Effect of Zr and B on Castability of Ni-Based Superalloy IN792

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The effect of Zr and B on hot tearing susceptibility of the Ni-based superalloy IN792 during directional solidification (DS) was studied. The Zr and B concentrations in the experimental alloys ranged from 0 to ~550 ppm. The results indicate that Zr or B does not influence the castability when added individually. However, when both Zr and B are present in the alloy, high hot tearing susceptibility was found, the effect being particularly strong if Zr concentration was high. The castability results cannot be explained by simple solidification characteristics such as total freezing range (obtained from differential scanning calorimetry (DSC)) or by the amount of eutectic liquid (derived from the fraction of interdendritic γ/γ' obtained from quantitative metallography). However, the present results can be interpreted in terms of formation of continuous films of liquid at grain boundaries (GBs) during the final stages of solidification rather than enclosed pockets. Such thin films of liquid may reduce GB cohesion and promote hot tearing.

I. INTRODUCTION

CRACK formation during directional solidification (DS) of Ni-based superalloys in investment casting is a well-known problem in the casting industry. Cracking occurs at the columnar grain boundaries in the last stages of the DS process. It has been well established that the DS versions of particular high chromium superalloys such as IN792* suffer from this problem prominently.[1,2]

The most common solution for the problem of hot tearing in Ni-based superalloys is compositional modification by addition of Hf.[2,3,4] However, a number of detrimental effects were found when Hf was added: (1) Hf is a reactive element that may cause reactions with the mold and formation of brittle Hf containing inclusions; and (2) Hf lowers the incipient melting point and thus the solutionizing temperature, which limits the possibility to homogenize the alloy and to dissolve coarse γ' precipitates. Consequently, DS alloys containing Hf show little or no strength advantage at all compared with the same alloy without Hf modification in the equiaxed condition. It is of particular interest, therefore, to study the mechanism of hot tearing and to try to improve hot tearing resistance of superalloys without additions of Hf.[2,5]

According to our previous work, the castability of IN792 can be improved significantly by control of the concentration of Ti[6] or the combination of Ti and Ta.[7] However, large changes of Ti and Ta content are not acceptable in practice since these elements are major strengthening agents in Ni-based superalloys. Therefore, in order to develop new DS alloys with improved castability, other compositional modifications must be considered.

It has long been known that hot tearing is a grain boundary (GB) phenomenon. The initiation or propagation of hot cracks is usually intergranular.[8] It is also well known that minor elements such as Zr and B are termed GB elements in Ni-based superalloys since they tend to segregate at GBs during solidification.[9] The present work is therefore focused on the effect of GB elements such as Zr and B on castability of the Ni-based superalloy IN792. Individual effects of Zr and B as well as their interaction will be reported. It will be shown that the castability of DS Ni-based superalloys can be improved significantly by proper control of the concentration of such minor alloying elements.

II. EXPERIMENTAL

The IN792 master heat was cast by Doncasters Precision Castings (DPC, Bochum). Table I lists the measured compositions in weight percent. The Zr and B concentrations were set to be as low as possible (B: <10 ppm, and Zr: <50 ppm) in order to be able to dope with Zr or B in different levels in our investigation. The master heat was remelted and different amounts of Zr or B were added in a vacuum arc furnace in house.

The content of sulfur and other contaminants was found to be very low in the experimental alloys. For example, sulfur was generally less than 10 ppm and phosphorus less than 50 ppm. Castability tests were performed in ceramic molds containing an inner ceramic tube serving as a core and an outer tube serving as an outer shell. During DS, hot tears may form due to stresses arisen from the different thermal contractions of the alloy and the ceramic core. Molds that give a tubelike superalloy casting with a wall thickness of 2 mm were used in the first stage to screen a large variety of Zr or B concentrations. Based on the results obtained from these castability trials, modified ceramic molds with a thinner wall thickness of 1.5 mm were used to study the effect of Zr and B within a constrained range. Castability tests were performed by a withdrawal method. The alloys were heated to 1520 °C and kept for 2 minutes before they were poured into the preheated mold (mold temperature: 1500 °C). A withdrawal speed of 3 mm/min was applied in all tests. The castability of an alloy was evaluated by measuring a "crack ratio" obtained from evaluation of the length and width of the cracks. The crack ratio r is defined as $r = \sum_{i=1}^{n} l_i w_i / LC$, where n is the number of the cracks; l_i and

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*IN792 is a trademark of INCO Alloys International, Huntington Woods, WV.

