases which can not be removed easily by homogenisation treatment.

Simulation tools are needed which are able to predict the remeltability as well as the quality and properties of the ingot for promising alloy compositions without the necessity of expensive solidification experiments. Simulation has to be done at a microscopic scale as composition primarily affects the microsegregation behaviour and macrosegregation is successfully prevented by modern remelting techniques. Even the freckles which usually extend over larger distances are eventually caused by segregation inside the mushy zone.

A steep increase in complexity arises from the fact that commercial Ni–based superalloys are multicomponent systems which cannot be successfully described without using sophisticated thermodynamic software packages like Thermo–Calc [1] together with extended thermody–
namic databases. Today several databases for Ni–based superalloys are available [2], which are assessed from a high number of experimental informations using the CALPHAD method [3] and which permit extrapolation of the thermodynamic behaviour to the desired alloy compositions.

In this paper a two–dimensional unit cell model is presented which describes dendritic solidification in industrial remelting processes. Microstructure and secondary phase formation is simulated using the multiphase–field method [4,5] which is online coupled to thermodynamic databases. This combination of tools, as described in this paper, allows the effective prediction of the remeltability of new alloys.

**Multiphase–Field Model Coupled to Realistic Thermodynamic Data**

The phase field method is a powerful tool for describing the spacial evolution of interfaces between different phases. Several phase–field models have been presented in literature which differ in terms of the free energy density in the interfacial region as well as in the way how they were derived [6–8].

The following approach is based on a multiphase–field concept which has been published earlier [4,5]. The development of the phase–field parameter $\phi_i$ of a phase $i$ in a multiphase system is described as the sum of the pair–wise interactions with all other phases $j$ (in the case of a double well potential):

$$
\frac{d \phi_i}{dt} = \sum_j \mu_{ij} \left[ \sigma_{ij} \left( \phi_i \nabla^2 \phi_j - \phi_j \nabla^2 \phi_i + \frac{36}{\eta_{ij}} \phi_i \phi_j (\phi_i - \phi_j) \right) + \frac{6}{\eta_{ij}} \phi_i \phi_j \Delta G_{ij} \right]
$$

(1)

Here $\mu_{ij}$ is the interface mobility, $\sigma_{ij}$ the surface energy, $\eta_{ij}$ the interface thickness, $N$ the number of coexisting phases and $\Delta G_{ij}$ the driving force for the transformation between the phases $i$ and $j$.

A distinctive feature of the multiphase–field model presented here regards the coupling to the diffusion equation. In contrast to the Wheeler–Boettinger model [6] instead of the overall composition $c^k$ the phase compositions $c^k_i$ and $c^k_j$ are used to determine the driving force $\Delta G_{ij}$. This makes the model more suitable for the input of realistic thermodynamic data. Multiphase diffusion for a component $k$ is then given as the sum of the fluxes in the individual phases which are calculated from the composition gradients $\nabla c^k_i$ using the diagonal terms $D_{ik}$ of the diffusivity matrix:

$$
\frac{dc^k}{dt} = \nabla \cdot \left( \sum_{i=1}^N \phi_i D_{ik} \nabla c^k_i \right)
$$

(2)

The thermodynamic calculation now has to provide three informations from the database, a) the relation between the phase compositions $c^k_i$ which are in contact, b) the thermodynamic driving force $\Delta G_{ij}$ in eq. (1) and c) some nucleation conditions for secondary phases.

For diffusion–controlled processes like those simulated in this paper a pseudo–equilibrium approach can be applied which assumes local equilibrium at the interface. The driving force $\Delta G_{ij}$ results from a slight deviation from equilibrium which we get by construction of a common tangent to the gibbs energy functions $f_i$ and $f_j$ ($a^k = df^k/c^k$ is the slope of the Gibbs energy curve which has to be identical for both phases):
\[
\Delta G_{ij} = f_i - f_j + a^k (c_i^k - c_j^k) \tag{3}
\]

Eq. (3) must be true for all components simultaneously, regarding as additional condition the conservation of composition at each interface point:

\[
\sum_i \phi_i c_i^k = c^k \tag{4}
\]

This is done in a pair–wise manner for all phase interactions \(ij\). Eq. (3) is solved by use of the software package Thermo–Calc [1] which has been enhanced by an extra routine in order to meet also eq. (4). Together with a realistic database even complex multicomponent and multi–phase problems can be solved in this way.

