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Structural and dimensional stabilities of tin–bismuth fusible cores

I. HAUBERT‡, Y. DAUPHIN*, J-L. DELPLANCKE‡, J. CHARLIER§ and R. WINAND‡
*Research and Technology Center of Solvay S.A., LC6, Rue de Ransbeek 310, B-1120 Bruxelles, Belgium
‡Métallurgie–Electrochimie CP165, and § Métallurgie Physique CP194/03, Université Libre de Bruxelles, Avenue F.D. Roosevelt 50, B-1050 Bruxelles, Belgium

Eutectic tin–bismuth alloys, used as fusible cores for high polymer injection moulding, were studied in order to identify structural and dimensional modifications during ageing at temperatures ranging from 4 to 110 °C. Optical and scanning electron microscopies together with X-ray diffraction were used to observe the coarsening of the eutectic structure and to plot an isothermal transformation diagram. Thermal cycles around the eutectic temperature promoted the dissociation of the eutectic structure into light tin dendrites at the top of the ingots and heavy bismuth crystals at the bottom. Differential scanning calorimetry and thermomechanical analysis were performed to observe possible phase transformations.

1. Introduction

Tin–bismuth eutectic alloy is used, together with other metallic alloys, in the plastic processing industry for the production of fusible cores for injection moulding. This process produces polymeric hollow parts of complex shape from which the core could not be mechanically removed. The three main stages of this process are represented in Fig. 1:

— casting of a low melting temperature metallic core,
— positioning the core in the moulding machine and enveloping it by injection moulding with a thermoplastic polymer (i.e. Polyamid 6-6 with 30 wt% glass fibres)
— positioning the injected part in a machine where, by means of eddy currents, the metallic core is melted out of the polymer part and is recycled back to the casting machine.

This process, developed by Solvay S.A. [1] and somehow similar to the old lost wax technique, is mainly used to produce intake manifolds with the goal of substituting the aluminium ones (see Fig. 2).

The main requirements of a good core alloy are the following:

— good castability in order to produce smooth metallic surfaces,
— no segregation during cooling,
— no expansion or shrinkage during solidification and melting,
— low oxidation rate in the liquid and solid phases,
— lower melting temperature than the injected polymer,
— high thermal conductivity to preserve the core integrity during the polymer injection,
— high mechanical properties to withstand deformation due to a compressive pressure as high as 65 MPa during the injection process,
— well-defined electric and magnetic properties,
— stable structure, composition and dimensions during ageing at temperatures lower than the melting point.

The eutectic tin–bismuth alloy fulfils nearly all these requirements for the injection of Polyamid 6-6 but little is known in the literature about its ageing behaviour. This is important, from the industrial point of view, in order to guarantee a high-quality thermoplastic hollow part production. It is the purpose of this paper to present experimental results related to the ageing behaviour of the eutectic alloy.

2. Experimental procedure

The eutectic tin–bismuth alloy (57 wt % Bi), given by Solvay S.A., was, before casting, remelted at 160 °C for 15 min.

The experimental casting mould is described in Fig. 3. Its smallness provided a more or less uniform quenching temperature. The 430 ferritic stainless-steel plates inserted in the middle of the mould and used as the mould bottom were electrochemically polished in an acetic/hydrochloric acid electrolyte to provide flat alloy surfaces without mechanical polishing. The mould was preheated to 150 °C before casting.

A Memmert thermostat, filled with monoethylene glycol, was used for the sample ageing.

The thermal cycles were performed in a programmed Haake TP32 thermostated bath filled with silicon oil. The heating rate ranged from 3 to 180 °C h^{-1}.

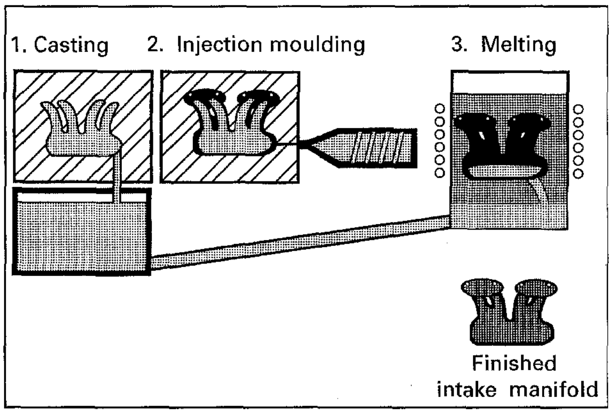


Figure 1 Production stages of fusible cores for injection moulding.

