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Interplay between α(Ti) nucleation and growth during peritectic solidification investigated by phase-field simulations

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Abstract

The properties of modern TiAl-based alloys with aluminum contents around 45 at.% critically depend on the as solidified α(Ti) grain structure. Commonly, a rather coarse grain structure is obtained if α(Ti) forms via the peritectic reaction 'liquid + β(Ti) $\rightarrow$ α(Ti)'. Phase-field simulations have been applied to perform a case study of grain structure formation during the early peritectic growth under unidirectional growth conditions. In the absence of foreign nucleation sites, the peritectic α(Ti) phase nucleates on the dendritic surface of the properitectic β(Ti) phase. For typical values of the critical nucleation undercooling, coarse structures with large elongated grains are reproduced. A delicate interplay between nucleation and growth is predicted for reduced values of the critical undercooling. In this case, the alloy composition is found to play an additional role. An effective grain refinement by frequent nucleation is obtained, if potent nucleants can reduce the critical undercooling below the local growth undercooling. Complementary Scheil calculations and Bridgman experiments show that *in situ* precipitation of TiB_2 particles can be controlled by adequate boron addition. Both, numerical predictions and experiments confirm that these particles can act as effective nucleation agents and significantly reduce the grain size of α(Ti).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Modern TiAl-based alloys solidify with β(Ti) as the primary phase. As can be inferred from the binary phase diagram displayed in figure 1, this phase is subject to subsequent transformations that finally lead to a lamellar microstructure, consisting of γ-TiAl and α_2-Ti_3Al. The rich dynamics associated with these transformations constitute the basis for various alloying concepts and process configurations [1–3].

For aluminum lean alloys, solidification is completed via β(Ti) only and accordingly α(Ti) forms in a solid-state transformation. For this case, it is known that low boron additions, e.g. 0.2 at.% B, lead to an efficient grain refinement of α(Ti), where heterogeneous nucleation on boride particles in the solid state is proposed to be the key mechanism [5]. It is less well understood, whether an efficient grain refining effect can be achieved by an analogous mechanism in the liquid melt for TiAl alloys with higher aluminum contents. Since in this case α(Ti) first forms in a peritectic reaction 'liquid + β(Ti) $\rightarrow$ α(Ti)', its grain structure will depend on the competitive interplay between nucleation and early growth of α(Ti) grains. If nucleation of α(Ti) occurs solely on the properitectic β(Ti) dendrites, a rather coarse grain structure is expected. A refined grain structure could be obtained by nucleation with reduced undercooling on seed particles, e.g. early precipitated TiB_2.

The aim of this paper is to investigate the grain structure formation of the α(Ti) phase in TiAl alloys by phase-field simulation. Unidirectional solidification with a defined temperature gradient and growth velocity is studied. Similar, though transient conditions, may be encountered in the columnar zone of technical castings. A general multiphase/multicomponent phase-field model [6] is used, coupled to a thermodynamic database for the binary system Ti–Al [4]. The simulations address the nucleation and early growth of the peritectic α(Ti) phase. A case study is performed to reveal the principal effect of a decreased

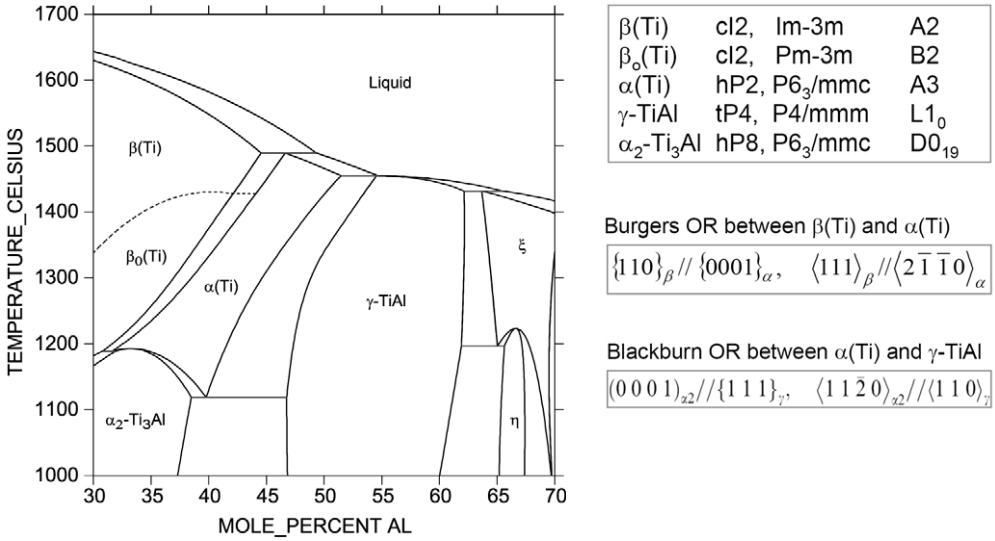

Figure 1. Phase diagram of the binary alloy system Ti–Al from the recent description by [4] along with the crystal structure of selected, relevant phases.

