ALUMINIUMBORATE REINFORCED Al-ALLOYS

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Abstract

Microstructure and mechanical properties of 30 vol% aluminiumborate whisker reinforced Al10.5Si3Cu-, Al9Si- and Al4.5Cu-alloy have been investigated. The composites were produced by squeeze casting with melt and preform temperature at 700°C and 800°C, respectively. The microstructure was slightly affected by the variation in processing temperature. Differences in mechanical properties as a function of processing conditions were, however, not observed.

Introduction

When the research on Metal Matrix Composites (MMC) started, about 25-30 years ago, the interest grew rapidly, and in the 1980s there was a strong worldwide interest in reinforced metals technology. The strong interest and the high activity on research on these materials have now, however, decreased, mostly due to high material- and production costs, which makes MMC-parts very expensive and limit the fields of application. A main goal for todays research on MMCs is therefore reduction in material- and production costs. The work presented here is a characterization of aluminiumborate-whisker reinforced aluminium. Whiskers of aluminiumborate ($9Al_2O_3x2B_2O_3$, abbreviated here as AlBO) have recently been synthesized in potassium flux[1]. Production of these whiskers is very cost efficient, they can be produced at 1/10 costs of the comparable siliconcarbide whiskers[2]. The AlBO-whiskers combination of low price together with high mechanical strength and low density (Table I), make them favourable as reinforcement in metals.

Table I. Mechanical and physical properties of the AlBO-whiskers [3]

Chemical formula	:	9Al2O3 x2B2O3
Diameter	:	0.5 - 1.0 μm
Length	:	10 - 30 μm
Tensile strength	:	8 GPa
Elastic modulus	:	400 GPa
Specific density	:	2.93 g/cm^3

Previous work on aluminiumborate whisker reinforced AlSiCu-alloy produced by squeeze casting[4] gave promising results on mechanical properties. In an Al-10 wt% Si-2 wt% Cu-alloy reinforced by 30 vol% AlBO an ultimate tensile strength of 400 MPa was obtained in as cast condition. The aim of the present work was to reproduce this result, by using a similar AlSiCu-alloy, and in addition study the microstructure and mechanical properties when a binary AlSi and AlCu-alloy were used as matrix.

In the literature[5,6] it is reported that the aluminiumborate whiskers have a high reactivity towards the surrounding metal base, when exposed to high temperature during processing or heat treatment. The whiskers stability towards the various matrix alloys and pure Al-alloy as a function of processing conditions, was therefore given attention.

Experimental procedure

Disc shaped preforms of 30 vol% aluminiumborate-whiskers with diameter of 53 mm and height of 18 mm were produced. A slurry of as received whiskers and binders were pressed and sucked in a die, in a way to promote random distribution of whiskers in the final preform. The preforms were dried in air at 80°C at least 24 hours before squeeze casting.

The 3 different Al-alloys and pure Al (Table II) reinforced with aluminiumborate whiskers were produced by squeeze casting as in the previous work[4]. The AlBO-preforms were preheated to 700°C and 800°C and infiltrated by molten metal at 700°C and 800°C, respectively. The castings were solidified at a pressure of 100 MPa. The high pressure was applied 7-10 seconds after the melt was poured, and was held for 3 minutes, before final aircooling.

After casting, the specimens went through macro- and micro characterization using optical- and scanning electron microscope (SEM). The composites and corresponding references of the monolithic material were further tested mechanically at room temperature. The tensile testing was done by an Instron 4206 testing machine, and ultimate tensile strength (UTS) and elongation (A) to fracture were measured.

Table II. Chemical composition of the matrix alloys used in the squeeze casting. The aluminium content balances the rest to 100%.