**Multi–Binary Extrapolation**

Even though the above description provides a complete solution within the local equilibrium approximation immense calculation times would be needed to include the thermodynamic calculations for multicomponent alloys in each time step and for all interface gridpoints. Therefore, together with the equilibrium calculation the slopes \(m_{ij}^k\) and \(m_{ji}^k\) of the liquidus (solvus) and the solidus plane are extracted at the equilibrium compositions \(c_{i0,k}^k\) and \(c_{j0,k}^k\) respectively in the directions of every component \(k\). By this procedure we get a number of linearized phase diagrams for each interface cell. These phase diagrams are additionally shifted by the temperature equivalent \(\Delta T^\text{off}_{ij}\) of the calculated equilibrium deviation \(\Delta G_{ij}\) from eq. (3) if \(\Delta S^\text{trans}_{ij}\) is the transformation entropy:

\[
\Delta T^\text{off}_{ij} = \Delta S^\text{trans}_{ij} \Delta G_{ij} \tag{5}
\]

From the local phase diagrams we get a good interpolation of the thermodynamic behaviour and time–consuming “real” equilibrium iterations have to be done only from time to time, when local compositions or the temperature show considerable deviation from the conditions at the last linearisation.

From the interpolation of the equilibrium temperatures

\[
T^\text{eq}_{ij} = T^\text{0.eq}_{ij} + \sum_k m_{ij}^k (c_i^k - c_{0.k}^k) \tag{6}
\]

(or the analogue expression using the solidus slopes \(m_{ij}^k\)) we obtain the interpolated driving force, if \(T\) is the actual temperature at this gridpoint:

\[
\Delta G_{ij}^* = -\Delta S^\text{trans}_{ij} (T - T^\text{eq}_{ij}) \tag{7}
\]

Using eq. (6) and the analogue formulation with \(m_{ij}^k\) together with eq. (4) finally the interpolated local phase compositions can be calculated:

\[
c^*_{i} = \frac{c^k - \sum_j \phi_j (c_{0.k}^j - c_{ij}^0 m_{ij}^k m_{ij}^k)}{\sum_j \phi_j m_{ij}^k m_{ij}^k} \tag{8}
\]

**The Unit Cell Approach**

In industrial remelting processes local solidification conditions are characterised by high thermal gradients and low cooling rates. This leads to dendritic morphology which is close to the cellular–dendritic transition region, i.e. tertiary arms are weakly developed, and due to grain
selection the dendrite trunks are oriented in the direction of the thermal gradient. Under such conditions segregation can be described in a isothermal two-dimensional cut through the primary dendrite [9–11] better than between secondary arms like in plate models.

Fig. 1 shows the unit cell used in the simulation throughout this paper. As dendrites often show fourfold shapes the dendritic cross section is assumed to be of such symmetry within a regular dendritic array. Due to this symmetry only a quarter of one dendritic cross section is included into the unit cell. The third dimension along the dendrite axis corresponds in this unit cell approach to the time variable which describes growth inside one fixed cross section or at the same time the gradient along the mushy zone. The side length of the unit cell is correlated to the dendritic primary spacing $\lambda$, and can be estimated from the thermal gradient $G$ and the solidification velocity $v$ using the theory of Hunt [12]:

$$\lambda = KG^{-1/2}v^{-1/4} \quad (9)$$

According to Goldschmidt [13] the factor $K$ can be considered as a unique constant for superalloys. Alternatively $K$ can be estimated from experiments.

Fig. 1: Comparison of the dendritic array given by the unit cell approach to a real dendritic array (CMSX–6). The small quadratic area indicated by the black square is the unit cell which is included into the simulation.

**Freckle Criterion**

In this paper a freckle criterion is derived which does not describe the effects of the solidification process parameters as done by other authors [14–17], but focuses on the specific tendency of the alloys for freckle formation. This tendency can be assessed from the composition distribution along the mushy zone which can be calculated using the unit cell model together with the multiphase-field approach described above. The composition change in direction of the temperature gradient is reconstructed from the time evolution of the average liquid composition calculated in the unit cell. The liquid density $\rho$ is determined using the empirical approach of Sung et al. [18]:

$$\rho^{-1} = \sum_{k} \frac{c_{liq}^k}{\rho_{ref}^k + \Lambda(T - T_{ref})} \quad (10)$$
According to this approximation $\rho$ is calculated from the densities of the pure element melts $\rho_{Ref}^k$ and the thermal expansion coefficients $\Lambda^k$ given at a reference temperature $T_{Ref}$ by molar volume averaging with the molar compositions $c_{liq}^k$. Now for all positions $h$ in the mushy zone a buoyancy force $f_B(h)$ is calculated. This is done by integration of the liquid density differences in the melt between this point and the top of the mushy zone weighted with the liquid fraction:

$$f_B(h) = \int_{z=0}^{h} f_L(z) (\rho(z) - \rho(0)) dz$$  \hspace{1cm} (11)

