Research Regarding the Formation of Micropores in a Ni-Ti-C Alloy During Directional Solidification under Vacuum

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The aim of this experiment was to study the origin and formation of microporosities in a Ni-5 % Ti-0.2 % C alloy which has been solidified and quenched, and to compare it to the previously developed mathematical model. In the selected alloy, the porosity may result from gases formed during solidification (for example by chemical reaction). The results show that solidification conditions influence microporosity formation through the fraction eutectic and this suggests that it is possible to relate susceptibility to microporosity formation to the fraction eutectic. The results also confirm that for solid solution alloys such as Ni-5 % Ti-0.2 % C, the fraction eutectic increases when the ratio G/R decreases.

Untersuchung der Bildung der Mikroporosität bei einer Ni-Ti-C - Legierung bei im Vakuum gerichteter Erstarrung. *Die Untersuchung wurde an einer Legierung Ni-5 % Ti-0,2 % C bei gerichteter Erstarrung vorgenommen. Dabei gelangte eine Erstarrungstechnik zur Anwendung, bei welcher eine Abschreckung zur Darstellung des Erstarrungsverlaufs vorgenommen wurde. Das Ziel der Untersuchung war das Studium des Verfahrens der Entstehung der Mikroporosität, um deren Ursache präzisieren und die hierfür entwickelten mathematischen Modelle verifizieren zu können. Für die untersuchte Legierung ist die Herkunft der Mikroporosität dem Gas zuzuschreiben, das sich beispielsweise bei der Erstarrung durch den Ablauf der chemischen Reaktionen bildet. Es könnte festgestellt werden, daß die Erstarrungsbedingungen für die Porositätsbildung mittels der eutektischen Fraktion von maßgeblicher Auswirkung sind. Tatsächlich ist die eutektische Fraktion ein empfindlicher Parameter für die Kennzeichnung der Neigung zur Porenbildung. Es ließ sich verifizieren, daß bei den Legierungen des Typs der festen Lösung, wie z.B. Ni-5 % Ti-0,2 % C, die eutektische Fraktion mit der Reduktion des Verhältnisses G/R zunimmt.*

Etude de la formation de microporosités dans l'alliage Ni-Ti-C en solidification dirigée sous vide. *Nous avons étudié l'alliage Ni-5 %Ti-0,2 % C en solidification dirigée. Nous avons utilisé la technique de la solidification suivie d'une trempe afin de figer la structure ce qui permet de suivre l'évolution de la solidification. Le but de ce travail est l'étude du processus de formation des microporosités afin d'en préciser l'origine et de vérifier les modèles mathématiques que nous avons développés. Pour l'alliage étudié, l'origine des microporosités est imputable au gaz se formant au cours de la solidification par des réactions chimiques par exemple. Nous avons montré que les conditions de solidification ont un effet marquant sur la formation des porosités par le biais de la fraction eutectique. En effet, la fraction eutectique est un paramètre sensible pour caractériser la propension à la formation de pores. Nous avons également vérifié que pour les alliages du type solution solide tels que le Ni-5 %Ti-0,2 % C la fraction eutectique augmente avec la réduction du rapport G/R.*

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Studie van de vorming van microporositeiten in legering Ni-Ti-C bij gerichte stolling onder vacuum. *Legering Ni-5 % Ti-0,2 % C werd onderzocht bij gerichte stolling. We hebben een stolling uitgevoerd, gevolgd door een afschrikking om de structuur te blokkeren, zodat de evolutie van de stolling kan gevolgd worden. Doel van dit werk is de studie van het vormingsproces van de microporositeiten, om de oorsprong ervan te bepalen en de door ons opgestelde wiskundige modellen te onderzoeken. In het geval van de bestudeerde legering kan de vorming van microporositeiten geweten worden aan het ontwikkelen van gas tijdens het stollen, b.v. door chemische reacties. We hebben getoond dat de stollingsvoorwaarden een grote invloed hebben op de vorming van microporositeiten, d.m.v. de eutectische fractie. Deze eutectische fractie is een gevoelige parameter ter kenschetsing van de neiging tot de porievorming. We hebben ook bevestigd dat, in legeringen met vaste oplossing als Ni-5 % Ti-0,2 % C, de eutectische fractie toeneemt wanneer de verhouding G/R afneemt.*

INTRODUCTION

The aim of this research is to study the origin and the mechanism of micropore formation using directional solidification under vacuum of a solid-solute Ni-Ti-C alloy. Some previously developed theoretical formulae [13] are also verified and are set forth in the appendix. Specimens were obtained by quenching during directional solidification in order to follow the solidification process. Microporosities are known to be extremely detrimental to the mechanical properties of these alloys. The further purpose of the study is to determine which factors related to the solidification process affect the occurrence of these defects. The thermal parameter considered in this analysis is the solidification rate.

EXPERIMENTAL ALLOY

We have studied the behaviour of the Ni-5 % Ti-0.2 % C alloy which composition may be considered as being the basis of numerous superalloys including IN 100 grades. Owing to its chemical simplicity, this ternary alloy allows easier interpretation of the results. Figure 1 illustrates the nickel-rich corner of the Ni-Ti-C ternary diagram : there are two ternary eutectics, one at a temperature of 1,270° C, the other at a temperature of 1,295° C.