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Table I. Composition of IN792 Master Heat Used in the Experiments, as Determined by XRF (in Weight Percent)

Cr	Co	Mo	W	Al	Ti	Ta	B	Zr	C	Ni
11.4	8.5	1.85	3.6	3.3	3.83	3.93	<0.001	<0.005	0.09	bal

w_i are the length and maximum width of a crack, respectively; L is the length of the casting tube; and C the outer circumference of the tube.

Compositions of DS castings were measured by X-ray fluorescence analysis (XRF). Differential scanning calorimetry (DSC) measurements were performed in a Netzsch* testing apparatus (model STA 409), using heating and cooling rates of 5 °C/min. The DSC specimens with masses ranging from 250 to 300 mg were cut from the DS alloys. All tests were conducted in a purged high-purity argon atmosphere using high-purity alumina crucibles. In order to monitor the phase transformation temperatures during solidification, the data obtained on cooling were used to determine the liquidus and solidus temperatures.

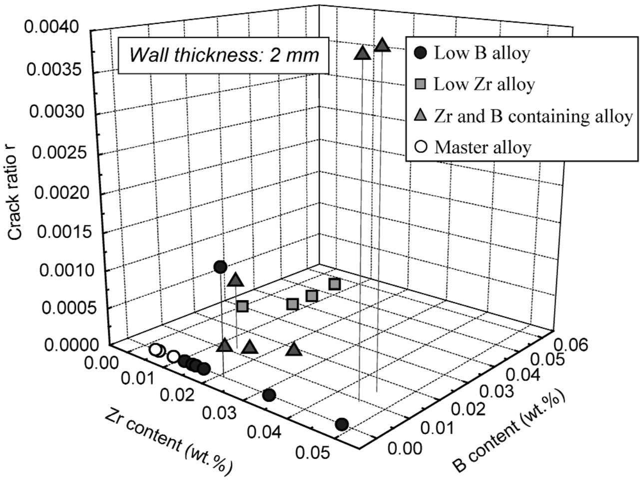
A quenched DS experiment was performed in a liquid metal cooling (LMC) furnace. IN792 specimens in the form of rods 180-mm long and 12 mm in diameter were directionally solidified into a tin bath for a length of 50 mm at a withdrawal speed of 1 mm/min. Then, the sample was rapidly quenched into the tin bath at a withdrawal speed of 120 mm/min. A pure Al_2O_3 mold was used in the quenching experiment.

Specimens for metallography were cut 60 mm from the chill end of the castability tubes. The volume fraction of coarse γ/γ' (including large γ' primary phase and the rosette microstructure generally known as γ/γ' eutectic) in interdendritic regions was determined by optical metallography in etched samples, using an image analysis system with OPTIMAS 6.2 software from (Analytical Imaging Solutions Group, Media Cybernetics, Gleichen, Germany.) Quenched DS specimens were polished and etched longitudinally (*i.e.,* parallel to the DS direction) to reveal the morphology of the mushy zone. A scanning electron microscopy (PHILIPS** XL30) was used for detailed microstructural observation.