In order to get a freckle criterion which is independent from the temperature gradient integration is done over the temperature $T$ instead of the height $h$:

$$f_B^*(T) = \int_{T=T_{liq}}^{T_{liq}} f_L(T) (\rho(T) - \rho(T_{liq})) dT$$  \hspace{1cm} (12)

The formation of a freckle will be initiated at the point where the value of $f_B^*$ is maximum, defining the freckle parameter $f_{FR}$:

$$f_{FR} = \max(f_B^*(T))$$  \hspace{1cm} (13)

If no liquid density inversion occurs at all the value of $f_B^*$ is arbitrarily taken at the temperature where the fraction liquid is 0.5.

**Results**

a) Simulation of IN706 Solidification:

For simulation of IN706 solidification under remelting conditions a 7 component equivalent composition has been chosen which includes all elements which play an important role in the solidification process. This composition is shown in tab. 1. Input parameters for calculation are the primary dendrite spacing $\lambda$ which according to experimental findings was set to 200 $\mu$m and a typical cooling rate of 0.5 K/s. Diffusion constants for the liquid phase were estimated as $1.0 \times 10^{-5}$ cm$^2$/s for Carbon and $5.0 \times 10^{-6}$ cm$^2$/s for the other elements. The temperature-dependent diffusion coefficients for fcc (the primary phase) are given in tab. 2. Due to the lack of literature data these values were also used in the secondary phases. All thermodynamic data were taken from the 11 component database nifedata [8] provided from Thermotech by online coupling to Thermo-Calc during simulation.

Tab. 1: Composition used for IN706 simulation

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>bal</td>
<td>37.7</td>
<td>17.1</td>
<td>1.83</td>
<td>1.8</td>
<td>0.55</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Tab. 2: Temperature dependent diffusion coefficients in the fcc phase expressed as $D=D^0 \times \exp(-Q/RT)$ [19,20]

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^0$ (cm$^2$/s)</td>
<td>10</td>
<td>1.8</td>
<td>5.2</td>
<td>1.3</td>
<td>4.1</td>
<td>0.01</td>
<td>1.87</td>
<td>0.0066</td>
<td>14.2</td>
</tr>
<tr>
<td>$Q$ (kJ/mol)</td>
<td>269</td>
<td>282</td>
<td>289</td>
<td>283</td>
<td>275</td>
<td>201</td>
<td>268</td>
<td>96</td>
<td>194.8</td>
</tr>
</tbody>
</table>
Fig. 2: Left side: Comparison of the fraction solid vs. temperature curve for the phasefield simulation (bold line) and a Thermo−Calc Scheil calculation. Right side: Corresponding microstructure evolution represented by the Nb composition in the unit cell. In frame 4 complete solidification is reached.
Fig. 2 shows the solidification progress predicted from simulation. In the diagram at the left side the fraction solid vs. temperature dependence for simulation is compared to the results of a Scheil Calculation done by Thermo−Calc using the same thermodynamic database. The differences between the two curves are relatively small at the beginning and get considerably large at the end of the solidification process. This is mainly due to back diffusion which is taken into account by our phase−field model. Another slight difference at the very beginning is caused by an initial undercooling of the dendrite (tip undercooling) which was set to 2 K in our model.

On the right side of fig. 2 the microstructure during solidification is shown for 4 timesteps, which are also indicated in the fraction−solid curve. Displayed is the Nb distribution within the isothermal cross−section through the dendritic unit cell. As can be seen the primary dendrite is growing according to the fourfold symmetry of the unit cell. Approaching the end of solidification secondary phases are formed which can be identified by their increased Nb composition (timesteps 3 and 4).

