5.   STRUCTURE: GRAIN REFINEMENT, MODIFICATION, AND MICROSEGREGATION

Much important work has been published in *Light Metals* on nucleation of grains and formation of intermetallics during solidi.cation. Grain refinement forms a major part of these works including the practical and economic aspects of grain refinement. From time to time papers on modification of Al-Si alloys have also been published in *Light Metals.* The so-called "fir tree" defect related to the formation of various iron intermetallics has received much attention, and these *Light Metals* papers are a very useful resource for anyone tackling this important industry problem.

GRAIN REFINEMENT IN ALUMINUM ALLOYS

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Abstract

The published information on the mechanism of grain refinement by Ti
and Ti + B additions is reviewed, with emphasis on the data in support
of nucleation by $TiAl_3$.

The various effects of grain refinement such as reduced cracking,
increased interdendritic spacing, coarser constituent distribution,
tendency for coarse primary crystals formation, are shown and explained
on the basis of the reduced undercooling due to early nucleation. Data
are presented showing the enhanced tendency for germination and reduced
hot formability produced by grain refinement.

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Mechanism of Grain Refinement

The marked improvement of properties produced in aluminum alloys by
small additions of Ti, Zr, V, etc. has been known for almost 50 years
(1,2) and its exploitation is standard practice in the casting of alumi-
num alloys. At first the improvement was attributed to a scavenging
effect (1), but soon (2) it was established that the better properties
resulted from pronounced grain refinement, mainly due to enhanced nuclea-
tion.

In spite of the long and widespread knowledge of its effect, the
exact mechanism of grain refinement is still under discussion. Two
main theories have been presented:

1. The carbide (or boride) theory (3, 4)
2. The peritectic reaction theory (5, 6)

Other theories based on viscosity (7) electronic shells (8),
liquid structure (9), do not seem to really explain the mechanism of
refinement.

The carbide theory attributes the nucleation to the presence in the
melt of abundant and well-dispersed crystals of Ti, Zr, V, etc. carbides
nitrides, or borides, on which the aluminum can nucleate. The peritectic
theory assumes that when the crystals of $TiAl_3$, $ZrAl_3$, $TaAl_3$, VAl_{10},
etc. react peritectically with the liquid above the melting point of
aluminum, they create small crystals of aluminum on which the freezing
metal can grow without further nucleation. There is a large amount of
experimental data, but a clear-cut decision on which of the two theories
is correct has not been reached.

In favor of the peritectic reaction militate the following factors:

1. Grain refinement in binary systems increases abruptly when the
    percent of refiner corresponds to the beginning of peritectic
    reaction (6, 10, 11, 12, 13, 14) (Fig. 1).

2. Undercooling for nucleation disappears completely when grain
    refiners are added (Fig. 2); in most cases the freezing starts
    at the peritectic temperature, or at least above the freezing
    point of the metal (15).

3. Optical and electron micro-examination and microprobe analyses
    reveal that $TiAl_3$ crystals are surrounded by a halo of Ti-rich
    Al solid solution (Fig. 3) (6, 16, 17, 18).

4. In Ti + B alloys the $TiAl_3$ crystals are mostly at the center of
    the grains, TiB_2 crystals mostly between the dendrites' arms
    (16) (Fig. 4).

5. The orientation relationships between $TiAl_3$ and Al have
    low disregistries (15, 16).

6. Similar results, although not always as clear-cut, can be obtained with other peritectically-reacting elements such as V, Zr, Mo, W, Nb, Ta, Hf, etc. and the refinement is most pronounced by those elements with the higher peritectic temperature (Ti, Ta, Hf) (4, 6, 11, 12, 13, 19, 20, 21).

In favor of the TiC or TiB$_2$ nucleation militate:

1. Addition of the carbides or borides produces grain refinement (3, 4, 19, 22, 23, 24, 25, 26, 27).

2. Undercooling for nucleation of Al by AlB$_2$ is small (15).

3. Electron microscope and microprobe analyses have revealed the existence of TiC or TiB$_2$ particles within Al crystals (28, 29).

4. Orientations relationships with low disregistry have been detected for TiC (29) and AlB$_2$ (15).

The main objection to direct nucleation of Al by carbides or borides in presence of TiAl$_3$, is that TiAl$_3$ nucleates aluminum at the peritectic temperature or close to it, that is above the freezing point of aluminum. AlB$_2$ nucleates aluminum a few degrees below its freezing point and the same is probably true for TiB$_2$ and TiC. It is well-known that, especially at the low cooling rates, only the nucleant that acts at the highest temperature can nucleate; less efficient ones do not get a chance to act.

