

Grain refinement by Al-Ti-B alloys in aluminium melts: a study of the mechanisms of poisoning by zirconium

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Conventional grain refining tests confirm that the presence of zirconium in commercial purity aluminium melts dramatically reduces the effectiveness of Al-Ti-B grain refiners. Quantitative comparisons suggest that this poisoning action cannot be attributed solely to reduction in growth restriction arising from changed solute contents in the melt. Microscopic analysis of TiB₂ particles in an aluminium based, zirconium containing metallic glass shows the potential for substitution of zirconium for titanium. Analysis of a conventional Al-5 wt-%Ti-1 wt-%B refiner doped with zirconium shows the potential for similar modification of Al₃Ti. Thus zirconium can affect the nucleation stage of grain refinement by substituting for titanium in the aluminide and/or the boride phase, consistent with earlier work suggesting that the key to the nucleation potency is the existence of a layer of Al₃Ti on TiB₂ particles.

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Introduction

In direct chill (DC) casting of aluminium, it is well established practice to add a grain refiner to promote the formation of a fine, equiaxed grain structure, improving many properties of the as cast metal and facilitating subsequent processing.^{1,2} Of various refiners available, those based on Al-Ti-B are particularly widely used; they are effective in giving a relatively uniform grain size of less than 200 µm. While Al-Ti-B refiners can be used in many aluminium alloys, their performance is dramatically worsened in the presence of certain elements, notably zirconium.³⁻⁸ Such a 'poisoning' action is undesirable, and the aim of the present work is to further the understanding of the underlying grain nucleation mechanisms, in order to develop ways to circumvent the problem, or indeed develop more potent grain refiners.

For effective grain refinement, the particles added to the melt in the refiner must be potent substrates for the heterogeneous nucleation of aluminium. However, such nucleation can occur only if there is sufficient undercooling in the melt, and that requires some solute in the melt to restrict the growth of the solid, either at a columnar front competing with equiaxed solidification or from particles where nucleation has already occurred. Thus, analysis of grain refinement must consider both the heterogeneous nucleation and the growth restriction. The present work attempts to elucidate whether the poisoning action of zirconium on Al-Ti-B refiners is attributable mainly to hindrance of the nucleation or of the growth restriction.

Al-Ti-B refiners consist of TiB₂ particles 0.1 to 10 µm in diameter and Al₃Ti particles 20 to 50 µm in diameter, dispersed in an aluminium matrix⁹ (confirmed in the present work). On addition to the melt, the matrix melts, the Al₃Ti particles should (at the operative dilution levels) completely dissolve, and only the TiB₂ particles survive as a stable solid phase. It has long been recognised^{2,10} that effective nucleation requires Al₃Ti to be present in some form. Recent microscopical studies of refining particles in an Al rich metallic glass matrix have provided evidence that thin Al₃Ti layers can be stabilised on the surface of the TiB₂ particles, even at low titanium levels where Al₃Ti would not otherwise be stable.¹¹⁻¹⁶ Thus if the poisoning action of zirconium occurs at the nucleation stage, it could be by affecting either the TiB₂ or the Al₃Ti phases.

Conventional grain refining tests have been carried out to confirm and quantify the poisoning action of zirconium in aluminium melts refined with Al-5Ti-1B (wt-%). However, microscopic aspects of the poisoning were studied using the metallic glass analogue technique developed by Schumacher and Greer.¹¹⁻¹⁶ Melt spinning was used to produce metallic glass ribbons with dissolved zirconium and with embedded refiner particles. The microstructure and composition at and around these particles could then be analysed by transmission electron microscopy (TEM). The advantages (and disadvantages) of the metallic glass technique have been discussed elsewhere,^{16,17} but two should be noted here. First, the preparation of electron transparent foils still containing particles appears to be much easier in glassy than in crystalline aluminium matrices. Second, even if particles in a conventional cast can be studied by TEM, the Al₃Ti phase of potential importance for the nucleation will probably have been removed by the peritectic reaction with the liquid during solidification; this is prevented in the metallic glass technique by stifling crystal growth after nucleation. To allow the investigation of how zirconium might affect the Al₃Ti phase in the refiner, a zirconium doped refiner was produced. The compositions of phases present in this refiner were studied by microanalysis in scanning electron microscopy (SEM).

Review of zirconium poisoning

The poisoning effect of zirconium has been observed in many studies.³⁻⁸ Birch¹⁸ found that when zirconium is added to an inoculated melt, there is a progressive development of poisoning; on the other hand, when refiner is added to a melt already containing zirconium, poisoning is immediate, i.e. the inoculation never gives effective refinement. As yet, there is no fully accepted understanding of how poisoning occurs. Its possible effects on growth restriction, on the TiB₂ phase and on the Al₃Ti phase are reviewed in the following sections.

GROWTH RESTRICTION

As briefly mentioned in the 'Introduction', grain refinement can occur only in melts which have some solute to restrict

crystal growth. As is well known,^{19,20} the degree of growth restriction can be quantified by the parameter P

$$P = -m(1 - k)C_0/k \quad \dots \quad (1)$$

where m is the liquidus slope, k is the equilibrium partition coefficient, and C_0 is the solute content. P is the temperature range over which equilibrium freezing of the alloy would occur and is a measure of the undercooling which can be attained in the bulk melt. As demonstrated by Spittle and Sadli²⁰ using inoculated binary alloy melts with a wide range of solute types and amounts, there appears to be a single curve relating relative grain size (i.e. relative to that in high purity aluminium with 0.01 wt-%Ti) to P . As P is increased, the grain size at first decreases steeply and then levels off when $P \geq 15$ K.²⁰ While the exact shape of this curve may depend on the casting conditions, including the dimensions of the cast and the type of refiner used, its general trend is likely to be universal. When there is more than one solute present, the overall growth restriction factor can be obtained by adding the P values for each element, provided that the addition levels are low and that the solutes do not react with each other in the melt.²¹ However, if the solutes do react to form complexes or precipitates, then the total solute level and overall growth restriction factor are reduced.^{8,22,23}

Commercial purity aluminium has a significant total solute level (0.1 to 0.5 wt-%), mostly iron and silicon. As pointed out by Spittle and Sadli,²⁴ these solutes can themselves restrict growth and can complicate the interpretation of poisoning effects. In particular, they suggest that zirconium has its poisoning effect by compound formation with iron and silicon, thus removing them from solution and reducing the overall solute level in the melt. To eliminate the effects of iron and silicon, Spittle and Sadli²⁴ used high purity (99.99 wt-%) aluminium; they found that in an inoculated high purity melt containing 0.01 wt-%Ti, the addition of 0.15 wt-%Zr alone significantly improved the grain refinement. A similar effect of adding the P factors for low addition levels of titanium and zirconium solutes was found by Johnsson.⁸ However, he found that for zirconium additions greater than the peritectic composition of 0.11 wt-%, precipitation of $Al_3(Zr,Ti)$ reduced the level of titanium in solution and impaired grain refinement.

