Banded regular/anomalous eutectic in rapidly solidified Co-61.8 at.% Si

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Abstract: A novel banded microstructure consisting of regular/anomalous eutectic has been found in hypoeutectic Co-61.8at%Si rapidly solidified by either copper mould casting and melt spinning. The bands originate because of varied undercooling and growth rate in the direction of heat flow towards the copper sinks. Diffusional effects (i. e. rejection of solute) in the presence of limited convection cause fluctuations in growth rates for which the role of recalescence is highlighted. Occasional primary phase/eutectic transitions were also found. The microstructures are contrasted with those seen in furnace cooled samples where diffusion fully occurred in a quiescent melt.

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Dear Editor,

I am writing to you this letter accompanying the submission of our manuscript entitled **"Banded regular/anomalous eutectic in rapidly solidified Co-61.8 at% Si"** to be considered for publication in *Scripta Materialia*.

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This manuscript describes original work and is not under consideration by any other journal. All authors approved the manuscript and this submission.

Thank you for considering our manuscript for review. We look forward to your response.

Kind Regards,

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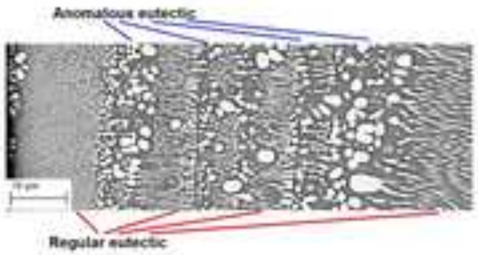
*Graphical Abstract



Banded regular/anomalous eutectic in rapidly solidified Co-61.8 at% Si

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Abstract
A novel banded microstructure consisting of regular/anomalous eutectic has been found in hypoeutectic Co-61.8at%Si rapidly solidified by either copper mould casting and melt spinning. The bands originate because of varied undercooling and growth rate in the direction of heat flow towards the copper sinks. Diffusional effects (i. e. rejection of solute) in the presence of limited convection cause fluctuations in growth rates for which the role of recalescence is highlighted. Occasional primary phase/eutectic transitions were also found. The microstructures are contrasted with those seen in furnace cooled samples where diffusion fully occurred in a quiescent melt.

Keywords: solidification microstructure, eutectic, undercooling, convection, Co-Si alloy

Microstructures in eutectics are determined by a complex interplay of nucleation of phases, both primary and coupled, solute segregation, solid/liquid interface morphology in relation to the rate of heat subtraction, and of crystal growth [1]. The model intermetallic compound-compound Co-Si system was earlier chosen for studying these features in undercooled droplets of composition Co-61.8 at%Si, i. e. slightly hypoeutectic, processed either by electromagnetic or electrostatic levitation [2, 3]. The alloy is constituted by the primary CoSi compound which admits about 1.5 at% excess solute Si in its structure and CoSi-$CoSi_2$ eutectic where $CoSi_2$ is a line compound and the eutectic occurs at 63.5 at% Si [4].

The varied undercooling achieved with the above techniques caused the formation of diverse microstructures. In electro-magnetically levitated (EML) samples (undercooling up to 127 K) mostly primary dendrites or cells with regular eutectic appeared. An irregular (or anomalous) eutectic made of primary $CoSi_2$ with intergranular CoSi of different size was obtained in electrostatic levitation (undercooling from 95 K to 304 K), EML and electromagnetic levitation accompanied by the application of a static magnetic field at high undercooling up to 150 K. Complex shape of primary phase with precipitates occurred in electromagnetic levitation + static magnetic field at undercooling of 199 K. The level of undercooling also gave rise to phase selection between CoSi and $CoSi_2$ according to nucleation rate and extent of convection, i.e. the turbulence of the melt ranging from strong in EML, damped when an electromagnetic field is applied, and weak in ESL [2, 3].

Overall it appears that the rod-like regular eutectic occurs at lower undercooling while the irregular one is favoured at high undercooling. No transition between these morphologies was ever reported nor were the microstructures formed in the presence of heat sinks, i. e. quenching media directing heat flow. Since the nucleation of phases is heterogeneous even in containerless techniques [2], it was devised to process the Co-Si alloy by rapid solidification with both melt spinning (MS) and copper mould casting (CMC) thereupon imposing a direction of the temperature gradient in fast cooling to reveal further aspects of the solidification mechanism, especially growth of crystals. At the other extreme of cooling rates a quiescent sample solidified in the cell of a high temperature calorimetry cell was studied.

