

SINGLE CRYSTAL GROWTH OF Ni-BASE SUPERALLOYS BY THE
CONVENTIONAL VERTICAL BRIDGMAN AND NOVEL SUBMERGED
BAFFLE METHODS

by

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ABSTRACT

SINGLE CRYSTAL GROWTH OF Ni-BASE SUPERALLOYS BY THE CONVENTIONAL VERTICAL BRIDGMAN AND NOVEL SUBMERGED BAFFLE METHODS

The purpose of this study is to develop a know-how on the growth of single crystal superalloys and investigate the effect of solidification rate and solidification technique on microstructural features of CMSX-4. Primary dendrite arm spacing (PDAS), dendrite core size, mushy zone length, melt-back transition length, porosity and microsegregation are investigated by comparing two different solidification techniques: the Vertical Bridgman (VB) technique and the Vertical Bridgman with a Submerged Baffle (VBSB) technique. The VBSB technique employs a ceramic disk (baffle) immersed in the melt. The melt is separated into two zones. The small zone below the baffle reduces the melt height, leading to a reduction convection. Samples produced by the VBSB technique show higher PDAs and dendrite core size than those produced by the VB technique. This effect is attributed to decreased convection. Along the height of all samples, PDAS and dendrite core size exhibit an increase. This is due to a decreasing thermal gradient at the s/l interface away from chill plate. Mushy zone and melt-back lengths are decreased for the samples grown with VBSB technique. This can be explained by the higher thermal gradients due to diminished convection. Samples produced by the VBSB technique show lower porosity than those produced by the VB technique, and the effect is more pronounced than for the mushy zone permeability and length. Overall the results show that the amount of convection has a considerable effect on the microstructure of directionally solidified superalloys. Moreover, the Vertical Bridgman with a Submerged Baffle technique can decrease the convection by decreasing the melt height above the solidification interface.

ÖZET

Ni BAZLI SÜPERALAŞIMLARIN KONVANSİYONEL BRIDGMAN VE ÖZGÜN SUBMERGED BAFFLE TEKNİĞİ İLE TEK KRİSTAL ÜRETİMİ

Bu çalışmanın amacı, tek kristal süperalaşım için know-how geliştirmek ve katılaşma hızı ve tekniğinin CMSX-4 mikroyapısına etkilerini araştırmaktır. Primer dendrit kol aralığı, dendrit göbek boyutu, peltemsi bölge uzunluğu, geri erimiş geçiş bölgesi uzunluğu, porozite ve mikrosegregasyon iki farklı teknik karşılaştırılarak incelenmiştir: Vertical Bridgman (VB) ve Vertical Bridgman with a Submerged Baffle (VBSB). VBSB tekniği ergimiş metale daldırılan bir seramik disk kullanmaktadır. Bu seramik disk katı/sıvı arayüzüne yaklaştırıldığında, ergimiş metali iki bölgeye ayırır. Seramik disk altındaki küçük bölge eriyik metal yüksekliğini azaltır ve konveksiyonda bir azalmaya neden olur. VBSB tekniğiyle üretilen numuneler VB tekniğiyle üretilenden daha yüksek PDA ve dendrit göbek boyutu gösterir. Bu etki, azalmış konveksiyona atfedilir. PDAS ve dendrit göbek boyutları tüm numunelerin uzunlukları boyunca artış gösterir. Bunun sebebi, numunenin üst kısımlarına doğru gittikçe soğutma yüzeyinden uzaklaşmış olmasıdır. İlk peltemsi bölge ve geri erimiş geçiş bölgesi uzunluğu VBSB tekniği ile büyütülen numuneler için oldukça düşüktür. Bu sonuçlar, azalan konveksiyonun etkisi ile artan thermal gradyanlara bağlanabilir. VBSB tekniği ile üretilen örnekler VB tekniği ile hazırlananlara göre daha düşük bir gözeneklilik oranı gösterir ve bu etki daha çok peltemsi bölge geçirgenliği ve uzunluğu ile ilgilidir. Sonuçlar konveksiyon miktarının yönlü katılaşırılan numunelerin mikroyapısında önemli bir etkiye sahip olduğunu gösterir. Dahası, Vertical Bridgman with a Submerged Baffle tekniği ergimiş metal içerisindeki konveksiyonu, ergimiş metal yüksekliğini düşürerek azaltabilir.

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LIST OF SYMBOLS

a_1	Primary dendrite calibration factor
C_0	Elemental composition at the beginning of solidification
C_L	Liquid composition
C_L^*	Liquid composition during solidification
C_S	Solid composition
C_S^*	Solid composition during solidification
D	Diffusion coefficient
f_l	Liquid fraction
f_s	Solidified fraction
G	Axial thermal gradient
h	Melt height
K	Permeability
k	Partition coefficient
L	Mushy zone length
l_z	Liquid zone length
m_L	Liquidus slope
P	Pressure
P_G	Dissolved gas pressure
P_A	Atmospheric pressure
r	Nucleus radius
r^*	Critical radius
Ra	Rayleigh number
s/l	Solid/liquid
T	Temperature
T_f	Local melting temperature
T_L	Liquidus temperature
T_m	Melting temperature
T_q	Imposed temperature field

V	Withdrawal velocity
v	Kinematic viscosity
x'	Distance from interface
β	Thermal volume expansion
β_{ss}	Coefficient of solidification shrinkage
γ'	Intermetallic phase in Ni-base superalloy
ΔG^*	Critical energy barrier
ΔG	The difference Gibbs free energies
ΔG_l	Gibbs free energy of the liquid per unit volume
ΔG_v	The volume Gibbs free energy
ΔG_s	Gibbs free energy of the solid per unit volume
ΔP	Pressure drop due to shrinkage
ΔS_f	Entropy of fusion
ΔT	Undercooling
$\Delta\rho/\rho_0$	Density gradient
ϵ	Perturbation amplitude
ϵ_T	Rate of temperature change
θ	Wetting angle
λ_1	Primary dendrite arm spacing
λ_2	Secondary dendrite arm spacing
μ	Viscosity
P_ρ	Metallostatic head pressure
P_σ	surface tension related pressure
σ	The solid/liquid interface energy

LIST OF ACRONYMS/ABBREVIATIONS

EDS	Energy-dispersive X-ray Spectroscopy
PDAS	Primary Dendrite Arm Spacing
SCR	Silicon Controlled Rectifier
SDAS	Secondary Dendrite Arm Spacing
SEM	Scanning Electron Microscopy
VB	Vertical Bridgman
VBSB	Vertical Bridgman with a Submerged Baffle

1. INTRODUCTION

Superalloys are defined as a class of materials with superior properties; high mechanical strength together with fatigue, creep, and corrosion and oxidation resistance at elevated temperatures especially above 800 °C [1]. They can be classified as polycrystal, directionally solidified and single crystal according to their microstructure. In addition, they are classified as Ni-base, Co-base and Fe-base according to their base element. Polycrystalline and directionally solidified superalloys are prone to creep deformation due to the presence of grain boundaries. Therefore, single crystal superalloys are the best performers since they do not have high angle grain boundaries and allow higher operating temperatures. As far as the base element is concerned, Ni-base superalloys have the best properties for high temperature operating conditions. Their performance can be attributed to ordered L12 γ' Ni₃ (Al, Ti, Ta, Nb) precipitates [2]. Moreover, single crystal superalloys do not include grain boundary strengthening elements like boron, carbon or hafnium. They are more solution-treatable and compositionally homogenizable, improving mechanical properties [1]. The absence of grain-boundary strengthening elements is characteristic of the first-generation single crystal superalloys. In addition, a large amount of W, Ta and Mo are added to increase the melting temperature of first-generation superalloys. Performance is improved in second generation superalloys by the addition of 3 wt.% Re, enhancing the creep rupture strength. The third generation contains more Re (6 wt.%) but less Cr to prevent the formation of unwanted phases. For the second and third generations, the segregation of refractory metals causes a convective instability during solidification and the formation of freckle type defects. The driving force to develop fourth-generation superalloys is to enhance the structural/phase stability. The addition of Ru and increased refractory elements provides better stability at high temperatures. However, superalloys become more expensive with the addition of more refractory elements. Recently, developed fifth and sixth-generation superalloys intend to provide better mechanical properties with reasonable performance to cost ratio. The effects of individual alloying elements on superalloy properties and performance are provided in Table 1.1 [1].

Table 1.1. Function of Alloying Elements in Ni-base Superalloys

Elements	Function
Ni:	Base element
Cr:	Forms a protective layer against oxidation and hot corrosion, solid solution strengthener
Co:	Solid solution strengthener
Al:	Forms protective layer against oxidation, precipitate former
Mo:	Solid solution strengthener
W:	Increases the incipient melting temperature
Re:	Improves the high temperature capability
Ta:	Segregates into the interdendritic regions and decreases density inversion and freckling
Ru:	Improves phase stability and enhances creep strength
Nb, Ti:	Strengthen γ' , form carbides
C, B, Z, Hf	Act as grain boundary strengtheners
Y, Hf:	Improves the adherence of the protective layer

Despite the already superior properties of the superalloys, new compositions are sought to increase the performance of devices using them. One of the major concerns with alloying is avoiding detrimental phases such as topologically closed-packed phases (TCPs). These are among the detrimental phases which are formed especially in alloys rich in refractory elements like Mo, W, Re, and Ta. Another group is the boride and carbide phases which are formed especially in alloys containing grain boundary strengtheners like C, B, Zr, and Hf together with Cr, Mo, Ti, and Ta [1]. Although carbides and borides can act as crack initiation sites especially under long-term stress conditions, they can also serve as pinning sites for dislocations and result in higher creep performance [1]. As a result, alloy design is constrained by the unwanted phases formed during high and complex alloying.

Investment casting is the primary technique for the production of superalloy articles because it allows complex geometries such as turbine blades with cooling channels. Casting can be equiaxed, columnar, or single crystal depending on the solidification

parameters and techniques used. An equiaxed microstructure is obtained with uniform cooling throughout the volume. When cooling is performed with an axial temperature gradient, the grain structure can be columnar. More stringent control of the temperature gradient and cooling velocity can yield a single crystal. Furthermore, production of a single crystal microstructure requires either a seed or a grain selector. The final properties and performance of a superalloy component are directly linked to the parameters present during the solidification process. The axial thermal gradient (G) and solidification velocity (V) are the two main parameters affecting the final microstructure. According to the literature [3–6], a high temperature gradient (G) increases the probability of having single crystals with a reliable microstructure characterized by low segregation, a fine microstructure, and a small mushy zone. The withdrawal rate should be carefully adjusted based on the thermal gradient. Otherwise, solidification could be successful even for high thermal gradients. The relation between G and V comes from the speed of withdrawal and speed of the solidification interface. Undercooling should be avoided to keep the interface stable. The microstructure formed during directional solidification consists of elongated dendrites along the temperature gradient. These elongated dendrites form a fiber-like structure and strengthen the material in a preferred direction. The distance between the dendrites is termed primary dendrite arm spacing (PDAS), and is a widely used parameter characterizing the microstructure. The PDAS is also dictated by the solidification parameters G and V . Directional solidification brings its own unique defects. Segregation of low density elements into the interdendritic melt can cause density inversion and hence melt plumps which can break the secondary dendrite arms (SDA), leading to formation of equiaxed grain chains called freckles [7, 8]. Freckles present around the perimeter and align with the solidification direction. Low temperature gradients (G), high segregation and large dendritic arms encourage the formation of freckle chains. Another type of defect are misaligned grains from arrays of dendrites which do not grow parallel to the solidification direction. They can form high angle grain boundaries and crack initiation sites under stress. These two defects can be considered as modern superalloy defects which result in the rejection of the components. Therefore, much research has been done to understand their nature and predict them. For example, the Rayleigh Number

(Ra) which is the ratio of the buoyancy force to frictional force in the mushy zone can be used as a predictive measure. A low Ra indicates a laminar flow, whereas a high one indicates a turbulent flow that can cause formation of freckles and misoriented grains. [9–11].

The Ra number can be kept low by solidifying with a reduced melt height. This suggests a novel solidification method called Vertical Bridgman with a submerged baffle (VBSB), in contrast to conventional vertical Bridgman method which is currently the sole production method for turbine blades with complex geometries.

2. OBJECTIVES

This research is conducted to compare microstructures of the second generation superalloy CMSX-4 as produced by the VB and VBSB methods. Thus, the viability of the VBSB as a production method for turbine blades is assessed. The objectives of this study are as follows:

- To successfully grow single crystal superalloys with the bottom seeding technique.
- To observe microstructural features of the grown samples (mushy zone, melt-back, dendrite, eutectic, carbide, precipitation).
- To observe microstructural differences along the sample (mushy zone length, melt-back length, PDAS, primary dendrite core size, SDAS, porosity).
- To observe the effect of growth velocity on the microstructure (mushy zone length, melt-back length, PDAS, primary dendrite core size, SDAS, porosity).
- To observe the reduced melt height effect on the microstructure (Mush zone length, melt-back length, PDAS, primary dendrite core size, SDAS, porosity). The VBSB technique can decrease the melt height.
- To observe the segregation characteristics of the grown samples.

3. BACKGROUND

3.1. Solidification Theories

Solidification is a phase transformation from the liquid to solid phase or phases. The solidification process includes mass and energy transport. It initiates with grain nucleation and proceed with grain growth.

3.1.1. Nucleation

If there are no foreign inclusions in the liquid phase and there is enough undercooling, homogeneous nucleation can occur by the formation of nucleants of solid phases homogeneously distributed in the liquid phase. Nucleation is driven by the change in the Gibbs free energy [12],

$$\Delta G = \Delta G_l + \Delta G_s = 4\pi r^2 \sigma - \frac{4\pi r^3}{3} \Delta G_v \quad (3.1)$$

where σ is the solid/liquid interface energy, r is the nucleus radius, and ΔG_v is the difference in the Gibbs free energies of solid (ΔG_s) and liquid (ΔG_l) phases per unit volume. As shown in Figure 3.1, a stable nucleus is formed if r exceeds a critical radius, r^* [12]. Atomic aggregates with radii less than r^* are called clusters or embryos. In addition, the Gibbs free energy at that critical radius, ΔG^* , is the energy barrier that has to be exceeded for the formation of a stable nucleus. This energy barrier is inversely proportional to the degree of undercooling, ΔT . [13]. Homogeneous nucleation requires the absence of impurities or nucleation sites like phases, defects, instabilities, or even mold wall. Thus, homogeneous nucleation can be formed just with special techniques or on small scales. If there is any nucleation site in the melt, heterogeneously distributed nuclei originate on them with much smaller undercoolings as compared to homogeneous nucleation. Figure 3.2 is a simple illustration of heterogeneous nucleation on a flat foreign substrate [12].

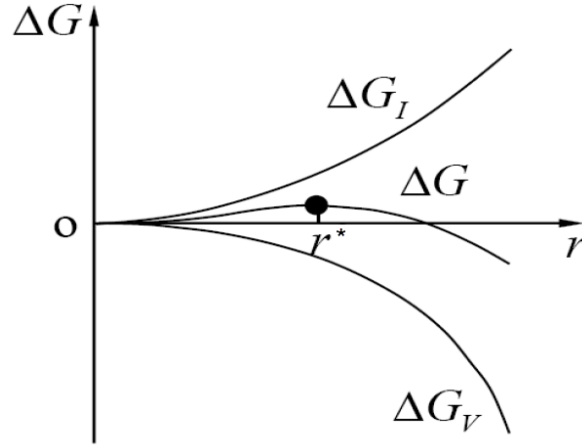


Figure 3.1. Critical radius for a nucleus

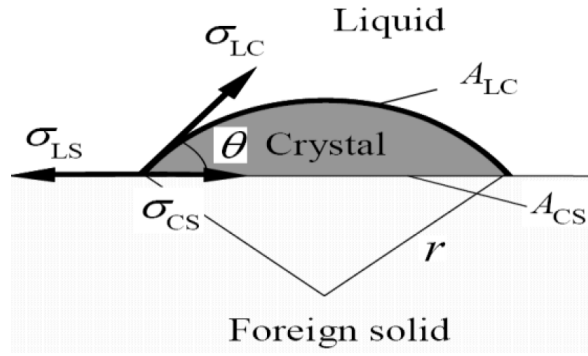


Figure 3.2. Heterogeneous nucleation

The driving force for heterogeneous nucleation is given by [12],

$$\Delta G_{Het} = \Delta G f(\theta)$$

$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \leq 1 \quad (3.2)$$

where θ is the wetting angle. Since $f(\theta)$ is always less than or equal to one, the energy requirement for heterogeneous nucleation is always less than or equal to that for homogeneous nucleation.

3.1.2. Growth

Once a nucleus with a radius greater than r^* forms, there is a thermodynamic driving force for it to grow.

3.1.2.1. Undercooling. Any phase transformation like solidification requires a driving force. In solidification, this force is related to the undercooling, ΔT , which is the deviation from the equilibrium melting temperature, T_m . Undercooling is alternatively defined as

$$\Delta T = \frac{\Delta G_v}{\Delta S_f} \quad (3.3)$$

where ΔS_f is the entropy of fusion. The driving force for solidification is zero if there is no undercooling, implying no transformation. For homogeneous nucleation undercoolings as high as 300K can be required, while only 2-10K is often enough for heterogeneous nucleation [14].

3.1.2.2. Stability of Solid/Liquid Interface. A solidifying interface can take one of two morphologies, planar or cellular/dendritic. A stable planar interface is achieved when the axial temperature gradient damps the perturbations that occur at the s/l interface. On the other hand, an instability can be caused by growing perturbations at the s/l interface, as shown in the Figure 3.3 [12]. In Figure 3.3 a, the T_q (temperature field) temperature always increases in the z direction indicating a positive thermal gradient. The interface position corresponds to T_f (melting temperature). A perturbation that has amplitude ϵ is formed during the directional solidification of a pure substance. The perturbation tip melts back and the interface stabilizes because the gradient at the tip of the perturbation increases (A-A) causing more heat flow to the tip and that then melts. However, the opposite happens for equiaxed solidification in Figure 3.3 b where the liquid is supercooled (T_q decreases along the z), so the thermal gradient is less than zero. The situation for pure substances can be summarized as follows: a perturbation is damped if the gradient at the s/l interface is positive, and grows if the gradient is

negative.

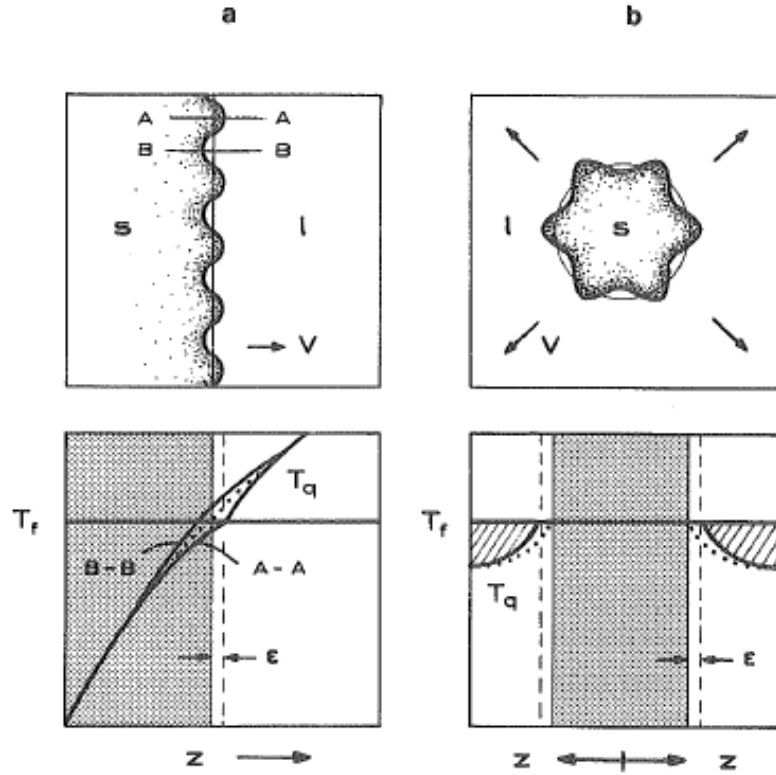


Figure 3.3. Decaying (a) and Growing (b) Interfaces

The situation is more complicated when considering segregation of alloying elements. Cellular/dendritic growth can occur even if the axial temperature gradient is positive. This phenomenon is called constitutional supercooling [12,13]. In Figure 3.4, a simple phase diagram is illustrated. The elemental composition just ahead of the interface (C_0/k) is higher than the solid concentration and also the initial concentration (C_0). This is due to the different solubility of the alloying element in the solid and the liquid. This differential solubility is quantified by the segregation coefficient (k) which is the ratio of the solute concentration in the solid to that in the liquid. A solute boundary layer forms just ahead of the interface as in Figure 3.5 for elements with segregation coefficient less than unity. As shown in Figure 3.5, the melting temperature (T_L) is a function of composition; more solute lowers the liquidus temperature (T_L). The cross-hatched region, where the imposed temperature (T_q) is less than the

liquidus temperature, is supercooled even if the axial temperature gradient is positive. However, if the imposed temperature gradient $(dT_q/dz)_{z=0}$ is greater than $(dT_L/dz)_{z=0}$, supercooling does not occur (Figure 3.5 a). Otherwise, cells and dendrites can grow along the z direction (Figure 3.5 b). By using the equality $dT_q/dz = dT_L/dz$ at the interface, the following stability requirement can be derived in terms of the solidification parameters G and V [15]:

$$\frac{G}{V} \geq -\frac{m_L C_0 (1 - k)}{k D_L} \quad (3.4)$$

where G is the imposed axial temperature gradient, m_L is the liquidus slope, D_L is the diffusion coefficient of the solute in the liquid, V is the solidification rate, and $k = C_S/C_L$. Even though there are many assumptions in the derivation of this equation, it still shows that the temperature gradient (G) and withdrawal velocity (V) are the main parameters controlling the stability of the s/l interface.

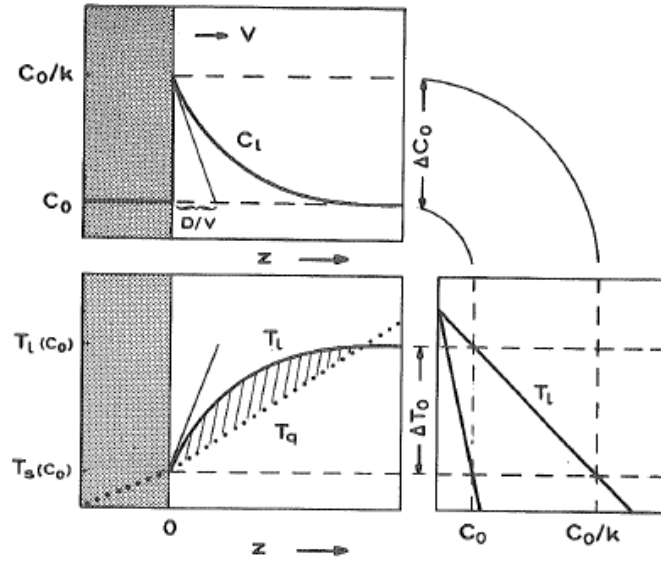


Figure 3.4. Melting temperature as a function of composition

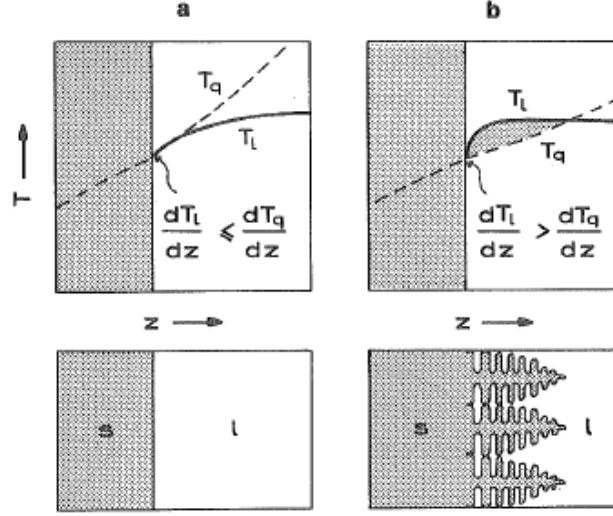


Figure 3.5. Planar (a) and dendritic interface (b)

3.2. Solute Redistribution

During solidification, solutes are either rejected to the liquid or incorporated to the solid according to their solubility. Rejected solutes can be carried away from the s/l interface by the diffusion and/or liquid convection. If there is considerable diffusion or convection, rejected solute can be distributed effectively, and result in less solute build up at s/l interface. On the contrary, if the solidification rate is faster than the rate of solute transport, a solute build up at the s/l interface takes place.

Depending on the mode of the solute transport in the melt, several analytical models have been suggested to predict the solute distribution in the solid. Some common assumption in the derivations are [13]:

- Equilibrium at the solid-liquid interface.
- Segregation coefficient (k) is a constant less than unity
- No significant undercooling before nucleation.

3.2.1. Equilibrium Solidification

When the diffusion of solutes is fast and the local solidification time is long, complete mixing in both the solid and liquid can theoretically be achieved. However, this type of redistribution is rare. As seen in Figure 3.6, solidification starts with the liquid composition C_0 and liquid is enriched (C_L^*) by the rejected solutes from the solid as solidification continues. Due to the fact that every solid layer is formed from an enriched liquid, composition of the solid (C_S^*) also increases from its very first value of kC_0 . At the end of the solidification, composition of the solid reaches C_0 uniformly all along the solid.

$$C_S = \frac{kC_0}{1 - (1 - k)f_S} \quad (3.5)$$

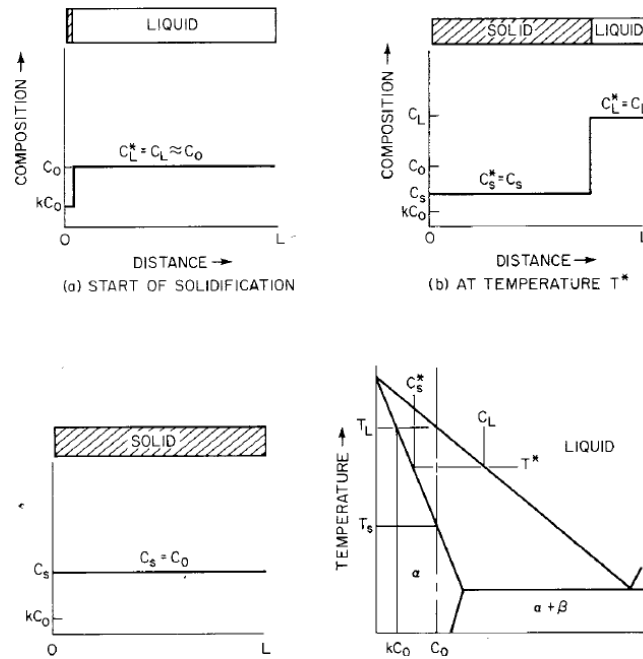


Figure 3.6. Plane front solute redistribution

3.2.2. No Diffusion in Solid and Complete Mixing in Liquid

In this model, there is no diffusion thus no mixing in the solid but complete convective mixing exists in the liquid. As solidification continues, liquid becomes enriched (C_L^*) in solute and so the solid (C_S^*) formed from a solute rich liquid. Since no diffusion takes place in the freezing solid, the final solid has a varying solute content along its length (L). Composition of the solid along the length is derived by Scheil as follows:

$$C_S^* = kC_0(1 - f_S)^{(k-1)} \quad (3.6)$$

where (f_S) is the fraction solidified. Predictions of the Scheil model are usually close to results.

