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Casting process for hypermonotectic alloys under terrestrial conditions

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Bearing materials are generally heterogeneous materials, containing hard as well as soft, phases. Hypermonotectic AlPb and AlBi alloys, especially, are considered as exceptionally qualified bearing materials if they also contain additional hard phases to decrease wear. Based on the considerable differences in the density of the decomposed fluid phases at high temperatures and the high velocity of separation, such alloys cannot, to date, be manufactured under terrestrial conditions. The results of microgravity experiments for the manufacturing of suitable sample material with a fine phase dispersion of the monotectic phases were rather disappointing. The cause of the rapid phase separation and local enrichment under microgravity conditions was found to be the Marangoni convection, the effects of which, to date, have been underestimated. The results of these space experiments are now utilized in a terrestrial casting process, whereby a comparatively high Marangoni convection is superposed in the opposite direction to the sedimentation action of gravity, thereby partially compensating the effects of gravity. Thus, cast strips of AlSiPb and AlSiBi alloys could be manufactured, the lead and bismuth phases being present in a characteristic fine dispersion over the length of the cast strips. The first tribological laboratory tests give an indication of the excellent suitability of such advanced bearing material for the future.

1. Structural characteristics of bearing materials: heterogeneous materials consisting of a strong matrix with compact inclusions of both soft and hard particles

Usually, a material used for sliding bearings subject to high stresses is of a heterogeneous structure with compact inclusions of both soft and hard phases in a mechanically strong matrix [1]. The soft phases provide good embedding characteristics, and whereas the hard phases are responsible for a considerable reduction of material wear.

The tribological behaviour of such alloys is not only determined by the amounts of such phases but also by their sizes and forms. In addition, the mechanical matrix characteristics are of major relevance, especially the modulus of elasticity. In particular, the soft phases, which are responsible for good embedding performance, should be of a compact structure. However, with traditional bearing materials, these phases crystallize as eutectic phases, which by nature are not of a very compact structure.

The above findings are reasons to assume that some of the monotectic alloys will show considerably better properties to meet sliding bearing requirements, in particular the hypermonotectic ternary alloys AlSiPb and AlSiBi, are considered as exceptionally qualified bearing materials.

2. Results of previous terrestrial and space experiments: difficulties in producing appropriate hypermonotectic alloys both on the ground and in the space

Unfortunately, it has not yet been possible technically to produce these alloys [2–5], because early in the cooling phase of the homogeneous liquid, these alloys separate into an aluminium-rich melt and a lead- or bismuth-rich melt. The latter phase, owing to its much higher density, moves to the bottom of a mould very quickly. As described by Stokes' Law, the sedimentation velocity of the droplets increases as the square of the particle radius, R^2: therefore, large droplets settle much more rapidly than small ones. When droplets of different diameters and thus different sedimentation velocities collide, they coagulate to form even larger droplets which settle even more rapidly.

Owing to this phenomenon, no casting process under terrestrial conditions has yet been able to produce the desired solidified dispersion of lead and bismuth spheres in the aluminium matrix, even if extremely high solidification rates were achieved. This was shown by a number of experiments where superheated homogeneous monotectic alloys were chilled extremely quickly in thin quartz tubes, but coagulation and sedimentation of the lead and bismuth spheres could not effectively be impeded (Fig. 1).

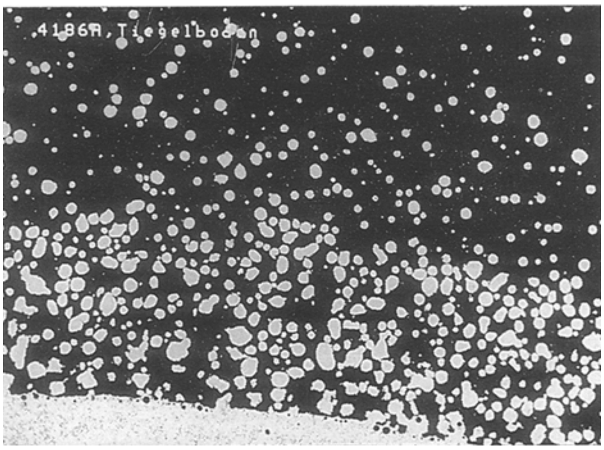

Figure 1 Distribution of the bismuth phase in AlSi5Bi20 near to the bottom of the sample (terrestrial conditions).