An alloy of nominal composition Co-61.8at%Si was made by arc melting high purity components. Portions of the ingot were rapidly solidified by melt spinning producing ribbons about 30 μm thick and by casting in a copper mould producing cylinders of either 1 mm or 2 mm in diameter. Samples were cut to observe the section parallel to the heat flow direction during quenching in optical and Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS).

$CoSi$ and $CoSi_2$ phases were identified in all samples by means of X-ray Diffraction (XRD) using Cu Kα radiation. High Temperature Differential Scanning Calorimetry (HTDSC) was employed at 5 K/min heating/cooling rate to monitor the melting and solidification of the alloy.

An exemplary image of the present alloy solidified as a 2 mm cylinder in CMC, i. e. imposing radial heat flux, is shown in Fig.1 which summarizes all varied features of the microstructure. Similar features were also found in the 1 mm cylinder, in the part of the arc melted ingot in contact with the copper hearth, and in portions of ribbons. The first phase nucleating heterogeneously on the external surface was most often the CoSi compound whose crystals grew to the size of some microns rejecting Si into the liquid phase. The $CoSi_2$ phase then surrounded the primary crystals, the composition of the melt approached the eutectic and a eutectic microstructure began to appear. However, in the adjacent melt more CoSi crystals were nucleated independently giving rise to an anomalous eutectic microstructure, i.e. with no coupled growth. At a distance of 10-15 μm from the external surface then a rod-like eutectic appeared. From the continuity of the $CoSi_2$ phase in the microstructure, it is deduced that this was the leading phase in solidification and the CoSi crystals were formed by re-nucleation. The regular eutectic band extended for about 10 μm with some local interruptions parallel to the external surface. Occasional large CoSi crystals were embedded in the eutectic. It is noted that only a few CoSi crystals display dendritic features whereas most are close to round shape, indicating they grew with limited constitutional supercooling. Four transitions from regular to anomalous eutectic and vice versa are then recognized with bands of variable size spanning overall about 30 μm. With the exception of some large primary CoSi crystals, the rod-like eutectic grew throughout. The coupled crystals are oriented along the direction of heat flow whereas they display a fan structure in the interior of the sample or around primary crystal. On approaching this zone the interruptions already mentioned are recognized again. More precisely, it appears that after growth of the rods to some micron length, the $CoSi_2$ phase took over forming a band of limited length being then replaced immediately by coupled crystals. This appears as a primary phase/eutectic transition. Bands apparently originated because of directional heat subtraction. On the contrary, in EM levitated droplets undergoing strong melt convection at the undercooling of 68 K, primary CoSi surrounded by $CoSi_2$ and regular eutectic were homogeneously found [2, 3].

Fig. 2a shows an enlarged zone of a banded microstructure of the cylinder. The interphase separation of the eutectic crystals increases from the outer surface towards the sample interior. The average thickness along lines parallel to the external surface was determined by digitizing the images and counting the pixels belonging to the white and dark zones to obtain the eutectic spacing, λ, which provides an estimate of the interfacial undercooling with respect to the eutectic temperature, ΔT, according to [5]

$$\Delta T = \frac{4\gamma_{\alpha\beta}}{\lambda \Delta S} \qquad (1)$$

where $\gamma_{\alpha\beta}$ is the interfacial energy between crystal phases and ΔS the entropy of fusion [6]. The undercooling values with respect to the eutectic temperature are plotted in Fig. 2b. They are limited to a few degrees whereas they are in between 40 K and 45 K with respect to the liquidus. The undercooling is highest in the portion of the samples which solidifies at first in contact with the quenching medium, then remains almost steady. At each temperature, the eutectic growth rate, V, is then determined [5] using

$$\lambda^2 V = \frac{8 D_L(T_I)\, 2\, \gamma_{\alpha\beta}}{\Delta S\, \bar{m}\, \Delta C} \qquad (2)$$

Where $D_L(T_I)$ is the interdiffusion coefficient at the interface temperature, T_I, $\overline{m}$ is the average liquidus slope, and ΔC the difference in composition between crystal phases. Parameters were taken from [6]. Growth rates range from a few millimetres per second to fraction of a millimetre per second according to the position of the eutectic in the sample as shown in Fig. 2b following the trend of the undercooling.