There is one way to reconcile the evidence for the carbides and borides, together with the peritectic reaction. The main assumption to be made is that TiC reacts with Al and/or with oxygen, so that some of the carbon is removed either as Al$_4$C$_3$ or as CO, and Ti becomes available to form a more or less continuous sheath of TiAl$_3$ on the TiC particle. In the case of TiB$_2$ the reaction would be TiB$_2$ + Al → (AlTi)B$_2$ + TiAl$_3$. The fact that heavy carbon additions to Ti (or Zr) bearing alloys reduce or even eliminate grain refinement (6, 30, 31) rather than enhance it, can be considered indirect support for TiAl$_3$ being necessary for grain refinement. More direct support for the reactions above can be found in the literature: the finding that no refinement can be obtained by adding TiC and melting and casting in vacuum, but that grain refinement can be obtained in air (24) points to oxidation of C to liberate Ti for TiAl$_3$ formation. In the photograph of (29) which shows nucleation of Al by TiC, there is an intermediate layer, which could be TiAl$_3$. The small particles of Al$_4$C$_3$ at the interface would result from the reaction of Al with some of the C liberated by the formation of TiAl$_3$. The presence of an orientation relationship--

(100)TiC||(100)Al   [001]TiC||[001]Al

does not preclude an intermediate layer of TiAl$_3$: a relationship between TiC and TiAl$_3$

(100)TiC||(100)TiAl$_3$;   [001]TiC||[001]TiAl$_3$

has been detected (32). Since nucleation of Al on TiAl$_3$ with the relationship

(001)TiAl$_3$||(001)Al;   [100]TiAl$_3$||[100]Al

is the second most frequent one (15), the presence of a TiAl$_3$ intermediate layer would not change the relationship between TiC and Al. It is interesting to note that a TiAl$_3$ layer formed on TiC, should have an expanded lattice to reduce disregistry and that this expansion would reduce the disregistry between TiAl$_3$ and Al (Fig. 5) and facilitate nucleation.

The same argument applies to TiB$_2$. The compound in equilibrium with Al is not TiB$_2$, but (AlTi)B$_2$, with variable Al and Ti contents (32). When TiB$_2$ is added to Al, some of the Ti is replaced and made available for the formation of TiAl$_3$. In the microprobe photos by Moriceau (28) of TiB$_2$ in Al, the B shadow is much smaller than the Ti shadow, indicating a TiB$_2$ particle surrounded by a Ti-rich, but B-poor layer. Positive evidence of this reaction has been shown by Bäckerud (33): TiB$_2$ immersed in liquid Al soon becomes coated with a sheath of TiAl$_3$. In this case, too, the TiB$_2$ substrate would facilitate nucleation by TiAl$_3$; assuming a relationship (001) TiB$_2$||[112] TiAl$_3$, the disregistry would force an expansion of the TiAl$_3$ lattice which would decrease the disregistry for nucleation of Al in the (112) TiAl$_3$||Al orientation.

The formation of a TiAl$_3$ layer on TiC or TiB$_2$ explains nucleation at hypo-peritectic concentrations. TiC and TiB$_2$, because of their high melting points and limited solubility in Al, can survive the superheating that dissolves hypo-peritectic TiAl$_3$ particles. In cooling they become coated with a layer of TiAl$_3$, which has no time to dissolve in the Al. Thus even in hypo-peritectic alloys TiAl$_3$ crystals are available to undergo the peritectic reaction and create nuclei for Al. Another objection to nucleation by TiAl$_3$, namely what nucleates TiAl$_3$, (34) also disappears. Even if the melt is heated above the melting points of TiC or TiB$_2$, in cooling they crystallize at temperatures well above the freezing point of Al, and can nucleate TiAl$_3$ before the peritectic temperature is reached.

Thus, all the available evidence is consistent with the peritectic reaction being the grain refining one, with carbide or boride nucleation of TiAl$_3$ being a preliminary step.

Effect of Grain Refinement

The change of grain size that results from the addition of grain refiners is accompanied by side effects, some beneficial, some deleterious.

One of the beneficial effects is shown in Figure 6, which shows the same metal DC cast in exactly the same conditions, the only difference being that 0.05 Ti, 0.01% B were added to billet B. Not only the grain size has been drastically reduced, but the center cracks have been eliminated. Elimination of crack results from earlier nucleation; alloys containing grain refiners are nucleated at their freezing point or above it (Figure 2) and crystallization with low undercooling is slower, thus reducing internal tensions.