Alloy*	Cu (wt%)	Si (wt%)	Mg (wt%)	Zn (wt%)	Fe (wt%)	Mn (wt%)
Al10.5Si3Cu	1.91	10.17	0.28	0.43	0.68	0.20
Al9Si	0.10	9.10	-	-	0.13	0.49
Al4.5Cu	4.49	0.10	-	-	0.13	0.05
Pure Al	0.001	0.003	-	-	0.004	-

* The Japanese specifications are: Al10.5Si3Cu = ADC12, Al9Si=AC4A, Al4.5Cu=AC1B

Results and discussion

Microstructure investigation

Characterization of the microstructure of the composites in as cast condition revealed a structure without pores or flaws. The whiskers were homogeneously distributed throughout the height of the preform, but a slight preferential orientation of the whiskers in the plane parallel to the castings baseplane was observed. This alignment had most probably occurred during preform processing.

The microstructure, by means of size, shape and distribution of intermetallic phases, changed significantly from the monolithic to the composite part of the casting. The eutectic growth mode, found in the monolithic part, was severely broken up by the presence of the whiskers. Neither needle shaped eutectic Si-phases nor typically Fe- or Mn-rich β-plates appeared. The size of the Cu-containing phases, Al_2Cu in the AlSiCu- and AlCu-based materials, decreased significantly compared with the monolithic part, and Al_2Cu were always located at a whisker surface.

In the Al10.5Si3Cu-based composites the silicon appeared in 2 modes, either as small (2-5 μm) spherical phases, or as large (7-10 μm) phases (Figure 1). The small Si-phases were most often located at or close to a whisker surface, but were also found isolated in the matrix. The large phases formed links, and covered the major part of 1 or more whiskers. The number of small phases was in general higher than the number of large Si-phases. A higher number of large phases was, however, observed in the composite prepared at 700°C, as compared to the composites prepared with melt and preform temperature at 800°C (Figure 2).

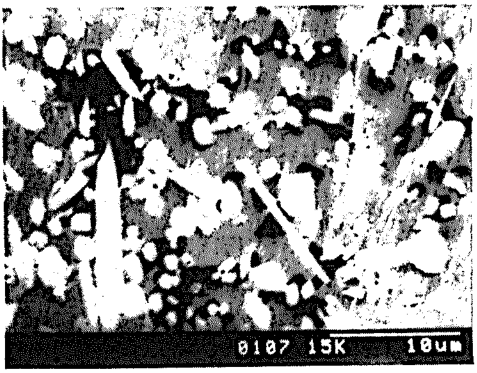

Figure 1. Small and large Si-phases (black) in Al10.5Si3Cu/30 vol% AlBO prepared at 700°C.

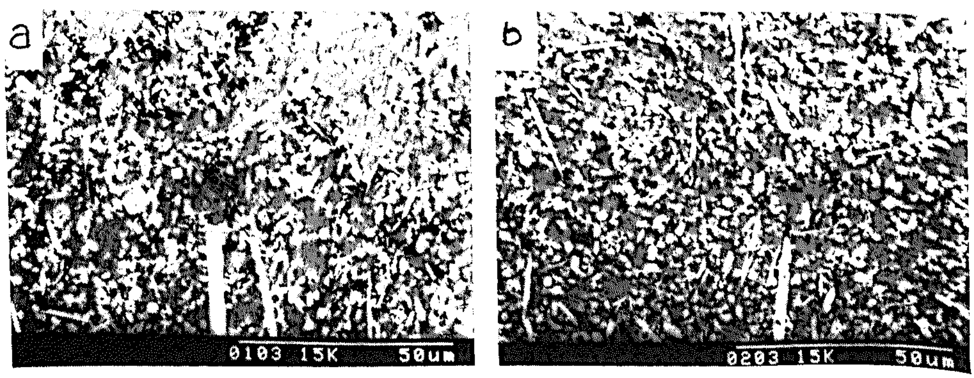

Figure 2. a) Large Si-phases in Al10.5Si3Cu/30 vol% AlBO prepared at 700°C. b) Small Si-phases in Al10.5Si3Cu/30 vol% AlBO prepared at 800°C.

The Al(Fe,Mn)Si-phases appeared as large (10-12 μm) squares, always surrounding 1 or more whiskers (Figure 3). Any differences in the amount of these phases as a function of processing conditions, were not observed, except at the border/interface between the monolithic and composite part. This interface was decorated by large Al(Fe,Mn)Si-phases (Figure 4) in the 700°C-sample, whereas much less was observed in the samples prepared at 800°C.

