Prediction of phase distribution pattern in phase field simulations on Mo$_5$SiB$_2$-primary areas in near eutectic Mo-Si-B alloy

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Abstract. A Mo-10.9Si-20.3B (if not stated otherwise all compositions are given in at.%) alloy was modeled using the phase field method with linearized phase diagrams and thermodynamic data. The simulation results showed that there are two specific microstructural constituents. According to the simulations and experimental microstructural investigations the primary Mo$_5$SiB$_2$ phase observed in this study was combined by the Mo$_3$Si-Mo$_5$SiB$_2$ eutectics. The overall composition of the both primary and eutectic area was probed and the phase evolution along with the concentration change of the core areas were explored and visualized in the solidification domain. To verify the accuracy of the simulation results, they were comprised with the experimental achievements. In terms of the fraction of phases, the portion of the primary phase and the eutectic constituent and the phase distribution pattern our results were in good agreement with the experimental observations.

1. Introduction

Materials applied in high temperature functions must maintain their mechanical and physical properties at high surface temperatures. Currently used Ni-based superalloys have met their limit near 1100 °C and therefore many efforts have been conducted to find an alternative to meet the high temperature application’s requirements and to reach the aim of an optimum use of resources. Regarding these aspects, Mo-Si-B alloys experienced great attention through the last years. The excellent creep behavior and acceptable oxidation resistance of these ternary alloys are favorable for high temperature applications [1-5].

In their recent thermodynamic calculations, Yang and Chang [5, 6] have shown that two-phase and three-phase alloys, which pass through eutectic reactions among the solidification, are located in the Mo-rich portion of the alloy. Liquidus projection conducted by Yang and Chang was considered to figure out the consequence of the reaction pathway with respect to the alloy’s composition in this study [5, 6].

In our previous studies [3, 4] we investigated the phase distribution pattern for the alloy Mo-17.5Si-8B which is located close to the ternary eutectic point and has finished in a volume fraction of almost 50 % Mo$_3$Si and equal amounts of Mo$_5$SiB$_2$ and Mo$_{ss}$ phases.

There are a couple of phases containing boron and silicon in the Mo-Si-B ternary system that have ascended the alloy’s melting point. However, the only ternary phase Mo$_5$SiB$_2$ (the so-called T2-phase) has received high attention because of its excellent mechanical properties at ultra-high temperatures which are superior compared to Ni-based superalloys [1, 2]. High creep strength along with the
relatively low density made this ternary phase of the Mo-Si-B system a favorable structural material. Furthermore, two-phase alloys like Mo$_5$-Mo$_3$SiB$_2$ or more complex alloys like Mo$_x$-Mo$_3$Si-Mo$_5$SiB$_2$ have shown improved toughness [1]. Accordingly, the Mo$_5$SiB$_2$ rich portion of the Mo-Si-B system is the focus of the present study. Moreover, because of favorite properties of the eutectic composition a combination of a primarily solidified Mo$_5$SiB$_2$ phase and a ternary eutectic constituent is preferred [7]. Therefore, we have modified the previous model with more detailed thermodynamic data [8] so that we could investigate the solidification behavior of an alloy located in the Mo$_5$SiB$_2$ primary area.

Microstructural evolution and solidification reactions of Mo-Si-B alloys in different primary solidification were studied using casting experiments by Ha et al. [1]. They reported a dendritic primary Mo$_5$SiB$_2$ phase along with a ternary Mo$_x$-Mo$_3$Si-Mo$_5$SiB$_2$ eutectic phase for alloy Mo-10.9Si-20.3B. Figure 1 shows the location of the alloys investigated in the both the current and the previous studies.

Figure 2 shows a SEM-BSE image of the as-cast microstructure of the assigned alloy. Probing the phase fractions resulted in 70 % Mo$_5$SiB$_2$ primary phase with the balance of the ternary eutectic Mo$_x$-Mo$_3$Si-Mo$_5$SiB$_2$.