In continuous casting often cracks can be eliminated by close control of the casting conditions, but it is much easier to add few pounds of grain refiner to the furnace and be sure that, even if the pouring temperature is off by some 30°C, the water temperature varies from morning to evening and the sprays are somewhat clogged with dirt, castings that can be rolled or extruded are obtainable. Another beneficial effect claimed for grain refinement: sheet or extrusions from grain refined billets tends to have a more homogeneous and brighter surface after anodizing and less tendency to streaking.

In Figure 7 is shown a streaked extrusion, that came from a grain refined billet. Examination of the structure of the as-cast billet (Figure 8A) gives a clue to the origin of the streaks: the grains are mostly small, but some larger ones are present. Examination of the same billet after homogenization and slow cooling (Figure 8B) shows that the large grains are very poor in solute and that homogenization has produced little diffusion into these grains. This low alloy zone, after extrusion, becomes a band, that responds to anodizing in a manner different from the alloy-rich material. The origin of the large crystals is simple to trace: they are crystals formed before the metal entered the mold and was subjected to the rapid cooling of the direct chill. This premature crystallization defeats the main purpose of DC casting; namely, to produce chilled ingots. It is not limited to grain refined melts: under particularly bad pouring conditions it can be found also in non-refined material. However grain refiners, that raise the temperature of beginning of crystallization, enhance the probability of its appearance.

The same is true of the defect shown in Figure 9: germination. Fine grained material is more prone to abnormal grain growth than coarse grained one. Also, the effect is more pronounced: a grain 1" diameter stands out in a material with an average grain size of 1/100" much more than if the average grain size is 1/10".

Another serious defect due to grain refinement is poor machinability of 2011. Figure 10AB show the microstructure of two 2011 billets without and with grain refiner. The non-refined ones has a coarse columnar grain, the refined one small equiaxed grains, as to be expected; but the fine-grained material has the larger interdendritic spacing. The micro-radiographs show the Pb and Bi distribution in the two materials. Obviously the much finer dispersion in the coarse-grained material leads to improved machinability.

Besides reducing machinability, grain refinement reduces hot formability and possibly cold formability as well. In Figure 11 is shown the extrudability of 6063 alloy as function of Mg and grain refiner content. Whether the difference is due to poorer response to homogenization because of the coarser distribution of soluble constituents, or to the larger number of grain boundaries that hinder slip or to some other cause was not ascertained, but there is a small, but clear-cut decrease of extrudability.

In some of the alloys of the 3,000 and 5,000 group the formation of primary crystals of Mn bearing compounds is occasionally a problem. The formula

$$\% \ Mn = 1.9 - (\% \ Fe) - 0.2 \ (\% \ Mg) - 0.3 \ (\% \ Cu) - 0.7 \ (\% \ Si)$$

$$- 3 \ (\% \ Cr) - 5 \ (\% \ Ti)$$

which delimits the line above which primary Mn compound crystals form, shows that many commercial alloys are very close or at the boundary and that slight segregations may shift them in the danger zone. Grain refiners affect the formation of primary crystals two ways:

1. By raising the temperature of the beginning of crystallization of aluminum they may prevent, or at least reduce, the amount of primary crystals formed.

2. Their addition has a pronounced effect on the position of the line. As can be seen in the formula, Ti is five times as effective as Fe in shifting the acceptable Mn to lower limits.

The first effect is relatively small compared with the second; thus, the balance is toward more primary compounds appearing in grain refined alloys, as shown in Figure 12.

One point that must be emphasized is that all the effects shown are not strictly limited to grain refined melts: most of the defects produced by grain refinement can also appear in refinement-free materials, but, generally, in refinement-free in materials adherence to optimum practice is less critical. Many people in the industry consider the grain refiners as some physicians consider antibiotics: a cure-all to be given to the patient in place of extensive examination and laboratory tests to establish the origin and causes of the illness. Like antibiotics, grain refiners can cure a lot of ills, but they too can produce side effects and allergies, that make the patient more sick than before the medication.

Acknowledgements

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Figure 1 – Relationship between grain size and equilibrium diagram in the Al-Ti, Al-Ta, Al-Hf systems. (After 13)

Figure 2 - Cooling curves of aluminum alloy 2011 - A) without grain refiner - B) with addition of Ti 0.05, B 0.01% - Notice disappearance of undercooling with Ti + B addition.

Figure 3A- Nuclei of $TiAl_3$ within Ti-rich Al dendrites. X490. Courtesy Dr. Biloni (17). Black $TiAl_3$, dark in relief Ti rich Al solid solution.

Figure 3B- Microprobe analysis of Ti of the same zone X525. Courtesy Dr. Biloni (17). Notice white spots corresponding to $TiAl_3$, mottled appearance of Ti-rich solution.

