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Alloy microstructures revealed by the technique of selective sublimation

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A new metallographic technique, selective sublimation, has been developed to remove as a gas the volatile matrix of certain two-phase alloys. In this way, microstructures of the remaining phase can be revealed to great depth into the specimen without damage to the phase exposed. Observations can then be made to advantage in the scanning electron microscope. The technique has been used on alloys based on Cd, Mg and Zn to reveal eutectic as well as dendritic micromorphologies. Very thin films of the Mg_2Si phase have been identified in the Mg–Mg_2Si eutectic.

1. Introduction

To obtain maximum information and reliability, observations of microstructures should be three-dimensional. While traditional metallography of planar sections is useful to determine the nature and the distribution of phases present in a specimen, it may be misleading to draw from it conclusions about the morphology of these phases in space. For example, the Cu–Cr eutectic has for a long time been mistakenly termed "globular" [1]. This situation can be remedied by the laborious technique of successive polishing [2, 3].

The unique depth of focus of the scanning electron microscope allows three-dimensional observations. To take advantage of it, one phase of the alloy can be removed to leave the other phase(s) standing free and ready for observations. This has been done by the selective dissolution of one phase in specimens of, for example, NiAl–Cr [4] and Al–Si [5]. However, this technique is limited in the depth of removal it achieves, and it occasionally damages fragile structures. Such limitations could be removed if one phase were eliminated via the gas phase.

In the present work, a new technique of selective sublimation has been developed to bring about this removal. Using this technique, the minor phase of an alloy was revealed by sublimating the volatile matrix in which it was embedded. This was achieved by the appropriate heating of samples under reduced pressure. This technique has been applied to the study of dendritic and eutectic structures in alloys based on Cd, Zn or Mg.

2. Experimental procedure

In order to reveal the non-volatile phase by removing the volatile matrix, the specimen was subjected to a sublimation treatment. This treatment involved heating the specimen under a dynamic vacuum of 10^{-4} mm Hg. The treatment temperature was about 70% of the relevant eutectic temperature (K). This ensured that the structure was not altered by the heat treatment.

The apparatus, in which the sublimation treatment was carried out, is shown in Fig. 1. It consisted of a moveable furnace, a "pyrex" vacuum chamber and a vacuum system composed of a mechanical pump and an oil diffusion pump. The oil diffusion pump could be bypassed by means of a butterfly-valve. This ensured a rapid change of specimens and minimized the waiting time between runs.

Preparation of the specimen before the treatment of sublimation involved a rapid mechanical polishing of the area to be revealed, down to 600 grit paper. This eliminated any surface contami-

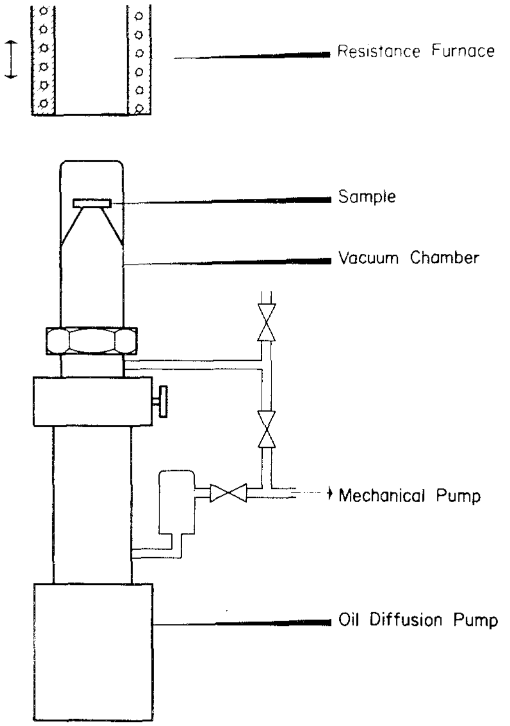

Figure 1 Apparatus for sublimation treatment.

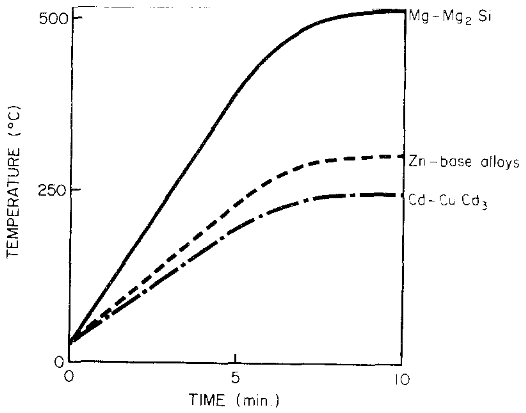

Figure 2 Temperature evolution in specimen for various alloy systems.

nation which would prevent or slow down the sublimation process; this also ensured that the removal of material started on a smooth specimen surface and thus proceeded evenly inwards.

