Physical Properties of Manganese-Bismuth Specimens Produced in Microgravity

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By contrast to other miscibility gap systems investigated in the micrgravity of space in which separation was caused by interfacial energy, the manganese-bismuth system showed no signs of separation under microgravity conditions. It was thus possible to take extensive physical and metallurgical measurements on the manganese-bismuth specimens, which were melted and cooled down during three space missions. The results of these measurements contribute to the knowledge of the manganese-bismuth system and to selective planning of a follow-up experiment in space.

Introduction

THE high costs for the development and preparation of compounds in migrogravity of space can only be justified when 1) preparation of these compounds is impossible under terrestrial conditions, 2) the experience from the space experiments can be used for improving terrestrial techniques, and 3) experimental data can be used for fundamental research or theoretical calculations that can help to solve problems with the preparation of materials.

In previous investigations specimens of metallic systems with a miscibility gap, which were melted and cooled down quickly under microgravity conditions, showed fine dispersions with a homogenous distribution in the matrix, new phases, and deviations of the electrical, magnetic, and thermal properties from terrestrial specimens. Examples are binary systems like Pb-Zn,[1] Ga-Bi,[2] Au-Ge,[3] Cu-Pb,[1] and Cu-Pb,[1] and Cu-Cr as well as the ternary systems Pb-Zn-Sb[3] and Pb-Sn-In.[3]

The results of the attempts to prepare these metallic systems during ballistic flights or onboard Skylab gave rise to optimistic speculations on the preparation of materials and possible new, unexpected properties. Compounds with a miscibility gap in the liquid phase were especially considered. The fineness of enclosed phases, with a typical particle size of 1 μm, and the corresponding increase of the particle surface were related to changes in surface-sensitive properties such as the coercivity. Later space experiments, e.g., the Apollo-Sojuz Test Project (ASTP) and the TEXUS flights, showed less homogeneous specimens than the earlier space experiments. Some specimens of systems with a miscibility gap in the liquid phase showed a large phase separation. Examples of this are the systems Zn-Pb in the Apollo-Sojuz flight,[2] Al-In and Al-Pb[4] in the flights of the rockets SPAR II and TEXUS I,[5,6] and Zn-Bi in the TEXUS II flight.[7] The main reasons for these negative results were considered to be surface-sensitive convection phenomena such as Maragoni convection.

To complement the microgravity experiments performed on alloys with a miscibility gap, Krupp Forschungsinstitut proposed that experiments be carried out with the manganese-bismuth system as a model for phase separation in systems with a peritectic reaction.

In the liquid state, the manganese-bismuth system exhibits a miscibility gap above the monotectic temperature of 1255°C. At 455°C, the intermetallic ferromagnetic compound $Mn_{1-x}Bi$ (with $x \approx 0.08$) forms peritectically. Upon further cooling, the high-temperature phase decomposes and forms the stoichiometric low-temperature phase MnBi, according to the reaction $Mn_{1.08}Bi \rightarrow MnBi + Mn$ at 340°C. When manganese-bismuth alloys are melted and solidified in gravity, the different densities of the alloy constituents cause the greater part of the manganese, separated as primary constituent, to rise in the melt so that it is no longer available for the peritectic reaction. The proportion of MnBi in the terrestrial specimens is well below 20% by weight. Under terrestrial conditions, therefore, it has hitherto only been possible to produce pure MnBi by powder technology,[8] as thin films,[9] and by growing small monocrystals.[10]

The microgravity experiments with the manganese-bismuth were intended to clarify 1) whether separation can be avoided in the absence of gravity-driven sedimentation and convections caused by density differences (which are therefore gravity dependent) even if there still may be some residual acceleration or surface-energy-driven convection, and 2) whether the peritectic reaction can run its full course to form the pure intermetallic compound MnBi in the absence of gravity dependent forces.

If the reaction could be completed, it would be the first time that large bulk samples of pure MnBi were available for physical (e.g., magnetic) experiments.

The space experiments with specimens of the MnBi system were planned to be carried out in two steps:

1) A ballistic flight. During this flight there is only a very short period of micrograyity, and this period should be used to check whether the system MnBi is suitable for further microgravity experiments. Particularly, whether or not surface energy-driven convection processes have influence on the MnBi system should be tested, as is the case for the systems Zn-Pb,[4] Al-In,[5] and Al-Pb.[6]

2) After a successful first step, a Shuttle flight should be carried out. The effect on the physical properties of a long microgravity treatment could be investigated.