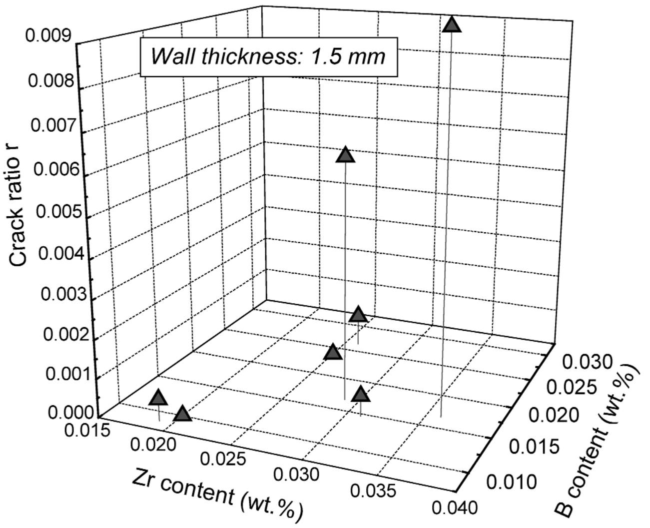
III. RESULTS

A. *Castability Tests*

Tubular samples were cast and the cross section was inspected by metallography to certify that casting cracks were located at GBs. Figures 1(a) and (b) summarize the results on hot tear formation for the various alloys from castability tests. In Figure 1(a), castability of alloys containing Zr ranging from 0 to ~500 ppm, and B ranging from 0 to ~550 ppm, have been tested by casting samples with a wall thickness of 2 mm. As shown in Figure 1(a), the master alloy without any Zr and B generally exhibits good castability. In the alloys without B content (<10 ppm), increasing Zr content does not lead to bad castability. Crack-free castings can be obtained even after increasing Zr content to 480 ppm. Similarly, without Zr content (<70 ppm), increasing B content does not result in bad castability either. Crack-free castings can be obtained when B content is as high as 560 ppm. When both Zr and B exist in the alloy at relatively low concentration, the hot tearing sensitivity of the alloy is still low. However, a further increase of Zr shows a significant detrimental effect on castability of the alloys, even when B content is kept at a relatively low level, *i.e.,* <150 ppm.



(*a*)



(*b*)

Fig. 1—Results of castability tests. (*a*) Castability tests performed by casting tube-shaped superalloy samples with a wall thickness of 2 mm. Master alloy without Zr and B and alloys containing only Zr or B individually do not crack. Severe cracking occurs when an alloy contains both B and Zr, in particular, when the Zr content is high. (*b*) Castability tests performed by casting tube-shaped superalloy samples with a wall thickness of 1.5 mm. The results are similar to (a).

Based on this information, further castability trials were performed in a narrower range of Zr and B concentrations: Zr ranging approximately from 150 to 400 ppm, and B ranging approximately from 100 to 300 ppm. Specimens with thinner wall thickness (1.5 mm) were used in these tests. The results are shown in Figure 1(b). A similar trend as discussed previously is observed. When Zr and B contents are low, the alloy is not prone to hot tearing, as expected. At medium high

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*Netzsch is a trademark of NETZSCH-Gerätebau GmbH, Selb, Germany.

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B content, increasing Zr significantly promotes the hot tearing susceptibility of the alloys. On the other hand, at medium high Zr content, increasing B only slightly increases the hot tearing sensitivity of the alloys.

B. *DSC Measurement*

A typical DSC curve during cooling is shown in Figure 2. Three major phase transformations during solidification are revealed: (1) the solidification of γ primary phase (corresponding to the liquidus), (2) carbide formation, and (3) the final formation of γ/γ' in interdendritic areas (generally known as γ/γ' eutectic in Ni-based superalloys, *i.e.,* corresponding to the solidus). Table II lists the measured Zr and B contents and the DSC temperatures in the experimental alloys. The results of Table II are plotted in Figure 3 in order to compare the effect of Zr and B.

