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Phase field simulation of a directional solidification of a ternary eutectic Mo-Si-B Alloy

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Abstract
We present a eutectic Phase-Field Model for a Mo-Si-B alloy at ternary eutectic composition (Mo-17.5Si-8B), under a constant thermal gradient. The process parameters like cooling rate and thermal gradient were obtained directly from the experimental procedure of zone melting. The equilibrium interface geometries and interface mobility were calculated using an isotropic model.
The phase equilibria and the other thermodynamic parameters are obtained by linearizing the Mo-Si-B ternary phase diagram.
We have investigated the effect of process parameters on the lamellar growth pattern and lamella pattern stability with respect to the Jackson-Hunt minimum undercooling spacing theory. In order to examine the generated results by the model, they were validated with experimental observed microstructures and measurements and showed to be in a good agreement with the experimental observations.

Keywords: Mo-Si-B alloy – Phase field simulation – Ternary Eutectic

1. Introduction

1.1. Phase-Field Method

Investigating the advancement of interface pattern and formation of complex microstructures during solidification, have been attractive subjects for the scientific researches. Predicting solidification behavior and microstructure pattern in alloys have been always interestingly focused, since having a good sight of the microstructure helps to predict the final physical and chemical properties of the alloy. One of the most powerful tools for predicting the interface evolution pattern is the Phase-Field Method [1 - 6].

The main logic behind the phase transformations indicates that the free energy reduction is the principal driving force of the phase transformations. Taking this attitude into account, the phase-field method has been implemented to simulate microstructure evolution during solidification [2]. In the phase-field models (PFM's), in order to define the distribution of the contacting phases and interface in the whole system, a phase field variable shown by Φ is announced. The value of the Φ in liquid region is adjusted to $\Phi = 0$, and in solid region $\Phi = 1$.

In the whole PFMs, the interface is considered as a thin layer but finite in width. In the classical assumptions which are abolished, the interfaces were assumed to be a sharp layer. However, recent investigations apply diffusive interface in which the interface is considered to be a combination of the liquid and the present solid phases. The phase field and diffusion field equations are derived from a definition of the free energy functional of the system, which is decreasing with time [1, 3].

During the past decades there are several attempts to perform a phase field simulation of the solidification process based on the Spinodal decomposition. In this approach, it is assumed that the crea-

tion of new nuclei will happen when the distance between lamellae get large enough. However, the experimental investigations proved that in some cases the prediction may not be accurate because despite the simulation's prediction, due to the abrupt tilting and oscillating of the lamellae the distance between them would slightly reduce and the potential position for the nucleation would be vanished.

Recently, Pezzolla and Steinbach have rearranged the multiphase field method by introducing a new variable called interface field. Thank to interface field variable, the changes of phase-field at each distinct point would be decomposed into sum of changes of independent interface fields at the point [1, 11].

1.2. Mo-Si-B Alloys

Newly Ni-based super-alloys have met their ultimate application limits in getting used in turbines and industry's further demands has induced lack of more efficient materials. An ongoing demand for the materials which are capable to operate in even increasing temperature has led to development of new ultrahigh temperature structural materials. A potential class of materials is Mo-Si-B alloys [7, 9].

A principal point for the current microstructural researches is to find appropriate alloy compositions and processing procedure to reach the optimal balance among the mechanical properties. In order to enhance the microstructures and recognize the correlation between microstructures and material properties, it is necessary to have a comprehensive knowledge of the phase equilibria and physical properties of the Mo–Si–B system [8].

In this paper we firstly derive isotropic phase-field and diffusion equations for eutectic solidification by using the interface-field method and the equal chemical potential condition and we perform a phase field simulation of Mo-Si-B ternary eutectic alloy's solidification. Consequently we present the results for conducting the simulation with the different operational parameters and then we investigate the instability of the lamellae and the interface in variation of lamella spacing and try to investigate the compatible range of lamellae spacing which adequately fits the Jackson-Hunt's minimum undercooling lamella spacing according to the given undercooling and growth velocity [13].

2. Eutectic Phase Field Model

In the eutectic solidification of Mo-Si-B alloy, there are three solid phases; Mo_3Si having an A15 crystal structure, Mo_5SiB_2 which has T2 structure and a Mo solid solution forming from the liquid phase; L [8]. Phases are designated by ϕ_i (i=0,1,2,3). According to the principles of phase field, sum of the ϕ_i at each region must be equal to 1 [1]. The main principle in determining the phase evolution pattern is to investigate the evolution of Phase field variable in the pass of the time. The time derivative of the ϕ shows the development of each phase clearly:

$$\dot{\Phi}_s(X,t) = \mu[\sigma(\nabla^2\Phi_s - \frac{(1-\Phi_s)(1-2\Phi_s)\Phi_s{}^2}{\eta}) + \frac{1}{\eta}\Delta G\Phi_s(1-\Phi_s)] \quad (1)$$

Where μ is interfacial mobility, η is interfacial thickness and σ denotes interfacial energy [1, 11].

