Rapid Quenching of Liquid Aluminum-Indium-Bismuth Alloys

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Abstract— Chill-block melt spinning technique was used to examine the possibility of casting Al-In-Bi monotectic alloys with possible homogeneous microstructure. The resulting microstructure was analysed by scanning electron microscopy and X-ray diffraction. The electrical resistivity, thermal parameters, internal friction, thermal diffusivity, elastic moduli and hardness of the melt-spun ribbons have been investigated as a function of composition. The results reveal that several combinations of strength, hardness, enthalpy, entropy change, resistivity and internal friction can be generated from the alloys to meet the needs of antifriction applications.

Index Term— Melt-spin technique, monotectic alloys, X-ray diffraction (XRD), scanning electron microscope (SEM), differential thermal analysis (DTA), elastic Moduli, internal friction, thermal diffusivity, hardness measurements, shear stress.

1. BACKGROUND AND MOTIVATION

The intent of this article is to continue and to describe in details the aluminum monotectic melt-spun ribbons. Aluminum base immiscible monotectic alloys have a wide range of applications as important structural and functional materials. Structural materials are selected to their load-bearing capacity, functional materials for the nature of their response to electrical, magnetic, optical, thermal and chemical stimuli, which are closely, related the crystallographic and electronic structures of the crystal [1].

Aluminum base immiscible monotectic alloys have significant potential for practical applications. These include self lubricating bearings, electrical contact materials, the fabrication of porous materials and superconducting materials [2-5]. Emmanuelle S. Freitas et al reported that Al-In monotectic alloys are potential alternatives for applications in the manufacture of wear-resistant automotive components [6].

Adrina P. Silva et al described that these kinds of aluminum alloys dispersed with bismuth are suitable for engineering applications, particularly self lubricating bearing materials in the tribology of automotive components [7], and Gandham Phanikumar et al reported that such dispersions exhibit flow easily under sliding conditions and low hardness, hence resulting in favorable tribological behaviors [8,9]. Indium when combined with aluminum forms an immiscible monotectic alloys system characterized by a monotectic reaction (L₁ → α + L₂) for a composition of 17.3 Wt. % In at a temperature of about 910K. Despite the potential for the use of Al-In monotectic alloys in tribological applications, detailed studies on the interaction between structure and physical behavior of these monotectic alloys using melt-spinning technique cannot be found in the literature. Kaban et al measured surface and bulk liquid phase transitions in Al-In monotectic alloys by a unique method currently used for determine surface and interfacial tension of liquid alloys [10]. Wislei R. Osório et al investigated experimentally electrochemical behavior of monotectic Al-In alloys. They also studied the effect of the scale of the interphase spacing of a microstructure, formed by indium droplet-like particles embedded in an aluminum matrix [11].

Umamaheswara Rao and Sastry reported that the melt-spun hypermonotectic Al-In alloys basically exhibit a microstructure of Al matrix with trimodal distribution of indium rich liquid [12]. Much of the work on Al-In as a simple monotectic phase diagram (Figure 1) with negligible mutual solubility in the solid–solid and solid–liquid domains have been aimed at a better understanding of nucleation phenomena associated with melting and freezing of small confined particles. Table (I) and (Figure 2) showed a systematic overview of ternary monotectic Al systems [13]. The present study aims to contribute to a better understanding of the effect of bismuth addition on the structure and properties of Al-In immiscible alloys prepared by chill-block melt-spinning [14] to investigate the structure evolution with composition.