At the highest undercooling near the surface of the sample the eutectic grows from the melt inside the coupled zone. Recalescence causes reduction of undercooling and the growth rate must fall below the values reported in Fig. 2b. CoSi nucleates in the melt in front of the growing solid because of the higher undercooling with respect to the liquidus, very likely on heterogeneous sites giving rise to the anomalous eutectic microstructure. Then the growth rate rises again and the regular eutectic occurs re-forms. Fluctuations in growth rate follow producing bands of the two types of eutectic. In the sample interior the undercooling must be limited and growth occurs within the coupled zone. The eutectic bands found in Co-Si correspond both in terms of rate of growth and size to the low velocity bands reported in Al-Fe for a cellular dendritic transition [7]. To the best of the Author's knowledge, only one case of regular/anomalous eutectic banding has been described in the literature to date. In directional solidification of an $Al_2O_3/Y_3Al_5O_{12}/ZrO_2$ eutectic ceramic prepared by laser floating zone, the YAG phase protruded from the interface in the same way as Co_2Si did epitactically in the present alloy [8]. The change in melt composition promoted the nucleation of Al_2O_3 in front of the interface and its free growth to the size of several microns, similarly to CoSi here. The relatively fast growth of the regular eutectic induces temperature changes in the melt which bring about a gradient in surface tension. The corresponding Marangoni flow destabilizes the eutectic interface, the rate of growth decreases and the anomalous eutectic occurs.

While the regular/anomalous eutectic banding is frequent in the present samples, eutectic/primary phase bands were found at places as in the right part of Fig. 1. Fig. S1 (Supplementary Information) shows their occurrence in the arc melted ingot. The transition from a eutectic to a single phase has been frequently reported [7, 9] and modelled [10] in off-eutectic alloys. Since the leading primary phase is Co_2Si, the local composition must have been shifted to the other side of the eutectic. This is understood by considering the formation of the large CoSi crystals at the beginning of solidification which must have consumed Co enriching the melt in Si along the liquidus line. Although it can be envisaged that the growth rates in the transition zone were of the order derived above, the verification with the current model [10] cannot be performed because of the uncertainty of the starting off-eutectic composition.

An example of the microstructure of the as-spun ribbon confirms the above picture (Fig. 3). The side in contact with the quenching Cu wheel was apparently undercooled to the extent of allowing regular eutectic growth inside the coupled zone. Recalescence because of latent heat release occurred in the still molten portion of ribbon, especially when the ribbon flew away from the wheel, therefore it solidified with primary CoSi dendrites, possibly fragmented by self-heating. The melt composition shifted to high Si content causing solidification of a Co_2Si matrix with very limited amount of regular eutectic. Only a layer of anomalous eutectic separates the two zones.

At the other extreme of cooling rates employed in this work, i. e. 5 K/min in HTDSC, the solidification occurred with a primary event at the undercooling of about 15 K with respect to the liquidus and a second one at the undercooling of 115 K below the liquidus and 65 K below the eutectic (Fig. 4). No transformation was detected down to room temperature, therefore the microstructure of the sample is representative of the solidification events (inset in Fig. 4). A primary CoSi phase constituted by large dendrites or dendrite fragments possibly re-joined together, is embedded in a Co_2Si matrix with very limited amount of eutectic. Apparently a CoSi dendritic skeleton solidified at high temperature and grew in the Si-enriched quiescent melt until its composition approached that of the other compound which eventually froze quickly as indicated by the sharp endothermal peak in the HTDSC trace. The substantial solidification undercooling of Co_2Si in the presence of CoSi crystals confirms that the latter does not promote its nucleation [2].