The solid alloy surfaces were etched in a 2 ml hydrochloric acid (37%)–5 ml nitric acid (52.5%)–93 ml methanol bath for 30 s at room temperature and then directly observed.

Optical micrographs were obtained with a Reichert-Jung MeF 3 microscope. Scanning Electron Microscopy (SEM) was performed with a Jeol JSM-820 microscope coupled with a 5525 Tracor Northern Energy Dispersive X-ray (EDX) analyser. X-ray diffraction analysis was performed with a Siemens D5000 apparatus.

Differential Scanning Calorimetry (DSC) experiments and Thermomechanical Analysis (TMA) were performed with a Perkin Elmer DSC 2 and a Shimadzu TMA 50 apparatus, respectively.

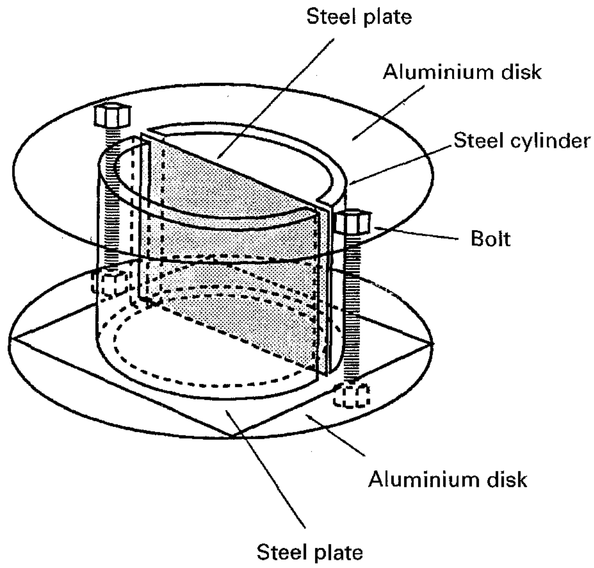


Figure 3 Casting mould for the eutectic tin–bismuth alloy.

3. Results and discussion

3.1. Structural modifications during ageing

3.1.1. Isothermal ageing

Two main equilibrium phase diagrams exist in the literature for the tin–bismuth alloy. The Hansen's diagram [2] corresponds to a pure eutectic diagram (see Fig. 4a) with a large solubility of bismuth in β-tin. This solubility decreases gradually from the eutectic temperature to room temperature. On the other hand,

