Detached Melt Nucleation during Diffusion Brazing of a Technical Ni-based Superalloy: A Phase-Field Study

B Böttger¹, M Apel¹, B Laux² and S Piegert²

1) Access, Aachen, Germany
2) Siemens AG, Power and Gas, Large Gas Turbines, Engineering, Berlin, Germany

E-mail: b.boettger@access.rwth-aachen.de

Abstract. Advanced solidification processes like welding, soldering, and brazing are often characterized by their specific solidification conditions. But they also may include different types of melting processes which themselves are strongly influenced by the initial microstructures and compositions of the applied materials and therefore are decisive for the final quality and mechanical properties of the joint. Such melting processes are often not well-understood because - compared to other fields of solidification science – relatively little research has been done on melting by now. Also, regarding microstructure simulation, melting has been strongly neglected in the past, although this process is substantially different from solidification due to the reversed diffusivities of the involved phases. In this paper we present phase-field simulations showing melting, solidification and precipitation of intermetallic phases during diffusion brazing of directionally solidified and heat-treated high-alloyed Ni-based gas turbine blade material using different boron containing braze alloys. Contrary to the common belief, melting of the base material is not always planar and can be further accompanied by detached nucleation and growth of a second liquid phase inside the base material leading to polycrystalline morphologies of the joint after solidification. These findings are consistent with results from brazed laboratory samples, which were characterized by EDX and optical microscopy, and can be explained in terms of specific alloy thermodynamics and inter-diffusion kinetics. Consequences of the gained new understanding for brazing of high-alloyed materials are discussed.

1. Introduction

Diffusion brazing is a process which has gained industrial importance, e.g. as build-up or repair brazing of gas and aircraft turbine components made of Ni-/Co-based high temperature materials [1]. To achieve an isothermal solidification process and hence to avoid formation of brittle eutectic phases, a filler material similar to the base metal is applied which has been modified by melting point depressing elements (typically boron) [2-4]. Figure 1 [5] shows the commonly assumed mechanism of the brazing process based on a simple binary Ni-B phase diagram. At brazing temperature, the filler melts due to its high content of boron (1). Then the base metal is rapidly melting until the liquid phase reaches equilibrium composition (2). But as boron rapidly diffuses into the base metal, isothermal solidification is possible (3). If the brazing time is long enough, complete solidification occurs (4), and the material can reach mechanical properties of the level of the base material (5).

For identifying suitable filler materials and process parameters, a deeper understanding of the microstructural changes during the brazing process including melting is needed, which can be...
achieved by computer simulation. The task is not only to minimize the brazing time, but also to avoid formation of new grain boundaries (epitaxial brazing).

For reaching this goal, among the different available simulation techniques, the phase-field approach appears to be most promising. Phase-field models have become very popular for the simulation of microstructure evolution during solidification [6-8]. The software MICRESS® [9] is based on the phase-field concept for multiphase systems which has been extended to multicomponent systems by direct coupling to thermodynamic databases [8,10]. Since then the software has been continuously developed not only for advanced scientific applications but also as a simulation tool for microstructure formation in technical processes [11-13].

In this paper, MICRESS® simulation results for brazing of CM247 using a Ni-15% Cr-4% B braze alloy are presented and compared to experimental results for various brazing times. A complex melting process with detached melt nucleation is suggested which accounts for the observed melting width and rows of new grains which typically emerge in the microstructure during brazing.

Figure 1: Principle of diffusion brazing [5]

2. Experimental

Brazing experiments were performed using small plate samples of solution heat treated equiaxed CM247 base material and melt-spun amorphous foils of the braze alloy with thickness of 50 µm. SEM images of three samples with different brazing times (½Δt, Δt, 2Δt, exact times are confidential), which have been cut perpendicular to the braze gap, are shown in Figure 2. Characteristic microstructural features are the polycrystalline nature of the molten zone with two or more rows of newly formed grains as well as boride precipitates on both sides of the gap which reach further into the base material with increasing brazing time.

Furthermore, the area covered by boride precipitates was evaluated using image analysis. For slices of 5 µm width parallel to the braze gap, the average area of all borides was measured and compared to simulation results (Figure 8). Individual types of borides were not distinguished.