The effect of limited convection in part of the melt spun sample and in the furnace cooled one with formation of primary CoSi and $CoSi_2$ matrix finds a counterpart in samples electromagnetically levitated with imposed static magnetic field with undercooling of 40 K and ESL samples with undercooling of 60 K [2].

In conclusion, novel banded microstructures have been found in hypoeutectic Co-61.8 at%Si rapidly solidified by either mould casting and melt spinning. It has been shown that the bands originate because of varied undercooling and growth rate in the direction of heat flow towards the copper sink which limits the convection so that diffusional effects (i. e. rejection of solute) become relevant. The role of recalescence was also highlighted for the transition in microstructure.

Acknowledgements

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Supplementary Information

The Supplementary Information section of this paper reports an example of CoSi nucleation and eutectic banding in the arc melted ingot of Co-61.8 at%Si.

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Figure captions.

Fig. 1. The cross section of a 2 mm cylinder of the Co-61.8at%Si alloy solidified by Copper Mould Casting. Starting from the external surface towards the interior a banded microstructure is apparent.

Fig. 2. a) Regular/anomalous eutectic bands in the 2 mm cylinder of the Co-61.8at%Si alloy. b) The undercooling with respect to the eutectic temperature derived from the spacing of the regular eutectic crystals (right scale), and the corresponding computed growth rates (left scale). The gray boxes indicate the alloy layers where the anomalous eutectic formed. Here, the growth rate could not be evaluated although it must be below that of the adjacent regular eutectic.

Fig. 3. The cross section of a melt spun Co-61.8at%Si sample showing regular eutectic on the wheel side and anomalous eutectic on the opposite side.

Fig. 4. HTDSC trace obtained with a Co-61.8at%Si alloy sample embedded in SiO_2 powder at the heating/cooling rate of 5 K/min under flowing Ar. The inset shows the sample microstructure.

Supplementary Information

Fig. S1. Eutectic/primary phase bands occurring in the arc melted Co-61.8at%Si ingot in addition to the more frequent regular/anomalous eutectic bands. The leading primary phase is Co_2Si. The local composition shifts to the other side of the eutectic (i. e. at% Si > 63.5) because thef large CoSi crystals being formed earlier seized amounts of Co.

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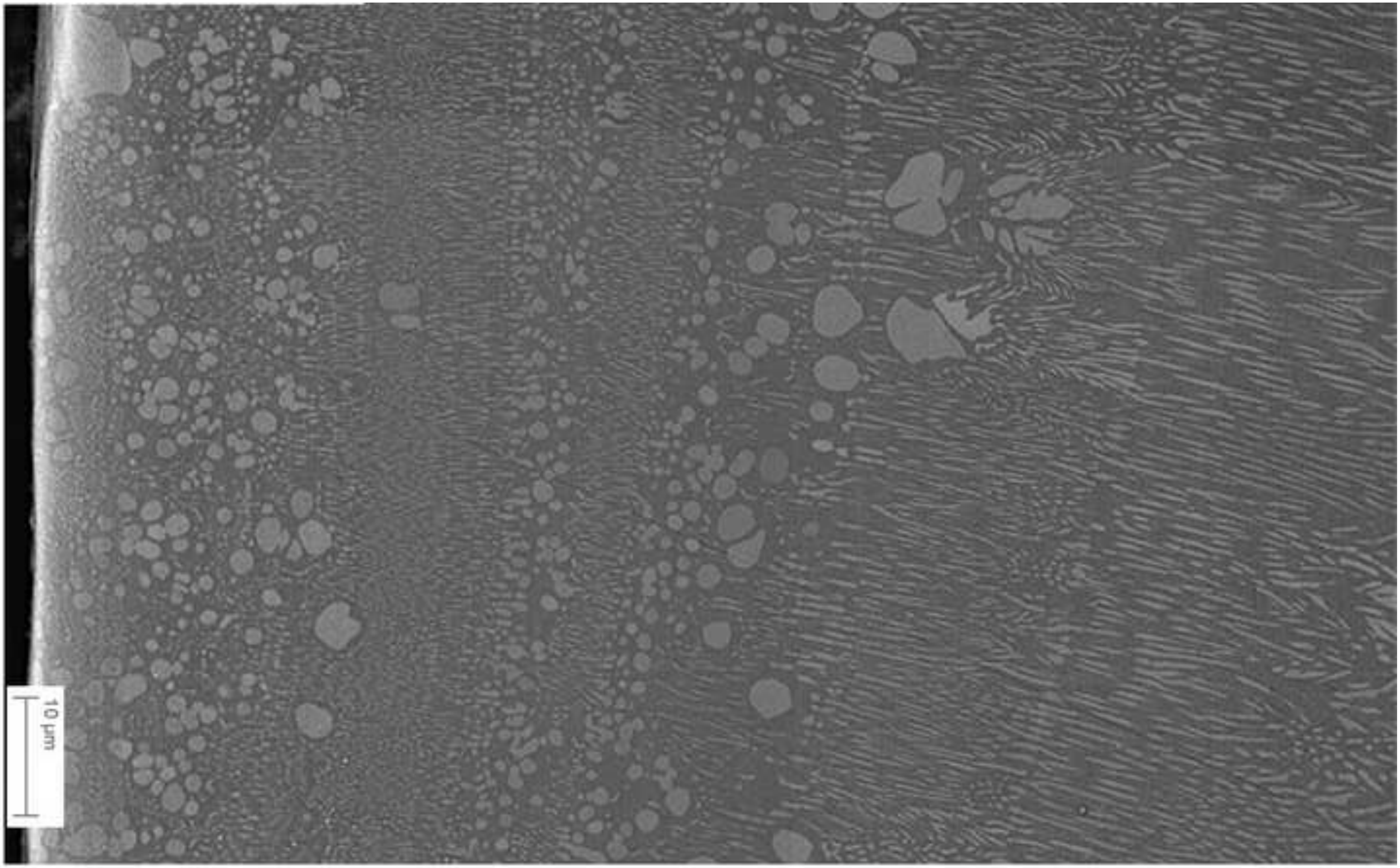