Space Experiments with Manganese-Bismuth Alloys

The processes taking place in the melting and solidification of the manganese-bismuth specimens under microgravity conditions were investigated during the following space missions:

Presented as Paper 89-0303 at the AIAA 27th Aerospace Sciences Meeting, Reno, NV, Jan. 9-12, 1989; received Jan. 21. 1989; revision received Aug. 14, 1989.

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TEXUS II sounding rocket flight[11] and MAUS mission STS 51 G onboard the Space Shuttle Discovery.[12]

For the space experiments, specimens containing 50 at.% Mn and 50 at.% Bi were produced under terrestrial conditions using a melting process followed by extremely rapid cooling. Prior to use in space, specimens were selected that displayed a high degree of chemical and structural homogeneity.

The first microgravity experiments on two MnBi specimens were carried out in a chamber of the TEM 01 isothermal furnace integrated in the payload of the TEXUS II mission. The experiment, which was performed at $10^{-4}g$ during the ballistic flight, lasted 6 min. In that time the specimens were heated to 1150°C and subsequently cooled at a rate of 400°C/min.

Postflight assessment of the results of the TEXUS II experiment produced the following findings.

1) In microgravity the manganese-bismuth alloys were not adversely affected by interfacial energy or residual acceleration and exhibited no signs of separation whatsoever.

2) The content of the intermetallic compound MnBi increased from 18% by weight (wt) in the terrestrial specimens to 23% by wt in the flight specimens. Figure 1 shows the fineness and uniform distribution of the MnBi particles in the flight specimens. The gray flakes in Fig. 1 are the intermetallic compound MnBi, the white platelets with the sharp edges are manganese, and the white matrix is bismuth. The structure shown in Fig. 1 brought about a marked improvement in the magnetic properties despite the substantial amount of Bi and antiferromagnetic Mn still present (see Table 1). These results obtained on the TEXUS II flight paved the way for and justified experiments under microgravity conditions of longer duration.

In the MAUS mission, STS 51 G onboard of the Space Shuttle Discovery from June 17–23, 1985, six manganese-bismuth specimens with the stoichiometric composition 50 at.% Mn and 50 at.% Bi were melted in three chambers of the TEM 01 isothermal furnace and subjected to temperature oscillations between 450 and 470°C with 10 min intervals for 3 h. As the MAUS payload did not include a gas supply, there was a need to dispense with homogenization at 1150°C with subsequent rapid cooling to the peritectic temperature. The microgravity experiments performed during this mission produced the following main results.

As was the case with the TEXUS II flight, the manganese-bismuth alloys investigated in the MAUS STS 51 G were not adversely affected by interfacial energy or residual acceleration. Figure 2a shows macrosections of the ground-based specimens displaying the separation behavior typical of specimens melted under terrestrial conditions. The sections of the macrostructure of the DG 206 flight specimens, on the other hand, exhibit no signs of separation whatsoever (Fig. 2b). Magnetic measurements over the length of the flight specimens also demonstrated a very good uniformity. Despite the not-yet-optimal temperature profile, the microstructure of the STS 51 G flight specimens shown in Fig. 3 displays an already advanced state of MnBi formation. The gray phase that covers a large part of Fig. 3 is MnBi, the white phase is Bi, and the small black particles consist of Mn.

The high proportion of MnBi in the DG 206 specimens from the STS 51 G flight enabled them to undergo subsequent thermomechanical treatment in the form of extrusion at 220°C. The extruded specimens were 2 mm in diameter and up to 80 mm in length. The result obtained from subsequent treatment of the flight specimens came as a complete surprise. As can be seen from Fig. 4, the extruded flight specimen consists almost entirely of the ferromagnetic compound MnBi. The gray phase in Fig. 4 is MnBi, the small white particles are Bi, and the black inclusions are small Mn crystallites. In contrast with this behavior of the flight specimens, the extrusion of terrestrial specimens always led to a complete destruction. The reason for this is easy to understand if we call to mind the very different hardness of the three phases of the manganese-bismuth system. The microhardness $HV_{0,01}$ is 10 units for bis-