Many tests have been performed during space experiments to achieve an appropriate phase distribution under microgravity conditions. The results, however, were rather disappointing, because even under these conditions a coarse-phase separation and rapid droplet coagulation occurred. The origin of this coarse demixing under microgravity conditions was found to be Marangoni motion of droplets, which is on Earth superimposed on gravity-driven sedimentation and often hidden behind its action. Marangoni motion stems from the temperature dependence of the interfacial tension. A temperature gradient leads to convection rolls inside a droplet and thus also outside in the fluid matrix, giving rise to a translational motion of the drop. For metals, the motion of the droplets is generally from the cold to the hot side in a melt. Marangoni motion depends linearly on the temperature gradient and the particle radius.

However, having studied the results of space experiments, a closer look at the terrestrial tests (Fig. 1) also reveals the presence of some Marangoni effect. The bismuth phase is not distributed uniformly along the crucible bottom, but concentrates in the centre. Thus, during the cooling phase, the enormous temperature gradient seems to have brought about some Marangoni transport towards the thermal centre of the samples [6].

In experiments under microgravity conditions, monotectic phase enrichment was observed either in the sample centre or on the surface of the samples. It was assumed that a different wetting effect of the monotectic phase and the crucible material was responsible for this different behaviour [7–9].

In our microgravity experiment during a TEXUS 20 flight, we intended to produce some appropriate sample material to verify empirically the assumption that hypermonotectic alloys demonstrate particularly suitable tribological properties [10]. For this experiment, ternary AlSiBi alloys (with 2.5 and 5 wt % Si and up to 20 wt % Bi) were selected for the following reasons.

1. We preferred bismuth to lead because the critical separation temperature of the Al–Bi system is clearly lower than that of the Al–Pb system. Therefore, the chance of achieving a completely homogeneous melt by superheating within the available period of time under microgravity conditions could be expected to be higher.

2. Silicon was added for two reasons. First, as already mentioned, bearing materials require not only soft but also hard phases. Secondly, we expected that, owing to the particular crystallization features of ternary alloys, the phase-separation effect would, at least, be inhibited by a network of rapidly growing primary aluminium dendrites.

The solidification process will be explained on the basis of the ternary phase diagram for AlSiBi established by Lukas and Sommer [11]. When, during the cooling of a homogeneous hypermonotectic melt, the miscibility gap is reached, the separation of this liquid into an aluminium-rich melt and a bismuth-rich one takes place. Both melts contain almost identical amounts of silicon. When cooling is continued, the aluminium content of the aluminium-rich melt is further enriched and finally the monotectic line is reached. At this point, aluminium dendrites will grow on solidification of the aluminium-rich melt, because of the given melt proportions. These dendrites build a kind of network throughout the melt.

As long as this dendrite-forming fraction is small as compared to the entire melt volume, this crystallization process will not take long, because only a small amount of latent heat will be set free. The assumption was made that the quickly growing network of dendrites would sufficiently restrict Marangoni transport of the droplets and so help to maintain a uniform distribution of particles throughout the melt.

On further cooling, the silicon concentration in both melts will rise and a univariant equilibrium of four phases will be reached. At this stage an aluminium–silicon eutectic results from the remaining aluminium-rich liquid and, additionally, a bismuth-rich phase forms. However, now the bismuth-rich phase, in its liquid form, is definitely included in a solidified matrix. Finally, at a temperature of 273 °C, the bismuth-rich phase forms a ternary eutectic, with the residual aluminium and silicon contents present in the liquid crystallizing on the surfaces of the bismuth droplets. So the droplets are of almost pure bismuth.