A typical sublimation run was as follows: once the specimen was in position inside the vacuum chamber, primary, and then secondary vacuum was established. When the pressure reached about 10^{-4} mm Hg, the furnace, which had been preheated to the appropriate temperature was lowered into position around the vacuum chamber. Between the lowering of the furnace and its removal at the end of the run, the time elapsed ranged from twenty to thirty minutes, depending upon the nature of the specimen. This duration will from now on be referred to as treatment time.

The temperature of the specimen was monitored for each type of alloy investigated. For this, a thermocouple was inserted in the centre of the specimen and the temperature was recorded to the nearest 2° C, as shown in Fig. 2 for Cd, Zn and Mg-base alloys. On these curves, the initial temperature is the room temperature just before the furnace is lowered into position. These curves proved to be reproducible. The temperature of the specimen rose for 5 to 7 minutes. The rate of heating and the maximum temperature reached were controlled by the furnace power supply. When the specimen reached a sufficient temperature, sublimation took place rapidly: a metallic mirror was deposited within minutes on the unheated, lower part of the walls of the vacuum chamber. The specimen was thus exposed to the sublimation temperature for a very short time, usually 5 min, which will be referred to as the sublimation time. Since sublimation is an endothermic process, it causes the specimen temperature to level off. The sublimation was stopped by removing the furnace. The specimen was then allowed to cool off and removed. The sublimation was found to affect only the area of the specimen which had been polished. Surface contamination prevented it elsewhere.

In the samples thus treated, the sublimation removed the volatile phase and thus exposed the remaining intermetallic non-volatile phase to a depth of 0.1 to 0.4 mm. These samples were then observed by scanning electron microscopy. In the microscope used, analyses could be carried out during the observations with an X-ray energy dispersive analyser.

Good perspective views of both dendritic and eutectic structures were thus obtained by scanning electron microscopy. Alloys based on cadmium, magnesium and zinc were investigated. These alloys are as follows: Cd–Cu, Cd–Al, Cd–Pb, Zn–Mg, Mg–Ni, Mg–Sb and Mg–Si.

3. Results

3.1. Eutectic morphology

The Cd–$CuCd_3$, Mg–Mg_2Si, Mg–Mg_2Ni and Mg–Mg_3Sb_2 eutectics have been investigated in the present work, using the procedure described above. The intermetallic phase was thus revealed to a depth of 150 to 400 μm after a 30 min sublimation treatment. Despite this deep removal of the matrix, no part of the intermetallic phase was observed to have collapsed. This indicates a very high degree of connectivity in the intermetallic phase, in turn indicating that repeated nucleation of that phase does not take place during freezing.

The results obtained concerning the morphologies of both the Cd–$CuCd_3$ and Mg–Mg_2Si eutectics, and their modifications by small tertiary additions, have been reported previously [6]. The findings concerning these two systems will therefore be only briefly summarized here.

3.1.1. Cd–$CuCd_3$ eutectic

The typical fibre morphology of this eutectic is shown in Fig. 3 in a directionally solidified eutectic sample. This micrograph shows that the fibre tips have been somewhat smeared during polishing. In the fibrous structure, plates developed when certain tertiary additives, such as Zn are added [6], as shown in Fig. 4.

3.1.2. Mg–Mg_2Si eutectic

The Mg–Mg_2Si eutectic was found to be primarily fibrous, but branched fibres and plates were present in all samples, as shown in Fig. 5. Some of these plates were thin enough to be transparent to 100 kV electrons upon observation by transmission electron microscopy, without any specimen preparation. They were identified by electron diffraction as being Mg_2Si, their thickness was estimated to be 0.1 μm or less. Two crystallographic orientations, (1 0 0) and (1 1 0) were found for these plates in the course of observing over 70 samples, as shown in Fig. 6.

Although these thin plates are very fragile, they were not damaged by the sublimation treatment, but were destroyed by chemical etching.

