Eutectic growth in space

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MS received 17 June 1980

Abstract. Defect-free eutectic components are favoured for certain applications in view of their improved performance and/or better stability. Eutectics produced even under best conditions possible on earth have some microstructural defects. Unavoidable density driven convectional currents in liquid are considered as a major cause for the production of these defects. Intensity of such convectional currents proportionally reduces with gravity. Therefore the defect density in the eutectics is expected to be very low when processed under microgravity conditions. The advantages and limitations of processing under microgravity conditions are examined. The potential of newly developed 'skin technology' for processing eutectic components in space is considered.

Keywords. Eutectic; in-situ composite; microgravity space; directional solidification; convectional currents.

1. Introduction

In the recent past much interest is shown in directionally solidified eutectic alloys due to their unique properties—mechanical, physical and electronic. Stability and performance demanded by some applications require defect-free structures. Some of the defects cannot be eliminated on earth due to unavoidable convection. The microgravity conditions in *Spacelab* facilitate production of eutectics under these conditions and assessing them. The present paper examines the potentials of microgravity-processed eutectics.

2. Background

The eutectic reaction is one in which a liquid decomposes into two or more solid phases at a temperature characteristic to that alloy. A eutectic reaction is possible only in multicomponent systems (*i.e.*, binary, ternary alloys, etc.). In a binary alloy the eutectic contains two solid phases, and in ternary alloy there are three solid phases. At the eutectic reaction point the compositions as also the temperature of all phases are fixed. Thus it has no degrees of freedom. Applying Gibb's phase rule, one derives the number of phases in a eutectic reaction as equal to the number of components at a constant pressure.

A simple binary phase diagram, that of the Ag-Cu system is shown in figure 1. In this alloy, a liquid containing 28.5% Cu freezes into two solid phases α and β

Figure 1. Equilibrium phase diagram of silver-copper.

at 780°C. One notices that the phases involved are solid solutions and not pure components or compounds. The relative proportions of the phases are given by mass balance equations (the Lever rule).

As shown in figure 2 the two solid phases are arranged as alternate lamellae. It is a monovariant eutectic alloy in the Fe-Ni-Al system containing alternate lamellae of a nickel rich (γ) phase and an iron rich (β) phase. Alternatively the second phase can be in the form of fibres embedded in matrix phase. Figure 3 shows a eutectic alloys of Al-Ni containing Al_3Ni fibres embedded in Al matrix. Thus eutectic alloys show the following characteristics.

- (i) Solidification front is planar;
- (ii) Volume fraction determines the structure : Near equal lamellar; Below 30% Rod structure
- (iii) Near eutectic compositions produce dendrites, cells, globules and divorced eutectics.

In addition this indicates that when the composition of the alloy is off eutectic, the microstructure will be different from that of the ideal eutectic.

Though eutectic alloys are known since about a century, the technological potential of their unique properties were recognised only a decade ago. Some interesting properties of eutectic alloys are listed below.

- (i) High strength

$$\sigma_E = \sigma_m V_m + (1 - V_m) \sigma_f.$$

- (ii) High directionality

- (a) better thermal fatigue,
- (b) better fracture resistance,
- (c) better polarisation, electrical and magnetic characteristics.

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Figure 2. Longitudinal microstructure of a Fe-Ni-Al (γ - β) alloy.

Figure 3. Transverse microstructure of a Al-Ni ($\text{Al-Al}_3\text{Ni}$) eutectic alloy.

- (iii) Excellent compatibility and good microstructural stability at high temperatures.

3. Directional solidification of eutectics under gravity

However these properties cannot be exploited unless the eutectic phases are aligned in one direction and are continuous throughout the body. For example, maximum strength is obtained when the phases are perfectly aligned and when the phase has an aspect ratio (l/d) greater than a critical value. Such a structure can be obtained by directionally solidifying the alloy. Directional solidification is obtained under conditions described below.

3.1. Directional solidification of eutectics

The following are the conditions necessary:

- (i) Heat flux should be unidirectional.
- (ii) Heat extracted at the solid/liquid interface should be equal to the heat given by liquid plus the heat generated at interface

$$K_s (\partial T / \partial x)_s = K_L \left(\frac{\partial T}{\partial x} \right)_L + R \frac{\Delta H}{V}, \quad (2)$$

where K_s and K_L are thermal conductivities of solid and liquid, ΔH , and V are enthalpy of fusion and atomic volume of the alloy and R the growth speed.

- (iii) Condition for plane front solidification

$$G/R \geq -m \frac{C - C_e}{D} = \Delta T/D, \quad (3)$$

where G is the temperature gradient; m the slope of liquidus; $C - C_e$ the deviation of composition from eutectic; ΔT the freezing range and D the coefficient of diffusion in liquid.