Figure 4 - Alloy with 5% Ti, 1% B - Notice the $TiAl_3$ needles at the center of the grains, the TiB_2 particles between the arms of the dendrites. X100

Figure 5 - Atomic distribution and spacing for the orientations

$(001)TiC||(001)TiAl_3||(001)Al$ and $(001)TiB_2||(114)TiAl_3$

$||(111)Al$

The two spacings shown for the $TiAl_3$ in the (114) plane correspond to the $[1\bar{1}0]$ and $[04\bar{1}]$ directions respectively.

Figure 6 - Macrostructure of two DC cast billets 1100 alloy. X1/2 At left with grain refiner, at right no grain refiners Notice cracks in center of non-refined billet.

Figure 7 - 6063 alloy extrusion, anodized - Streaks resulting from segregation.

Figure 8 - Structure of 6063 billet of the type from which extrusion in Figure 9 was made A) as cast X10; B) after homogenization X500. Notice scarcity of precipitate at center of large grains, indicating lack of solute.

Figure 9 - 6063 Billet, 7" dia. after homogenization. A) Without grain refiner, B) With grain refiner X 1/2, Tucker's etch. Notice slight grain coarsening in A, Germination in B.

Figure 10- 2011 billets - A, B, micros X100, Keller's etc.; CD Microradiographs X25 - A, C no grain refiner, coarse columnar grain, fine Pb distribution - B, D with grain refiner. Fine grain, coarse interdentric spacing and Pb distribution.

Figure 11 - Extrudability of 6063 as function of Mg and grain
          refiner content.

