GRAIN REFINEMENT IN CASTINGS AND WELDS

Edited by G. J. Abbaschian and S. A. David

CONFERENCE PROCEEDINGS

The Metallurgical Society of AIME

GRAIN REFINEMENT IN CASTINGS AND WELDS

Proceedings of a symposium sponsored by the Solidification Committee of The Metallurgical Society of AIME, held at the Fall Meeting of The Metallurgical Society of AIME, St. Louis, Missouri, October 25-26, 1982.

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FOREWORD

The grain structure of a cast alloy or a weld is of great importance since many of the alloy properties are directly related to the size, shape, and distribution of the grains. Fine-grained structures generally have improved low-temperature strength and toughness, reduced anisotropy, reduced microsegregation, better heat treatment response, and reduced hot tearing or hot cracking tendency. Grain refiners in use today throughout the casting industry were found by trail and error, and the fundamentals of grain refining are not well understood. For some alloy systems, such as superalloys, no effective inoculant has yet been developed, In the welding industry, grain refining is still in its infancy. From an economic and scientific point of view, it is necessary to study the basic principles of grain refining and to optimize the conditions that enhance the effectiveness of the inoculants.

In view of the above, the organizers felt that it was timely and desirable to organize a symposium focusing on the currect status of grain refinement in castings and welds. The symposium was held at the fall meeting of The Metallurgical Society of AIME in St. Louis, Missouri, October 25-26, 1982. It brought together university and industrial researchers and manufacturers to discuss the current status of grain refinement, both theory and practice, in castings and welds.

The proceedings of the symposium has been divided into two parts, namely, grain refinement in castings and grain refinement in welds. The first part covers grain refinement in nonferrous alloys, with particular reference to aluminum castings, capabilities, mechanisms, and limitations of aluminum-titanium grain refiners; grain refining of ferrous alloys; inoculants; supercooling and cooling rate effects; coarsening; and inoculation by oxide dispersions. The second part covers the current status of grain refinement techniques in electroslag welds and gas tungsten arc welds. Materials of interest include stainless steels, structural steels, and titanium and iridium alloys. The book is intended to serve manufacturers, industrial researchers, and the academic community.

The organizers wish to express their appreciation to the members of the Solidification Committee of The Metallurgical Society of AIME for their support and encouragement. Also they would like to thank the speakers and session chairmen, Drs. Bruce A. MacDonald of the Office of Naval Research and John Vitek of Oak Ridge National Laboratory.

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GRAIN REFINEMENT IN CASTINGS

GRAIN REFINEMENT IN THE CASTING OF NON-FERROUS ALLOYS

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Abstract

Substantial grain refinement in castings is obtained by enhancing nucleation so that a large number of crystals is formed, that soon impinge on each other and prevent further growth. This enhancement comes from heterogeneous nucleation produced by solid nucleants either present in the melt or intentionally added. After a brief review of present knowledge on the nature of nucleants, the techniques available for grain refinement are discussed under the headings: rapid cooling, dynamic methods, growth-hindering additions, nucleating additions, denucleation.

快速，动力方法，阻碍 [illegible] 形核剂

非核化

Introduction

Most of the properties of metals and alloys are affected by the as cast structure, even after extensive deformation, heat treatment and recrystallization, because these processes do not change substantially the distribution of constituents and inclusions. Hence the most important step in the control of the properties of metallic materials is the production of the best possible as-cast structure. Generally this has been assumed to correspond to a structure of fine, equiaxed grains with random orientation, and great effort has been spent in determining the conditions that produce the finest grain possible. Actually fine grain is not always the most important condition for optimum properties; especially in multiphase alloys and in materials to be extensively worked, a small interdendritic spacing that produces a good distribution of phases and inclusions may be much more important than fine grain. However grain refinement may also result in a small interdendritic spacing and thus fine grain has become synonimous with good quality.

Grain refinement in castings can be produced only by increasing the number of nucleating centers, so that a large number of crystals is formed which soon impinge on each other and prevent each other growth. Hence enhanced nucleation is the key to grain refinement. This nucleation is heterogeneous, in the sense that it arises from solid nucleants either already present in the melt or added purposely, which act as centers for abundant nucleation.