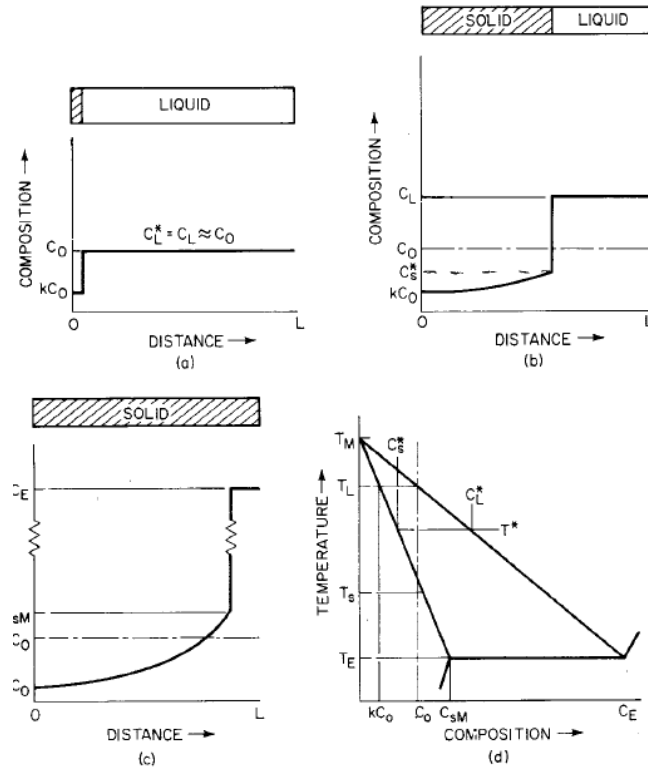


Figure 3.7. Solute redistribution in solidification with no solid diffusion and complete mixing in liquid.

3.2.3. No Diffusion in Solid and Diffusional Mixing in Liquid

In this model, diffusion in the solid is again neglected and the mixing in the liquid is assumed to be diffusional. This assumption allows formation of a solute boundary layer ahead of the interface. The solute concentration in the liquid within the boundary layer drops from C_0/k at the interface to the far field value C_0 . Final solid has a uniform solute composition, C_0 , in the steady state region with initial and final transient before and after this region. As shown in Figure 3.8, there is an initial transient region that ends when the solute concentration reaches C_0 . A final transient occurs toward the end of the sample where the solute boundary layer reaches the end of the sample. In the final transient region, the rejected solute cannot be diffused away totally due to the end effect, thus leading to an elevated solute concentration. According to this model, the liquid composition at the steady state in terms of solid fraction is given as follows:

$$C_L = C_0 \left(1 + \frac{(1-k)}{k} e^{((-V/D_L)x')} \right) \quad (3.7)$$

where x' is the distance from the interface to the end of the specimen and V is the solidification velocity.

The equation of solute redistribution in solid during the initial transient is given as:

$$C_S = C_0 \left(1 - (1-k) e^{(-k \frac{V}{D} x')} \right) \quad (3.8)$$

As shown in Figure 3.8 the final transient is much smaller than the initial transient since the length of the final transient is the order of the solute boundary layer.

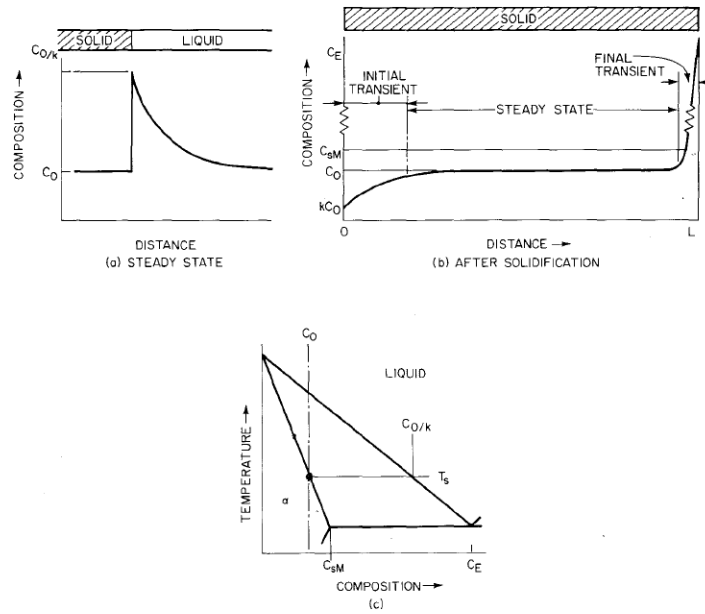


Figure 3.8. No Diffusion in Solid and Limited Diffusion in Liquid

3.2.4. Zone Melting

In this method, an induction coil melts a thin layer of the seed and a portion of the charge, which makes the melt in front of the seed finite. Therefore, equations for the complete diffusion in liquid and the limited diffusion in liquid must be modified. Pfann [16] developed an equation for the case of complete mixing in the liquid zone:

$$C_S(z) = C_0(1 - (1 - k)e^{-\frac{kz}{h}}) \quad (3.9)$$

where h is the liquid zone length. Pure diffusion in the liquid zone, is treated by Tiller [15]. The solute distribution in the initial transient and the steady state region is characterized as:

$$C_S(z) = C_0(1 - (1 - k)e^{-\beta Z}) \quad (3.10)$$

where

$$\beta = k \frac{V}{D} [1 - e^{(-\frac{V}{D}h)}]^{-1} \quad (3.11)$$

when the liquid zone length h is smaller than the solute boundary layer. Note that the zone melting method is similar to the VBSB method used in the present study.

3.2.5. Redistribution in Dendritic Front

Solute redistribution in the plane front solidification has been threated above. When cells or dendrites form at the s/l interface, the behaviour is different. A dendritic/columnar structure is shown in Figure 3.9 [12]. The trunk of the tree-like structure is called a primary dendrite, and grows parallel to the imposed temperature gradient while secondary dendrites grows perpendicular to the gradient. The distance between two primary trunks is called primary dendrite arm spacing (λ_1) and the distance between the secondary dendrites is called secondary dendrite arm spacing (λ_2). These two parameters are crucial to characterize a solidified material, so many models have been developed to correlate them to the solidification parameters.

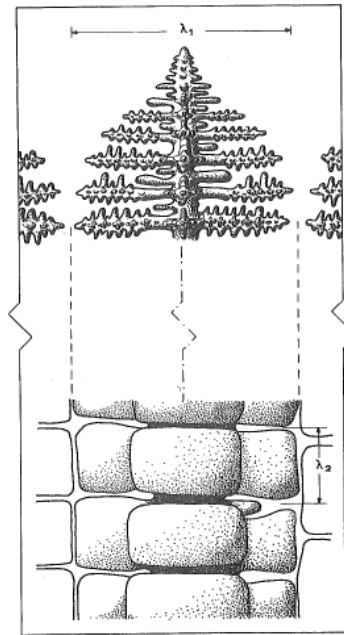


Figure 3.9. Dendritic solidification front

There are several significant differences between a plane front and a dendritic front. First, the contact area between the solid and the liquid phases in a dendritic front is much higher than that in a plane front. This results in a more effective transfer of the latent heat to the liquid. Second, there is solute transport by diffusion and convection within the liquid ahead of the dendrites and between the dendrites within the mushy zone. This enriches the dendrite tips as solidification proceeds, changing the dendrite morphology and segregation characteristics. Finally, fluid flow between the dendrites (mushy zone) can break or melt some secondary dendrites and deposit them in other regions, leading to freckles. The redistribution behavior mainly depends on the solidification rate, the temperature gradient, segregation coefficient of the alloying elements, and the arm spacing. Redistribution characteristics are much more complex for a dendritic interface, and current models are still incomplete.

A simple case for the dendritic solidification is shown in Figure 3.5 [12]. Due to solute rejection, constitutional undercooling occurs ahead of the s/l interface and is the driving force for the dendritic growth. However, there is also an inhomogeneous distribution perpendicular to the growth direction.

Localized radial, uneven solute distribution, or microsegregation, is due to the rejection of solutes by the recently formed solid phase into the interdendritic liquid inside the mushy zone. The segregation coefficient (k) dictates whether an element segregated to the dendritic core or to the interdendritic melt as seen in Figure 3.10. In fact, the segregation coefficient in dendritic structures is found as the ratio of the dendrite core composition to the interdendritic composition. Figure 3.10 shows representative composition profiles for elements that tend to be rejected to the interdendritic region and segregated to the core.

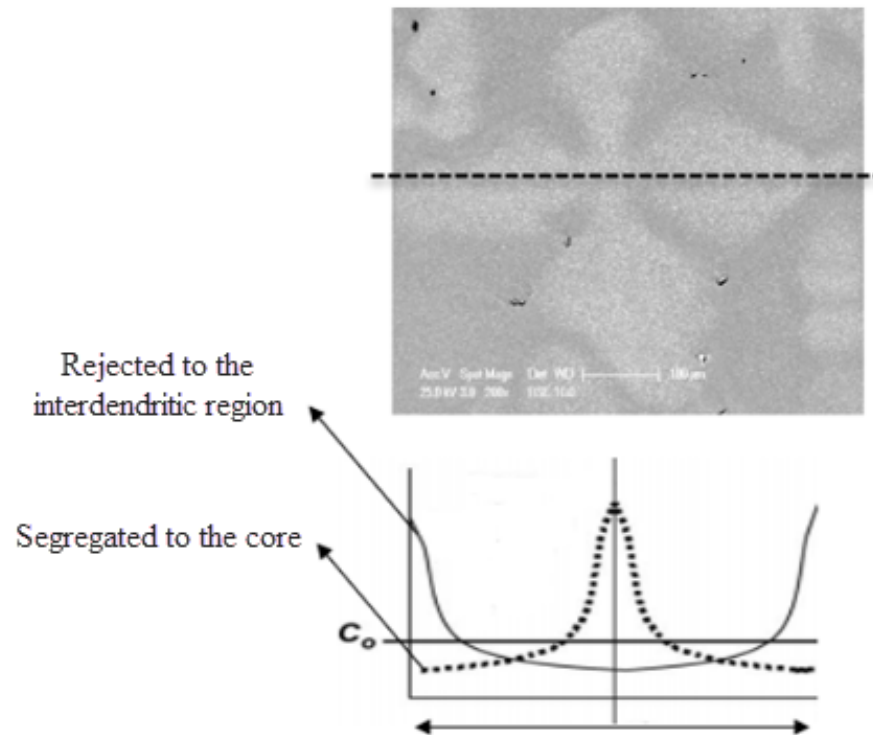


Figure 3.10. Microsegregation profile in a dendrite. The chemical analysis is conducted on the dashed line.

3.3. Microstructural Features

3.3.1. Mushy Zone and Melt-back Transition Length

During vertical directional solidification of the superalloys, there forms a region between the position of the the solidus and the liquidus temperatures of the alloy. Obviously, the solid and liquid phase coexist between this region which is called the mushy zone. The mushy zone length is directly influenced by the thermal gradient and the heat extraction rate from the system in addition to the range between the solidus and the liquidus temperatures. The dendrites in the mushy zone are soft because of their semi-solid nature. Therefore, any melt-flow based disturbances can destroy the dendritic structure in the mushy zone and cause the formation of misoriented dendrites

and even grainy regions. This disturbed region is called the melt-back transition region. The melt-back transition length is highly influenced by the convection in the melt which especially disturbs the top of the mushy zone where the velocity of convection is expected to be highest.

3.3.2. Primary Dendrite Arm Spacing and Primary Dendrite Core Size

Characterizing the primary dendrite arm spacing (PDAS) in directionally solidified samples is crucial to reveal the influence of processing parameters on microstructure. Hunt [17] developed the first theoretical formulation linking the imposed process parameters to the PDAS. According to his study, PDAS is reversely proportional to the thermal gradient (G) and the withdrawal velocity (V), as follows:

$$\lambda \sim (G)^{-1/2}(V)^{-1/4} \quad (3.12)$$

The number of dendrite cores in a specific area is correlated with the PDAS and the PDAS (λ_1) can be found via the equation as follows [18]:

$$\lambda_1 = c\sqrt{\frac{A}{n}} \quad (3.13)$$

where λ_1 is PDAS, c is a coefficient depending on the shape of the dendritic array, A is the area, and n is the number of dendrites in that area A . The c takes a value of 0.5 for a random, 1 for a square, and 1.075 for a hexagonal dendritic array. The dendrites of superalloys form a square array. Moreover, dendrite core size is the diameter of the individual dendrite cores assumed to cover a circular area. The main factor influencing the dendrite core size is the withdrawal velocity.

3.3.3. Secodary Dendrite Arm Spacing

The secondary dendrite arm spacing (SDAS) is defined as the distance between the protruding adjacent secondary arms on a primary dendrite trunk. It has been used together with PDAS to describe the process and property relationship. The samples having lower SDAS give better tensile but lower creep resistance, especially for aluminum alloys [19]. Various theoretical approaches relate the SDAS (λ_2) with the local solidification time (t_f) and with the cooling rate [20]. t_f is the product of temperature gradient (G) and solidification rate (V), as follows:

$$\lambda_2 \sim (t_f)^{1/3} \sim \left(\frac{1}{GV}\right)^{1/3} \quad (3.14)$$

SDAS is determined by soldification time through the mushy zone. Longer solidification time results in a larger SDAS. In addition, reducing G and V causes coarser dendrites due to the increased solidification time.

3.3.4. Porosity

The nucleation of a pore can occur due to the dissolved gas pressure (P_G) and pressure drop (ΔP) because of solidification shrinkage inside the mushy zone. On the other hand, atmospheric pressure (P_A), metallostatic head pressure (P_ρ), and surface tension related pressure (P_σ) try to close the pore [21]. The (ΔP) is proportional to the mushy zone length (L), flow velocity (V), and permeability (K) of the mushy zone through the Darcy's Law as follows [21, 22],

$$\Delta P = \frac{V\mu L}{K} \quad (3.15)$$

where μ is the viscosity of the melt. Reduced V and L can decrease the porosity, although decreased permeability of the mushy zone can increase the porosity of the sample.

3.4. Convection

Superalloys are solidified in vertical Bridgman mode where a positive axial temperature gradient is imposed to stabilize the melt convection. However, radial temperature gradients can set in considerable convection in the melt. Various microstructural occurrences such as solidification shrinkage, thermal and solutal buoyancy, nucleated or floating solid fragments, and forced flows due to vibration, rotation, or pouring can cause fluid motion. As expected, fluid motion during solidification has a significant effect on the microscopic and macroscopic features of the solids. For instance, freckle formation, segregation of solutes, and porosity are major consequences of the thermo-solutal convection. To understand the mechanisms and quantitatively predict the results beforehand, a great effort has been made to model the fluid flow during solidification. However, due to the complex nature of dendritic solidification, there is no comprehensive theory representing the fluid flow during solidification of superalloys. As for dendritic solidification of superalloys, the melt flow can be treated as two separate but interacting regions, namely the mushy zone and the bulk liquid ahead of the dendrite tips. Early models to simulate the fluid flow considered the flow inside the mushy zone but neglected the flow in the bulk the melt. For example, the macrosegregation model developed by Flemings et al. in 1960s [23–25] considered a fixed dendritic mushy network. By performing a mass and species balance there, the local solute redistribution equation (LSRE) was derived to be:

$$\frac{df_l}{dC_l} = -\frac{1-\beta}{1-k} \left[1 + \frac{V \cdot \nabla T}{\epsilon} \right] \frac{f_l}{C_l} \quad (3.16)$$

where f_l is the liquid fraction, C_l is the solute concentration in the liquid, β is the coefficient of solidification shrinkage, V is the velocity vector of the liquid, ∇T is the temperature gradient, and ϵ is the rate of temperature change. This formulation simply links the interdendritic fluid flow and segregation. Mehrabian et al [26] defined a porous medium representing the mushy zone, and the velocity of the fluid flow inside

that region was found to be:

$$V = -\frac{K}{\mu}(\nabla P + gC_l) \quad (3.17)$$

where K is the permeability, μ is the viscosity, ∇P is the pressure gradient, and g is the gravitational constant. These type of equations have a common limitation which is the interdependence of the mushy zone morphology and permeability. While the permeability affects the convection by affecting the dendrite arm spacing, the convection alters the permeability. This limitation precludes the exact solution of the problem. Therefore, a non-dimensional Rayleigh number inside the mushy zone has been derived to describe the extent of convection in this region, which avoids the bulk flow [27–31]:

$$R_a = \frac{(\Delta\rho/\rho_0)gKL}{\alpha V} \quad (3.18)$$

where $\Delta\rho/\rho_0$ is the density gradient in the liquid, α is the thermal diffusivity and v is the kinematic viscosity. In this formulation, $\Delta\rho/\rho_0$, α , and V are inherently dependent on the alloy chemistry. The viscosity and diffusivity can affect the extent of the convection, while the density gradient can change even the flow direction depending on its sign. A positive density gradient can set in an upward plume, while a negative gradient can stabilize the vertical fluid motions. On the other hand, the convection is directly related to the permeability which is linked to the dendrite arm spacing and length of the mushy zone.

Furthermore, flow characteristics of the bulk melt have a considerable effect on the interdendritic melt flow. This has been reported in various studies [9,32–34]. For instance, reduced convection in the bulk melt can decrease the interdendritic convection. The reduction in the interdendritic convection can substantially change the as-grown microstructure of the casting. The detailed discussion will be given in Section 7.

3.4.1. Effect of Convection on Primary Dendrite Arm Spacing

The primary dendrite arm spacing is considered to be the main microstructural feature that is related to material [35]. Hence, numerous studies have been carried out to reveal the parameters affecting the fineness of the primary dendrite spacing. Two main parameters, the axial temperature gradient at the s/l interface (G) and the solidification velocity (V), are found to have considerable effects on the primary dendrite arm spacing (PDAS) [36–38]. Certain theoretical and empirical formulations relating the solidification parameters to the PDAS have been derived by other researchers. The first two theories developed by Hunt [17] and Kurz and Fisher [39] characterized the PDAS (λ_1) as a function of the temperature gradient (G), the withdrawal rate (V), and the composition (C_0). Under the steady state conditions in the high velocity regime, these models are:

Hunt Model:

$$\lambda_1 = 2.83[m_L(k-1)D\Gamma]^{0.25}C_0^{0.25}V^{-0.25}G^{-0.25} \quad (3.19)$$

Kurz and Fisher model:

$$\lambda_1 = 4.3[m_L(k-1)D\Gamma/k^2]^{0.25}C_0^{0.25}V^{-0.25}G^{-0.25} \quad (3.20)$$

where Γ is the Gibbs–Thomson coefficient. Trivedi [40] improved Hunt’s theory by including a constant (l) relating to the interface perturbation:

$$\lambda_1 = 2.83[m(k-1)D\Gamma l]^{0.25}C_0^{0.25}V^{-0.25}G^{-0.25} \quad (3.21)$$

These equations are derived for steady-state conditions with diffusional mass transport, and do not agree well with experimentals because convection due to thermo-solutal gradients is inevitable. Hunt-Lu [22] and Bouchard-Kirkaldy [41, 42] proposed

formulations to characterize the PDAS considering this convection. In their model, the temperature gradient and the solidification velocity change during solidification, unlike the steady-state models. The equations for their models are:

Hunt and Lu model:

$$\lambda' = 0.07798V'^{a-0.75}(V' - G')^{0.75}G' - 0.6028 \quad (3.22)$$

where $\lambda' = \lambda\Delta T_0/(\Gamma k)$, $G' = G\Gamma k/(\Delta T_0)^2$, $\Delta T_0 = mC_0(k - 1)/k$, $V' = V\Gamma k/(D\Delta T_0)$, and $a = -1.131 - 0.1555 \log G' - 0.007589(\log G')^2$,

Bouchard and Kirkaldy model:

$$\lambda = a_1 \frac{16C_0^{0.5}G_0\epsilon\Gamma D}{(1 - k)mGV} \quad (3.23)$$

where G_0 is a characteristic parameter and a_1 is the primary dendrite calibrating factor.

3.5. Directional Solidification With A Submerged Baffle

Directional solidification is a crystal growth technique to yield a columnar or single crystal microstructure. This technique uses a furnace with one or multiple heaters. In addition, a chiller can cool one end to aid the directional alignment. The earliest directional solidification system with a single heater is named after P. W. Bridgman [43]. Later, Stockbarger [44] improved it by adding a second heater with a lower temperature than the first one. In this technique, melting takes place inside a crucible where a seed-charge couple is placed, and the crucible is positioned inside the furnace so that the s/l interface is established at a position within the seed. The initial (just before solidification) position of the crucible inside the furnace is decided according to the liquidus temperature of the solidifying alloy and controlled via the readings from thermocouples mounted on the crucible. After partially melting the seed, solidification is started by moving down the crucible to a lower-temperature region of the furnace with a velocity. Vertical Bridgman technique is widely used in the directional solidifica-

tion of superalloys due to its ease of use and effectiveness in producing both columnar polycrystal and single crystal ingots. Weaknesses of the technique are a non-planar interface due to radial temperature gradients and buoyancy-driven liquid convection. As a remedy to these problems, first Golyshev and Gonik [45] and then Ostrogorsky [46] have patented a technique respectively called the Axial Heat Processing (AHP) and the Submerged Heater Method (SHM). Although the names are different, they are essentially the same. They make use of a baffle (with a heater) submerged in the melt and positioned near the s/l interface. This baffle not only can minimize the radial temperature gradient by supplying heat axially, but also allows close monitoring of the s/l interface via thermocouples inside it. In addition, the baffle divides the bulk melt into two regions. As a result of this separation, the effective melt height above the s/l interface decreases and so does the amount of natural convection. The Vertical Bridgman with a Submerged Baffle technique is very similar to AHP and SHM, with the difference that a high purity alumina baffle is used without a heater as shown in Figure 3.11. In this technique, a ceramic baffle is positioned at a predetermined height (h) above the s/l interface to decrease the melt height. The position of the baffle is fixed during the solidification.

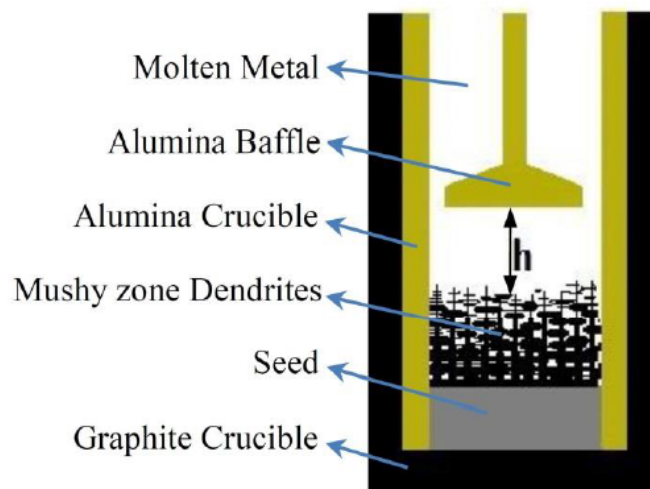


Figure 3.11. Vertical Bridgman with a submerged baffle technique

4. EQUIPMENT

The solidification system, seen in Figure 4.1, at the Bogazici University Crystal Growth Laboratory was specifically designed for single crystal and directional solidification experiments and is able to integrate a submerged baffle. The system is composed of a furnace, a servo motor, a chiller, a vacuum pump, and a data acquisition and control system. The latter consists of data input/output cards, power controllers (SCRs), temperature sensors (C-type thermocouples), and a control software developed on the Labview platform in-house.



Figure 4.1. Solidification system

A four-zone tubular furnace is made by winding molybdenum wire around a high purity (99.8%), dense alumina tube. The wire is shielded with high purity alumina beads to prevent electrical shorting of windings. Each zone is separately controllable up to a maximum temperature of about 1600 °C. Thermal insulation, in the form of

two cylindrical Mo sheets and graphite felt, is placed around the furnace. A water cooled double wall stainless steel chamber encapsulates the heating system.

A graphite casing attached to a molybdenum rod is used as a thermocouple housing and an outer casing for the alumina crucible. The molybdenum rod is connected to a stainless steel water chilled shaft and keeps the chilled shaft 20 cm away from the heating zone. Otherwise, the stainless steel shaft could be damaged or the chilling water could evaporate due to the high temperature in the heating zone. The chilled shaft is connected to a servo motor, servo drive, and a power gear which converts the rotational motion of the motor to a vertical translation. The chilled shaft enters the stainless steel chamber through a Wilson vacuum seal.

An alumina ceramic tube as the melting crucible is inserted into the graphite casing. In order to prevent damage to the graphite casing from molten metal leakage, the melting crucible bottom is closed with a 3 mm thick graphite disk that fits inside the melting pot. The clearance between the graphite disk and the melting crucible is filled with graphite foil.

There are 7 C-type thermocouples on the system. Four of them (TCH1-TCH4) are used to monitor and control the temperatures of each heater while the others (TC5-TC7) are used to measure the thermal profile near the s/l interface. C-type thermocouples have been produced from Tungsten- 5% Rhenium and Tungsten-26% Rhenium wires. The thermocouple junctions have been formed by a TIG welder. Two types of insulators have been used to insulate them both thermally and electrically. For the first part that is inside the furnace, double-hole and single-hole alumina ceramic sleeves are used, and for the rest that extends out of the furnace, fiber glass insulators are used. The heater thermocouples are attached to the middle of each heating zone with an extra ceramic protection tube. Graphite casing thermocouples are fastened to the grooves of the graphite casing via Tungsten-26% Rhenium wires, starting from the bottom of the graphite casing (seed bottom), with 15 mm spacing upward. Graphite casing thermocouples are fed from the bottom of the stainless steel shaft through a center hole. Sealing is provided by feeding the thermocouples between two rubbers

pressed against each other.

Thermocouples are interfaced to a computer by a Keithley 7700 differential multiplexer module attached to a Kiethley 2700 data acquisition and switching system. The Kiethley system receives voltages from the thermocouples, amplifies and sends them to the Labview software whose output is then sent to the Kiethley PCI3130 analog output card. A cold junction compensation is done by reading the junction temperatures with a K-type thermocouple and converting this temperature to voltage. The cold junction in Kiethley 2700 is done internally. The data acquisition card is interfaced with Labview Software, which is used to convert the voltage signals to temperature data. 0.1 Hz real time data acquisition is accomplished.

Each furnace heater is controlled by a different Eurotherm single phase power thyristor 7100A (Silicon Controlled Rectifier). PID algorithms in the Labview interface compare the set temperature and actual temperature for each furnace heater. Accordingly, the PCI3130 output card sends a voltage to the SCRs, and then the SCRs regulate the current to the heaters.