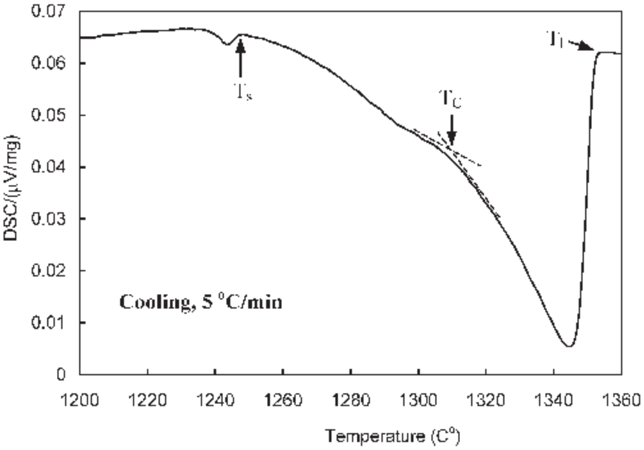


Fig. 2—Typical DSC curve of an alloy containing both B and Zr during cooling at 5 °C/min. The way liquidus temperature T_l, carbide formation temperature T_C, and solidus temperature T_s are determined is indicated in the plot.

Table II. Liquidus Temperature (T_l), Carbide Formation Temperature (T_C), and Solidus Temperature (T_s) of the Experimental Alloys, as Determined by DSC during Cooling Using a Cooling Rate of 5 °C/min (Concentrations of Zr and B Are Determined by XRF; Total Freezing Range ΔT ($\Delta T = T_l - T_s$) Is Also Listed)

Alloy	Zr Content (ppm)	B Content (ppm)	T_l (°C)	T_C (°C)	T_s (°C)	ΔT (°C)
Master	40	<10	1358	1326	*	—
Low B	110	<10	1359	1324	*	—
	130	<10	1356	1324	*	—
	160	<10	1359	1324	*	—
	210	<10	1357	1322	*	—
Low Zr	60	560	1357	1310	1230	127
	70	390	1362	1321	1238	124
	70	460	1357	1312	1234	123
Zr and B containing	120	106	1352	1316	1252	100
	140	120	1359	1316	1248	111
	160	135	1352	*	1252	100
	230	188	1352	1310	1248	104
	300	250	1349	1318	1239	110
	310	147	1352	1320	1241	111

*Temperature not detectable by DSC.