Table 1. Material data used as input for the phase-field simulations.

Diffusion coefficients ($m^2\ s^{-1}$) for aluminum in the liquid, β(Ti) and α(Ti)		
$D_L = 10^{-9}$	$D_\beta = 1.94 \times 10^{-4} \exp(-324\,155/RT)$	$D_\alpha = 6.6 \times 10^{-3} \exp(-328\,979/RT)$
Interfacial energies σ ($J\ m^{-2}$) and their anisotropy δ^σ		
$\sigma_{L\beta} = 0.1$ $\delta^\sigma_{L\beta} = 0.02$	$\sigma_{L\alpha} = 0.1$ $\delta^\sigma_{L\alpha} = 0$	$\sigma_{\beta\alpha} = 0.1$ (for Burgers OR) $\delta^\beta_{L\alpha} = 0$
Phase-field mobilities ($m^4\ (J\ s)^{-1}$) and their anisotropy δ^{kin}		
$M_{L\beta} = 10^{-6}$ $\delta^M_{L\beta} = 0.05$	$M_{L\alpha} = 10^{-6}$ $\delta^{kin}_{L\alpha} = 0$	$M_{\beta\alpha} = 10^{-9}$ $\delta^{kin}_{\beta\alpha} = 0$

nucleation undercooling on the α(Ti) grain structure for varied aluminum compositions. Complementary to the simulations, Scheil calculations and Bridgman experiments are performed for Ti–Al–xB alloys to study the *in situ* precipitation of TiB_2 particles, which can act as potent nucleants for the α(Ti) phase. On the basis of the experimental observations, the particle size and distribution are estimated in order to simulate their grain refining effect.

2. Definition of the simulation scenario and input data

Simulations are performed using the phase-field software MICRESS [7]. Thermodynamic data for the Ti–Al system are derived via the ThermoCalc [8] software from a recently re-assessed Calphad database [4]. Rather simple, well-defined scenarios are chosen to model the primary dendritic growth of the β(Ti) phase. The simulations start from explicitly set β(Ti) nuclei at the bottom of the calculation domain. The distance between the nuclei (approx. 200 μm) corresponds to an average primary spacing, which has been evaluated in preliminary simulations. A constant temperature gradient ($G = 2 \times 10^4$ K mm^{-1}) is assumed in the vertical direction and the system is cooled by a constant rate $\dot{T} = 0.667$ K s^{-1}, which corresponds to the imposed velocity of $v = 3.33 \times 10^{-5}$ m s^{-1} in the Bridgman experiments described in section 4. Table 1 gives the material data used as input for the simulations. The diffusion data for the solid phases are taken from Mishin and Herzig [9], while the diffusion coefficient in the liquid and the liquid–solid interfacial energies just represent an order of magnitude estimate. Because of the Burgers orientation relationship, the energy for the β(Ti)/α(Ti) interfaces is selected much lower than ordinary solid/solid interface energies. The solid-state transformation 'β(Ti) $\rightarrow$ α(Ti)' does however only play a major role during the subsequent peritectic transformation and is of minor importance for the here studied early peritectic reaction.

In the general case, α(Ti) grains are supposed to nucleate with a Burgers orientation relationship on the properitectic β(Ti) phase. This is described by a critical undercooling model based on an explicitly defined value for the critical nucleation undercooling ΔT_{nuc} and a minimum distance between nucleation sites. A new nucleus is set whenever the local undercooling, which is determined as function of the local temperature, the concentration and the curvature of the β(Ti) surface, exceeds the specified critical value. For numerical reasons a minimum distance between the nuclei is defined, which, however, does not impair the general trends, deduced from the parameter variations.