A mechanical pump which can supply a maximum of 4×10^{-2} mbar vacuum is used to remove oxygen and contaminants from the crystal growth system. In addition, a high purity (99.999 %) argon supply tank is connected to the system. Before heating the system, the chamber is evacuated to 4×10^{-2} mbar and purged with argon. This cycle is repeated twice to decrease the oxygen content of the chamber. Then, heating starts in vacuum up to 500 °C so that contaminants from degassing can be evacuated. Finally, the chamber is filled with argon to 0.5 bar over the atmospheric pressure and argon flow continues throughout the experiment at 0.5 bar inside the chamber. The pressure is shown by a pressure gauge. Argon outlet is connected to a bottle partially filled with water; bubbles in the water indicate the argon flow inside the chamber.

5. PRELIMINARY EXPERIMENTS

5.1. Furnace Gradient and Thermal Profile Experiment

Experiments have been conducted to obtain the highest possible and at the same time stable thermal gradient in the four zone directional solidification furnace. This is important because the scale of a solidification microstructure is proportional to the thermal gradient in the case of directional growth of superalloys, as reported in the literature [3–6].

Figure 5.1 shows the furnace zones and temperature profiles obtained by three thermocouples (TC5 - TC7). First, aiming to find the maximum thermal gradient in the furnace, only the top heater of the four zone furnace H4 was heated to 1500 °C. As expected, after TCH4 reached its set temperature, the thermocouples (TCH1 to TCH3) also heated up despite the other heaters being off. After 1 hour of stabilization time, the heater thermocouples showed the following: TCH4 = 1500 °C, TCH3 = 1301 °C, TCH2 = 1108 °C, and TCH1 : 885 °C. Then the average thermal gradient formed along the furnace was calculated by using the temperatures shown by TCH4 and TCH1 and the distance between them, $L_{furnace}$, in $(TCH4-TCH1)/L_{furnace}$. The calculated thermal gradient was 29.3 °C/cm, and this is the maximum temperature gradient that can be created by the furnace. However, the furnace thermocouples was not stable. Alternatively, the average thermal gradient could be determined by the crucible thermocouples when the crucible was set to its initial position before the solidification. After the furnace temperatures reached their set values, the crucible thermocouples showed the following: TC7 = 1381 °C, TC5 = 1278 °C. The average thermal gradient along the crucible was calculated by using $(TC7-TC5)/a$, where a is the distance between TC5 and TC7 (30 mm). The gradient was found to be 33.3 °C/cm using the thermocouples around the graphite casing. However, the temperature was not stable for these furnace settings and TC1 to TC3 tended to increase by 0.5 °C every ten seconds. The stability of the furnace temperature is important to conduct a controlled solidification experiment. Otherwise, an uncontrolled, continuously varying

solidification temperature would not allow a parametric solidification study.

A new temperature combination for the heaters was tested as; TCH4 = 1550 °C, TCH3 = 1408 °C, TCH2 = 1198 °C, and TCH1 = 936 °C. Accordingly, the crucible thermocouples showed the following when the crucible was at its initial position; TC7 = 1370 °C and TC5 = 1298 °C. The thermal gradient along the furnace was calculated using the temperatures shown by TC4 and TC1 and the distance between them as before. The thermal gradient was found to be 29.2° C/cm. However, using TC7 and TC5 and the distance between them gave 24 °C/cm. A lower gradient was calculated using the crucible thermocouples compared to gradient calculated by using the heater thermocouples. Temperature stability was preserved with these set temperatures. The temperature readings of the TC's and the experimental gradients are tabulated in Table 5.1.

Table 5.1. Furnace Gradient and Thermal Profile Experiments

	TCH4	TCH3	TCH2	TCH1	TC5	TC6	TC7	Gradient °C/cm	Remark
1	1500 °C	1301 °C	1108 °C	885 °C	1278 °C	1328 °C	1381 °C	33.3	Unstable
2	1550 °C	1408 °C	1198 °C	936 °C	1298 °C	1333 °C	1370 °C	24	Stable and Profiling

To determine the temperature profile along the furnace, an experiment was conducted with an empty crucible-pedestal assembly. The crucible was initially positioned such that the top of the crucible was at the same level with the top of the furnace. The temperatures of the heater thermocouples were: TCH4 = 1550 °C, TCH3 = 1408 °C, TCH2 = 1198 °, and TCH1 = 936 °C (Second set in Table 5.1). After the furnace temperatures reached their set values, temperature data collection was performed at 8 different vertical positions with 30 mm spacing along the furnace. 20 minutes of stabilization time was given at each data collection position. The temperature versus position graph can be seen to be linear in Figure 5.1.

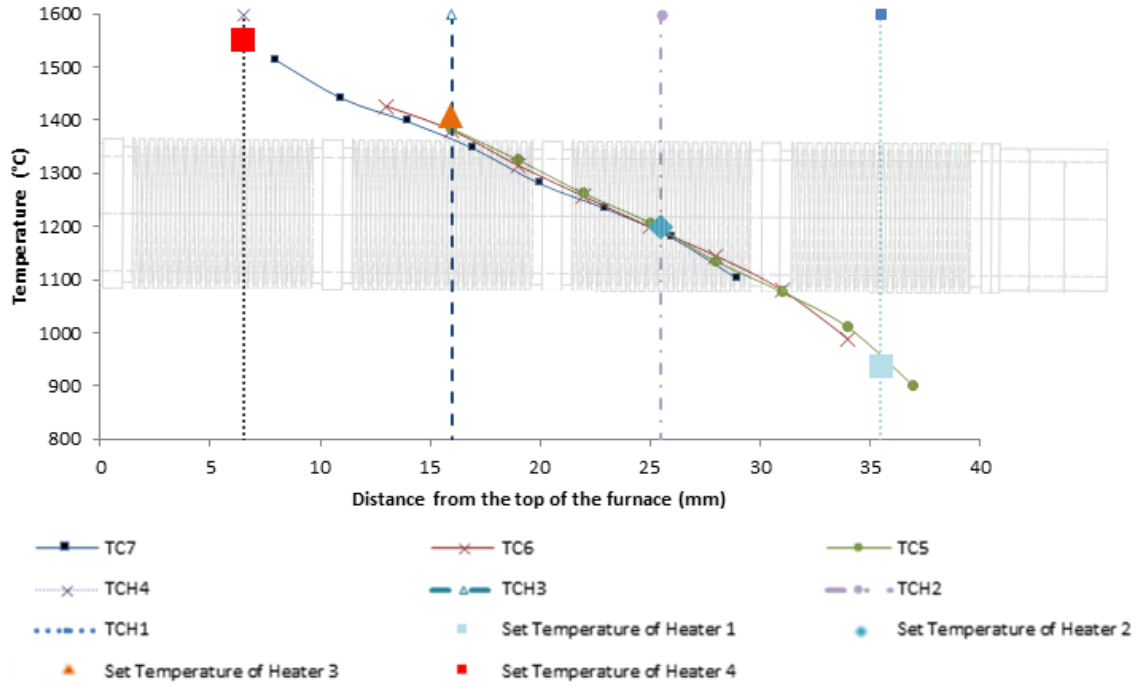


Figure 5.1. Temperature profile of the furnace

5.2. Trial Directional Solidification Experiments

5.2.1. Differential Scanning Calorimetry

The second generation superalloy CMSX-4 was used in the solidification experiments in this study. To find the liquidus and solidus temperatures of the purchased CMSX-4 superalloy, a differential scanning calorimetry (DSC) test was conducted. A DSC specimen with a mass of 50 mg was cut from a CMSX-4 bar to the required size of 3x3x3 cubic mm. The heating/cooling rate was 10 °C/min. The experiment was carried out within a temperature range from 25 to 1450 °C. After reaching the temperature of 1450 °C (after melting), the sample was cooled to 25 °C. The test was performed in a protective atmosphere of inert argon with high-purity (99.999 %). In order to monitor the phase transformation temperatures during melting and solidification, the data obtained on heating were used to determine the liquidus and solidus temperatures. Figure 5.2 shows the results of the DSC experiment. Analysis of the results shows that the melting temperature of the alloy is almost 1385 °C. The liq-

liquidus temperature was taken to be at the minimum of endothermic peak. The solidus temperature also was measured to be 1322 °C which is compatible with the literature findings [47]. The γ' solvus temperature was found to be 1180 °C. Furthermore, many articles have reported the liquidus and solidus temperatures of CMSX-4 as 1326 °C and 1385 °C [47]; 1306 °C and 1375 °C [48]; 1321 °C and 1381 °C [49], respectively. They are similar to the DSC findings in the present work.

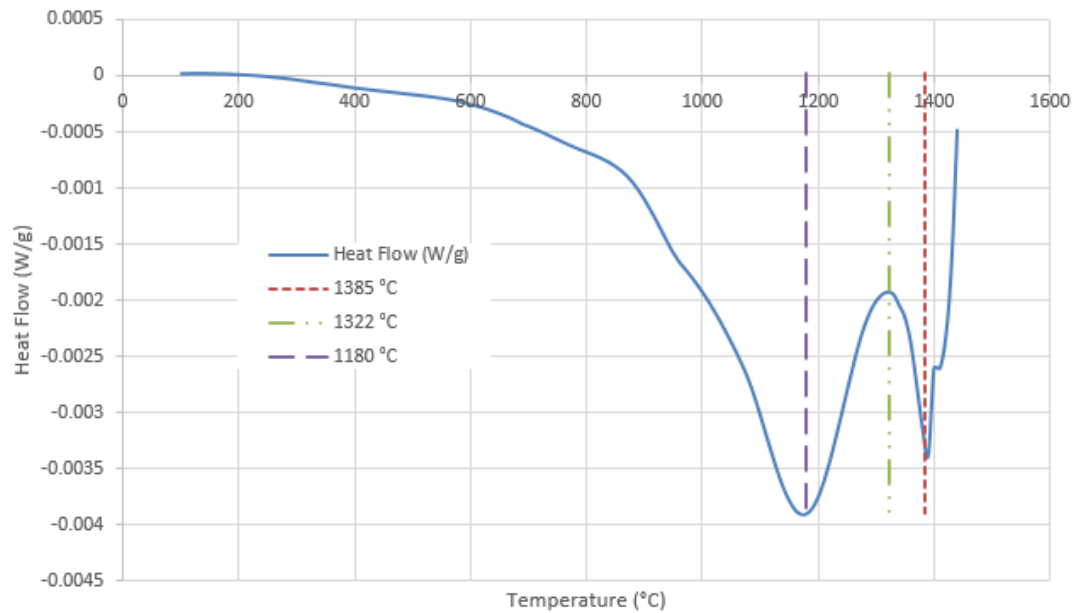


Figure 5.2. Differential Scanning Calorimeter (DSC) results for CMSX-4 alloy with vertical dashed lines determining liquidus, solidus and γ' solvus temperatures

5.2.2. Bottom Seeding Technique

Single crystal solidification can be initiated either using a grain selector or a seed. When a seed is used, the technique is called bottom seeding. Growth with a grain selector has the advantages that it does not require any single crystal seed and can be accomplished with lower thermal gradients than bottom seeding. However, the yield of successful single crystal production is higher with the bottom seeding technique. Moreover, the complex geometry of the grain selector as shown in Figure 5.3 requires investment casting procedures which were not available in the BU – CGL. Hence, the bottom seeding was chosen as the method of growing single crystal superalloys in the

current study.

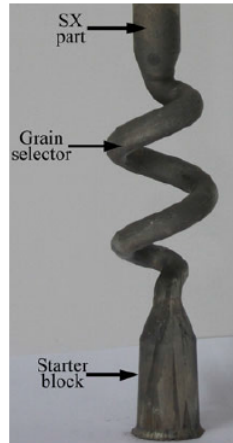


Figure 5.3. Grain selection during casting of single-crystal superalloys with grain selector

The method of bottom seeding to grow single crystals necessitates careful calibration of certain parameters. These are the thermal gradient (G) and withdrawal velocity (V) as external parameters imposed by the solidification system. Other parameters are the seed material and seed height (L_{seed}). A single crystal seed with a (001) orientation was used. Its solidus temperature was reported to be 1325 °C [50], and liquidus temperature was reported to be 1402 °C [50] or 1395 °C [51].

To grow single crystals by the bottom seeding technique, at least few micrometers of the top of the seed should be melted to initiate epitaxy from the seed. Furthermore, there should be an unmelted portion at the bottom of the seed. This means that at the top of the seed, the temperature should be greater than its liquidus temperature ($T_{L_{seed}}$) and at the bottom, the temperature should be less than its solidus temperature ($T_{S_{seed}}$). By satisfying these two conditions, the minimum length of the seed can be calculated as $L_{seedmin} = (T_{L_{seed}} - T_{S_{seed}})/G$. For the used single crystal seed, $L_{seedmin} = (1402\text{ °C} - 1352\text{ °C})/24 = 2.08\text{ cm}$ is the theoretical minimum length of the seed to have a successful single crystal solidification. As the $L_{seedmin}$ actually gives the mushy length (melting/solidification range), any shorter seed will melt to the bottom from several interdendritic sites where multiple grains can form.

5.2.3. Selection of the Withdrawal Velocity

Figure 5.4 shows some typical microstructures obtained using a superalloy with a melting range of 50K. The product $G \cdot V$, which is equivalent to cooling rate $\dot{T}$, controls the scale of the microstructure. Microstructural refinement without changing the morphology is obtained by moving from lower left to upper right. The ratio G/V controls the morphology, and occurs when going from lower right to upper left. The area of interest to produce single crystal superalloys is labeled "oriented dendritic" in Figure 5.4 [12].

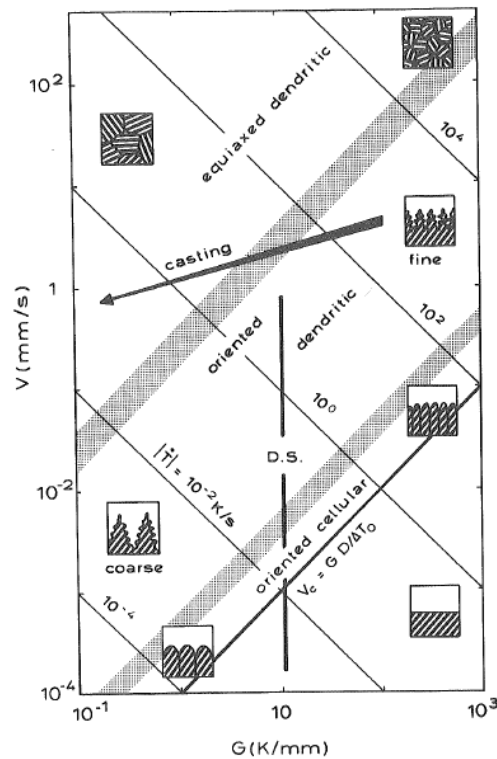


Figure 5.4. Solidification morphologies

Data on the withdrawal rate according to the imposed thermal gradient in the furnace is very scarce in the literature due to confidentiality surrounding the defense industry. Still, the data in the literature is enough to estimate the range of the withdrawal rate to obtain single crystals. In the case of a fixed thermal gradient, as in this current work, the microstructure is determined by the withdrawal velocity. The data

in Table 5.2 show that withdrawal rate can be between 0.288 and 72 cm/hour. More specific withdrawal velocities can be extracted from the microstructural maps available in the literature, like the one in Figure 5.5. In this work, the growth system can impose a thermal gradient of 24 °C/cm. By taking a gradient interval between 20 °C/cm to 30 °C/cm, a velocity range from 5 to 40 cm/hour will be used for the single crystal growth experiments.

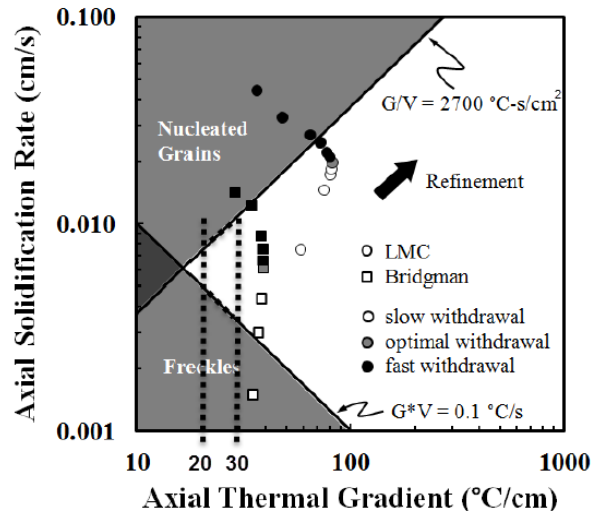


Figure 5.5. Solidification morphologies

Table 5.2. Withdrawal Velocity Speeds for the Single Crystal Growth

	Withdrawal speeds (cm/hour)	
	Minimum	Maximum
CMSX-486 [6]	14.4	32.4
CMSX-3 [52]	0.288	21.6
Rene N5 [50]	25.2	72

5.2.4. Trial Experiments

The polycrystalline CMSX-4 has been used as both the seed and charge for trial growth experiments in order not to waste the single crystal seeds before perfecting the

single crystal growth procedure. The aim of these experiments was to position the s/l interface at a desired location in the furnace. Eight trial solidifications were conducted before using a single crystal as the seed. Four experiments were done with single crystal seeds. All twelve experiments are summarized in Table 5.3.

The interface position was determined from the readings of TC5, TC6 and TC7. TC5 was on the crucible and corresponded to the bottom of the seed. TC6 and TC7 were fixed on the crucible 15 mm and 30 mm above the seed bottom (TC5), respectively. The TC locations are shown in Figure 5.6. The temperature difference between outside and inside of the crucible complicates positioning the interface at a desired position, though. Therefore, a calibration relating thermocouple readings and interface position was needed. The first three of the trial experiments established this calibration.

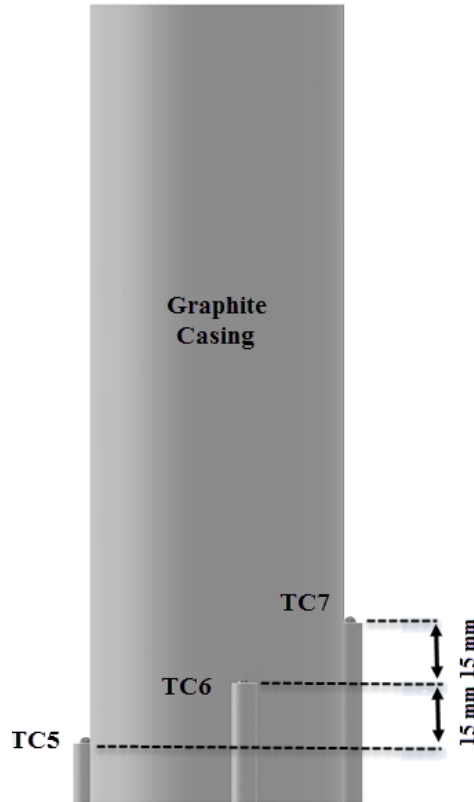


Figure 5.6. TC5, TC6, and TC7 locations on the graphite casing

Table 5.3. Furnace Gradient and Thermal Profile Experiments

Sample Name	Purpose	G ($^{\circ}\text{C}/\text{cm}$)	V (cm/h)	Remarks
S1	CMSX-4 melting	27	No Withdrawal	CMSX-4 melted
S2	To observe liquidus position	27	75	Calibration established
S3	To double check the calibration	27	75	Liquidus position could be located
S4	Single crystal growth imitation	24	22.5	An oxidation scale observed between the seed and the charge
S5	Accelerated furnace heating	24	22.5	An oxidation scale observed between the seed and the charge
S6	To check the newly inserted TCs	24	22.5	TCs and calibration work properly
S7	Single crystal growth imitation	-	No Withdrawal	Neutral cable failure in furnace
S8	To measure G_L and $T_{s/l}$ with TC Baffle	24	22.5	G_L and $T_{s/l}$ measured as $16^{\circ}\text{C}/\text{cm}$ and 1390°C , respectively
S9	Repeat the experiment 8 by using a single crystal seed	24	22.5	"W" shape interface and inconsistent $T_{s/l}$
S10	Repeat the experiment 9 with new TC Baffle	24	22.5	$T_{s/l}$ measured as 1391°C which is consistent with S8
S11	To prevent oxide scale	24	22.5	Solidus position was pushed down resulting mis-oriented dendritic alignment
S12	To prevent oxide scale	24	22.5	Full epitaxy with no oxide scale observed

5.2.4.1. Experiments 1-3. In experiment 1, the objective was to melt the entire charge to test the graphite casing-alumina crucible assembly for leaks. Two 15 mm diameter and 49 mm and 35 mm long CMSX-4 cylindrical pieces were put inside the alumina crucible, one on top of the other. After reaching the furnace set temperatures, the furnace was shut down and cooling was performed without the crucible pulling. This experiment showed, in addition to the s/l interface position, whether there was a leak or any cracking in the alumina crucible and graphite casing. After the solidification, the melting equipment including the graphite casing and ceramic crucible were all safe. Nevertheless, due to the diameter difference between the charge and the alumina crucible, molten metal leaked down to the bottom of the sample. Moreover, although the charge melted fully, the original interface between the two charge cylinders was observable. A longitudinal surface section of this sample (S1) showed an equiaxed dendritic microstructure and big porous regions between the secondary dendrite arms due to rapid cooling, as seen in Figure 5.7.

In experiment 2, the objective was to observe the liquidus position. A 92 mm long and 15.9 mm diameter CMSX-4 cylindrical piece was used as the charge. After reaching the set temperatures and desired crucible position in the furnace, the crucible was withdrawn with a speed of 75 cm/hour. After solidification, the observations showed an oxidation cap and perimeter leakage in this sample (S2). A sharp change in the dendritic microstructure in the longitudinal cut denoted the liquidus position in Figure 5.8. The liquidus position was detected 44 mm above the bottom of the sample, while TC5, located at the seed base, showed 1256 °C. Considering the average thermal gradient as 24 °C/cm; then liquidus was formed at the temperature of; $1256\text{ °C} + (24\text{ °C/cm}) \cdot 44\text{ mm} = 1361.6\text{ °C}$. This is the temperature outside of crucible at the position where liquidus occurs. As reported previously, CMSX-4 has liquidus temperature around 1380 °C, which is temperature inside of the crucible where liquidus line occurs. This roughly 20 °C difference is the temperature difference between inside and outside of graphite casing. By means of this, calibration was found between thermocouple readings and the s/l interface position.

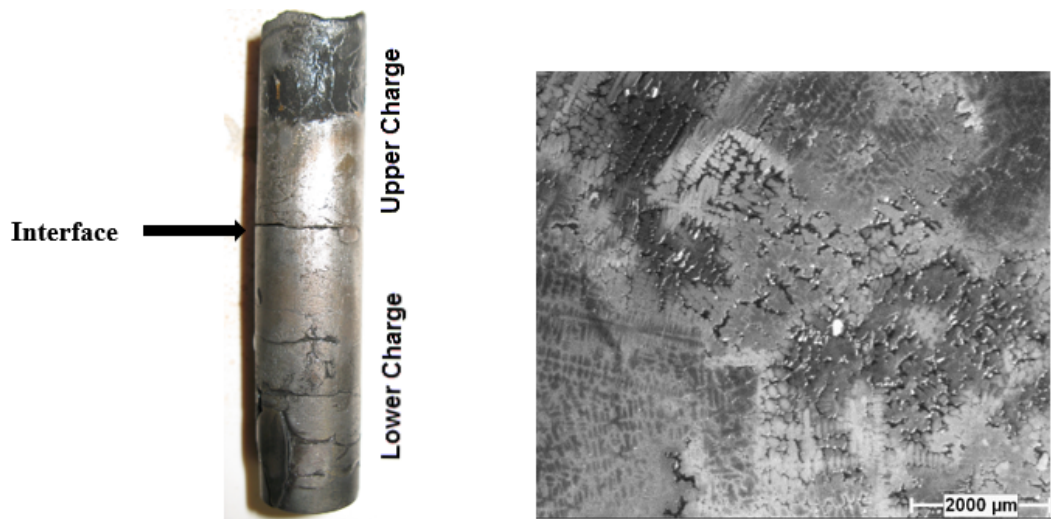


Figure 5.7. As cast sample S1 and its axial microstructure

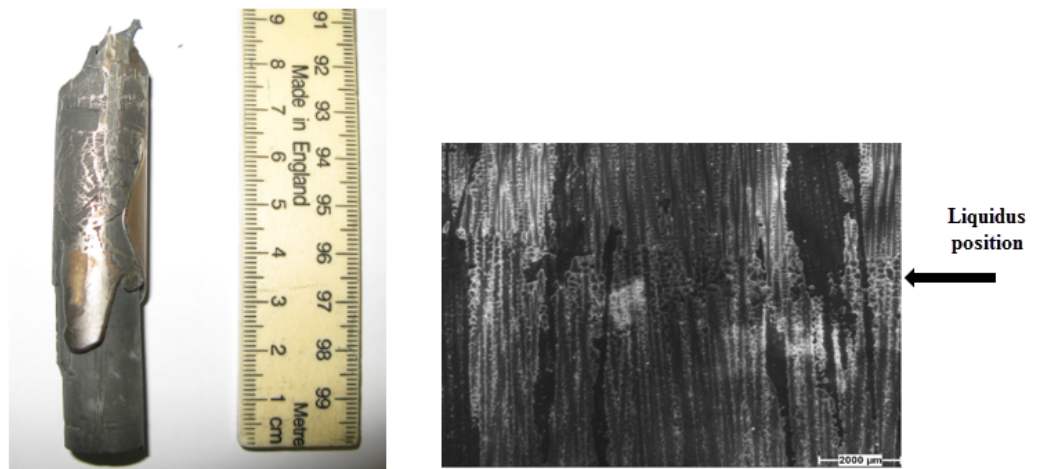


Figure 5.8. As cast sample S2 and its axial microstructure

In experiment 3, a 13 mm long and 15 mm diameter low C steel pieve was used as a fake seed; 85 mm long and 15 mm diameter CMSX-4 cylindrical sample was used as the charge. To double check the temperature calibration, the crucible was positioned such that TC7 read 1362°C and liquidus was expected to be seen at the level of TC7. The temperature reading of 1362°C from the outside of the crucible at TC7 position would result in 1380°C inside of the crucible at the same level referring to the calibration obtained in experiment 2. Withdrawal speed was 75 cm/hour. The

oxidation cap and perimeter leakage were also observed on S3. Additionally, argon bubbles were trapped above the fake seed and led to a big cavity there. Liquidus position was sharp, straight and as expected leveled with TC7 as shown in Figure 5.9. Thus, through this experiment, we learned to position the initial s/l interface at a desired axial level within the furnace.

