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Microstructural evaluation of arc-melted Al–Li–Be alloys

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A microstructural investigation has been carried out on a series of small castings of arc-melted Al–Li–Be alloys. The alloy composition included amounts of lithium up to 3 wt% and beryllium up to 10 wt%. Optical metallographic examination has revealed gross macrosegregation in the highly alloyed compositions. On the microstructural level, the structure consists of primary beryllium particles in a matrix of primary aluminium containing eutectic structure at the cell walls. A detailed Auger electron spectroscopy examination has been carried out on a section of an Al–3Li–10Be arc-cast alloy to determine the precise compositional variations. This approach is demonstrated to be a necessary prerequisite for selection of material for rapid solidification processing by techniques such as splat quenching.

1. Introduction

In recent years one of the major areas of research in advanced aluminium alloys has been directed toward the development of low-density alloys. The major emphasis of this research has been in alloys based on the Al–Li system; indeed, interest in these alloys is sufficiently great that three international conferences on this subject have been held since 1980 [1–3]. The reason that the Al–Li system is central to the above development is based on the recognition that lithium is both the most efficient density-decreasing and elastic modulus increasing of all metallic elements when added to aluminium. In determining potential weight savings in aerospace structures it is now well accepted that low density is an overriding consideration but that increased modulus is also important [4]. There appear to be only three elements which added to aluminium both decrease the density and increase the modulus; lithium, beryllium and silicon (there is some uncertainty about the influence of boron on the modulus of aluminium although it is known to decrease the density of aluminium). Of these three elements, only lithium and beryllium significantly offer the simultaneous benefits of decreased density and increased modulus.

The combination of lithium and beryllium in aluminium alloys has not been attempted because of the limited solubility of beryllium in aluminium (less than 0.03 wt % [5]) as shown in Fig. 1. In binary alloys of aluminium and beryllium the low solubility of beryllium leads to massive segregation of the beryllium-rich phase upon solidification under normal ingot production, and poor mechanical properties result. Another disadvantage of beryllium is the well-known toxicity of its oxide, and this requires precautions in the handling and machining of beryllium metal or beryllium-based alloys.

Despite the above disadvantages, there are significant advantages to be gained from the development of fine-structured Al–Be or Al–Li–Be alloys. This is because in order to take further advantage of density decreases in Al–Li alloys, it is not possible simply to continue to increase the lithium content. Beyond a level of about 3 wt % Li in Al–Li alloys, deleterious effects of lithium are observed on toughness and ductility [1–3]. As a result of this restriction, Al–Li–Be alloys become attractive if the beryllium can be dispersed in a very fine form.

Rapid solidification processing (RSP) is a unique and potentially practical method for the development of high-modulus and high-strength microstructures in Al–Li alloys containing more than about 0.03 wt % Be. Rapid solidification would eliminate segregation of beryllium and greatly refine the microstructure of the alloy. Although beryllium has only a small solubility in aluminium at low temperatures, at increased temperatures (Fig. 1) it shows an increasing liquid solubility reaching about 10 wt % at 1025° C. The successful development of Al–Li–Be alloys would result in ultra-low density, high-modulus and high-strength aluminium alloys, competing with the most promising metal-matrix and non-metal matrix composites with respect to weight savings in advanced aerospace structures. The potential for weight savings in such structures is significantly higher for Al–Li–Be alloys than for any other aluminium alloy system, including metal-matrix composites. In a preliminary study of Al–Li–Be alloys [6] using the S-3A Naval Patrol Aircraft as a structural example [4, 7], the weight savings were calculated for two illustrative Al–Li–Be compositions: Al–3Li–3Be and Al–3Li–10Be. The results, together with similar calculations (made using experimental data [8–10]) for other advanced aluminium alloys, as well as for a metal-matrix composite [11], have clearly demonstrated the important potential benefits of the Al–Li–Be alloys. For example, by comparison with Al-7075, an Al–3Li–10Be alloy exhibited a 26% weight saving and an Al–3Li–3Be a