In the state of equilibrium, the alloy is a solid solution, but in the practical solidification conditions the non equilibrium ternary eutectic occurs.
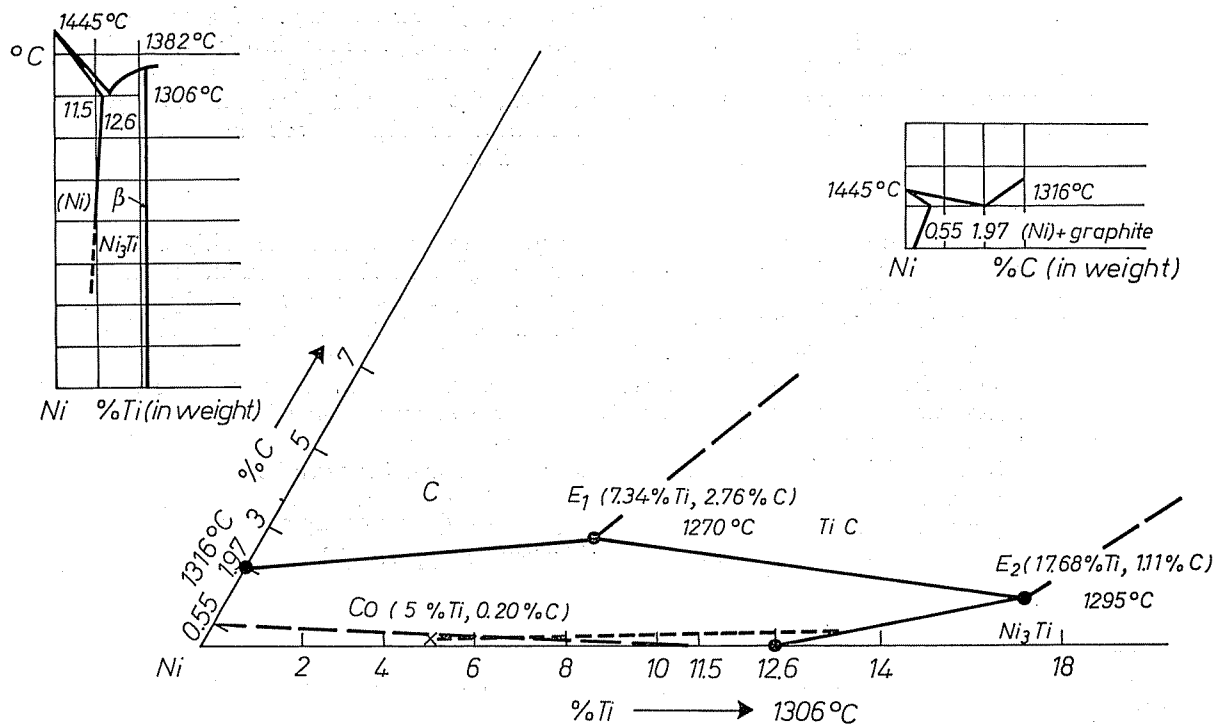

FIG. 1. Ternary diagram Ni-Ti-C [4] [5].

PREPARATION OF THE SPECIMENS

The alloy was prepared in an induction furnace. We took specimens 10 cm in diameter and 110 cm in length. The apparatus specially devised for this study is shown in Figure 2. This apparatus is placed in a chamber under vacuum in which fusion, directional solidification and helium quenching are carried out successively. Figure 3 illustrates the process of solidification which can be established by this method.

SOLIDIFICATION CONDITIONS

Several specimens were made under different solidification conditions. In each case, we determined the speed of solidification and the mean temperature gradient. The speed of solidification is taken as the quotient obtained when the total length of the entirely solidified zone is divided by the time during which the solidification occurred. The temperature gradient is calculated as the quotient of the solidification range by the length of the mushy zone.
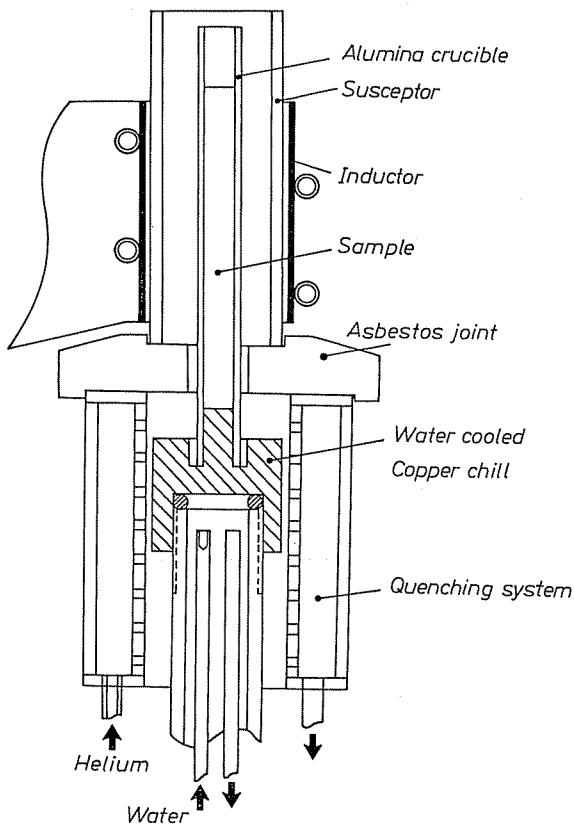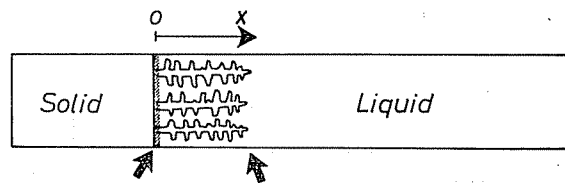

FIG. 2. Apparatus for the directional solidification.