Fig. 1. A Simple phase diagram of Al-In monotectic alloy
The surface speed of aluminum wheel (coated with copper metal) was about 30.4m.s⁻¹ to obtain well shaped ribbons. Melt-spun ribbons (thicknesses 50-120 μm, width about 3-5 mm, cooling rate 10⁶K.s⁻¹) were prepared from pure aluminum, indium and bismuth. Extrusion was performed at about 772 Kelvin. The structure of the quenched ribbons was investigated by X-ray diffraction using Cu Kα radiation (λ=1.5406Å) with Ni-filter at room temperature. The microstructure analysis was carried out on a scanning electron microscope (SEM) of type (JEOL JSM-6510LV, Japan) operate at 30Kv with high resolution 3nm. Differential thermal analysis (DTA) was carried out on a (SDT Q600, USA) with a heat rate 10°C min⁻¹. The elastic moduli, the internal friction and the thermal diffusivity of the melt-quenched ribbons were calculated from the resonant frequency, which was measured using a modified dynamic resonance method. The hardness of the melt-quenched ribbons was measured using a digital Vickers micro hardness tester (model FM-7). Applying a load of 10 gf for 5sec via a Vickers diamond pyramid. More than fifteen indents were made on each sample to bring out any hardness variation due to presence of more phases, with one phase soft and ductile and another phase considerably harder, so that the average value Hv would be obtained [16].

3- RESULTS AND DISCUSSIONS

A. Structural analysis

The X-ray patterns of the melt-quenched ribbons showed only the elemental peaks of aluminum, indium and bismuth. No lines of new phases as were detected on X-ray diffraction patterns in the region of bismuth concentrations, such as that shown in (Figure 3).

2- EXPERIMENTAL PROCEDURE

The apparatus used to produce the melt-quenched ribbons in based on the design by Kamal et al [15]. The melt-spun ribbons under investigation were prepared by a chill-block melt-spinning as listed in a table (II).

![Diagram](image-url)
Fig. 3 (a, b, c)

Scanning electron microscopy (SEM) indicates the presence of dispersed particles in the aluminum matrix, as shown in Figure 4, a, b. It shows a typical SEM micrograph of the melt-spun ribbons of (light) revealing a fine dispersion of the indium particles and the bismuth particles (grey) in the aluminum matrix (dark). The microstructure reveals distribution of fine submicron particles.

Fig. 4. a. SEM micrograph of the melt-spun ribbons

Al-17.3 Wt. % In

(3b)

(3c)
Measurement of the lattice parameter of Al, Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 wt. % Bi melt-spun ribbons is made difficult by the smallness of the changes in interplanar spacing as the solute concentrations varies. On the bases of the known spacings for pure aluminum as melt-quenched ribbons, the lattice parameter of the melt-quenched Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 wt. % Bi was found to be 5x10^{-5} nm, as shown in table (III).

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>a (Å)</th>
<th>cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al pure</td>
<td>4.049</td>
<td>66.4</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In</td>
<td>4.059</td>
<td>66.8739</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>4.055</td>
<td>66.6764</td>
</tr>
</tbody>
</table>

This behavior of lattice parameters was due to the undissolved indium and bismuth in aluminum matrix, and was confirmed with the aid of scanning images. The number of atoms per unit cell in any crystal is partially dependant on its Bravais lattice. It was found that the number of atoms per unit cell in a crystal based on a face centered cubic lattice such as in our case must be a multiple of 4. In practice, a cell containing a non integer number of atoms also exists, but this type of melt-quenched ribbons usually contains point defects and is called a nonstoichiometric melt-quenched ribbons [16,17], see table (IV).

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>No. of atoms per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al pure</td>
<td>4</td>
</tr>
<tr>
<td>Al-7.3 Wt. %In</td>
<td>2.7311</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>3.2102</td>
</tr>
</tbody>
</table>

The rapid solidification from melt of monotectic alloys has been shown to produce appreciable changes in the intensity distribution of diffracted X-rays as indicated by G. K. Williamson and W. H. Hall [18]. The most conspicuous of these effects are changes in line shape and in integrated intensity. It was suggested that the broadening in produce by either lattice strains alone, or by lattice strains and small particle size simultaneously. The broadening of an observed diffraction peak can be characterized in a simplistic way by its FWHM (Full Width at Half Maximum) value at a particular 2θ angle. Line widths B, both FWHM and integral, were used in a Williamson-Hall plot [19] as illustrated in (Figure 5), to drive information about the size of coherent zones (crystallite size D_{eff}) and local lattice distortion <Σ^2> in aluminum phases.
The $1/D_{\text{eff}}$ and $5 < \Sigma^2 > ^{1/2}$ parameters are given in Table (V).