The results of Birch,¹⁸ that there is progressive poisoning when zirconium is added to an inoculated melt but instant poisoning when refiner is added to a zirconium doped melt, appear to offer strong support for the idea that zirconium exerts its poisoning effect by reactions in the melt, such as those proposed by Spittle and Sadli.²⁴ The zirconium doped melt would already have undergone the reactions between zirconium and the iron and silicon in solution to give it a low overall solute content, and when the refiner is added the low value of P then gives instant poisoning. On the other hand, zirconium added to an inoculated melt would take time to react with the iron and silicon in solution, and so the poisoning effect would be progressive. However, it is known that refiners may require some contact time to become effective. During this time the particles are in some way conditioned by contact with the melt. For modern, potent refiners the contact time is very short and not readily detected, but the conditioning can still be seen in the way poor refiners improve their performance with holding in the melt.²⁵ The instant poisoning when refiner is added to a zirconium doped melt could arise because the zirconium interferes with the conditioning process so that the refiner can never become effective, an explanation originally suggested by Birch.¹⁸ On the other hand, zirconium added to an inoculated melt may take some time to destroy the effectiveness of particles which have already been conditioned. Thus, the results of Birch are not conclusive in deciding whether poisoning by zirconium

is mainly attributable to reduction in growth restriction or to direct interference with the nucleation potency of the refiner particles.

NUCLEATION MECHANISM

Before considering what effects zirconium might have on refiner particles, it is worthwhile to consider the nucleation mechanism in Al-Ti-B refiners. When the refiner is added to the melt, the TiB_2 particles disperse and, being denser than liquid aluminium, tend to settle out, depending on the local melt agitation. The Al_3Ti particles in the refiner are expected to dissolve quickly when added to the melt, since the overall titanium content is then well within the solubility limit, and measurements confirm this.²⁶ However, a good refining action is achieved only if there is excess titanium in the refiner beyond that combined in the TiB_2 particles, suggesting (as noted in the 'Introduction') that Al_3Ti , not TiB_2 itself, might be the potent nucleation substrate. A number of ways have been suggested in which the presence of TiB_2 particles might stabilise or prolong the life of the Al_3Ti phase in the melt; metallic glass matrix studies have given strong support to the suggestion that the Al_3Ti is stabilised as an epitaxial layer on the TiB_2 particles. The metallic glass studies are important in revealing the crystallographic relationships involved in the nucleation of aluminium.

Schumacher and Greer¹¹⁻¹⁶ found that, even at the very high effective undercooling in a metallic glass matrix, nucleation occurs only on the basal {0001} faces of the hexagonal TiB_2 particles. The particles are coated with a layer of Al_3Ti , as thin as three atomic layers.¹⁵ The orientation relationships between the phases are straightforward, the close packed planes and directions being parallel in each case

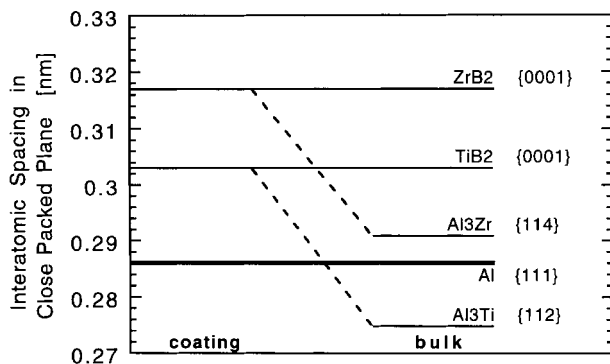
$$\{111\}_{Al} \parallel \{112\}_{Al_3Ti} \parallel \{0001\}_{TiB_2} \\ \langle \bar{1}\bar{1}0 \rangle_{Al} \parallel \langle 20\bar{1} \rangle_{Al_3Ti} \text{ or } \langle \bar{1}\bar{1}0 \rangle_{Al_3Ti} \parallel \langle 11\bar{2}0 \rangle_{TiB_2}$$

The {112} faces of the Al_3Ti are not equilibrium faces for Al_3Ti particles in the melt, but Klang has pointed out that they may be particularly effective nucleation substrates.²⁷ The degree of lattice matching of the various phases during nucleation can be estimated from the known lattice parameters at room temperature. The interatomic distance in $\{111\}_{Al}$ is 0.286 nm. In $\{0001\}_{TiB_2}$ the corresponding distance is 0.303 nm, 5.9% greater. In $\{112\}_{Al_3Ti}$ the atomic arrangement does not have exact hexagonal symmetry. As discussed in Ref. 16, the weighted average interatomic distance in the plane is 0.275 nm, 3.7% smaller than for α -Al. However, as shown in Ref. 15, the Al_3Ti layer when very thin is coherent with its TiB_2 substrate and would have an expanded interatomic distance. As the Al_3Ti gets thicker, its spacing will relax towards the bulk value, as illustrated schematically in Fig. 1. Thus the lattice matching of aluminium on the Al_3Ti layer is always better than that on TiB_2 , but may be much better, depending on how much the spacings in the layer are relaxed towards their bulk value.

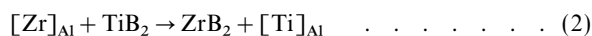
Since nucleation of aluminium occurs only on the basal faces of the boride particles, lattice matching must play an important role. Substitution of zirconium into either TiB_2 or Al_3Ti may affect the ease of nucleation depending on how this substitution alters the interatomic distance in the boundary plane and the consequent lattice match with aluminium. However, nucleation potency may be governed by chemical effects in addition to lattice matching; substitution of zirconium may alter such effects also.