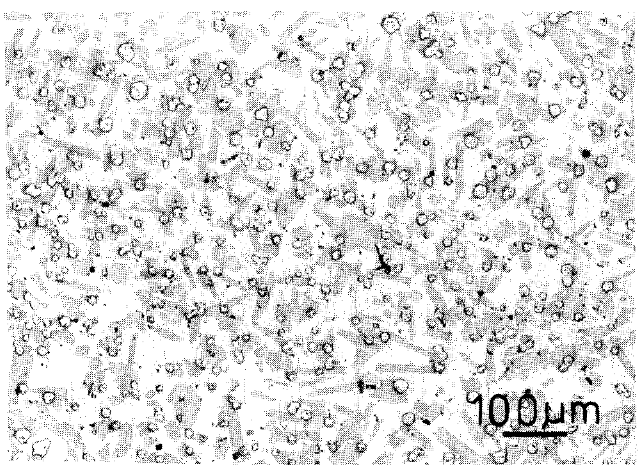

Fig. 1 Microstructure of a TEXUS II flight specimen.

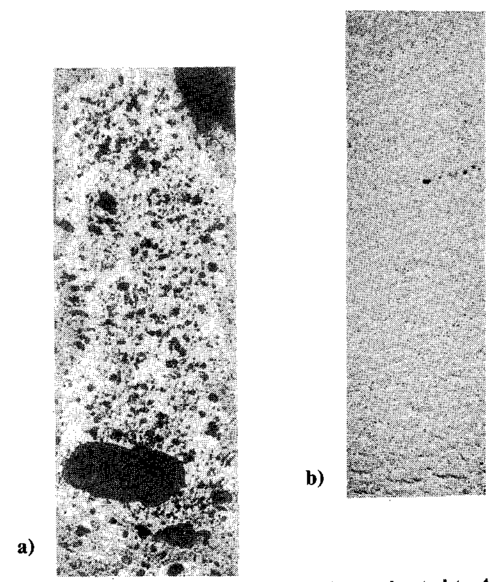

Fig. 2 Macrostructure of a) MnBi specimens heated to 470°C under terrestrial conditions; and b) DG 206 flight specimen.

Table 1 Magnetic properties of 1-*g* and TEXUS II flight specimens

Experiment FC 1	Temperature, K	Magnetizing coercivity, kA/m	Magnetic values B_r,[a] mT	Magnetic values $_JH_c$,[b] kA/m
Ground specimen	4.2	4800	15	5
	77	1400	10	5
	295	1000	15	6
TEXUS II specimen	4.2	4800	40	160
	77	1400	25	64
	295	1000	45	64

[a] B = remanence; [b] H = coercivity of polarization.

Table 2 Results of cryogenic measurements on DG 206 specimens

Specimen	ρ, g/cm^3	$\sigma(17)$, emu/g	$\sigma(\infty)$, emu/g	B_r, mT	$_JH_c$, kA/m	MnBi, %
DG 206/2	9.0	32.7	33.3	63	9.7	44.4
DG 206/5	9.0	70.4	71.8	272	10.8	95.7

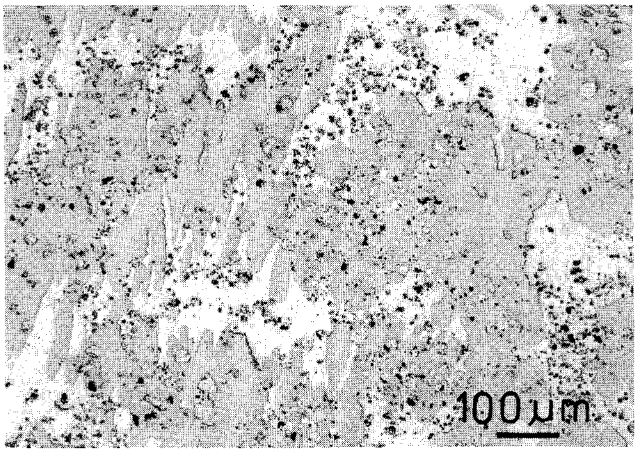

Fig. 3 Microstructure of a DG 206 flight specimen from STS 51 G.