For the aluminum phase is immeasurable low, in drawing a conclusion to a good crystallization state. So the indium and bismuth phases are more disorder than aluminum matrix for both compositions supporting the stacking-fault segregation origin of the indium and bismuth lattices. What kinds of stacking are possible in a F.C.C lattice? For the sake of simplicity let us consider a close-packed lattice made up of spheres of equal size as indicated in (Figure 6). If we already have a layer, in which the centers of the spheres are indicated by A a further layer can be placed above either of two sets of hollows in the first layers. If the layers follow each other so that the centers of spheres are in order over points A, B, C, A, B, C, ..., then a close-packed cubic (face-centered) lattice is obtained, the close-packed layers forming its {111} planes [20].

Thus, it may easily occurs that as a result of some effect the otherwise regular stacking sequence becomes disordered, and a stacking-fault is created for instance in the following way:

\[
\downarrow
\]

\[\ldots ABC ABABC ABC \ldots\]

At the position indicated by the arrow there is a stacking-fault. Since two layers of identical character cannot follow by introducing the stacking operator [20]. Stacking faults are created whenever there is more than one possibility for the arrangement of the atomic layers. The more complicated the structure, the more numerous are the possible stacking orders. In ordered alloys the boundaries of the anti-phase domains are also stacking-faults.

### B. Resistivity and the thermal conductivity

In this work, the resistivity is measured around room temperature. This corresponds to the formation of ordered alloys. Moreover, by addition of 10Wt. % Bi to the monotectic Al-17.3 Wt. %In causes a pronounced increase of the electrical resistivity. The value of electrical conductivity $\sigma$ according to the quantum theory is:

\[
\sigma = \frac{ne^2r_f}{m_e}
\]
The value of the collision time of an electron at Fermi surface, $\tau_{\text{F}}$, may be computed directly from equation (2) provided the conductivity is known [21]. Table (VI) gives a list of the electrical conductivities and other transport parameters of Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi rapidly quenched ribbons from the melt. Values of the equivalent Fermi temperature, Fermi velocities $V_F$, and Fermi wave vector, $K_F$, are also given. Another important aspect of the electrical conduction process in general is that it enables us to compute the density of states at the Fermi surface $g(E_F)$ within the framework of band theory [22], which leads finally to the following expression for the electrical conductivity:

$$\sigma = \frac{1}{3} e^2 V_F^2 \tau_F g(E_F)$$

(3)

It is observed that the electrical conductivity depends on the density of states at the Fermi surface $g(E_F)$). Table (VII) shows the density of states for rapidly quenched ribbons of Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi, indicating the position of the Fermi level for rapidly quenched ribbons. The thermal conductivity changes in a similar way as was developed for the electrical conductivity. There is a definite relationship between the electrical and thermal conductivities of the alloy; although the Weidman-Franz ratio does not hold [23]. It is found that the values of the thermal conductivity of the quenched ribbons from melt of Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi is summarized in Table (VIII).

C. Thermodynamic fraction from DSC

Zu et al [24] suggested that structural changes take place to some extent in molten alloys as a function of temperature, which have been confirmed by the corresponding calorimetric peak in a differential scanning calorimeter. So in this section, it is noted that further work is needed to probe the concrete change of structures with the help of a differential scanning calorimeter. Specimens approximately 7 mg in mass were cut from the melt-spun ribbons and were submitted to heating from 323.15 K to 1073.2 K at rates of 10 K.min$^{-1}$ in a SDTQ600 differential scanning calorimeter DSC. A typical output is depicted in (Figure 7). The results of the melting temperature, enthalpy, entropy change and the average specific heat are tabulated in Table (IX). On the basis of thermodynamic functions from DSC results Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi quenched ribbons from melt exhibit notably
different behaviors. On the basis of these results we claim that, by indicated in Table (IX).

