FRECKLES IN REMELTED NIOBIUM CONTAINING SUPERALLOYS

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Abstract

Freckle defects can be found in several niobium-containing nickel base superalloys. The freckles in VAR or ESR ingots of 718, 706, 625 and other model alloys were analyzed using Scanning Electron Microscopy (SEM) / Energy Dispersive Spectrometry (EDS) and Differential Thermal Analysis (DTA). The compositions and the transformation temperatures of the freckled areas were determined. It is found that for most of the alloys the composition and melting temperature of the freckle body usually correspond to a solidification moment when about 70% liquid has transformed into solid, though in some alloys the correspondent volume fraction was found to be higher. Freckle criterion considering the compositional effect is proposed for the evaluation of the freckle potential of alloys. Quantitative calculation results of the alloys using the criterion are presented and discussed in terms of the experimental measurements.

Introduction

Freckle has been of concern in remelted superalloy ingots as the alloys are strengthened with higher amount of niobium or titanium and large diameter ingots are demanded in the market, particularly for landbased gas turbine. Melting experiences in vacuum arc remelting (VAR) and electroslag remelting (ESR) have indicated that freckle formation is strongly influenced by melting practices, especially the stability of melt rate. On the other hand, chemical composition is also an important limiting factor in achieving large diameters of remelted ingots.

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Theoretical analysis and experimental observations using transparent analog systems have proved that freckle is formed by the hydrodynamic instability inside the mushy zone[1-4]. Tests have been carried out in different alloy systems by various solidification configurations to clarify the formation mechanism and critical conditions for freckling in metallic systems. Criteria such as Rayleigh number and the well-known Flemings' can be found in several published works[1,5-7]. Due to the complexity of the physical nature and limited understanding, the verification of the proposed criteria using experimental results is very limited. In a recent publication[8], the authors were able to compare the experimental tests on upward directional solidification of lead alloy systems to the most widely recognized freckle criteria. It was found that among the criteria suggested, Flemings' one provides the best fit to experimental data. Besides, the criterion has a very concise physical meaning: freckle forms inside the mushy zone if the interdendritic liquid moves away from the growing dendrites. The criterion, when it is expressed in the form of a Rayleigh number, is

$$Ra = \frac{\Delta \rho g \Pi}{\nu f_L R} \tag{1}$$

Where $\Delta\rho$ is the density difference, Π is permeability of the mushy zone, and f_L is the liquid fraction, g is gravitational constant, ν is the viscosity of interdendritic liquid, R is the growth speed of dendrites.

It is generally believed that freckle is initiated inside the mushy zone[1,2,9]. The final structure usually contains low melting point constituents and dendrite debris. This was demonstrated in the paper by Giamei et al.[10]. Experimental work on carbon steel ingot castings by Suzuki et al suggested that freckle flow is inside the mushy zone[9]. Freckle is formed at a solid fraction of fs=0.4 in the mushy zone in 0.7% carbon steel, even though this solid fraction can be as high as fs=0.7 if the cooling rate is slowed down[9,11]. Auburtin et al found that the composition of freckles in superalloys corresponds to the interdendritic liquid composition at fs=0.7[12]. Experiments carried out on transparent analog NH_4Cl-H_2O system support the observation results in metallic systems. Theoretical analysis by Worster also indicated that the plume flow of freckle is initiated inside mushy zone[1].

The present research analyzed the freckle samples from industrial scale ingots and specially designed model alloys, which had exaggerated compositions to facilitate freckle formation. The composition of the freckles and the transformation temperatures are measured and compared with theoretical prediction of Equation 1).

Experimental

The alloys

Compositions of the ingots obtained by wet chemical analysis are listed in Table I. The freckle in alloy 718 were produced by a special melting procedure[13]. Freckles in 625 and 706 alloys were sampled from scrapped ingot or billet with abnormal melting rate excursions. The last three in the table are experimental alloys which were solidified by horizontal directional solidification (HDS), as detailed in another paper[13]. Among the alloys, 625 was annealed and hot worked. The inhomogeneity in the base metal was completely removed before the test. The rest of the alloys are in as-solidified condition.