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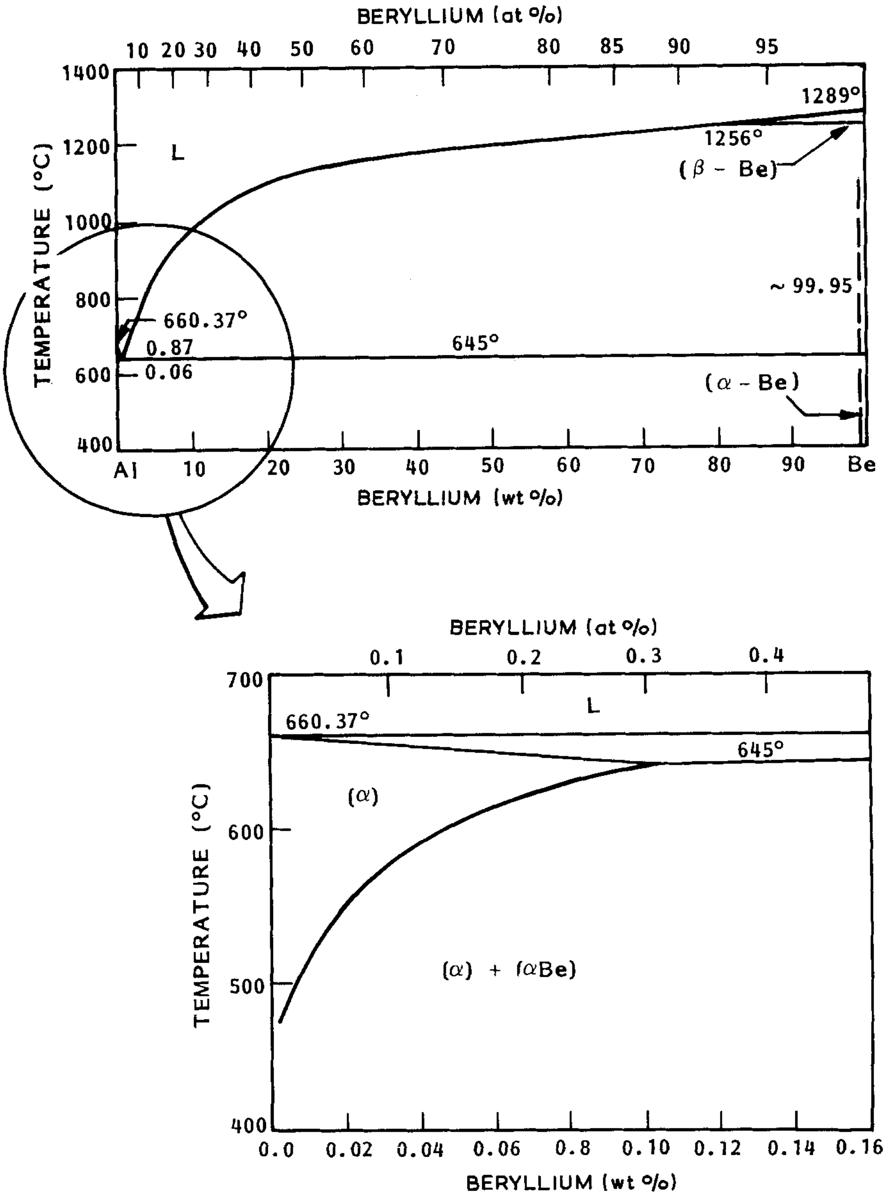

Figure 1 The aluminium–beryllium equilibrium phase diagram.

20% weight saving. The Al–Li–Be alloys are therefore a group of alloys which could have applications in aerospace stuctural components resulting in major increases in range, payload and service life.

During the course of initial attempts by the present authors to make RSP Al–Li–Be alloys, it was discovered that the segregation effects in the as-cast starting material required special attention. This was necessary because it is important to understand precisely the composition of the starting material from which RSP particulate or ribbon is to be manufactured. This is especially true if small quantities are to be made, for example, by splat quenching methods. In the present paper, detailed metallographic examinations of such starting material from Al–3 wt % Li + 2, 5, and 10 wt % Be alloys are described.

2. Experimental procedures

The materials used for manufacturing the Al–Li–Be ternary alloys were: pure aluminium (99.95%) from high-purity ingot stock; high-purity battery-grade lithium containing less than 1000 p.p.m. Na (and typically less than 300 p.p.m. Na), and electrolytic induction-melted beryllium stock (99.6%) the main impurities being oxygen, iron and aluminium. The aluminium was cleaned by chemically etching in a mixture of HNO_3 and HF, the lithium was handled in a low-humidity (1%) room, and the beryllium was cleaned by chemical etching in dilute H_2SO_4.