Mushy zone (length: L)

Bottom of dendrites where solidification is complete = end of solidification.

Top of dendrites where solidification begins and from which solidification advances = solidification beginning.

FIG. 3. Process of solidification.

The solidification range was measured by differential thermal analysis. The curve that was obtained is shown in Figure 4. Table 1 gives the temperatures of the transformation points obtained during heating. We have selected five specimens of which the solidification conditions are given in Table II.

METALLOGRAPHIC EXAMINATIONS

We made longitudinal and transverse sections of the specimens.

In accordance with eutectic morphology we observed the solidifications in the transverse sections. In the zone that is wholly liquid before quenching, the eutectic presents very fine irregular particles that are scattered in a homogeneous way. In the mushy zone, the eutectic is larger and more and more oriented as solidification continues. In the zone that is entirely solid before quenching, the eutectic becomes finer and is well oriented in the direction of solidification. Figure 5 illustrates these different zones of which the lengths are shown in Table II, and Figure 6 shows the macrographs of two specimens.

The transverse and longitudinal sections were subjected to quantitative metallographic examinations in order to measure the dimensions, quantity and distribution of the micropores and of the eutectic.

EXPERIMENTAL RESULTS

(a) *Fraction liquid and eutectic.*

The measurement of the fraction liquid on the longitudinal section in the mushy zone is not easy, because the interdendritic liquid after quenching contains a large quantity of solid solution which looks like dendrites. But at the end of the solidification the interdendritic liquid is greatly enriched in alloy elements, and after quenching it is almost entirely transformed into non-equilibrium eutectic. This enables us to compare the non-equilibrium

TABLE I. Transformation points obtained by heating.

Transformation points	Notations	Specimens No.			Mean values
		001	002	003	
Ni-Ni$_3$Ti-TiC : ternary eutectic ± 5° C in non-equilibrium conditions	TE3	1,305	1,295	1,304	1,301
	TE2	1,334	1,327	1,319	1,330
Liquidus ± 5° C	TLH	1,395	1,383	1,383	1,387

Note. — Metallographic examinations carried out on the specimens after differential thermal analysis (therefore close to equilibrium) show that a solid solution is obtained.

For this reason, in order to obtain the non-equilibrium transformation temperatures we considered the transformation points, obtained during heating, on a specimen taken from a bar solidified in the usual way (and therefore not homogenized).

TABLE II. Conditions of solidification of some specimens.

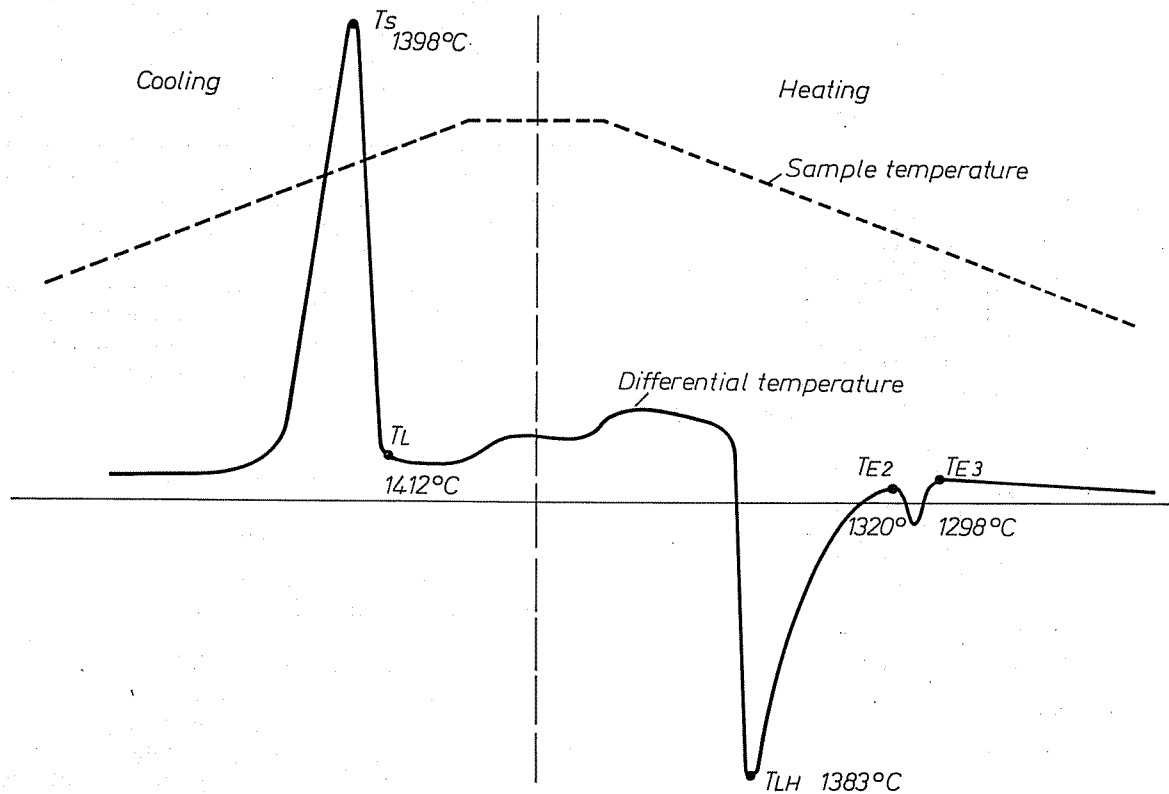| Number of the sample	Solidification range	Length of entirely solid zone (cm)	Length of the mushy zone (cm)	Speed of solidification R (cm/s)	Temperature gradient G (°C/cm)	Vacuum	G/R
05		2.928	1.072	0.00856	80.22		9.3 × 10³
06		1.586	0.544	0.00294	155.23		5.28 × 10⁴
10	86°	1.376	0.814	0.00036	105.65	1.33 Pa	2.93 × 10⁵
12		1.311	0.782	0.00437	109.97		2.54 × 10⁴
13		1.452	1.021	0.00487	84.23		1.74 × 10⁴

