

# The Mechanisms of Grain Refinement in Dilute Aluminum Alloys

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The contribution of the peritectic reaction in producing grain refinement in aluminum alloys has been studied in three binary aluminum systems. It appears that titanium has a unique effect compared with zirconium or chromium; there is evidence of a refinement mechanism associated with the peritectic reaction in Al-Ti alloys which was not observed in the other two systems. Additions of boron to Al-Ti and Al-Zr alloys emphasizes the difference in effect of these two transition elements as grain refiners. The significance of the present work is discussed with reference to conflicts apparent in earlier experimental data.

THE mechanism of grain refinement of aluminum alloys by titanium and certain other transition elements has provoked considerable controversy. It has been suggested,<sup>1</sup> following the work of Iwasé *et al.*,<sup>2</sup> that the peritectic reaction occurring between intermetallic compounds, *e.g.* TiAl<sub>3</sub>, and the melt provides efficient substrates by sheathing the intermetallic crystals via the peritectic reaction in a layer of aluminum. Alternatively, the refining action has been explained<sup>3</sup> by the formation of simple interstitial carbides or borides of the refining addition which, because of close matching with the aluminum lattice, enhance nucleation of the solid phase. Experimental evidence in support of both suggested mechanisms has been summarized by Glasson and Emley,<sup>4</sup> but much of this earlier work is difficult to assess objectively because of wide variations in purity of the base materials and melt thermal history, and also in the methods employed to determine grain size. This investigation was undertaken to determine the relative contribution of each mechanism in promoting refinement in high purity aluminum when solidified under controlled conditions.

## EXPERIMENTAL WORK

The experimental technique resembled that of Crossley and Mondolfo<sup>1</sup> but with modifications to improve the reliability of grain size estimation and using base materials of higher purity, Table I. Master alloys were prepared and cast *in vacuo* to avoid contamination and possible uncontrollable effects on refinement by the use of fluxes.<sup>3</sup> Calculated amounts of master alloy and pure aluminum sufficient to produce a 150 g ingot of the required composition were placed in an alumina crucible which was then heated in a resistance furnace to 100°C above the alloy liquidus. After stirring, the crucible was transferred to a rig positioned between poles of an electromagnet and the alloy solidified in a unidirectional field of 2000 gauss. This procedure minimized gravity segregation of the crystallites and resulted in a more uniform vertical size distribution of grains. Without freezing in a magnetic field, a vertical section of an ingot would display a marked and

variable variation in grain size, rendering a single grain-size value of doubtful significance.

The ingots were sectioned horizontally 1 cm from the base and the bottom slice milled to 0.3 cm, the millings from the last two cuts being collected for analysis. Grain size was estimated by a linear intercept method across random diameters of this section;

Table I(a). Compositions and Suppliers of Materials Used

Metal	Form	Impurity Level, ppm	Method of Analysis	Source
Aluminum	Ingot	B 0.1	Mass Spectrograph	Aluminium Research and Development Ltd., Banbury.
		Ti 1		
		Zr 0.4		
		Cr 0.6		
		Fe 2		
		Si 11		
Titanium	Sponge	Na 100	Spectrograph	Johnson, Matthey and Co. Ltd.
		Sn 100		
		Fe 20		
		Si 2		
		Cu 1		
		Mg <1		
Zirconium	Rod	Fe 200	Spectrograph	Johnson, Matthey and Co. Ltd.
		Si 20		
		Ti 20		
		Al 10		
		Cu 5		
		Mg <1		
Chromium	Pellets	Fe 3	Spectrograph	Johnson, Matthey and Co. Ltd.
		Cu 1		
		Mg <1		
Iron	Sponge	Si 3	Spectrograph	Johnson, Matthey and Co. Ltd.
		Mn 2		
		Cu 1		
		Mg 1		
		Al 1		
		Ag 1		

Table I(b). Estimates\* of Carbon Contents of Alloying Additions

Metal	Carbon Content, wt pct
Titanium Sponge	<0.05
Zirconium Rod	0.03
Chromium	0.008
Iron Sponge	0.002

\*Supplied by Johnson, Matthey & Co. Ltd.