In order to make Al–Li–Be ternaries, master alloys of Al–Be were prepared by arc melting. The arc melting was carried out in a small depression in a water-cooled copper hearth in a chamber containing an argon atmosphere. A getter button of pure titanium was melted prior to melting the small (20 g) charges of aluminium and beryllium, in order to reduce the partial pressures of N_2 and O_2 in argon. The small castings of Al–Be thus produced were remelted several times (inverting the solidified ingot on each occasion) to promote homogeneity. These master alloys were chemically cleaned prior to the addition of lithium which was made by placing the elemental lithium underneath the Al–Be arc-melted buttons, and slowly melting the lithium by conduction from the top side of the buttons (at which point the arc was located). This procedure avoided evaporative losses of lithium and permitted its diffusion into the master alloy prior to the mass becoming molten. This molten pool was puddled for several minutes, allowed to solidify and then the button was remelted three times.

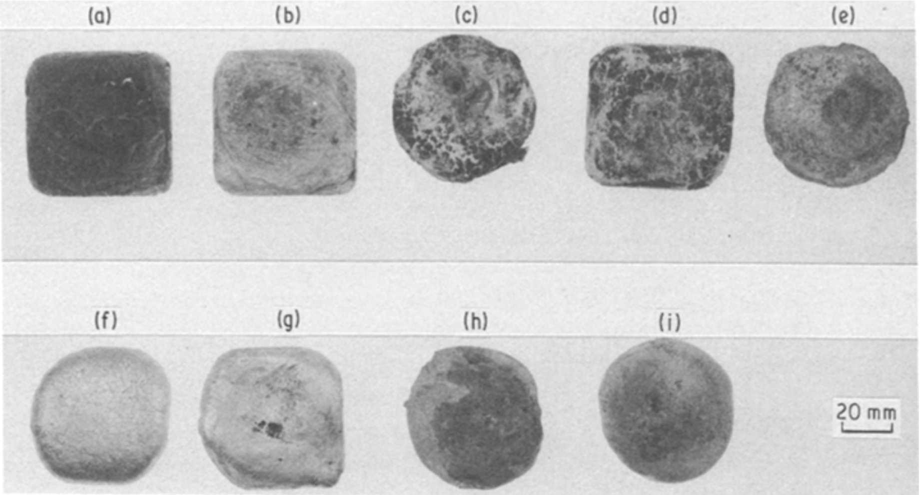

Figure 2 Arc-melted, acid-etched castings of Al–Li, Al–Be and Al–Li–Be alloys: (a) Al–3Li, (b) Al–3Li–1Be, (c) Al–3Li–2Be, (d) Al–3Li–3Be, (e) Al–3Li–5Be, (f) Al-10Be, (g) Al–1Li–10Be, (h) Al–2Li–10Be, (i) Al–3Li–10Be.

A number of analyses on these arc-melted buttons was carried out, primarily by optical metallography and Auger electron spectroscopy. Because of the severe segregation that was observed using optical metallography, it was necessary to determine the precise compositions at locations within the button. This was carried out using Auger electron spectroscopy.

3. Results and discussion

Typical castings produced by arc melting, for a range of Al–Li–Be alloys, are shown in Fig. 2. Generally, a rather thick oxide surface was observed on each alloy. Upon sectioning, it was revealed that macrosegregation was apparent in each of the castings, but much more severely so in the case of the highly alloyed compositions. Examples of the coarse macrostructures of two of the alloys are given in Fig. 3. As may be seen, the Al–3Li–10Be alloy showed an especially segregated structure; it was subsequently determined that the upper part of the casting (the light area of Fig. 3b) was rich in lithium. A small degree of porosity was also evident in some of the castings. Three castings (Al–3Li–2Be, Al–3Li–5Be and Al–3Li–10Be) were investigated using optical microscopy and one was investigated (Al–3Li–10Be) for compositional details using Auger electron spectroscopy.