Theories of homogeneous nucleation have been developed and the mathematical treatment for it is well established. Several of these theories have been extended to cover heterogeneous nucleation (1-3), but the fit between theory and experimental data is far from perfect (4). The main reason for this discrepancy is that the mechanisms of homogeneous and heterogeneous nucleation are different: whereas homogeneous nucleation results from the stabilization of a transient grouping of atoms, so that a nucleus consisting of many atoms is formed all at once, in heterogeneous nucleation formation of the nucleus is an atom by atom accretion, in which the atoms of the metal to be nucleated attach themselves to the best locations in the nucleant. Moreover reports of intermediate lattices formed between nucleant and nucleus (5-8) may indicate that heterogeneous nucleation is not a continuous process, but that growth of both nucleant and nucleus can take place at the same time on the same plane.

The best location for nucleation is a nucleant plane with an atomic spacing and distribution similar to that of a plane of the nucleus, so that disregistry is held at a minimum. Often there are several plane couples with low disregistry and nucleation has been found to take place in most of them, although disregistry may be different in the different couples.

Another characteristic of heterogeneous nucleation is the variability of fit. In some cases the planes with low disregistry have extactly the same atomic distribution, so that nucleation takes place by an atom to atom replacement in the lattice (Fig. 1a); in other cases the fit is limited to few atoms, one here, one there (Fig. 1b). In most cases the fit is between these two extremes. Also, when an intermetallic compound is the nucleant the plane in which nucleation takes place may be constituted wholly or in part of atoms that are the same as those of the nucleus, most times however are different ones. Most probably this produces some difference in nucleating ability.

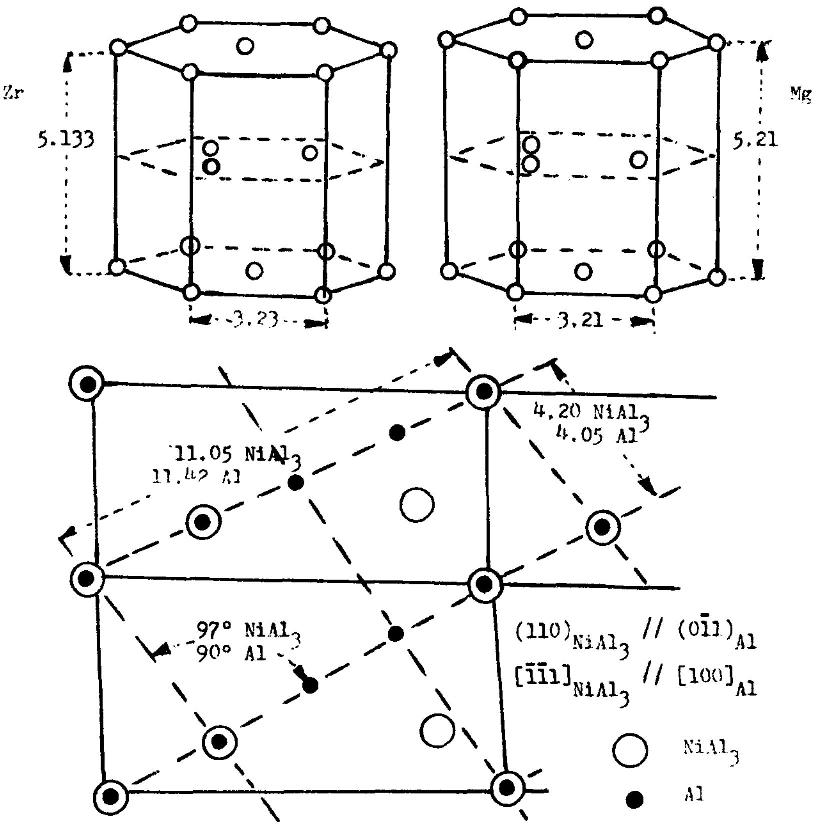

Fig. 1 - Lattice fit in nucleation--In the nucleation of Mg by Zr the two lattices are very similar, with only a small difference in dimensions. In the nucleation of Al by $NiAl_3$ only a few atoms coincide.