From the last equation it is clear that for truly eutectic alloys the G/R ratio required is zero, as $\Delta T = 0$. However, alloys always contain some impurities and therefore G/R is never zero for commercial alloys. It is also clear from the same equation that a ternary or higher component alloys, on eutectic troughs where liquid ultimately goes to two phase solid region with $\Delta T \neq 0$, can also be directionally solidified with plane front solidification to obtain composite structures. The G/R ratio required for some recently developed eutectic alloys are shown in table 1.

A directional solidification set-up has to satisfy a number of requirements so as to produce a satisfactory structure. These requirements are summarised below.

3.2. Requirements of experimental set-up

- (i) High G because of high R requirement
- (ii) Absence of metal-mould reaction
- (iii) Flat isotherm for melting point of the alloy

Table 1. G/R ratios required for some eutectic alloys.

Matrix	Second phase	$(G/R)_{critical}$ (K s cm ⁻² , $\times 10^4$)
Co, Cr, Ni	TaC	25
Co Cr	(Cr, Co) ₇ C ₃	2.5
Ni ₃ Al	Ni ₃ Nb	8.3
Ni/Ni ₃ Al	Ni ₃ Nb	1.8

(iv) Stable and vibration free set-up

(v) Positive temperature gradient in the liquid

(vi) Protective atmosphere.

An experimental set-up meeting these requirements was fabricated at DMRL and is sketched in figure 4. In this apparatus, an alloy bar contained in a recrystallised alumina tube, surrounded by a graphite susceptor enclosed in a quartz tube, is heated using a RF generator. The alloy and susceptor are protected by passing high purity argon. Once the molten metal temperature, judged by optical pyrometer stabilises, the alumina tube is lowered through a closely fitting water cooled copper toroid. In this set-up temperature gradients of about 150° C/cm have been obtained.

A monovariant eutectic alloy Ni-Mo-Al which was directionally solidified at 1.17 cm/hr in the above set-up has a perfect microstructure as shown in figure 5. This consists of continuous fibres of molybdenum embedded in nickel-base superalloy matrix. Production of such a perfect microstructure was possible, because of a nearly planar interface as shown in figure 6. The interface was revealed by abruptly stopping the withdrawal of the alloy from the furnace.

3.3. Defects in eutectic structures

Usually eutectic alloys contain various defects arising from different reasons such as subcritical G/R thermal fluctuations, jerks/vibration and convective currents. Examples of such defects are (i) cells, (ii) dendrites, (iii) growth bands, (iv) branching and (v) ROD termination.

When G/R is subcritical a cellular structure is produced as shown in figure 7. Here the planar solidification breaks down leading to curved fibres at the cell walls as shown in this figure. Figure 8 shows a more serious defect called dendrite in one of the phases of Ni-base superalloy.

Figure 9 shows a band produced by sudden change in withdrawal speed. Defects like fibre branching and rod termination cannot be easily observed. Though these are not as serious as other defects, which affect mechanical properties even in the as-grown condition, they reduce the strength when the material is exposed to high temperatures for long periods.

Figure 10 shows fibre branching and rod termination in a Ni-Al-Cr alloy. Such defects are produced due to changes in withdrawal speed and provide a means of changing inter-fibre spacing.

Bridgman directional solidification apparatus.

Figure 4. Experimental set-up for directional solidification of high temperature alloys.

Figure 5. Longitudinal microstructure of a Ni-Mo-Al (γ/γ' -Mo) alloy.

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Figure 6. Solid/liquid interface in a Ni-Mo-Al (γ/γ' -Mo) alloy. **Figure 7.** Cellular microstructure in γ/γ' -Mo alloy. **Figure 8.** Dendritic microstructure in a γ/γ' -Mo alloy.

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Figure 9. Banded microstructure in a γ/γ' -Mo alloy; **Figure 10.** Fibre branchings and rod terminations in Ni-Al-Cr alloy; **Figure 12.** Typical morphology of graphite in a grey cast iron.

4. Processing under microgravity conditions

Even under ideal conditions it is not possible to produce completely perfect eutectic structures due to unavoidable convection. Though a positive temperature gradient in liquid ahead of solidification interface greatly reduces convection, it cannot completely eliminate it. It is observed that the segregation profiles obtained in directional solidification of γ/γ' -TaC alloy obey Pfann's equation which assumes complete mixing in the liquid. A condition for stability against convection, taking temperature and composition effects into consideration, is

$$\partial\rho/\partial x \leq 0$$

$$[\partial\rho/\partial x(c)] + [\partial\rho/\partial x(T)] \leq 0$$

$$[-\partial\rho/\partial x(c)] \geq [\partial\rho/\partial x(T)].$$

The critical velocity is given by

$$V_c = \frac{2\pi^2 g (\rho_d - \rho_m)}{9 M_m}$$

where V_c is critical velocity; g is acceleration due to gravity; ρ_d = density of region considered; ρ_m = density of surroundings; and M_m = viscosity of surroundings.

Convective currents are produced wherever this condition is not met in the liquid. The intensity of convective current is qualitatively given by the critical velocity. This equation suggests that the bulk movement in the liquid can be avoided by two methods; firstly by eliminating the density gradients completely and, secondly, by reducing gravitational force g to very low values. The other variable, viscosity, cannot be considered as a true variable for a given alloy system.