Because of the degree of macrosegregation (the structure varied considerably depending upon the precise location within the casting), it is difficult to present representative microstructures of each alloy. However, examples from the approximate mid-sections of each of the three arc-cast compositions are illustrated in Figs 4a, b and c at increasing magnifications for the Al–3Li–2Be, Al–3Li–5Be and Al– 3Li–10Be alloys. The microstructures of the alloys show an increasing amount of primary beryllium phase as the total beryllium content is increased. The matrix of each alloy, as clearly evident in the high-magnification photomicrographs of Fig. 4c, shows the relatively fine eutectic structure. It is important to emphasize the inhomogeneity of these castings, and a detailed examination of the Al–3Li– 10Be alloy was carried out. Optical photomicrographs are shown in Fig. 5 from within one of the castings (the Al–3Li–10Be composition). Despite the variation in structure within individual castings, some general observations can be made from Figs 4 and 5. As for the case of Al–Be binary alloys, the beryllium in the Al–Li–Be alloys is extremely insoluble and precipitates upon cooling from the melt in coarse, microsegregated form in a variety of irregular shapes and sizes. This is the predominant phase visible in Figs 4 and 5. This primary

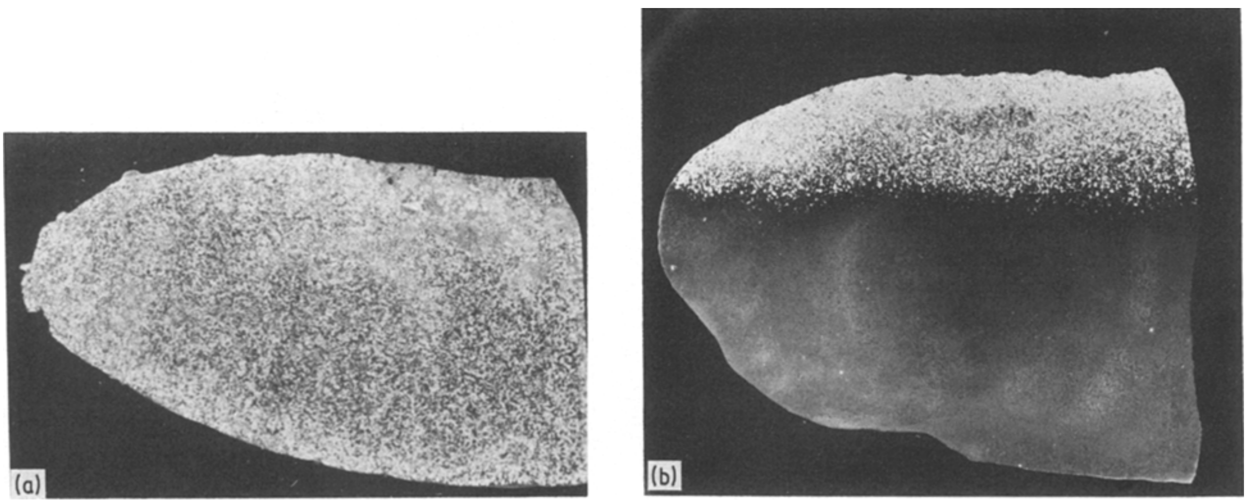

Figure 3 Sections of the arc-melted castings of (a) Al–3Li–2Be and (b) Al–3Li–10Be alloys.