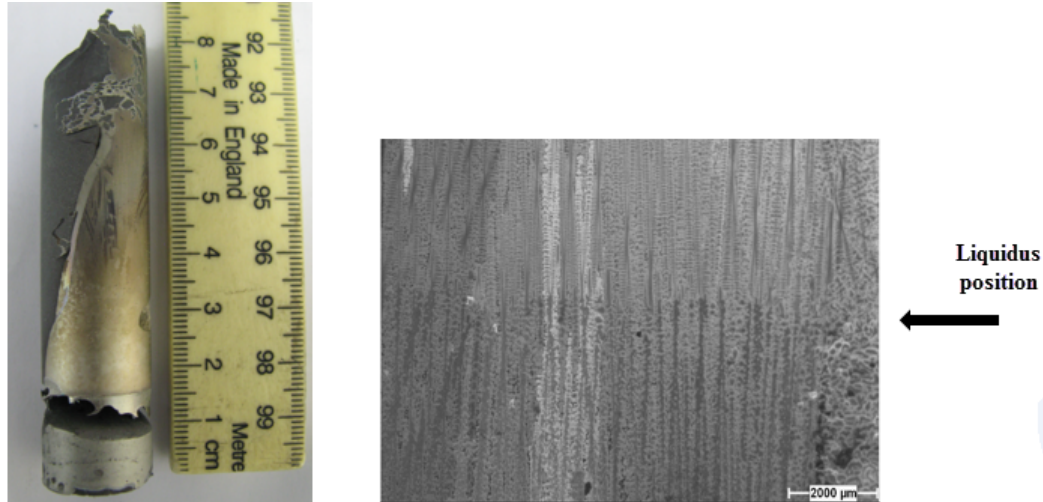


Figure 5.9. As cast sample S3 and axial microstructure

5.2.4.2. Experiments 4-7. In experiment 4, to imitate the real solidification, a 15 mm long CMSX-4 seed and a 45 mm long CMSX-4 charge were put on top of each other. Seed and charge were both induction melted and polycrystalline. The solidification rate was 22.5 cm/hour. As seen in Figure 5.10 showing the longitudinal microstructure of the sample (S4), a line between the seed and the charge was apparent while epitaxy formed between them. This contradictory result showed that while heating the sample to the desired temperature, an oxide layer covered the top surface of the seed and inhibited full joining between the melted seed and charge.

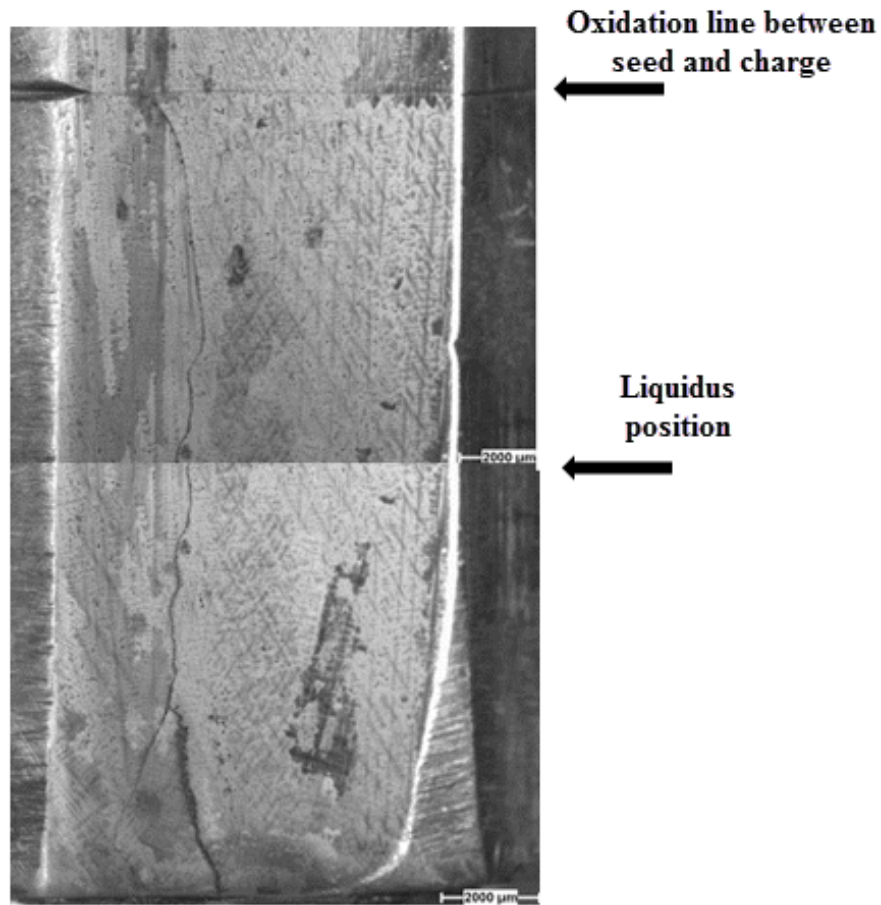


Figure 5.10. Axial microstructure of S4

In experiment 5, a 15 mm long CMSX-4 fake seed and a 38 mm long CMSX-4 charge were inserted into the alumina melting crucible. The solidification rate was 22.5 cm/hour. This time, the heating and melting periods were accelerated to decrease the oxidation time and prevent the formation of the oxide layer. However, the oxide layer again formed between the seed and the charge and prevented full epitaxy, as shown in Figure 5.11.

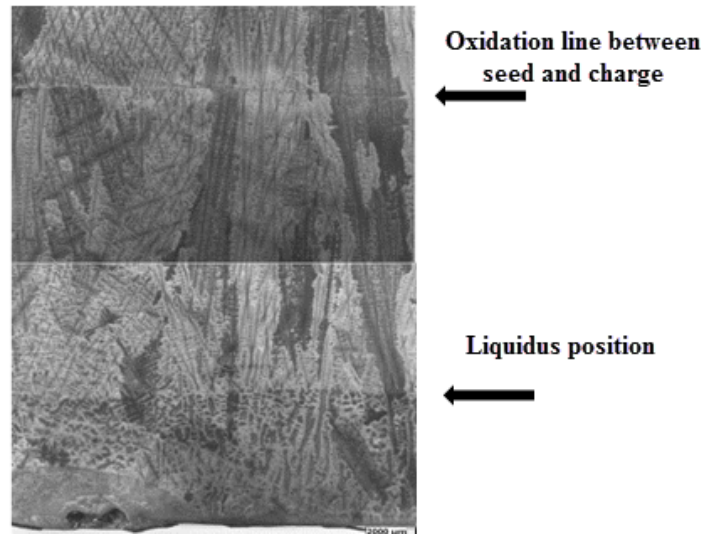


Figure 5.11. Axial microstructure of S5

High temperatures make the W-Re thermocouples brittle and mechanical friction during the withdrawal period can damage them. That is why a periodical repair or replacement is needed. After experiment 5, the thermocouples needed to be replaced and experiment 6 was conducted to check the newly inserted TC's and the already established calibration. A 39 mm long and 15 mm diameter CMSX4 alloy was used as a charge. The solidification rate was 22.5 cm/hour. The liquidus interface, as shown in Figure 5.12, was seen at the predicted position.

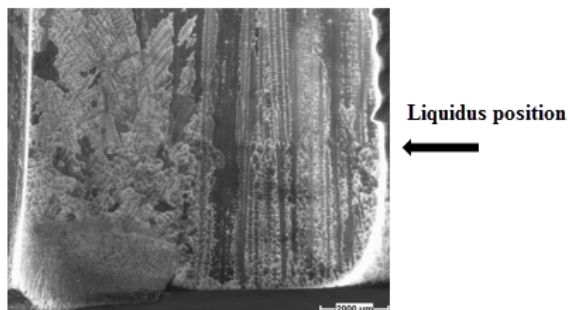


Figure 5.12. Axial microstructure of S6

In experiment 7, the neutral cable of the furnace failed due to continuous overload

and corrosion, so the experiment was halted.

5.2.4.3. Experiment 8. To have further information about the interface position, an alumina rod having a center hole was coupled with a thermocouple (TCBaffle) and integrated to the submerged baffle system. With TCBaffle, extra information could be obtained such as the liquid temperature gradient and the actual temperature of the liquidus position, the s/l interface.

In experiment 8, a 13.4 mm long and 18.3 mm diameter induction melted CMSX-4 was used as seed and a 77 mm long 14.7 mm diameter CMSX-4 was used as charge. Before heating the furnace, the position of the TCBaffle was calibrated by touching its tip to the solid charge whose position was precisely known. To eliminate errors due to thermal expansion of metals and other articles, at 1200 °C, the solid charge was again touched by the TCBaffle and the position information updated. A 10 mm total system expansion was observed at 1200 °C. Just before withdrawal period, the TCBaffle was moved away from the charge with two 5 mm intervals inside the molten metal. There was a 10 minute dwell time at each position during which the temperature data were recorded. The averaged temperature for the first position was 1407 °C and for the second 1397 °C. Solidification rate was 22.5 cm/hour.

From the temperature readings, G_{Liquid} was calculated as $(1405-1397)/0.5 = 16\text{ °C/cm}$. Please note that G_{Liquid} was calculated 24 °C/cm in the subsequent experiment done to only measure the G_{Liquid} . Furthermore, the TCBaffle was dipped into the molten metal until it was blocked by the s/l interface. At that position, it waited 10 minutes for stabilization and temperature data was recorded. This gave the actual liquidus temperature, 1390 °C. As seen in Figure 5.13, a small indentation formed at the interface because of the dipped TCBaffle. Clearly, the TCBaffle tip was strong enough to slightly deform the top of the mushy zone.

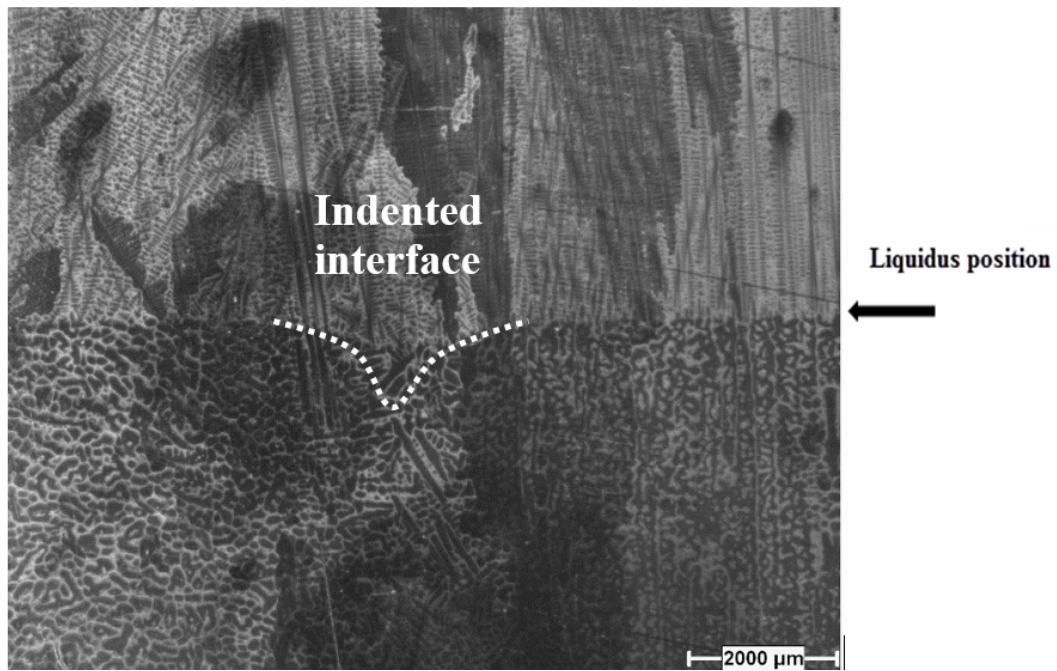


Figure 5.13. Axial microstructure of S8

5.2.4.4. Experiments 9-11. In these experiments, single crystal seeds were used. However, the growth direction was chosen to be perpendicular to the primary dendritic direction of the seed. Thus, the growth was initiated parallel to the secondary dendrite direction. In the rest of the trial experiments, the aim was to simulate the single crystal growth by using single crystal seeds. However, single crystal seeds with shorter length than the minimum single crystal seed length (20.8 mm) were used to keep longer seeds for the real experiments.

In experiment 9, a 16.2 mm long and 18.6 mm diameter single crystal seed and a 77 mm long CMSX-4 charge were used. Again the TC Baffle was integrated into the system to touch and measure the position and temperature of the liquidus interface. After reaching the furnace set temperatures and desired crucible position, the TC Baffle was touched to the interface two times. Each time, it waited 10 minutes for stabilization and temperature readings were recorded as 1355 °C and 1366 °C, respectively. The solidification rate was 18 cm/hour.

These temperature readings were not consistent with the previous readings showing the temperature of the liquidus as 1390°C . This might stem from a malfunction in the TC Baffle. A small indentation again was seen at the s/l interface where the TC Baffle made contact as seen in Figure 5.14. In addition, it was apparent that an oxide layer formed and hindered full epitaxy between the seed and the charge. Moreover, a “W” shape interface was seen instead of a straight one.

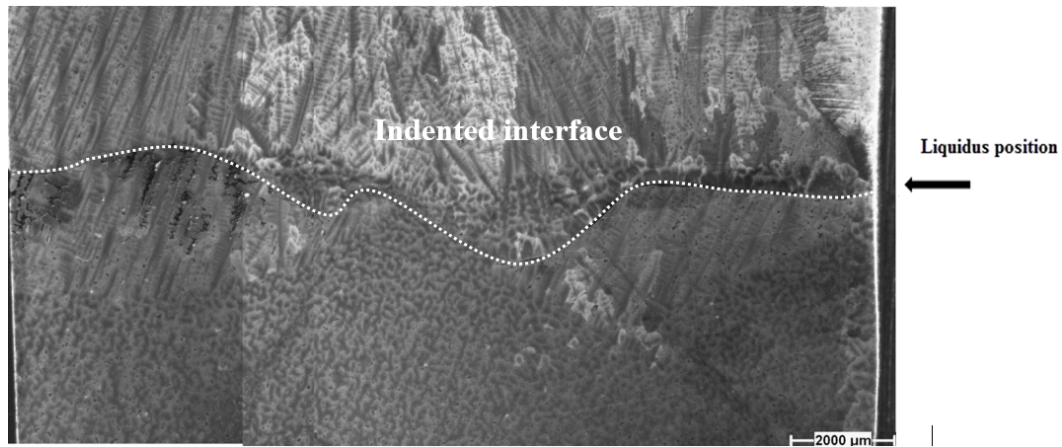


Figure 5.14. Axial microstructure of S9

Owing to the inconsistent results observed in experiment 9 in terms of the s/l interface temperature, the TC Baffle was replaced in experiment 10. The TC Baffle was touched to the s/l interface three times and data were recorded as 1393°C , 1391°C , 1389°C , respectively. These temperature readings of the TC Baffle from the s/l interface matched the DSC data in this study and those reported in literature [50,51].

In experiment 11, a 17 mm long and 18.5 mm diameter single crystal seed and 60 mm long CMSX-4 charge were used. To break the oxide layer and promote better epitaxy, the s/l position was lowered (crucible moved up) which provides a higher temperature at the position (seed/charge interface) where the oxide layer generally forms. Solidification rate was 18 cm/hour. As a result, the oxide layer was not observed in resultant microstructure, as seen in Figure 5.15. However, pushing down the interface caused the seed to melt down to its base and the loss of the single crystal structure. Therefore, single crystal growth could not be initiated.

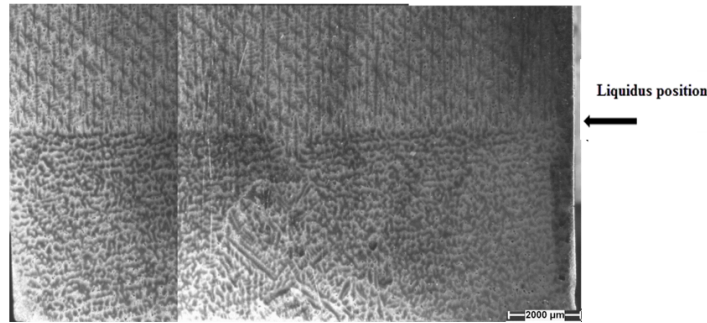


Figure 5.15. Axial microstructure of S11

5.2.4.5. Experiments 12. The final pre-experiment before the real growth experiments was done with a 17.2 mm long and 18 mm diameter single crystal seed and 62 mm long CMSX-4 charge. The interface was positioned 10 mm above the seed base and the solidification rate was 18 cm/hour. To provide a better epitaxy between the seed and the charge, their contact surfaces were flattened with a lathe beforehand. By doing this, the clearance between the touching surfaces was decreased. As a result, the oxide film forming between the seed and the charge was eliminated, as seen in Figure 5.16. This approach to eliminate the oxide layer was a better one than that in experiment 11 where the solidus was below the seed base.



Figure 5.16. Axial microstructure of S12

After these preliminary experiments, significant experience was gained in terms of positioning the interface, preventing oxidation at seed/charge interface, and measuring real interface temperature. It was time to start growing the superalloy single crystals.

6. CRYSTAL GROWTH EXPERIMENTS

After establishing the procedure for the growth of a successful single crystal with the bottom seeding technique, a total of 8 crystals were grown by the Vertical Bridgman (VB) and the Vertical Bridgman with a submerged baffle (VBSB) methods. Five crystals were grown by the VB at five different withdrawal rates of 6, 12, 18, 30, and 40 cm/hour, while three crystals were grown by the VBSB at three different withdrawal rates of 12, 18 and 30 cm/hour. Table 6.1 provides the experimental parameters for the grown crystals.

Table 6.1. Grown Crystals with Their Experimental Parameters

	Technique	V (cm/hour)	G($^{\circ}\text{C}/\text{cm}$)	Seed (mm)	Unmelted Seed (mm)	Mush (mm)	Melt-back (mm)	Total length (mm)
VB6	VB	6	24	33	14	19	1.6	105
VB12	VB	12	24	33	14.5	18.5	3.2	105
VBSB12	VBSB	12	24	30	13	17	2.2	102
VB18	VB	18	24	32	10	22	3.4	104
VBSB18	VBSB	18	24	30	9.5	20.5	2.1	102
VB30	VB	30	24	33	8.7	24.3	4.4	105
VBSB30	VBSB	30	24	29	6	23	4.3	101
VB40	VB	40	24	29	10	19	4	101

In all experiments, a 15 mm diameter single crystal seed and 72 mm long and 14.5 mm diameter CMSX-4 charge were used. The seeds were cut to the cylindrical shape by Electron Discharge Machining (EDM) from an originally rectangular slab. The charge was cut to a proper size by a SiC rotating disc. Contact surfaces of the seeds and the charges were all flattened via lathe and the transverse surfaces of all samples were ground with 800 grid sand paper to smoothen the machined surface. Once the seed and the charge were prepared, they were put inside the alumina melting crucible. The bottom of the melting crucible was sealed with a 3mm thick graphite insert and graphite foil. Then, the melting crucible was inserted into the graphite casing

crucible. Before heating the system, the growth chamber was evacuated to 4×10^{-2} mbar and backfilled with argon to 0.2 Bar. This cycle was repeated twice to decrease the oxygen content in the chamber. Then, while the chamber was under vacuum, the system was heated up to 500°C and kept for 10 minutes so that contamination due to degassing could be evacuated. Finally, the chamber was slowly filled to 0.5 Bar argon overpressure. The argon outlet was connected to a bottle partially filled with water. Bubbles in the water indicated the continuous argon flow and a pressure gage showed the argon overpressure inside the chamber.

In the VB experiments, the furnace was heated up to the set temperatures while the crucible was kept in the cold zone of the furnace. After stabilization of the furnace zone temperatures, the crucible was moved up to the hot zone at a rate of 10 cm/hour. The crucible was stopped at a position where 3 to 5 mm of the seed melted. In this position, it was waited for 20 minutes. Finally, the crucible assembly was withdrawn with a selected speed. In the VBSB experiments, in addition to the VB procedure, the baffle was immersed into the liquid until it touched the s/l interface. Then, the baffle was moved 10 mm up to set the initial effective melt height. Then, the crucible assembly was withdrawn with a selected velocity to start the solidification. After the withdrawal period, the furnace was allowed to cool slowly. Argon and cooling water continued to flow until the furnace reached 250°C . After cooling, the unit was disassembled and melting crucible was taken out of the graphite casing with pliers. The crystal was extracted from the melting pot by careful mechanical strikes. After solidification, the samples were radially cut at 6 cm from their bottom. Then, the bottom parts were longitudinally halved. One of the halves and the top parts were further sectioned transversely at distances of 5 mm below the initial s/l interface (I-5), at the initial s/l interface (I), and at 5 (I5), 10 (I10), 15 (I15), 25 (I25), 35 (I35), and 45 (I45) mm above the initial s/l interface. The sectioning is shown in Figure 6.1 The samples were ground with a rough 50 grit SiC abrasive paper followed by 80, 120, 240, 400, 600, 800, 1200 and 2000 grit SiC papers. After the finest grinding step, they were polished on polishing cloths loaded with 10, 3, and $1\text{ }\mu\text{m}$ alumina powder, consecutively. After grinding and polishing, the samples were etched with a solution of $4\text{g CuSO}_4 + 20\text{cc HCl} + 20\text{cc H}_2\text{O}$.

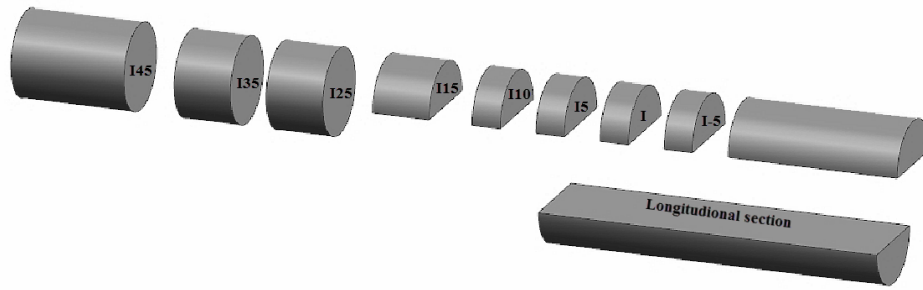


Figure 6.1. The representative sectioning of the grown samples

The optical microscope was used to observe the microstructural phenomena such as liquidus position, solidus position, mushy and melt-back zones, primary and secondary dendrites, and porosity. The longitudinal images and the radial images were taken with 0.5X magnification and with 40X magnification under the optical microscope, respectively. Then, they were evaluated to calculate the microstructural parameters such as mushy and melt-back zone length, PDAS, primary dendrite core size, SDAS, and porosity. For the calculation of the mushy and melt-back zone lengths, at least five different measurements were taken from at least five different horizontal position of the s/l interface of each sample. Three 30X magnification radial images were used to calculate the average PDAS and primary dendrite core size for each sample. SDAS was measured by using the longitudinal images and choosing at least three different primary dendrite trunks from different horizontal positions of the related elevation. SDAS was determined as a ratio of length of the selected dendrite to the number of secondary arms. Finally, at least three unetched sample images were used to determine the area fraction of the micropores on transverse sections using the ImageJ software. Their length averaged value was used as an overall estimate of the microporosity in a sample. Scanning Electron Microscopy (SEM) was used to characterize the finer sections; interdendritic regions, carbides, eutectics, and precipitations. Additionally, compositional analysis (EDS) of microstructural features were done. Backscattered and secondary electron images of radial sections were generated by employing SEM with an accelerating voltage of 20-30 kV. The samples were in the polished condition.

7. RESULTS AND DISCUSSION

In this chapter, results for the microstructural features such as the mushy and melt-back transition zone, primary dendrite arm spacing, primary dendrite core size, porosity, existing phases, and solute segregation are presented and discussed in terms of the solidification parameters.

7.1. General Macro and Microstructural Features

Figure 7.2 is a representative photo showing five different solidification zones along the samples: unmelted seed below the solidus, mushy zone, melt-back region, s/l interface, and newly formed dendrites. The initial mushy zone is formed in the seed and bounded by the solidus and the liquidus temperatures. This zone is composed of partially melted dendrites. The melt-back transition region appears in the last portion of the mushy zone, just below the s/l interface. This region comprises of partially melted dendrite arms together with pinched off secondary dendrites and sparsely nucleated equiaxed grains. At the beginning of solidification, convection in the melt and in the mushy zone is strong enough to break/bend the dendrite arms. Additionally, turbulent mixing of the melt can smear out the thermal field near the s/l interface because of the transportation of the hot liquid to the s/l interface. Moreover, latent heat evolution in the mushy zone also reduces the thermal gradient near the s/l interface. These might form a thermal undercooling near the s/l interface, which makes the region prone to equiaxed grain formation [14]. In total, the combined effects of the turbulent melt flow and the thermal undercooling results in broken/bend dendrites together with grainy microstructure in the melt-back region. In addition, the melt-back region including broken dendrites and grains negatively affect the newly formed dendrites. Misaligned dendrites just above the s/l interface are shown in Figure 7.1. The s/l interface appears to be a radially straight separation between the melt-back and newly formed regions.

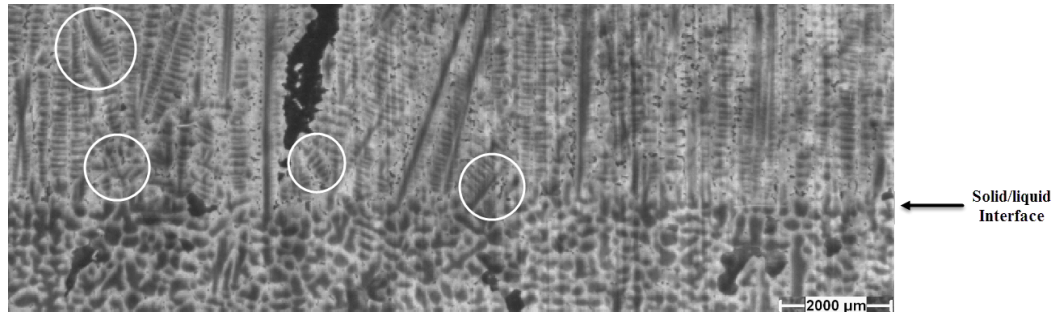


Figure 7.1. Representative misaligned dendrites just above the s/l interface of S14

The longitudinal and the radial image of the grown samples are shown in Figures 7.3 to 7.10. The radial sections of I-5, I, I5, I10, I25, I35, I45 for each sample are shown with its respective macro photo in this order from bottom up. As seen in the radial image, the I-5 sections comprise of partially melted dendrites. Obviously, dendrite arms were fragmented and fused to each other so it is difficult to observe the dendrite cores and dendrite arms. However, the I sections appear to have broken/bent dendrites and circular grains. In addition, the I5 radial photos show misoriented dendritic structure compared to the radial sections above them. The highly misoriented dendrites can also be seen between the I and I5 radial sections of the longitudinal photos. A detailed discussion will be given in the following sections.