In fig. 3 the composition distribution after complete solidification is shown for all elements. In addition to a strong microsegregation for almost all elements, three different secondary phases can be distinguished: The small MC carbides which are forming first during solidification can be identified by their high carbon content. The Laves phase covers a bigger area in the cross−section and is relatively high in Nb. Just before freezing of the remaining liquid, \( \eta \) appears as third phase, indicated by its low content of Fe and Cr.

b) Homogenisation:
More important than their formation is the sissolution of these phases during the production process of steam engine parts, especially if brittle phases are involved. As secondary phase formation during solidification is a metastable process most of them can be dissolved by heating at a temperature just below the melting point. This homogenisation treatment can also be of importance because it increases the melting temperature which directly after solidification can be very low due to strong segregation. If this temperature is exceeded during forging, the material can be destroyed by incipient melting.

Homogenisation can be observed also in simulation, where this process is demonstrated for IN706 (fig. 4). In this calculation the temperature after solidification was raised to 1093°C for several hours. As can be seen the Laves and \( \eta \) phase is vanishing slowly due to the diffusion process while MC carbides are stable and show only ripening after 33 hours. In reality transformation to \( \text{M}_2\text{C}_6 \) would be expected, which has not been taken into account here.

c) Prediction of the Freckle Risk:
As shown above the freckle risk can be estimated from the liquid density inversion which is caused by segregation during solidification. The resulting freckle number has been calculated from phase−field simulations for the three candidate alloys IN706, Waspaloy and IN617, which have been chosen as a reference for the development of new steam turbine alloys [21].
Fig. 3: Microstructure after solidification represented by the distribution of the different alloying elements in the unit cell. The secondary phases MC, Laves and η can be distinguished by their characteristic compositions.

Fig. 4: Secondary phase dissolution by heat treatment at 1093°C. Shown is theNb composition in atomic percent.
Tab. 3 summarizes the compositions and tab. 4 the calculated freckle numbers for the three alloys. The negative values for IN706 and IN617 demonstrates that no density inversion is observed at all. At the contrary Waspaloy shows a positive freckle number. The results are in good agreement with practical experience: While IN706 and IN617 can be used for production of even large ingots, Waspaloy is known to be very critical with respect to freckle formation so that the remelting of ingots bigger than 1 meter in diameter is effectively impossible. From the freckle calculations also a modified Waspaloy composition has been proposed for use in steam turbines [21].

Tab. 3: Compositions of Waspaloy and IN617

<table>
<thead>
<tr>
<th>at%</th>
<th>Ni</th>
<th>Fe</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN617</td>
<td>bal</td>
<td>0.55</td>
<td>12.7</td>
<td>24.6</td>
<td>5.48</td>
<td>0.67</td>
<td>–</td>
<td>2.39</td>
<td>–</td>
<td>0.29</td>
</tr>
<tr>
<td>Waspaloy</td>
<td>bal</td>
<td>0.58</td>
<td>13.5</td>
<td>21.2</td>
<td>2.68</td>
<td>3.73</td>
<td>0.006</td>
<td>2.58</td>
<td>0.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Tab. 4: Calculated freckle numbers

<table>
<thead>
<tr>
<th>alloy</th>
<th>IN617</th>
<th>Waspaloy</th>
<th>IN706</th>
</tr>
</thead>
<tbody>
<tr>
<td>freckle number [gKcm⁻³]</td>
<td>–0.224</td>
<td>0.069</td>
<td>–0.354</td>
</tr>
</tbody>
</table>

Conclusion

It has been shown that the multiphase–field model coupled to thermodynamic databases is a powerful tool for the prediction of microstructural evolution at a microscopic scale. The pragmatic multi–binary extrapolation of the local phasediagrams allows the application to complex multicomponent and multiphase problems like Ni–based superalloys and precipitation of secondary phases at reasonable calculation times.

Using a unit cell approach for dendritic solidification under remelting conditions the tool was applied to the prediction of the remeltability of potential ultra high temperature steam turbine alloys. While in the paper results for the commercial alloys IN706, Waspaloy and IN617 are shown, the future potential consists in the application to modified alloy compositions. Important parameters like brittle phase formation, incipient melting temperatures and heat treatment cycles needed for homogenisation can be estimated without need for expensive experiments. The risk of freckle formation during remelting is evaluated by an alloy–specific freckle criterion. For the three model alloys a good coincidence between this criterion and industrial experience has been found.

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References