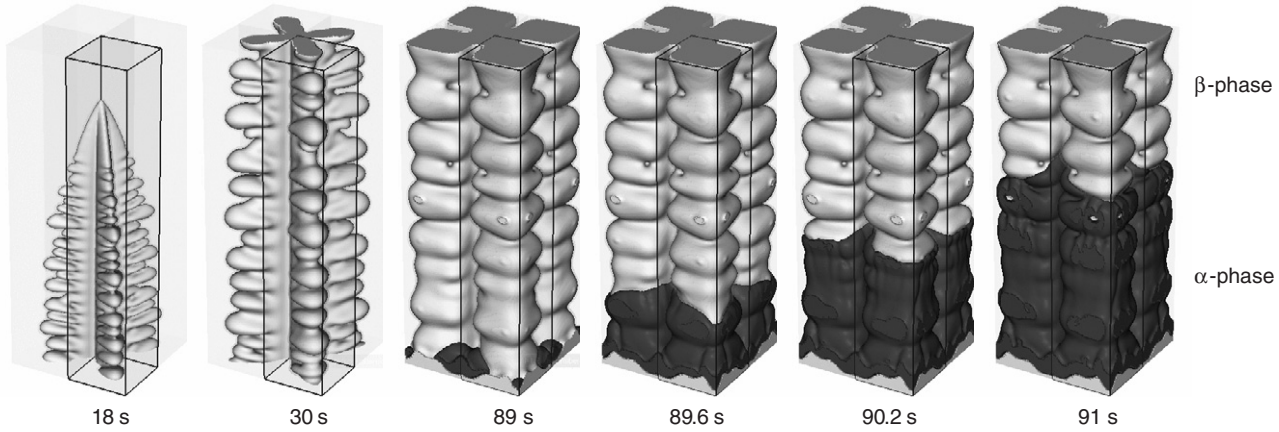

Figure 2. 3D phase-field simulation of the growth of a primary β(Ti) dendrite and the subsequent peritectic reaction to α(Ti) in Ti–45%Al.

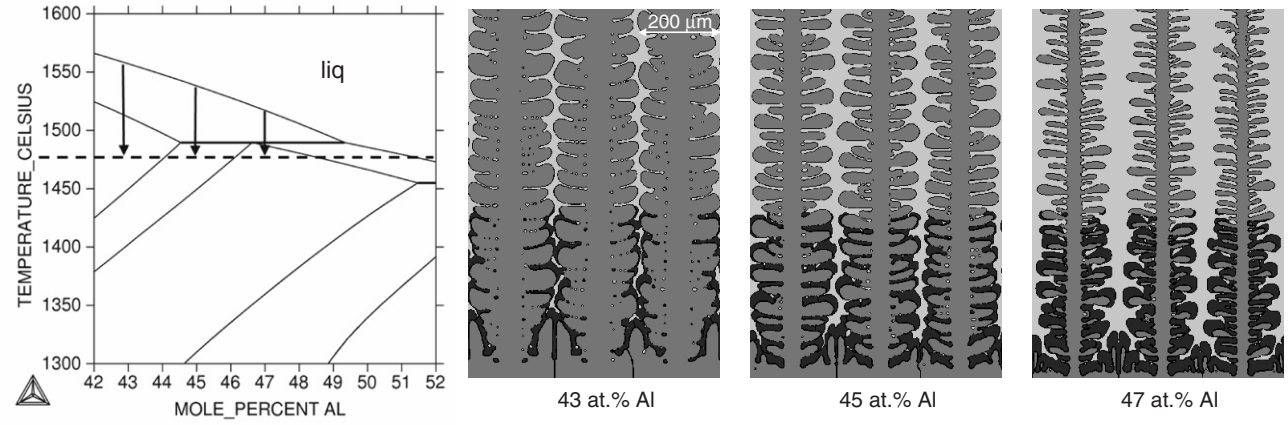

Figure 3. Microstructures at the early stage of the peritectic reaction in comparison for three selected aluminum contents (simulated in 2D).

In the present phase-field simulations, three major simplifications are made: (i) the crystalline anisotropy of α(Ti), as well as its Burgers orientation relationship to the β(Ti) phase are not yet considered; (ii) *in situ* formation of nucleant particles, e.g. TiB_2 is not modeled explicitly but treated by a simplifying sub-model, detailed in section 4; (iii) the thermodynamic and kinetic effects of boron addition are not yet taken into account. All three aspects are subject of further investigations.