Figure 1. Schematic view of the primary solidification areas according to Yang and Chang [5, 6] and the chemical composition of investigated alloys; alloy shown in red was examined in a previous study [3, 4], the alloy marked in green is subject of the current study.

Figure 2. SEM-BSE micrograph of Mo-10.9Si-20.3B, thankfully provided by Ha et al. [1].
First of all we performed the simulation for predicting the solidification of Mo-10.9Si-20.3B alloy within the phase-field method to examine the evolution of the $\text{Mo}_5\text{SiB}_2$ primary phase and the $\text{Mo}_3\text{Si-Mo}_5\text{SiB}_2$ ternary eutectic phase. A comparison between the simulations and experimental observation of Ha et al. [1] proved that the simulations results were in a good agreement with the experimental achievements.

In the following the phase evolution in dependence on the temperature was investigated. In order to probe the dispersion pattern of the elements, their change in the temperature field was examined for both the eutectic and primary area.

2. Simulation procedure
The solidification process was considered to include three solid phases: $\text{Mo}_3\text{Si}$, $\text{Mo}_5\text{Si}$ and $\text{Mo}_5\text{SiB}_2$ [6]. In order to define the correlation between phases and phase fractions, the liquidus projection was performed using the Factsage software [8].

The domain was considered to be a two-dimensional field. The size of the calculation domain along with the grid size has a considerable effect on the calculation time and accuracy. The calculation domain should have an optimal size so that along with generating the most accurate results, the calculation must be performed in a reasonable time. Therefore, after examining various numerical setups, the domain size was adjusted to 24×24 microns containing 90,000 cells with a grid size of 0.08 microns.

In order to apply the actual operational parameter precisely, a thermal gradient was not considered in the model. The temperature trend was applied linearly changing over the time, starting from a temperature in which the whole domain is liquid.

In the simulation domain both of the side walls were adjusted to periodic boundary conditions. Since there is no flux of materials during the solidification, the insulation boundary condition was set for both the top and the bottom wall.

Latent heat release of the produced phases can affect the temperature changes and from a microscopic point of view it may cause some early generated nuclei to melt, which might change the phase distribution pattern. However, the overall phase fractions will be preserved. Due to the serious impact on the computational time, the latent heat was not considered in this study. Nevertheless, the microstructure and phase distribution pattern were acceptably compatible with the experimental observation. It is planned to apply this variable for all phases in prospective studies.

Initial concentrations for the components of the simulation domain were assumed to be at equilibrium situation. At the beginning of the process it was presumed that the composition of the whole domain is unified and equal to Mo-10.9Si-20.3B.

The phase evolution was studied by setting up the nucleation procedure for the phases out of liquid. In order to predict the potential points for the new nuclei of each phase, it was set up into the model to check the possibility of phase generation in each grid cell based on three credentials: the temperature, the composition of the cell and melting temperatures of each phase. The new generated nuclei were supposed to be randomly oriented and it was adjusted to check their stability at every time step to vanish the metastable ones.

The time step was set to automatic and the initial temperature was set to 2370 K. At this temperature, all of the domain must be liquid, based on Factsage prediction. In order to predict the solidification pathway, the correlation between phases and element repartitioning during solidification were taken from the phase diagram. To define the boundary conditions for the used phase field software Micress, two isothermal cross sections of the ternary phase diagram must be incorporated, i.e. one cross section for each phase. The composition changing rate for each element along with the two cross sections should be defined. Table 1 shows the input of the phase diagram for all three phases. It is noteworthy that the phase $\text{Mo}_3\text{Si}$ is considered as stoichiometric composition. Further it should be noted that all the calculations in this study were performed in the isotropic condition.
Table 1. Applied values for the definition of the phase diagram; reference points 1 and 2 stand for the isothermal section at 2275 K and 2278 K, respectively.