Table I Chemical compositions of the alloys

Alloy	Melting	Status	Ni	Cr	Fe	Nb	Mo	Ti	Al	C
718	VAR	As-cast	53.35	18.15	18.32	5.13	3.16	0.99	0.54	0.045
625	VAR	Annealed	60.11	22.09	4.40	3.53	9.10	0.29	0.26	0.02
706	ESR,VIM	As-cast	41.39	16.30	37.03	2.98	0.12	1.70	0.19	0.01
RN902	HDS	As-cast	54.43	19.95	17.76	7.13				0.014
RN903	HDS	As-cast	70.57	20.09		8.57				0.004
RN904	HDS	As-cast	74.15	20.17				5.7		0.009

Composition analysis of the freckles

The freckles in the alloys were analyzed by SEM/EDS. Different freckle areas on the longitudinal and transverse cross sections were analyzed. During the composition measurement, freckle free areas at the chill side of directional growth were used as the multi-element standards, the composition of which were calibrated to wet chemical analysis results. Pure Nb and Mo were also used for standards since the Mo and Nb L peaks are too close together for the software to correctly discern them. Samples were in the as-polished state. The SEM used was JSM JOEL6400 with Princeton Gamma Tech EDS detector. Testing conditions were accelerating voltage: 20KeV, condense lens current: 0.1nA, live time: 60 seconds, magnification was varied between 150x to 1000x to cover only the freckle body.

Transformation temperature

Freckle samples were tested by differential thermal analysis (DTA). Specimens were cut from the materials to include freckles. Since the volume of freckle in each sample varies, at least three samples were tested for each alloy to better identify the reaction peaks. For comparison, materials from the same ingot without freckles were also tested. The tests were carried out using TA DTA1600 machine. Calibration was done using pure nickel and silver before the tests. The heating and cooling rates were 20°C/min.

Results

Macrostructure of freckles

The longitudinal sections of the freckles in alloy 625 billet are shown in Figure 1. Figure 1a) shows a cross section located at mid-radius of the billet. Since the location is off the billet axis, freckles are revealed as elliptical spots in the micrograph. An enlarged photo of an individual freckle spot is also embedded in the picture. These freckles are revealed as line type defects if the longitudinal cut-up surface is located on the billet axis, such as the one shown in Figure 1b). The diameter of individual freckle line is around 1mm. Generally, it is well recognized that freckles are discrete lines following the pool profiles in three-dimension space. This distribution pattern of freckles indicates that the defect is formed by a long distance mass transport mechanism such as convection rather than diffusion. The distance between freckle lines is several times higher than dendrite spacing. If freckles were formed by diffusion, they would have about the same periodicity in space as dendrites. The uniform distribution of freckle lines in the solidification front indicates that the driving force for the defect formation is homogeneous present. But the defect formed is only heterogeneous: not the whole surface of the solidification front, but individual lines. A rationale is that something such as convective instability of fluid flow sets in and releases the driving potential from the front, and freckles are formed as a result.

All the freckles carry a common feature that the boundary on the chill side is sharper than the other side, where the heat source is located (the enlarged view in Figure 1a and Figure 1b). Segregation of heavy elements such as Nb and Mo and delta or Laves phases was found in freckles formed in 718 type alloys (Figure 2).

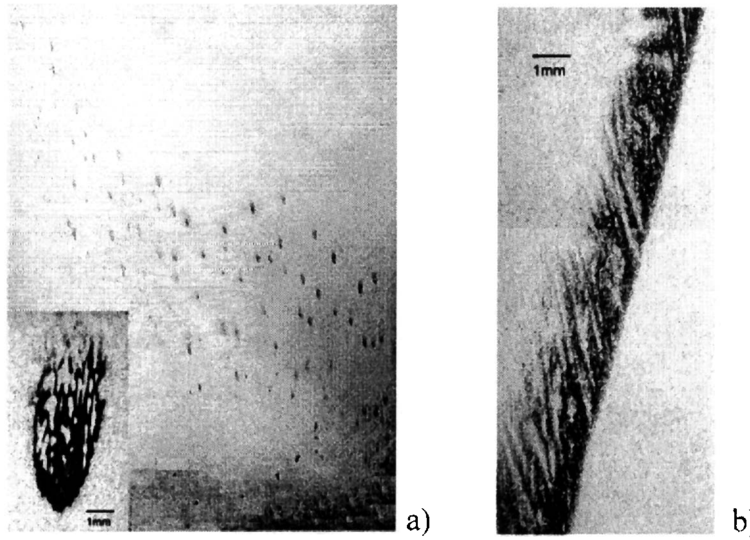


Figure 1 The optical macrostructure of freckles in alloy 625 billet after annealing and deformation. a) longitudinal section at mid radius; b) longitudinal section at billet axis