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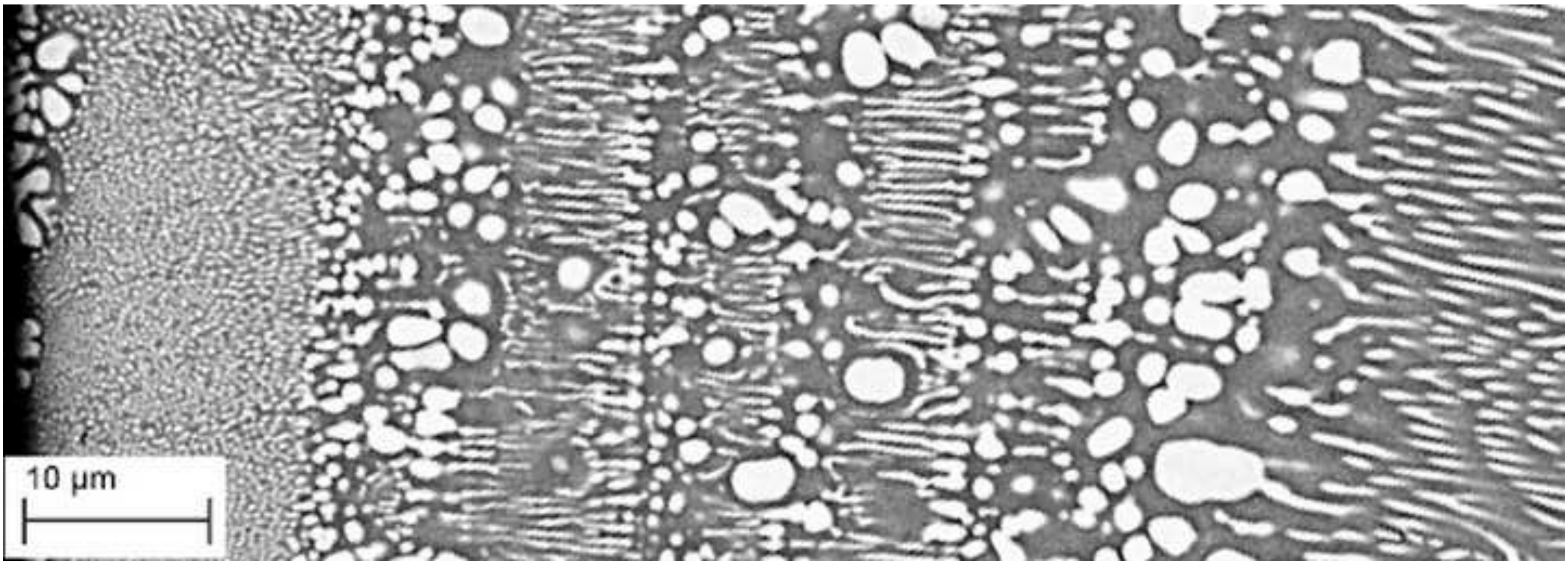