3. Simulations of primary dendritic growth and peritectic reaction

Figure 2 shows the growth of a single Ti–45 at.%Al dendrite simulated in 3D. In the first stage of solidification, the tip of the primary β(Ti) dendrite still lies within the simulation domain, while later only the growth and ripening of the secondary arms are simulated. The peritectic α(Ti) phase nucleates near the bottom of the simulation domain, where the critical undercooling is first exceeded. The α(Ti) then grows in a direct peritectic reaction: liquid + β(Ti) $\rightarrow$ α(Ti). Its spatial propagation depends on the local compositions and curvatures. It can be seen that α(Ti) first grows along the surface of the stem in vertical directions before the arms are enveloped.

For the sake of computation time, extended simulations with several dendrites and series of simulations with systematic variation of input parameters have still to be run in 2D. Figure 3 gives a 2D scenario with three parallel growing dendrites, which has been run for varied aluminum concentrations (43, 45, 47 at.%). Comparison with the previous 3D simulation reveals two major artifacts of the 2D simulations: (a) the peritectic phase cannot grow around the dendrites, which limits the grain size in the horizontal direction to the primary dendrite spacing. (b) The changed growth path of the peritectic phase around the secondary arms slightly effects the local growth undercooling. Apart from this, the 2D simulations reproduce qualitatively the same mechanisms as the 3D simulation.

The most noticeable effect of the composition variation is that significantly different fractions of the primary β(Ti) phase are present at the start of the peritectic reaction. For the lowest content (43 at.%), solidification is almost completed. Here, α(Ti) will mainly form from the solid β(Ti) phase, whereas it still grows to a large extent from the liquid for the highest aluminum content (47 at.%). Another effect of a higher aluminum content is the increased growth restriction. As will be discussed further in section 4, the peritectic phase evolves with a higher growth undercooling, if more solute has to be redistributed during the transformation.

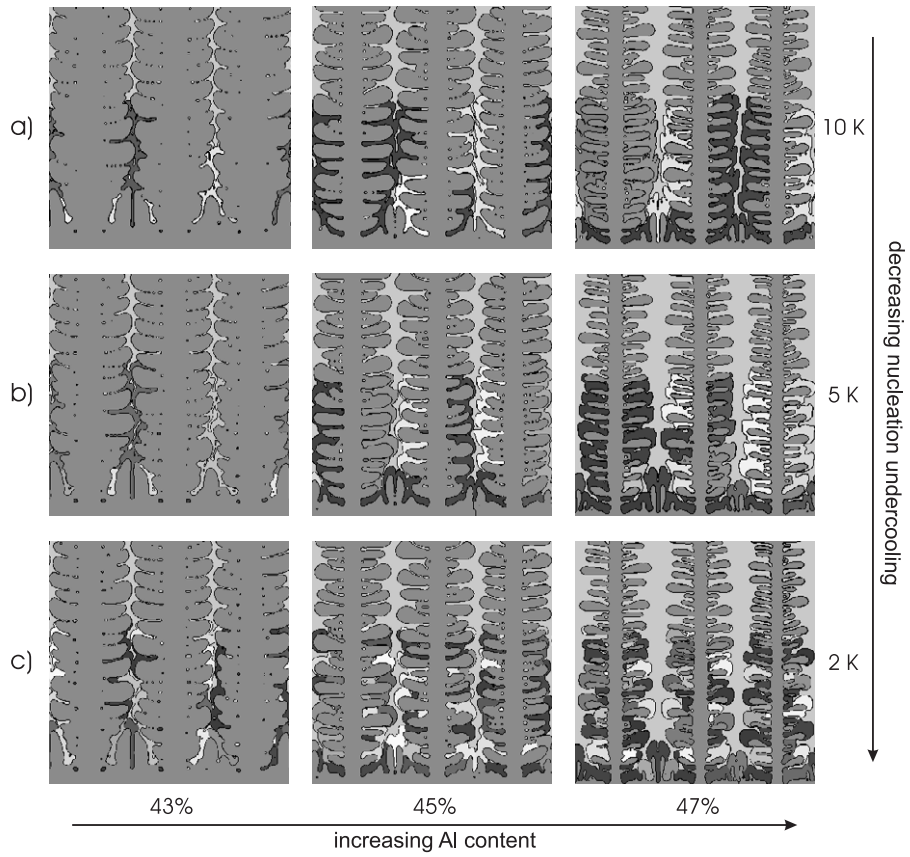

Figure 4. Case study to investigate the effect of a decreased nucleation undercooling on the number and morphology of α(Ti) grains. The colors (gray levels) distinguish grains which originated from independent nucleation events.