Figure 2: SEM images of three samples with different brazing times: a) ½Δt, b) Δt, c) 2Δt. The width of the molten zone was about 90 µm in all cases.
3. Phase-Field Modelling

3.1. Multiphase-field model and MICRESS® software

The multiphase-field theory describes the evolution of multiple phase-field parameters \( \phi_\alpha(x,t) \) in time and space. They reflect the spatial distribution of multiple grains with different orientation and/or of multiple phases with different thermodynamic properties. At the interfaces, the phase-field variables change continuously over an interface thickness \( \eta \) which can be defined as being large compared to the atomic interface thickness but small compared to the microstructure length scale. Their time evolution is calculated by a set of phase-field equations deduced by the minimization of the free energy functional [8]:

\[
\phi_\alpha = \sum_\beta M_{\alpha\beta} (\hat{n}) \left( \sigma_{\alpha\beta} (\hat{n}) K_{\alpha\beta} + \frac{\xi}{\eta} \sqrt{\phi_\alpha \phi_\beta} \Delta G_{\alpha\beta} (\vec{c}, T) \right)
\]

(1)

\[
K_{\alpha\beta} = \phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + (\pi / \eta) (\phi_\alpha - \phi_\beta)
\]

(2)

In equation (1), \( M_{\alpha\beta} \) is the mobility of the interface as a function of the interface orientation, described by the normal vector \( \hat{n} \). \( \sigma_{\alpha\beta} \) is the anisotropic surface stiffness, and \( K_{\alpha\beta} \) is related to the local curvature of the interface. The interface, on the one hand, is driven by the curvature contribution \( \sigma_{\alpha\beta} K_{\alpha\beta} \) and on the other hand by the thermodynamic driving force \( \Delta G_{\alpha\beta} \). This driving force which is a function of temperature \( T \) and local composition \( \vec{c} \) couples the phase-field equations to the multi-phase diffusion equations

\[
\vec{c} = \nabla \sum_\alpha \phi_\alpha \vec{D}_\alpha \nabla \vec{c}_\alpha \quad \text{with} \quad \vec{c} \quad \text{defined by} \quad \vec{c} = \sum_\alpha \phi_\alpha \vec{c}_\alpha
\]

(3)

and \( \vec{D}_\alpha \) being the multicomponent diffusion coefficient matrix for phase \( \alpha \). \( \vec{D}_\alpha \) and \( \Delta G_{\alpha\beta} \) are calculated online from databases for the given concentration and temperature.

The above equations are implemented in the software package MICRESS® [9] being used for the simulations throughout this paper. Direct coupling to thermodynamic and mobility databases is accomplished via the TQ-interface of Thermo-Calc Software [14]. The thermodynamic driving force \( \Delta G \) and the solute partitioning are calculated separately using the quasi-equilibrium approach [8], and are introduced into the equation for the multiple phase-fields (equation (1)).

3.2. Model parameters and data

Thermodynamic data were provided by online coupling to the database TTNI7 [15] using the elements given in Table 1 and the phases listed in Table 2. In the same way, diffusion data for \( \gamma \) including cross-terms were taken from the MOBNI1 mobility database [14]. As MOBNI1 has no corresponding data for \( \gamma' \) and MOBNI2 is not compatible to the coupled TTNI7 thermodynamic database, the diffusion matrix of \( \gamma' \) was tabulated as function of temperature along equilibrium for the base metal.

Compositions of both materials are shown in Table 1. Phase-related data like nucleation conditions, interface mobility \( \mu \) and interface energy \( \sigma \) between all phases and melt or \( \gamma \) are given in Table 2.

3.3. Initial Microstructure

Creating the initial microstructure of the base metal from metallographic images was not the preferred method in view of the complexity of the observed microstructures, the small size of precipitates, and the difficulty to obtain concentration distributions which are consistent with the nominal alloy composition. Therefore, the initial microstructure was created by 2D phase-field simulation of solidification with subsequent solution heat treatment according to the Siemens internal material specification. Solidification was simulated at the scale of two \( \frac{1}{4} \) equiaxed grains including a grain boundary and essentially using the parameter sets given in Table 1 and 2. A self-consistent homoenthalpic approach [16] was applied to assure that microstructure formation was consistent with the macroscopic temperature boundary condition which leads to a realistic initial microstructure.
Table 1: Chemical compositions (in wt %) used for simulation

|      | C   | Cr  | Co  | Mo  | W   | Ti  | Al  | B   | Ta  | Hf  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| CM247 | 0.07 | 8.0 | 9.0 | 0.4 | 9.3 | 0.6 | 5.45 | 0.01 | 3.1 | 1.2 |
| braze foil | 0.06 | 15.0 | -   | -   | -   | -   | -   | 4.0 | -   | -   |

