INFLUENCE OF THE CHEMICAL COMPOSITION OF NICKEL-BASE SUPER- ALLOYS ON THEIR SOLIDIFICATION BEHAVIOR AND FOUNDRY PERFORMANCE

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An investigation of the solidification behavior of several nickel-base superalloys has been carried out to get a better understanding of their foundry performance.

The program was centered around vacuum melted and cast superalloys : IN 100, IN 792, IN 792 + Hf, B 1914 and B 1925. Differential thermal analysis and metallographic observations of directionally solidified and quenched samples were used for determining the solidification sequences of the alloys. The morphology of the mushy zone of each alloy was characterized by means of a texture analyser on quenched samples which were solidified in controlled thermal conditions before quenching.

Alloys were tentatively compared according to the ease with which capillary feeding of liquid can balance the solidification shrinkage during the last stages of solidification. From this view-point, the superiority of the BC alloys over the alloys containing carbon was clearly demonstrated.

Several observations on the microporosity levels in production castings were analysed in the light of this study.

INTRODUCTION

Microporosity, caused by gas or shrinkage, is a common defect in castings. Porosity formation in nickel base superalloys can be greatly affected by the casting conditions and by the chemical composition of the melt (1). This work is concerned with the potential influence of minor chemical modifications of a few nickel-base superalloys on shrinkage porosity, sometimes called microporosity because of pore size.

From empirical correlations, it is sometimes concluded that chemical modifications which tend to increase the freezing range of an alloy increase microporosity in castings (2-

4). Unfortunately, these correlations can seldom be analysed in depth from a metallurgical standpoint. Moreover it is now generally agreed that the substitution of boron for carbon in cast nickel-base superalloys offers significant improvement in castability (5) ; this fact might be in contradiction with the idea that microporosity increases with the solidification range as boron is likely to increase the solidification range of nickel-base alloys. It might be that knowledge of the solidification range is insufficient to predict foundry performance. Therefore closer investigation of the solidification behavior of several nickel-base superalloys has been carried out.

Basic considerations on the mechanisms of microporosity formation have been summarized in the next section to introduce our experimental analysis of solidification sequences which is presented in the following sections along with our main results and conclusions.

BASIC CONSIDERATIONS ON MICROPOROSITY FORMATION

Nickel-base superalloys contract on solidifying. Most of this contraction takes place when efficient feeding mechanisms are still operative : liquid and mass feeding (6). However, since these alloys solidify in a mushy manner, mass feeding stops when about 70% of the alloy is solidified (7) ; capillary (that is interdendritic and intergranular) feeding then becomes the only operative feeding mode. Microporosity formation occurs during the last stages of solidification when capillary feeding becomes insufficient. This can be formalized in terms of pressure : microporosity is thought to occur when the local liquid metal pressure, p^l , becomes smaller than a critical pressure, p^* , because of solidification shrinkage and sometimes segregation of gaseous solutes. In the following, p^* will be assumed a constant close to zero.

The local pressure, p^l , is the sum of three terms :

$$p^l = p_o + p_m - \Delta P \quad |1|$$

where p_o and p_m are the external and the metallostatic pressures respectively and where ΔP is the pressure drop associated with the liquid metal flow through the mushy zone. As solidification proceeds, ΔP continuously increases and the local pressure p^l may eventually become negative. In the following, microporosity formation will then be discussed in terms of a pressure drop ΔP .

It has been proposed to calculate the pressure drop in the mushy zone during solidification with the help of fluid flow calculations already available for porous media where Darcy's law applies (8,9), i.e. where the local gradient of pressure drop is proportional to the local flow velocity $\vec{v}$:

$$\text{grad}(\Delta P) = \frac{\mu}{k} \vec{v} \quad |2|$$

where $\vec{v}$ is the effective mean flow velocity, μ the viscosity of the liquid and k the permeability of the porous medium. Since nickel-base superalloys have similar chemical compositions and liquidus temperature, viscosity is thought not to vary by a large amount and is assumed constant.

The permeability, k , of a porous medium strongly depends on its internal structure (10). For our purpose, it is sufficient to consider that k is proportional to f_l^3/σ^2 , where f_l is the volume fraction of liquid and σ the specific area of liquid/solid interface (area of the interface per unit volume of mushy zone).