4. Prediction of the grain structure for varied nucleation undercoolings

The phase-field model does not only distinguish between different thermodynamic phases, i.e. liquid, β(Ti) and α(Ti), but also between grains which originated from independent nucleation events. In figure 4, the grain structure of the α(Ti) phase is indicated by different colors. Nucleation of a new grain is modeled whenever the local undercooling—dependent on temperature, concentration and curvature—exceeds a specified critical value. The value for nucleation of α(Ti) on the peritectic β(Ti) phase is supposed to be at least 10 K [10]. Figure 4(a) reveals that under the assumption of such a critical undercooling, nucleation takes place almost solely in the early stage. Subsequently, α(Ti) grows continuously in a coupled peritectic reaction along the dendrite surfaces. Ongoing nucleation is only found in isolated liquid pockets, but no longer on the surface. Even in the simulation with the highest aluminum content (47 at.%), the critical undercooling value is never exceeded again, implying that the growth undercooling for α(Ti) is always below this value. During subsequent peritectic transformation, this will result in a structure with large elongated α(Ti) grains.

In the numerical model, the critical nucleation undercooling is defined as an explicit input parameter, which allows its independent variation. A case study is performed to investigate how the α(Ti) grain structure would be affected, if the nucleation undercooling could be reduced by some means. The nucleation undercooling is first reduced to 5 K. Figure 4(b) displays the simulated grain structures at the time of early peritectic reaction for all three examined aluminum contents. Only in the simulation with the highest aluminum content, a small effect is observed. Here, the local growth undercooling already exceeds at some critical sites the required nucleation undercooling. This can be explained by the increased growth restriction for higher solute concentrations. To obtain a considerable grain refining effect, the nucleation undercooling has to be reduced further. This can be inferred from figure 4(c) where the value of $\Delta T_{\mathrm{nuc}} = 2$ K yields frequent nucleation even for the lowest aluminum content. Due to the growth restriction effect, the nucleation rate increases with increasing content.

This case study demonstrates that a refined grain structure is only achieved if the nucleation undercooling falls below the growth undercooling of the peritectic phase ($\Delta T_{\mathrm{nuc}} < \Delta T_{\mathrm{growth}}$). Principally, this can be realized by two different measures: either the growth undercooling is increased, e.g. by a higher growth rate, or the nucleation undercooling is reduced by providing preferred sites for heterogeneous nucleation. In the following, the latter possibility will be studied in more detail.

5. Complementary studies of heterogeneous nucleation on TiB_2 particles

TiB_2 particles are known to act as potent agents for heterogeneous nucleation of α(Ti). This is supported by recent

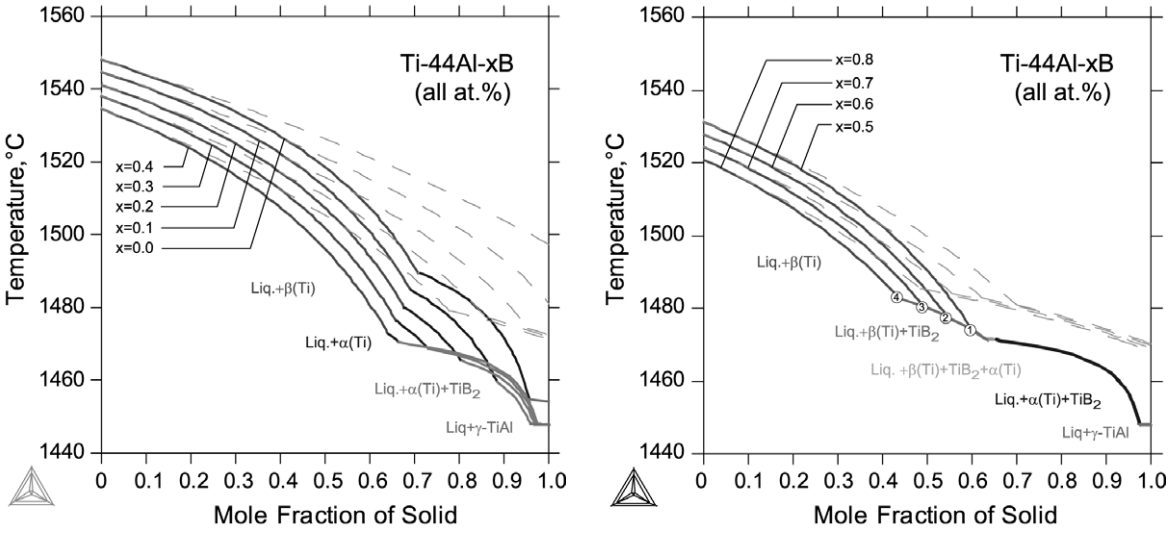

Figure 5. Scheil curves evaluated for ternary Ti–44%Al–xB alloys from the Calphad database [12] using ThermoCalc. For boron contents above approx. 0.5%, the TiB_2 phase precipitates prior to the α(Ti) phase.