FIG. 4. Differential thermal analysis diagram.
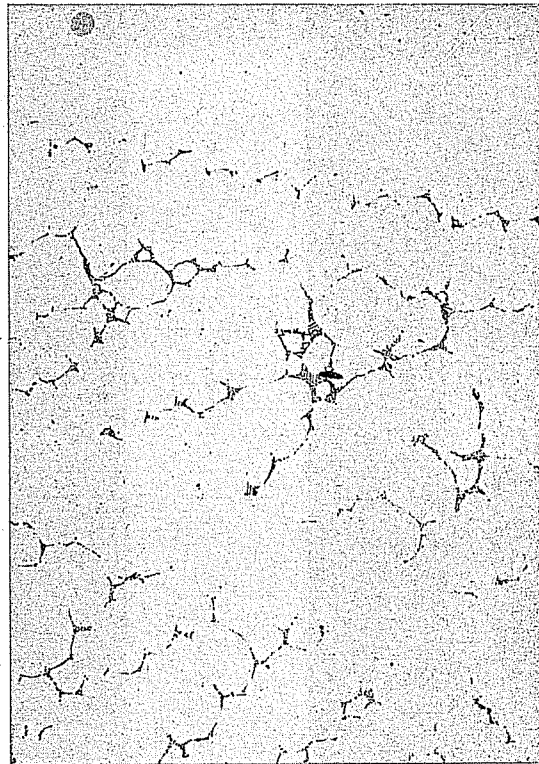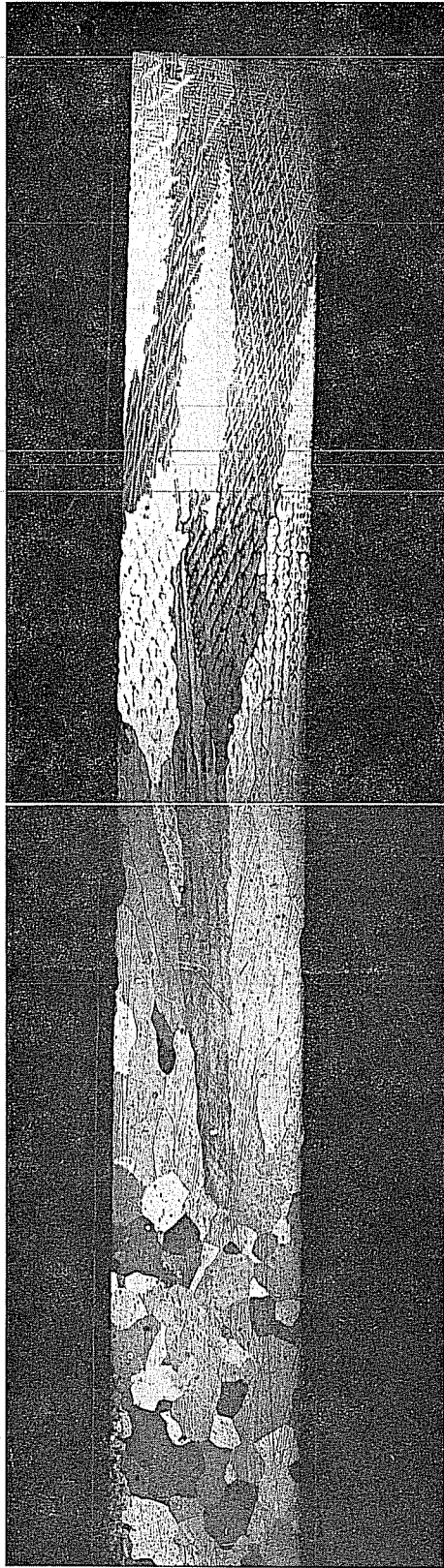
Solidification beginning

Middle of the mushy zone
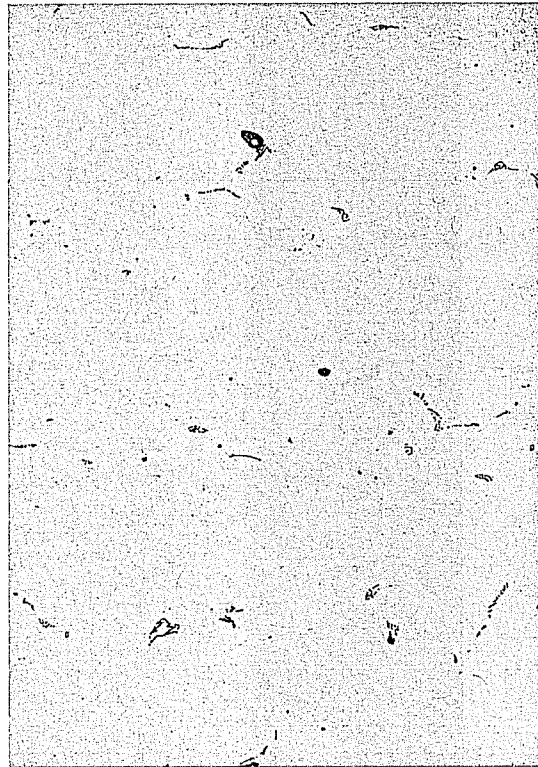
End of solidification

FIG. 5. Microporosities morphological features (sample No. 5 ; G = 80,22 °C/cm = ; R 0,00856 cm/s).