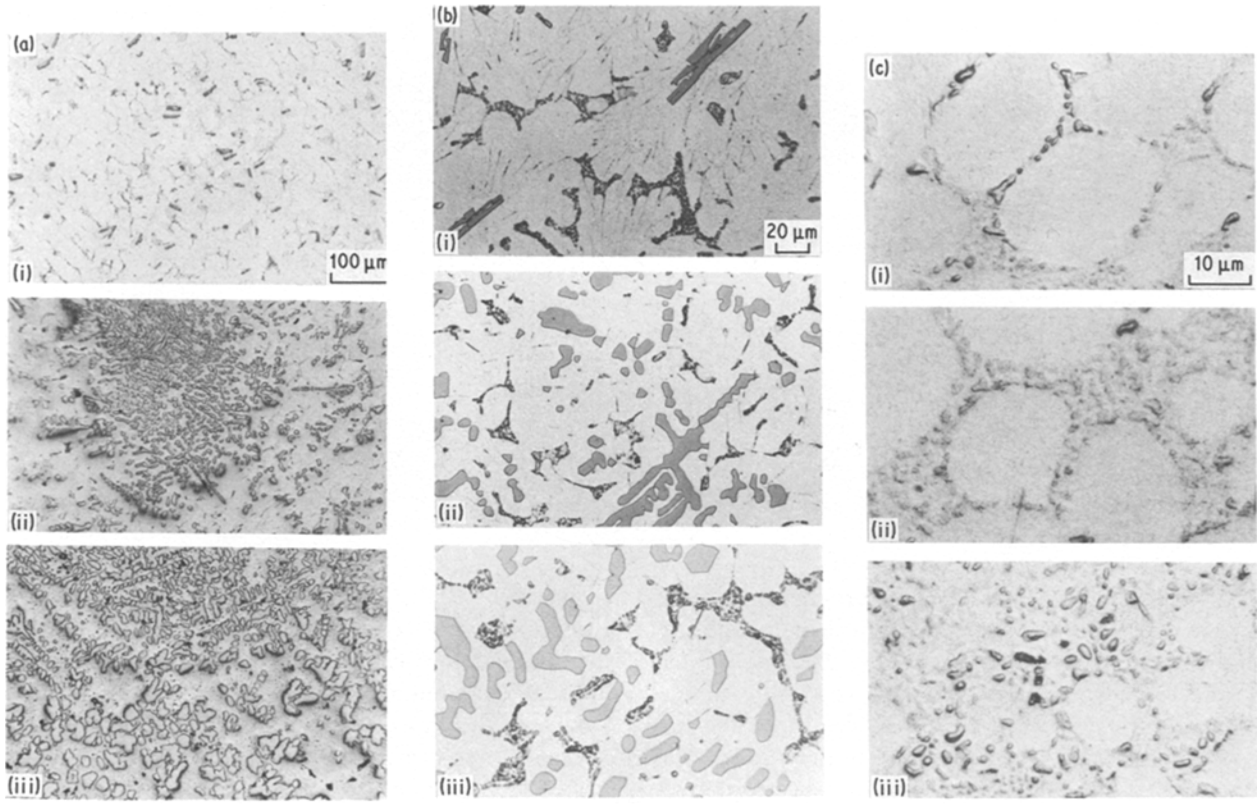

Figure 4 Optical photomicrographs at (a) low, (b) medium and (c) high magnification for the (i) Al–3Li–2Be, (ii) Al–3Li–5Be and (iii) Al–3Li–10Be alloys in the arc-melted condition.

beryllium has a large size range from about 2 to 70 μm. Within these segregated regions, a cellular eutectic structure exists and at the cell walls are found both the beryllium phase as well as, presumably, the lithium-containing phases (assumed to be δ' or δ). This type of microstructure is most undesirable from the viewpoint of mechanical properties because the large particles result in brittle behaviour. Refinement of such microstructures provides the driving force to produce these compositions of Al–Li–Be alloys by RSP. Furthermore, because of the uncertainty of the compositional ranges within these castings, it was not possible to simply cut pieces for splat-quenching experiments and assume nominal compositions. A detailed Auger analysis was therefore carried out to measure the composition fluctuations in a polished half-section of the Al–3Li–10Be alloy ingot in order to locate precisely regions for further study.

3.1. Compositional variations in Al–3Li–10Be arc-melted buttons

A common procedure in the preparation of alloy splats involves making a master alloy button (or casting) of a nominal composition and then using a small portion of it (e.g. a cube of side 2.5 mm) to melt and rapidly solidify by splatting. A source of composition fluctuation in splats arises from any inhomogeneity present in the master alloy button. The composition of the alloy can also change during each melting step due to evaporation losses and oxidation. These losses can be particularly high for lithium and beryllium, leaving the splat deficient in these elements. Thus, an assurance of homogeneity in the master alloy, and careful melting practice to avoid oxidation and evaporation losses, are important factors in achieving alloy splats of the desired composition. This section of the study was aimed at understanding the nature of macrosegregation present in the master alloy and is considered an essential step in preparing splats with preselected compositions.

The alloy with a nominal composition of Al–3Li–10Be was selected for this macrosegregtion study. This alloy had the greatest beryllium and lithium concentrations and was determined to exhibit the greatest degree of inhomogeneity among the various alloys. The macrosegregation study was conducted on a polished thin slice, shown in Fig. 6, which was cut from the master alloy button.