| Phase | Mo₃Si | Mo₅SiB₂ | Mo₆ss |
|-------|-------|---------|-------|
| Temperature of reference point (K) | 2275 | 2275 | 2275 |
| Temperature difference of crosses (K) | 3 | 3 | 3 |
| Si content at reference point 1 (at.%) | 19.5 | 18.6 | 18.6 |
| Si content at reference point 2 (at.%) | 25 | 10.4 | 4 |
| B content at reference point 1 (at.%) | 5.9 | 6.8 | 6.8 |
| B content at reference point 2 (at.%) | 0 | 25 | 0 |
| dT/dC (K/at.%) for Si at reference point 1 | 10 | -10 | -10 |
| dT/dC (K/at.%) for Si at reference point 2 | Inf | 10 | Inf |
| dT/dC (K/at.%) for B at reference point 1 | -7.5 | 15 | 15 |
| dT/dC (K/at.%) for B at reference point 2 | Inf | 15 | Inf |

The mechanical interaction between phases would affect the phase boundary evolution and consequently the solidification pattern. The surface energy and mobility between different phases are applied from our previous study [3, 4]. Table 2 simplifies the applied values for the required variables.

The diffusion of the elements into different phases was considered by applying the modified values of diffusion coefficients which were used in our previous study. Table 3 shows the diffusion variables of the components in the phases. The simulations were performed with different interface thicknesses and an interface with a width of seven cells proved to result in the most compatible results.

Table 2. Applied values for the operational and thermodynamic parameters.

| Parameter | Value |
|-----------|-------|
| Cooling rate [K/s] | 100 |
| Surface energy between liquid and phases [J/cm²] | 10⁻⁴ |
| Entropy of fusion in solid phases [J/cm³K] | 0.1 |
| Entropy of fusion in liquid phases [J/cm³K] | 0.9 |
| Diffusion coefficient in liquid [cm²/s] | 2 · 10⁻⁴ |

Table 3. Applied values for the required diffusion parameters.

| Phase | Mo₅SiB₂ | Mo₃Si | Mo₆ss |
|-------|---------|-------|-------|
| Diffusion coefficient (cm²/s) | 10⁻⁸ | 10⁻⁹ | 10⁻⁹ |

3. Results and discussion

According to Ha et al.’s research, solidification of the referred alloy composition would result in about 70 % of the domain occupied by the primary Mo₅SiB₂ phase [1]. The balance is occupied with the ternary eutectic composition: Mo₆ss, Mo₃Si and Mo₅SiB₂. The phase distribution and the distribution of components among the phases for the solidified domain are shown in Figure 3.

The phase distribution pattern as well as the volume fractions of the primary and the eutectic phases were entirely compatible with the Ha et al.’s [1] observations. Figure 4 shows the phase distribution pattern for the Mo-10.9Si-20.3B alloy during the arc melting process. In order to have a thorough comparison of the phase distribution, the phase fraction in both experimental results and simulations are compared to each other in Table 4.

After reproducing Ha et al.’s [1] experimental observations via phase field method, the results were compared to each other and proved to be completely compatible. Figure 5 compares the simulation’s prediction of phase distribution and experimental achievements.
Figure 3. Schematic distribution of components in the solidified Mo-10.9Si-20.3B alloy.

Table 4. Comparison of phase fraction of Mo-10.9Si-20.3B for experiments and simulations.

| Phase        | Mo₅SiB₂ | Mo₅Si | Mo₆n |
|--------------|---------|-------|-------|
| Fraction (%) in experiments | 76      | 17.1  | 6.9   |
| Fraction (%) in simulations   | 74      | 18.6  | 7.4   |

Figure 4. The phase distribution evolution and pattern of Mo-10.9Si-20.3B during cooling down the simulation domain from 2380 K to 2258 K.

The solidification pattern was studied by considering the concentration evolution of each component in the all phases over the time. The visualized results showed that the solidifying paths of all phases meet each other in a ternary point which is supposed to be the ternary eutectic point. Figure 6 shows the solidification path for both the primary and the eutectic phases.
Figure 5. Microstructural evolution of alloy Mo-10.9Si-20.3B in experimental observations vs. simulation.