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error bars in the figures represent 95 pct confidence limits for the mean of six measurements.

The top sections of some of the ingots were remelted and solidified in the rig to determine the undercooling before solidification. A 30 SWG thermocouple, sheathed in an alumina tube except at the bead, was fixed 1 mm from the crucible base and allowed measurements to within  $\pm 0.1^\circ\text{C}$ .

This sequence of experiments was carried out on alloys of three binary systems, viz. Al-Ti, Al-Zr, and Al-Cr, on the assumption that if the "peritectic theory" was valid, the grain count/composition curves would be of the same form, whereas the curves for Al-Ti and Al-Zr would be similar but differ markedly from that for Al-Cr if the "carbide theory" held. The effect of boron in conjunction with titanium and zirconium was also examined by producing a series of casts of varying titanium and zirconium content together with a fixed, nominal, boron content of 0.005 wt pct.

In addition, several ingots of Al-Zr alloys were produced containing small additions of iron, an element which forms a eutectic with aluminum at  $655^\circ\text{C}$ . It was intended that the segregation of iron in the liquid ahead of the interface should depress the interface temperature to an extent comparable with Al-Ti binary alloys, *i.e.*, to generate equivalent "solute fields". Additions of antimony to Al-Cr alloys were also made.

### RESULTS

Grain size/composition relationships for the three systems are shown in Figs. 1 to 3 and typical values of

nucleation undercooling in Table II. The following points are significant:

1) The Al-Ti system differs from the other two in that very small titanium additions, (up to 0.02 pct), produce a sharp decrease in grain size followed by a slower rate of decrease up to approximately 0.15 wt pct Ti, the point at which primary  $\text{TiAl}_3$  crystals would first be expected to form. Beyond this level, grain size again decreases markedly. Both discontinuities are

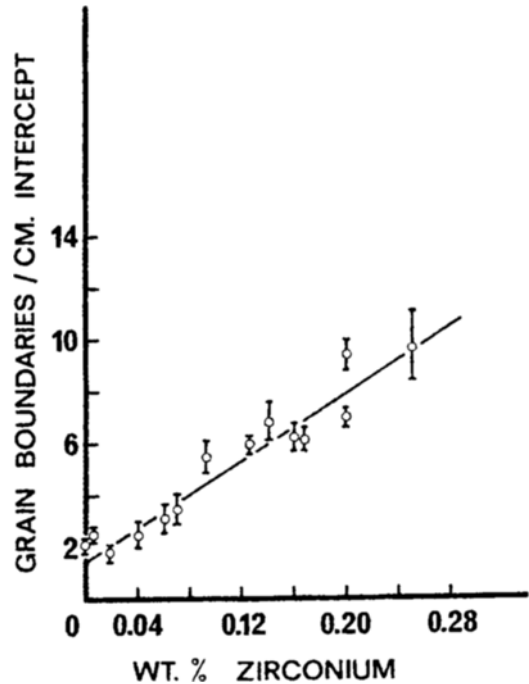


Fig. 2—Change in grain count on the addition of zirconium to aluminum.