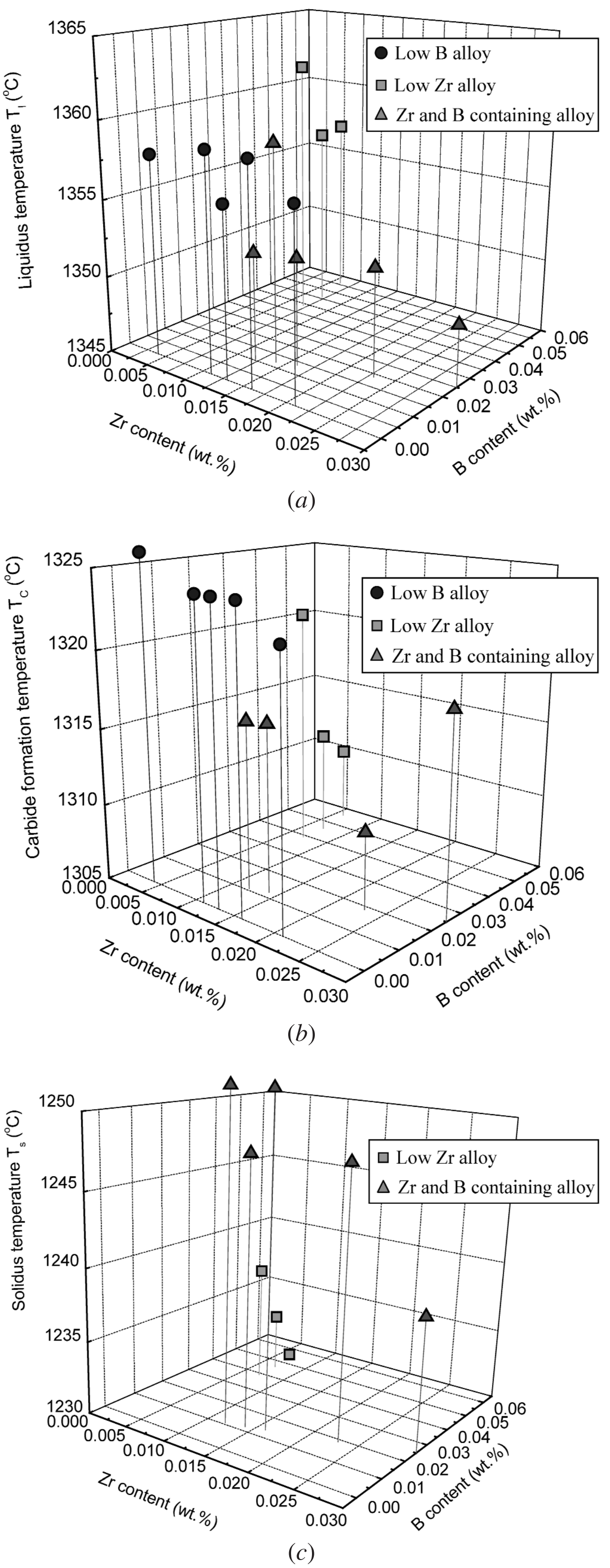


Fig. 3—Phase transformation temperatures as determined by DSC measurements (Fig. 2 for the definition of the temperatures). (*a*) Effect of Zr and B on liquidus temperature, (*b*) effect of Zr and B on carbide formation temperature, and (*c*) effect of Zr and B on solidus temperature. B is found to decrease the solidus temperature considerably.

One can see from Figure 3 that the *liquidus temperature* is not strongly influenced by varying Zr and B content in the alloys. It seems that Zr or B does not influence the liquidus temperature of the alloy individually, while Zr and B together slightly decrease the liquidus. *Carbide formation temperature* T_C is slightly decreased by increasing Zr content in alloys that do not contain any B. A relatively large decrease of T_C can be found when increasing B in an alloy that does not contain Zr. The combined influence of Zr and B on T_C also seems to be negative, *i.e.,* increasing the overall Zr and B concentration results in decreasing T_C. The most striking influence of B can be found in Figure 3(c), where the *solidus temperature* is considered. The B content significantly decreases the solidus temperature of an alloy. Moreover, this effect seems only to be correlated with B content, *i.e.,* Zr content shows hardly any influence on the solidus. In fact, no data for low B alloys are included in the figure as the peak corresponding to the formation of coarse γ/γ', the solidus, cannot be detected by DSC in such alloys.

C. *Microstructure Observation*

The volume fraction of coarse interdendritic γ/γ' was measured by quantitative metallography. The results are shown in Figure 4. It is clearly seen that B strongly promotes the formation of coarse γ/γ' at interdendritic area. On the other hand, Zr almost shows no influence.

The LMC quenching experiment reveals the morphology of the mushy zone during DS (Figure 5). The upper (hotter) portion of the mushy zone cannot be distinguished clearly due to the insufficient cooling rate during the rapid quenching. However, the residual liquid can be observed without a doubt in the lower part of the mushy zone. A continuous liquid film is found, probably following a GB. (It is hard to locate the exact position of a grain boundary in Figures 5 and 6, since the cross section of the sample was not examined.) Figure 6 shows the detailed microstructure of the film structure. Since the etchant used in the present experiments attacks only γ' phase in the alloy, one can deduce from Figure 6(b) that the film structure is composed of large γ' primary phase, γ/γ' eutectic, and probably filmlike carbides. (For a detailed discussion of the sequence of events that turns the remaining liquid in the last stages of solidification into γ/γ' eutectic, the reader is referred to Reference 4.)