Table 2: Phases and phase related parameters

| No | name in database [15] | identity/constitution | diffusion data | nucleation in phase | $\mu_0x$ (cm$^2$/Js) | $\mu_1x$ (cm$^2$/Js) | $\sigma_{0x}/\sigma_{1x}$ (J/cm$^2$) |
|----|------------------------|-----------------------|----------------|---------------------|----------------------|----------------------|----------------------------------|
| 0  | LIQUID                 | melt                  | $10^{-6}$ cm$^2$/s | 1 (region)          | -                    | $1 \times 10^{-7}$  | $7 \times 10^{-6}$               |
| 1  | FCC_A1#1               | $\gamma$ MOBN1        | 0              | 1                    | $1 \times 10^{-7}$  | $7 \times 10^{-5}$  | $1 \times 10^{-5}$               |
| 2  | FCC_A1#2               | (Hf,Ta)C              | 0.1            | 1                    | $8.2 \times 10^{-9}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 3  | MB2_C32                | (Ti,Hf)B$_2$          | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 4  | FCC_L12                | $\gamma'$ MOBN12      | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 5  | M3B2_TETR              | (W,Cr,Mo)$_3$B$_2$    | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 6  | M2B ORTH               | (Cr,Mo,W)$_2$B        | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 7  | MB ORTH                | (Cr,Mo,W)B           | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 8  | CR5B3                  | (Cr,Mo)$_3$B$_2$      | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 9  | M2B TETR               | (W,Cr,Mo)$_3$B       | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |
| 10 | M3B                    | (Cr,Mo,W)B$_2$       | 0.1            | 1                    | $2.4 \times 10^{-8}$| $1 \times 10^{-4}$  | $1 \times 10^{-4}$               |

Figure 3: Simulated Al-distribution (wt%) during solidification at a) 1365 °C, b) 1345 °C, after solidification at c) 800 °C and d) after homogenisation and subsequent cooling to 800 °C.

Figure 3a-c shows the Al-distribution during the solidification process. Dark particles are carbides (FCC_A1#2) which nucleate in the melt modelled by a seed density model [13,17]. The $\gamma'$ phase appears as bright regions along the grain boundary. Although grid resolution was rather low (500x200 cells with $\Delta x=1\mu m$), $\gamma'$ precipitation from the solid was simulated as individual small particles represented by a small phase fraction in a single grid cell (analytical curvature model [13]).

Solution heat treatment was simulated for the specified industrial conditions including heating from 800 °C. As shown in Figure 3d, the concentration gradients of Al and small $\gamma'$ particles were dissolved while larger eutectic $\gamma'$ remained nearly unchanged. Few smaller $\gamma'$ precipitates formed during cooling down to 800 °C afterwards. The resulting microstructure was stored for use in the brazing simulations.
3.4. Simulation of Diffusion Brazing

The simulation domain for brazing had a size of 500x550 grid cells (∆x=1 µm) and consisted of three grains representing half of the filler (grain 1), one side of the base metal (grain 2) and a connection zone for a one-dimensional extension for far-field diffusion of boron (grain 3, see Figure 4a). While grain 1 and 3 were defined to have a constant composition corresponding to the braze alloy and base metal composition in Table 1, respectively, grain 2 was replaced by the initial microstructure in Figure 3d. This was achieved using a specific restart algorithm which reads the detailed microstructure information from the previous simulation and further allows complete filling of the space originally covered by grain 2 using mirror symmetry (Figure 4b). The zones where melting and boride precipitation is expected and mirror symmetry at the bottom are also indicated in Figure 4b).