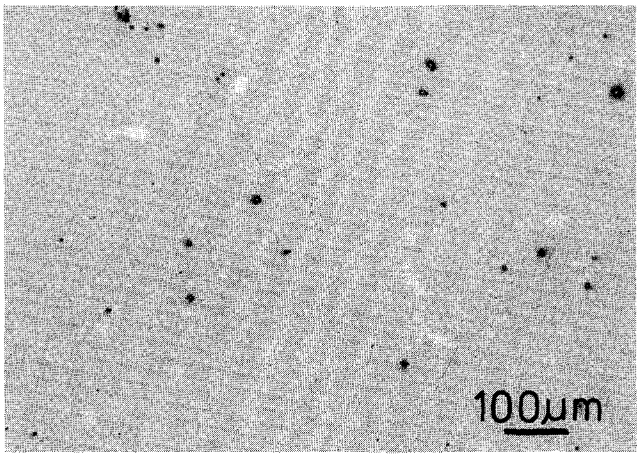

Fig. 4 Microsection of an extruded DG 206 specimen.

muth, 1100 units for manganese, and 170 units for MnBi. The hardness of MnBi is of the same order as that of easily deformable kinds of steel. The flight specimens consist predominantly of MnBi, and this is the reason that these specimens can be easily deformed. Terrestrial specimens contain too much Mn and are simply too hard for extrusion. The reason for the observed nearly 100% formation of MnBi during the extrusion is probably that the high pressure achieved during extrusion just below the melting point (a temperature where the Bi atoms already have a high mobility) induces rapid diffusion and subsequent formation of the MnBi phase.

Low Temperature Measurements of MnBi Specimens

The measurements were taken at 4 K in a Foner vibrating sample magnetometer with continuous magnetic field variation between -17 *kOe* and $+17$ *kOe*. The saturation moment per unit mass (*emu*/g) was determined at the highest field strength attained. By extrapolation of the magnetization curve σ vs H, the saturation moment per unit of mass in an infinitely strong field $\sigma(H) = \sigma(\infty) - a/H^2$ was calculated. The percentage by mass of the ferromagnetic MnBi phase was determined from the ratio of the saturation moment at infinitely strong field to the value for pure MnBi: $\sigma(\infty)_{\text{specimen}} = \sigma(\infty)_{\text{MnBi}} * A$ (A = proportion of MnBi).

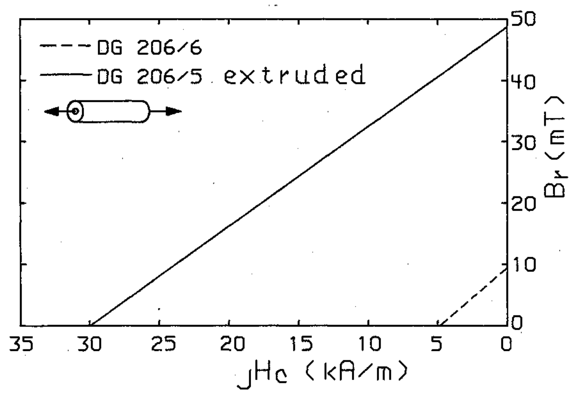

Fig. 5 Demagnetization curves of the DG 206/6 flight specimen and of the extruded DG 206/5 flight specimen (parallel to the direction of extrusion).

Table 2 gives the results of the measurements described: the flux density B_r, the intrinsic coercivity $_JH_c$ values determined for the flight specimen DG 206/2, and the extruded flight specimen DG 206/5 from the hysteresis loop.

In x-ray diffraction measurements, two reflections could be clearly ascribed to ferromagnetic MnBi, the 011 and 110 reflections. In the flight specimen DG 206, these reflections were of moderate intensity. In the extruded specimen DG 206/5, the intensity of these reflections had increased, which confirmed the increased amount of MnBi as was also concluded from the magnetic measurements. From the observed reflections, the cell parameters of both the flight specimen DG 206/2 and DG 206/5 were calculated to be $a = 0.429$ nm and $c = 0.615$ nm. This is in reasonable agreement with the values $a = 0.429$ nm and $c = 0.612$ nm reported by Andresen et al.[13] for the low temperature phase of MnBi. The quenched high temperature phase has cell parameters $a = 0.434$ nm and $c = 0.597$ nm.[13]

Magnetic Measurements at Room Temperature

The demagnetization curve of the DG 206/6 flight specimen and the demagnetization curve, measured parallel to the direction of extrusion of the extruded DG 206/5 flight specimen, which are presented in Fig. 5, demonstrate that extrusion of the flight specimens not only results in the formation of MnBi but also imparts a texture that yields an improvement in the magnetic values in a preferred location.