SEM-BSE images of the VB and VBSB samples with 200X magnification can be seen in Figures 7.11 to 7.13. The dendritic regions appear bright and the interdendritic regions appear dark. Dendritic regions are surrounded by interdendritic regions in all samples. A closer look at the microstructure shows brighter pools inside dark interdendritic regions. These sections are called eutectic islands, seen in Figures 7.14 to 7.17. Typically, the γ' forming elements, such as Al, Ti and Ta, enrich the interdendritic melt, while the elements W and Cr are segregated toward the dendrite cores. Then, γ' grow to larger sizes in the interdendritic regions. This segregation also lead to the formation of the eutectic islands in the interdendritic regions which solidify last. Compositional analysis of the eutectic islands shows that they lack W, Re and Cr and have high amounts of Ta, Ti and Hf (Table 7.1). The mosaic appearance of the eutectic

islands with different magnifications can be clearly seen in Figures 7.15 to 7.17.

Carbides that appear as bright white phases are located inside the interdendritic regions but close to the boundaries of dendrite arms. The compositional analysis of the carbides seen on radial sections matches the compositions of MC type carbides reported in various studies [53–55]. Typically, high concentration of Ta and Hf but small amount of W and Re are found, as shown in Table 7.1. Their Cr, Co, and Ni concentrations are significantly lower than the nominal composition of CMSX-4. MC carbides are categorized in terms of their shapes. Script-like and blocky MC carbides, as shown in Figures 6.30 to 6.32, are widely observed in all the samples.

The microstructure at higher magnification in the dendritic regions exhibits rows of γ' precipitates with cuboidal morphology and an average size of about 500 nm, as shown in Figures 7.22 to 7.24. The γ phase is seen to be bright and the γ' phase dark. Moreover, the results showed significant increase in size of the γ' precipitates in the interdendritic region with an average size of 1000 nm, as shown in Figures 7.25 to 7.27. The average volume fraction of the γ' is measured to be in the range of 63-68 % for all the samples.

Table 7.1. Compositional Analysis of Eutectic Regions and Carbides

	Al	Ta	W	Re	Mo	Ti	Cr	Co	Ni	Hf	C
CMSX-4	5.15	5.57	7.24	4	0.63	0.8	6.7	9.54	60.2	0.1	-
Eutectics	5.97	13.83	2.52	2.14	0.81	1.34	4.79	7.47	50.8	2.31	-
Carbides	0.63	74.1	-	-	-	5.57	0.74	1.09	4.9	9.63	3.36