MODIFICATION OF TiB_2

Jones and Pearson³ proposed that the poisoning effect of zirconium arises through the reaction



1 Relative values of the interatomic spacings in the close packed planes of the phases possibly involved in the nucleation of aluminium. The aluminium phase is a coating on the boride, and when thin enough is coherent with the boride adopting the same interatomic spacing. Diagram shows schematically how the spacing in the aluminides would decrease towards the value characteristic of the bulk phases as interfacial dislocations are introduced when the coatings are thicker



giving a layer of ZrB_2 on the surface of the TiB_2 particles. They suggested this would decrease the nucleation potency for α -Al because, although ZrB_2 is isomorphous with TiB_2 , it would have larger lattice parameters than TiB_2 and therefore be a less good match for the aluminium lattice (Fig. 1). The interatomic distance in the basal plane of ZrB_2 is 0.317 nm, 10.8% greater than that in $\{111\}_{\text{Al}}$. Thermodynamic estimations suggested that reaction (2) would occur only if the concentration of zirconium in solution were at least four times that of the residual titanium.³ Abdel-Hamid⁶ considered that it was likely that a solid solution phase $(\text{Ti}_{1-x}\text{Zr}_x)\text{B}_2$ would be most stable. Zdaniewski²⁸ has discussed how substitution of zirconium for titanium affects the lattice parameters of TiB_2 . The c parameter is changed more than the a because the covalently bonded boron network perpendicular to c is not easily deformed. For each wt-%Zr substituted in TiB_2 , increases of 0.017 nm in a and of 0.037 nm in c are found. The effects of lattice parameter changes would appear only for thicker zirconium modified layers, as a thin layer on the surface of a TiB_2 particle would probably be coherent with the main particle and therefore have the same interatomic spacing in the $\{0001\}$ plane. However, any modification of TiB_2 by zirconium would be expected to hinder nucleation, since the lattice matching with aluminium can only be worsened.

It has also been suggested that the TiB_2 particles might become coated in elemental zirconium,²⁹ though this suggestion does not seem to have been explored further.

MODIFICATION OF Al_3Ti

When added in sufficient amounts, zirconium could lead to the formation of Al_3Zr particles which would be competitors to Al_3Ti as nucleation substrates.³⁰ The thermodynamics of formation of Al_3Zr have been analysed.³¹ Although it has been claimed that Al_3Zr itself is an effective nucleant,³² its appearance in the presence of Ti leads to an overall worsening of grain refinement.⁸ Alternatively, as reviewed by Abdel-Hamid,⁶ substitution of Zr for Ti could lead to the formation of a solid solution phase $\text{Al}_3(\text{Ti}_{1-x}\text{Zr}_x)$, which could form in individual aluminide particles or in layers of Al_3Ti stabilised on TiB_2 . Since only the surface need be modified, the effect could be seen for small zirconium additions.

The unit cell of Al_3Zr (trigonal, D_{023} structure) is essentially four aluminium unit cells stacked parallel to the

c axis with an ordered substitution of Zr atoms. In contrast, Al_3Ti (D_{022}) is a stack of two aluminium cells. For Al_3Zr , the closed packed plane likely to be parallel to $\{0001\}_{\text{TiB}_2}$, and forming the substrate for $\{111\}_{\text{Al}}$, is $\{114\}$. The close packed directions in (114) for example are $[\bar{1}10]$, $[\bar{4}01]$, and $[0\bar{4}1]$, for which the weighted average interatomic spacing is 0.291 nm, 1.7% greater than that for aluminium (0.286 nm).

Structural studies show that Al_3Ti and Al_3Zr form a pseudobinary system, with a very narrow two phase region at low zirconium content, from 2.75 to 6.25 at.-%Zr (Ref. 33). Substitution of zirconium for titanium in Al_3Ti increases its lattice parameters, as for TiB_2 , while substitution of titanium for zirconium in Al_3Zr gives corresponding decreases. However, the weighted average interatomic distance in the close packed plane ($\{112\}$ for Al_3Ti and $\{114\}$ for Al_3Zr) shows an essentially linear variation across the composition range from Al_3Ti to Al_3Zr ; thus the lattice match of aluminium to the aluminide is dependent on the composition of the latter, but does not show any significant discontinuity at the phase change between the two aluminide structures. As the zirconium content in the aluminide increases, the lattice matching with aluminium first improves, and should always be better than for bulk Al_3Ti . On the other hand, if the aluminide is a thin layer on the boride and coherent with it, then any substitution of zirconium for titanium in the boride will greatly degrade the overall lattice matching with aluminium.

The aluminide can undergo a peritectic reaction with liquid aluminium to give solid aluminium. It is very significant that the peritectic temperature for Al_3Ti is 665°C (4.5 K above the melting point of pure aluminium), while that of Al_3Zr is only 660.8°C.³⁴ Thus, if aluminides of two compositions were present, the one richer in titanium would always be expected to dominate as the more potent nucleant. In this way it is clear that even if Al_3Zr were an effective nucleant on its own, partial substitution of zirconium for titanium would be likely to impair the grain refining performance.

Experimental methods

In the grain refining tests and in glassy matrix studies, a commercial Al-5Ti-1B (wt.-%) refiner was used, as supplied in rod form by London and Scandinavian Metallurgical Co. Ltd (LSM). The composition of this refiner is given in Table 1.

Grain refining tests were carried out on commercial purity (CP) aluminium, for which the specification was that the content of the main solutes (iron and silicon) would not exceed 0.3 wt.-% in total; the measured composition is given in Table 1. Of all the solutes present, the only ones giving a significant contribution (>0.1 K) to the growth restriction factor are iron, nickel, silicon, sodium, and gallium (Table 2). The grain refining tests were conducted at LSM according to the Aluminum Association procedures (TP-1).³⁵ Melts of 10 kg of the CP aluminium were held to within ± 10 K in resistively heated furnaces. After melting and temperature stabilisation, a TP-1 cone sample was taken for reference, and then grain refiner was added to the main melt to a level of 1 part per thousand (ppt) by weight. At this addition level, the only significant contribution of the refiner to the overall growth restriction in the alloy comes from the titanium. As detailed in Table 2, the 1 ppt addition of refiner contributes ~ 0.003 wt.-% free titanium (i.e. not combined with boron) to the melt. Samples were taken for grain refining tests after 1, 3, 7.5, 10, 15, 30, 45, 60, 120, 240, and 360 min; in each case the melt was thoroughly stirred prior to sampling. As noted in earlier work²⁵ and discussed below in the next section on

'Grain refinement in presence of Zr', the stirring prevents apparent 'fading' of the refiner action through settling of particles out of the melt. Test samples are removed from the metal bath in a conical, mild steel ladle. The ladle is then lowered into the retaining ring of a quenching tank through which water runs until solidification is complete. For grain size analysis, samples were sectioned transversely at a fixed distance of 38 mm from the base of the cone.³⁵ The sections were polished and etched with Poulton's reagent. The grain size was measured from optical micrographs using the linear intercept method. Since solidification occurs from the base of the sample it is notable that the transverse sectioning may not reveal if the growth is columnar rather than equiaxed as intended; in this way the mean grain size may be underestimated. The error in the grain size measurements is estimated to be $\pm 10\%$.