The total free energy function of the system volume V is given by

$$F = \int_V [f^p + f^t + \lambda_L(\sum_i \Phi_i - 1)]dV \quad (2)$$

In which the λ_L is the Lagrange multiplier and f^p is defined as follow:

$$f^p = \sum_{j>i}\sum_{i}[-\frac{\varepsilon_{ij}^2}{2}\nabla\Phi_i \cdot \nabla\Phi_j + \omega_{ij}\Phi_i\Phi_j] \quad (3)$$

Where ε_{ij} is the gradient energy coefficient and ω_{ij} is the height of double well potential.

And f^t, which is thermodynamic potential could be defined by:

$$f^t = \sum_i \Phi_i f^i(c_i) \quad (4)$$

The $f^i(c_i)$ is the free energy density of i phase with composition of c_i [1].

2.1. Phase-field equation

Kim et al. have defined a step function $S_i(x, t) = 1$ when $\phi_i > 0$ and $S_i(x, t) = 0$ otherwise. So the number of coexisting phases could be given by:

$$n(x,t) = \sum_{i=0}^{3} s_i(x,t) \quad (5)$$

Taking account to this concept the time derivative of the phase field variable could be shown as following:

$$\frac{\partial\Phi_i}{\partial t} = \frac{1}{n}\sum_{j\neq i} s_{ij}(\frac{\partial\Phi_i}{\partial t} - \frac{\partial\Phi_j}{\partial t}) \quad (6)$$

Thank to this consideration, the change of phase field takes place at the interface. It emphasizes that motions of the interface of each phase with the other participating phases will affect the changes of the phase field variable contributing to it. It should be noted that these equations are derived with keeping the assumption that all the coexisting phases have equal chemical potential [1].

2.2. Diffusion equation

The main concept in deriving the diffusion equation is mass conservation. Accompanying the free energy of the system it could be mentioned as following:

$$\frac{\partial c}{\partial t} = \nabla D\sum_i \Phi_i \nabla c_i \quad (6)$$

In which the D is diffusivity dependent on the phase field [1].

It is worth noting here that all of the calculations in this study were assumed to be in isotropic condition.

3. Methods and Parameters

The most important part of conducting a transition simulation is to identify the phase equilibria and recognize the thermodynamic description and material characteristics of the present phases. The Mo rich part of Mo-Si-B system has been the subject of many researches. It was firstly review by Nowotny et al. and they have performed the isothermal section at 1600 °C and have extracted the involved phases in assistance with XRD [10].

Nunes et al. have studied the liquidus projection of the Mo rich portion of Mo-Si-B system and reported that there are six principal reactions along the solidification. They found that a ternary eutectic reaction occurs in the system and have reported that it is as following:

$L \rightarrow Mo_3Si + Mo_5SiB_2 + Mo_{(ss)}$ [8].

Performing the liquid projection process with the Factsage™ software has proved that the eutectic transition occurs at about 2260 ºK. Figure 1 shows the prediction of the phase equilibria and temperature of the phase transitions.