In the formulas depicting heterogeneous nucleation the requirement of the proper couple of planes being active is to some extent accounted for by the requirement that the nucleus - nucleant interfacial energy be low, but no provisions are made for multiple orientation relationships between nucleant and nucleus, the presence or absence of the best nucleating plane, nor for the variability of fit. Unless all these features can be translated into numerical coefficients to be inserted into the nucleation formulas, any formula is not going to be representative of the facts.

One step toward a basic understanding of grain refinement would be the knowledge of what are the characteristics of a good nucleant. Unless one knows what nucleates and what does not in a given melt, all grain refinement methods boil down to a trial and error system. Unfortunately, there is not sufficient information to describe the characteristics of a good nucleant.

Many authors have listed requirements for a good nucleant, but since these listing are based on a limited amount of experimental data, none of them can be applied generally. For example Doherty (9), lists a high Tn/Ts ratio, where Tn and Ts are respectively the melting point of the nucleant and of the nucleus. Generally this is true, if nothing else because the nucleant must be solid in the melt, but for example in the eutectic system lead-tin, tin nucleates lead (10,11), in spite that the Tn/Ts ratio is 0.7. A metallic bond in the nucleant stronger than in the metal to be nucleated has also been mentioned by Doherty. This may apply to nucleation of lead by copper or nickel (10), but fails for the nucleation of zinc by Zn_2TiO_4 (12), or for nickle by its oxide (13). The reverse rule has been proposed by Samsonov, Lamikhov (14), who state that electron acceptors are good nucleants. Rama Rao (15) on the other hand, suggests that electronegativity of the nucleant should be the same as that of the nucleus. According to Löhberg (16) the nucleant must have a work function higher than that of the nucleus. Again this is true to some extent, because the work function is approximately proportional to the melting point but, as shown in Table 1 (17), there are enough exceptions to nullify the rule. Based on reported grain refinement of aluminum by carbides, Nakao et al. (18) describe a good nucleant as having a large heat of formation, a low density and a small size factor with a NaCl structure. This may be true for carbides and can be stretched to fit nucleation of copper by iron, but not nucleation of magnesium by zirconium (19).

Table I. Relationship Between Nucleating Ability, Melting Point Entropy of Fusion and Work Function - The Elements are in Order of Increasing Nucleating Ability (17)

Element	Melting Point °K	Entropy of Fusion Cal/Mole/°K	Work Function in eV
Tl	577	1.78	3.70
Pb	601	1.81	4.00
Ag	1233	2.18	4.30
Au	1336	2.28	4.30
Cu	1357	2.09	4.40
Ni	1726	2.44	4.50
Co	1768	2.12	4.41
Fe	1812	2.01	4.31
Ge	1210	5.93	4.76
Sn	505	3.32	4.38
Zn	692	2.51	4.24
Bi	544	4.83	4.40
Sb	903	5.25	4.08

The most accepted relationship between nucleant and nucleus is the similarity of lattice: the nucleant must have a crystal structure and lattice parameters very close to those of the nucleus. This theory, that originated with rain making by seeding clouds with AgI, originally required the same crystal structure for nucleant and nucleus, but had to be stretched to accept crystallographic fit in one plane only. However, the main objection to it is that crystallographic fit is reciprocal: if α fits β, β also fits α, whereas the evidence indicates that nucleation is nonreciprocal: if α nucleates β, β does not nucleate α at low undercooling.

Although non reciprocal nucleation has been alledgely disproven by Southin and Chadwick (20) and by Hunter (21) careful scrutiny of their work reveals that the conclusion of reciprocal nucleation was based on a "post hoc, propter hoc" philosophy and that no attempt was made to insure that the nucleation events assumed to be nucleation of α by β were not due to nucleation by some impurity of β. Some of the results reported by Southin and Chadwick strongly indicate this: multiple nucleation events at widely differing undercoolings are shown in few alloys, which must be due to a variety of nucleants, none of which needs be the β phase. On the other hand, nonreciprocal nucleation is supported not only by the early work of Lamplough and Scott (22), Sundquist and Mondolfo (10), Powell and Colligan (23), but also by the more recent work of Perepezko et al. (24), Lemaignan (25), etc.