Melt spinning to obtain metallic glass ribbons was carried out at the University of Oxford, UK. An inductively heated 5 g melt was held at 1150°C for 5 min in an atmosphere of 200 mbar He before ejection from a BN crucible on to the rim of a copper wheel rotating with a peripheral velocity of 50 m s⁻¹. The melt holding temperature represents a superheat of 100 to 200 K and was found to be necessary for sufficient fluidity to eject the glass forming melt through the 0.8 mm diameter orifice of the crucible. The ribbons had typical width 3 mm and thickness 50 μm , giving an estimated cooling rate of 10⁵ to 10⁶ K s⁻¹. Further details of the melt spinning apparatus have been given elsewhere.³⁶ The base alloy was Al₈₇Ni₈Zr₅ (at.-%) with Al-5Ti-1B rod added to a level of 0.5 wt.-%, giving a calculated 0.01 wt.-% of dissolved titanium in the melt. The ribbons were found by X-ray diffraction and TEM to be glassy, with embedded, randomly distributed particles.

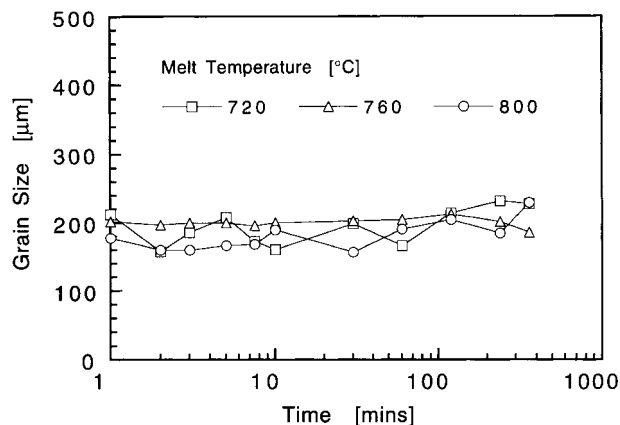
Samples of melt spun ribbon were prepared for TEM by jet polishing using a 4% perchloric acid in ethanol solution at -40°C with a voltage of 20 V. Examination by TEM took place in a Philips CM30 microscope. Selected samples were examined in a VG HB501 scanning transmission electron microscope (STEM). A Link AN10000 spectrometer on this instrument was used for energy dispersive X-ray spectroscopy (EDS) to perform compositional mapping.

A zirconium doped refiner was produced at LSM by adding 0.1 wt.-%Zr during conventional grain refiner production.² Following the zirconium addition, the melt was held at 950°C for 30 min to ensure complete mixing,

Table 1 Solute contents of alloys used in present work*

Alloy	Solute	Content, wt-ppm or wt-%
	Fe	825 ppm
	Si	475 ppm
	Ga	125 ppm
	Ni	51 ppm
	V	79 ppm
	Ti	42 ppm
	Zn	18 ppm
	Pb	16 ppm
	Na	15 ppm
	Mn	14 ppm
	Cr	12 ppm
	Cu	8 ppm
	Sn	4 ppm
	Mg	4 ppm
	B	4 ppm
Al-5Ti-1B refiner	Ti	5.01%
	B	1.00%
	Fe	0.12%
	V	700 ppm
	K	600 ppm
	Si	500 ppm
	others	Each < 500 ppm

*The batch-to-batch variability of these measured values is $\pm 10\%$.



2 Grain refining performance of Al-5Ti-1B refiner added to a level of 1 part by weight in 1000 (1ppt) into commercial purity aluminium (Table 1), as a function of holding time in the stirred melt in temperature range 720-800°C

and the refiner was then cast into waffle form. A sample of this was sectioned, polished, and lightly etched in Poulton's reagent before examination by SEM using a Jeol 820 microscope. Compositional mapping by EDS was performed using a Link AN10000 spectrometer.

Grain refining tests

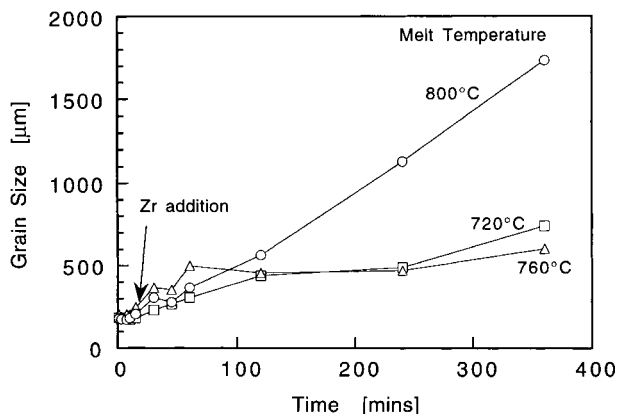
GRAIN REFINEMENT IN PRESENCE OF Zr

To study poisoning, it is first necessary to characterise the behaviour in melts without zirconium. The effects of holding Al-Ti-B refiner in the melt were tested at 720, 760, and 800°C for times up to 6 h. The melt was stirred before each test sample was taken. As shown in Fig. 2, for these experiments in the absence of zirconium, there is no evidence of 'fade'. Previous workers have seen an apparent loss of refiner potency over similar holding times, but the prevention of such effects simply by stirring suggests that they can be attributed solely to settling effects. The behaviour appears to be the same at all three test temperatures, giving identical grain size to within experimental error.

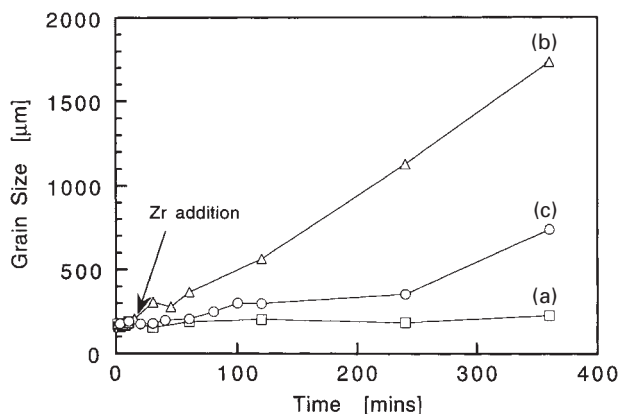
The effects of addition of 0.05 wt.-%Zr are shown in Fig. 3. The grain size becomes progressively coarser,

Table 2 The values of liquidus slope m , equilibrium partition coefficient k , solute content C_0 , and P (growth restriction factor, calculated from equation (1)) for the solutes of interest in the present work. The m and k values are calculated from parameters in Ref. 34. Of the solutes present in CP aluminium, only those contributing >0.1 K to the overall growth restriction factor are given. The addition of refiner increases the titanium content, and for some tests there are additions of zirconium and iron