The results of these experiments were, however, disappointing. A transverse microsection of a sample reveals both types of bismuth concentrations (Fig. 2), that were also found in experiments by other researchers [2, 7–9]. First, a bismuth film had formed on the sample surface. In this area, droplets and interdendritic shapes of bismuth were also found. These interdendritic shapes might originally have been droplets that were then drawn into the interdendritic shrinkage cavities. Secondly, occasional occurrences of big droplets were observed near to the centre of the sample, i.e. in the thermal centre during cooling. This phase distribution is supposed to be due to experimental conditions that cannot be influenced. Given that the samples must be heated very quickly, the thermal gradients between the centre and the superheated surface are correspondingly high. This favours the Marangoni transport of bismuth droplets towards

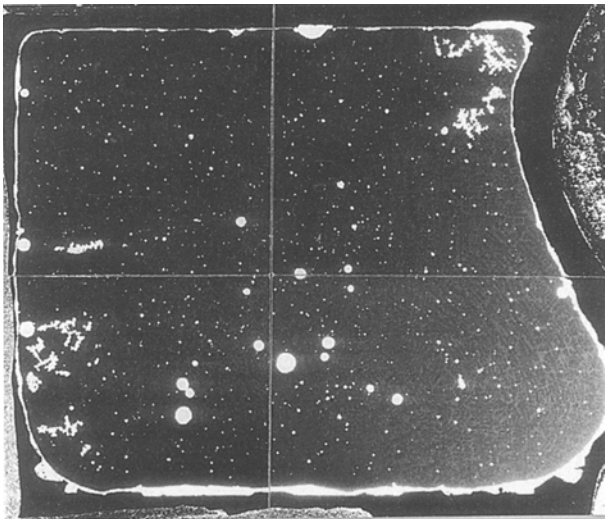

Figure 2 Distribution of the bismuth phase in AlSi5Bi20 processed under microgravity conditions (TEXUS 20).

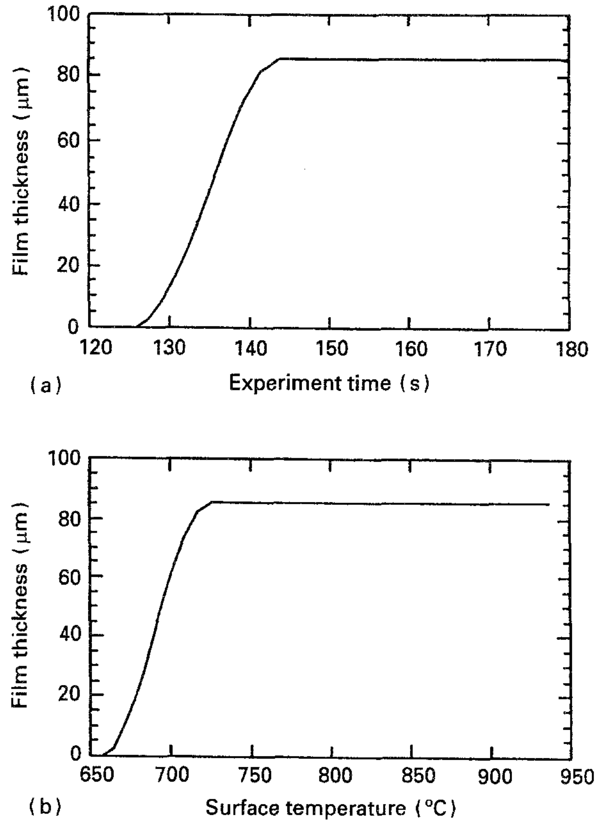

Figure 3 (a,b) Calculated film thickness on the surface of the sample under microgravity conditions.

the crucible wall, where the droplets coagulate to form a bismuth-rich film on the sample surface. As the critical separation temperature cannot be exceeded and the times available for the melt system to form a homogeneous liquid are extremely short, the major part of this film will remain as such. When crystallization starts, i.e. when the thermal gradient is reversed in the cooling phase, this bismuth-enrichment will be fixed in place. Only the bismuth dissolved in the bulk melt will precipitate as dispersed droplets and then be subject to Marangoni convection towards the sample centre, according to the prevailing thermal gradients.

The film thickness observed in the TEXUS experiment can be calculated using the following model. Heating of the cylindrical samples through the surface leads to an advance of a melting front into the sample. Its speed and position and the temperature field in the melt was calculated in a one-dimensional model. The bismuth droplets move in the molten zone by Marangoni motion towards the hotter surface. With their motion into the hotter region they also shrink in accordance with the binodal line compositions given by the phase diagram. The shrinkage is described as a diffusion process. Taking into account the experimental temperature profile at the sample surface as a function of time, the thickness can be calculated as a function of surface temperature or experiment time. The result is shown in Fig. 3, which demonstrates clearly that heating from the surface leads within a few tens of seconds to a mean layer thickness which is in agreement with the experiment.