It is expensive to eliminate density gradients in the directional solidification of complex components as the processing has to be designed separately for every component, whereas, the reduction of the gravitational force will reduce convection currents in all components with equal effectiveness. Thus, processing under microgravity conditions is an attractive proposition.

It is, however, costly to transport melting furnaces and moulds to space. Further, a large amount of power is not available in space. To overcome these handicaps a new technology has been developed recently known as "skin technology processing of components". This method consists of the following steps:

- (i) The alloy piece is shaped either by conventional casting or by machining;
- (ii) The shaped component is coated with a thin layer of refractory which is compatible with the alloy and which has sufficient strength at these temperatures;
- (iii) The skin coated alloy component is melted and directionally solidified.
- (iv) The processed alloy component is transported back to earth and coating removed before use. If coating is beneficial in service, then the component can be used with the coating itself. These processing steps are shown in figure 11.

Figure 11. Processing steps in skin technology.

In the beginning it was considered that the large difference in thermal expansion coefficients between the alloy and its refractory coating could be a major problem as the skin material (coating) is inherently brittle. However, initial ground based experiments on ceramic-coated IN 100 showed that the ceramic coating deformed rather than cracked, under the force of differential expansion and metallosstatic pressure. The coating was Al_2O_3 formed by processing like plasma spray, detonation gun plating or chemical vapour deposition to thicknesses in the range of 100 to 200 μ . It is possible to use thicknesses in the range of few microns in microgravity conditions. This also facilitates production of higher temperature gradients than is possible on earth, and consequently, faster solidification associated with finer microstructures. The finer microstructure exhibit better mechanical properties.

Experiments using skin technology were done successfully during six minutes free fall of the *Texus* (Spranger *et al* 1979) rocket flights. In the *Texus-I* flight experiment, an IN 100 specimen was coated with a skin of Al_2O_3 and was directionally solidified. Some deformation of the skin was observed which was attributed to differential thermal expansion during melting and directional solidification. It was thought that this deformation would be avoided by proper design modification. The *Texus-II* flight experiment in which the design modifications were effected failed since the furnace did not work. However, some useful data were collected.

The *Texus* experiments were limited to the conventional alloy IN 100 as the free fall time was only 6 minutes. Much longer periods of microgravity can be obtained in the *Spacelab*. So directional solidification of eutectic alloy γ/γ' -Mo have been planned with solidification speeds of 0.1, 0.4, 0.7 and 1 mm/min. These experiments are aimed at proving the superiority of processing of eutectics under microgravity conditions and will also demonstrate the stability of skin in contact with liquid metal for longer periods.

Though at first sight solidification of eutectic alloys under microgravity looks attractive, several difficulties can arise in actual practice. The most important one is the difficulty in determining the accurate composition of eutectic alloys. The composition of most of the eutectics is known only to an accuracy of about 5000 ppm. Even the smallest composition deviations lead to breakdown of plane front solidification. This problem is especially severe in microgravity due to the absence of convection in liquid which can reduce solute concentration ahead of solid-liquid interface. Thus space processing of eutectic alloys demands an

accurate knowledge of composition. Another difficulty that stands in the way of space processing technology development for eutectics is non-availability of quantitative methods of sufficient accuracy to distinguish between the levels of microstructural perfection of space processed and earth-grown alloys. Therefore methods for quantitative studies of alloy structure should be improved. These points were stressed by Malmejac (1976), who also listed the following indispensable precautions to be taken for a successful experiment in microgravity.

- (i) The viscosity of the eutectic liquid studied has to be as high as possible.
- (ii) Systems studied must have vapour pressures as low as possible.
- (iii) The walls of the containers must be wetted by every element of the alloy to avoid segregation.
- (iv) The containers must be filled as completely as possible by the liquid eutectic alloy to avoid parasitic oscillations.
- (v) All mechanisms, except gravity, giving convection movements must be suppressed.

In addition to the developmental work, several experiments which were impossible on earth, were conducted in space. One such interesting case is study of sulphur segregation in liquid cast iron (Luyendijk and Nieswaag 1979). In the Bridgman technique of directional solidification on earth the rejected sulphur from solid cast iron builds up in the liquid at the interface. This leads to precipitation of a sulphur rich liquid phase of lower density leading to severe convection. Therefore the true sulphur segregation profiles cannot be studied on earth. Experiments have been planned for *Spacelab* to study the segregation of sulphur in the absence of convection and to study the effect of sulphur on the morphology of graphite.

Figure 12 shows the typical morphology of graphite in a cast iron. It is expected that the absence of convection will affect the morphology of graphite.

5. Conclusions

- (i) Absence of convection in directional solidification is likely to produce defect-free eutectic structures.
- (ii) Newly developed skin technology can be applied to produce directionally solidified components. This gives additional benefit of higher temperature gradient.
- (iii) Microgravity conditions can help to conduct experiments which are impossible on earth.

References

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