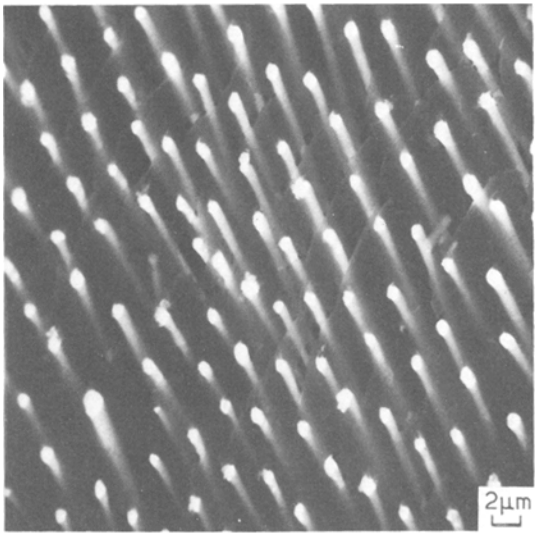

Figure 3 Fibres of $CuCd_3$ phase revealed by sublimating the Cd matrix in Cu–$CuCd_3$ eutectic. Directionally solidified samples (growth rate: 10 cm h^{-1}, temperature gradient: 80° C cm^{-1}).

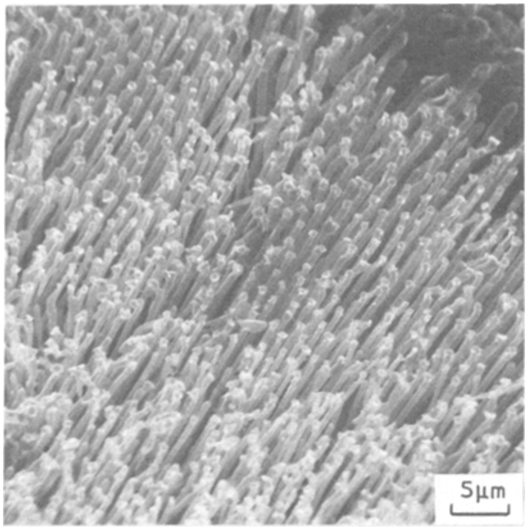

Figure 4 $CuCd_3$ phase modified by addition of 0.8 wt% zinc.

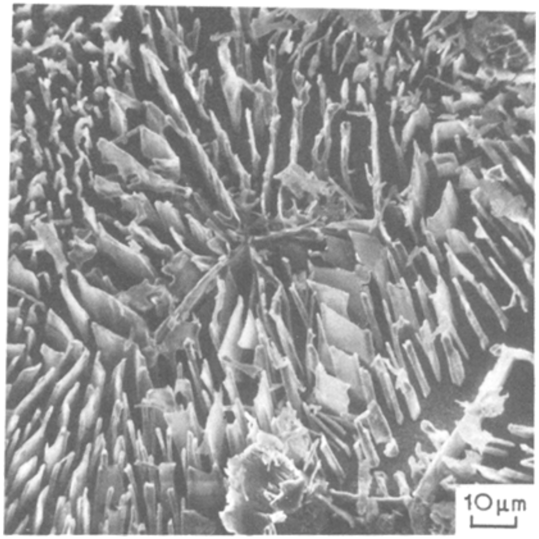

Figure 5 Rods and thin plates of Mg_2Si phase revealed by sublimating the Mg matrix in Mg–Mg_2Si eutectic. Directionally solidified sample growth rate: 8 cm h^{-1}, gradient: 80° C cm^{-1}).

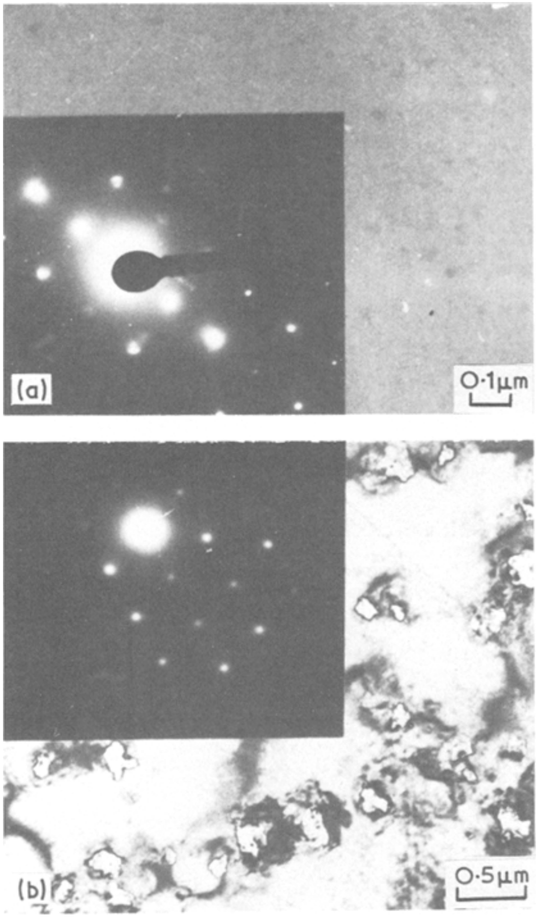

Figure 6 Thin plates of Mg_2Si phase. Transmission electron micrographs and diffraction patterns (a) (1 0 0) plane; (b) (1 1 0) plane.