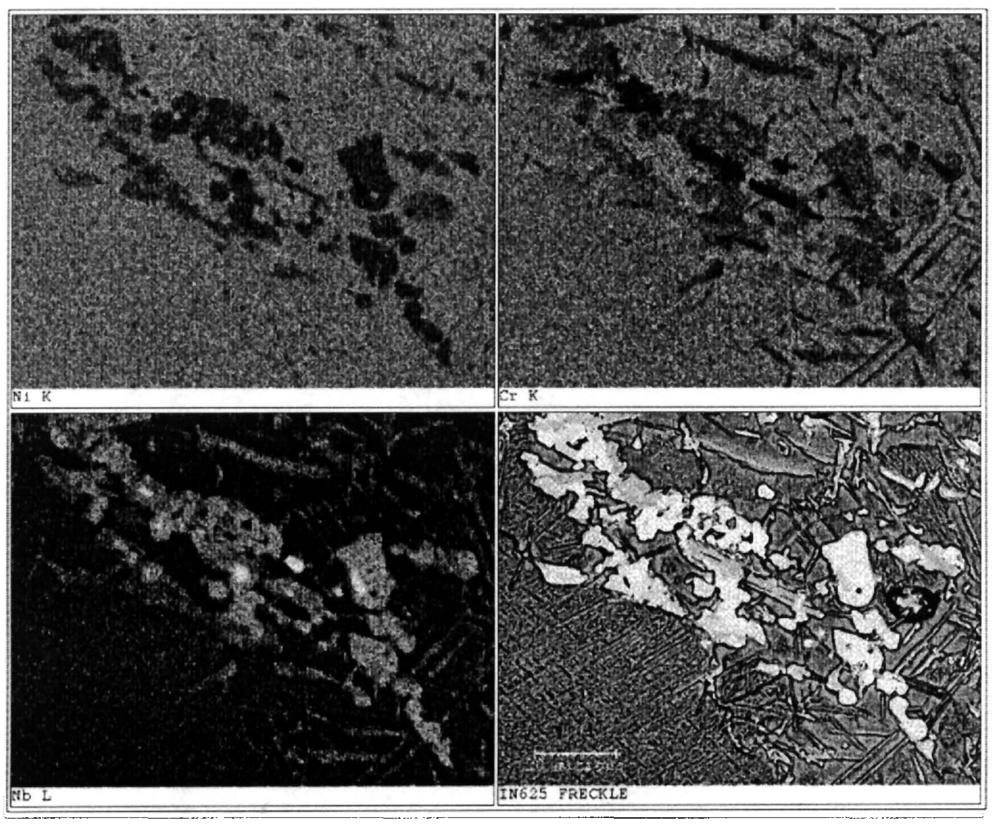


Figure 2 SEM/EDS X-ray mapping of a freckle area in alloy 625. a) upper left: X-ray map of Ni, b) upper right: X-ray map of Cr, c) lower left: X-ray map of Nb, and d) lower right: backscattered electron image. Freckle is rich in Nb and depleted in Ni and Cr. Phases present: Carbides, bright spots in c). δ-phase(Ni_3Nb), gray phase in d), which are dark in b), no contrast in a). Laves phase, bright phases in d), which are bright in c), dark in both a) and b).

Solid fraction of freckles

The results of SEM/EDS measurement of the freckle composition are shown in Table II. The results include measurements from both longitudinal and transverse cross sections. The standard deviation of the measurements at different locations is not very significant. This is quite surprising considering the deliberation in selecting analysis areas. Comparing the freckle compositions to the base alloy compositions, freckles are found enriched with Nb and/or Ti, which is expected from the strengthening element additions in the alloys.