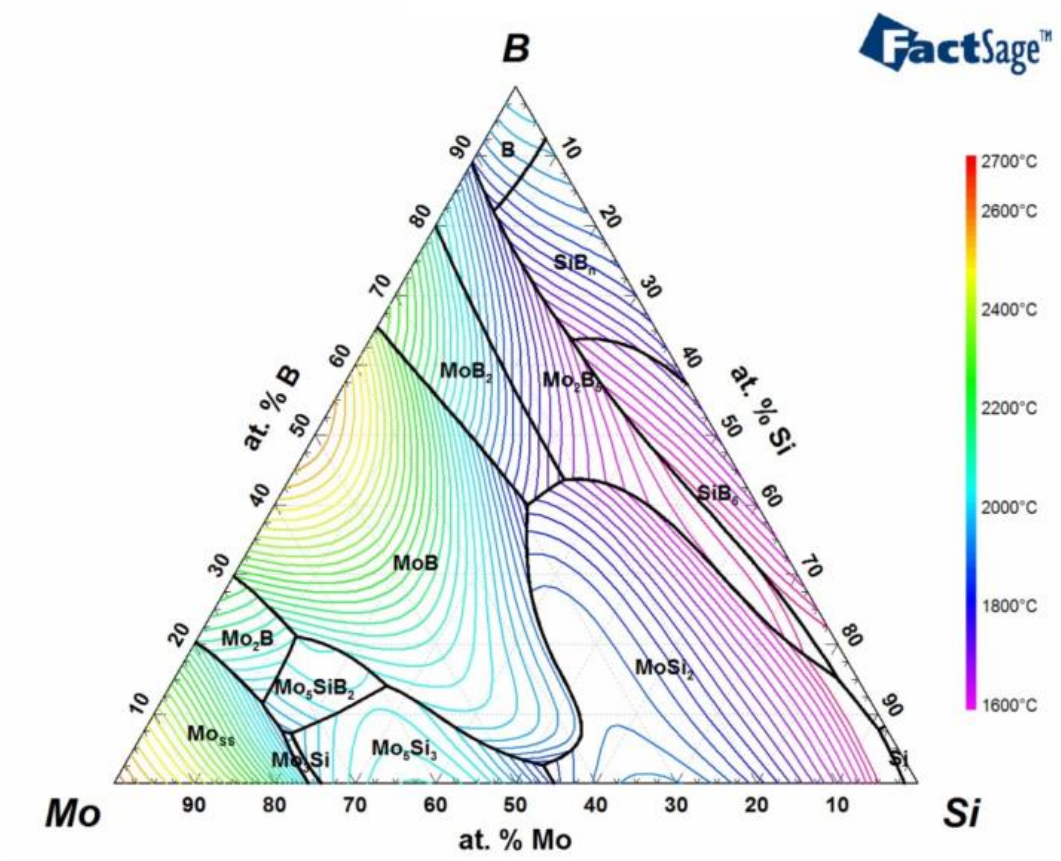

Figure 1: Liquidus projection of Mo-Si-B system, predicted by Factsage

In order to simulate the eutectic solidification process using the phase field method, a well cited scientific software called MICRESS was applied. To perform the simulation three major types of data were required: Material parameters such as diffusion data, phase interaction data like the mobility between phases, interface energy and thermodynamics data, process parameters like cooling rate and thermal gradient and the other numerical parameters for instance grid resolution and time step. The latter have to be adjusted to optimal values since although small values lead in more accurate results, but would increase the simulation time significantly. Otherwise the big enough amounts would result in unreliable consequences.

To carry out the simulation, a model containing the predicted phases was developed. The initial composition of the liquid was adjusted precisely to the ternary eutectic composition; Mo - Si 17 at % - B 7.7 at%. All the composition values are indicated in atomic percent in following.

Concerning the verification of the created results, they were compared with the experimentally observed outcomes. In this regard the cooling rate and thermal gradient were obtained from the experiments. Table 1 shows the parameter adjustments.

Table 1. Applied values for the required parameters

Cooling rate [K/s]	Thermal Gradient [K/cm]	Surface energy between liquid and phases [J/cm^2]	Entropy of fusion in solid phases [J/cm^{3}K]	Entropy of fusion in liquid phases [J/cm^{3}K]	Diffusion coefficient in liquid [cm^2/s]
200	10	10^{-4}	0.1	0.9	2×10^{-4}

The simulations were performed with different interface thickness and an interface with three cells width has proved to result in the most compatible results.

4. Results and Discussion

Preliminary results showed to be in adequate accordance with the experimentally obtained ones. Figure 2 presents a schematic comparison between the initially achieved results of simulation and the observations of experiments.