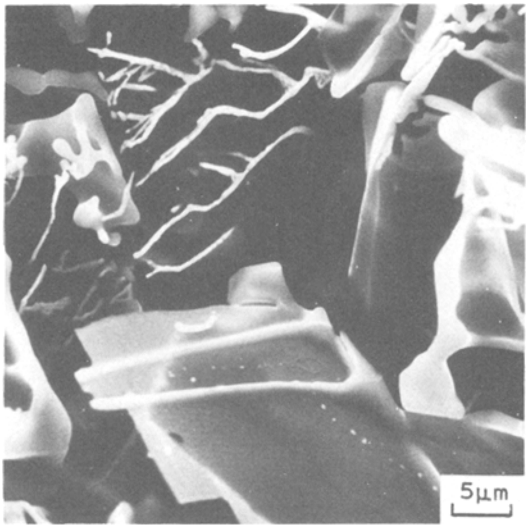

Figure 7 Rods and plates of Mg_2Ni phase revealed in Mg–Mg_2Ni eutectic.

In fact, in chemically etched samples no thin plates were observed.

3.1.3. Mg–Mg_2Ni eutectic

The Mg_2Ni phase, exposed by sublimation of the magnesium matrix out of the eutectic, is shown in Fig. 7 in a cast and air-cooled sample. Both lamellae and fibres are present. A detailed study of directionally grown Mg–Mg_2Ni eutectic should be of particular interest since the volume fraction of the Mg_2Ni phase (~ 35%) in the eutectic is close to the predicted breaking point between lamellar and fibrous morphologies [1].

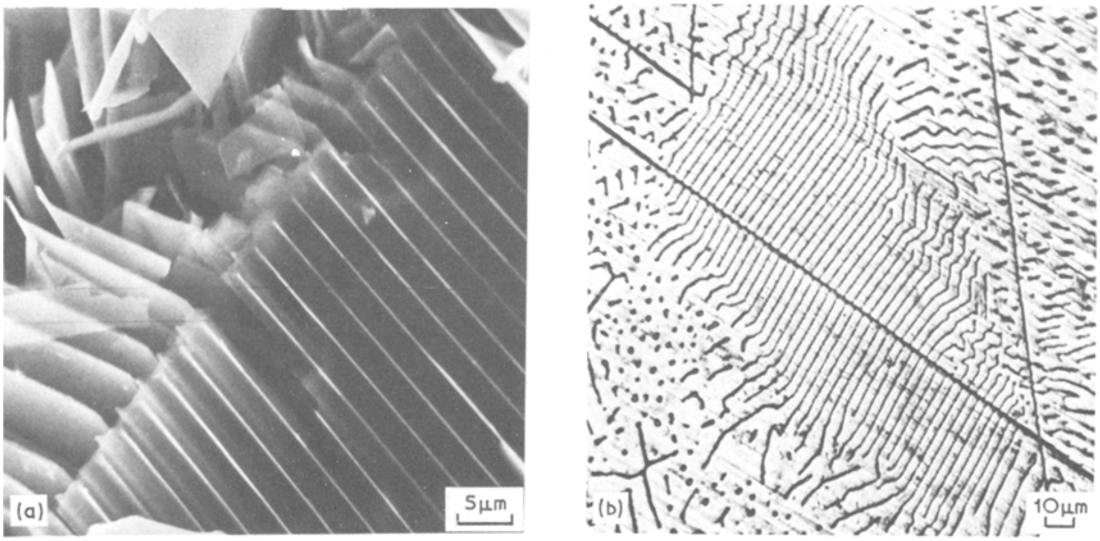

Figure 8 Array of Mg_2Si plates in Mg–Mg_2Si alloy. (a) Scanning electron micrograph; (b) optical micrograph.