Figure 3. Al(Fe,Mn)Si-phase surrounding whiskers in Al10.5Si3Cu-based composite.

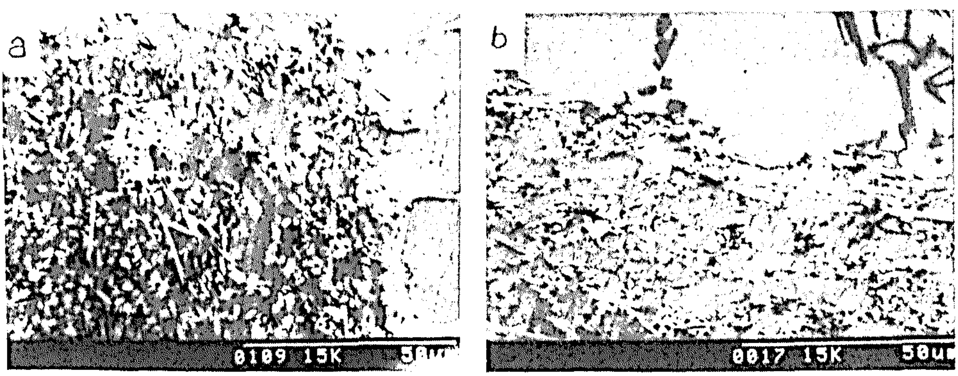

Figure 4. a) Al(Fe,Mn)Si-phases decorating the monolithic/composite interface in Al10.5Si3Cu/30 vol% AlBO prepared at 700°C. b) The monolithic/composite interface in Al10.5Si3Cu/30 vol% AlBO prepared at 800°C.

The microstructure in the Al9Si-based materials was in general found to be much the same as in the AlSiCu-based composites. One significant difference was, however, that only a very limited amount of large Si-phases were found. The structure was dominated by a uniform distribution of small (2-5 μm) Si-phases, and larger (7-10 μm) Al(Mn,Fe)Si-phases. A slight tendency of segregation of large Mn-rich phases was observed at the interface between the monolithic and composite part of castings prepared at 700°C, this segregation was, however, much less than observed in the AlSiCu-based material, as discussed above.

The location of the intermetallic phases, close to or at the whisker surface, and sometimes surrounding 1 or more whiskers, indicated that the intermetallics were precipitated during infiltration and solidification, and that the whiskers act as nucleation sites for the precipitation. During solidification, the melt will solidify last at the surface of and in the vicinity of the whiskers, because of low thermal conductivity of the whiskers. The melt solidifying last will be enriched in alloying elements, giving intermetallic phases in these areas. According to the Al-Si-Cu phase diagram [7], the melt will, during solidification, be enriched mainly in Cu, Mn and Fe, and not so much in Si. This probably explains why small Si-phases were observed isolated in the matrix, and why Fe- and Cu bearing phases never were observed isolated in the matrix. Several authors [8, 9] confirm however, that the whiskers to some extent act as nucleation sites for Si-precipitation.

Both observations that the composite prepared at 700°C contained more large Si-phases, and that the monolithic/composite-interface was decorated with large Al(Fe,Mn)Si-phases in the 700°C-sample, might be a result of premature solidification that is strongest in the samples prepared at low temperature. Just before infiltration, the melt temperature has most probably been close to or below the liquidus temperature (liquidus temperature for Al10.5Si3Cu is 580°C [10]). This means that the alloy starts to solidify before or during infiltration. As the solidification proceeds, the melt will gradually be enriched in alloying elements and Al(Fe,Mn)Si and Si will start to precipitate [11]. This incipient eutectic and AlFeSi-particle containing melt will be squeezed into the preform. In the preform the cooling rate of the melt will decrease due to the high whisker temperature, and the already precipitated Si-phases and the small AlFeSi-phases will have time to grow. At the same time, the eutectic solidification proceeds, giving "new" Si-phases with a size dependent of the solidification rate. In the final composite, the early precipitated "old" Si-phases are recognized as the large phases, while the phases precipitated during and after infiltration most probably are the small and more spherical Si-phases.