Unless nonreciprocal nucleation is not accepted, the most probable criterion for nucleation is the energy balance as in Fig. 2. If $\sigma_{NL} > \sigma_{NS} + \sigma_{SL} \cos \theta$, the nucleus S can spread on the nucleant N and grow. If σ_{NL} is smaller than the sum of $\sigma_{NS} + \sigma_{SL}$ the nucleus must shrink and disappear. σ_{NS} is generally small because the orientation relationship between nucleant and nucleus is one of low disregistry and epitaxial growth of the nucleus on the nucleant is facilitated by good crystallographic fit that results in a very low interfacial energy between the two. Since the σ_{NS} is small enough to be negligible in most cases, it would seem that a comparison of the solid-liquid interfacial energies of the nucleant and the nucleus is all that is needed to decide if a crystal is a good nucleant or not. Unfortunately few, if any, reliable values are available for solid-liquid interfacial energies. Admittedly these energies are to some extent proportional to the melting point, but are also affected by crystal structure and most probably by other factors about which little is known. Direct experimental measurements of solid-liquid interfacial energies are extremely difficult, if not impossible. Hence most of the values found in the literature were determined by indirect methods, usually on the basis that the highest undercooling for crystallization recorded represents homogeneous nucleation. In the fifties it was accepted that undercoolings for homogeneous nucleation were of the order of 0.18 - 0.20 Tm (where Tm is the melting point in °K) and extensive calculations of interfacial energies and contact angles, based on these values were published. More recently undercoolings up to 0.5 Tm have been recorded and the evidence available indicates that nucleation at these undercoolings may still be heterogeneous. Thus most of the published values of solid-liquid interfacial energies can only be considered as lower limits, with the actual value possibly higher by 50 or even 100%.

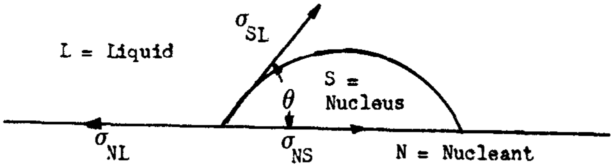

Fig. 2 - Energies balance in heterogeneous nucleation.

Even if the values in the literature were correct, they would represent the surface energy of α crystal in contact with α liquid, not the surface energy of α crystals in a liquid that contains a substantial amount of β phase component. Especially if the β metal has a lower energy than the α one, this may make a substantial difference.

There are now in the literature a few values of solid-liquid energies (26,27) obtained by measuring the dihedral angle formed when the primary phase is in equilibrium with the molten alloy. These values do not contain the error of the α solid in equilibrium with the α liquid. However they were obtained by equilibrating the solid with the liquid by holding at temperature for a relatively long time. Thus they represent the average interfacial energy of those faces that are most stable and that means in general, the closest packed ones, which have the lower index planes and the lowest energy. However, as mentioned before, even if the low index planes of the nucleant and nucleus have a good crystallographic fit, the evidence available (28-30) indicates that nucleation takes place in loosely packed planes which have the highest energy and consequently tend to disappear as the nucleant crystal moves toward equilibrium. It is true that in the more symmetrical crystals (face centered cubic, hexagonal close packed) the surface energy change with orientation has been reported as small (31-35) as shown in Fig. 3 (35), but two factors have been neglected in these measurements:

1) The crystals in which measurements were made were equilibrated and the high energy faces may have disappeared.
2) The measurements represent averages over an area and the presence of a small high energy face that would produce a spike on the energy-orientation plot would get smoothed down.

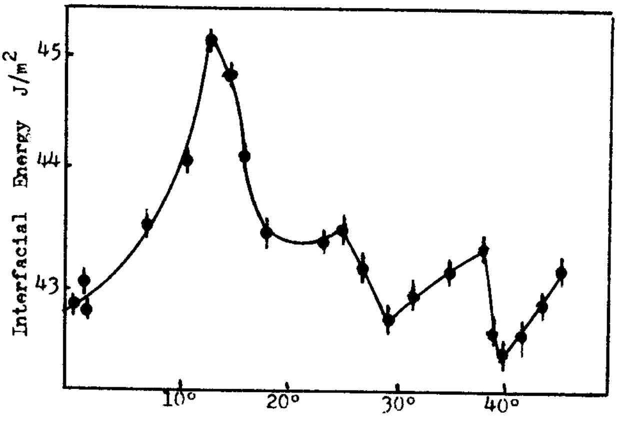

Fig. 3 - Interfacial energy of tin--germanium boundaries as a function of rotation about the axis perpendicular to the boundary (After (35)).