The technique of Auger electron spectroscopy (AES) was used in evaluation of the lateral compositional inhomogeneity of the alloy. A Perkin-Elmer model PHI 560 ESCA/SAM system was used which has a minimum electron beam diameter of 1 μm. In practice, the scanning Auger microprobe (SAM) electron beam was rastered to cover large areas of 400 μm $\times$ 400 μm. AES spectra and selected energy region multiplexes were obtained from various regions of the alloy slice, and quantitative estimates made using elemental sensitivity factors. It should be pointed out that these quantitative estimates may have a $\pm 30\%$ relative error for most elements and possibly larger errors for lithium concentrations. The errors in lithium estimates are larger due to its peak occurring in the very low energy range (36 to 43 eV), which is also dominated by true secondary electrons. The large errors also arise due to changes in chemical states, e.g., when the elements are present in their oxide forms or mixed states. Attempts at better quantification are

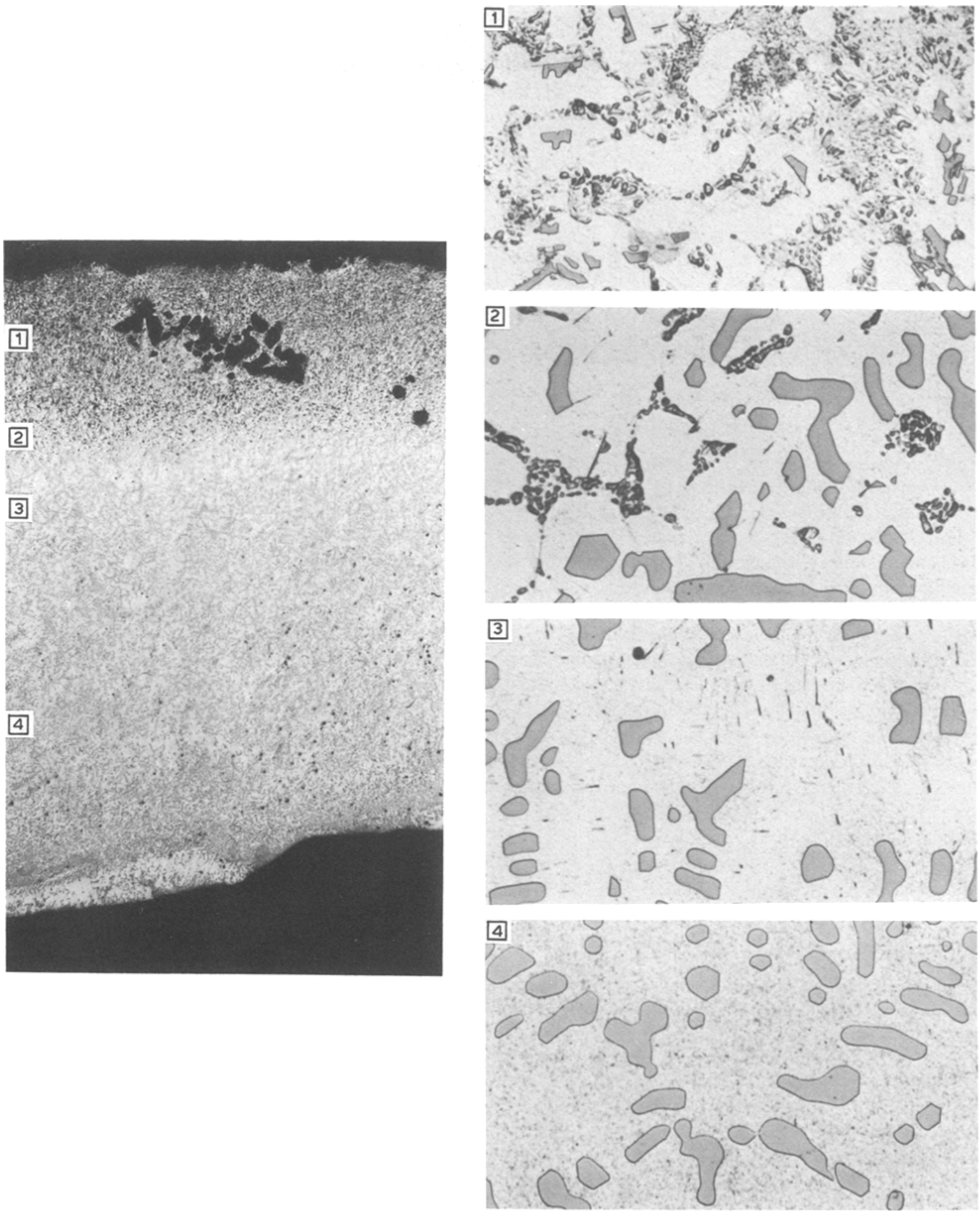

Figure 5 Variations of microstructure within the arc-melted Al–3Li–10Be alloy.