When the preform is infiltrated by melt enriched in Fe and Cu, the content of these elements will be higher in the composite part than in the average composition of the casting. This is expected to result in an increase in size, and to some extent density of Al(Fe,Mn)Si- and Al_2Cu-phases [7], and can possible explain the large size of the Al(Fe,Mn)Si-phases that is observed in the composite part of these castings.

Also, as the preform is infiltrated by the Al(Fe,Mn)Si- and incipient eutectic melt, the preform will act as a filter stopping the largest phases. This can explain the enrichment of large Al(Fe,Mn)Si-phases observed at the top of the preform in the composites prepared at 700°C.

Any temperature experiments to confirm or measure the degree of premature solidification was not done in this work. Premature solidification was, however, observed by several authors [12,13] on other composite systems. Mathiesen and Johnsen [12] report that high melt- and preform temperature (800°C) was necessary to avoid premature solidification in AlCu-alloys reinforced by SiC-whiskers. Tsuchitori et al [13] worked on potassium titanate whisker reinforced Al7.5SiCuMg-alloy produced by squeeze casting. They report that the melt temperature dropped from 800°C to below the liquidus temperature just a few seconds after the melt was poured and the solidification pressure was applied.

The fact that many of the whiskers were covered by intermetallic phases, made the whisker/intermetallic interface just as important as the whisker/Al-matrix interface. SEM investigation at high magnification revealed, however, good bonding between the whisker and the various covering phases. No visible degradation of the whiskers was found in the as cast condition in any of the investigated materials.

Mechanical properties

The results from mechanical testing are given in Table III. The ultimate tensile strength (UTS) of the AlSiCu-, AlSi- and AlCu-based composites were more than twice the unreinforced alloy. Furthermore, the strength of the pure Al-based composites reached to almost 7 times the monolithic material, although the strength in pure Al-based composites was significantly lower than in the Al-alloy-based. Any significant differences in the strength for samples prepared at 700°C and 800°C, respectively, were not found. This result gave another indication and confirmed the microscope observation that there was no destructive degradation of the whiskers during processing. The observed variation in amount of large Si-phases, is not likely to have to have any influence on the mechanical properties.

The elongation (A) in the AlSiCu- and AlSi- based materials was very low and almost the same with and without reinforcement. Low ductility is a common problem in Al-Si alloys, due to the formation of brittle needle- and plate shaped pre-eutectic and eutectic phases. More spherical phases, like the small Si-phases found in the AlSiCu- and AlSi-based composites in this work will normally contribute to increased ductility. The whiskers, however, give the opposite effect, as the pure Al-based materials very clearly showed, and the result is no significant difference in ductility. The obtained elongation in the AlCu-based composites were higher, probably due to the more uniform distribution of small intermetallic phases in these materials. In general the results from this work indicated that high melt fluidity alloys such as Al10Si is not a prerequisite for successful infiltration of the AlBO-preforms, and the avoidance of embrittling constituents should probably be given higher priority in future work on these composites.

Table III. Results from mechanical testing of the composites and their corresponding references of unreinforced material.

Alloy	Melt and preform temperature	UTS (MPa) Composite	UTS (MPa) Matrix	A (%) Composite	A (%) Matrix
Al10.5Si3Cu	700°C	475	217	1.2	1.2
Al10.5Si3Cu	800°C	468	209	1.3	1.7
Al9Si	700°C	358		1.5	
Al9Si	800°C	377	161	1.4	5.8
Al4.5Cu	700°C	444		3.0	
Al4.5Cu	800°C	421	171	3.0	13
Pure Al	800°C	303	45	6.1	25

Heat treatment experiments

The results from the mechanical testing and the microstructure investigation indicated that there was no formation of undesired and destructive reaction products on the whisker surface during squeeze casting. Squeeze casting is, however, a quick process were the heated whiskers are exposed to melt at high temperature for less than 1 minute. In order to study the whisker stability at longer time at high temperature, additional heat treatment experiments at 700°C were undertaken. Microscope investigations of the samples showed that the whiskers were strongly attacked after 30 min at 700°C. Both in AlSiCu- and pure Al-based composites severe amounts of reaction products were covering the whisker surface, and a significant part of each whisker seemed to be consumed (Figure 5). The reaction products were identified by X-ray as Al_2O_3.The pure Al-based sample was slightly less attacked than the AlSiCu-based sample.