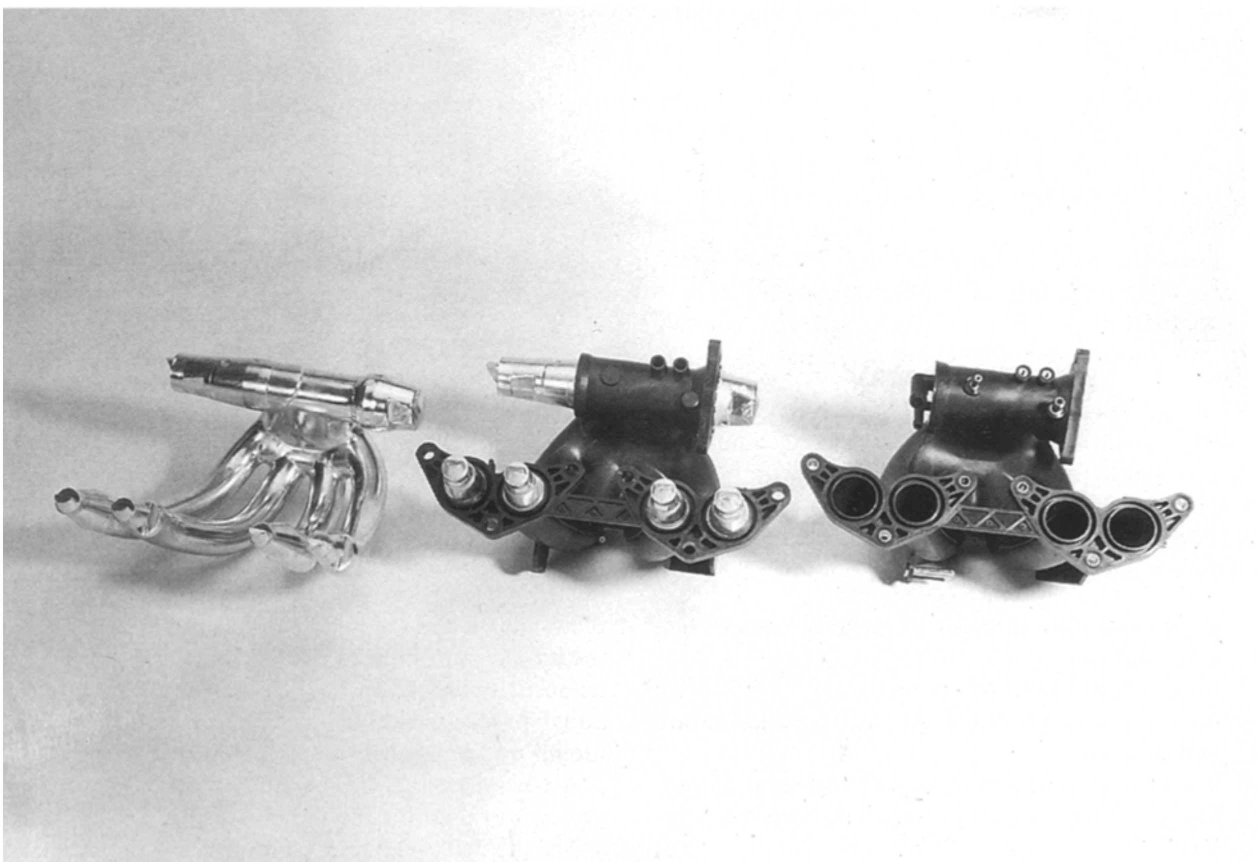


Figure 2 Example of polymer manifold produced by injection moulding.

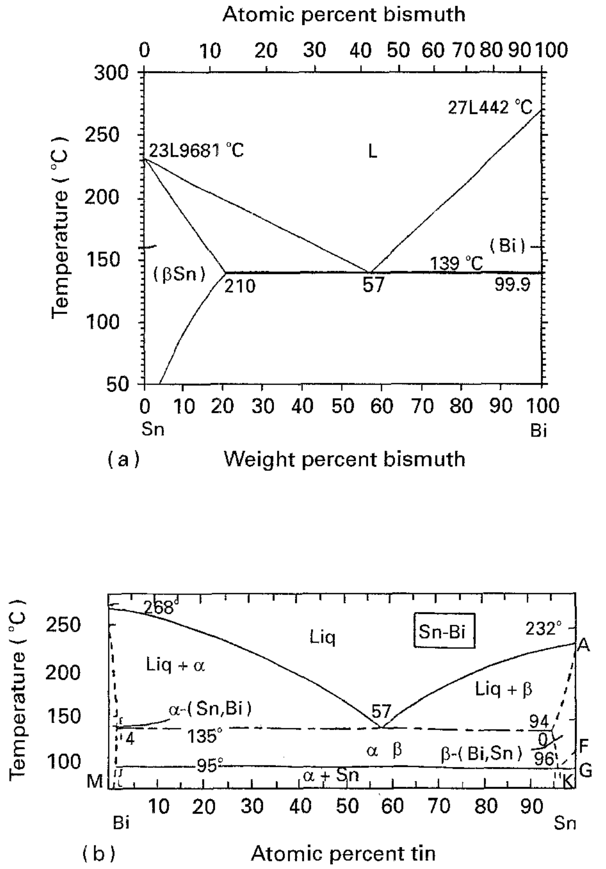


Figure 4 Tin–bismuth phase diagrams: (a) Hansen's diagram [2], (b) Kapp's diagram [3].