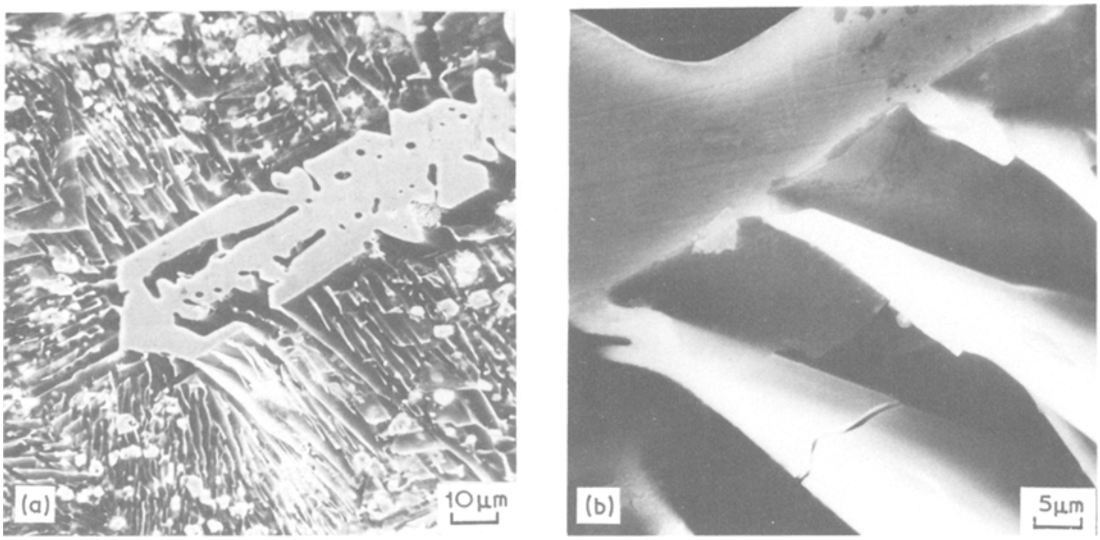

Figure 9 Dendrite and plates of Mg_2Si phase in Mg–Mg_2Si alloy. (a) Continuity between dendrite and eutectic; (b) junction between dendrite and eutectic (enlargement of above micrograph).

3.1.4. Mg–Mg_3Sb_2 eutectic

Preliminary experiments have been carried out on the Mg–Mg_3Sb_2 eutectic. A 10 min sublimation time (at 340° C) uncovered the Mg_3Sb_2 phase to a depth of 300 μm. This phase consists of plates.

3.2. Dendritic morphology

The selective sublimation technique has been used in the present work to reveal as-grown dendritic morphologies. As previously, this was done by the removal of the more volatile phase. The following systems were studied in this way: Mg–Si, Mg–Pb, Cd–Al and Pb–Cd.

3.2.1. Mg–Si alloy

In this system, good perspective views were obtained of arrays of primary Mg_2Si plates, as shown in Fig. 8. It was thus possible to have a much better representation of this morphology, than allowed by conventional optical metallography (Fig. 8).

Faceted "arrow head" dendrites of the Mg_2Si phase were shown to present some continuity with the same phase in the eutectic, as shown in Fig. 9. This results from the nucleation during growth of the eutectic phase by the dendrite.

3.2.2. Mg–Pb alloy

In this system, the Mg_2Pb phase of the Mg–Mg_2Pb eutectic has been revealed by the removal of magnesium, as shown in Fig. 10. It was positively identified by X-ray microanalysis. Here also continuity of the Mg_2Pb phase between the primary phase and the interdendritic eutectic morphology of a Mg_2Pb faceted dendrite is shown in Fig. 11.

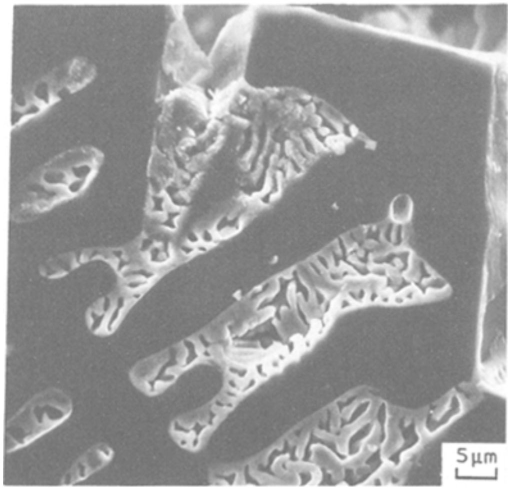

Figure 10 Continuity of Mg_2Pb phase between dendrite and eutectic in Mg–Mg_2Pb alloy.