Figure 12 - 3004 alloy billets X100. A without grain refiner, B with
          grain refiner. Notice larger size and angularity of Mn
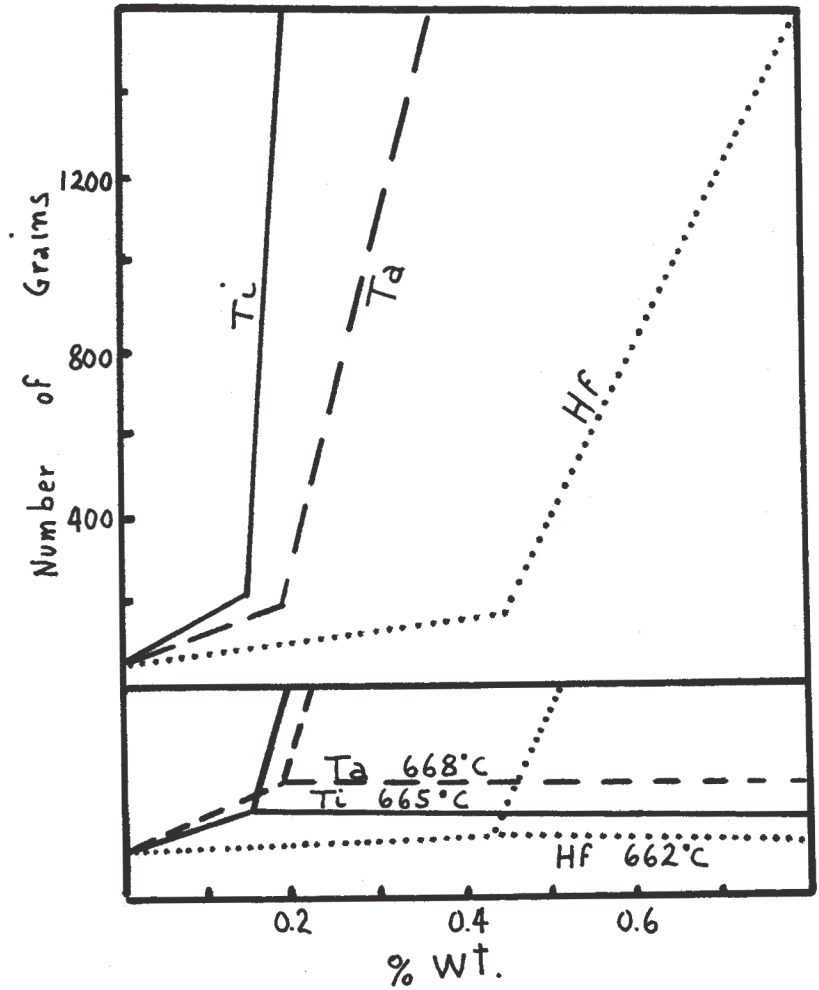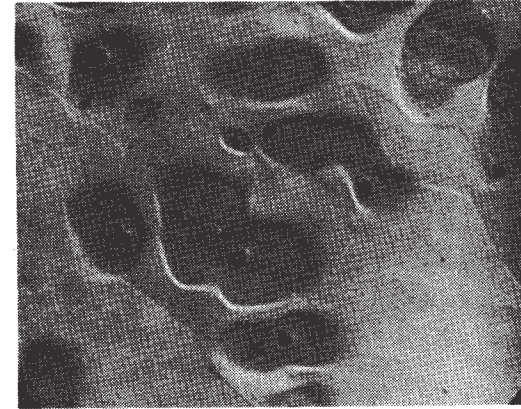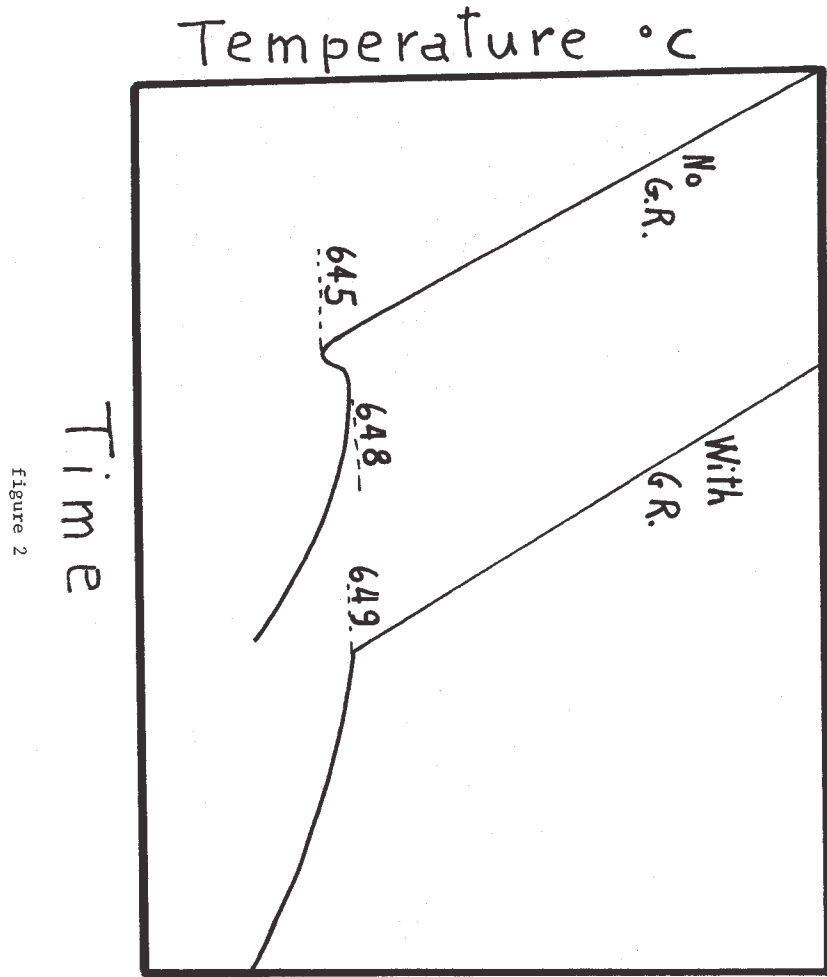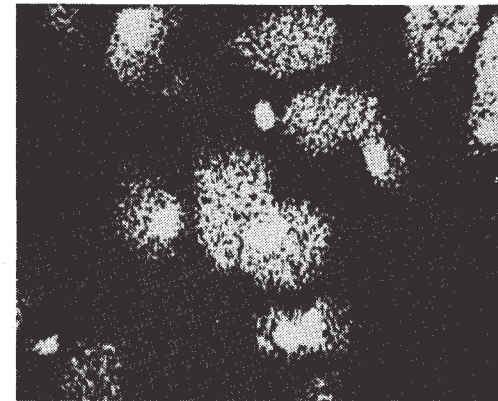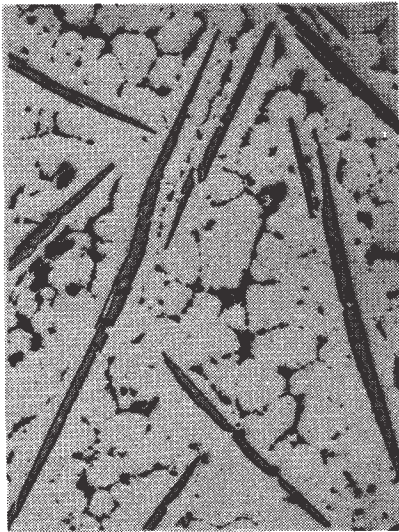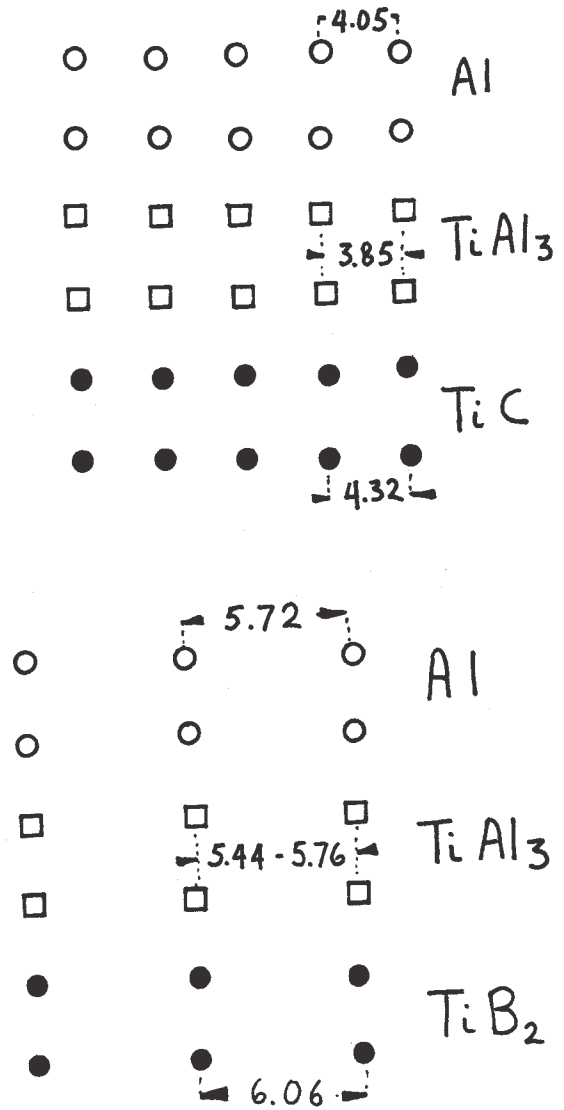   bearing compounds in B.
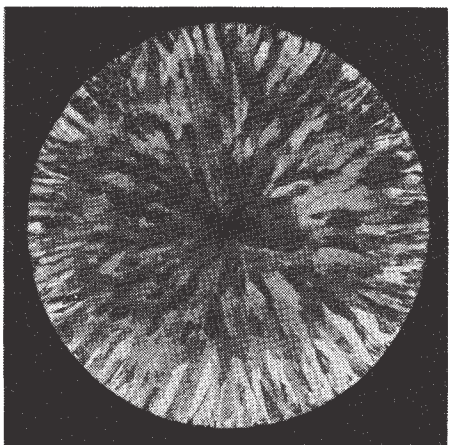