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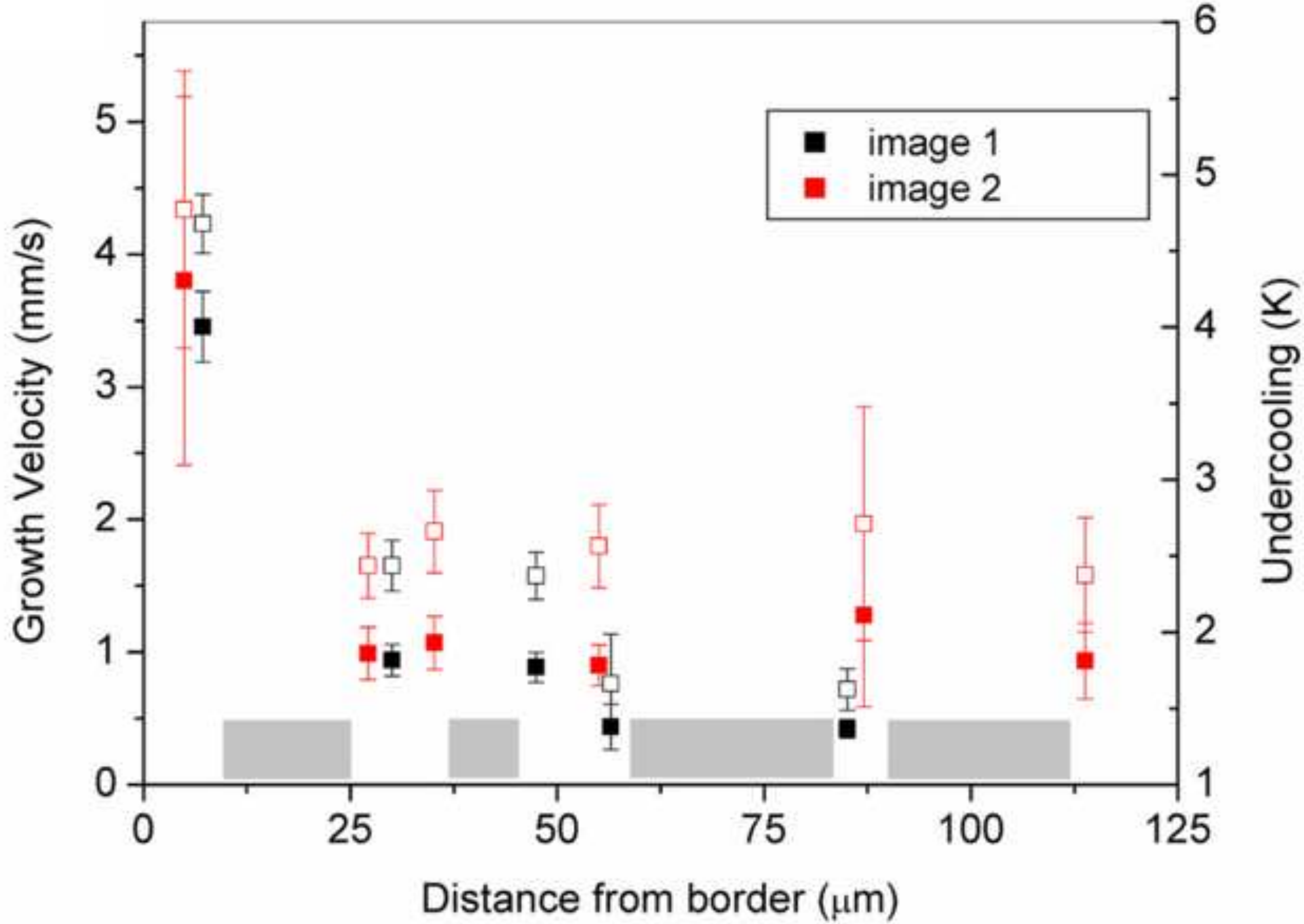