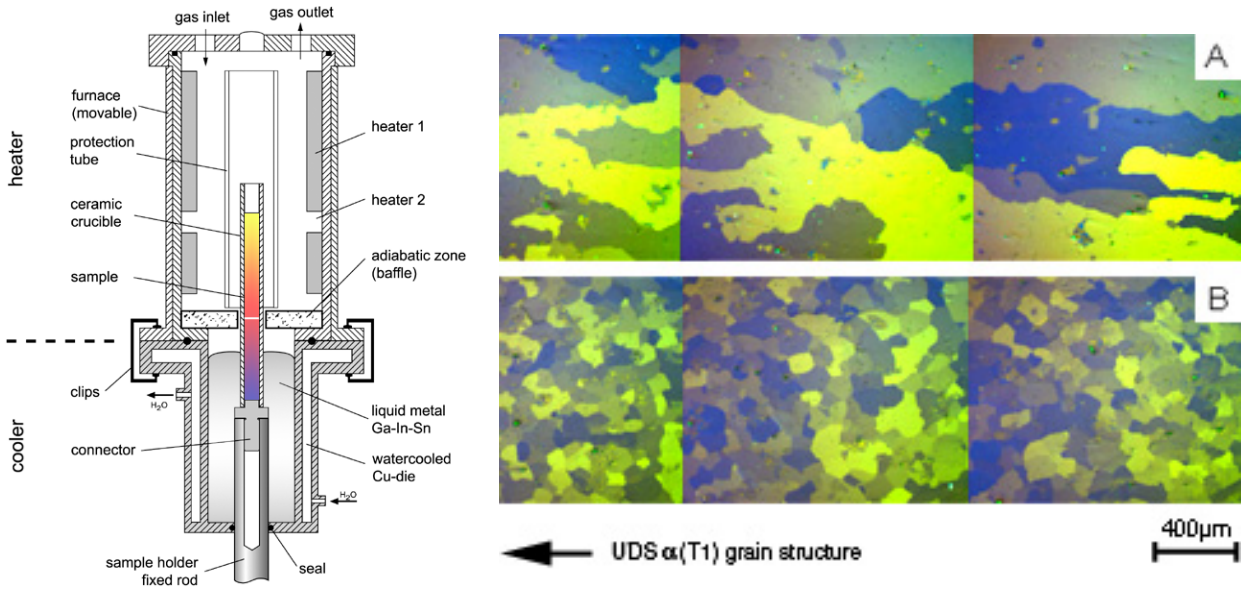

Figure 6. Unidirectional solidification (UDS) in a Bridgman furnace (left) was performed with a furnace velocity $v = 3.3 \times 10^{-5}$ m s^{-1} and a temperature gradient $G = 2 \times 10^4$ K m^{-1} for (A) Ti–44.8Al–0.2B and (B) Ti–44.7Al–0.5B. Considerably differing grain structures are observed for the two boron contents (right). For the low B content, where α(Ti) is supposed to have nucleated on β(Ti), a coarse structure with elongated grains is obtained. For the higher boron content, where TiB_2 particles formed prior to α(Ti) and served as agents for heterogeneous nucleation, much smaller grains with an average size of 220 μm are achieved.

work by Gosslar *et al* [11], who showed that the basal {0001} planes of hexagonal TiB_2 particles show low crystallographic misfit strains towards {0001} planes of α(Ti). This misfit strain is about a factor of three lower than the misfit strain between {110} planes of β(Ti) and {0001} planes of α(Ti), which corresponds to the Burgers orientation relationship. It is found that the *in situ* formation of TiB_2 particles in TiAl alloys can actively be controlled by boron addition. A prerequisite for the grain refining mechanism is that TiB_2 precipitates before α(Ti). Scheil calculations performed for ternary Ti–Al–xB alloys using the re-assessed Calphad database [4], reveal that the boron content can always be adjusted to the aluminum content in order to fulfil this criterion. Figure 5 illustrates that for an aluminum content of 44 at.%, a minimum boron content of 0.5 at.% is required to make TiB_2 precipitate prior to α(Ti).