Figure 1

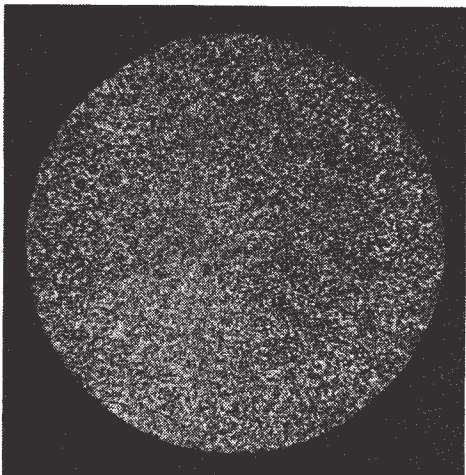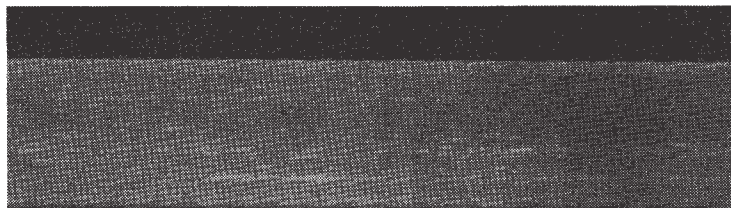figure 2