Solute element	m , K/wt-%	k	$-m \left(\frac{1-k}{k} \right)$, K/wt-%	C_0 , wt-%	P , K
Fe	-2.925	0.03	94.57	0.0825	7.8
Ni	-3.50	0.004	871.5	0.0051	4.4
Si	-6.62	0.12	48.55	0.0475	2.3
Ti	25.63	7	21.97	0.0042	
From refiner				0.0028	
Total				0.0070	0.15
Na	-7.84	0.013	595.2	0.0015	0.9
Ga	-2.52	0.14	15.48	0.0125	0.2
Zr addition	3.45	2.33	1.97	0.05	0.1
Fe addition	-2.925	0.03	94.57	0.05	4.7



3 Effect of 0.05 wt-%Zr addition (at 10 min) on performance of Al-5Ti-1B refiner added to a level of 1 ppt into commercial purity aluminium, as a function of holding time in the stirred melt, in temperature range 720–800°C



a commercial purity aluminium; b as a but with subsequent addition of 0.05 wt-%Zr (at 10 min); c as for b but with prior addition of an extra 0.05 wt-%Fe

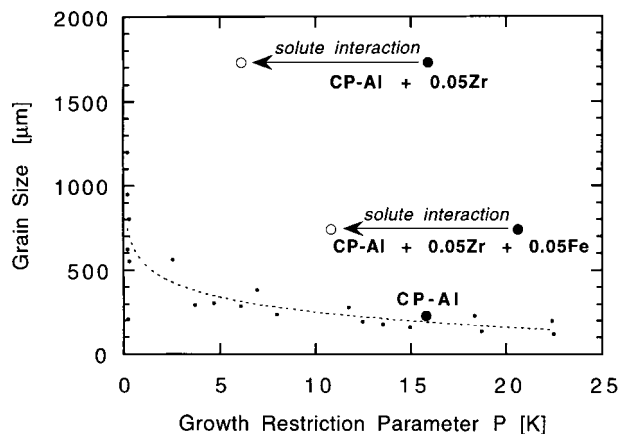
4 Effects of holding stirred melt at 800°C on the grain refinement by a 1 ppt of Al-5Ti-1B refiner added to given melts

particularly at the highest temperature studied, 800°C, at which the grain size dramatically changes from $\sim 225 \mu\text{m}$ at 5 min after zirconium addition to $\sim 1800 \mu\text{m}$ after nearly 6 h. Thermodynamically, the increased poisoning at higher temperatures is not consistent with the formation of complexes in the melt, since these would be expected to be less stable at higher temperatures.

GRAIN REFINEMENT WITH COMPENSATING Zr AND Fe ADDITIONS

A possible model for the poisoning effect of zirconium is that it reacts with iron, nickel, or silicon solute, effectively reducing the overall solute level in the melt. However, if extra solute is added it should be possible to compensate for this effect and restore the original value of the growth restriction factor. In the present work it is assumed that iron is the main solute and that the most likely product of reaction with zirconium would be Fe_2Zr complexes or precipitates (corresponding to the highest melting compound in the Fe-Zr system). Reaction with 0.05 wt-%Zr would remove up to 0.06 wt-%Fe from solution. In the present work the Fe solute level is increased by 0.05 wt-% to approximately compensate for this. As can be seen in Table 2, the growth restriction factor for 0.05 wt-%Zr itself is negligible compared to the effects of Fe solute.

An additional 0.05 wt-%Fe was dissolved in the melt, 30 min later the refiner was added, and then, after a further 10 min, 0.05 wt-%Zr was added. Throughout, the melt was

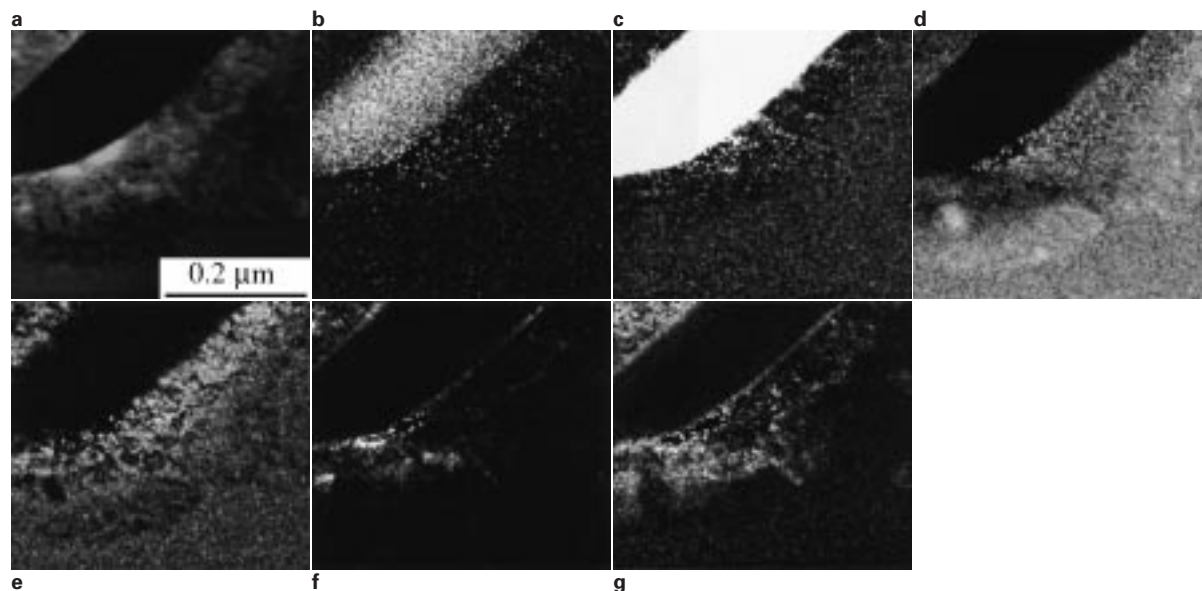


5 Variation of grain size with growth restriction parameter P for a variety of grain refined alloys. The small points, their trend shown by the broken line, are the data of Spittle and Sadli²⁰ on various solutes and solute levels in high purity aluminium. The data from the present work are shown by full circles. These grain sizes were measured in a standard refining test³⁵ (cooling rate of 4.5 K s^{-1}) with a refiner addition level of 1 ppt after a hold for 6 h at 800°C. The grain size measured in CP-Al is in excellent agreement with the trend in Ref. 20. Additions of 0.05 wt-%Zr with or without 0.05 wt-%Fe raise the grain size above this trend. The arrows and open circles indicate the maximum likely amounts by which the P values would be reduced by solute interaction in the melt. It is assumed that Ni_2Zr and Fe_2Zr complexes or precipitates are formed

held at 800°C and was stirred. As shown in the comparison in Fig. 4, the higher iron content reduces the poisoning effect of zirconium, but does not eliminate it; a straightforward compensation has not been achieved. Thus it seems that the formation of Fe-Zr intermetallic phases cannot be the dominant poisoning mechanism. If a different composition of Fe-Zr complexes is assumed (Fe_3Zr is the next most likely), this argument is not substantially changed. However, if zirconium interference with nucleant particles were the dominant mechanism, poisoning would still be expected. As is clear in Fig. 4, a lower grain size is obtained with the greater iron content. Two possible origins for this can be distinguished: (a) whatever the nucleation behaviour, a greater overall solute level gives a larger growth restriction factor, or (b) the effect of zirconium on the nucleant particles could be reduced if the concentration or activity of zirconium in the melt is reduced by interactions with the higher iron content.