During brazing a homogeneous temperature is assumed. In the simulation scenario, heating starts from 800 °C with a rate of 25 K/min up to the brazing temperature. Then, temperature is kept constant for \( \frac{1}{4} \Delta t, \Delta t, \text{or } 2 \Delta t \) followed by cooling to 800 °C with -25 K/min. Melting of the filler was assumed to occur instantaneously at 1061 °C (according to DSC experiments). This “Melting” was implemented as a sudden raise of the diffusivity in grain 1 to \( D_{liq} \) and of the interface mobilities \( \mu^0/\Delta x \) from 0 to the values specified in Table 2. In order to obtain a realistic solidification time, the diffusivities of B in \( \gamma \) from MOBN1 had to be reduced by a factor of 5.

The progression of the liquid-solid interface during brazing is shown in Figure 5. If the simulation is performed according to the simple mechanism of Figure 1, melting of the base metal is observed, with a maximum shortly after brazing temperature is reached (Figure 5a). Due to the inhomogeneous microstructure of the base metal non-planar melting is observed. But there is no indication that formation of new grains during solidification should occur. And the average width of the (total) molten zone does not exceed 65 µm in contrary to the experimentally found ~90 µm (Figure 2). Nevertheless, this smaller simulated value is supported by thermodynamic calculations: a mixture of 50 parts braze alloy and 40 parts base metal (corresponding to 90 µm maximum melting width) according to Thermo-Calc equilibrium calculations using the TTN17 database should consist only to 73.3% of liquid at brazing temperature!

Therefore, an alternative mechanism including detached nucleation of liquid inside the base metal was taken into consideration. In a first simple approach, nucleation of liquid was allowed along a fixed row at 15 µm behind the initial solid-liquid interface. This relatively large distance was chosen to prevent early mixing of the new liquid with the liquid braze alloy. Interestingly, the simulations clearly showed that detached liquid nucleation leads to rapid melting inside the base metal which is accompanied by \( \gamma' \) precipitation and formation of a semisolid region inside the base material. In Figure 5b we can observe that this semi-solid region finally breaks up and gets connected to the main
liquid in the more segregated central region around the grain boundary, while accelerated solidification is observed laterally. Later (Figure 5b, right) the remaining semi-solid regions have vanished and the liquid gap starts closing.

Thus, the new mechanism which includes detached melt nucleation, with the simple approach of a nucleation line, seems to explain as well the formation of new grains as the increased width of the brazing gap in the experiments (Figure 6).

![Figure 5: Cr composition profile (wt%) in the lower part of the simulation domain (Figure 4) during the initial stage of the brazing process, showing melting and re-solidification during brazing: a) without, and b) with detached melt nucleation. The bright zones indicate liquid regions.](image)

![Figure 6: a) Formation of new grains during brazing. Shown is the grain orientation (in degrees) after $2\Delta t$ brazing for simulation a) without and b) with detached melt nucleation. c): SEM image of a brazed sample after $2\Delta t$.](image)

Besides of the melting and re-solidification process, precipitation of borides was observed. Nucleation of the different boride types listed in Table 2 was allowed as well at the interfaces to the melt as inside the $\gamma$ phase. Figure 7 shows the location of the borides after $\Delta t$. Most abundant are the Ti-rich MB2_C32 borides. They form bigger precipitates close to the gap, which have grown from the melt, and smaller particles which nucleate inside the base metal. The size of the latter increases with the distance from the gap, which is due to their decreasing growth rate and the fact that growth is limited by the available amount of Ti. This observation is consistent with experimental microstructures (Figure 2), though the morphology change to needle-like structures could not be correctly modelled owing to the low resolution of the simulation. The lower amounts of W-rich M3B3_TETR borides visible in Figure 7 left could not be directly identified in the experimental micrographs.

Finally, Figure 8 compares the simulation results with the measured distribution of the total boride area for three different brazing times. There is a good qualitative agreement with respect to the maximum and width of the distribution as well as to the shift and broadening with increasing brazing time. The plot of the simulated borides over time (Figure 8b) reveals that during brazing MB2_C32 is
the most abundant boride type. All others appear intermediately but vanish at longer times, with the exception of M3B3_TETR. Note that this phase slightly grows again at the end due to cooling.

**Figure 7:** Concentration distribution of W, Ti and B indicating the location of borides after $\Delta t$.

**Figure 8:** Area of total borides after brazing as a function of the distance from the gap center (left) and simulated average molar fraction of individual boride types during the $2\Delta t$ brazing cycle.