Kapp's diagram [3] presents an eutectic diagram with a small solubility of bismuth in β-tin at the eutectic temperature and with an abrupt decrease in this solubility at 95 °C (see Fig. 4b).

Accordingly, the isotherms for the ageing experiments, ranging from 4 to 110 °C, were selected to surround this 95 °C transition temperature. The isothermal durations ranged from 5 min to 3 months. It has to be noted that in the industrial injection moulding process, the maximum delay between casting and fusion of a core corresponds to about 1 h.

The as-cast and quenched samples presented eutectic anomalous structures in Croker *et al.*'s classification [4–6]. A mixture of quasi-regular, complex-regular and irregular microstructures was observed (see Fig. 5). This was probably due to the fact that the quenching temperature was maintained constant instead of the solid growth rate imposed by Croker *et al.* [6].

Tin dendrites covered with a thin layer of bismuth were often observed. This was in agreement with Hunt and Jackson's theory [7], if the tin dendrites could grow faster than the eutectic structure. Indeed, in this case, the tin dendrites crystallized first. They could be used as nuclei for the bismuth crystallization and could be covered by a thin bismuth layer. This layer promoted very fast nucleation of the eutectic structure. As tin was a poor nucleating constituent for bismuth [8–11], many tin dendrites could grow before being completely covered with bismuth. The liquid phase was enriched in the idiomorph constituent (Bi) and complex-regular structures surrounded by bismuth crystals could be observed [12–14]. These bismuth crystals were observed for all the experimental conditions, mainly in the centre of the ingots.

A decrease in the quenching temperature decreased the grain size but did not globally affect the observed microstructures.

Isothermal ageing promoted the coarsening (see Fig. 6 (TTT diagram)) of the structure even at room temperature (especially for the complex-regular microstructures). The lower the quenching temperature, the longer the ageing duration needed to observe the coarsening effect (see Fig. 7).

No phase transition was observed around 95 °C even for long isothermal durations. This result was confirmed by the X-ray diffraction patterns that were not affected by the quenching temperature and the ageing process. Accordingly, Hansen's diagram was favoured.