The data in Fig. 3 indicate the existence of high energy planes. Further proof can be found in the fact that multiple relationships between nucleus and nucleant appear, often with different disregistries that require different undercoolings, as shown in Fig. 4 (36). If all nucleation sites were available at all times, obviously the one with the lowest disregistry would be the only active one. In the nucleation of aluminum by $TiAl_3$, if the alloy is rapidly cooled the orientation relationship predominates which has matching high index planes and the lowest disregistry (37). Nucleation takes places with 0 °K undercooling and substantial grain refinement results (38). If the alloy is slowly cooled or held slightly above the peritectic temperature so that the $TiAl_3$ has a chance to equilibrate, the dominant orientation relationship is one of the lower index planes with higher disregistry and requiring a 4 °K undercooling.

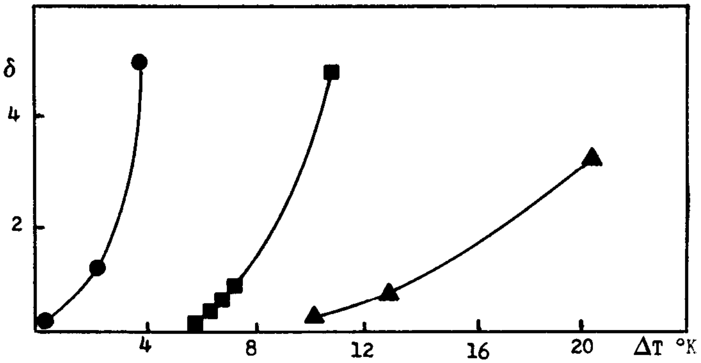

Fig. 4 - Effect of disregistry δ on undercooling for nucleation ΔT. ● Al by $TiAl_3$, ■ Pb by Sb, ▲ Pb by Fe. (36)

From the above it is obvious that even if the interfacial energies balance is the controlling factor in nucleation, little use of this knowledge can be made, since values for the interfacial energy of specific faces with the liquid to be nucleated are not available and most probably will not become available in the near future, if ever.

The energy balance shown in Fig. 2 is also complicated by the possible presence of impurities. As shown in Fig. 5, if an impurity I is present the balance of energies may change. In Fig. 5 there is a triangle of forces also at A, but it can be considered inoperative because the movement of point A can take place only by diffusion in the solid, which is 100 to 1000 times slower than movement in the liquid. On this basis growth of nucleus S depends on the balance of forces where the nucleus contacts the nucleant, against the area where it contacts the impurity. If for simplicity the nucleus is assumed to have the shape of a spherical cap, growth of the nucleus can take place if $\sigma_{NL} \times C_N + \sigma_{IL} \times C_I > \sigma_{SL} \times C + \sigma_{NS} \times C_N + \sigma_{NI} \times C_I$, in which: C is the circumference of the nucleus, C_I is the fraction in contact with the impurity, C_N the fraction in contact with the nucleant and $C_I + C_N = C$.

If $\sigma_{NL} \times C_N < \sigma_{IL} \times C_I$ and $\sigma_{IS} \times C_I < \sigma_{NS} \times C_N$ the impurity helps nucleation, which means that nucleation takes place at a lesser undercooling. If $\sigma_{NL} \times C_N > \sigma_{IL} \times C_I$ and $\sigma_{IS} \times C_I > \sigma_{NS} \times C_I > \sigma_{NS} \times C_N$ the impurity increases the undercooling needed for nucleation. If $\sigma_{NL} \times C_N > \sigma_{IL} \times C_I$ and $\sigma_{IS} \times C_I < \sigma_{NS} \times C_N$ or vice versa, nucleation may be hindered, favored or little affected by the presence of the impurity, depending on the actual values of the forces.

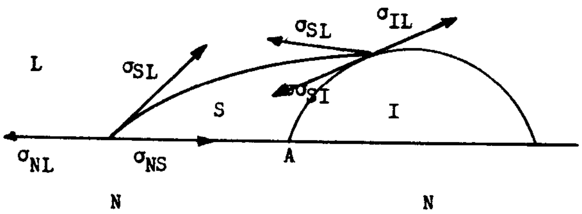

Fig. 5 - Effect of an impurity on the energy balance in heterogeneous nucleation. L = Liquid, S = Nucleus, I = impurity, N = Nucleant. For discussion see text.