The compositions of the freckles were compared to the profiles of the interdendritic liquid of alloys obtained by the random mapping method from solidified structure[15]. The method is illustrated in Figure 3 for alloy 625. The solid fractions obtained therefrom for all the alloys are listed in Table II. A difference in the predicted solid fractions is always observed between elements. The elements segregating to dendrite core, such as Cr and Fe, give a lower solid fraction. The elements segregated to interdendritic area give a higher fraction. The consistency among each category of elements is very good. Therefore, it is believed that the difference in predicted solid fractions is related to the melting and re-solidification nature of freckles. Considering that freckle flow results in remelting of formed dendrites, the composition of freckled area would be the mixing of dendrite core rich in Cr and Fe and the interdendritic liquid rich in Nb, Mo and Ti. Details of the mixing and the resultant composition are to be explored.

Table II Composition of freckles in industrial ingots and HDS model alloys

Alloy	*Samples*	*Element*	*Alloy*	*Freckle*	*StDev*	*Fs*
VAR625	24	Cr	22.09	21.71	0.32	0.38
		Mo	9.1	12.33	0.69	0.84
		Nb	3.53	7.29	0.31	0.84
ESR706	3	Cr	16.3	15.38	0.10	0.48
		Fe	37.03	34	0.91	0.52
		Nb	2.98	5.78	1.09	0.75
		Ti	1.7	2.73	0.29	0.80
VIM706	10	Cr	16.3	14.7	0.24	0.63
		Fe	37.03	31.44	0.69	0.72
		Nb	2.98	7.4	0.42	0.87
		Ti	1.70	3.32	0.26	>.90
VAR718	27	Cr	18.1	17.03	0.33	0.90
		Fe	18	16.02	0.41	0.87
		Mo	3.12	4.04	0.29	0.85
		Nb	5.22	9.03	0.73	>.95
		Ti	1.03	1.46	0.13	>.95
RN904	8	Cr	20.17	17.37	0.48	0.62
		Ti	5.7	8.74	0.55	0.80
RN902	6	Cr	19.95	16.83	0.70	0.53
		Fe	17.75	14.22	0.66	0.75
		Nb	7.13	14.70	1.05	>.85
RN903	6	Cr	20.09	17.54	0.08	>.85
		Nb	8.57	13.68	0.46	0.88

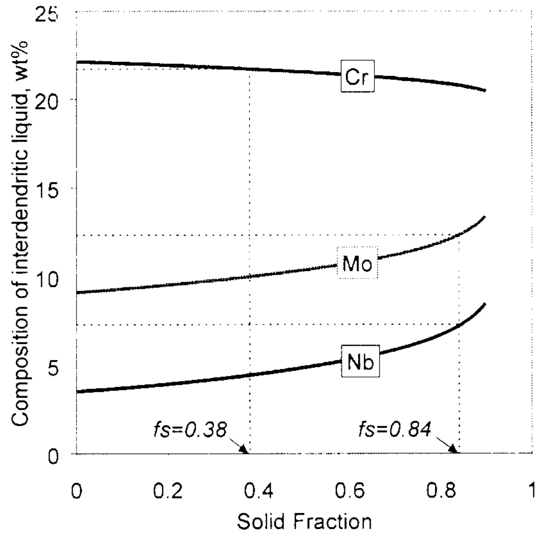


Figure 3 Determination of the correspondent solid fraction from the segregation profiles obtained by random mapping for alloy 625

Among all the alloys listed in the table, freckles in the VAR718 ingot and RN903 ingot correspond to higher solid fraction, at about fs=0.9. For the rest, fs is about 0.5~0.7 by the prediction using either the composition of Fe or Cr. The same number is predicted to be 0.8~0.9 using the composition of Nb or Ti. For the 706 ingots, freckles in the VIM ingot were located at high solid fraction, about 10% higher than in ESR ingot. This may be related to the slow cooling in VIM ingot, since slow cooling can expand the range of the solid fraction[9].

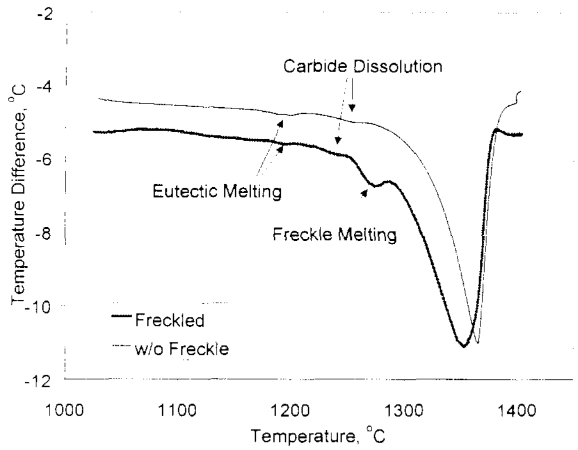
The measured fractions for different alloys increases in the order : 625 < 706 < RN902 < RN904 < RN903 < 718 if rated by the matrix elements Cr and Fe. The order is slightly different if it is sorted by Nb and Ti: RN904 < 706 < 625 < RN903 < RN902 < 718.