Figure 3A

Figure 3B
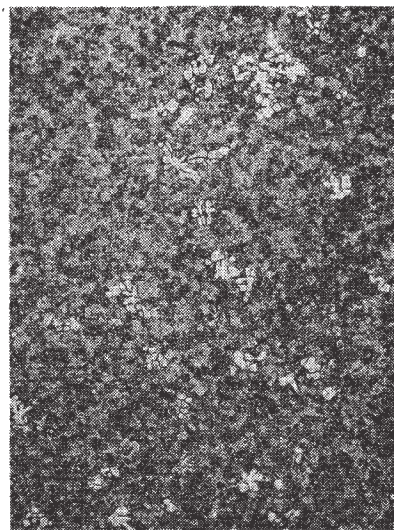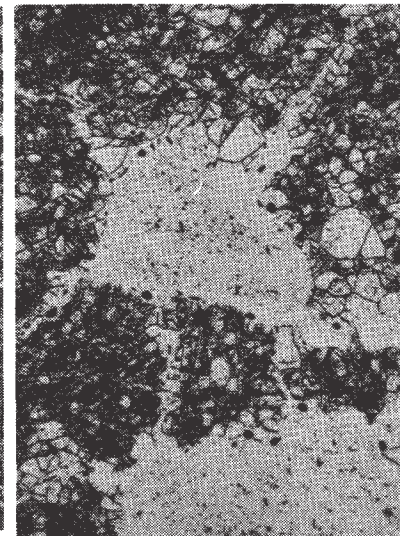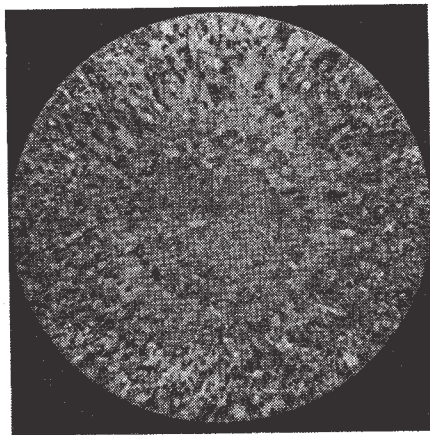
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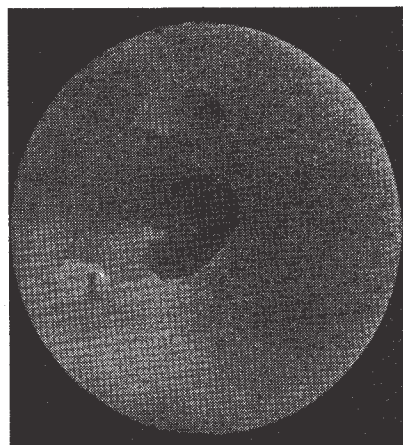

Figure 5

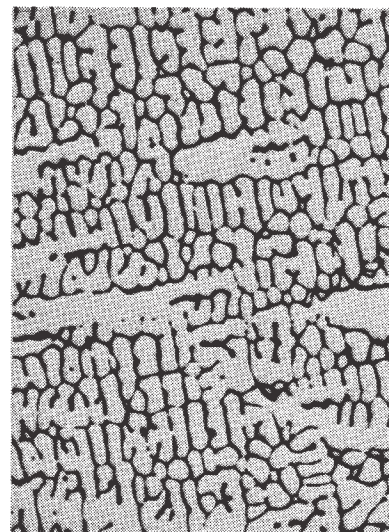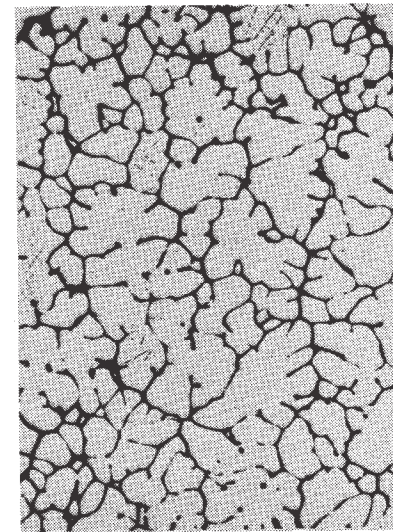Figure 6A

Figure 7
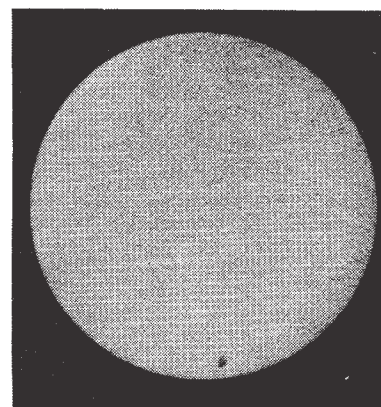

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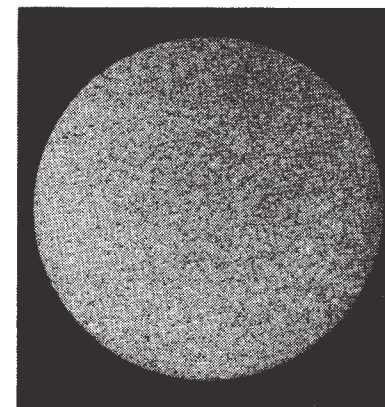