Since most melts contain many impurities, it is obvious that the situation is very complicated and that to obtain the same undercooling for nucleation in two different batches of metal it is necessary that they contain the same impurities. This explains why even when two experimenters agree on nucleation of β by α, they may find different undercoolings for the same nucleation.

Examination of the known cases of nucleation indicates that lattice symmetry could be a criterion for a good nucleating agent: the more complex the lattice, the better the nucleant. Unfortunately there is no way to assign numbers to lattice symmetry. However entropy of fusion can to some extent be used as a measure of lattice symmetry. Although there is not a one to one correlation between entropy of fusion and lattice complexity, generally less symmetrical lattices have higher entropies of fusion, as shown in Table I. As can be seen good nucleants have a high entropy of fusion, easily nucleated metals a low one. The nucleation of copper by iron however is a good example of the imperfection of entropy of fusion as measure of lattice symmetry. Although the body centered cubic lattice is less symmetrical than the face centered cubic, the entropy of fusion of iron is lower than that of copper.

This lattice symmetry criterion most probably is still an interfacial energy criterion: the more symmetrical the lattice, the smaller the difference of energy between the various faces. Thus the low index face of α, say orthorhombic, may have lower energy than the low index face of β (face centered cubic) with similar spacing and a β crystal cannot grow on that face of α. However the energy of a high index α plane may be higher than that of the corresponding β plane and, if the atomic spacing is favorable, epitaxial growth is possible. Most of this is speculative and extensive experimental work is needed before a heterogeneous nucleation theory based on experimental data can be formulated.

Summarizing the probable requirements for a good nucleant can be listed as:

1) High melting point
2) High solid-liquid interfacial energy
3) Low symmetry lattice (high entropy of fusion)
4) Ability to nucleate at very low undercooling
5) One or more planes with atomic spacing and distribution close to those of one plane of the crystal to be nucleated.

None of these characteristics is absolutely necessary, but generally a crystal that satisfies all or most of them has a strong probability of being a good nucleant.

In the following table are collected data on nucleants for nonferrous metals and compounds as found in the literature. These data come from a variety of sources; some of the data are well documented, others are little more than educated guesses. Every effort has been made to collect all the information available and the data are presented more as a starting point for a search than an authoritative list. For example many of the orientation relationships were determined on coupled eutectics. Comparison with the few relationships determined also in nucleation reveal that most of the time they are different. It is not known if this results from multiple relationships, or because in the eutectic the orientations must be tridimensional, whereas in nucleation only a planar fit is needed.

Although the data in Table II cover a large number of nucleants and nucleated metals, definite conclusions cannot be drawn. Many of the nucleants have been identified only through grain refinement. Unless it is definitely proven that grain refinement is produced by nucleation by the nucleant, and not by growth hindering or by some impurity of the nucleant, any relationship derived from the table is open to question. Also, if one considers a good nucleant to be one that can nucleate at low undercooling before extraneous impurities can act, how does one qualify for example Zn in Bi, that is reported to require 146 °K undercooling?

In the following pages is discussed the existing knowledge on nucleation as a basis for grain refinement. In the following section will be described the methods available to achieve grain refinement, their efficiency, advantages and disadvantages. This will be covered under the headings:

1) Rapid Cooling
2) Dynamic Methods
3) Growth Hindering Additions
4) Nucleating Additions
5) Denucleation

Rapid Cooling

It is well known that the more rapid the cooling, the smaller the grain size. Hence sand castings, with cooling rates of the order of 0.1 °C/sec. show grain sizes ranging from 0.5 to 5 mm dia. whereas in splat cooling, that may produce cooling rates up to 10^8 to 10^9 °C/sec., grain sizes of 3 nm have been reported (167). In Fig. 6 is shown the variation of grain size with cooling rate in Nb and V (168). One of the factors that may produce this decrease may be a shortening of the time during which the metal, partially or completely solidified, is held at temperatures at which grain growth can take place. This effect may be appreciable in pure metals, in which no second phase at the grain boundaries prevents the α grain to α grain contact necessary for the growth of one crystal into the other.