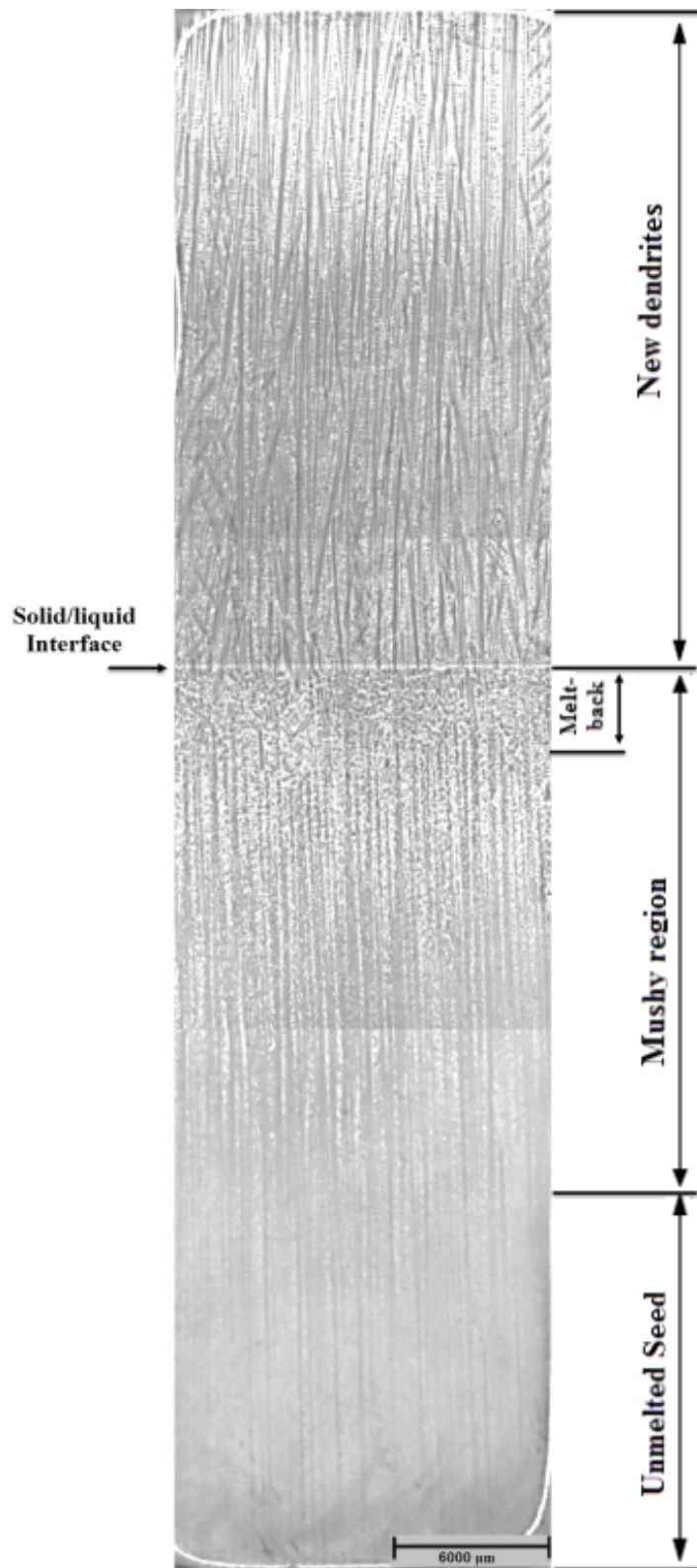


Figure 7.2. Solidification zones in the longitudinal cross section of the VB18

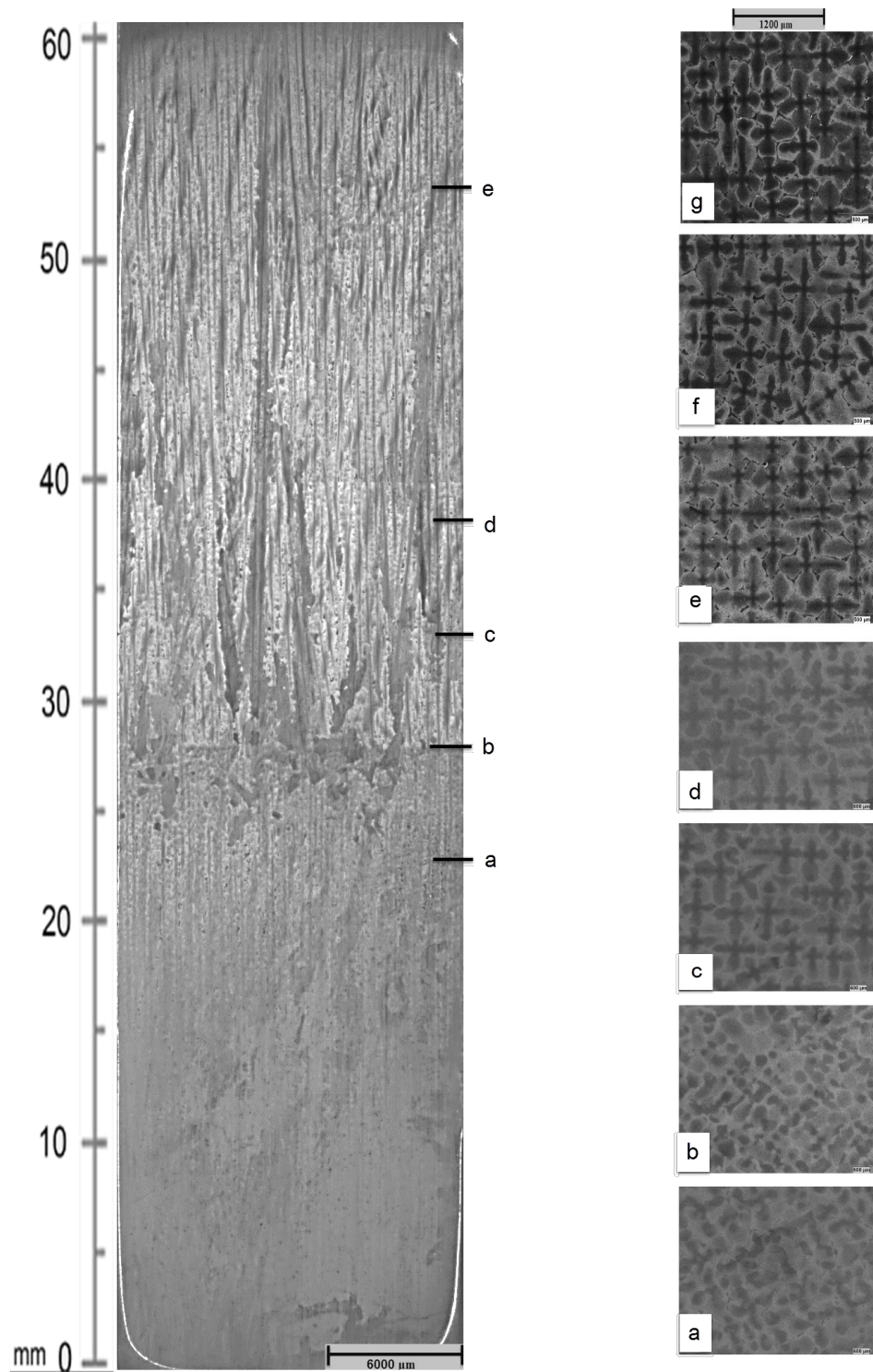


Figure 7.3. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VB6

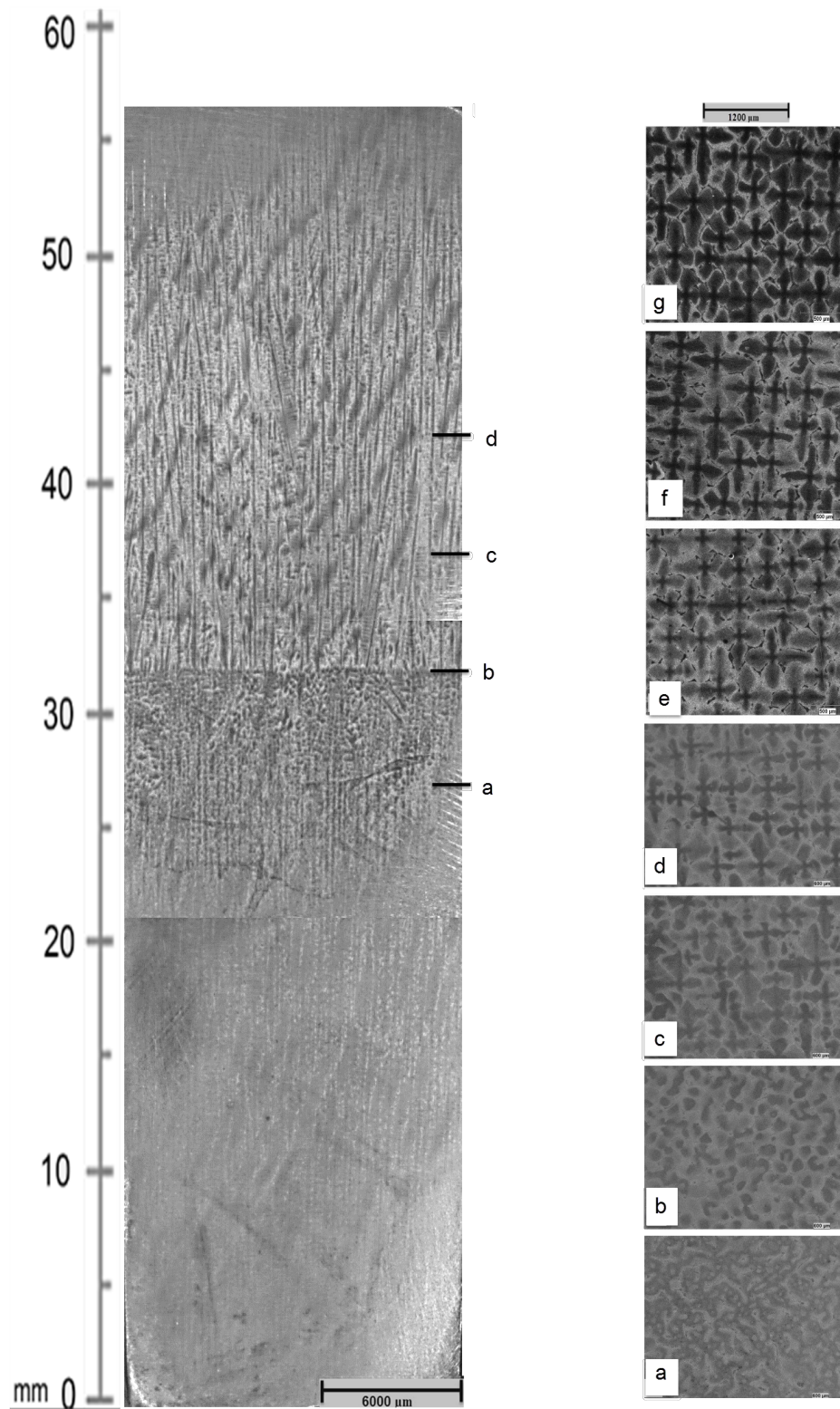


Figure 7.4. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VB12

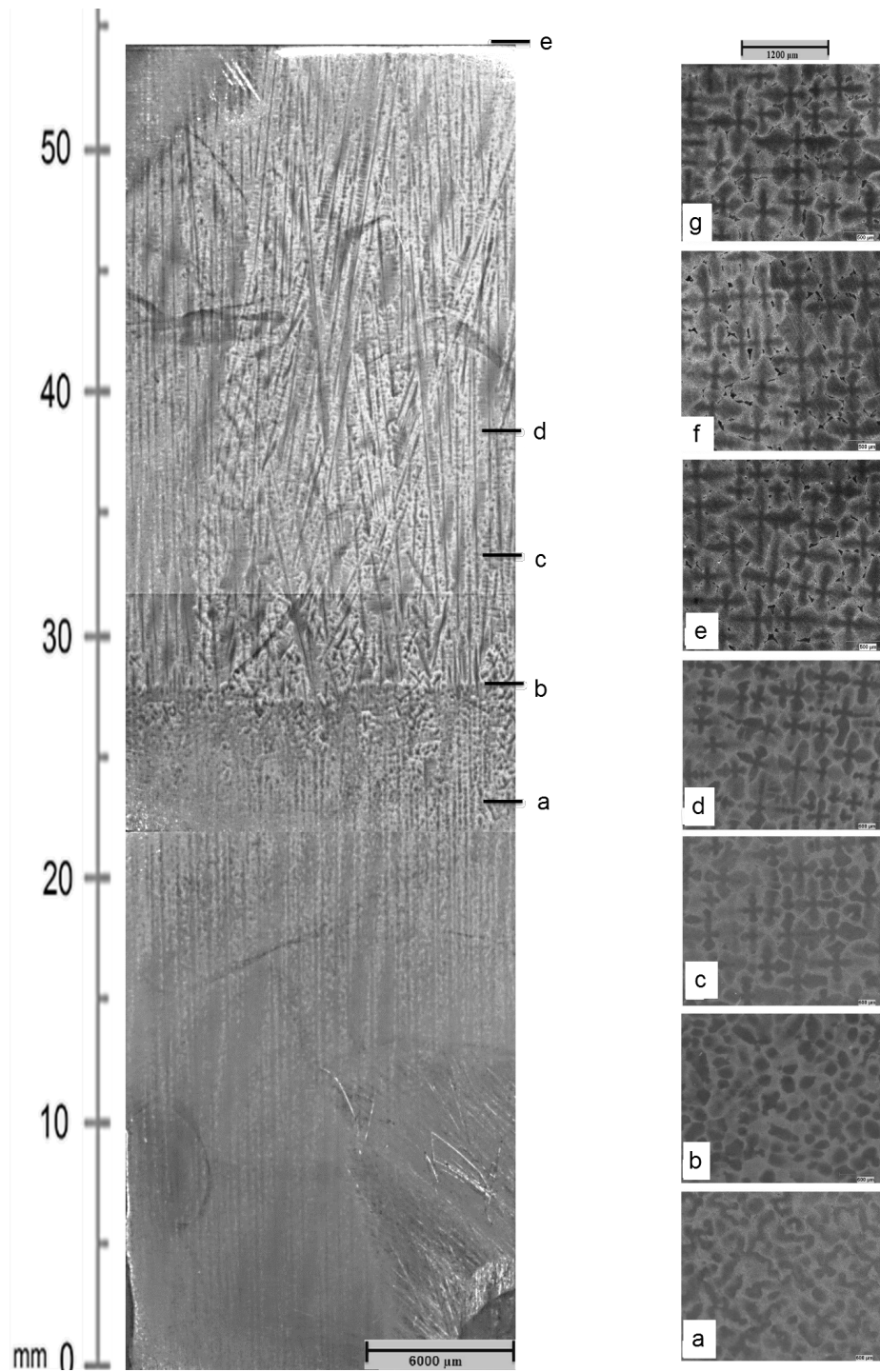


Figure 7.5. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VBSB12

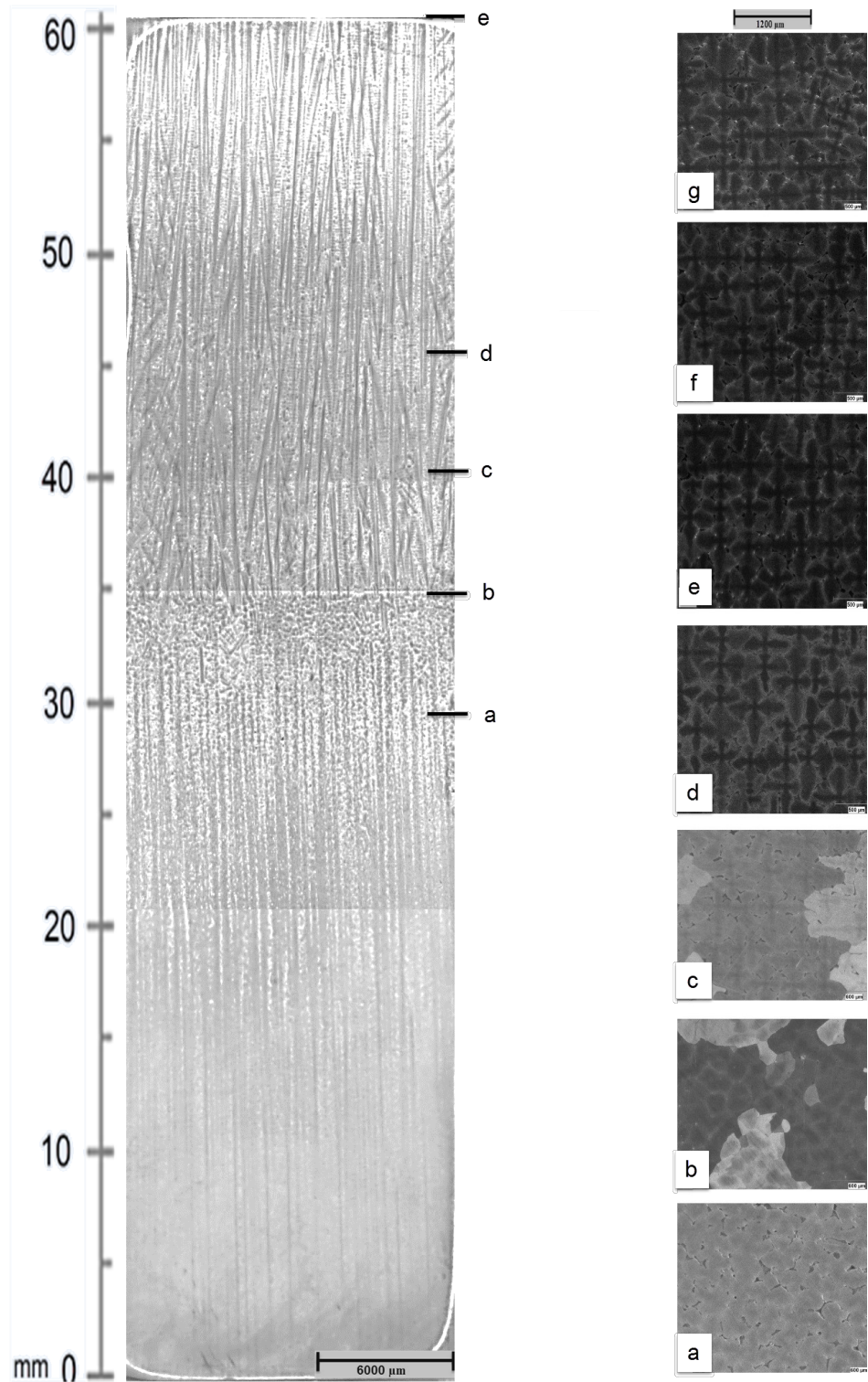


Figure 7.6. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VB18

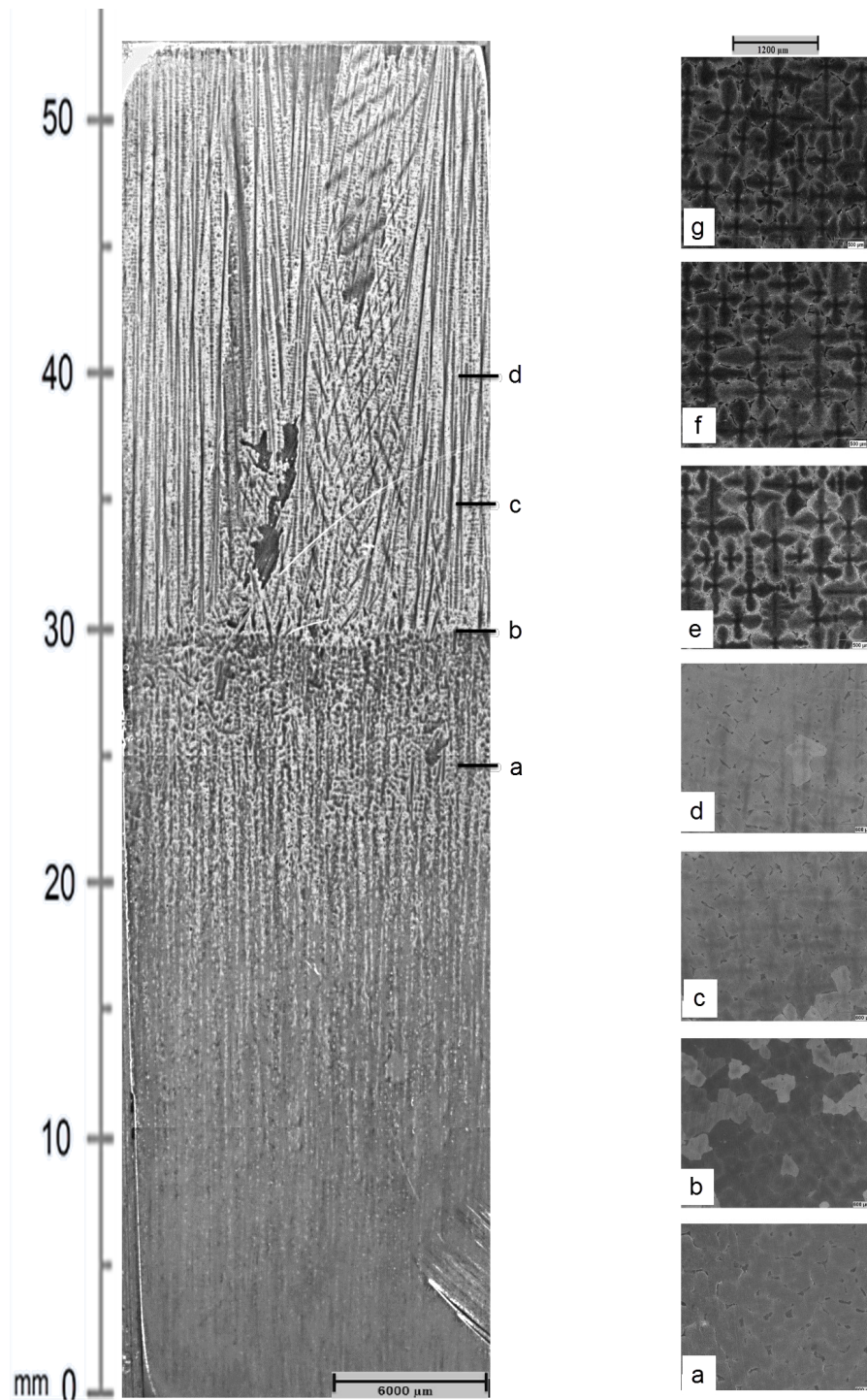


Figure 7.7. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VBSB18

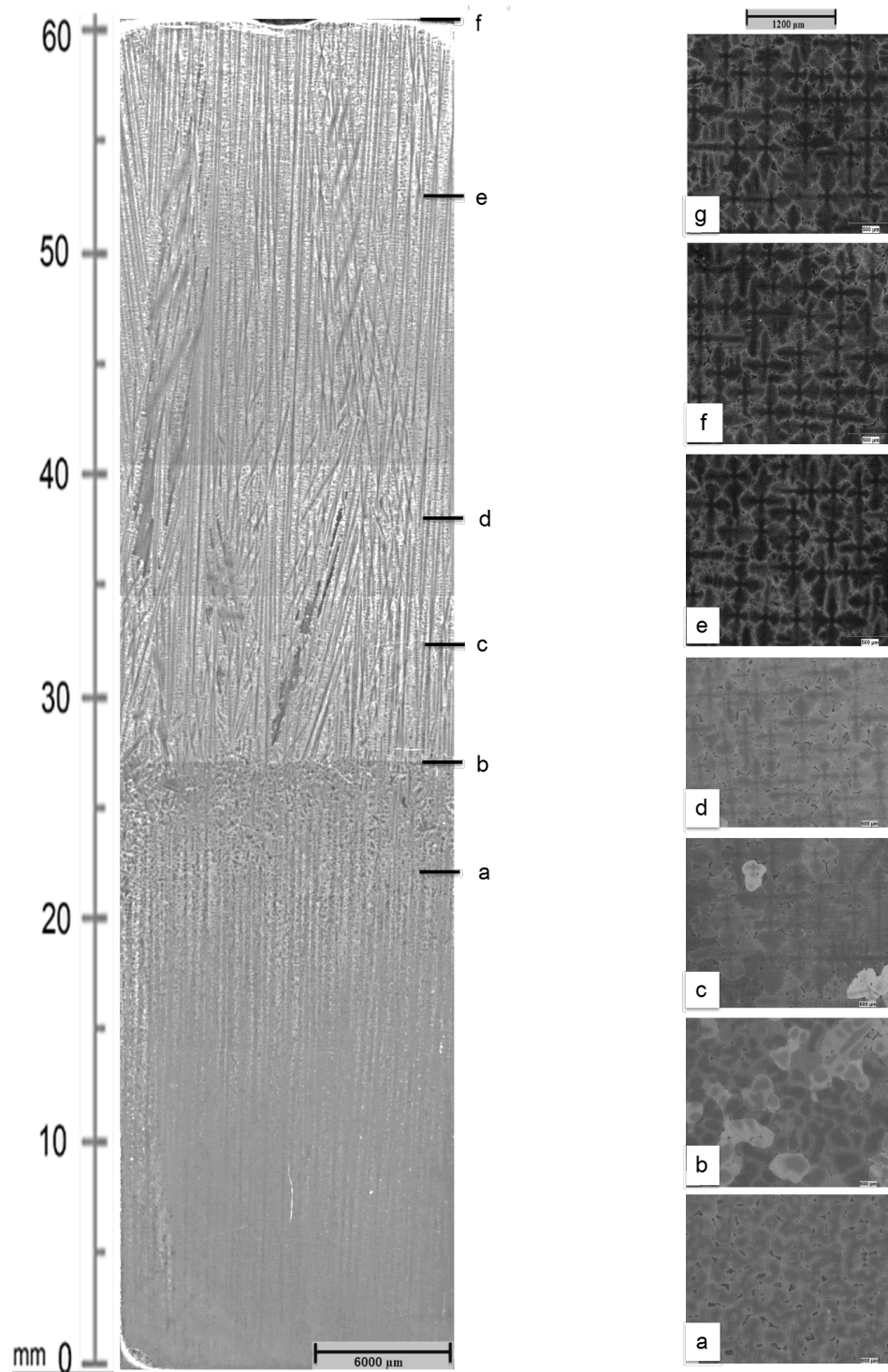


Figure 7.8. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VB30

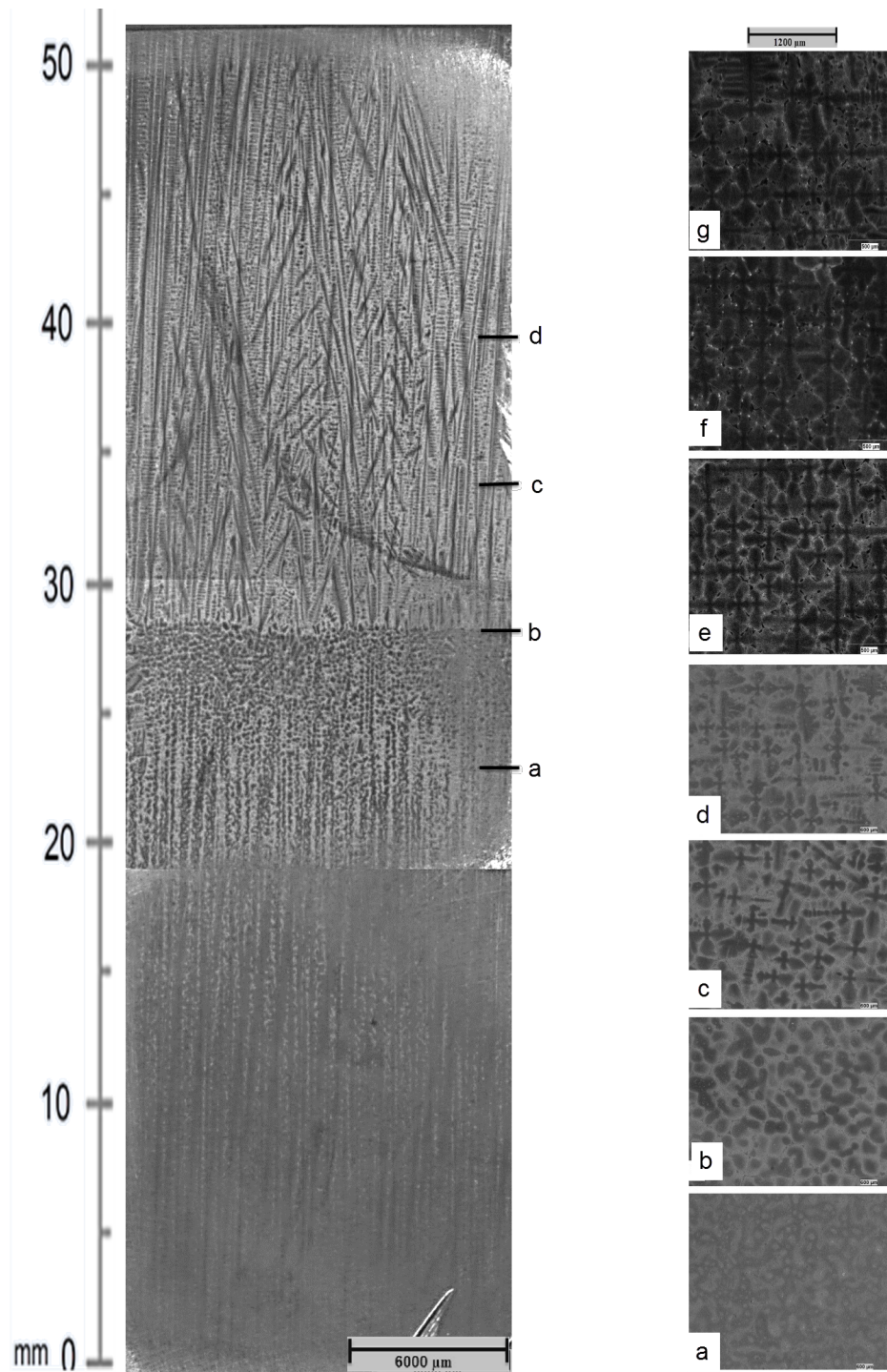


Figure 7.9. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VBSB30

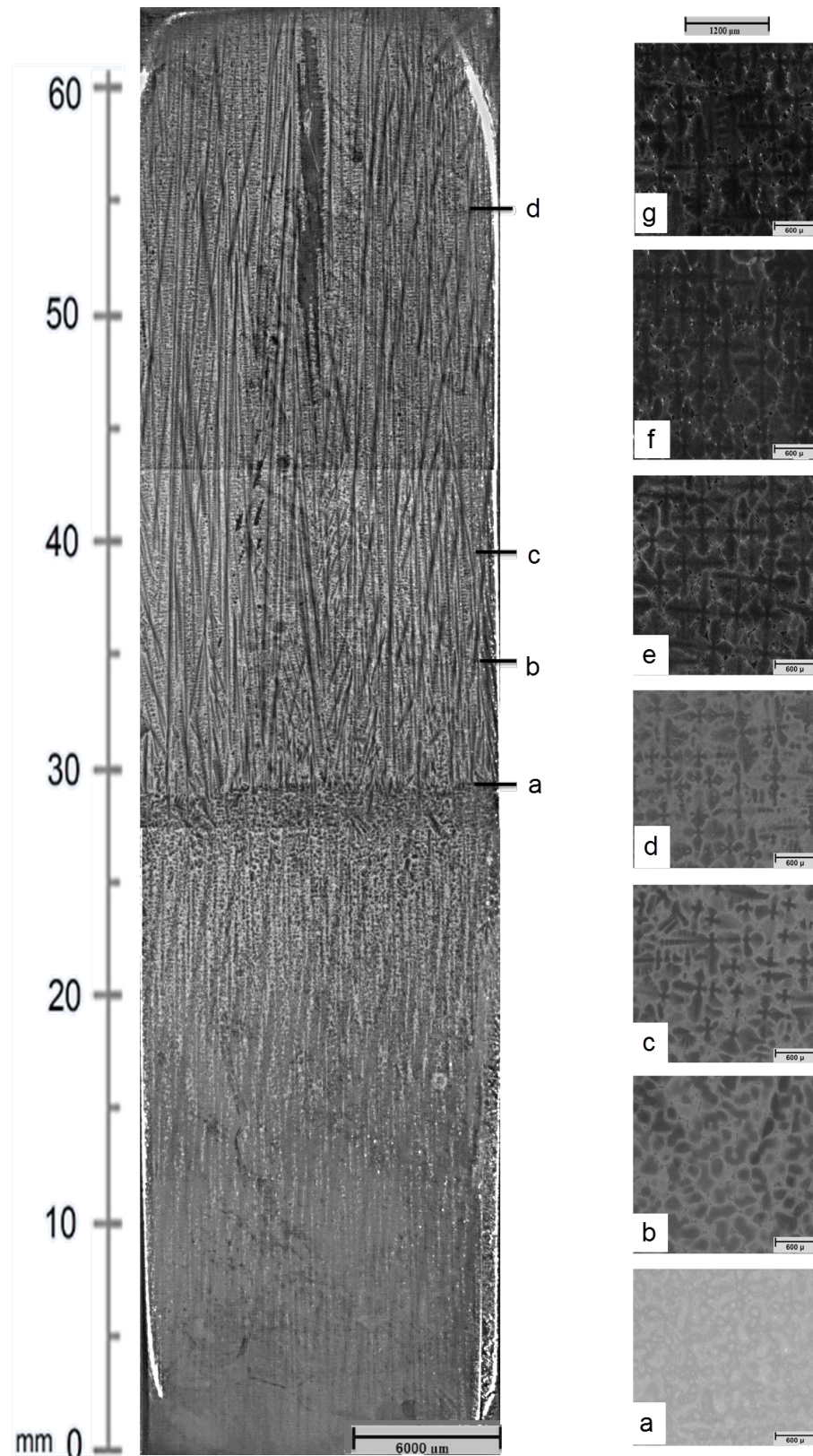


Figure 7.10. Longitudinal microstructure and radial microstructures of I-5(a), I(b), I5(c), I10(d), I25(e), I35(f), I45(g) of the VB40