No. 10
R : 0.0036 cm/s
G : 105.65 °C/cm

No. 6
R : 0.00294 cm/s
G : 155.23 °C/cm

× 6

× 6

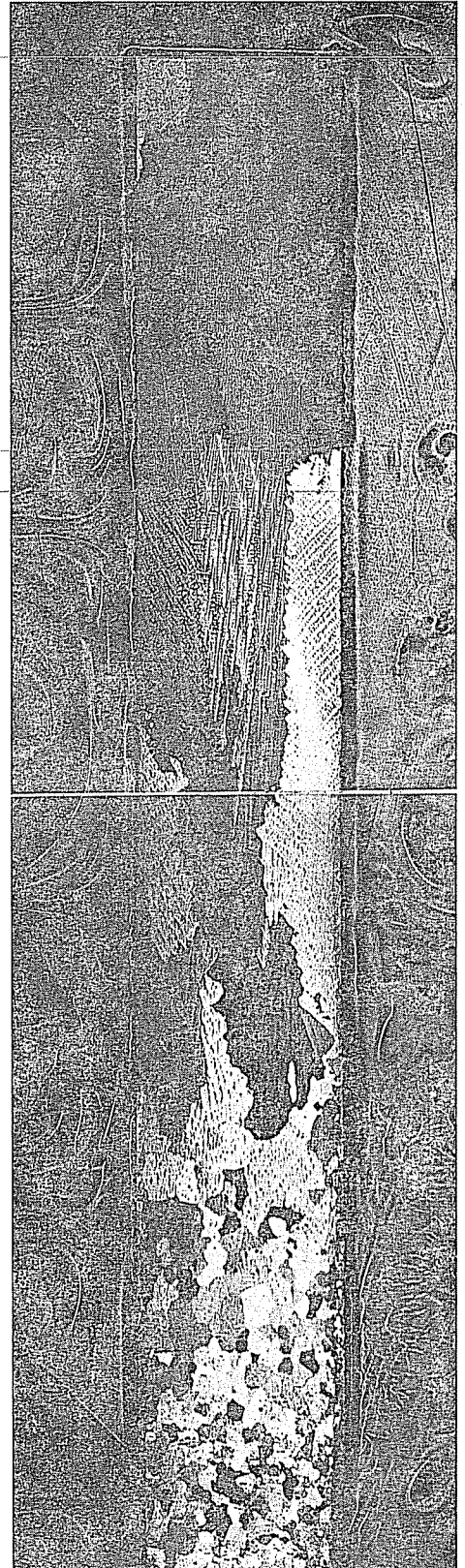FIG. 6. Macrographies of two samples.

eutectic to the interdendritic liquid and to measure it directly. It is of course to be noted that in general the measured values of the fraction eutectic are large.

Figure 7 shows the manner in which the fraction liquid on the longitudinal section varies according to the solidification conditions. The fraction liquid falls rapidly after the beginning of solidification. Near the top of the primary dendrites the remaining fraction liquid is only a small percentage. The solidification parameters have a marked effect on the fraction liquid (or eutectic); this regularly increases as the G/R ratio becomes smaller.

We have also measured the fraction eutectic on the transverse sections in the wholly solidified zone.

The variation of the fraction eutectic with the G/R ratio is identical. We note in Figure 8 that : the fraction eutectic g_E increases if the G/R ratio decreases.

(b) Micropores.

The micropores appear very close to the primary dendrites top and increase in number and in size from the time when they appear to the end of the solidification process. The examinations of the longitudinal sections and of the transverse sections in the wholly solidified zone show that the number and the mean diameter of the micropores are greater when the G/R ratio is greater.

It is probable that there are two parallel processes during solidification : the occurrence of new pores and the amalgamation of the micropores. Thus, the very fine micropores which are the first to be formed become larger by encountering other micropores and combining with them.

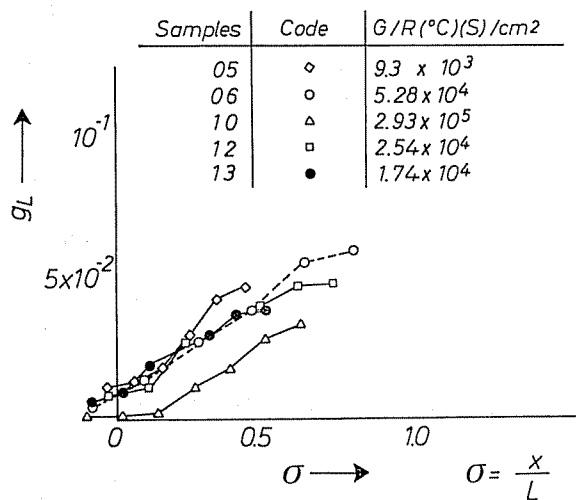The surfacial ratio which is related both to the number and to the size of the micropores can