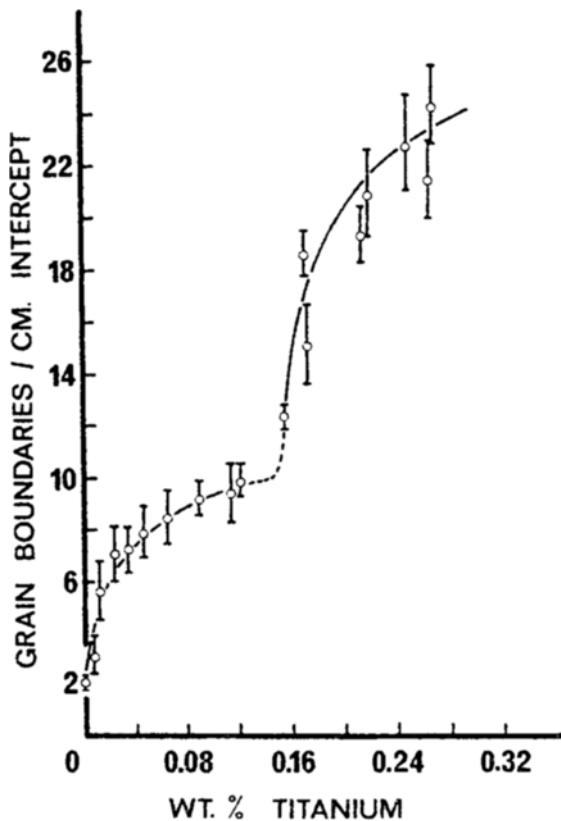


Fig. 1—Change in grain count on the addition of titanium to aluminum.

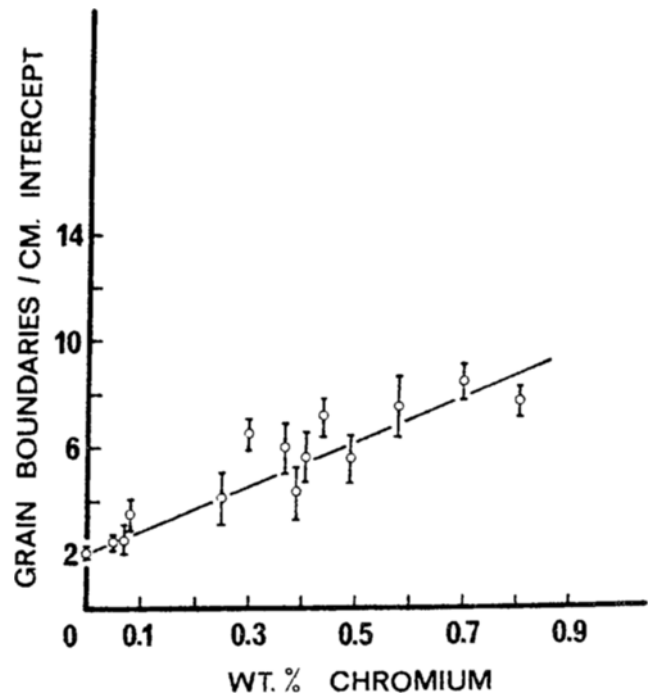


Fig. 3—Change in grain count on the addition of chromium to aluminum.

Table II. Undercooling Measurements

System	Composition, wt pct Addition	Measured Undercooling, °C	Average Undercooling, °C
Al		1.00	
		1.12	
		0.88	
		0.88	0.97
Al/Ti	0.034	0.37	
		0.50	
		0.50	0.46
	0.087	0.37	
		0.25	
		0.25	0.31
	0.215	0.87	
		0.62	
		0.50	0.67
	0.267	1.12	
		0.80	
		1.00	0.97
Al/Cr	0.073	4.40	
		5.25	
		2.90	4.20
	0.70	1.89	
		2.12	2.00
Al/Zr	0.063	1.12	
		0.75	
		1.12	
		1.00	1.00
	0.092	1.62	
		0.94	
		0.71	
		0.71	1.09
	0.20	0.55	
		0.50	
		0.50	
		0.67	0.57

Note: Each group of alloys is divided into those which would not be expected to freeze peritectically and those that would.

absent in the Al-Cr and Al-Zr systems, grain size decreasing steadily across the range of compositions examined.

2) Small additions of titanium reduce the undercooling for nucleation in Al-Ti alloys to low levels compared with equivalent amounts of chromium and, to lesser extent, zirconium. Peritectic Al-Ti alloys require larger undercoolings than nonperitectic alloys while the reverse is true in the other systems.

3) The singular effect of titanium compared with zirconium persists when boron is added to the melt. This is demonstrated when Figs. 4 and 5 are compared with Figs. 1 and 2, respectively. It should be noted that the ordinate intercepts in Figs. 4 and 5 indicate the grain size of the (Al + 0.005 wt pct B) alloy and not of aluminum. Marked grain-refinement occurs when boron is present in Al-Ti alloys whereas little change is observed for Al-Zr alloys.