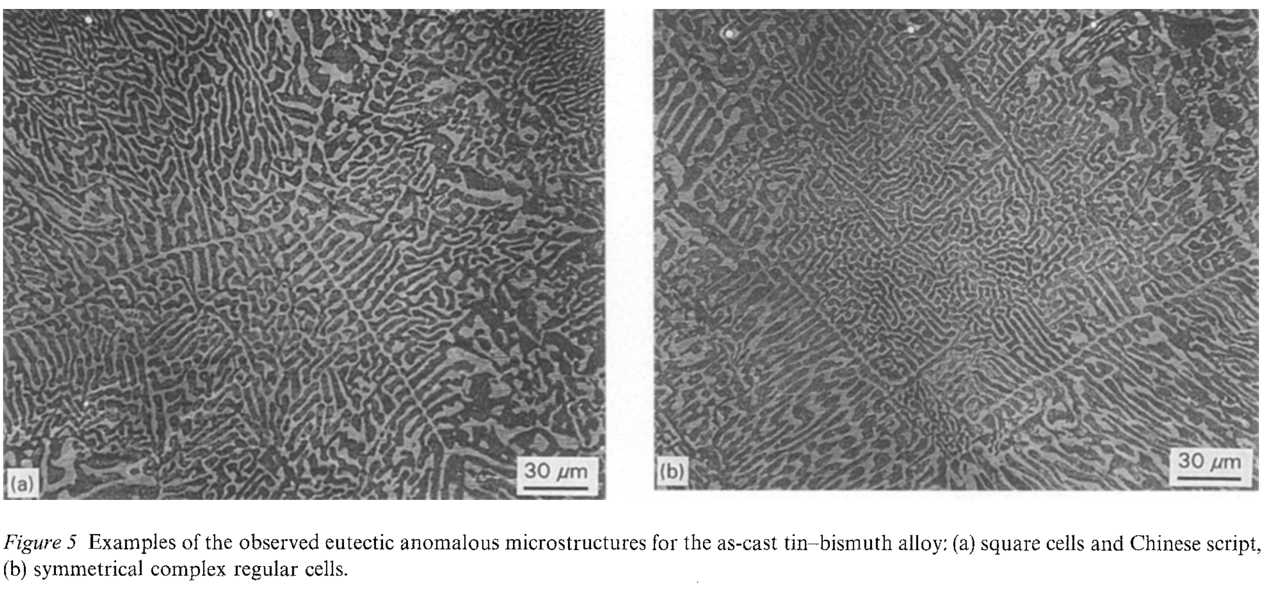


Figure 5 Examples of the observed eutectic anomalous microstructures for the as-cast tin–bismuth alloy: (a) square cells and Chinese script, (b) symmetrical complex regular cells.

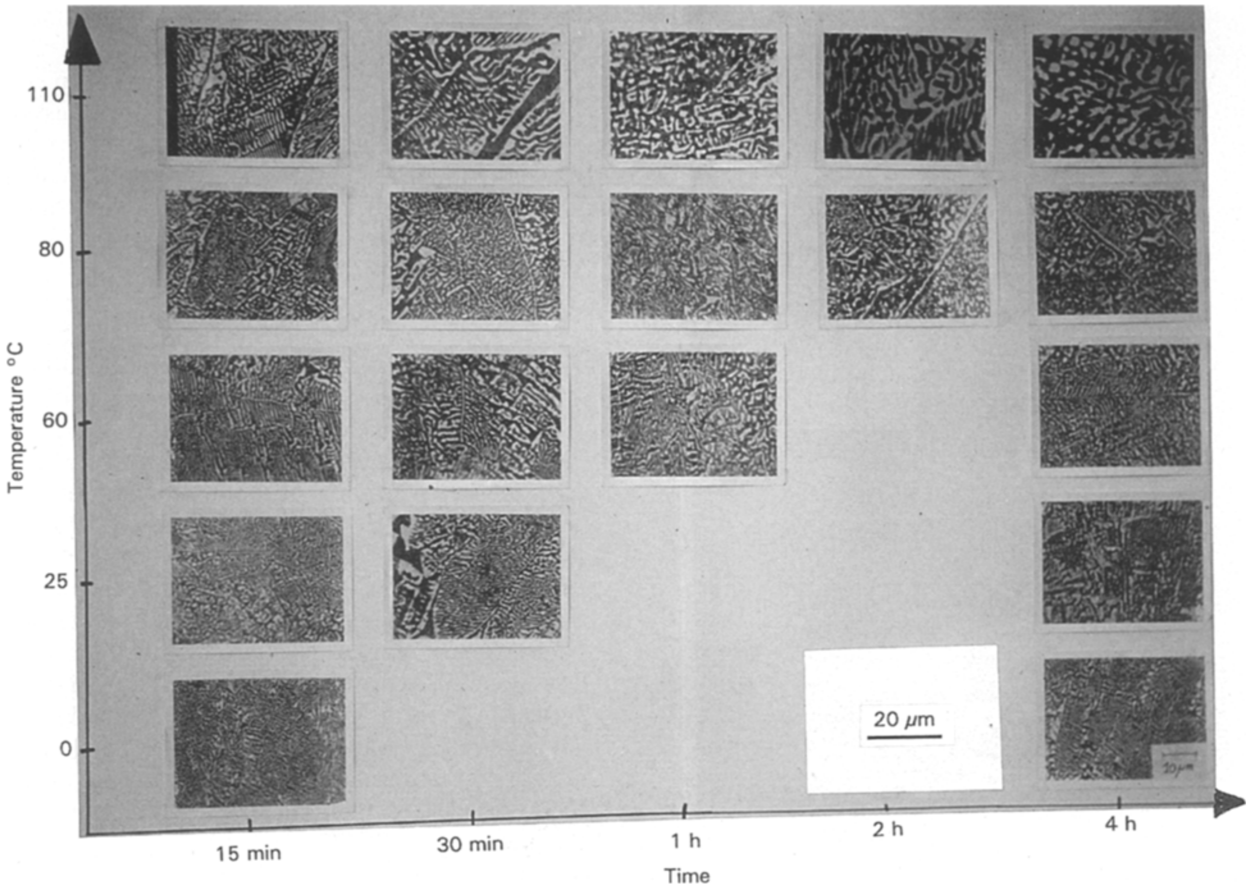


Figure 6 Temperature–time–transformation diagram of the eutectic tin–bismuth alloy.