![Graph](image1)

**D. Elastic constant**

The elastic constant such as young’s modulus $E$, shear modulus $G$, bulk modulus $B$ and poisson’s ratio $\nu$ for isotropic polycrystalline melt-spun ribbons can be estimate approximately from the following equations:

$$E = \frac{38.32\rho T^4}{t^2}$$  \hspace{1cm} (4)  

$$G = \frac{E}{2(1+\nu)}$$  \hspace{1cm} (5)  

$$B = \frac{E}{3(1-2\nu)}$$  \hspace{1cm} (6)

Table (X) shows the young’s modulus, the shear modulus, the bulk modulus and the poisson’s ratio for Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi. Both young’s modulus and the shear modulus for Al-17.3 Wt. % In-10 Wt. % Bi are twice those of Al-17.3 Wt. % In, and the poisson’s ratio in abut (0.370) and for Al-17.3 Wt. % In-10 Wt. % Bi is about (0.365).

![Graph](image2)

Table (IX)

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>$T_{m1}$ (K)</th>
<th>$T_{m2}$ (K)</th>
<th>$T1$ (K)</th>
<th>$T2$ (K)</th>
<th>Enthalpy $H$ (J/g)</th>
<th>Specific heat $C_p$ (J/Kg.K)</th>
<th>Entropy change $S$ (J/Kg.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. % In</td>
<td>339.9</td>
<td>341.35</td>
<td>338.5</td>
<td>353</td>
<td>96.56</td>
<td>6659.31</td>
<td>279.36</td>
</tr>
<tr>
<td></td>
<td>905.21</td>
<td>913.5</td>
<td>903</td>
<td>938</td>
<td>167.3</td>
<td>4780</td>
<td>181.80</td>
</tr>
<tr>
<td>Al-17.3 Wt%In-10Wt%Bi</td>
<td>898.95</td>
<td>919.31</td>
<td>897</td>
<td>920</td>
<td>158.1</td>
<td>6873.91</td>
<td>174.06</td>
</tr>
<tr>
<td></td>
<td>919.31</td>
<td>940.97</td>
<td>920</td>
<td>943</td>
<td>738.1</td>
<td>32091.30</td>
<td>792.56</td>
</tr>
</tbody>
</table>
In a paper Ledbetter [25] and Gorecki [26] reported a theoretical basis for the experimental relationship between young’s modulus $E$ and the shear modulus $G$ which has recognized for many years:

$$\frac{G}{E} \approx 365 \quad (7)$$

So if we take into account the well-known relation between young’s modulus, the shear modulus and the bulk modulus:

$$\frac{G}{E} = \frac{3+G/B}{9} \quad (8)$$

The aim of this part is to check the validity of relationship (8), for typical F.C.C. structures by searching for experimental relationships for the ratios $G/E$, $G/B$, and $E/B$ for each melt-spun ribbon separately. Table (XI) showed statistical analysis results of the relationships between $G$, $E$ and $B$ for melt quenched Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi ribbons.

Table XI

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>Young modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Bulk modulus (GPa)</th>
<th>poisson's ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In</td>
<td>15.94</td>
<td>5.82</td>
<td>20.43</td>
<td>0.370</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>33.84</td>
<td>12.39</td>
<td>41.87</td>
<td>0.365</td>
</tr>
</tbody>
</table>

Where $f$ is a critical frequency of quenched ribbons. Table (XII) shows the internal friction melt quenched Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi ribbons.

Table XII

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>Internal friction $Q^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In</td>
<td>0.0542</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>0.0366</td>
</tr>
</tbody>
</table>

From Table (XII) it can be seen the internal friction $Q^{-1}$ is more sensitive than the elastic moduli to the phase changes occurring in the quenched ribbons [28]. We observe decreased value of the internal friction when adding 10 Wt. % Bi to the monotectic Al-17.3 Wt. % In is also confirmed that internal friction measurement has been quite for learning about the small change in the mechanical state of a material.