DISCUSSION OF REFINING TESTS

It is useful to consider growth restriction effects more quantitatively using the parameter P as given in equation (1).²⁰ Table 2 gives the values of m and k for the solutes of present concern, and P values estimated for the various cases in Figs. 3 and 4. The CP aluminium itself is estimated to have a growth restriction factor of 15.6 K (assuming additivity of P values, as discussed in Ref. 21), increased to 15.8 K by the addition of refiner (Table 3). Addition of 0.05 wt-%Zr to the melt would increase P to 15.9 K if there were no reaction between solutes in the melt. It is useful to estimate the maximum amount by which P would be reduced by reaction. To do this it has been assumed that the added zirconium first reacts with the nickel (the most potent restricting solute of those present), forming Ni_2Zr , and then with iron, forming Fe_2Zr . The 0.005 wt-% of nickel present would combine with 0.004 wt-% of the added zirconium, leaving the remainder to react with 0.056 wt-% of the iron. Thus the assumed



a bright field image; b-g EDS (X-ray) composition maps for b titanium (using the Ti K line), c zirconium (Zr K_{α} + Zr L), d aluminium (Al K), e nickel (Ni K), f carbon (C K), and g oxygen (O K)

6 Examination by STEM of region around a boride particle in a melt spun glassy matrix specimen

reactions in the melt remove the growth restriction effects of all of the nickel, all of the zirconium, and nearly 70% of the iron. Figure 5 shows how the measured grain sizes after long holding time (6 h) correlate with the P values estimated with and without reaction in the melt (from Table 3). It is readily seen that, when zirconium is present, the grain sizes do not lie on the curve found by Spittle and Sadli,²⁰ even when the maximum possible extent of reaction between zirconium and other solutes is taken into account. Even with complete reaction, the overall P values lie outside the range in which the grain size is strongly sensitive to P ; this is especially true of the experiments with added iron.

It is concluded that the poisoning phenomena cannot be explained by growth restriction effects alone and that nucleation must be involved.

Microstructural studies in a glassy matrix

JUSTIFICATION OF TECHNIQUE

To study nucleation events it is necessary to suppress growth at a very early stage of solidification. This can be achieved if the melt is rapidly quenched to give a mostly glassy product, with small amounts of crystallisation only

Table 3 Overall growth restriction factors P for the alloys used in the present work, obtained by summing the values in Table 2. It is assumed that zirconium in the melt reacts completely with nickel and iron in the melt forming Ni_2Zr and Fe_2Zr . In this way, all of the nickel and much of the iron are consumed. This is used to estimate the maximum possible effect of solute interactions in the melt

Sample	Alloy	P, K
1	Commercial purity Al (CP Al)	15.6
2	CP Al + 1 ppt Al-5Ti-1B refiner*	15.8
3	CP Al + refiner + 0.05 wt-%Zr; unreacted	15.9
4	As 3; reacted (residual: Zr, 0 wt-%; Ni, 0 wt-%; Fe, 0.026 wt-%)	6.1
5	CP Al + refiner + 0.05 wt-% Zr + 0.05 wt-% Fe; unreacted	20.6
6	As 5; reacted (residual: Zr, 0 wt-%; Ni, 0 wt-%; Fe, 0.076 wt-%)	10.8

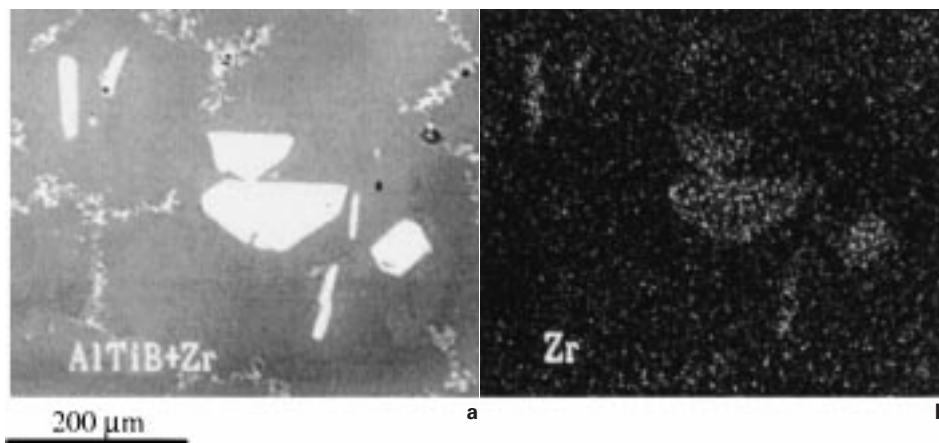
*ppt: 1 part per thousand.

at potent nucleation sites. As in earlier work,¹¹⁻¹⁶ a grain refining addition was melted together with a glass forming alloy and then melt spun. However, in the present work the chosen glass forming composition, $Al_{87}Ni_8Zr_5$ (at.-%), contains zirconium to permit the study of poisoning effects.

STEM ANALYSIS

As quenched specimens were thinned and examined by TEM to identify those thin foils suitable for compositional analysis of poisoning effects in STEM. It was necessary to have a uniform thin area including an embedded boride particle. Figure 6 shows STEM images from one such specimen, including the EDS results which although not quantitative do give a useful qualitative indication of the elemental distributions. The bright field image (Fig. 6a) shows a boride particle (dark) viewed perpendicular to its hexad axis. The boron content could not be analysed, but the X-ray map in Fig. 6b does confirm the presence of titanium in the particle. It is clear that some titanium has penetrated into the matrix around the particle. The most striking result is in Fig. 6c, which shows that the zirconium content of the particle is very much greater than in the matrix. This suggests substantial substitution of zirconium for titanium in TiB_2 , with consequent release of titanium into the matrix. Figure 6b appears to show this release, the enhanced Ti concentration around the boride being preserved by the rapid quench.