currently being made utilizing X-ray photoelectron spectoscopy (XPS) for large-area (5 mm diameter) surface analysis and inductively coupled plasma (ICP) for high-accuracy bulk analysis. Surface analysis efforts using AES does offer a combination of attributes for the present study that include: (i) light-element sensitivity (lithium, beryllium, etc.) with the exception of hydrogen and helium, (ii) high lateral resolution as low as 1 μm, (iii) surface sensitivity (2 to 5 nm region of the surface), (iv) depth-profiling capability in conjunction with ion sputtering and, (v) chemical state information such as is needed in distinguishing oxide states from elemental states.

AES estimates of aluminium, beryllium, lithium and oxygen concentrations were obtained from the areas shown in Fig. 6. These data were obtained after sputter cleaning of surfaces to remove atmospheric oxides and contamination. The top portion of the button, represented by the light area of Fig. 6, had a mottled appearance. An AES spectrum (Fig. 7) obtained from Area 4 within this region indicated high concentrations of lithium, determined to be present in

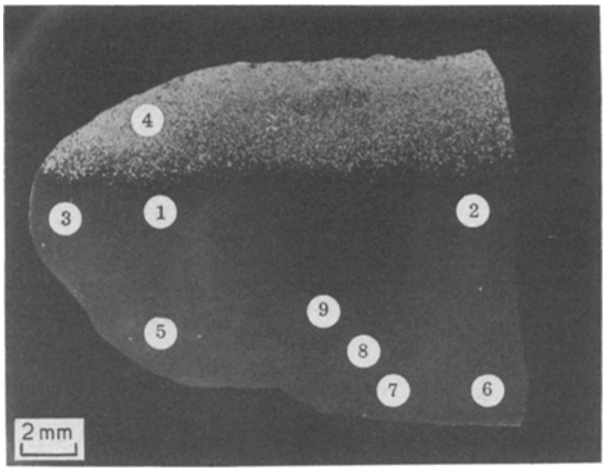

Figure 6 Cast slice of Al–3Li–10Be alloy showing the areas studied by Auger analysis.

TABLE I AES compositional estimates from various locations shown in Fig. 6

Area/location*	Composition (at %)				Comments
	Al	Be	Li	O	
1	53	34	13	–	
2	45	41	13	1	
3	43	46	10	1	
4	38	36	17	10	
5	41	53	5	1	
6	23	70	3	4	
7	21	68	9	2	
8	25	68	4	2	
9	38	44	16	2	
1(a)*	76	10	13	1	Dark phase
1(b)*	35	53	11	–	Light phase
1(c)*	26	63	11	–	Light phase
Bulk concentration	68	23	9	–	

*1(a), (b) and (c) represent 20 μm × 20 μm areas. All others are 400 μm × 400 μm areas.

the form of an oxide (based upon its peak position). The estimated atomic concentrations from various locations marked in Fig. 6 are shown in Table I. The data clearly indicate substantial variations in lithium and beryllium concentrations at the various locations. It is generally found that lithium is richer near the top surface of the button and in a form combined with oxygen. On the other hand, beryllium is enriched near the bottom of the button in concentrations estimated to be as high as 70 at %. The abolute quantities described above may be in error, but the relative comparison of data from different areas leads to the conclusion that large-scale macrosegregation occurs during the preparation of these master alloy buttons. Hence, caution must be exercised in selecting portions for splat-alloy preparation.

Table I also shows compositional information obtained from light and dark microscopic phases present in the sample. These data, for Locations 1(a), (b) and (c), obtained from the general Area 1, indicate that little or no variation in lithium concentration occurs in these microscopic regions. On the other

