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Off-Eutectic Composite Solidification and Properties in Al-Ni and Al-Co Alloys

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To investigate the range of "coupled" eutectic growth in Al-Co alloys from 1 to 4 wt% Co and Al-Ni alloys from 5 to 10 wt% Ni directional solidification, using rates from 0.8×10^{-2} cm/sec to 10.6×10^{-2} cm/sec, was employed. Both alloy systems exhibited coupled zones skewed towards the hypereutectic compositions. Fully eutectic structures were obtained in the ranges Al-1 wt% Co to Al-3 wt% Co and Al-5.7 wt% Ni to Al-9.2 wt% Ni.

The off-eutectic alloys which exhibit a fully eutectic structure behave as reinforcing composite materials, with the tensile strength and microhardness increasing as the volume fraction of the strengthening phase increases.

1. Introduction

The demonstration by Hertzberg *et al* [1] of the composite behaviour of aligned eutectics and the evidence of Mollard and Flemings [2], Cline [3] and Sheppard [4] that aligned eutectics could be grown at off-eutectic compositions, have indicated the potential usefulness of directionally solidified eutectics in reinforced composite applications. Unfortunately, alloy systems whose eutectic phases are suited for composite behaviour usually exhibit equilibrium diagrams which make the practical application of the solidification conditions proposed by the Mollard and Flemings' criterion extremely difficult.

Recently Cline and Livingston [5] have demonstrated that compositional variation in the Sn-Pb eutectic and a consequent variation in the volume fractions of the eutectic phases can be achieved by another approach, the employment of high growth rates. They were also able to maintain the unidirectionality of the microstructure by suitable design of the solidification apparatus.

The conditions necessary for interface stability at off-eutectic compositions have yet to be quantitatively established [6]. However, the Pb-Sn alloys behaved in a manner qualitatively predictable by the competitive growth concept originated by Tammann and Botschwar [7] and more recently applied to metal systems by Hunt and Jackson [8]. The basis of this concept is that the structure formed, eutectic or eutectic plus dendrites, depends on which structure grows with the smallest degree of undercooling at a given growth rate. Thus, if the two phases can solidify simultaneously in a diffusion coupled fashion at a smaller degree of undercooling than dendrites of either single phase, then no dendrites will form.

The Pb-Sn system was convenient to study the high-rate coupled-growth which produced an aligned structure. However, neither of the eutectic phases in this system shows significant strength. It was decided, therefore, to apply the high growth rate technique to determine the range of "coupled" growth in Al-Co and Al-Ni alloys. The alloys exhibiting coupled microstructures could then be mechanically tested for reinforcing composite behaviour.

2. Experimental Procedure

2.1. Directional Solidification

Aluminium (99.999%)-cobalt (99.87%) alloys in the range 1 to 4 wt% Co and aluminium-nickel (99.99%) alloys in the range 5 to 10 wt% Ni were melted in graphite crucibles and cast into graphite moulds to produce rods 6 mm in diameter and 180 mm long. These alloy rods were unidirectionally solidified at rates from 0.8×10^{-2} to 10.6×10^{-2} cm/sec. For some samples, not required for mechanical testing, growth rates as low as 2.8×10^{-3} cm/sec were used.

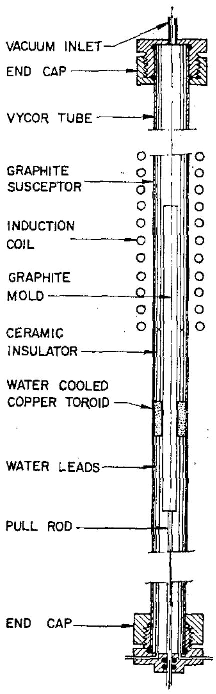

Figure 1 Schematic diagram of directional solidification apparatus.

Fig. 1 is a schematic of the apparatus used for directional solidification. A 200 mm long induction coil surrounds a Vycor tube enclosing a graphite susceptor. The graphite susceptor is separated from the bottom cooling coil by a ceramic insert. Vertical directional solidification was accomplished by first melting alloy samples contained in graphite moulds of 9 mm outer diameter and 200 mm long and then withdrawing them through the bottom cooling toroid. Solidification was carried out under argon.

The directionally solidified rods were sectioned transversely, electrolytically polished and etched in a 5 vol % perchloric acid-methanol electrolyte and examined for the presence of primary dendrites. Samples exhibiting entirely "coupled" microstructures were also examined on a scanning electron microscope.

2.2. Mechanical Testing

Tensile specimens of 3.2 mm diameter and 13 mm gauge length were machined from all rods which exhibited a "coupled" microstructure. These were tested on an Instron testing machine at a strain rate of 6.7×10^{-4} sec^{-1}.