Figure 6a shows that there is crystallinity immediately around the boride. The contrast within the crystalline region shown in the bright field image correlates with complementary contrast variations in the aluminium (Fig. 6d) and nickel (Fig. 6e) X-ray maps. These results would be consistent with eutectic crystallisation, for example to $Al + Al_3Ni$, as has been found for related glassy compositions.³⁷ They do not show nucleation of single phase aluminium on the borides as seen in earlier studies using zirconium free glassy matrices.¹⁶ There is no evidence for substantial substitution of aluminium or nickel into the boride. Figure 6f and g show some contamination by carbon and oxygen, concentrated around the thinnest part of the STEM specimen adjacent to the boride particle. This contamination probably arises from the jet polishing and during the TEM and STEM examination, but it does not affect the boride itself, for which the EDS results unambiguously indicate zirconium substitution.



a backscattered electron image; b EDS composition map for Zr

7 Examination by SEM of a polished cross-section of Al-5Ti-1B refiner doped with 0.1 wt-%Zr

DISCUSSION OF MATRIX STUDIES

In all particles analysed there was substantial, if not total, substitution of zirconium for titanium, giving a mixed $(Zr_xTi_{1-x})B_2$ particle. This substitution is expected to give an increase in the lattice parameter of the boride. AlB_2 also has the same structure as TiB_2 , but no evidence was found for aluminium substituting for titanium in the boride particles. This is in agreement with other work which has shown that no such substitution occurs when excess titanium is present.³⁸

Before using microstructural observations in the glassy matrix to interpret the poisoning seen in grain refinement, it is essential to note some fundamental differences between the experimental conditions. First, the melt holding temperature in the melt spinning experiments ($\sim 1150^\circ C$) is considerably higher than that during grain refinement tests ($720\text{--}800^\circ C$). Since there is a strong temperature dependence of poisoning (Fig. 3), entirely different boride-melt reactions could arise in the metallic glass and in the conventional grain refinement experiments.

Second, the melt compositions are quite different in the two cases. While the grain refinement tests deal with essentially commercial purity aluminium with 0.05 wt-%Zr, the glass forming alloy necessarily has much higher solute levels. While the nickel content does not appear to interact with the boride particles, the enhanced zirconium content (two orders of magnitude greater than in the grain refinement tests) may alter the effects of the zirconium on the borides.

Analysis of zirconium doped refiner

MOTIVATION

It has, up to this point, not been possible to explore any interaction between the aluminide and zirconium in the melt, since no aluminide phase was observed in the glassy matrix experiments. A specimen of Al-5Ti-1B refiner rod doped with 0.1 wt-%Zr was prepared for elemental analysis. In this way, the presence of the aluminide phase was ensured and other solutes such as in the glassy matrix were avoided. With refiner rod it is difficult to prepare thin foils for TEM which retain all the phases. For this reason, and because its resolution was adequate, microanalysis was carried out using SEM.

MICROANALYSIS

As expected, the refiner shows boride and aluminide particles in an aluminium matrix. In the backscattered electron image (Fig. 7a) the aluminide appears as large

white particles, the boride as smaller speckled particles. Within the resolution of the experiment, there is no evidence for zirconium substitution into the boride phase. However, as the zirconium X-ray map (Fig. 7b) shows, there is zirconium substitution into the aluminide phase. The overall zirconium content of the refiner is so low that one would not expect to see any contrast in this map unless there were zirconium segregation to the aluminide.

DISCUSSION OF DOPED REFINER STUDIES

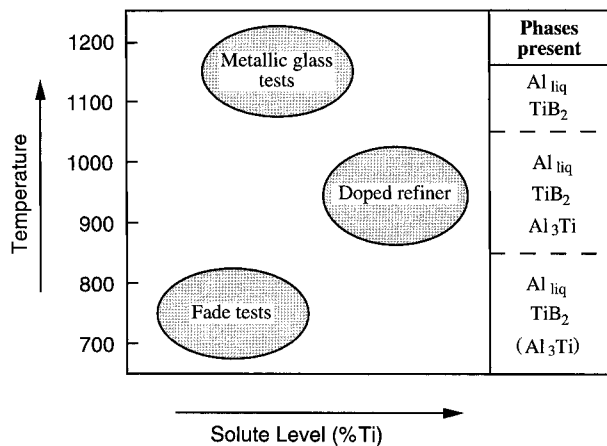
The lack of zirconium substitution in the boride particles is in marked contrast to the glassy matrix studies, but may be understood in terms of the much higher melt holding temperature in the latter case. The clear segregation of zirconium into the aluminide is in agreement with the suggestions (outlined in the section above on 'Modification of Al_3Ti ') that the formation of a mixed $Al_3(Zr_xTi_{1-x})$ phase may be responsible for the dramatic effect on grain refining efficiency caused by trace additions of zirconium.

Discussion

Figure 8 summarises the solidification conditions and phases present during holding in the melt in all three types of experiment. It has been shown that at high melt temperatures (in the glassy matrix studies) zirconium can substitute for titanium in TiB_2 ; however there is not expected to be any aluminide present under these conditions. In earlier glassy matrix studies,¹¹⁻¹⁶ an aluminide layer is present on borides held in a zirconium free aluminium alloy, but this layer is expected to form during the quench and not to be present during holding. If there is zirconium substitution for titanium in the TiB_2 particles during holding, then the lattice parameter of the boride increases, and it would be more difficult for an Al_3Ti layer to form on the surface of the boride phase because of the increased lattice mismatch. Thus the presence of zirconium in the boride particles, by preventing stabilisation of an aluminide layer on their surfaces, degrades their nucleation potency for aluminium.

If, however, the zirconium interferes with the aluminide phase then it may also destroy the potency of the nucleants, since although an aluminide layer may survive on the surface of borides, it is of a different and possibly less potent composition for the nucleation of aluminium.

In the doped refiner specimens both boride and aluminide particles are present and it is found that zirconium preferentially substitutes for titanium in the aluminide phase. In the grain refinement tests it is less obvious which



8 Schematic diagram of solidification conditions and phases expected to be present during holding in the melt in the three types of experiment in the present work: conventional grain refining tests, glassy matrix studies, and production of a doped refiner

phase is being interfered with. However, it is clear that both boride and aluminide can be affected by the presence of zirconium in the melt. For thin aluminide coatings coherent with the TiB₂ substrate, substitution of zirconium into the aluminide would have no effect on the in-plane atomic spacings, and therefore would be unlikely to have any effect on nucleation potency. For thicker layers, substitution of zirconium may even (Fig. 1) increase the potency. However, substitution of zirconium into the boride would always degrade the direct lattice matching with aluminium and make stabilization of an aluminide coating less likely.

Recently developed grain refiners based on the Al-Ti-C alloy system appear to be immune to poisoning by zirconium in high strength alloys.^{39,40} This distinctive behaviour further supports the view that the effect of zirconium is primarily on the nucleants themselves rather than on the alloy constitution, which should be affected similarly for both Al-Ti-B and Al-Ti-C systems. Mechanisms of refinement by Al-Ti-C will be investigated in future work.