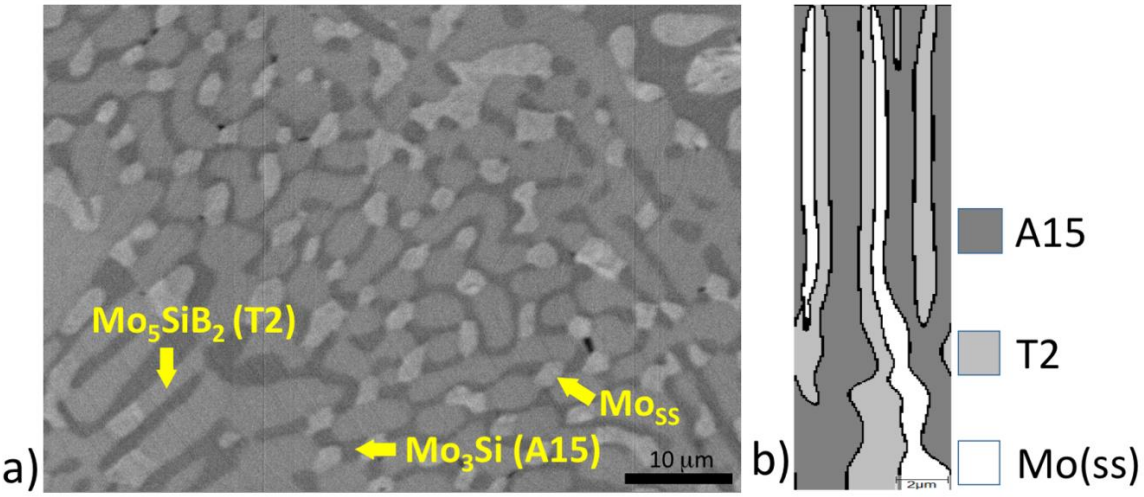

Figure 2. Eutectic lamellae observed in: a) experiments b) MICRESS simulation; the nuclei position was adjusted at the bottom so that from left the phases are presenting A15, T2 and $Mo_{(ss)}$ consequently. It is proved by simulations and experiments that almost 50 % of domain would be A15 and the other phases have almost equal volume fractions.

For the further studies we have investigated the instability of the ternary eutectic growth. For this purpose we have explored the Jackson-Hunt (JH) theory to address the minimum undercooling lamellae distances for the eutectic composition alloy. In this investigation the velocity of solid-liquid front was assumed to be constant and the simulation domain was containing three lamellae standing for three solid phases. Taking periodic boundary conditions into account, the generated results are capable to get mirrored for better consideration.

Choudhury et al. have proposed a generalized form of classical JH model [13] to examine the undercooling vs the lamella spacing in ternary systems [12]. We have followed their suggested procedure to study the changes of undercooling vs lamellae distance. Figure 3 shows the undercooling as a function of lamellae distance based on the theoretical assumptions in [12].

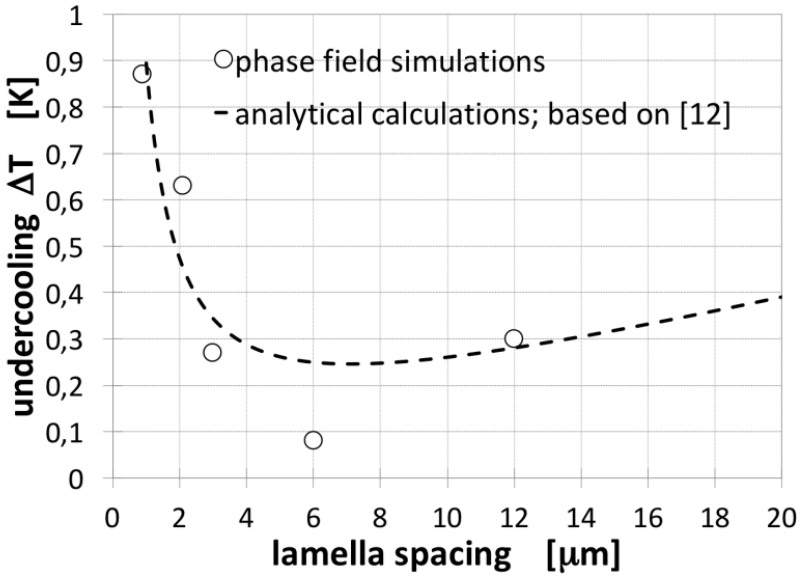

Figure 3. Variation of undercooling as a function of lamellae spacing for the Mo-Si-B ternary eutectic alloy, the lamellae spacing in this graph is showing the width of a unit containing three lamellae of solid phases

According to the Kim et al. we have defined a dimensionless variable ʌ which is λ / λ_{JH} and have carried out the simulation with the different ʌ values to probe the possible instabilities in the system [1]. We have calculated the JH lamellae spacing for our system $\lambda_{JH} = 7$ μm connected to the minimum in undercooling (see Figure 3). This will be considered in following as a width of three lamellae in which lamellae are assumed to have equal width. For a ternary system, Choudhury et al. have suggested there are various instability patterns. Two mainly probed are patterns with different repeating units. According to Choudhury's work, if we call the three existing solid phases as A, B, and C, the dominant repeating units are ABC and ABAC [12]. It implies that along with the tilting and oscillating instability, the lamellae could shape different arrangement pattern during the solidification. They have also proposed that other permutations are possible. Confirming by the simulation and experimental investigations, the most predominant repeating pattern in Mo-Si-B eutectic alloy looks to be ABAC, however depending to the adjusted lamellae spacing, the phase field simulations proved the transition of the ABAC pattern to the other arrangements. This conversion happens following elimination of a lamellae or pinning or bifurcation of one lamella during evolution of the other lamellas. The growth pattern of the lamellae in Mo-Si-B ternary eutectic composition with constant proceeding velocity of solid phases into the liquid phase v = 0.05 μm/s, for ʌ = 0.12, 0.17, 0.3, 0.85 and ʌ = 1.7 is shown in Figure 4. According to the simulations, a transition to an intermittent oscillating growth pattern happens at ʌ = 1.7.