Code	G/R (°C)(S)/cm²
◇	9.3 x 10³
●	1.74x 10⁴
□	2.54x 10⁴
○	5.28x 10⁴
△	2.93 x 10⁵

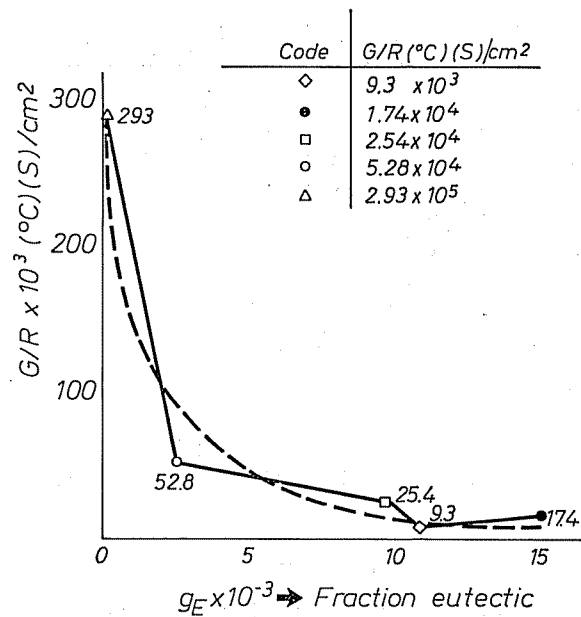$g_E x 10^{-3} \rightarrow$ Fraction eutectic

FIG. 8. Evolution of the fraction eutectic in the solidified zone in different solidification conditions.

serve as a good indicator of the compactness of the alloy. Figure 9 illustrates the way in which the incidence of micropores varies during solidification. This ratio is greater when the G/R ratio is greater. Figure 10 shows the way in which the surfacial ratio of micropores varies, in the wholly solid zone, as a function of the fraction eutectic; the surfacial ratio increases regularly as the fraction eutectic g_E decreases. On the other hand, no relationship is found between the surfacial ratio of micropores and the partial pressure drop due to the interdendritic flux :

$$\left[\frac{G}{R} \cdot (PS)_E^2\right]$$

Samples	Code	G/R (°C)(S)/cm²
05	◇	9.3 x 10³
06	○	5.28x 10⁴
10	△	2.93x 10⁵
12	□	2.54x 10⁴
13	●	1.74x 10⁴

$\sigma \longrightarrow$ $\sigma = \dfrac{x}{L}$

FIG. 7. Evolution of the fraction liquid along the solidification direction in different solidification conditions.

Code	G/R (°C)(S)/cm²
◇	9.3 x 10³
●	1.74 x 10⁴
□	2.54 x 10⁴
○	5.28 x 10⁴
△	2.93 x 10⁵

τ surfacial ratio of microporosities x 10⁻⁵

$\sigma \longrightarrow$ $\sigma = \dfrac{x}{L}$
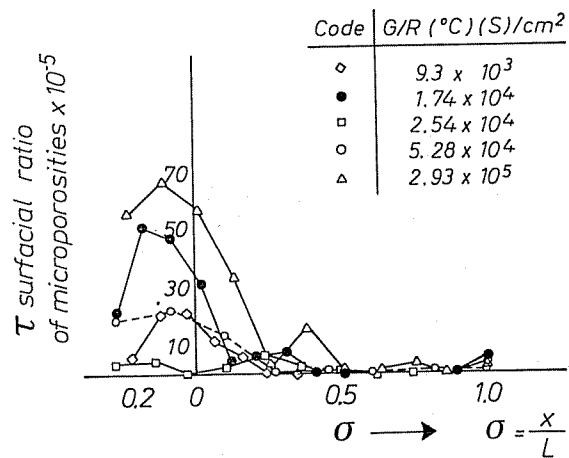
FIG. 9. Average of microporosities along the solidification direction.

Samples	Code	G/R (°C)(S)/cm²
05	◇	9.3 x 10³
13	●	1.74 x 10⁴
12	□	2.54 x 10⁴
06	○	5.28 x 10⁴
10	△	2.93 x 10⁵

$g_E \rightarrow$ Fraction eutectic
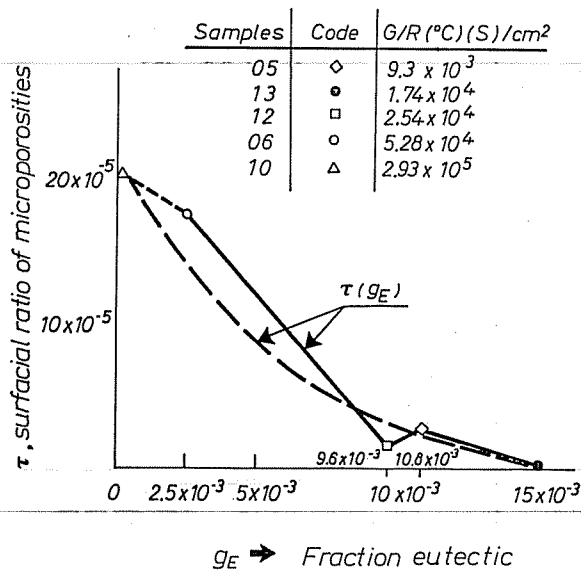
FIG. 10. Evolution of the surfacial ratio of microporosities in the solidified zone, with the fraction eutectic.