Complementary Bridgman experiments (figure 6) are in line with the numerical predictions. For low boron addition (figure 6(A)), a coarse microstructure with large elongated grains is obtained, similar to the simulated structure in figure 4(a). In this alloy, α(Ti) is supposed to have nucleated and grown in a peritectic reaction on the surface of the properitectic β(Ti) phase. Considerably smaller grains with an average size of 220 μm are obtained for an increased boron content of 0.5%. The observed grain refinement

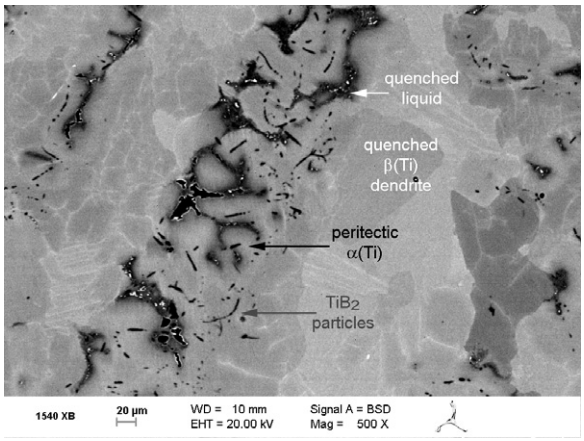

Figure 7. SEM/BSE micrographs showing precipitated TiB_2 particles in the interdendritic regions of the Ti–44.7%Al–0.5B alloy with refined grain size.

is attributed to heterogeneous nucleation of α(Ti) on TiB_2 particles. This can indirectly be concluded from the crystal orientation distribution [13] and also from micrographs which show clear-cut TiB_2 particles in the interdendritic regions of the Ti–44%Al–0.5%B alloy (figure 7). To further verify this interpretation, phase-field simulations are performed with an integrated sub-model, that takes into account nucleants (seeds for heterogeneous nucleation) with size and distribution similar to those of the experimentally detected TiB_2 particles.

6. Modeling of heterogeneous nucleation of α(Ti) on TiB_2 particles

To model heterogeneous nucleation of α(Ti) grains on boride particles, a special sub-model is used [14]. An exponential distribution function is approximated to describe the distribution density versus the size of the boride particles (figure 8(a)). According to this function, potential sites for nucleation of α(Ti) with reduced critical undercooling are randomly placed in the simulation domain. As illustrated in figure 8(b), the value for the critical undercooling is calculated from the particle size according to the hemispherical cap model [15, 16]. The assumed mean particle radius of $r_{nuc} = 2\ \mu$m, which has been estimated from the experimental data, corresponds to a nucleation undercooling of $\Delta T_{nuc} = 0.71$ K. Using these data, simulations are performed for the three selected aluminum contents (43, 45, 47 at.%). The results in figure 9 show that boride particles of the observed size lead to a significant grain refinement. The predicted nucleation density is again highest for high aluminum contents. In contrast to the previous simulations (figure 4(c)), this is not only an effect of growth restriction, but also of the higher liquid fraction at the peritectic temperature. Since nucleation no longer occurs on the β(Ti) surface, a divorced peritectic growth might have been expected. However, this is found only in the simulation for 47 at.%Al, where the amount of residual liquid is still high. In the other simulations, most α(Ti) grains soon come in contact with the β(Ti) phase and continue their growth as in the previous simulations (figure 4) in a coupled peritectic mode.

7. Discussion and outlook

A phase-field model has been applied to simulate the interaction between nucleation and growth of the peritectic α(Ti) in Ti–43%Al, Ti–45%Al, and Ti–47%Al. With increasing aluminum content, the fraction of the properitectic β(Ti) phase present at the peritectic temperature decreases. Without explicit grain refining measures, α(Ti) grains are supposed to nucleate on the surface of the primary β(Ti) phase. For typical values of the critical nucleation undercooling (larger than 10 K), nucleation occurs only once and the further evolution of α(Ti) is dominated solely by growth. This is independent of the aluminum content and results in large vertically elongated grains, as also observed experimentally. Repeated nucleation, which is desired to get finer grains, is only possible for values of the critical nucleation undercooling below the local growth undercooling (approx. 5 K for the conditions studied). For such reduced undercooling, an increased aluminum content additionally increases the grain refining effect due to growth restriction.