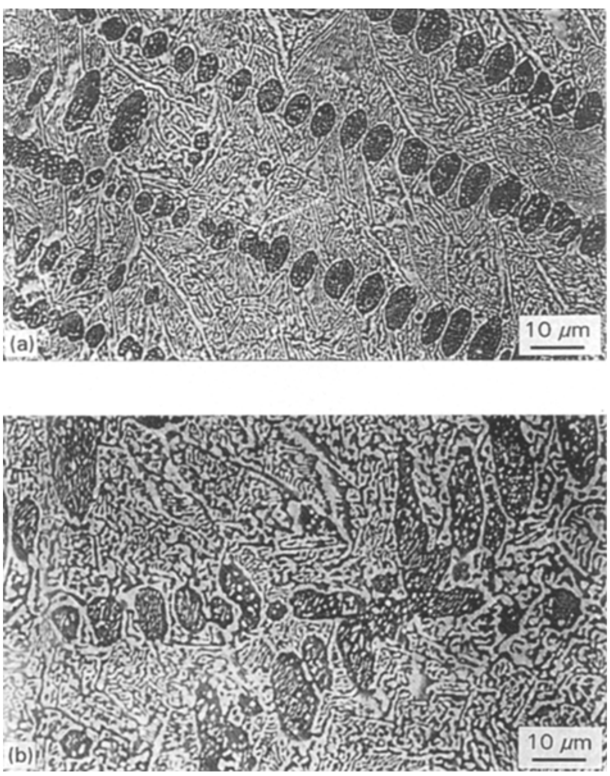


Figure 7 Room-temperature modifications of the eutectic tin–bismuth alloy: (a) 3 hours after casting, (b) 3 days after casting, (c) 3 months after casting.

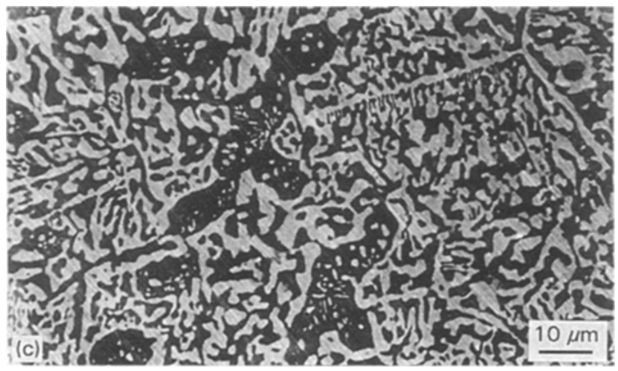
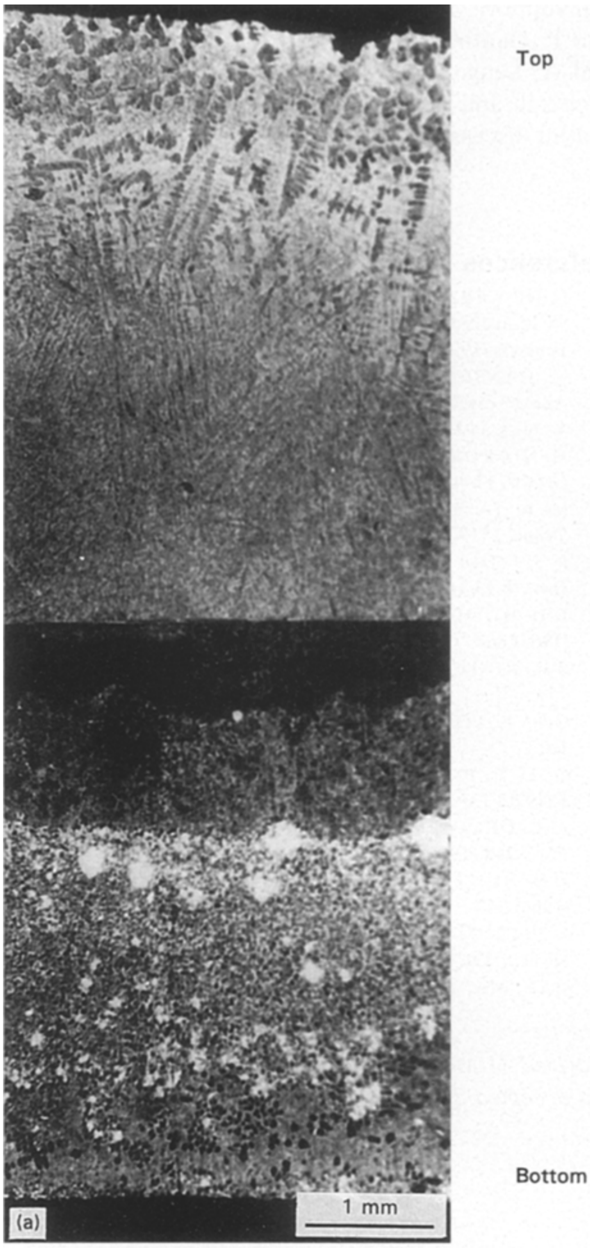