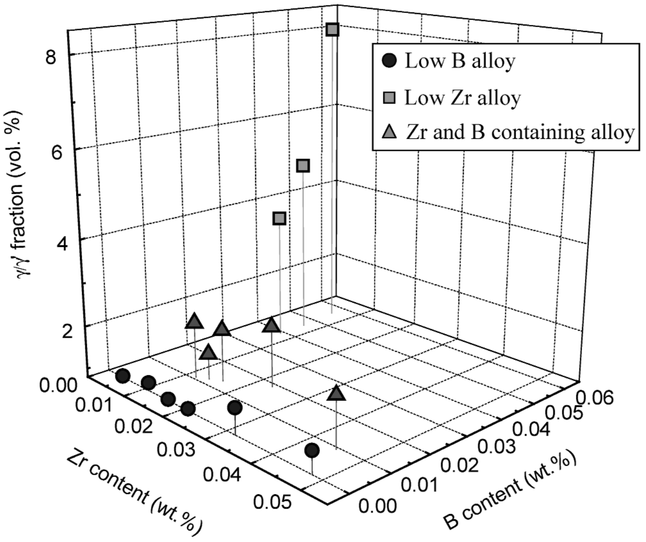


Fig. 4—Volume fraction of coarse interdendritic γ/γ' in the experimental alloys measured by quantitative metallography. The B can be observed to significantly promote the formation of the interdendritic γ/γ'. On the contrary, Zr shows little influence.

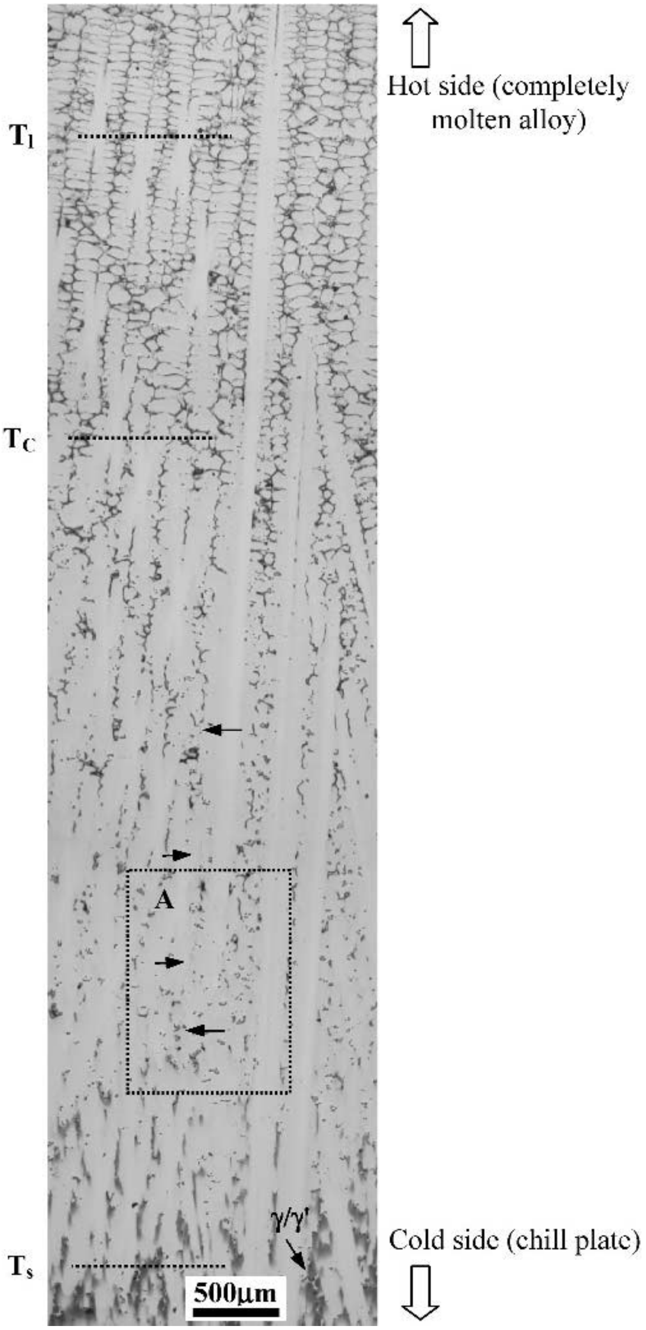
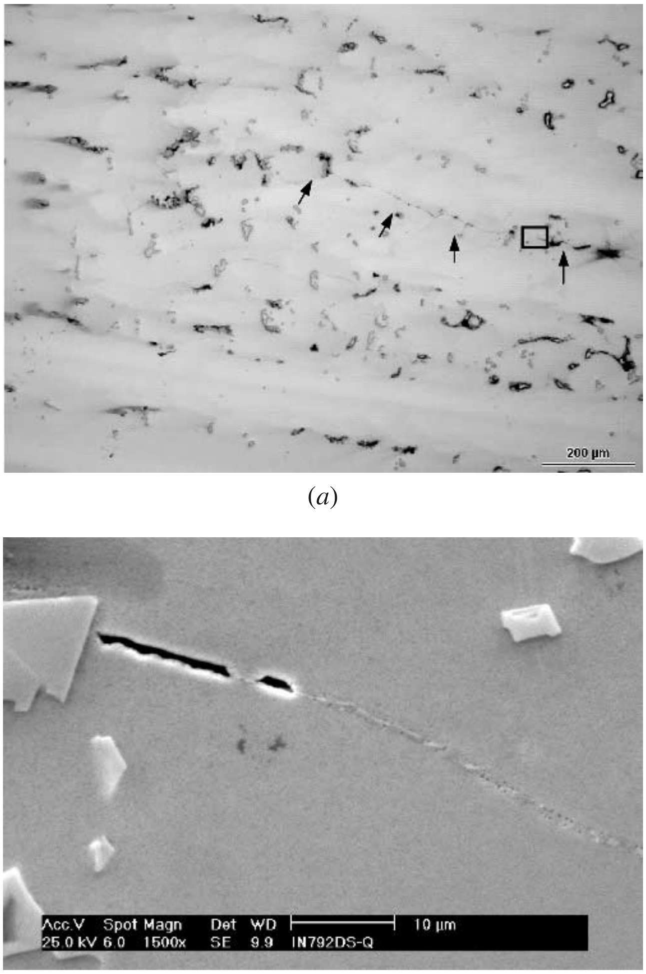