Potential sites for heterogeneous nucleation of α(Ti) grains with reduced nucleation undercooling are supposed

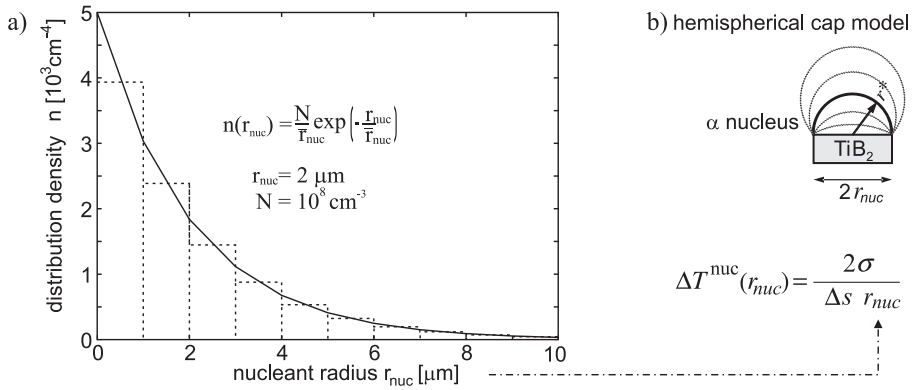

Figure 8. (a) Exponential distribution versus size function to model the TiB_2 particles, which are supposed to serve as agents for heterogeneous nucleation of the peritectic phase. (b) The critical nucleation undercooling is approximated according to the hemispherical cap model.

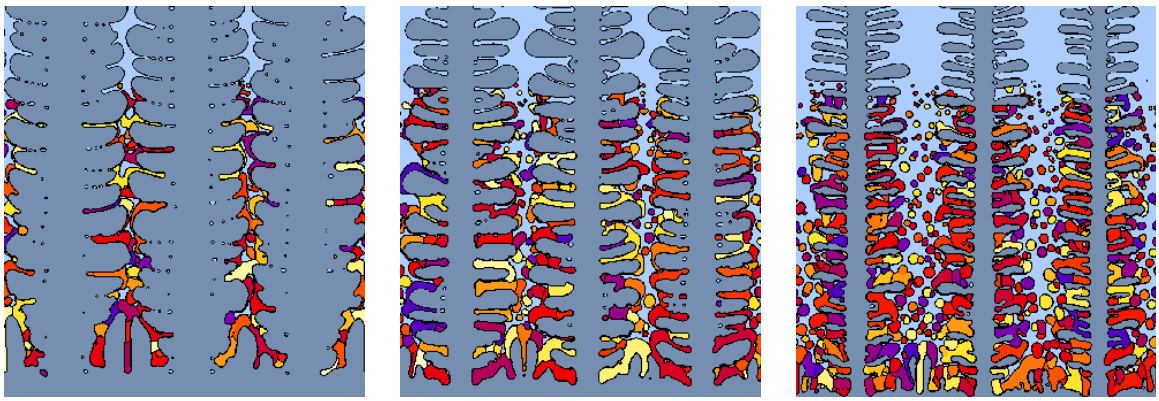

Figure 9. Simulations of nucleation and early growth of α(Ti) grains for different aluminum contents. Boride particles of different sizes have been assumed to be distributed randomly in the melt and act as agents for heterogeneous nucleation.

to be provided by *in situ* precipitation of TiB_2. Scheil calculations allow the estimation of the required amount of boron addition. Bridgman experiments performed for Ti–44.7%Al with the calculated boron addition of 0.5 at.%, indeed revealed precipitated TiB_2 particles and moreover a significant grain refinement. The conclusion that this refinement can be attributed to heterogeneous nucleation on TiB_2 particles has been supported by phase-field simulations, in which nucleants with size and distribution similar to those of the experimentally detected particles resulted in a strong increase of the grain density.

Due to the lack of accurate material data for the diffusion coefficients in the melt and the interfacial energies and mobilities, the present studies can only be regarded as qualitative. Improved data are expected to become available in the near future, both by experiments and *ab initio* calculations. To further increase the quantitative character, future simulations shall no longer be restricted to the binary Ti–Al system but take into account the additional effect of boron on the growth kinetics and phase fractions.

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