Transformation temperature

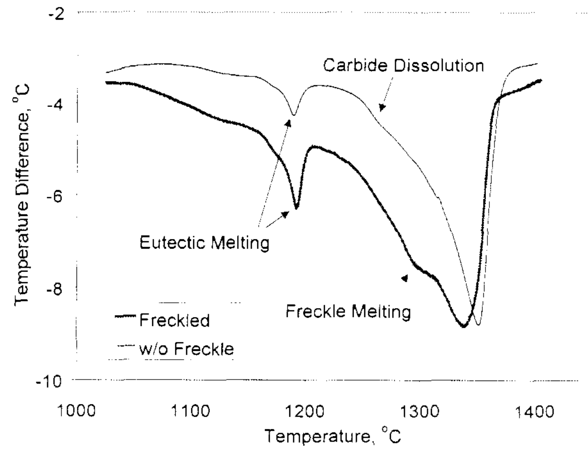
Figure 4 illustrates the DTA test results of freckled materials. The baseline DTA curves are provided by the freckle-free materials processed under the same conditions. Only the heating curves are shown in the figure because the macrostructural inhomogeneity due to freckles was present only at the heating stage but not the cooling. Several tests were repeated for the freckled specimens. They gave almost the same transformation information even though the peak heights may be different from the one presented here because the volume of freckled material in each sample may vary.

All the three alloys gave similar feature. Freckle peak is observed somewhere between alloy melting point and the eutectic temperature. This is reflected typically in the DTA curve of 625. Since the alloy was homogeneous, the peak associated freckle transformation is from the freckle body only. However, in 718 and 706, because that the structures were as-cast, the freckle transformation is partly mixed with eutectic phases formed between dendrites. Even in this case, the end of freckle body reaction can still be clearly discerned in between the eutectic point and the alloy melting point. In both alloys it can also be observed that the eutectic peaks are significantly magnified, indicating there are a lot of eutectic phases in freckles.

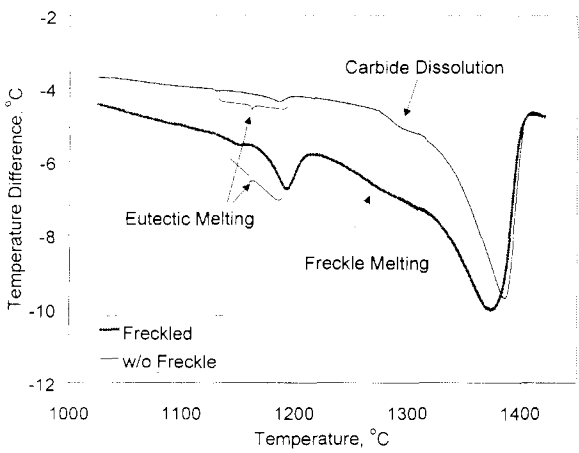
To summarize, both composition and DTA tests indicate freckle is formed at a certain solid fraction, usually at about fs=0.7~0.8. The formation temperature is about midway between the alloy melting point and eutectic point for the three industrial alloys.



a) alloy 625



b) alloy 718



c) alloy 706

Figure 4 DTA heating curves of freckled materials. The curves in higher positions in the figures are the baselines of normal freckle free materials

Discussion

Equation 1) is the freckle criterion verified by experimental data. As a simplification, when only the compositional effect of an alloy is considered, a reduced freckle criterion from Equation 1) can be obtained[15], i.e.,

$$Ra_r = \frac{\Delta\rho\Pi(f_L)}{f_L} \tag{2}$$

Where $\Delta\rho$ is the density difference, $\Pi(f_L)$ is the permeability related to the solid precipitation in the mushy zone, and f_L is the liquid fraction. The density difference is caused by the segregation of alloying elements into the interdendritic regions. This is the normalized density difference with reference to alloy density at the melting point of the alloy.