Microhardness measurements were taken from transverse sections of these alloys, employing a pyramid diamond indenter and a load of 16.5 grams. Since all the samples displayed a cellular structure, these measurements were confined to the central portion of the cells.

3. Experimental Results and Discussion

3.1. Microstructure

All specimens contained some percentage of eutectic growth, in the form of rods of the intermetallic phase in an aluminium matrix.

Figs. 2 and 3 indicate the range of the entirely "coupled" growth region as a function of growth rate and alloy composition for the Al-Co and Al-Ni systems. In both cases, the zone of "coupled" growth is skewed towards the hypereutectic compositions. That is, alloys increasingly rich in Ni or Co can be grown in a eutectic manner by increasing the growth rates. In the Al-1 wt % Co alloys (the eutectic composition), primary aluminium dendrites appear at the faster growth rates, whereas in the Al-Ni system the eutectic composition is included in the coupled region for the growth rates investigated.

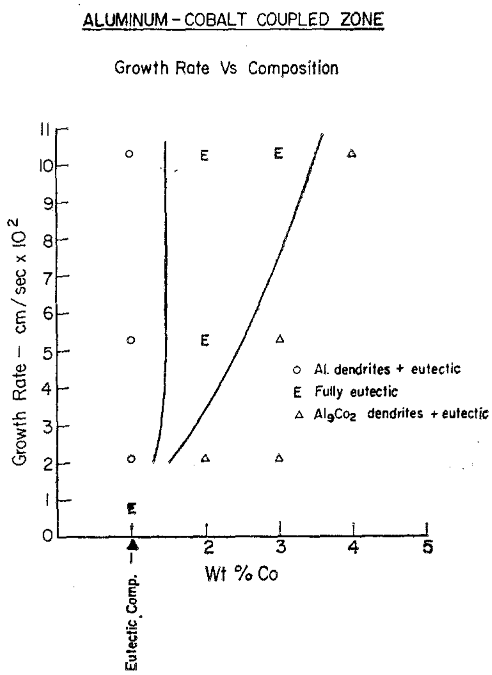

Figure 2 Growth-rate versus alloy composition plot showing range of coupled growth for Al-Co alloys.

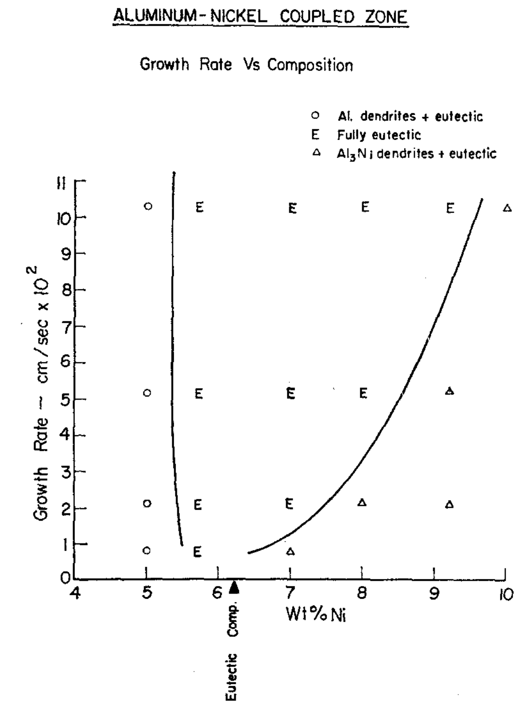

Figure 3 **Growth-rate versus alloy composition plot showing range of coupled growth for Al-Ni alloys.**

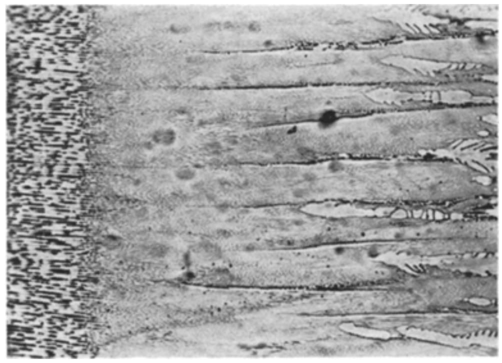

Figure 4 **Longitudinal section of the quenched interface of an Al-1 wt % Co alloy directionally solidified at 2.8×10^{-3} cm/sec prior to quenching, growth direction from left to right (× 175).**

In the coupled growth region of these alloys the eutectic structure has grown with smaller degrees of undercooling for a given growth rate than the respective faceted proeutectic Al_3Ni or Al_9Co_2 phase. To maintain this condition at increasingly hypereutectic concentrations and correspondingly higher liquidus temperatures, higher growth rates are required. It is possible in this case that the "coupled" zone is enlarged somewhat by the imposed temperature gradient [5] which would serve to stifle dendritic growth. This competitive aspect is observed in the start end of the hypereutectic rods where primary dendrites started to grow, but were replaced within 1 cm of growth by a fully eutectic structure.