#### DISCUSSION

When the data of Crossley and Mondolfo<sup>1</sup> and of Cibula<sup>3</sup> are examined, the experimental results appear to fit the particular theory being advanced in a most strikingly tidy fashion. This apparent tidiness is all the more surprising when it is recognized that each piece of work is claimed to refute the theory advanced by the other. In view of this, it would appear appropriate to bring together the present work with these earlier studies for the purpose of comparison. Un-

fortunately, Cibula's<sup>3</sup> results are such as to afford only a qualitative comparison with the others. This is given in Table III.

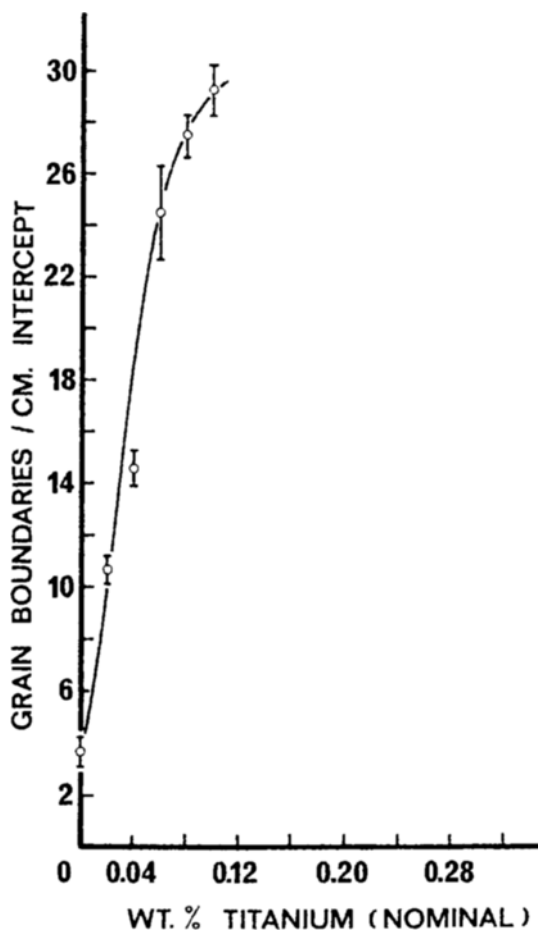


Fig. 4—Change in grain count on the addition of titanium to aluminum containing 0.005 wt pct boron.

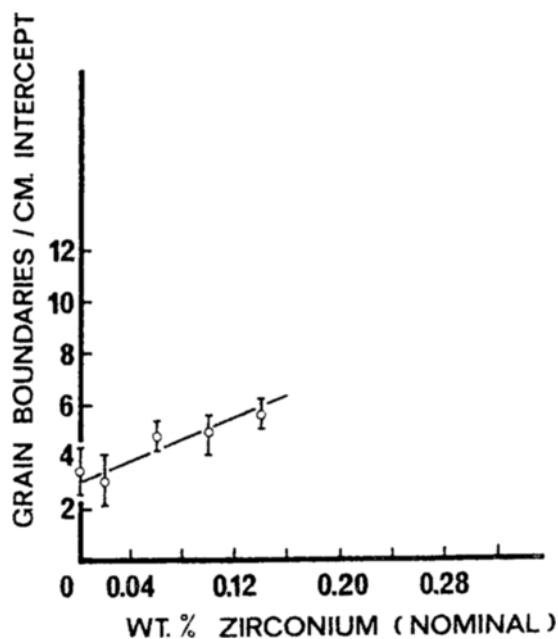


Fig. 5—Change in grain count on the addition of zirconium to aluminum containing 0.005 wt pct boron.