$$\Delta\rho = (\rho - \rho_0)/\rho_0 \tag{3}$$

Permeability can be obtained by the empirical relationship suggested by Poirier[16]

$$\Pi(f_L) = f_L^{\,3.34} \tag{4}$$

A computer program was written to estimate the freckle tendency of different alloy compositions according to Equation 2)~4). Segregation profiles obtained by the square mesh random sampling were used for calculation of the density and alloy melting temperature. Density calculation is done by the software "Metals", provided by the National Physics Laboratory of UK [17]. The interdendritic liquid temperature was estimated using the empirical relation in reference [15]. An integration scheme was carried out for the permeability calculation in order to consider the effect of the overall mushy zone length, as recommended in reference [8].

Figure 5 shows the calculated result. The horizontal axis is the variation of liquid fraction f_L (f_L=1-fs). It can be visualized as the depth into the mushy zone. At the mushy zone top, on the dendrite tips, the liquid fraction equals unity. Inside the solidifying mushy zone, the liquid fraction decreases. At the same time, the degree of segregation increases. For most alloys calculated, the Rayleigh number initially increases as the depth into mushy zone increases. But there are maxima in the curves, such as those shown in Figure 5. The solid fractions correspond to the maxima location follow this order : 706 < RN904 < 625 < RN902 < RN903 < 718. The order is close to the one predicted by the matrix element Cr and Fe. The peak values of the curves are located around fs=0.5 for most alloys. For alloy 718, calculated maximum appears at a solid fraction greater than fs=0.7. Comparing to the experimentally measured fs=0.5~0.7, the coincidence between the calculation and the experiment is obvious.

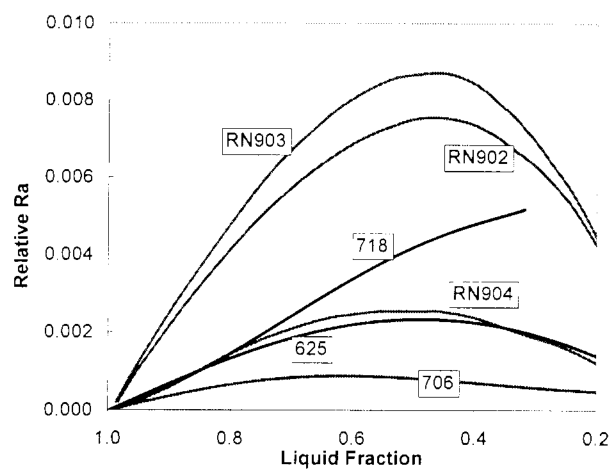


Figure 5 Calculated Rayleigh number for different alloys

The capability of the present freckle criterion to predict the occurrence of the peak values midway in the mushy zone partly proves its validity in reality, compared to some other criteria which may either predict the maxiuma at the very dendrite tip or the end of solidification[8]. In either case, it will be very difficult to explain why freckle dose not always have a composition at a fixed solid fraction. The freckle criterion in equation 1) predicts that the occurrence of maxima depends on the alloy solidification characteristics. If an alloy contains a large amount of eutectic, the maximum value will most likely be reached at the eutectic point. The resultant freckle will have the eutectic composition. For most industrial alloys, the eutectic amount is low, therefore the peak value can only be reached somewhere midway in the mushy zone.

It is worthwhile pointing out that the location where fs equals 0.5 is not deep in the mushy zone as commonly regarded or described in literature. Instead it is very close to the dendrite tip. For the industrial alloys studied, a temperature at which 50% liquid solidifies is only about 20°C from the alloy liquidus, compared to a solidification range of about 100~150C from alloy liquidus to its eutectic temperature.

Conclusions

Freckles in industrial and model alloys are analyzed by SEM/EDS and differential thermal analysis. It is found that freckle has a composition corresponding to the interdendritic liquid at solid fraction fs=0.7~0.8 for most of the alloys studied. There exists a difference in the solid fractions predicted by different alloying elements. Matrix forming elements give lower predicted solid fractions compared to interdendritically segregated species. The measured solid fraction is compared to the Rayleigh number considering only compositional effect. A fair agreement is noted between the experiment and the theory. The Rayleigh number is able to predict the occurrence of peak values in the mushy zone.

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