Although the experimental result was very unsatisfactory, the experiment itself was certainly of some use.

3. Principles of a new terrestrial continuous strip casting process: partial compensation of the effects of gravity by superposition of strong Marangoni convection in the opposite direction

The production of appropriate samples for the TEXUS experiments required much consideration and many calculations based on the results of previous space experiments, particularly those of Ahlborn and Löhberg [12]. This work gave rise to the first ideas of how to produce hypermonotectic alloys under terrestrial conditions.

In this process, the sedimentation of the heavy bismuth phase caused by gravity is to be compensated, at least in part, by a similarly strong Marangoni effect acting in the opposite direction [13]. This has to take place under stationary conditions of a continuous casting process. Unfortunately, it has not yet been possible to quantify the required process parameters. However, some basic prerequisites for the process could be established.

1. Only a continuous casting process is suitable, which allows appropriate stationary conditions to be established and maintained throughout the entire casting operation.
2. The direction of the thermal gradients ahead of the solidification front, i.e. the direction of crystallization, must be opposite that of gravity. Therefore, only a vertical process is possible.
3. The period of time between phase separation in the melt and solidification of the primary phase must be kept as small as possible. This requires very high cooling rates and, at the same time, high temperature gradients ahead of the solidification front.
4. Such conditions can only be obtained in the centre of castings of moderate thickness or small diameter. In our own casting process, strips 10 mm thick were cast. Cooling rates of more than 600 $K\,s^{-1}$ have been reached with temperature gradients ahead of the solidification front greater than 500 $K\,cm^{-1}$.

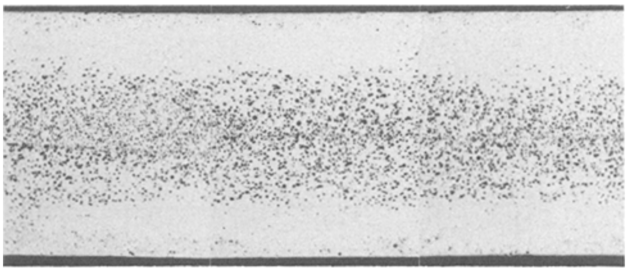

Figure 4 As-cast microstructure of a 10 mm thick strip of AlSi5Bi 10 hypermonotectic alloy.

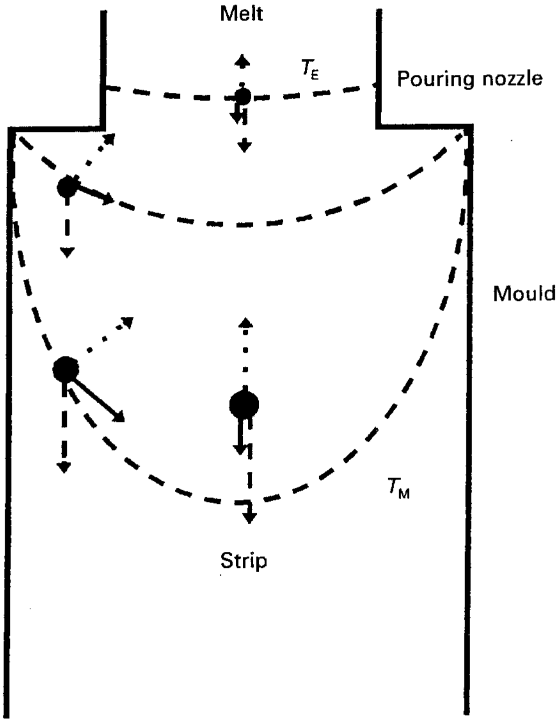

Figure 5 Mechanisms controlling the movement of bismuth droplets during the continuous casting process. (– – –) Sedimentation due to gravity (Stokes) $\approx R^2$; (...) Marangoni convection $\approx R$, gradient T; (——) resulting movement of droplets. T_E, separation temperature; T_M, monotectic temperature.