Figure 7 continued.

3.1.2. Thermal cycles

Thermal cycles were then performed around the eutectic temperature in order to study the influence of the core recycling procedure on the structure of the solidified alloy. Four thermal cycles between 120 and 140 °C (heating and cooling rates equal to 1 °C $\min^{-1}$ and 10 min isothermal ageing at 140 °C) modified the ingots structurally. A macrosegregation was observed. The eutectic structure was partially decomposed with the formation of tin dendrites and bismuth crystals. Due to density differences (tin 7.8, eutectic alloy 8.72 and bismuth 9.3), the bismuth crystals were found preferentially at the bottom of the ingots and the tin dendrites at the top (see Fig. 8a). These crystals and dendrites were not remelted by the short-term isothermal ageing at 140 °C and they grew progressively during the cycles. This segregation effect seemed to be initiated during the cooling of the liquid phase. Indeed, above the bismuth crystals, a coarser eutectic



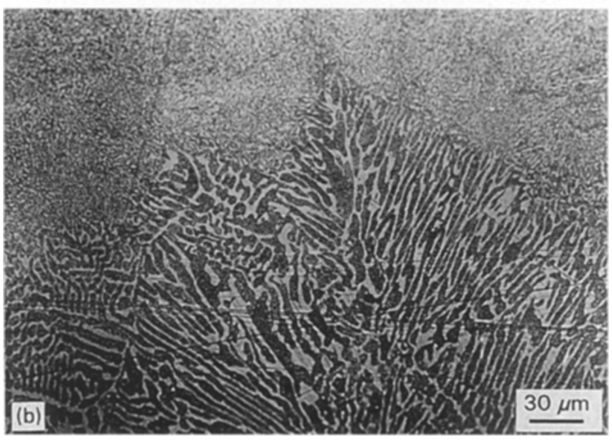


Figure 8 Macrosegregation of tin dendrites (black) and bismuth crystals (white) in the alloy ingot after 4 thermal cycles between 120 and 140 °C: (a) general view of the ingot, (b) 'Arrow head' interface observed above the bismuth crystals.

structure with an 'arrow head' interface was observed (see Fig. 8b). Moreover, thermal cycles below the eutectic temperature did not show the formation of tin dendrites and bismuth crystals even after numerous cycles.