Figure 8A

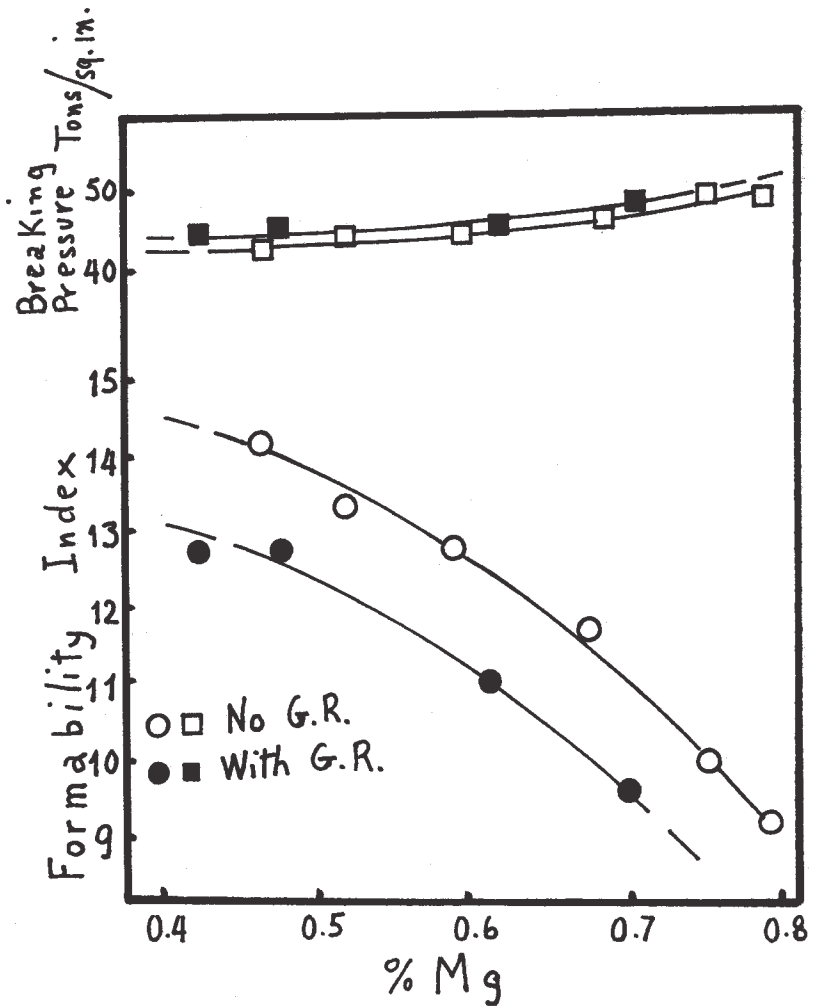
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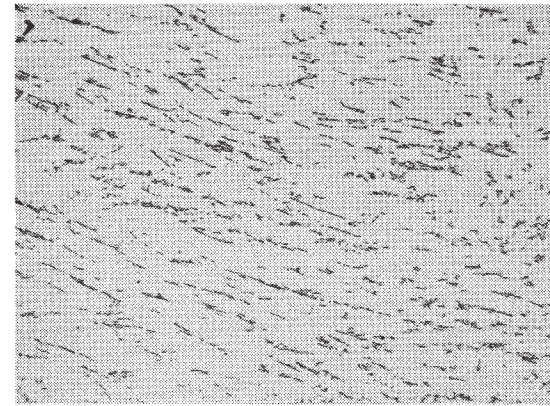
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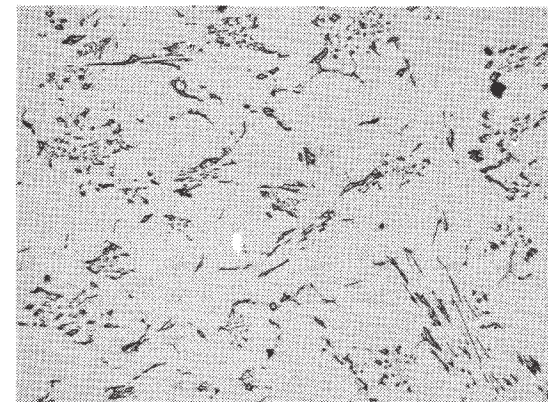

Figure 9B

Figure 10A

Figure 10B

Figure 10C

Figure 10D

Figure 11

Figure 12A

Figure 12B