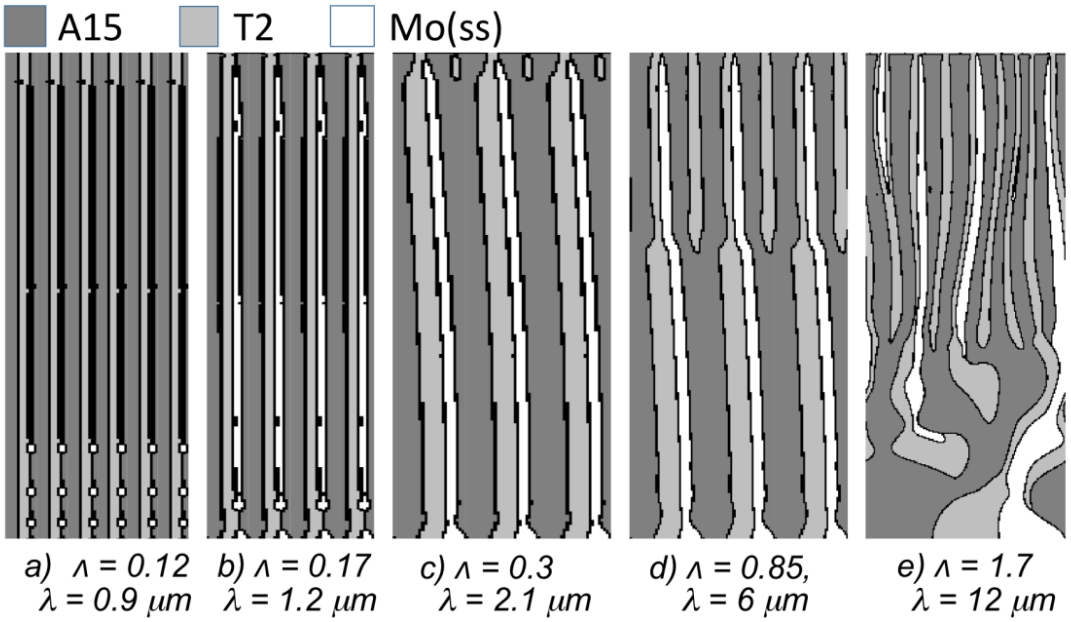

Figure 4. Growth pattern from the PFM computation at different $\Lambda = \lambda / \lambda_{JH}$

In the model proposed by Choudhury et al. it is assumed that all the solid phases have equal volume fraction regardless to the number of lamellae of each phase and width of each lamella. They have also considered that the undercooling at the interface of all solid phases with the liquid are equal to each other. Moreover, in their projected model it was assumed that all the phase diagram of binary composition of existing phases have similar characteristics such as liquidus slope. Despite to these assumptions the phase field simulation and model predictions are in good agreement with each other. Especially the stable lamellar spacing of 7 μm will be predicted in both models as the same.

5. Conclusions

Although several phase-field studies have been conducted for predicting a eutectic solidification's behavior, there is not adequate number of simulations for a ternary eutectic composition alloy. Several computations have been performed to predict the instability pattern in binary eutectic compositions but for the ternary eutectics there has not been a quantitative number of models. Despite of lack of sufficient verified models, we have derived the isotropic ternary eutectic model using MICRESS software with some major simplifications. Furthermore, we have investigated the minimum undercooling lamella distance for a fixed interface evolution velocity to probe the lamella spacing which results in a stable growth.

Performing the phase field simulation has shown a variety of growth patterns and instabilities in growing of lamellae which have been observed in the experimental investigations. Thanks to a generalized form of Jackson-Hunt theory for ternary alloys, the interval of lamellae spacing which results in a stable lamella growth was derived for the interface proceeding speed of 0.05 micrometer per second. The computation has shown that performing the simulation with the lamella spacing satisfactorily larger than the optimal JH lamella spacing would result in oscillating instability.

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