F. Thermal diffusivity

Using dynamic resonance method for measuring the thermal diffusivity of quenched of Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi ribbons. From the frequency $f$, at which the peak damping occurs, the thermal diffusivity $D_{\text{th}}$ can be obtained directly from the relation:

$$D_{\text{th}} = \frac{2\pi f}{t} \quad (10)$$

Where $t$ is the thickness of quenched ribbons. For Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi ,as indicated in Table(XIII), the thermal diffusivity are approximately in Al-17.3 Wt. %In half than for the others compositions of the quenched ribbons.
pure aluminum as melt-quenched ribbons, the lattice parameter of the melt-quenched Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 wt. %Bi was found to be 5x10^{-4} nm. The average crystal size well be increasing by adding 10 Wt. %Bi which explains the change in the hardness and the elastic modulus of the alloys. As in the case electrical resistivity increases with adding 10 Wt. %Bi, on the other hand, there is improvement in mechanical properties, and sufficient internal friction. Hence the Al-17.3 Wt. %In-10 Wt. %Bi alloy has better properties for bearing applications. Composites made of multicomponent alloys with liquid– liquid miscibility are the focus of basic and applied research on design of new materials with exceptional functional properties, as showed in the table (XV) and (XVI).

### Table XIII

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>Thermal diffusivity $D_n (m^2 \cdot sec^{-1}) \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In</td>
<td>1.359</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>2.160</td>
</tr>
</tbody>
</table>

### Table XIV

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>HV (MP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In</td>
<td>573.198</td>
</tr>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>473.371</td>
</tr>
</tbody>
</table>

The maximum shear stress that is created by a local applied pressure occurs on the central axis below the pressurized region [29,30]. Assuming that the value given by elasticity theory for a circular pressurized region will be approximated in a hardness measurement, the maximum shear stress will be:

$$\tau_{m}=0.5 \mu R \left[ (1-2v)/(1+v) + 0.22(1+v)[2(1+v)]^{1/2} \right]$$  \hspace{1cm} (11)

Using $v=0.370$ for Al-17.3 Wt. % In, $\tau_{m}$ is equal to (217.5 MPa). And using $v=0.365$ for Al-17.3 Wt. % In-10 Wt. % Bi this leading to $\tau_{m}$ is equal to (526.9 MPa). Therefore, hardness measurements can be used to obtain yield stress for their melt-quenched Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 Wt. % Bi ribbons and to estimate the impact yield stress.

### CONCLUSION

The study concludes that melt-spin technique is an effective technique for producing a uniform dispersion of indium droplets in aluminum monometal alloys. The estimated compositions of the resultant alloys were almost the same as target compositions. The Al-In alloys consisted of a very homogeneous microstructure throughout all sections. The solid-state microstructure of monometal alloys is essentially determined by their thermophysical properties and solidification parameters. The X-ray measurements of the lattice parameter of Al pure, Al-17.3 Wt. % In and Al-17.3 Wt. % In-10 wt. %Bi melt-spun ribbons is made difficult by the smallness of the changes in interplanar spacing as the solute concentrations varies. On the bases of the known spacings for

### Table XV

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>Young modulus (GPa)</th>
<th>Shear stress (GPa)</th>
<th>Internal friction $Q'$</th>
<th>Thermal diffusivity $D_n (m^2 \cdot sec^{-1}) \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>33.84</td>
<td>12.39</td>
<td>0.0366</td>
<td>2.160</td>
</tr>
</tbody>
</table>

### Table XVI

<table>
<thead>
<tr>
<th>Melt-spun ribbons</th>
<th>Hardness (MPa)</th>
<th>Poisons Ratio</th>
<th>Maximum shear stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-17.3 Wt. %In-10 Wt. %Bi</td>
<td>473.371</td>
<td>0.365</td>
<td>526.9</td>
</tr>
</tbody>
</table>

### REFERENCES