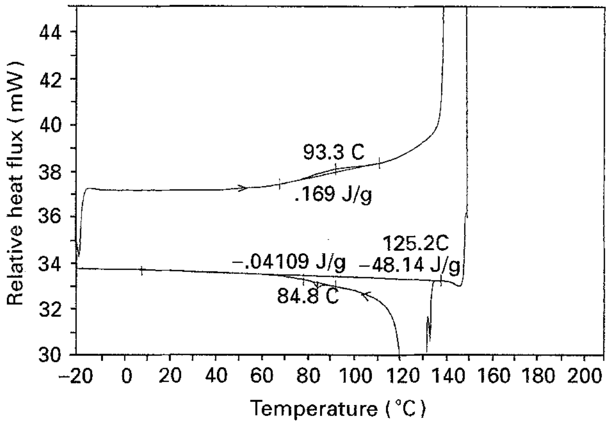


Figure 9 Differential scanning calorimetry of an eutectic tin–bismuth sample.

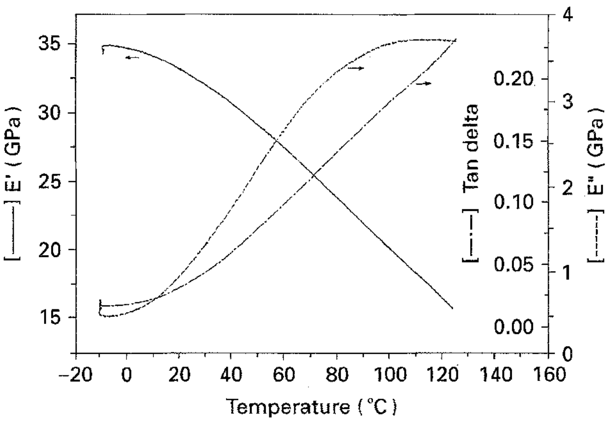


Figure 10 Thermomechanical properties of the eutectic tin–bismuth alloy (E': elastic modulus; E'': viscous modulus; tan delta: phase difference).

Due to differences between the thermal expansion coefficients of bismuth, tin and the eutectic alloy, the macrosegregation effect could progressively affect some properties of the cores used in the casting–solidifying–melting cycles. Therefore, Solvay S.A. periodically samples the alloys and if such defects occur, they could be cured by heating the alloys to a temperature higher than the fusion temperatures of tin and bismuth.

The influence of the thermal history on the sample behaviour was reflected in the differential scanning calorimetry experiments. A first fusion decreased the fusion temperature of the alloy from 140.3 ± 0.2 °C to 138.4 ± 0.2 °C for further fusions. This first fusion on the other hand, did not affect the latent heat of fusion (46.3 ± 0.2 kJ kg^{-1}), the latent heat of crystallization (− 45.8 ± 0.2 kJ kg^{-1}) and the crystallization temperature (129.8 ± 0.2 °C).

The endothermal increase started at a low temperature and was very progressive (see Fig. 9). This could be due to the presence of impurities; however, eutectic alloys prepared from 99.99% pure tin and bismuth metals showed the same behaviour.

During the heating procedure, a small endothermal peak was observed at 93 °C (first cycle) or at 125 °C (successive cycles). During the sample cooling, a small exothermal peak was observed at 84.8 ± 0.2 °C if the sample had been melted (analysis with isothermal ageing during 10 min at 145 °C). If the thermal cycle in the DSC apparatus corresponded to a maximum temperature of 120 °C, this exothermal peak was not observed.

These peaks did not seem to correspond to the presence of adsorbed water, to a structural modification of the samples, to an order–disorder transition (no modification of the X-ray diffraction patterns), to a modification of the alloy resistivity or to a modification of the dynamic thermomechanical properties of the alloy (elastic and viscous modulus) (see Fig.10). Nevertheless, the temperatures corresponding to these peaks were close to the Kapp's 95 °C temperature related to a sudden decrease of bismuth solubility in tin.

4. Conclusions

This study showed that the eutectic tin–bismuth alloy fulfilled all the industrial requirements for the injection of thermoplastics if careful attention was paid to a possible decomposition of the Croker's anomalous eutectic structure of this alloy into tin dendrites and bismuth crystals by thermal cycles around the eutectic temperature. Isothermal ageing in the 4–110 °C temperature range only promoted coarsening of the microstructure.

From a fundamental point of view, Hansen's phase diagram was favoured by this study, although some unexplained phenomena detected by differential scanning calorimetry could be related to the transition temperature mentioned in Kapp's diagram.

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