Figure 6. Solidification path derived by simulations for a) primary $\text{Mo}_5\text{SiB}_2$ and b) eutectic composition in the context of Yang and Chang’s prediction of the solidification path and primary areas [5]. The orange line refers to primary $\text{Mo}_5\text{SiB}_2$, the blue line refers to $\text{Mo}_\alpha$ and the red line refers to $\text{Mo}_3\text{Si}$. The green point shows the initial composition of the melt. Path a) shows that the liquid start to solidify from the initial composition and by reducing the temperature follows the shown way to eutectic point.

As is apparent in the graphs, the primary $\text{Mo}_5\text{SiB}_2$ phase starts to solidify from the initial composition Mo-10.9Si-20.3B and evolve to the stoichiometric composition. Afterwards the residual melt enriches in its Mo concentration until it reaches the ternary eutectic composition at the ternary point. At this point a coexistence of the four phases, namely liquid, $\text{Mo}_\alpha$, $\text{Mo}_3\text{Si}$ and $\text{Mo}_5\text{SiB}_2$ is present and determines the ternary eutectic reaction. By calculation of the Si and B content of each phase it was concluded that $\text{Mo}_\alpha$ tends to the assumed maximum solubility of 4 at.% for Si [9]. Also it was found that both $\text{Mo}_5\text{SiB}_2$ and $\text{Mo}_3\text{Si}$ are stoichiometric compositions with respect to the Si content as defined in the model.
As shown in ternary graphs, there is a slight difference between the ternary eutectic point predicted by Yang and Chang and our simulation results. It is worth mentioning that, for their thermodynamic calculations, Yang and Chang assumed a possible variation of the composition of the phase Mo$_5$SiB$_2$ by (Mo)$_{0.625}$(B,Si,Va)$_{0.375}$ due to the presence of vacancies (Va) in the Mo$_5$SiB$_2$ lattice. However, in order to generate the phase diagram within the Factsage data along with preserving Yang and Chang’s database we have considered a solubility range for B in Mo$_5$SiB$_2$ as (Mo,B)$_{0.625}$(B,Si,Va)$_{0.375}$. Moreover, Yang and Chang assumed the phase transitions to be in equilibrium conversion but due to the high cooling rate in the simulation setup, which is a typical boundary condition in casting processes, it is not expected to really meet the equilibrium phase transition.

5. Conclusions

The main objective of this research was to investigate the solidification of the alloy Mo-10.9Si-20.3B using the phase field method to extend the already published model [3, 4] which was only able to predict the solidification and microstructure evolution for an eutectic alloy composition. In order to perform this study the Micress software was used. To verify the software’s generated phase fractions, micro-structural morphologies and component distribution pattern, the experimental study of Ha et al. [1] was used. The before-mentioned composition was selected for this investigation, because it consists of a considerable amount of primary Mo$_5$SiB$_2$ phase, which is supposed to perform an enhanced mechanical behavior in combination with the ternary eutectic Mo$_5$-Mo$_3$Si-Mo$_5$SiB$_2$ microstructural constituent. The simulation results showed to be in a good agreement with the experimental observations and the presented model is able to predict the observed phase formation patterns and the amount of the individual phases.

The solidification path extracted from the compositional changes of the components in the phases has shown that the melt solidifies from its initial composition and then, after producing a high amount of primary Mo$_5$SiB$_2$, the residual melt turns into a ternary composition at the ternary eutectic point. The point varies slightly from Yang and Chang’s calculations [5] due to the fast cooling and also slightly different assumptions in thermodynamic calculations. However, the practical and simulation results were in a good agreement.

In order to improve the current study the release of latent heat might be considered. For future studies it is planned to calculate the heat capacity data for the phases and apply them to the model. Also the boundary condition which is derived from the experimental process affects the solidification behavior and the microstructure. It must be reviewed if the simulations could also be performed considering other solidification processes such as zone melting.

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