4. First results: confirmation of the applicability of the process and of the superior tribological suitability of hypermonotectic alloys

Fig. 4 shows the results of the cast strip (cross-section). The completely uniform concentration and distribution of the bismuth phase in the strip matrix (which consists of the primary aluminium dendrites and the AlSi eutectic) remains unchanged throughout the entire casting process. A characteristic feature is the enrichment of bismuth towards the centre of the strip, while the surface regions, which are approximately 1.5 mm wide, are largely free of any bismuth phase. The size of the bismuth droplets in the cast strip depends on the alloy composition. For identical composition, however, the droplet size obtained in different experiments demonstrates notable variation depending on the special casting conditions, while remaining constant within any single strip. Owing to droplet enrichment in the centre of the strip, the mean bismuth concentration at that point was found to be approximately double that of the initial composition of the melt. When defining the alloy composition with regard to the desired phase concentration, this phenomenon must be taken into consideration.

The reasons for the particular phase distribution with bismuth enrichment in the thermal centre are explained in Fig. 5. In the centre of the cast strip, the vector of Stokes' sedimentation velocity is pointing downwards, while that of the Marangoni motion is always normal to the isotherms. In this way, sedimentation is, at least partly, counteracted. The resulting droplet movement is dominated by Marangoni motion for small droplets and by Stokes' motion for large droplets, owing to the different radial dependence of both kinds of motion. Towards the surfaces of the strip, gravity sedimentation is also directed downwards, but the vector of sedimentation velocity is smaller than that in the centre because of the smaller droplet diameter. As the cooling process inevitably is applied to the sample surface, the temperature gradients in the surface region are directed to the centre of the strip. Thus the Marangoni effect on the bismuth droplets in the surface regions is directed to the centre, and at some distance from the surface its vector is perpendicular to the isotherm curves and to the curvature of the solidification profile. The resulting droplet movement is from the surfaces to the centre. Whether the droplets simultaneously slightly rise or sink remains to be shown.

At the moment, the mechanisms outlined above unfortunately cannot be proved quantitatively, because the process parameters cannot be varied to the extent required. Nevertheless we believe that this is a very plausible theory, which confirms the considerations that have led to the development of this special casting process. With the cast strips, thus obtained, it has been possible for the first time to produce a material of hypermonotectic alloys whose monotectic phase is well defined in size and distribution. Because the strips were solidified under stationary conditions, the phase distribution throughout the strip length is uniform, independent of the point of sampling. This made the strips a sufficiently defined test material which we could use during the course of already performed microgravity experiments (TEXUS 28 [14], D2[15]) to study the processes taking place during transport and growth of dispersed monotectic droplets in quantitative terms.

For our technical purposes the cast strips are an appropriate test material to verify the good tribological properties of such materials for sliding bearings. It should be pointed out that the cast strips cannot be used directly as a sliding bearing. First, it must be formed by rolling and is usually cladded on steel. Therefore, the inclusions, which are in the as-cast

TABLE I Tribological characteristics of some aluminium-based bearing alloys

Alloy	Mean friction coefficient, μ	Mean running time, t (min)	Mean wear of samples, Δl (μm)	Number of samples, n
AlSn20Cu (rolled)	0.05	43	n.d.[a]	0
AlZn5SiCuMg (rolled)	0.07	32	175	1
AlSi2,5Bi5 (as cast)	0.04	48	238	2
AlSi5Bi10 (rolled)	0.03	54	57	3
AlSi5Bi10 (rolled and treated)	0.03	$\geqslant 90$	16	18

[a] Not determined.

condition spheres, are transformed after the mentioned treatment into long plates. However, in order to achieve a favourable tribological behaviour, a subsequent recoagulation process is required [16].

These cast strips made of monotectic alloys are generally new materials and their behaviour during forming, cladding on steel and heat treatment for recoagulation has very little in common with that of conventional bearing materials. Therefore, it will be necessary to develop the appropriate process conditions required for each process step.

The results of the first tribological pin-on-disc tests with our strip material are shown in Table I. Both the measured friction coefficients and the wear data measured by pin-on-disc tests show that under the same test conditions the new hypermonotectic material is superior to conventional alloys, provided that the conditions for all subsequent process steps are optimized.

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