Measurements of the Electrical Resistivity

The electrical resistivity of the flight specimens was measured between 4.2 and 300 K. A constant ac current of 100 mA with a frequency of 83 Hz was applied, and the voltage drop between the two contact points was measured. The results are given in Fig. 6. The residual resistivity at $T = 0$ in metallic specimens is due to atomic disorder and the presence of foreign atoms in the crystalline phases. The residual resistivity therefore provides information about the quality of the specimen. The residual resistivity of the TEXUS II flight specimen (curve 1) is about 280×10^{-8} Ωm. The residual resistivities of the Space Shuttle specimens are much lower, indicating higher homogeneity and crystallinity. The DG 206 flight specimen (curve 2) has a residual resistivity of 13×10^{-8} Ωm and the extruded DG 206 specimen $6.7 * 10^{-8}$ Ωm (curve 3). Values for the residual resistivity of MnBi reported in the literature are $\approx 100 \times 10^{-8}$ Ωm for evaporated thin films[14] and

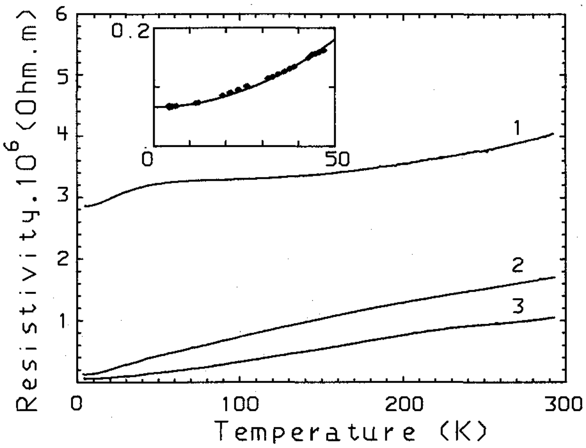

Fig. 6 Electrical resistivity of MnBi specimens, prepared during TEXUS II flight (curve 1), Space Shuttle flight (curve 2) and the extruded space specimens (curve 3) (inset shows the T^2-dependence between 0 and 50 K for the extruded specimen).

$0.05 - 0.5 \times 10^{-8}$ Ωm for single crystals.[15] From comparison with these single crystal data, the conclusion has to be drawn that in the extruded flight specimen, there is still a considerable amount of atomic disorder and atomic defects, probably caused during the extrusion process.

For the extruded specimen, containing 95% MnBi, the electrical resistivity at the low temperature could be represented quite well by $\rho = \rho_0 + AT^2$ between 4 and 45 K, with $\rho_0 = 6.7 \times 10^{-8}$ Ωm and $A = 4.6 \times 10^{-11}$ Ωm/deg.^{2} A T^2-temperature dependence is expected at low temperatures for a number of scattering processes. First there is $s-d$ electron-electron scattering.[16] A large value for A indicates a large difference in effective mass between s and d electrons. A value of 10^{-13} Ωm/deg^2 is typical for transition metals so that our value is rather large for such a scattering process. Another type of scattering process that leads to a T^2 dependence of the resistivity is magnon scattering.[17] Stutius et al.[15] suggested that interstitial atoms also induce a T^2 term in the resistivity. However our value for A is of the same order of magnitude as the value reported by Stutius et al.[15] for single crystals, whereas the residual resistivity in our specimens is larger by a factor of 10–100. This indicates that impurity scattering is not the origin of the T^2 term but that it should be ascribed to magnon scattering.

Other interesting transport properties of MnBi are the Seebeck and the anomalous Hall effect. These effects have been studied extensively in the literature.[15] Studies of these properties, which we plan to carry out using DG 206 space specimens, will probably furnish more information about the transport mechanism in these specimens.

Conclusions

The results presented here have shown that microgravity alloys of the manganese-bismuth system do not display any tendency of phase separation and that, given further optimalization of the process parameters, it is possible to obtain the pure intermetallic compound in the microgravity of space.

Further optimalization of the process parameters will be possible by engineering new MAUS payloads featuring a freon cooling circuit: heating up to 1150°C, very rapid cooling to the peritectic temperature, and oscillation treatment near the peritectic temperature. Rapid cooling guarantees an extremely fine-grained structure of the precipitated phases Mn and MnBi within the Bi matrix and thus provides a large reaction surface for the subsequent diffusion treatment.

As already indicated by the results of the physical measurements taken on space specimens, the production of large MnBi monocrystals under microgravity conditions will be of major importance for further investigations in the field of magnetics and magneto-optics.

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Associate Editor