Table III. Collected Grain Refinement Results

Authors	Proposed Grain Refining Mechanisms	Element	Alloy System	Range of Composition	Expected Refinement	Observed Refinement	Observed Undercooling, Approximate °C	
							Alloys	Base Aluminum
Crossley & Mondolfo <sup>1</sup>	Primary intermetallic compounds react peritectically to give aluminum crystallization centers	Ti	Peritectic	S.S.	Insignificant	Insignificant	—	—
		Zr	Peritectic	S.S.	Significant	Very Significant	—	—
		Cr	Peritectic	S.S.	Insignificant	Insignificant	—	—
Cibula <sup>3</sup>	If $\frac{\text{Carbon atom Rad. (Rc)}}{\text{Solute atom Rad. (Rm)}} < 0.59$ a simple carbide forms which is an effective substrate for aluminum crystallization. Final grain size will depend on the effectiveness of the addition present in producing growth restricting solute fields.	Ti	Rc/Rm = 0.53 Forms simple carbide	S.S.	Significant	Significant	0	1 to 2
		Zr	Rc/Rm = 0.49 Forms simple carbide	S.S.	Significant	Slight	2.8	<0.5
		Cr	Rc/Rm = 0.63 Forms complex carbide	S.S.	Insignificant	Insignificant	—	—
Present Work <sup>5</sup>		Ti		S.S.		Very Significant	0.4	1
		Zr		S.S.		Very Significant	0.8	
				P.		Insignificant	1.0	
		Cr		P.		Significant	0.6	
				S.S.		Insignificant	4.2	
				P.		Significant	2.0	

S.S. Solid solution Alloys.

P. Peritectic Alloys.

A more detailed comparison of the present work with that of Crossley and Mondolfo<sup>1</sup> is shown in Fig. 6, in which the curves from Figs. 1, 2, and 3 are assembled together with data points abstracted from the latter's work. Whilst these workers<sup>1</sup> show their results in terms of grains per sq cm, they report that "the grain size of the specimens was measured by counting the grains intercepted by a line running horizontally on the polished face 0.3 in. from the bottom (of the ingot)". Presumably the grain count values were squared to give a grain count per unit area. Following this assumption, the square roots of the reported values have been plotted against composition for the Al-Ti, Al-Zr, and Al-Cr systems. To avoid confusion with the present work, no 'best fit' curves have been included to this data.

As seen in Table III, the present work shows that additions of zirconium and chromium produce very similar grain refinement. This would be predicted by the peritectic theory but runs contrary to expectation from Cibula's carbide theory. However, Table III shows that all the experimental data for the Al-Zr and Al-Cr solid solution alloys are in agreement, *i.e.*, little grain-refinement. Thus, on closer inspection, Cibula's own data does not support the generality of his postulate that transition metal carbides with simple structures grain refine aluminum.

The present work also shows that peritectic Al-Zr and Al-Cr behave similarly, in accord with the findings of Crossley and Mondolfo but not of Cibula in that the latter found virtually no refinement in any of the Al-Cr alloys, evidence used to dismiss the peritectic theory of refinement. Thus the Al-Zr and Al-Cr results of