3.2.3. Cd–Al alloy

Directionally solidified Cd-rich Cd–Al alloys containing 0.5 to 1 wt% Al, were revealed by sublimating out the cadmium. This provided good perspective views of the aluminium dendrite morphology, as shown in Fig. 12. Secondary branches are clearly revealed, with strictions at their points of attachment to the main stalk.

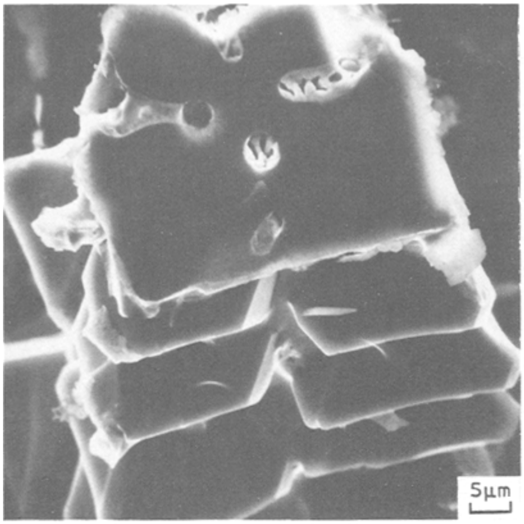

Figure 11 Mg_2Pb dendrite in $Mg-Mg_2Pb$ system.

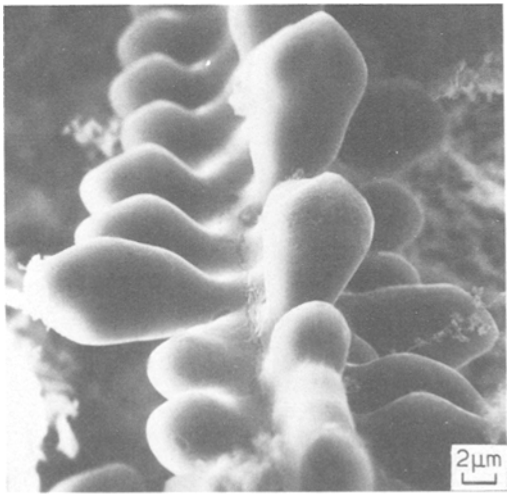

Figure 12 Aluminium dendrite revealed by sublimating Cd matrix out of a Cd–Al alloy.

Some faceting of the dendritic lobes was observed. In aluminium (f c c symmetry), dendrites grow along the (1 0 0) direction and the facets are (1 1 1) planes. Such faceting has been attributed to a population effect encountered in very dilute alloys [7], as in the present case.

3.2.4. Pb–Cd alloy

In this system, the volatile (cadmium) phase is the minor (dendritic) phase, instead of being the major matrix phase, as was the case in previous systems. The sublimation of the cadmium thus eliminated the dendrites, resulting in the structure shown in Fig. 13. Here, the direct observation of dendritic morphologies is not possible.

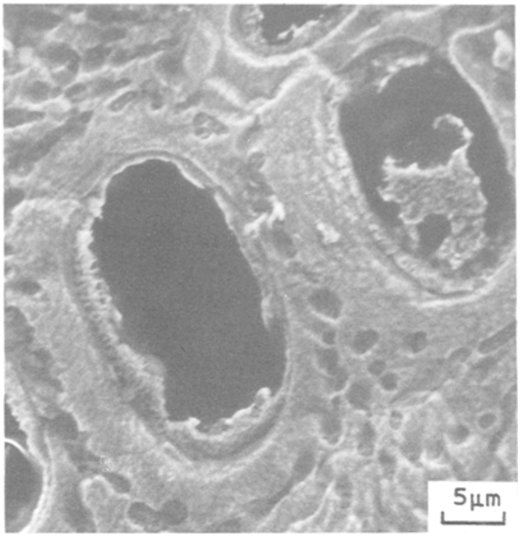

Figure 13 Pb phase in Pb–Cd alloy after sublimation of Cd dendrites.

Preliminary experiments indicate however that a three-dimensional replication technique can provide an indirect means of observation. Resin can be cast into a sample, in which the primary phase has been sublimated out. After the resin has set, the sample is dissolved in concentrated nitric acid. The resin thus obtained was found to replicate well the contours of the sample. A conductive, coating, aluminium for example, could be used to permit scanning electron microscopy observations of the replica thus obtained.

4. Discussion of the technique of selective sublimation

4.1. Sublimation of the volatile phase

The evaporation rate of a substance is given by the Hertz–Knudsen equation [8]:

$$i = \alpha(P-P')/\sqrt{(2\pi MRT)}$$

where

α = evaporation coefficient.
i = flux of evaporated molecules (mol sec^{-1} cm^{-2}),
P = vapour pressure of the substance at temperature T (K),
M = molecular weight of evaporated substance,
R = gas constant,
P' = actual vapour pressure of substance during sublimation.