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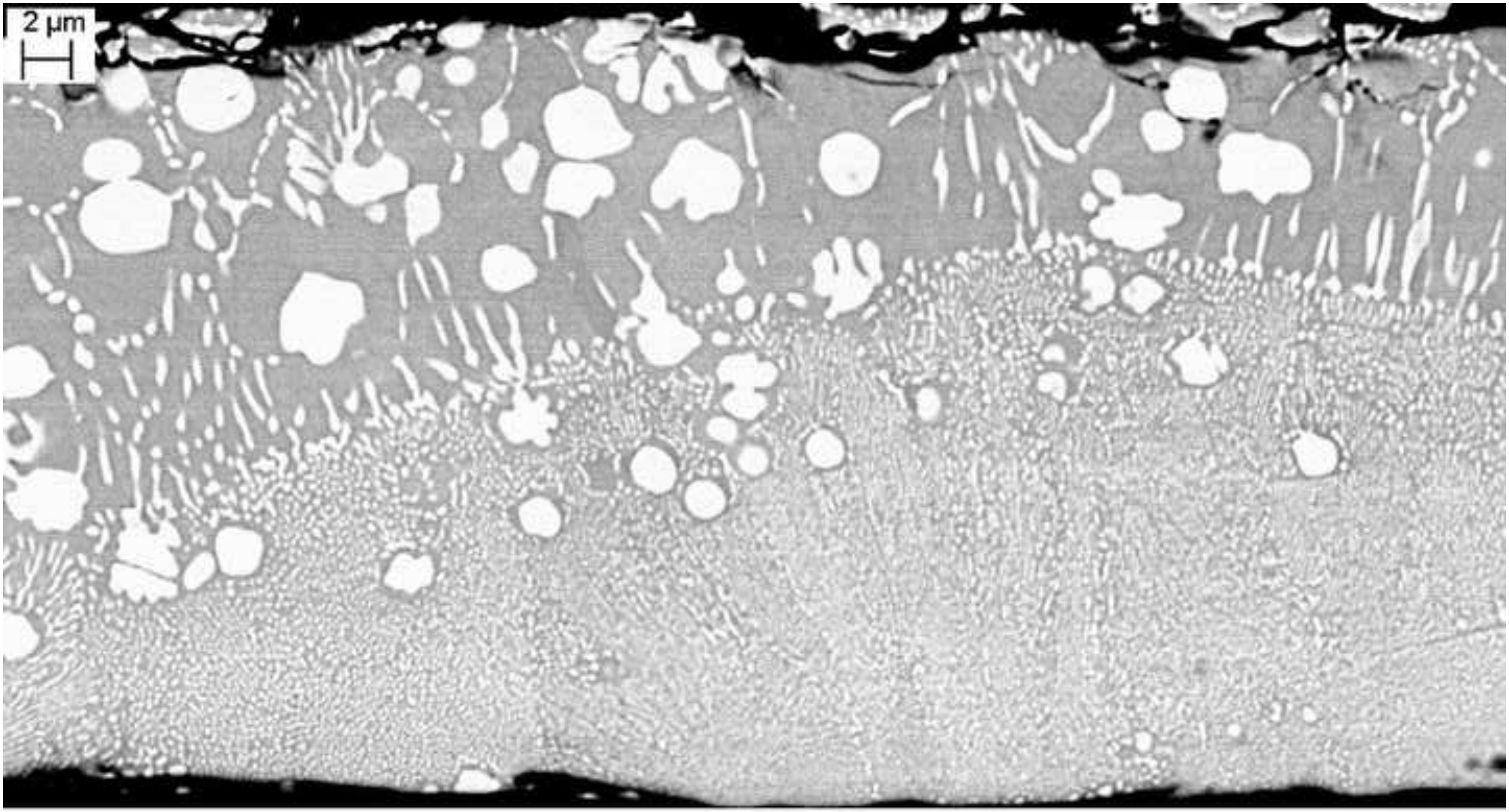