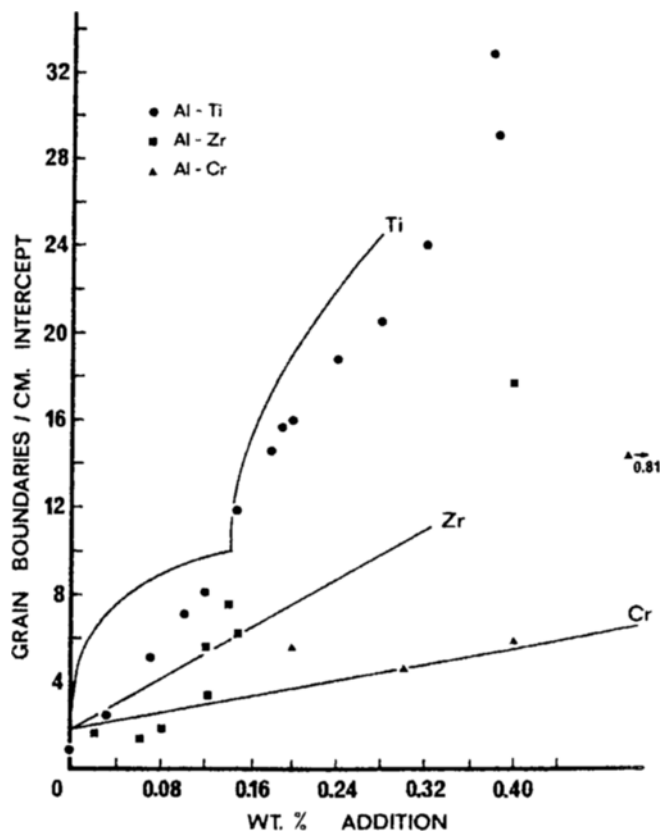


Fig. 6—Comparison of present work with that of Crossley and Mondolfo.<sup>1</sup> Full lines represent the curves transposed from Figs. 1, 2, and 3; data points are those obtained from the results of Crossley and Mondolfo.

Table III indicate that whereas the peritectic reaction might produce grain refining, unless the results are due solely to solute concentration effects, the ability of the transition element addition to form a simple carbide most certainly is not a sufficient condition.

The case of titanium as a grain-refining element is unique, since the present work shows significant grain refinement occurs even in solid-solution alloys. This was not observed by Crossley and Mondolfo but forms the basis on which Cibula constructed his own (carbide) theory of the action of aluminum hardener alloys. The various implications of the Al-Ti results may be explored further with the aid of Figs. 1, 2, 3, and 6.

The grain size/composition plots show that as Ti, Zr, or Cr are added to aluminum, the grain size decreases. In the case of titanium additions, Fig. 1, this decrease is initially very marked, then falls off as alloy composition approaches the peritectic range, in which it decreases sharply again. This would suggest a two-stage refinement process, possibly nucleation by a compound in the solid solution alloys, and via a peritectic reaction in the others. However, no sharp changes of grain size with composition were observed with the zirconium, Fig. 2, or chromium alloys, Fig. 3, merely a gradual decrease of grain size with increasing composition. Thus it may be concluded that the peritectic reaction is not inevitably a grain-refinement mechanism in aluminum alloys since its effectiveness may be linked to other variables, such as the growth restriction potentially available in any particular system.

It was noted that the peritectic horizontals in the Al-Ti, Al-Zr, and Al-Cr systems are 5°, 0.5°, and 1°C, respectively, above the melting point of pure aluminum and so growth restriction would be likely to be more effective in the Al-Ti system than in the other two. Because of this, the small additions of iron to several Al-Zr alloys and antimony to Al-Cr alloys were made to provide growth restricting solute fields around growth centers comparable with those likely in the Al-Ti alloys. The results of these experiments<sup>5</sup> showed that growth restriction is not the major factor in determining the difference in refining action of titanium as compared with zirconium and chromium.

For the peritectic reaction to provide a source of grain refinement as compared with solid solution alloys or base aluminum, it is necessary that a) the peritectic reaction occurs with less undercooling than that necessary to activate the heterogeneous nuclei normally responsible for the initiation of freezing in the solid solution alloys or base aluminum; or b) these heterogeneous nuclei be rendered inactive, possibly by being consumed as a result of nucleating the primary intermetallic phase; in addition, c) more crystallites of aluminum must exist in the melt immediately peritectic action ceases than would normally be present after the initiation of freezing in the non-peritectic range material. This last requirement could be met with contributions from either or both of two multiplication mechanisms. The first of these takes note of the fact that the liquidus curves bounding the intermetallic phase is very steep and hence significant undercooling may take place before the primary intermetallic phase appears. Dendrite remelting<sup>6</sup> could then provide many growth centers from a single nucleation event. The second multiplication mechanism is concerned with the manner in which the peritectic reaction can break up the primary phase

and so produce many aluminum crystallites from a single primary intermetallic crystal.<sup>2</sup> It has been demonstrated<sup>7</sup> that, in some systems at least, the peritectic phase may isolate dendrite arms by complete reaction at the neck; convective movement in the melt may then allow partial remelting of the peritectic phase and separate side arms from the main dendritic stem. This type of mechanism can be operative even when the primary intermetallic phase does not form a branched structure to any extent and so no metallographic evidence of fragmentation would be obtained.<sup>1</sup>

Further insight into the nucleating processes occurring in the present work may be obtained by examining the undercoolings recorded for the various alloys. With the exception of the Al-Ti alloys, the peritectic alloys\*

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\*The undercooling recorded is that occurring at the peritectic horizontal.