Metals are vaporized as monatomic molecules and have an evaporation coefficient close to unity.

The imposed pressure of 10^{-4} mm Hg in the vacuum chamber was chosen because it is low enough to prevent oxidation of the specimens and to yield sufficient Cd, Zn and Mg evaporation rates at moderate temperatures. At this pressure, the mean free path of the gas molecules is such that the vapour emanating from the specimen is removed from its surface without bouncing back onto it. The pressure P' can thus be considered very close to the imposed pressure of 10^{-4} mm Hg and, at any rate, much smaller than P.

The weight loss G resulting from sublimation is obtained by multiplying by the molecular weight the rate i given by Hertz–Knudsen equation:

$$G = \frac{P - P'}{17.14} \cdot \sqrt{\left(\frac{M}{T}\right)}$$

where G is in $\mathrm{g\,sec^{-1}\,cm^{-2}}$ of metal and P and P' are in mm Hg.

Weight losses after a five-minute sublimation time were measured by weighing specimens before and after the treatment and by measuring the area affected by it. As noted earlier, this area is the surface of the specimen which was mechanically polished before the treatment.

At the temperature of the sublimation treatment, the vapour pressure is 1.54×10^{-3} mm Hg for Cd (at 220° C), 9×10^{-2} mm Hg for Mg (at 500° C) and 10^{-2} mm Hg for Zn (at 340° C). Corresponding values for G were calculated and found to tally with measured weight losses in alloys based on cadmium, magnesium or zinc.

The removal of the volatile matrix was found to be uniform over the sublimated area. Larger depths of removal could be achieved by prolonged times of sublimation. It was found, however, that as sublimation progresses deeper into the specimen, its rate decreases. According to the calculated weight loss G, a 400 μm depth should be achieved in Mg–Mg_2Si, for example, after eleven minutes of sublimation treatment. In reality, double the amount of time was found necessary. This slowing down of the evaporation rate is attributed to a more difficult path of escape for the gaseous molecules. As sublimation progresses deeper, the bouncing of molecules into the features of the microstructure creates a locally high vapour pressure. This reduces the driving force of the sublimation treatment.

4.2. Applicability of the technique

The technique of selective sublimation is applicable to alloys in which the vapour pressure of one phase is higher and much larger than that of any other phases present in the alloy. The non-volatile phase may be a solid solution, an intermetallic compound or a pure metal.

A further requirement is that the volatile phase be a metal with little or no solubility for the other constituents of the alloy. This requirement is met by the alloys which have been the subject of calculations and measurements in previous sections.

If the volatile metal forms a solid solution with the non-volatile solute, its sublimation is slowed down and cannot progress deep into the alloy; the vapour pressure of the solid solution is lower than that of the pure matrix. In dilute solutions (less than 10 at% of solute), this lowering is expressed by Rauolt's law:

$$p_A - p_S = x_B p_A$$

with

p_A = vapour pressure of pure volatile metal,
p_S = vapour pressure of volatile metal in solution,
x_B = atomic fraction of solute.

This decrease in vapour pressure reduces the evaporation rate i by the same ratio x_B. For higher solute concentrations, the decrease in i is

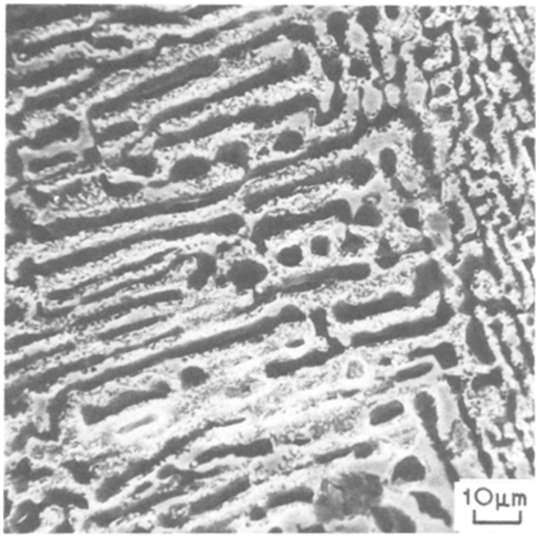

Figure 14 Mg_2Cu phase in Mg–Mg_2Cu alloy after sublimation of Mg.

more or less rapid than linearity, depending upon the deviation of the solid solutions from ideality.