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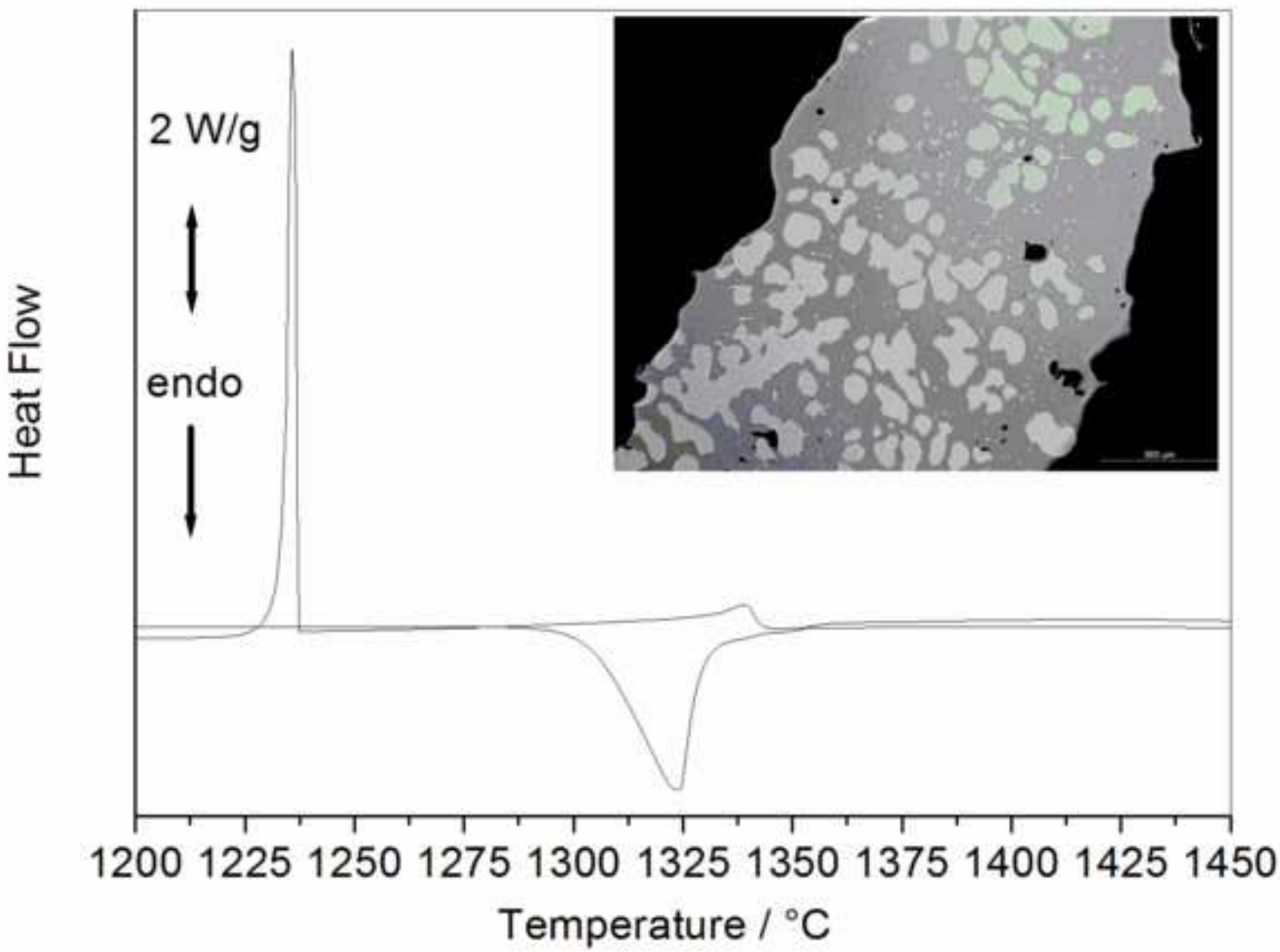

Supplementary Material

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