We have also analysed the form of the micropores; both in the longitudinal sections and in the transverse sections, the form factor is kept constant and is of the order of 0.06 (Fig. 11).

This form factor F is defined as follows :

$$F = \frac{S}{P_e^2}$$

where P_e is the perimeter surrounding the surface S.

when $S/P_e^2 = 0$, the particle is extremely irregular; when $S/P_e^2 = 0.08$, the particle is entirely circular.

The solidification parameters are not found to have any effect on the form factor.

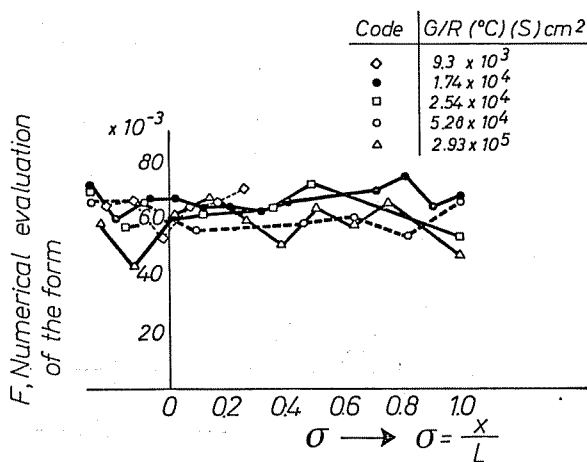| Code	G/R (°C)(S)cm²
◇	9.3 x 10³
●	1.74 x 10⁴
□	2.54 x 10⁴
○	5.28 x 10⁴
△	2.93 x 10⁵

FIG. 11. Evolution of the form of microporosities along the solidification direction.

DISCUSSION

1. — Model of the mushy zone.

There are two well-known models for the mushy zone; one compares it to a porous mass in which the interdendritic liquid flows between parallel cylinders, while the other also compares it to a porous mass but regards the tubes as conical [1], [2].

Our experiments seem to show that the channels in which the interdendritic liquid flows are neither cylindrical nor conical. They have a form close to that of equation (2) in the appendix. Thus, the expressions for the pressure drop which we have deduced from this model correspond better with reality.

2. — Origin of the micropores.

The study of the process of formation and of the morphology of the micropores permits us to believe that their origin may be mainly attributed to the gas contained in the alloy and that the effect of the solidification shrinkage is secondary.

Actually, on the one hand most of the micropores present a more circular shape. Moreover, in our experiments the surfacial ratio of micropores has no regular relationship with the pressure drop due to the interdendritic flux.

3. — The effect of the solidification parameters on the fraction eutectic.

The Ni-5 % Ti-0.2 % C alloy which we studied is a solid solution type alloy. For this, the non-equilibrium fraction eutectic increases as the G/R ratio becomes smaller. This confirmed the theory which we developed for a binary system, on the assumption that this is also applicable to a ternary system.

However, there is a difference which must not be ignored. This lies in the values of the fraction eutectic which are greater, by two orders of magnitude, than those which can be obtained theoretically for the binary Ni-5 % Ti alloy. In accordance with equation (1) in the appendix, it is clear that the partition ratio K has a dominant effect on the fraction eutectic, more particularly when the chemical composition of the alloy is much lower than that of the eutectic. Now, according to Figure 1 the partition ratio of titanium in the Ni-Ti-C alloy is always lower than in the case of the Ni-Ti alloy. This implies a remarkable increase of the fraction eutectic in the ternary alloy.

4. — Sources of the gas contained in the alloy.

Since the alloy solidifies under a vacuum of 1.33 Pa, the partial pressure of the dissolved gas at the beginning of solidification cannot possibly exceed 1.33 Pa. If the value of $k' = \dfrac{k_s}{k_L}$,

which is the ratio of the coefficients of solubility of the gas in the solid and in the liquid, is estimated at 0.1, in accordance with equation (4) in the appendix, then the maximum partial pressure of the gas at the end of the solidification process is not more than 1.33 Pa.

Also, in our experiments the static pressure of the liquid alloy on the solidification front is of the order of 4.10^3 Pa (equivalent to 5 cm in height). Obviously a static pressure of this kind can totally inhibit the formation of micropores. It therefore seems, in point of fact, that the gas producing the micropores does not arise from the dissolved gas. On the other hand, it is probable that the gas may be produced during solidification, by chemical reaction such as the reaction of reduction of carbon. Under vacuum, the carbon is very reactive and gives the following reaction [12] :

$$[C] + [O] \rightarrow [CO] \nearrow$$
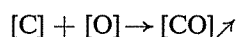
The micropores would be formed at the expense of the carbon; the carbon monoxide serves as gas source.

5. — *Criteria characterising the propensity of the alloys towards the formation of micropores.*

Starting from the gas dissolved in the alloy and the solidification contraction, we showed theoretically (the equations are given in the appendix) that the fraction eutectic and the pressure drop due to the interdendritic flux may be taken as criteria characterising the propensity to the formation of pores.

But in our experiments the micropores do not originate in the dissolved gas nor in the solidification contraction. It might seem strange that in this case also the fraction eutectic conditions the formation of micropores. Actually, during solidification the fraction eutectic becomes smaller, and this increases the rate of enrichment in carbon and oxygen (or other reacting elements producing gas). Under solidification conditions that give rise to increasingly high fractions eutectic, the phenomenon becomes still more marked. Thus, the fraction eutectic represents a criterion that is valid in this case also. On the other hand, the partial pressure drop due to the interdendritic flux loses its property as a criterion in this case, because the fraction eutectic is great in all the specimens.