Fig. 5—Mushy zone morphology of IN792 (containing both Zr and B) obtained by the LMC quenching method. The residual liquid in interdendritic areas in the high-temperature part of the mushy zone is clearly visible due to its darker color. A continuous liquid film can be observed that extends deeply into the mushy zone toward the fully solidified side, as indicated by the arrows. According to DSC data, approximate positions of T_l, T_C, and T_s are also shown in the picture.



(*a*)

(*b*)

Fig. 6—Detailed microstructure of the film structure observed in Fig. 5. (*a*) Optical micrograph showing morphology of the film structure inside the region marked A in Fig. 5, and (*b*) SEM image of the film structure marked by the dark rectangle in (a). In the SEM, the film structure is shown to correspond to a multitude of tiny holes and grooves that are produced by the etchant used (refer to text).

IV. DISCUSSION

A. *Industrial Application*

From an industrial point of view, our results underline how important it is to carefully control the minor element content when it comes to hot tearing. Effects can be very surprising. Alloys that contain both B and Zr apparently are to be avoided, with high Zr contents being particularly harmful.

Another interesting finding is that B significantly promotes the formation of coarse γ/γ' in interdendritic areas and decreases the solidus temperature. This is not desirable in terms of heat treatment: coarse γ/γ' will be more difficult to dissolve if the volume fraction is high and if the acceptable heat treatment temperature is low.

The Zr acts as a getter element in superalloys, *i.e.,* Zr is traditionally used to reduce the detrimental effect of trace elements such as sulfur.[3,9] This particular role of Zr may not be as important in modern superalloys as it used to be in the past since the detrimental trace elements have been depressed to a very low level today.

From the preceding arguments, to decrease the B and Zr content in Ni-based superalloys seems a good suggestion. However, in order to find the optimum alloy composition for commercial application, the effect of B and Zr on the mechanical properties must be considered too.

B. *Hot Tearing Mechanism*

In terms of the mechanisms governing hot tearing, it is clear that our current experimental results do not show any simple correlation between castability and the solidification characteristics of an alloy. For instance, one cannot predict the hot tearing susceptibility by looking at the total freezing range, as listed in Table II. The amount of coarse γ/γ' (generally known as eutectic) also cannot be used as a criterion to explain the castability of an alloy. Both criteria would suggest that high B containing alloys are somewhat distinct with respect to their hot tearing susceptibility, but they are not.