In the case of the hypoeutectic or eutectic compositions, the growth rate versus undercooling relationship is somewhat different, in that the growth kinetics of the primary nonfaceted aluminium dendrites are similar to those of the eutectic. For the Al-Co system at the eutectic composition primary aluminium dendrites grow at smaller degrees of undercooling than the eutectic structure for growth rates in excess of 2.1×10^{-2} cm/sec. This feature is shown in fig. 4 which is the quenched interface of an Al-1 wt % Co alloy (eutectic composition) directionally solidified at 2.8×10^{-3} cm/sec prior to quenching. In the quenched zone where the growth rate is considerably higher the eutectic microstructure has been replaced by the aluminium dendrites plus eutectic microstructure.

Several authors [9, 10] have shown that the presence of impurities can cause the breakdown of a planar eutectic interface into a cellular or colony structure unless proper control is maintained over the growth rate and thermal gradient in the liquid at the interface. The growth conditions employed in these experiments were not adequate to prevent some constitutional undercooling and all the eutectic structures exhibited a cellular structure which became finer with increasing growth rate.

The number of rods of Al_3Ni per unit area were measured from scanning electron photomicrographs taken near the central section of the cells. These measurements were converted to average rod spacings by applying the following formula [11],

$$\bar{\lambda} = \sqrt{\frac{2}{\sqrt{3}.\rho}}\,. \qquad (1)$$

where $\bar{\lambda}$ is the average spacing from the centre of one rod to the centre of its nearest neighbour and ρ is the number of rods per unit area.

When the results of these measurements were plotted versus the corresponding solidification rates, the $\bar{\lambda}$ versus $R^{-\frac{1}{2}}$ relationship proposed by Tiller [12] (where R is the growth rate) appears to be maintained for the Al-Ni off-eutectic alloys.

Similar measurements were done on the Al-2

TABLE I

Alloy	Solidification rate ($\times 10^{-2}$ cm/sec)	Average rod spacing $\bar{\lambda}$ (μm)	VHN	UTS (kg/mm²)
Al-1 wt % Co	0.8	—	33	9.9
Al-2 wt % Co	5.3	—	49	21.1
Al-2 wt % Co	10.6	0.30	57	20.0
Al-3 wt % Co	10.6	0.32	59	20.3
Al-5.7 wt % Ni	0.8	0.60	55	29.5
				26.1
				33.3
	2.1	0.44	60	26.3
				21.7
	5.3	0.32	67	26.3
				29.4
	10.6	0.23	79	27.7
				28.7
				29.2
Al-7 wt % Ni	2.1	0.43	66	27.7
	5.3	0.33	77	27.5
	10.6	0.21	83	31.6
				32.2
				36.1
Al-8 wt % Ni	5.3	0.28	78	22.2
				23.3
	10.6	0.22	89	32.2
				34.4
				34.9
Al-9.2 wt % Ni	10.6	0.18	100	37.5
				38.6
				33.5

wt % and 3 wt % Co alloys which exhibited a rod-like morphology at a growth rate of 10.6×10^{-2} cm/sec. These data have been included in table I.

3.2. Mechanical Properties

The tensile and microhardness data for the Al-Co and Al-Ni alloys are presented in table I. The tensile data has also been comparatively evaluated with the theoretical analysis of Hertzberg *et al* for composite behaviour of Al-Ni alloys in fig. 5. It is felt that the inclusion of the Al-Co data in this comparison is reasonable since the alloy exhibits a eutectic microstructure similar to that of Al-Ni, and the Al_9Co_2 strengthening phase has a microhardness value [13] close to that of Al_3Ni. It is noted that an increase in the microhardness and the tensile strength occurs as the volume fraction of the intermetallic constituent increases. However, a considerable degree of scatter is associated with the tensile data and these values fall below the predicted values with higher volume fractions of the strengthening phase.

Investigation of the fracture surfaces and the microstructure in the area of the fracture showed evidence of three microstructural defects which could contribute to this scatter and less-than-ideal strengths. Some samples, notably Al-3 wt % Co, 10.6×10^{-2} cm/sec, exhibited primary Al_9Co_2 dendrites oriented transversely to the growth axis. Presumably these dendrites had nucleated heterogeneously ahead of the advancing coupled interface. Although the central portion of the specimen exhibited a "coupled" microstructure the presence and orientation of these dendrites acted to reduce the overall strength of the sample. The second defect observed was the presence of voids in almost all the samples. The voids appear to be gas voids rather than shrinkage cavities and were apparently present in the as-cast rods.