Considering situations where the metal temperature is practically homogeneous at any time during freezing is a good starting point for the study of the casting of mushy freezing alloys. In this case, the flow velocity is proportional to the rate of formation of the solid and to the solidification shrinkage β . Therefore, in castings with zero temperature gradients and for a fixed rate of formation of solid, the local gradient of pressure drop during solidification is expected to depend only of f_l , σ and β :

$$|\text{grad}(\Delta P)| = A \cdot \beta \cdot \frac{1}{f_l^3/\sigma^2} \quad |3|$$

where A is a constant of proportionality.

This result suggests that it is possible to relate the susceptibility to microporosity formation of cast alloys and morphological features of their mushy zone during freezing. The present study is an attempt to characterize quantitatively the morphology of the mushy zone of a few nickel-base superalloys in order to understand their foundry performance.

EXPERIMENTAL

This paper is centered around five vacuum-melted and cast superalloys : two conventional alloys IN 100 and IN 792,

their BC versions B 1914 and B 1925, and a modified version of the alloy IN 792 containing hafnium. Chemical compositions of the alloys are given in Table 1.

Differential thermal analysis (D.T.A.) and metallographic observations of directionally solidified and quenched samples (D.S.Q.) were used for determining the solidification sequences of each alloy. D.T.A. was performed in a SETARAM 2000 K thermal analysis system on small samples (≈ 0.5 g) with heating and cooling rates ranging between 2 and 35 K mn^{-1} . Temperatures were measured during heating and cooling, plotted versus heating and cooling rate respectively, and extrapolated to zero rate. The extrapolated values only will be reported here.

Directional solidification of 250 mm long rods was performed in a conventional vertical apparatus with a static induction coil under controlled thermal conditions as shown in Table 2. Controlled solidification was achieved for a distance of about 10 cm. The power was then turned off and the specimen was dropped through the hot zone and quenched in a water-cooled box. Temperature profile in the metal was known by recording the temperature versus time curve of a thermocouple moving with the solid with respect to the mushy zone.

After solidification, a longitudinal section containing the quenched mushy zone was taken and mounted first to identify the various phases precipitating from the melt and to determine the temperature at which they precipitate. Transverse sections of the mushy zone were then taken at known distances from the liquidus zone to carry out morphological studies. Examples of such sections are shown in Fig. 1.

Table 1 - Chemical analyses (wt %)

Alloy	Co	W	V	Mo	Cr	B	C	Ta	Hf	Ti	Al	Zr
IN100	14.9	-	1.02	3.1	10.1	0.01	0.18	-	-	4.57	5.53	0.05
B 1914	9.8	0.2	0.05	3.0	9.8	0.09	0.02	-	-	5.30	5.50	0.03
IN792	8.7	4.05	-	1.85	11.8	-	0.10	3.5	-	3.95	3.6	-
B 1925	8.5	4.50	-	1.80	12.0	0.10	0.02	4.0	-	4.00	3.5	-
IN792 + Hf	8.8	4.00	-	1.80	12.5	0.01	0.13	3.5	0.8	4.00	3.6	0.12

Table 2 - Thermal conditions for directional solidification

Alloy :	IN100	B 1914	IN792	B 1925	IN792 + Hf
V (cm h^{-1}):	12	12	6	6	6
G (K cm^{-1}):	45	45	27	29	32

Fig. 1 - Micrograph montage of a B 1925 directionally solidified specimen after quenching. Left : longitudinal section : right : transverse sections.

Specific area of quenched liquid, S_a , (area of quenched liquid over total area of the section) and specific length of liquid/solid interface, L_a , (length of liquid/solid interface over total area of the section) were measured by means of a texture analyser (11). Morphological studies were carried out directly on properly etched metallographic sections for alloys IN 100 and B 1914 ; the same analysis was carried out on touched-up micrographs for alloys IN 792 (with and without hafnium) and B 1925. Although interdendritic liquid channels had complex shapes, they were extremely elongated due to the fact that the structure was columnar. Therefore, S_a and L_a have been

assumed to be reasonable estimates for r^1 and σ respectively.

SOLIDIFICATION SEQUENCES

Results of both differential thermal analysis and micrographic observation of directionally solidified samples are reported in Fig. 2 : temperature at which phases precipitate from the melt during slow cooling, nature of the solid phases in a given temperature range, nature of the reactions of precipitation from the melt. Related to the aim of this paper, the main points are the following :

- In carbon alloys, IN 100, IN 792 and IN 792 + Hf, primary carbides precipitate near the liquidus temperature whereas precipitation of γ' phase completes the solidification.
- In boron alloys, B 1914 and B 1925, solidification is completed by primary borides precipitation several tens of degrees below the precipitation of the γ' phase.