CONCLUSIONS

In the Ni-5 % Ti-0.2 % C alloy subjected to directional solidification under vacuum, the origin of the formation of micropores can be attributed to the gas which is formed during solidification. The sources of gas might be chemical reactions producing gas, such as deoxidizing reaction by carbon.

The solidification parameters have a great effect on the formation of micropores, by way of the fraction eutectic. The surfacial ratio of micropores is greater when the fraction eutectic is smaller.

In accordance with our experiments we have concluded that for alloys of the solid solution type such as Ni-5 % Ti-0.2 % C the fraction eutectic becomes greater as the ratio G/R becomes smaller. For alloys containing a certain quantity of eutectic in equilibrium in the solid state, we only have the conclusion set forth in the appendix : the fraction eutectic increases as the ratio G/R increases.

The fraction eutectic, as ascertained in our experiments, is a sensitive parameter for the formation of micropores and can therefore be taken as a criterion characterising the propensity of the alloys that contain a large fraction eutectic, towards the formation of micropores.

APPENDIX

MATHEMATICAL MODEL
OF DIRECTIONAL SOLIDIFICATION

In a previous article we developed some theoretical aspects regarding the formation of micropores during directional solidification. We briefly give the conclusions, more particularly those which we have sought to confirm in this analysis.

(1) *The effect of the solidification conditions on the fraction liquid.*

If certain hypotheses are admitted, in general the fraction liquid is expressed by :

$$g_L = \left[\frac{\dfrac{C_L}{C_0} - \dfrac{a}{K-1}}{1 - \dfrac{aK}{K-1}} \right] \frac{1}{K-1}$$

We have introduced the expression of the fraction liquid as a function of the position on the axis of the dendrites, in the form :

$$g_L = (g_E{}^{K-1} - A\sigma)^{\frac{1}{K-1}} \qquad (1)$$

K is the equilibrium partition ratio.

$\sigma = \dfrac{X}{L}$ is the relative length along the dendrites axis.

A is a coefficient which depends on the solidification conditions and the nature of the alloy.

A mathematical treatment has led us to the following conclusions :
when the alloy concentration exceeds the solubility limit $C_0 > KC_E$, the fraction liquid becomes greater if G/R becomes greater.

The fraction solid is expressed by :

$$g_S = 1 - g_L$$

$$g_S = 1 - (g_E^{K-1} - A\sigma)^{\frac{1}{K-1}} \tag{2}$$

Taking the Ni-5 % Ti alloy as an example, we obtain the contours of the two primary dendrites under the different solidification conditions indicated in Figure A1.
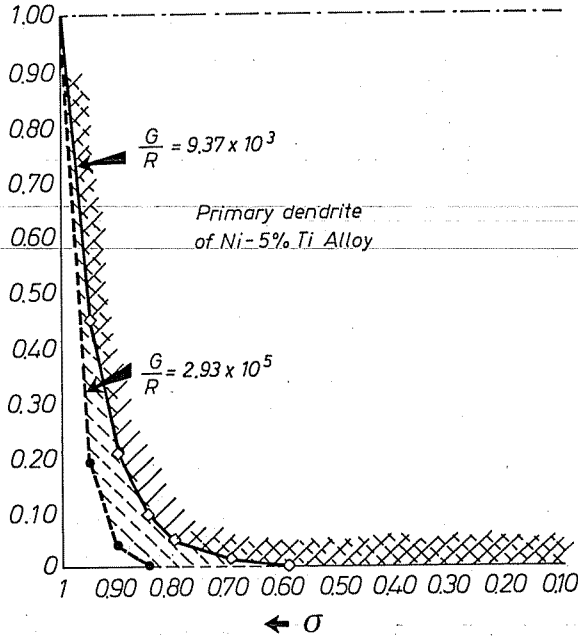

FIG. A1. Form of the primary dendrite in two different solidification conditions.

(2) *Pressure drop.*

Starting from this expression of the fraction liquid, and by way of certain calculations, it is possible to write the expression of the pressure drop as a function of the relative position as :

$$\Delta p = -\frac{B}{A}(1 - g_L^{K-2}) + \frac{\rho_L g_r L}{A}(1 - g_L^{K-1}) \tag{3}$$

where the first term represents the effect of the solidification contraction and the second represents that of gravity.

(ρ_L = density of the liquid, g_r = gravitational acceleration). B is a coefficient which depends on the nature of the alloy and the solidification conditions.

(3) *Criteria characterising the propensity of the alloy towards the formation of micropores.*

(*a*) For the alloys rich in eutectic in which the fraction eutectic is greater than 10^{-3}, the formation of the micropores is mainly due to the gas dissolved in the alloy, and the propensity towards the formation of micropores can be characterised by the expression :

$$(p_g)_{\text{max}} = \frac{(p_g)_0}{(K' + g_E)^2} \tag{4}$$

$(p_g)_0$ = initial pressure of gas dissolved in the alloy.

$K' = \dfrac{K_S}{K_L}$, K_S, K_L = constant of solubility of the gas in the solid and liquid respectively. The greater this expression, the greater the microporosity.

(*b*) For alloys poor in eutectic, the following expression is used :

$$(\Delta p)_{\text{characteristic}} = \Delta T \frac{R}{G}(PS)_E^2 \tag{5}$$

where $(PS)_E$ is the specific perimeter of the eutectic.

The greater this expression, the greater the microporosity.

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