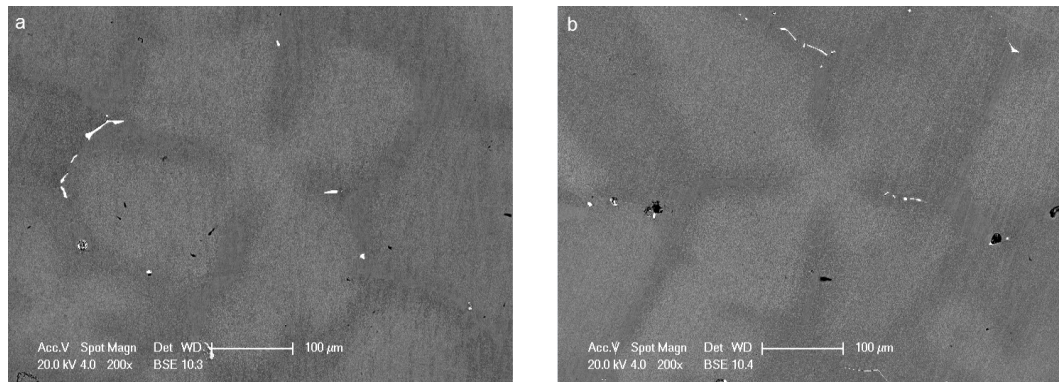


Figure 7.11. SEM-BSE image of VB12 (a) and VBSB12 (b) showing dendrite region

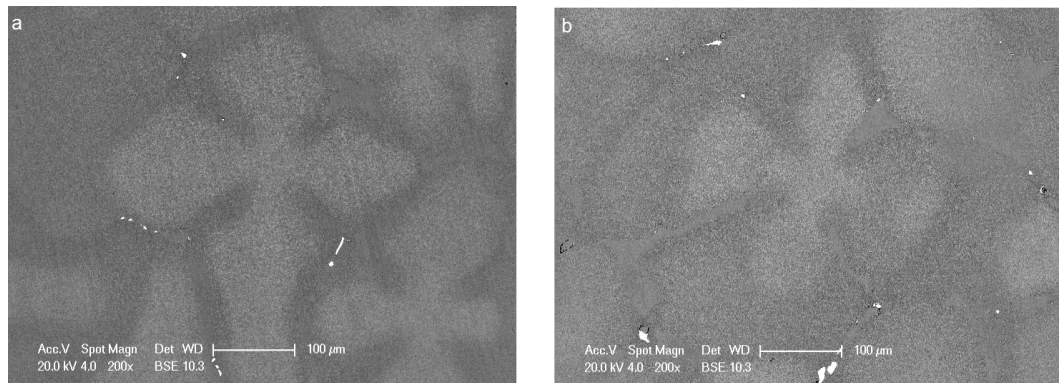


Figure 7.12. SEM-BSE image of VB18 (a) and VBSB18 (b) showing dendrite region

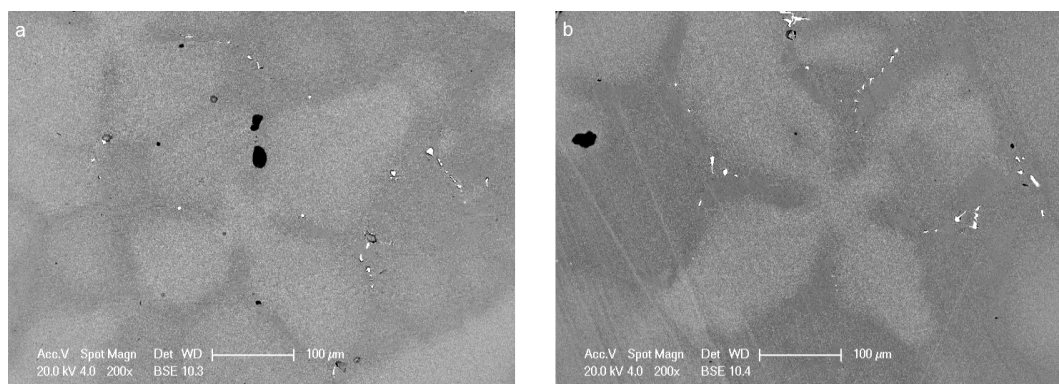


Figure 7.13. SEM-BSE image of VB30 (a) and VBSB30 (b) showing dendrite region

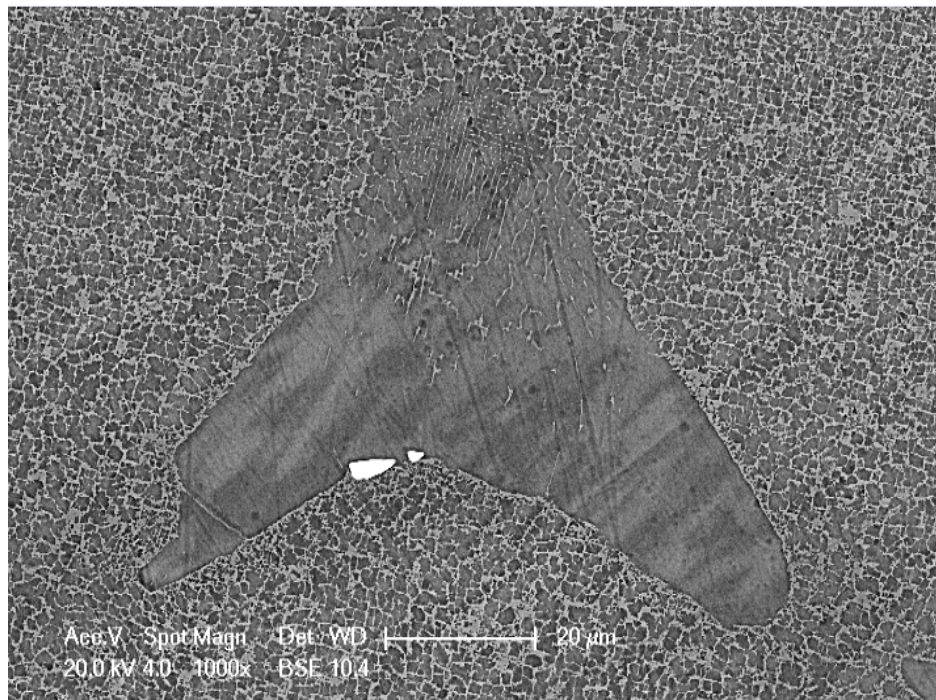


Figure 7.14. SEM-BSE image showing eutectic region

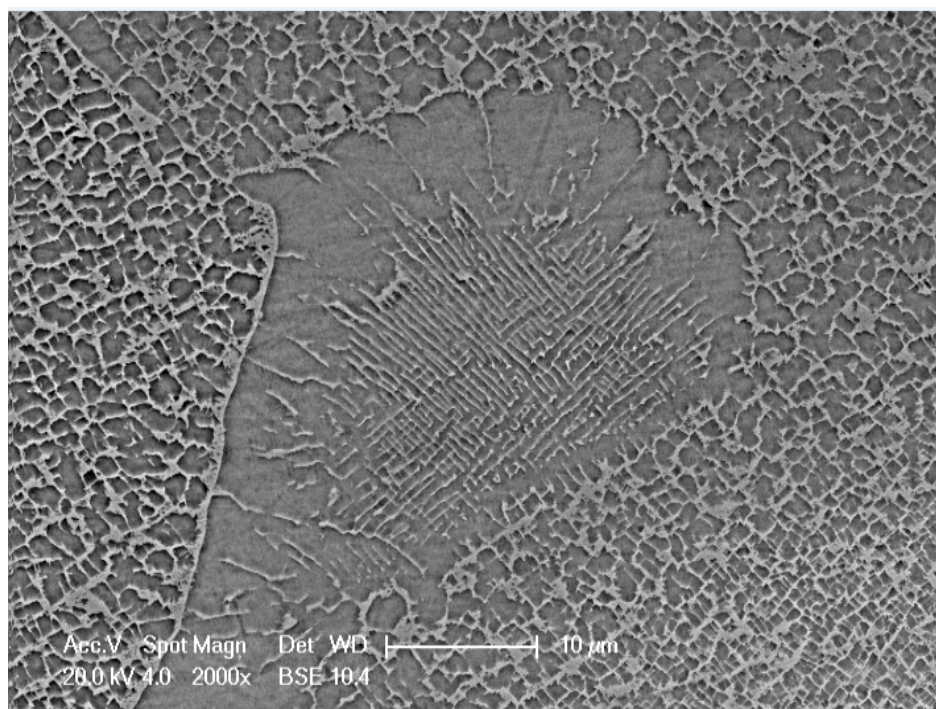


Figure 7.15. SEM-BSE image showing eutectic region

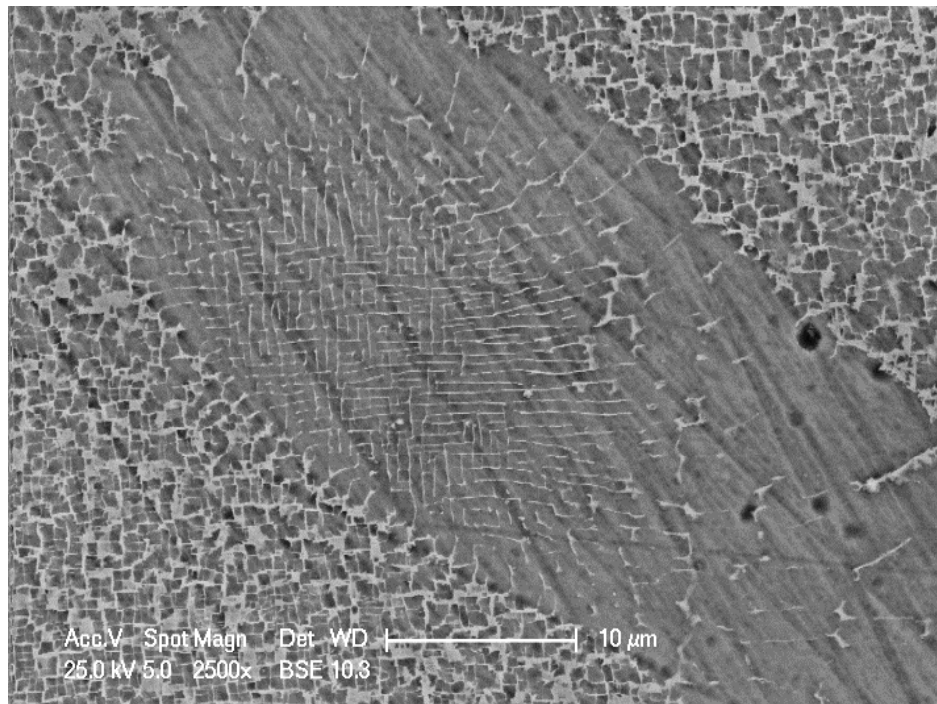


Figure 7.16. SEM-BSE image showing eutectic region

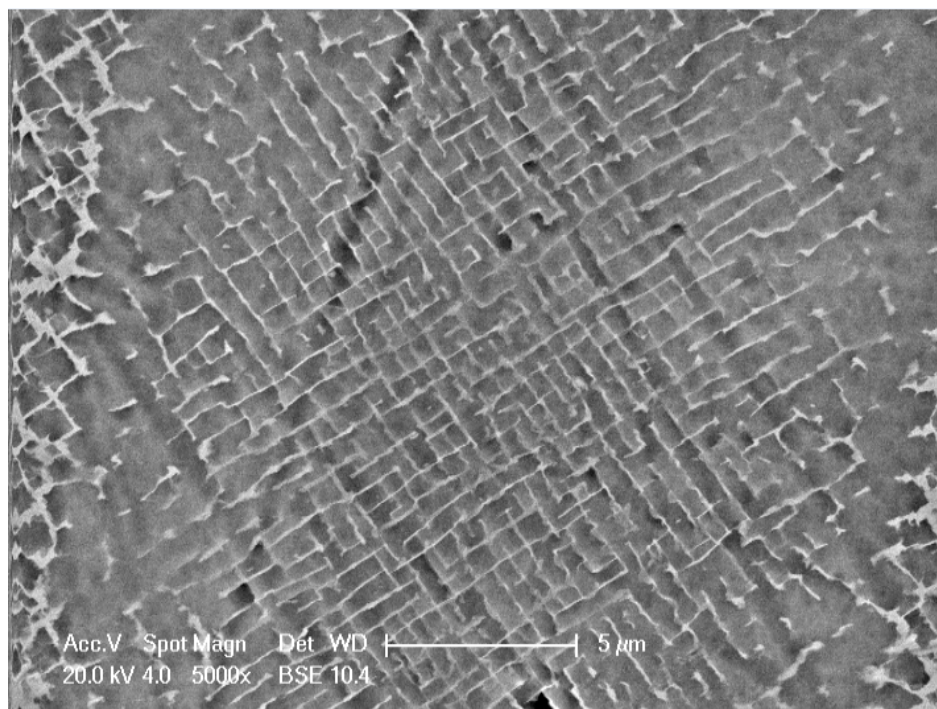


Figure 7.17. SEM-BSE image showing eutectic region

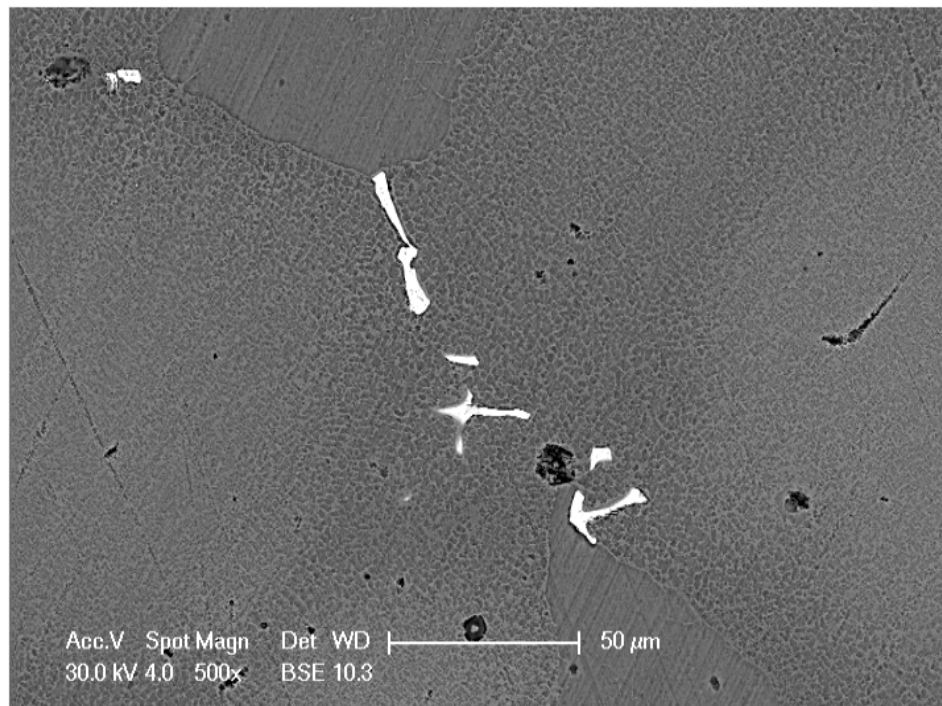


Figure 7.18. SEM-BSE image showing carbide

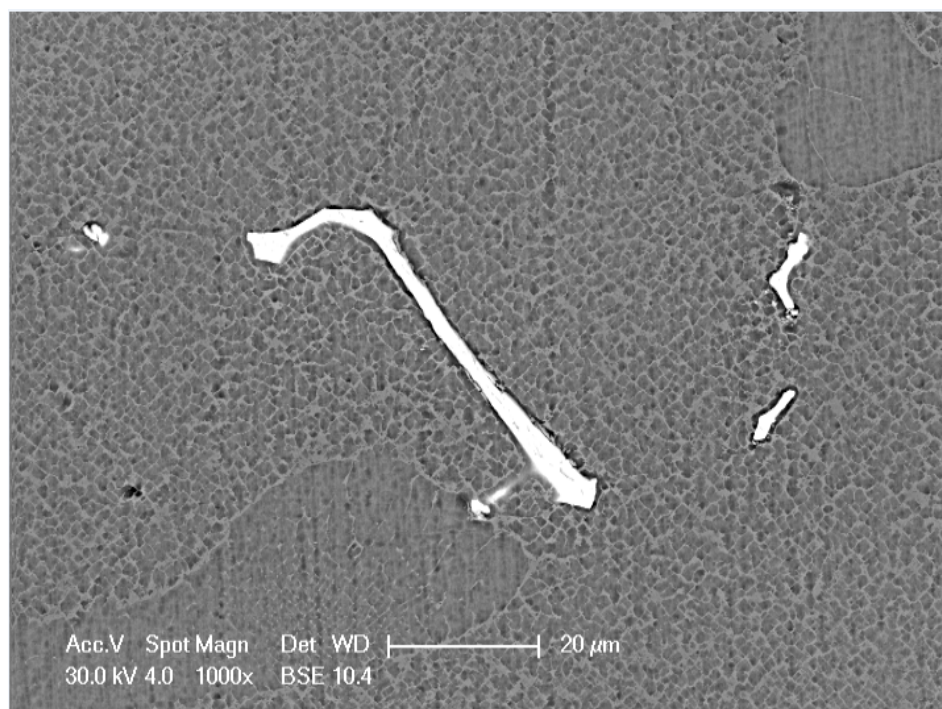


Figure 7.19. SEM-BSE image showing carbide

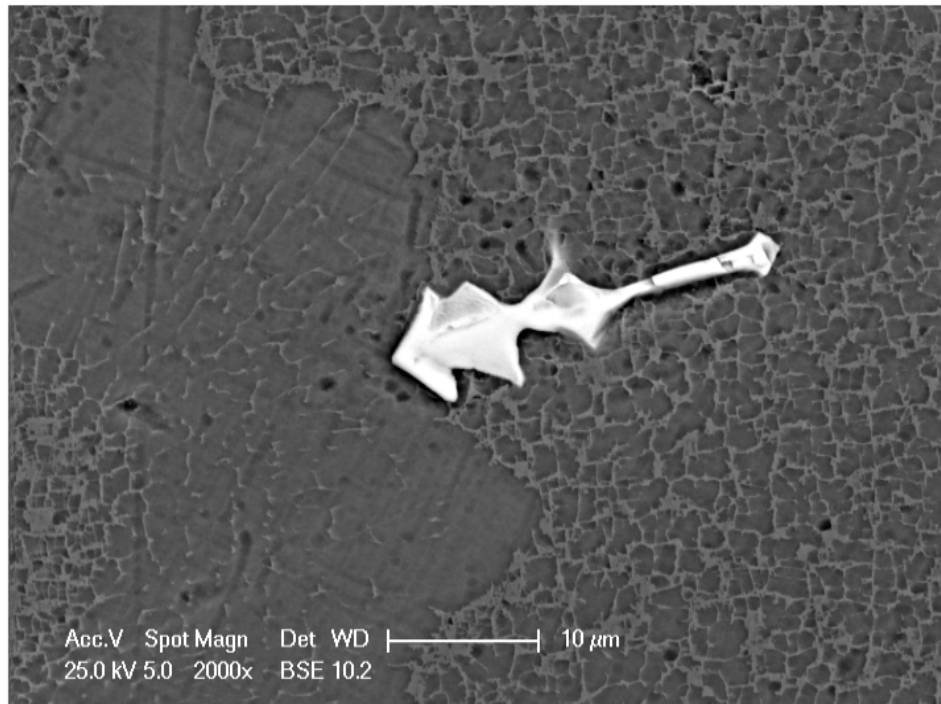


Figure 7.20. SEM-BSE image showing carbide

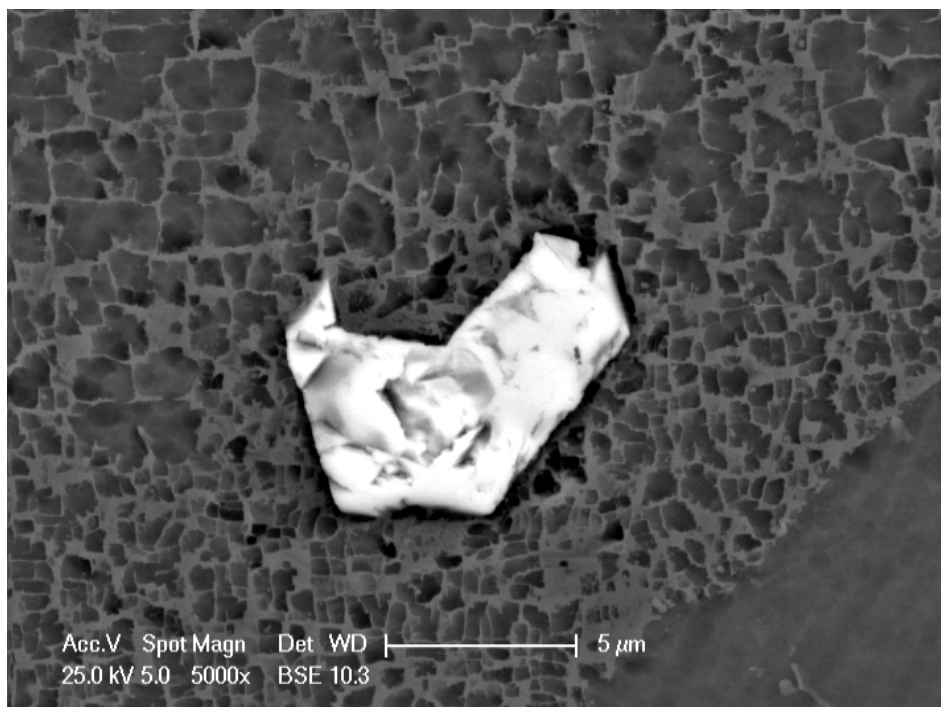


Figure 7.21. SEM-BSE image showing carbide

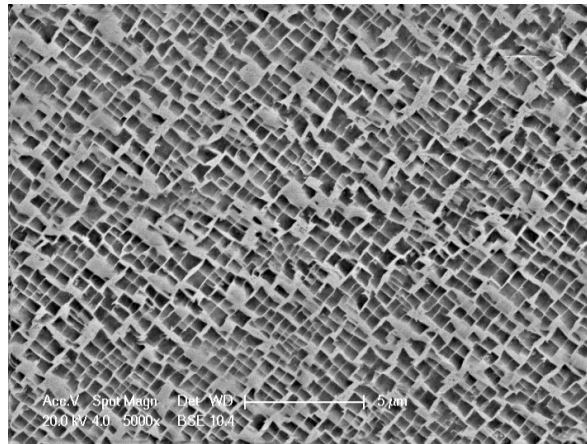


Figure 7.22. Precipitation in the dendritic region(5000X)

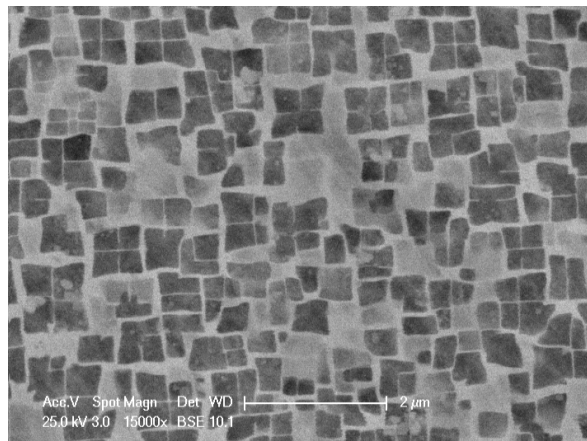


Figure 7.23. Precipitation in the dendritic region(15000X)

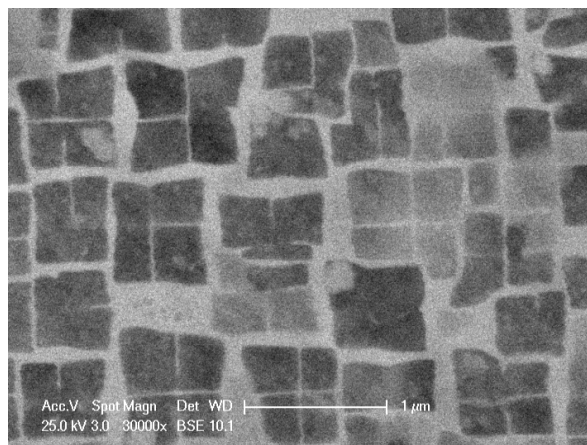


Figure 7.24. Precipitation in the dendritic region(30000X)

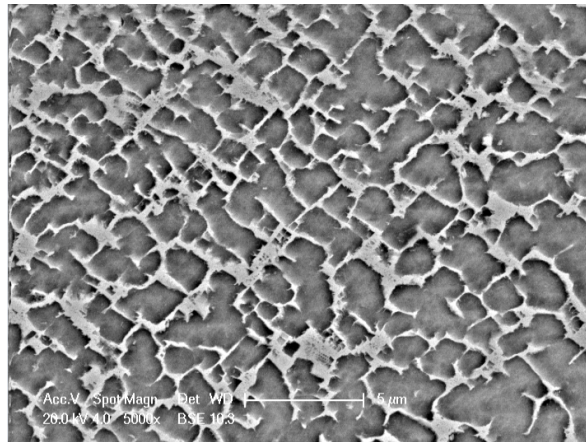


Figure 7.25. Precipitation in the interdendritic region(5000X)

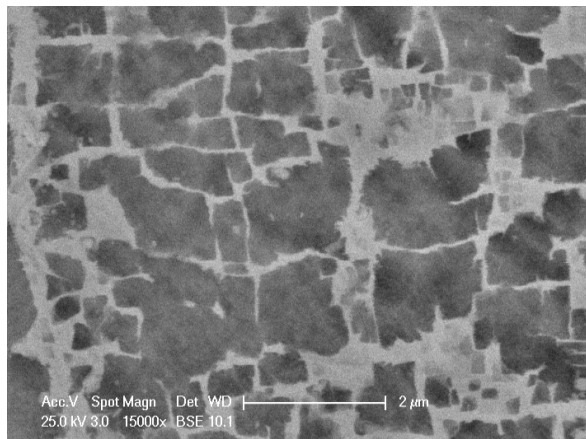


Figure 7.26. Precipitation in the interdendritic region(15000X)

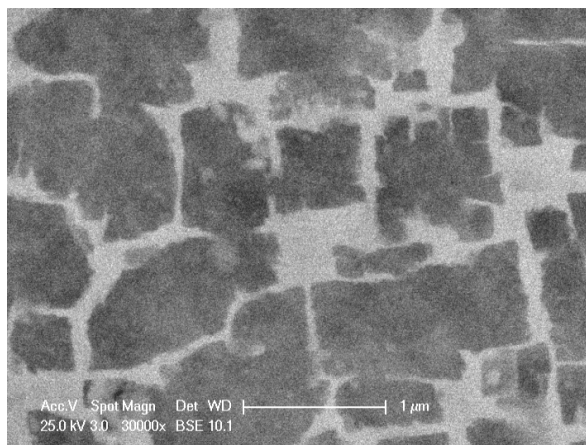


Figure 7.27. Precipitation in the interdendritic region(30000X)

7.2. Mushy Zone Length

Figure 7.28 shows an increasing trend for mushy zone length with growth velocity. Because of the fact that measured values are the initial mushy zone lengths, differences come from the amount of latent heat liberation and the amount of hot liquid transported to the mushy zone. Latent heat release increases as the growth velocity increases [56]. Furthermore, a faster velocity brings down a hotter liquid from the bulk to the interface [57]. This hot liquid might increase the length of the mushy zone. As a result, more latent heat liberation and more hot liquid transport to the mushy zone increase the mushy zone length as velocity increases.

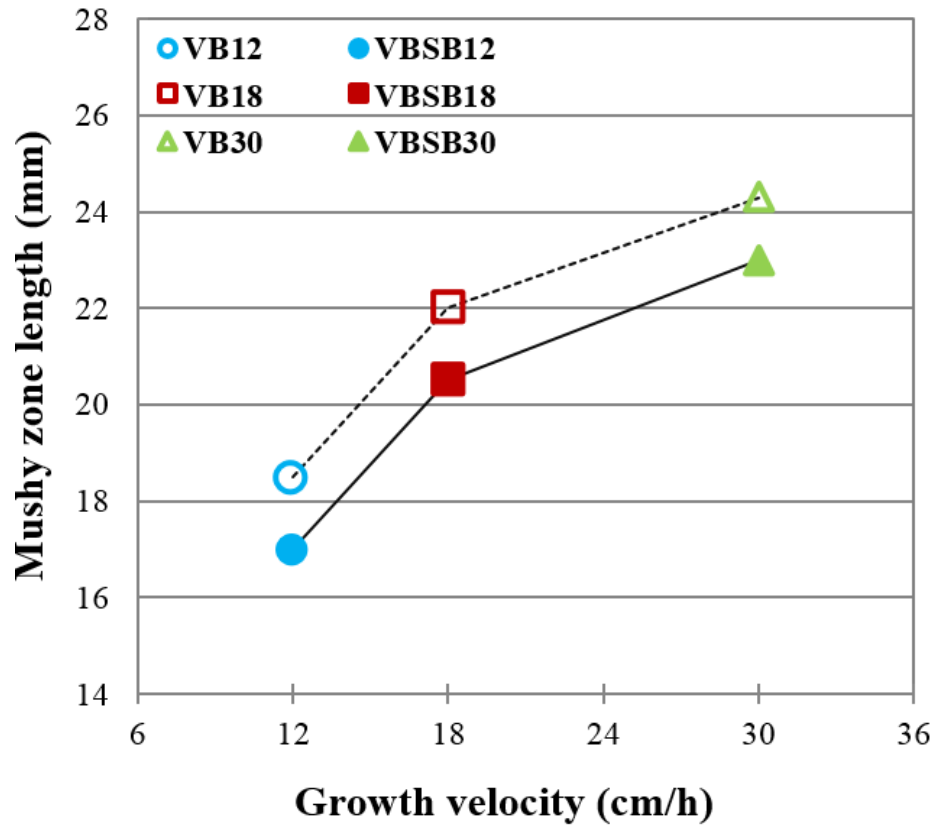


Figure 7.28. Mushy zone length with respect to growth velocity

Figure 7.28 demonstrates that VBSB samples show a lower length for the mushy zone, which may point to a convective melt flow for the VB samples and a diffusive flow for the VBSB ones. Low gravity (minimal convection) experiments have already

showed thinner mushy layers compared to the terrestrial samples with similar growth parameters [58]. Hence, the VBSB method mimics the diffusional growth mode which is dominant in low gravity space environments. Reduced initial mushy zone lengths are attributed to the decreased convection by using the submerged baffle. A lowered mushy layer thickness has benefits that include reducing the possibility for the formation of stray grains, freckles, and pores in a directionally solidified sample.

7.3. Melt-back Transition Length

In the mushy region of the crystals, there is a melt-back transition region just below the initial s/l interface position as shown in Figures 7.2 to 7.9. This region forms in the upper part of the mushy zone since liquid fraction and melt flow strength are higher there. The pulling induced hot flow at the beginning of the solidification melts back and/or breaks/bends the dendrites in the upper part of the mushy zone. In addition, the inability of the cooling system to remove the accumulated latent heat causes thermal undercooling near the s/l interface, and leads to formation of grainy regions and misoriented dendrites seen in the melt-back transition region [59–61].

As seen in Figure 7.29, the length of the melt-back region increases as the growth velocity increases. This is expected because the hot melt flow can penetrate deeper into the mushy region and destroy the dendritic structure for faster velocities since the solidification is slower for them at the beginning of solidification [57]. Moreover, the s/l interface is displaced down more for faster growth velocities, which results in a larger thermally undercooled liquid region. Therefore, the length of the region affected by the thermal undercooling increases as the growth velocity increases.

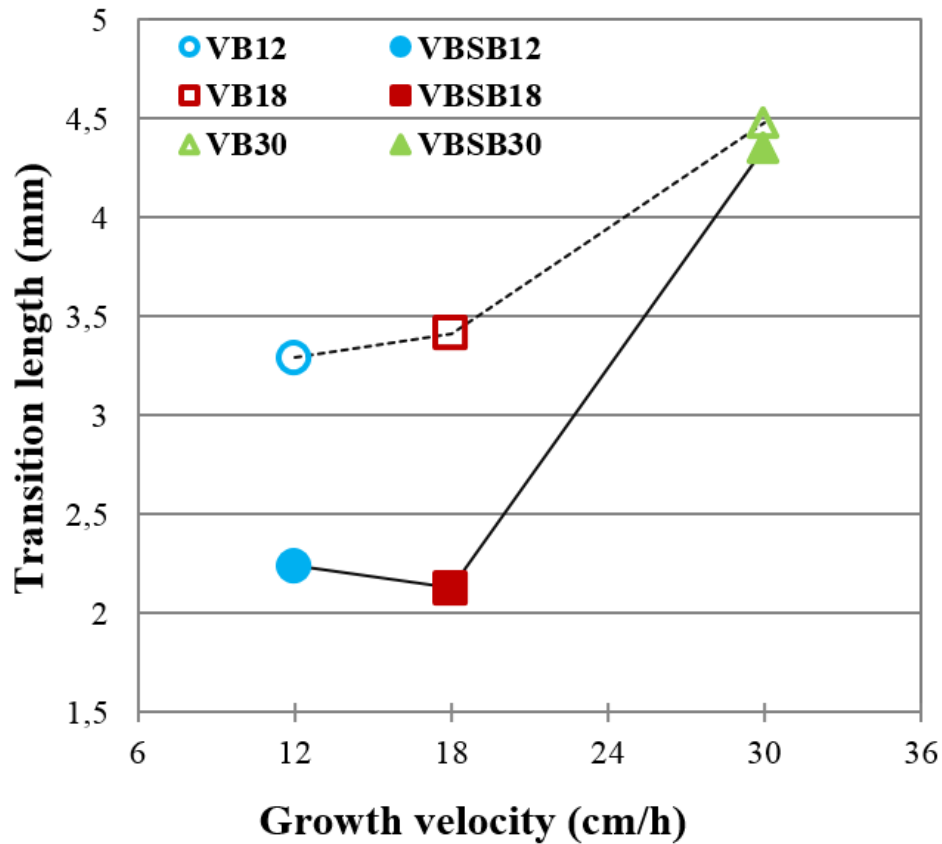


Figure 7.29. Melt-Back transition length with respect to growth velocity

Another finding of melt-back transition length analysis is that the VBSB samples have smaller melt-back transition length than the VB samples. First, using the submerged baffle decreases convection by decreasing the melt height. This results in fewer broken/bent dendrites near the s/l interface. Second, the submerged baffle diminishes turbulent mixing of the hot and cold molten metal by separating the melt into two regions. This reduces the decrease in the thermal gradients, and decreases the formation of grainy regions in the melt-back transition region. Therefore, employing a submerged baffle is beneficial by reducing the convection and the associated broken/bent dendrites and grainy regions.

7.4. Primary Dendrite Arm Spacing

The primary dendrite arm spacing (PDAS) of directionally solidified superalloys is very crucial feature related to the mechanical properties of the cast products. In addition, PDAS is a useful parameter that reflects the process variables, mainly the axial thermal gradient (G), the withdrawal velocity (V), and the extent of convection in the mushy region and the bulk melt. Many researches have been done to explain the variation of dendritic spacing with V and G [62, 63]. However, experimental data on superalloys solidified at low thermal gradients ($20 - 30\text{ }^{\circ}\text{C/cm}$) are limited. Moreover, PDAS can vary along the sample again depending on the process variables which change during solidification due to the transient nature of the interface growth velocities (V) [57] and the consistently decreasing axial thermal gradient (G). Experimental data on the evolving morphology along the length of the grown samples are limited. In the current study, the crystals were solidified with a fixed thermal gradient but with varying pull velocities. However, the most important contribution of this present study is the utilization of the baffle in the VBSB method. This is the first in the superalloy directional/single crystal solidification. This allowed a comparison between the results obtained by the VB and VBSB methods with respect to many microstructural features presented and discussed below, including the primary dendrite arm spacing.

The PDAS values along the length are plotted in Figure 7.30. Please note that PDAS for the single crystal seed is $405\text{ }\mu\text{m}$. PDAS in grown samples along the length can be analysed in two ranges, from I5 to I10 and from I10 to I45. A decreasing PDAS can be seen from the I5 to I10. The microstructures in this range are shown in the I, I5 and I10 radial photos of Figure 7.3 to 7.10. The radial microstructures of I are composed of cellular and broken/bent dendrites. Indeed, at the beginning of solidification, there was accumulation of solidification latent heat. Due to insufficient heat extraction, latent heat could not be removed from the initial interface region (I). This latent heat did not allow the s/l interface to solidify for a few mm, although withdrawal proceeded. Then, the section that could not be solidified by withdrawal turned into a thermally undercooled region. As a result, grainy/cellular/misoriented dendritic microstructure was formed near the s/l interface (I). Starting from the I5 section, the microstructure

started to become dendritic. Grainy regions no longer appeared in the I5 radial photos. While the microstructure was cellular and had grains near the s/l the interface, the dendritic structure became more and more dominant away from the interface (I). Since dendrites were formed from I5 to I10, more dendrite cores could be observed decreasing the PDAS. After the I10 section, as seen in the I10 radial photos, dendrites started to obtain a more oriented pattern and the misoriented dendritic structure was no longer dominant. Further from the interface, the primary dendrite arm spacings increase. This is due to a reduced thermal gradient with distance from the heat extracting surface. This result has been reported also in another study [64].

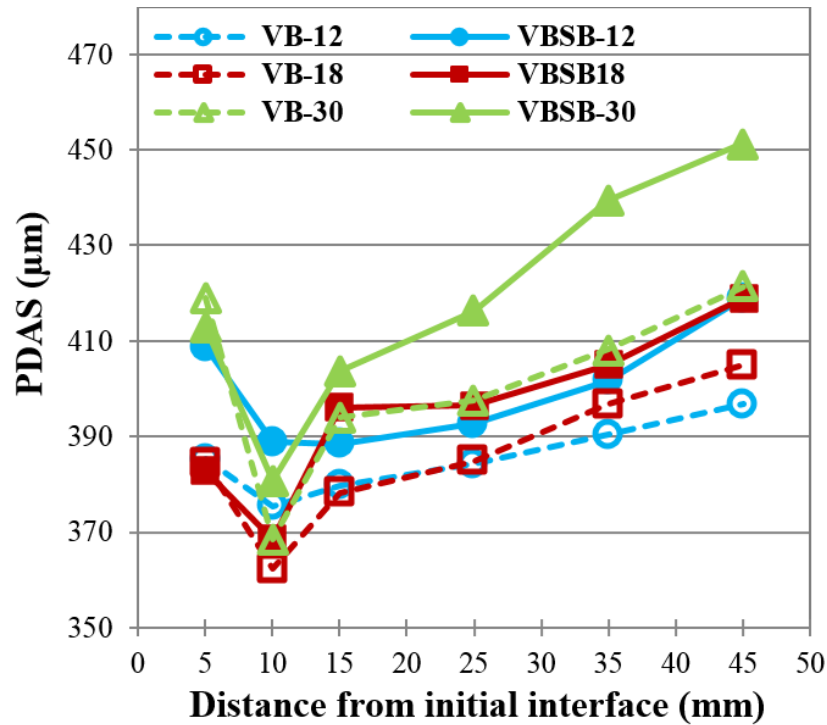


Figure 7.30. Primary dendrite arm spacing with respect to the distance from interface for VB and VBSB pairs

It has been shown that the primary dendrite arm spacing (PDAS) decreases with increasing withdrawal rates (V) [62]. However in this study, PDAS generally increases as growth velocity increases. A larger PDAS with a higher growth velocity is in agreement with the literature [63] for low thermal gradients (<28 °C/cm). This behavior is explicitly shown in Figure 7.30. During the solidification, the s/l interface

position can shift down into cooler regions [57]. This is more apparent for the highest pulling velocity. Once the s/l interface was shifted down, radial temperature gradients can become more influential. The radial thermal gradients enhance the growth of secondary dendrite arms. These overgrown secondary dendrite arms can be seen in Figure 7.31, and block and inhibit the growth of primary dendrites.

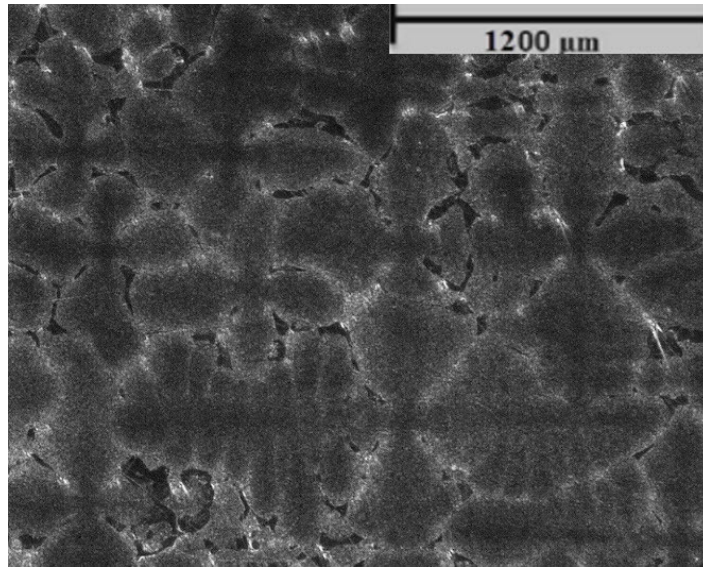


Figure 7.31. Dendritic region with overgrown secondary dendrite arms

The effect of buoyancy driven convection inside and ahead of the mushy zone has been investigated by various techniques such as low- and high-gravity [65] and downward solidification [66,67] experiments. In these experiments, the effect of thermosolutal convection on segregation and PDAS is considered due to the strong impact on the mechanical properties. As for dendritic spacing, all researchers have agreed that convection decreases the PDAS by the formation of new primary dendrite arms from the tertiary dendrite arms, as shown in Figure 7.32 [68]. During solidification, rejected solute is carried away from the s/l interface in the mushy region via diffusional convective flows. Since the solute can not be washed away effectively in the mushy network, the rejected solute atoms forms a solute build up at the s/l interface. This build up can constitutionally supercool the surfaces of the secondary dendrites resulting in the formation of cells and then dendrites parallel to the solidification direction. These newly formed dendrites are called tertiaries. Newly formed tertiary dendrites growing

along the growth direction refine the microstructure.

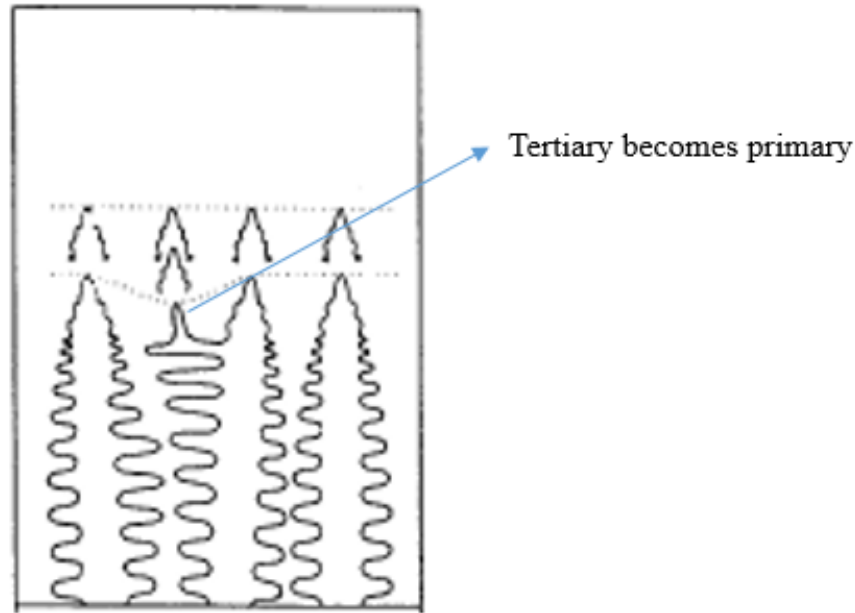


Figure 7.32. Formation of tertiary dendrites

The aforementioned studies regarding the thermosolutal convection have considered only the convection inside the mushy zone. Bulk convection ahead of the mushy zone has not been generally considered by many researchers. However, Ridder et al [32] conducted one of the first studies presenting a model that couples the interdendritic flow and the bulk flow ahead of the s/l interface. They treated the mushy zone as a porous medium and conducted several experiments with Sn–Pb to validate their model. In this study, it has been shown that there is a considerable effect of bulk convection on the macrosegregation depending on the flow direction in the molten metal. If the bulk flow rotation is in the same direction as the interdendritic flow, it increases macrosegregation. Otherwise, counter rotating flows in these regions decrease the macrosegregation by confining the mushy zone plumes. This is shown in Figures 7.33 to 7.36.