Conclusions

The solute content in the melt has a strong effect on grain refinement through the growth restriction factor. However, the poisoning of Al-5Ti-1B refiner by zirconium leads to large increases in grain size, to which a decrease in growth restriction can make only a small contribution. Thus the main poisoning effect can be attributed to interference with the nucleation stage of grain refinement. As shown in earlier work, in the absence of zirconium, nucleation is on TiB₂ particles coated with Al₃Ti.¹⁶ It is found that, depending on the experimental conditions and crucially on the phases available, zirconium can interfere with both the aluminide and the boride phase during holding in the melt. If both phases are present, zirconium preferentially substitutes in the aluminide phase. However, the most probable reason for the destruction of potency of Al-Ti-B refiners is zirconium substitution into the boride phase, a process known to be enhanced by higher holding temperatures in the melt. The consequent expansion of the boride lattice parameter (in the basal plane) inhibits formation of an aluminide coating on the boride. Since aluminide coatings are known to be essential for effective nucleation, poisoning of the refiner action results.

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References

- M. E. J. BIRCH and P. FISHER: in 'Solidification processing 1987', (ed. J. Beech and H. Jones), 500-502; 1988, London, The Institute of Metals.
- D. G. McCARTNEY: *Int. Mater. Rev.*, 1989, **34**, 247-260.
- G. P. JONES and J. PEARSON: *Metall. Trans. B*, 1976, **7B**, 223-234.
- W. REIF and W. SCHNEIDER: *Giessereiforschung*, 1980, **32**, 53-60.
- M. E. J. BIRCH: in 'Aluminium-lithium alloys III', 152-158; 1986, London, The Institute of Metals.
- A. A. ABDEL-HAMID: *Z. Metallkd.*, 1989, **80**, 643-647.
- S. M. AHMADY, D. G. McCARTNEY, and S. R. THISTLETHWAITE: Proc. Conf. 'Light metals 1990', 837-843; 1990, Warrendale, PA, TMS.
- M. JOHNSON: *Z. Metallkd.*, 1994, **85**, 786-789.
- L. ARNBERG, L. BÄCKERUD, and H. KLANG: *Met. Technol.*, 1982, **9**, 7-13.
- G. W. DELAMORE and R. W. SMITH: *Metall. Trans.*, 1971, **2**, 1733-1738.
- P. SCHUMACHER: PhD thesis, University of Cambridge, UK, 1994.
- P. SCHUMACHER and A. L. GREER: *Mater. Sci. Eng. A*, 1994, **A178**, 309-313.
- P. SCHUMACHER and A. L. GREER: *Mater. Sci. Eng. A*, 1994, **A181/A182**, 1335-1339.
- P. SCHUMACHER and A. L. GREER: Proc. Conf. 'Light metals 1995', (ed. J. W. Evans), 869-877; 1995, Warrendale, PA, TMS.
- P. SCHUMACHER and A. L. GREER: Proc. Conf. 'Light metals 1996', (ed. W. Hale), 745-753; 1996, Warrendale, PA, TMS.
- P. SCHUMACHER, A. L. GREER, J. WORTH, P. V. EVANS, M. A. KEARNS, P. FISHER, and A. H. GREEN: *Mater. Sci. Technol.*, 1998, **14**, 394-404.
- A. L. GREER: *Metall. Mater. Trans. A*, 1996, **27A**, 549-555.
- M. E. J. BIRCH: Unpublished work.
- C. A. TARSHIS, J. L. WALKER, and J. W. RUTTER: *Metall. Trans.*, 1971, **2**, 2589-2597.
- J. A. SPITTLE and S. B. SADLI: *Mater. Sci. Technol.*, 1995, **11**, 533-537.
- M. JOHNSON: *Z. Metallkd.*, 1994, **85**, 781-785.
- S. E. NAESS and O. BERG: *Z. Metallkd.*, 1974, **65**, 599-602.
- M. A. KEARNS and P. S. COOPER: *Mater. Sci. Technol.*, 1997, **13**, 650-654.
- J. A. SPITTLE and S. B. SADLI: *Cast Met.*, 1994, **7**, 247-253.
- A. M. BUNN, A. L. GREER, A. H. GREEN, and M. A. KEARNS: in 'Solidification processing 1997', (ed. J. Beech and H. Jones), 264-267; 1997, Sheffield, The University of Sheffield.
- T. W. CLYNE and M. H. ROBERT: *Met. Technol.*, 1980, **7**, 177-185.
- H. KLANG: *Chem. Commun. Univ. Stockholm*, 1981, (4).
- W. A. ZDANIEWSKI: *J. Am. Ceram. Soc.*, 1987, **70**, 793-797.
- H. KOCH and W. REIF: Proc. 1st Int. Conf. on 'Production engineering and design for development', Vol. 2, 345-360; 1984, Cairo, Ain Shams University.
- F. A. CROSSLEY and L. F. MONDOLFO: *Trans. AIME*, 1951, **191**, 1143-1148.
- I. ANSARA: in 'Thermochemical database for light metal alloys', 53-56, 66-70, 1995, Brussels, European Commission.
- J. A. MARCANTONIO and L. F. MONDOLFO: *J. Inst. Met.*, 1970, **98**, 23-27.
- S. TSUREKAWA and M. E. FINE: *Scr. Metall.*, 1982, **16**, 391-392.

34. T. B. MASSALSKI (ed.): 'Binary alloy phase diagrams', 2nd edn, Vol. 1, 225–227, 241–243; 1990, Materials Park, ASM International.
35. 'Standard test procedure for aluminum alloy grain refiners: TP-1', The Aluminium Association, Washington, DC, USA, 1987.
36. P. SCHUMACHER, K. A. Q. O'REILLY, and B. CANTOR: in 'Solidification processing 1997', (ed. J. Beech and H. Jones), 281–284; 1997, Sheffield, The University of Sheffield.
37. W. T. KIM, M. GÖGEBAKAN, and B. CANTOR: *Mater. Sci. Eng.*, 1997, **A226-A228**, 178–182.
38. U. K. STOLZ, F. SOMMER, and B. PREDEL: *Aluminium*, 1995, **71**, 350–355.
39. P. HOEFS, W. REIF, A. H. GREEN, P. C. van WIGGEN, W. SCHNEIDER, and D. BRANDNER: Proc. Conf. 'Light metals 1997', (ed. R. Huglen), 777–784; 1997, Warrendale, PA, TMS.
40. W. SCHNEIDER, M. A. KEARNS, M. J. MCGARRY, and A. J. WHITEHEAD: Proc. Conf. 'Light metals 1998', (ed. B. Welch), 953–961; 1997, Warrendale, PA, TMS.



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