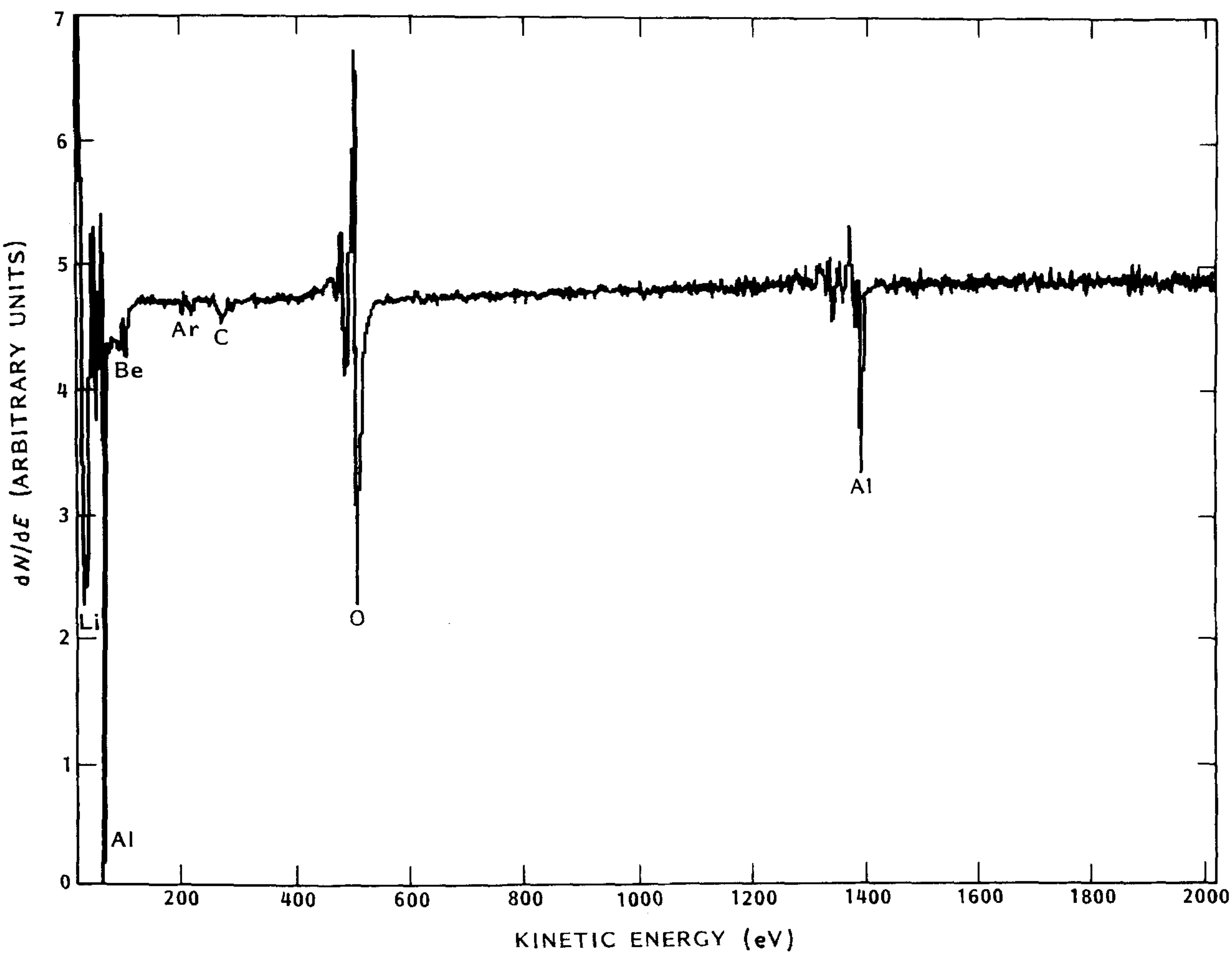

Figure 7 AES spectrum from Area 4 of Fig. 6.

hand, the Al/Be ratio varied substantially, suggesting precipitation of beryllium-rich and beryllium-deficient phases within the matrix.

4. Summary

A series of small castings of Al–Li–Be alloys has been prepared by arc melting. The compositions of the alloy contain up to 3 wt % Li and 10 wt % Be. Despite attempts to homogenize the alloys by remelting techniques, severe macrosegregation is observed in all alloys but particularly so in the heavily alloyed compositions. The alloy microstructures consist of coarse primary beryllium particles in an aluminium matrix containing a relatively fine eutectic structure at cell walls. A detailed Auger electron spectroscopy analysis of a section of the most heavily alloyed casting (Al–3 wt % Li–10 wt % Be) has been carried out to obtain a detailed understanding of the compositional variations in the alloy. This procedure is considered to be essential in order to select material of known composition for study by rapid solidification processes such as splat quenching.

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