The final microstructural defect is the presence of the cell structure mentioned earlier. Cell walls would be weaker than an ideal composite because of the presence of fibre depleted zones and the misoriented fibres there [9, 12]. This is

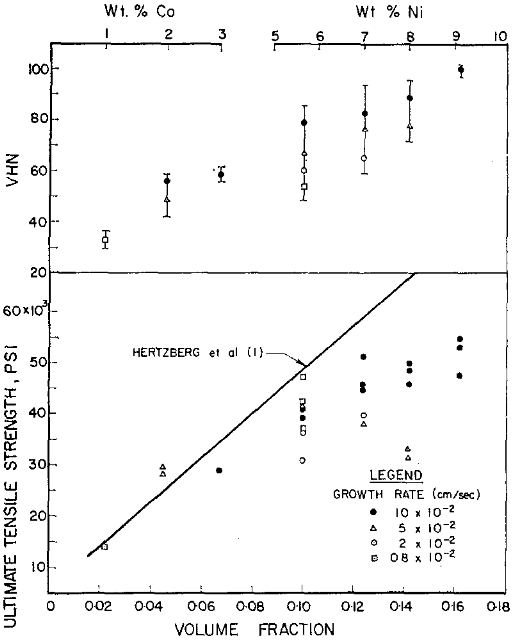

Figure 5 Ultimate tensile strength and microhardness values versus alloy composition for the Al-Co and Al-Ni alloys exhibiting "coupled" microstructures.

shown in fig. 6 where the fracture has followed the cell walls.

It is anticipated that by improving the heat transfer in the directional solidification equipment, proper processing of the alloy rods, e.g. vacuum melting or extrusion, and using higher purity alloys, these defects could be minimised.

The possible improvement in tensile strength by virtue of an increased growth rate and thus finer structures [14] is borne out by the microhardness results for the Al 5.7-wt % Ni and Al-7 wt % Ni alloys, since in both cases an increase in microhardness is noted with increasing growth rate.

In regions where dendrites and voids were absent, fractographic examination showed that the alloys behaved much like other composite materials. It was observed that fibre fracture occurred in front of the crack tip, indicating that the load was being transferred from the matrix to the fibres.

After fracture of the fibres, failure of the surrounding matrix is by shear, with the shear crack linking up the voids formed by the fibre fractures. This is illustrated in fig. 7, where a large number of the dimples, which are characteristic of such ductile shear failures, can be seen.

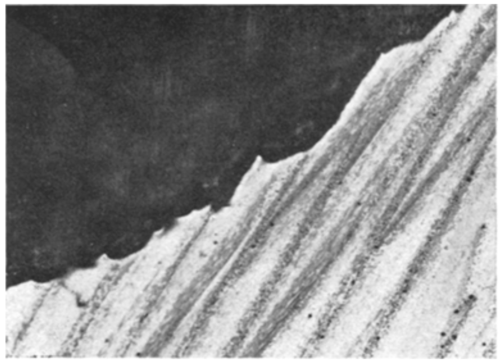

Figure 6 Longitudinal section of the fracture surface in an Al-8 wt % Ni alloy directionally solidified at 5.3×10^{-2} cm/sec showing how the fracture has followed the cell walls ($\times$ 160).

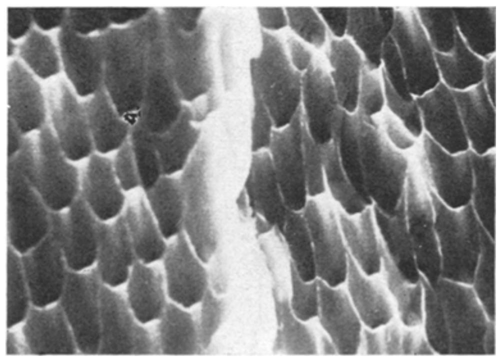

Figure 7 Scanning electron photomicrograph of the fracture surface in an Al-5.7 wt % Ni alloy directionally solidified at 0.8×10^{-2} cm/sec showing shear failure of the matrix. Examination at the base of "cupped" regions showed the presence of a number of fibre fracture surfaces ($\times$ 7000).

The white band across the centre of this figure is the step at a cell wall, so that the focus on one side of the step is much better than on the other side. Observation of the surface at the base of the sheared matrix regions showed the presence of a number of fractured fibres, indicating possible simultaneous failure of groups of fibres.

4. Conclusions

(1) At high solidification rates the Al-Co and Al-Ni alloys exhibit a compositional range in eutectic structures skewed towards the hyper-eutectic compositions.

(2) The $\bar{\lambda}\ \alpha\ R^{-\frac{1}{2}}$ relationship for the Al-Ni alloys persists at off-eutectic compositions.

(3) The Al-Co eutectic undergoes a transition

from a broken-lamellar to a rod-like morphology with increasing growth rate.
(4) The off-eutectic alloys behave as reinforcing composite materials with the tensile strength and microhardness increasing as the volume fraction of the strengthening phase increases.
(5) The presence of a cellular microstructure, non-directional proeutectic constituents, and gas voids decreases the ultimate tensile strengths below their theoretical values.

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