Our D.T.A. results on alloys IN 100 and B 1914 are in good agreement with previous published data as far as freezing range is concerned (12). There appears to be a difference of about -20 K between our results on absolute values of temperature and those published by Burton (12) due perhaps to a different experimental set-up. Nonetheless melting of samples of high purity nickel was always observed at 1453°C in our apparatus.

Fig. 2 - Solidification sequences

Fig. 3 - Results of the morphological analysis on transverse sections. Top : S_a , the estimate for f^1 ; middle : L_a , the estimate for σ ; bottom : (S_a^3/L_a^2) , the estimate for the permeability of the mushy zone.

STRUCTURE OF THE MUSHY ZONE

Results for IN 100 family and IN 792 family are reported separately on Fig. 3 since they correspond to slightly different thermal conditions during solidification.

In the upper part of Figure 3, specific area of quenched liquid in transverse sections, S_a , is plotted against $(T_L - T)$, where T_L is the liquidus temperature and T the temperature of the section just before quenching ; the quantity S_a is our estimate for f_L^1 , the volume fraction of liquid. The most important effect of the chemical modifications is related to the starting of the solidification : 75% of the solid forms within a range of about 15-20 K below the liquidus temperature in the case of carbon containing alloys ; the same solid fraction forms within a two times larger temperature range for boron containing alloys. Addition of hafnium slows down the formation of solid on freezing, like substitution of boron for carbon.

In the middle part of Figure 3, specific length of liquid/solid interface in transverse sections, L_a , is plotted against $(T_L - T)$; the quantity L_a is our estimate for σ , the specific area of liquid/solid interface. Different scales have been used since structures of IN 100 grown at higher solidification rates are finer than those of IN 792 grown at lower rates.

In the lower part of Figure 3, the product (S_a^3/L_a^2) is plotted against $(T_L - T)$. This quantity is our estimate for the product (f_L^3/σ^2) which is proportional to the permeability of the mushy zone ; the constant of proportionality is of the order of one half. During freezing, this quantity is observed to decrease continuously from infinity to more or less small values at the end of solidification. The following conclusions can be drawn from Fig. 3 : the values of the permeability of the mushy zone of the alloys containing boron are markedly higher than that of the related carbon containing alloys. Adding hafnium to IN 792 also definitely increases the permeability.

DISCUSSION

Evaluation by investment casting foundries has confirmed that the BC alloys, especially B 1924 and B 1925, show low microporosity levels (13). A comparison between the respective foundry performances of IN 792 (without Hf) and B 1925 has already been published (5) ; the results obtained on metallographic examination are reported in Fig. 4. On the other hand,

Fig. 4 - Comparison of the microporosity levels found in the aerofoil section of blades cast in B 1925 and IN 792 Mod 5A (after Durber (5)).

basic studies on directionally solidified samples and flat rectangular or wedge shaped castings definitely showed that B 1914 castings contain always a much lower microporosity level than IN 100 (14). These results cannot be explained in terms of freezing range since 0.1% boron significantly affects the freezing range of nickel-base superalloys, but in a manner opposed to that favorable for improvement of castability. On the contrary, the concept of permeability of the mushy zone is useful in understanding these foundry performances as shown below.

It has been concluded from basic fluid flow considerations that susceptibility of an alloy to form microporosity in a casting increases with decreasing permeability of the mushy zone during freezing. It has been shown that it is possible to estimate permeability as a function of measurable morphological quantities on columnar structures. It has been found that small chemical modifications can markedly change this permeability for nickel-base superalloys. Substitution of boron for carbon causes remarkable increases of the permeability ; this modification is thus expected to considerably improve castability although it causes a large increase of the freezing range of the alloy. Results from investment casting foundries agree with this conclusion. More surprisingly, it was found that adding 1% hafnium to IN 792 also increased permeability and therefore was expected to improve castability. In fact, some early Martin Metals work on MAR-M-004 concluded that hafnium additions might reduce microshrinkage in IN 713 LC castings (15) ; the result of the present study on the influence of adding hafnium on the permeability of the mushy zone of IN 792 might have some

connection with earlier Martin Metals findings.

It is concluded that it is possible and useful to relate the intrinsic susceptibility of an alloy to form microporosity in castings and the estimate of the permeability of the mushy zone of the freezing alloy under standard thermal conditions.

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