In two previous articles,[4,6] we found evidence suggesting that hot tearing susceptibility might be explained by the way the volume fraction of remaining liquid changes with temperature in the final stages of solidification. A simple mathematical model showed that a strong change in the fraction of liquid results in high strains and strain rates during solidification, and this may lead to crack formation and bad castability. Within the limits of experimental resolution, there seems to be no difference in solidification behavior between the various alloying modifications investigated in the present case, *i.e.,* there must be other phenomena causing the different hot tearing susceptibility.

In another article by the present authors,[10] the effect of GB misorientation on hot tearing susceptibility was studied. High misorientations promote tearing. This cannot be explained in terms of feeding behavior, as feeding should become easier rather than more difficult. It cannot be caused by solidification effects (as previously discussed), as the composition remains the same in the experiments. We therefore attributed the effects to GB cohesion. In particular, we assumed that bridging of secondary arms is important; *i.e.,* the strength of the solidifying skeleton determines hot tear formation.

This argument shall be further refined in the following to explain the effect of minor elements studied in the present investigation. It is obvious that bridging will be affected by the way the remaining melt is distributed. Figure 7 is a schematic diagram, showing two possibilities. A situation is considered where the volume of the remaining melt is about the same. In Figure 7(a), the remaining melt is present in the form of isolated pockets, while in Figure 7(b), the melt forms a continuous liquid film. Obviously, GB cohesion will be less in the film case.

The difference in melt distribution can be brought about by differences in surface tension. It is well known that the surface tension of any solvent can be markedly reduced by the presence of relatively low levels of certain solute elements that are preferentially adsorbed at the surface or interface.[11] In the present case, one would expect a lowered surface tension of the residual liquid in Zr and B containing alloys because of the enrichment of Zr and B in the liquid. The GB therefore could be almost completely wetted (Figure 7(b)), which results in much less solid bridging and bad castability.

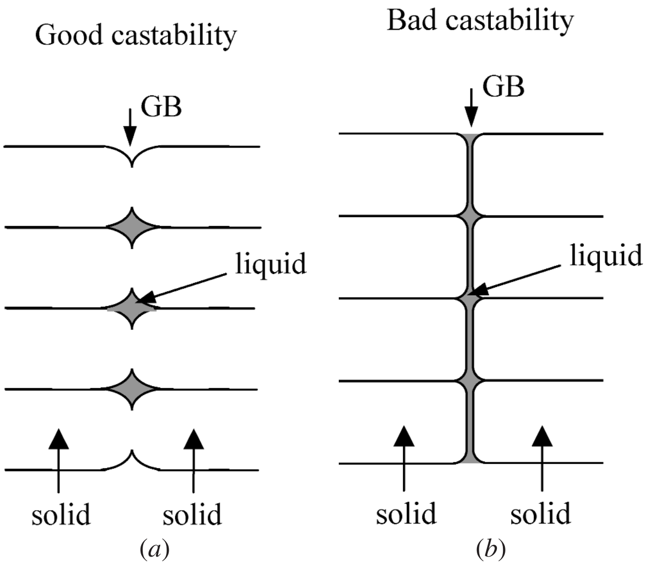


Fig. 7—Schematic illustration of the assumed effect of Zr and B on mushy zone morphology of Ni-based superalloys in the final stages of DS processing. (*a*) In alloys containing either Zr (and no B) or B (and no Zr), the residual liquid probably exists in form of isolated pockets at the GB. Therefore, bridging of secondary dendrite arms and strong boundary cohesion is favored. (*b*) In alloys containing Zr and B simultaneously, surface tension effects may cause the remaining liquid to be present as a continuous thin film. Consequently, there is no bridging of secondary dendrite arms. The hot tearing susceptibility is very high.

Unfortunately, the preceding mechanism is hard to experimentally verify. As such, our explanation for the effect of minor elements on castability must remain a hypothesis for the time being. In future work, wettability of simplified systems will be studied in order to verify the preceding mechanism.

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