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tended to undercool less to form aluminum than did the solid solution alloys, thus indicating that the peritectic reaction might well promote refinement, although it should be pointed out that in the absence of more active nuclei, a combination of effective growth-restricting solute fields and a crop of a particular relatively inactive nuclei could give a refined structure. That the recorded undercooling for the Al-Cr solid solution alloys was significantly greater than that for the base aluminum would indicate that chromium additions modify the heterogeneous nuclei in the aluminum.

The undercoolings observed for the Al-Ti alloys are particularly interesting in that the solid solution alloys undercool appreciably less and the peritectic alloys slightly less than the base aluminum. One interpretation of this is that, on the addition of titanium to aluminum, very efficient substrates form but that these are consumed in the formation of a shower of primary intermetallic particles. Then, as the latter move through the peritectic reaction and because no more effective substrates are present, they will act as the major growth centers. This hypothesis overcomes the objection which has been raised<sup>8</sup> that examples of peritectic reaction nucleation evade the question of how the primary phase is itself nucleated. Thus, the very special behavior of titanium as a grain-refining addition is believed to be linked with the formation of particles in the melt, perhaps carbides, which are capable of refining not only the aluminum solid solution at compositions <0.15 wt pct Ti but also the TiAl<sub>3</sub> phase in peritectic alloys. The two refinement steps in the grain count/composition plot, Fig. 1, are therefore interdependent—the second would not exist in such a pronounced form without the first.

It is seen, Table III, that the few recorded undercoolings of Cibula are in general agreement with those of the present study.

The grain count/composition data of Crossley and Mondolfo, when replotted in Fig. 6, are most interesting. Gone are the very marked kinks which had been drawn in as occurring at the peritectic plateau termination composition, being replaced by what would be a small inflection in the case of Al-Ti, a somewhat larger inflection for Al-Zr, but none for Al-Cr. Had any estimates of the experimental error been given in this earlier work, then the picture might be different. As it is, the present authors conclude that the results of Crossley and Mondolfo give only scant support to the hypothesis that the peritectic reaction "per se"

provides grain refinement. It is, however, acknowledged that Mondolfo's more recent work<sup>9</sup> demonstrates that primary intermetallic phases can nucleate aluminum with little or no undercooling.

#### ALLOYS CONTAINING BORON

It has been generally accepted that small additions of boron to Al-Ti alloys enhance refinement by producing  $TiB_2$  crystals which are particularly effective nucleating substrates. More recently, Davies *et al.*<sup>10</sup> suggested that the action of boron is to allow formation of  $TiAl_3$  at low titanium concentrations and that these particles rather than  $TiB_2$  are the growth centers. The present results, Figs. 4 and 5, indicated marked enhancement of refinement in Al-Ti alloys by small boron additions but similar additions to aluminum-zirconium alloys produce no extra refinement compared with melts containing no boron. These results confirm the earlier work of Cibula and are in line with the difference in effect noted here between the Al-Ti and Al-Zr binary systems. It is not possible to distinguish between the alternative suggestions on the basis of these results but it is clear that any proposed mechanism of refinement must account for these differences.

#### CONCLUSIONS

1) The generalized grouping of certain transition metals as strong grain refiners of aluminum based on their ability to form simple interstitial carbides is not supported by this investigation since the refinement

mechanism of zirconium does not resemble that of titanium.

2) A peritectic reaction in aluminum alloys is not automatically associated with grain refinement although it appears to provide an additional source of refinement in the Al-Ti system.

3) The addition of boron to Al-Zr alloys produces no enhancement of grain refinement, as compared with Al-Zr binary alloys, whereas grain-size is reduced by a factor of 2 to 3 in the case of Al-Ti alloys.

#### ACKNOWLEDGMENTS

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