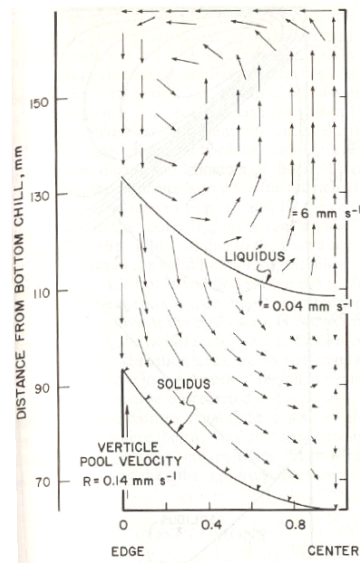


Figure 7.33. Calculated flow velocities in the Sn 16 pct Pb ingot. Taken from the study of Ridder et al [32]

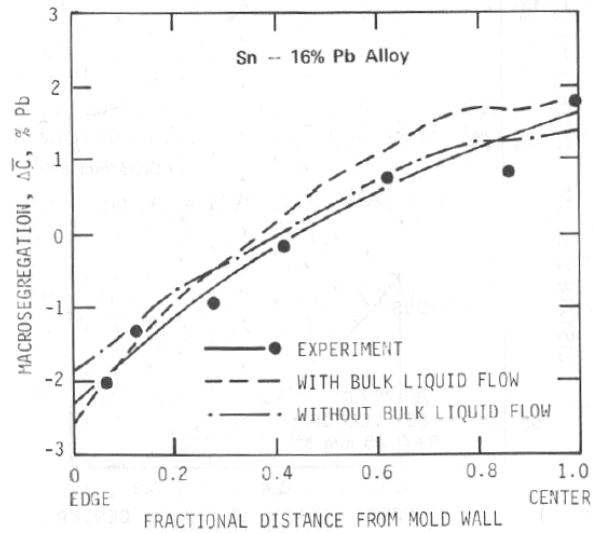


Figure 7.34. Comparison on experimental and theoretical segregation profiles in the Sn 16 pct Pb ingot. Taken from the study of Ridder et al [32]

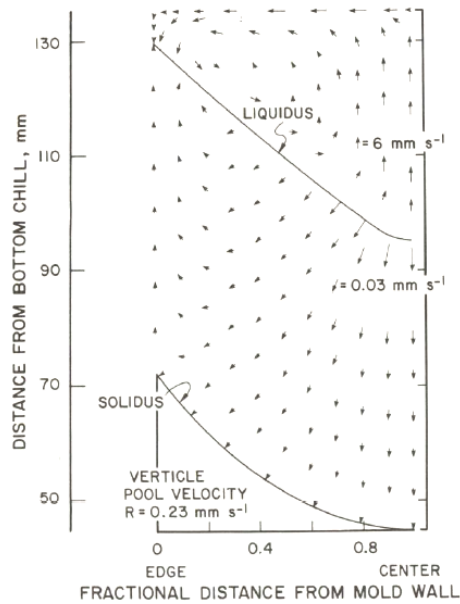


Figure 7.35. Calculated flow velocities in the Pb 26.5 pct Sn ingot. Taken from the study of Ridder et al [32]

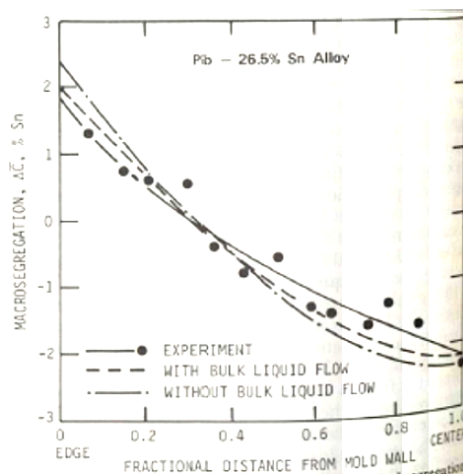


Figure 7.36. Comparison on experimental and theoretical segregation profiles in the Pb 26.5 pct Sn ingot. Taken from the study of Ridder et al [32].

Moreover, Bennon and Incopera [33] have developed a continuum model for a binary system in a rectangular cavity. Advective transport of fluids across the mushy zone has been investigated and its interaction with the bulk liquid has been studied. According to their study, fluid flow in the mushy zone is characterized by solutal gra-

dients while the convective motion in the bulk fluid is highly dependent on the thermal gradient (G). If there is a strong, counter-rotating fluid inside the bulk fluid, most of the interdendritic flow is confined to circulate within the mushy zone. Otherwise, the interdendritic fluid can penetrate into the bulk fluid which results in segregation, localized growth rate change, an irregular s/l interface and local remelting.

To show the extent of the bulk convection, Szekely and Jassal [34] reported numerical and experimental results that include the temperature and velocity profiles of fluids both in the mushy zone and the bulk fluid. In this study, it has been shown that the velocities in the bulk liquid are at least ten times larger than the velocities inside the mushy region. This research is important in showing that the fluid motion in bulk liquid is not too small to be neglected as seen in Figure 7.37.

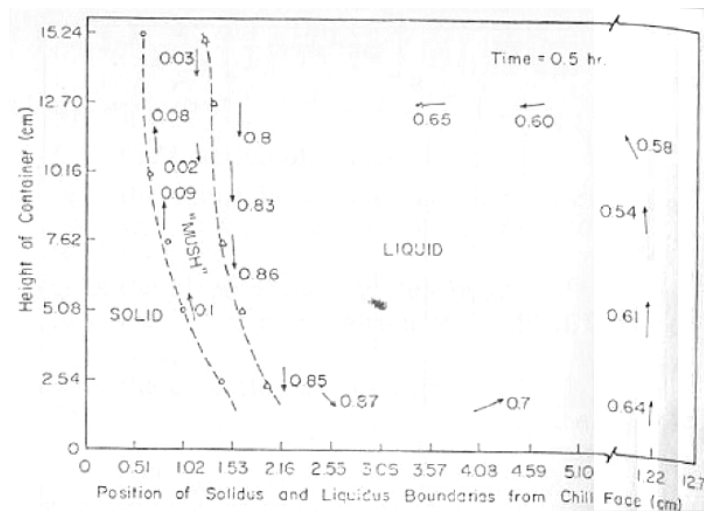


Figure 7.37. Velocity distribution in the mushy zone and in the bulk liquid. Taken from the study of Szekely and Jassal [34]

Finally, Sample and Hellawell [9] conducted a study that investigated the effect of forced convection of the bulk liquid on the channel segregation. They aimed to prevent upward interdendritic flows by forming a downward forced bulk flow ahead of the s/l interface with the help of rotation and inclination of the crucible. They found out that forced downward bulk flow can effectively stop the formation or propagation of density inversion channels. These can be regarded as a strong evidence that bulk

liquid movement has a great effect on the macrosegregation behavior and should not be neglected. Therefore, it can be asserted that bulk convection has a great effect on the micro and macrostructure, so assessments made without considering the bulk convection would be incomplete.

In the light of aforementioned findings, the submerged baffle experiments were designed in order to decrease the bulk melt height. The reduced melt height reduces the bulk convection as the bulk convection is proportional to the melt height via the Rayleigh number. The effect of employing a baffle on PDAS characteristics can be seen in Figure 7.30. PDAS of the samples grown with the Vertical Bridgman with Submerged Baffle (VBSB) technique are larger than those of the samples grown with the Vertical Bridgman (VB). This is a clear proof that using submerged baffle can effectively decrease the melt height, and that decreased melt height results in weaker thermosolutal convection. Weaker convection reduces the formation of new tertiary dendrites which decrease the spacing between primary dendrite arms.

7.5. Primary Dendrite Core Size

To better analyze the behavior of dendrites, dendrite core sizes were measured for all the samples and the seed. Please note that primary dendrite core size for the single crystal seed is $110\ \mu m$. As seen in Figure 7.38, dendrite core size decreases as withdrawal velocity (V) increases. This is consistent with diffusional interface growth theories [39]. To adjust to the faster growth rate, dendrite tips get sharper to have an increased interface for an efficient rejection of the solutes. However, it is interesting that the primary dendrite arm spacing and the dendrite core size show opposite trends in terms of withdrawal velocity. To understand this contradictory finding, it is beneficial to look at the study by Ma and Sahm [69] proposing that primary dendrite arm spacing is resolved into 2 different parts, the diameter of dendrite core and two times the secondary dendrite arm length. They claimed that the primary dendrite core size depends highly on the growth velocity while the secondary arm length is related to the growth velocity as well as the local radial free growth time. In this study, as the withdrawal velocity increases, the dendrite core gets thinner while the secondary

dendrite arms overgrow due to insufficient axial thermal gradient (G). That is the reason why primary dendrites with fine core and coarse secondary arm are seen as the growth velocity increases.

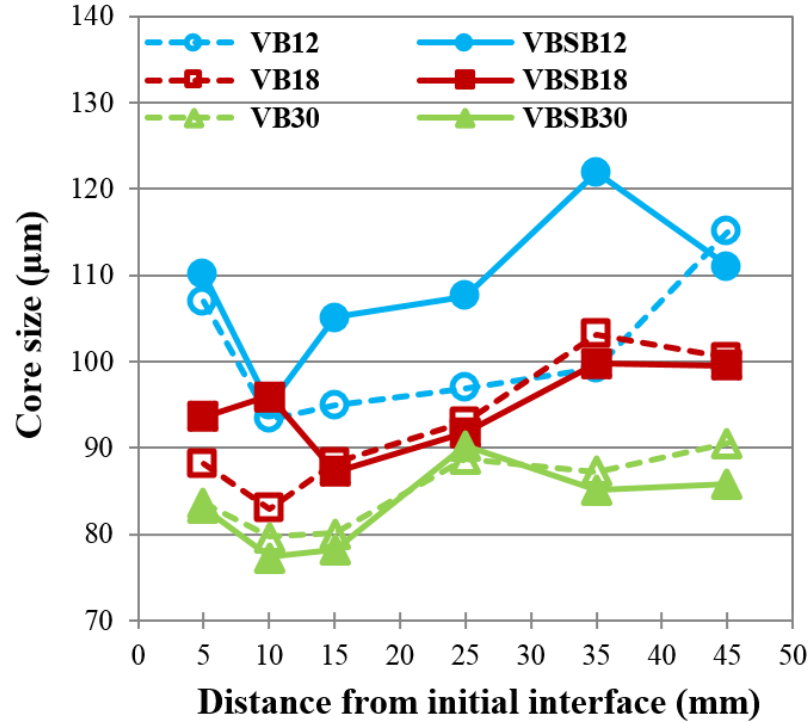


Figure 7.38. Dendrite core size with respect to axial distance

Dendrite core size over the sample length can be analysed in two regions similar to the PDAS. First, the core size decreases from I5 to I10. Second, the core size increases from I10 to I45. During solidification, the withdrawal velocity is not equal to the solidification velocity due to the inadequate heat extraction from the system. In other words, the s/l interface shifts down as solidification proceeds [57]. The sluggish solidification at the beginning of withdrawal results in coarser primary dendrite cores at I5 than at I10. After dendrites start to form a more oriented structure (I10), dendrite core size increases with distance from the interface owing to increased distance from the chill plate, and decreased G (I10 to I45).

As for the effect of the submerged baffle on dendrite core size, the dendrite cores of VBSB samples are slightly coarser than VB samples. The decreased melt height

and melt convection for VBSB samples promote the diffusional growth mode during solidification which leads to thicker dendrite cores.

7.6. Secondary Dendrite Arm Spacing

SDAS values over the length are plotted in Figure 7.39. SDAS for the single crystal seed is measured as $96\text{ }\mu\text{m}$. It should be considered that SDAS is strongly correlated to the G and V , as discussed in Section 1. In our study, V is the main parameter controlling the SDAS values since G is fixed.

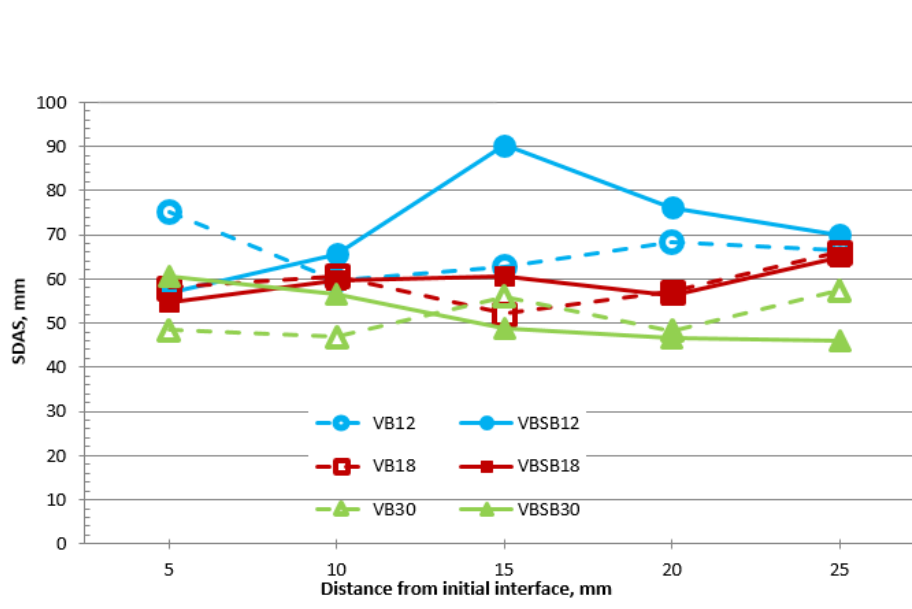


Figure 7.39. Secondary dendrite arm spacings with respect to axial distance

There is no distinctive variation of SDAS over the length for any sample. However, the reduction of withdrawal velocity leads to a slight increase in the SDAS, especially after the I10 section. This may be attributed to the increased solidification time by the decreased withdrawal velocity. Up to the I10 section, samples grown with different velocities show similar SDAS values. The sluggish solidification rate for all samples in the beginning of the solidification (I-I10) [57] could lead to similar SDAS between the I5 and I10 sections. Using the submerged baffle considerably reduced the convection, as discussed earlier. However, there seems to be no distinctive/consistent effect of

the submerged baffle on the SDAS. In fact, the effect of convection on SDAS was studied earlier by Spinelli et al [70] and it was shown that the SDAS was not affected significantly by convection.

7.7. Porosity

Pore area fractions over the length and average pore area fraction on radial surfaces for each sample are plotted in Figure 7.40 and Figure 7.41, respectively. Assuming the pore shape is spherical, the average pore diameters are also plotted in Figure 7.42 with respect to distance from the interface.

To interpret the porosity results, the mechanism behind the microporosity formation should be well understood. As introduced in Section 1, P_G and ΔP try to nucleate a pore within the mushy zone during solidification. According to Darcy's law, ΔP is directly proportional to the flow velocity (V), viscosity (μ) and the mushy length (L), and inversely proportional to the permeability (K) of the mushy zone. Additionally, it has been reported that alloys with finer structure have higher porosity with smaller pore size [71]. This is attributed to inadequate fluid feeding of micro-shrinkage sites due to low permeability of the mushy zone with finer structure. Therefore, microporosity is directly related to microstructural features like the primary dendrite arm spacing, primary dendrite core size, development of secondary and tertiary arms, and convection.

Figure 7.41 shows the least porosity in samples grown at 12 cm/hour and the highest porosity in samples grown at 18 cm/hour. Porosity in the 30 cm/hour samples is between the other two. Here, the interesting result is that the 12 cm/hour sample has the lowest porosity despite having the finer structure in terms of PDAS. This velocity has the largest core size, too. Having the largest core size and the lowest PDAS may imply a reduced permeability of the mushy zone. However, radial micrographs of samples grown at 12 cm/hour show no sign of secondary dendrite arm overdevelopment. Therefore, the permeability of the mushy zone is not disturbed by overgrown secondaries. The bulk liquid flow can fill more efficiently the micro-shrinkage sites in the

last solidified parts. Moreover, the VB12 sample has the smallest mushy zone length. This decreases the ΔP according to Darcy's law. These are the reasons why the lowest porosity is observed in the samples grown with 12 cm/hour velocity. By increasing the growth velocity to 18 cm/h, there is a slight increase in the PDAS; however, there is a considerable increase in the microporosity. It seems that permeability of the structure is reduced considerably at this velocity. This could be due to an increase in the mushy length and especially elongated secondary dendrite arms. On the other hand, there seems to be a decrease in the porosity of samples grown with 18 cm/hour to 30 cm/hour. This can be understood by looking at their PDAS values. PDAS values of the samples grown with 30 cm/hour are considerably larger than those of the 18 cm/hour samples. This much coarser structure dominates over the fluid feeding blocking effect of the overgrown secondaries. Moreover, for the samples grown with 30 cm/hour, excessively grown tertiary arms hinder the growth and coalescence of micropores.

Considering the effect of the submerged baffle, VBSB samples show a lower porosity in all axial positions. The VBSB samples show up to 38 % lower area fraction of porosity as seen in Figure 7.41. The PDAS is higher for the VBSB samples, which means more permeability (K). In addition, a lower mushy zone length (L) for the VBSB samples also provide better interdendritic feeding and fewer nucleation sites for micropores. Darcy's law also shows that a reduced melt flow (V) can reduce ΔP . In fact, the VBSB technique reduces the convection in the melt by reducing the melt height. Therefore, the melt flow velocity is also reduced. On the other hand, in the presence of a gas in the melt, it has been found that gas bubbles attach themselves to the baffle base and move with it out of the melt [21]. This lowers the gas content in the interdendritic regions and reduces the P_G .

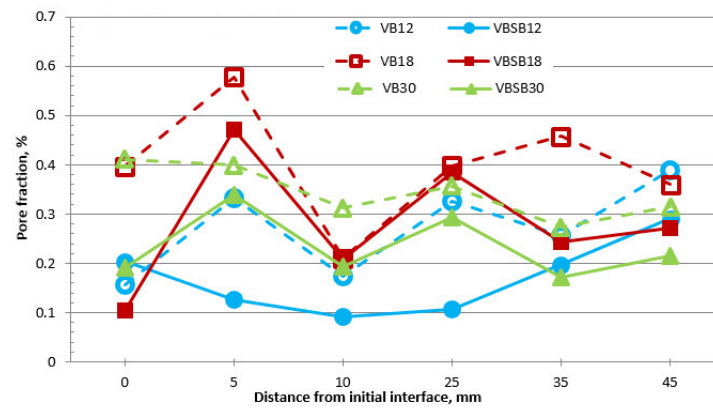


Figure 7.40. Porosity with respect to distance from initial interface

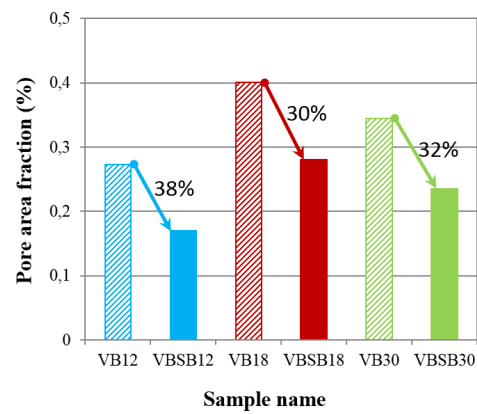


Figure 7.41. Porosity fraction with respect to growth velocities for VB and VBSB samples

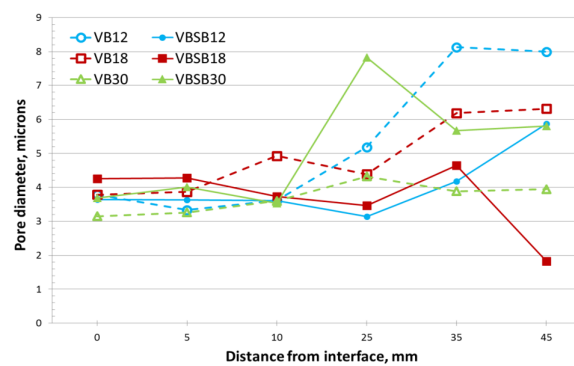


Figure 7.42. Average pore diameters with respect to distance from interface

7.8. Segregation Characteristics

Table 7.2 shows the values of the average microsegregation (partition) coefficient k for the samples grown with the VB and the VBSB techniques. Partition coefficients are obtained by dividing the concentration of each element at the dendrite core (Point 1 in Figure 7.43) by the average concentration of the interdendritic region (Points 2-4 in Figure 7.43) as measured by SEM-EDS. The shown k values are the average k values of the I25, I35, and I45 sections of each sample. Two dendrites were arbitrarily chosen from each elevations. In fact, the microsegregation behavior in the as-grown microstructure does not appear to be a strong function of the distance from the interface. Note that the elements which segregate to the dendrite cores have coefficients greater than unity. The greater the coefficient, the greater the partitioning to the dendrite core. For the elements that have partitioning coefficients less than unity, they tend to segregate to the liquid during solidification and enrich the interdendritic regions. The smaller the coefficient, the greater the degree of segregation to the interdendritic region. Table 7.2 indicates that elements Al, Ta, Ti, and Hf show negative segregation behavior as they tend to segregate to the interdendritic region while W, Re and Co show positive segregation behavior during solidification. On the other hand, Mo, Cr and Ni exhibit a nearly uniform distribution between the dendrite core and interdendritic region in all samples.

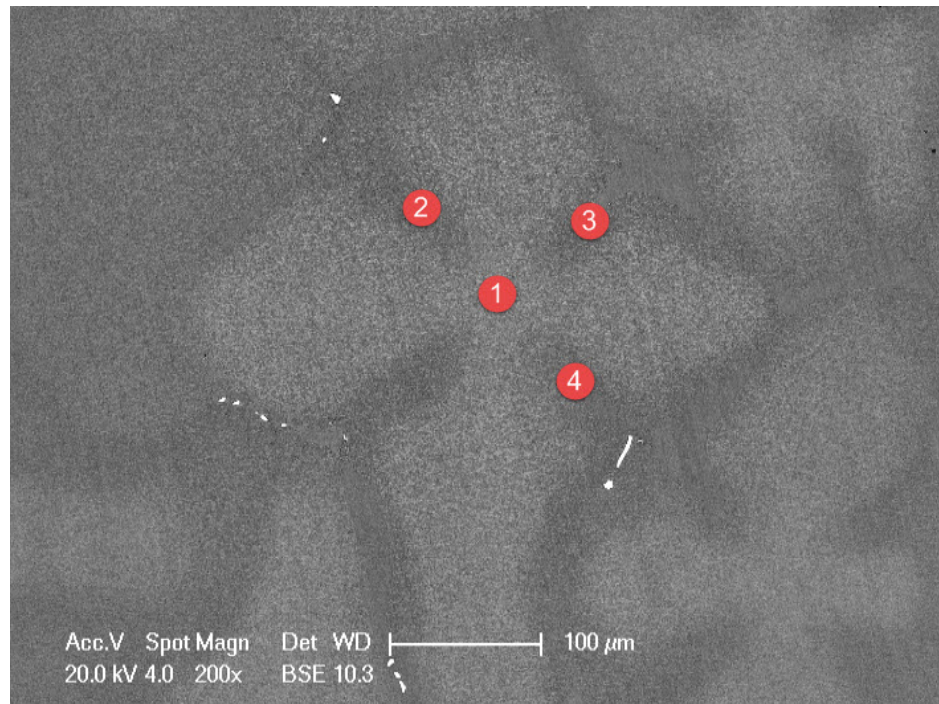


Figure 7.43. The SEM-EDS compositional analysis locations. The compositional analysis on the point 1 represents the composition of the dendrite core and the average of points 2-4 represents the composition of the interdendritic region

Table 7.2. Microsegregation Partition Coefficient of the VB and the VBSB Samples

	Al	Ta	W	Re	Mo	Ti	Cr	Co	Ni	Hf
VB12	0.88	0.72	2.13	1.37	0.84	0.63	0.95	1.10	0.97	0.16
VBSB12	0.88	0.71	2.26	1.44	0.94	0.64	1.02	1.11	0.96	0.32
VB18	0.89	0.77	2.26	1.70	0.96	0.64	0.92	1.06	0.95	0.34
VBSB18	0.89	0.76	2.06	1.44	1.06	0.52	0.94	1.07	0.96	0.17
VB30	0.85	0.71	2.35	1.48	0.81	0.57	0.97	1.09	0.98	0.07
VBSB30	0.84	0.70	2.39	1.70	1.00	0.58	1.03	1.11	0.94	0.24

According to the average k values, there is no considerable distinction between the microsegregation characteristics of the samples grown with the VB and VBSB. This

is an interesting result since all findings discussed in the previous sections clearly show that the VBSB technique promotes diffusional growth while the VB technique is more convectional. Therefore, it can be asserted that the SEM-EDS used in this study was capable of showing the segregation characteristics of each element since the k values are consistent with the literature findings. However, the compositional analysis was not sensitive enough to reflect the segregation differences between the VB and VBSB samples. Wavelength-Dispersive X-Ray Spectroscopy (WDS) could be utilized used to detect the segregation differences between the samples grown with the VB and VBSB, since WDS exhibits superior peak resolution of elements compared to EDS.

8. CONCLUSION

A new solidification method, the vertical Bridgman with a submerged baffle (VBSB), has been employed to investigate the solidification microstructures in a superalloy. In order to judge the improvement brought about by the new method, corresponding samples also have been solidified with the conventional Bridgman (VB) method. Growth velocities of 6, 12, 18, 30 and 40 cm/hour have been used to grow the VB samples and 12, 18, 30 cm/hour have been used to grow the VBSB samples. The axial thermal gradient was 24 °C/cm for all experiments. The comparative results of this study can be summarized as follows:

- The mushy zone length and the melt-back transition length were decreased for the VBSB method.
- PDAS and primary dendrite core size were increased along the length of the samples.
- The VBSB method yielded a larger PDAS and increased dendrite core size.
- The porosity was reduced up to 38 pct by the VBSB method.

This study showed that the VBSB method can be successfully employed to the growth of single crystal superalloys. It is a promising technique since considerable reductions in porosity provide an advantage in the creep-fatigue life of the parts.

9. FUTURE WORK

In this study, the samples grown with the VBSB technique have larger PDAS than the samples grown with the VB technique. As discussed earlier, the VBSB decreases the convection and decreased convection increases the PDAS. However, PDAS should be decreased to have better fatigue properties. Therefore, the intend can be growing crystals with a finer structure in a future study. For this, samples can be grown with an increased axial thermal gradient (G). This consequently increases the convection in the melt. Meanwhile, implementation of the VBSB technique can decrease the melt height, so the convection. As a result, cystals with a finer structure and decreased porosity can be produced. Moreover, effect of changing the melt height below the submerged baffle (h) on the microstructure has not been examined in this study. The same set of VBSB experiments can be conducted with different melt heights to find the optimum h in terms of decreasing the convection.

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