4. Discussion

Although this has not yet been discussed in literature, it is obvious that detached melting during brazing may occur if the base metal plus the additional high boron activity provided by fast B diffusion results in a lower melting point compared to the braze alloy itself. This is the case for the high-alloyed CM247 when combined with a braze alloy which has only 15% Cr.

The reason why we believe the base metal is not melting from the surface is shown in Figure 9. After equilibrium is reached at the solid-liquid interface, there is a depletion of substitutional elements close to the solid-liquid interface which prevents further melting (1). Instead, there is a region closely behind this zone with unchanged compositions where the B activity is high and may lead to melting. Therefore, a thin detached liquid film can form below the surface (2) which has a composition different to the primary melt and which rapidly grows due to fast B diffusion (3). In case of CM247 simultaneous $\gamma'$ precipitation occurs in this zone. As the original solid layer which separates the two liquids can be very thin, material inhomogeneity or other effects may easily lead to its rupture (4). The remnants of the solid layer form a row of new grains (5). Alternatively, if the layer melts completely, nucleation may also occur on the $\gamma'$ particles which start dissolving once the liquid composition is altered by mixing. After complete mixing of the two liquids, the same process 1)-(5) may be repeated deeper into the base metal while the inner part of the gap is already partially
solidified. The fact that detached melting and solidification of the primary liquid occur simultaneously can explain the observed width of the molten zone of 90 µm without contradicting the equilibrium calculations mentioned in Section 3.4.

Figure 9: Schematic representation of detached melting. Shown are the solid-liquid interfaces with the temperature and concentration profiles of B and an arbitrary substitutional element X.

5. Conclusions and Outlook
It has been shown that, despite of the high complexity of the alloys and the process, simulation of brazing can be achieved using the phase-field method. Good agreement with experiments was reached with respect to morphology and boride distribution. Furthermore, a new mechanism of detached melting has been postulated and discussed, which allows explaining not only the formation of new grains, but also of an increased width of the molten zone compared to thermodynamic estimations. Although, due to the low grid resolution, including this mechanism into modelling was rather rough, the effect of detached melting was clearly confirmed and turned out to be of utmost importance for understanding the experimental findings.

The results of this paper also shed new light on the criteria for choosing braze alloys, especially for the case of epitaxial brazing. The question arises whether new high-alloyed filler materials or improved process parameters can prevent formation of new grains in case of high-alloyed materials.

References
[1] Demo W A and Ferrigno S J. 1992 Adv. Mater. Process. 141 43–5
[2] Duvall D S, Owczarski W A and Paulonis D F 1974 Weld. J. 53 203–14
[3] Ekrami A, Moeinifar S and Kokabi A H 2007 Mat. Sci. Eng. A 456 93–8
[4] MacDonald W D and Eagar T W 1998 Metall. Mater. Trans. A, 29 315–25
[5] Hoppe B 2003 Dissertation Technische Universität Braunschweig/Germany
[6] Wheeler A A, Boettinger W J and Mc Fadden G B 1993 Phys. Rev. E 47 1893-909
[7] Kim S G, Kim W T and Suzuki T 1999 Phys. Rev. E 60 7186-97
[8] Eiken J, Böttger B and Steinbach I 2006 Phys. Rev. E 73 066122
[9] MICRESS software, http://www.micress.de
[10] Böttger B, Grafe U, Ma D and Fries S G 2000 Mater. Sci. Technol. 16 1425-28
[11] Schmitz G J et al 2012 Int. J. Adv. Eng. Sci. Appl. Math. 2 4 126-39
[12] Böttger B, Apel M, Eiken J, Schaffnit P and Steinbach I 2008 Steel Res. Int. 79 608-16
[13] Böttger B, Eiken J and Steinbach I 2006 Acta Mater. 54 2697-704
[14] Thermo-Calc Software, http://www.thermocalc.se
[15] Thermotech Ltd., http://www.thermotech.co.uk
[16] Böttger B, Eiken J and Apel M 2009 J. Comput. Phys. 228 6784-95
[17] Böttger B, Apel M, Santillana B and Eskin D G 2013 Metall. Mater. Trans. A 44A 3765-77