As sublimation progresses, the volatile metal is removed, leaving behind a solid solution enriched in the non-volatile solute. The vapour pressure of the solid solution decreases and eventually the sublimation stops. This results in a shallow removal of material, as in systems such as Mg–Mg_2Sn and Mg–Mg_2Cu. As a result, the sublimation treatment reveals the Mg_2Sn phase to a depth of 10 to 15 μm only, even after prolonged times (40 min). The situation is the reverse in the Mg–Mg_2Cu eutectic: magnesium is soluble in the intermetallic phase Mg_2Cu. The Mg_2Cu phase is thus altered by the removal of magnesium by sublimation, as though it had been partially dissolved (Fig. 14).

4.3. Effect of heat treatment on microstructure

The heat treatment during sublimation is moderate. Indeed, the specimen is heated at no more than 70% of the eutectic temperature of the alloy for a few minutes. It should not affect the microstructure of the alloy.

In order to make sure that such is the case, etched and sublimated specimens of the same sample were observed. They showed the same features. Specimens were also heated in evacuated ampules at the sublimation temperature for periods of up to 100 h. No effect on the morphology was observed. It is therefore felt that the technique of selective sublimation allows observations of as-grown morphologies, unmodified by the sublimation treatment.

4.4. Advantages of the techniques

To improve the two-dimensional observations of classical metallography, two methods can be used to remove one phase in an alloy for scanning electron microscopy observations. One method is selective dissolution, the other is selective sublimation, which was developed in the present work and first reported in 1974 [9]. When both of these methods are applicable, they offer the possibility of checking the reliability and selectivity of each technique, but selective sublimation has the following advantages:

(1) *Larger depth of removal.* Selective dissolution reveals the phase to be observed to a typical depth of 15 to 20 μm. The depth is limited both due to the difficulty of removing the reaction products retained in the alloy microstructure by liquid–solid interfacial tension and due to the formation of non-reactive secondary reaction products which then prevent further dissolution of the matrix. Some systems, such as NiAl–Cr, do not present these problems and the NiAl phase can be removed in depth and with good selectivity [4] after prolonged exposure to the etchant. As a rule, however, selective etching is limited to a depth of removal of 20 to 30 μm.

In contrast, alloy microstructures can be revealed by selective sublimation to depths of 100 to 400 μm with excellent selectivity. A very large volume of specimen is thus exposed and can be explored by scanning electron microscopy to yield a lot of information on its micromorphology.

(2) *Material removed in the gas state.* During a deep etching operation, gases are often violently given off, causing damage to the fragile microstructure of the alloy. In the selective sublimation technique, material is removed as a gas, making the removal much more gentle. The microstructure is therefore fully preserved, however fragile. Indeed, the thin plates of Mg_2Si (about 0.1 μm thick) destroyed by the effervescence accompanying the chemical attack of the magnesium matrix, are, on the other hand, preserved by the selective sublimation technique, as indicated earlier.

4.5. Further possible applications

Many systems based on cadmium, magnesium or zinc lend themselves well to selective sublimation, such as Cd–Sb, Mg–Mg_2Co, Zn–Ge, Zn–Zn_8Ni, Zn–$ZnSb_2$. Systems with other less volatile bases, such as calcium or manganese (vapour pressure: 10^{-2} mm Hg at 600° C) should also be suitable.

The applicability of the technique could be extended to many other alloys by combining a chemical reaction with the process of sublimation. A jet of gas could be blown into the sample, which would react selectively with one of the phases present in the alloy to yield a volatile compound. The latter would then be removed by sublimation. Chlorine is suitable for such a "vapour-etch", as chlorides such as $CoCl_2$, CuCl, $FeCl_2$ or $TiCl_4$ are volatile compounds with vapour pressures of the order of 10^{-3} mm Hg at 600° C. They could therefore be removed by sublimation under either dynamic or static vacuum by using a set-up similar to the one used in crystal growth from the vapour.

In systems where the minor phase, and not the matrix phase, is removed, replica techniques could also be used, as indicated earlier. This would provide an indirect means of obtaining perspective views of the minor phase morphology.

5. Conclusion

The technique of selective sublimation offers a new alternative to traditional metallography. Its main advantage is to reveal micromorphologies in depth without damage even to fragile features. This improvement over selective dissolution is due to the fact that material is removed via the gas state. The scope of the technique could be significantly increased by forming a volatile compound from one of the phases to be removed out of the specimen.

Acknowledgements

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