Reduced time at 700°C (7.5 min) gave a significant decrease in the amount of reaction products (Figure 6). Some Al_2O_3 was still observed at the whisker surface in the AlSiCu-based sample, but in the pure Al-based sample no reaction products or degradation of the whisker surface were observed by investigation in SEM. This showed that when exposed to high temperature for a long time, the whiskers are more sensitive to alloys with Si, Cu and Fe than pure Al.

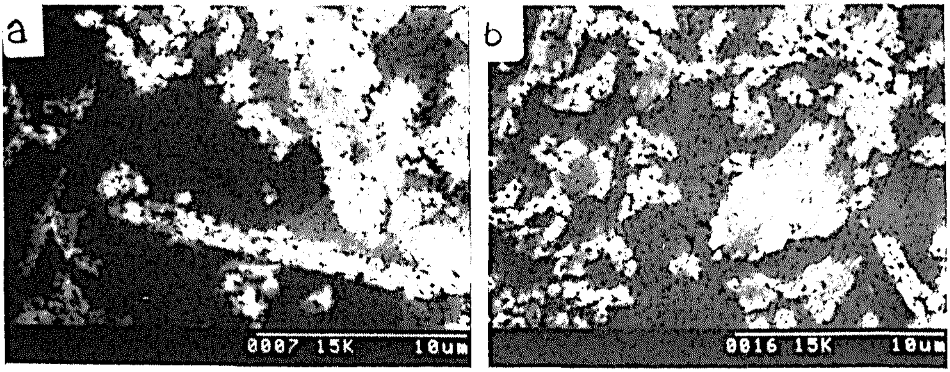

Figure 5. Whiskers covered by reaction products after heat treatment at 700°C for 30 minutes, a) Al10.5Si3Cu/30 vol% AlBO, b) Pure Al/30 vol% AlBO.

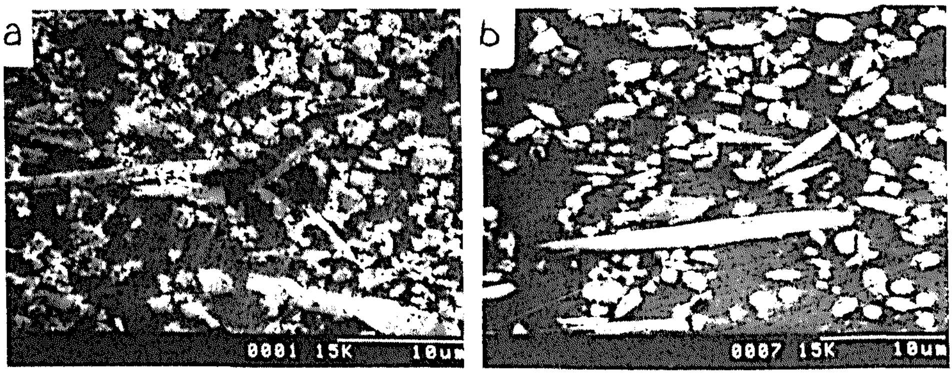

Figure 6. a) Al10.5Si3Cu/30 vol% AlBO heat treated at 700°C for 7.5 minutes, b) Pure Al/30 vol% AlBO heat treated at 700°C for 7.5 minutes.

Conclusions

1) The microstructure, by means of size, shape and distribution of intermetallic phases, is severely affected by the presence of whiskers. The structure is also slightly affected by processing conditions, probably due to premature solidification in samples cast at low temperature.

2) The interfacial structure is not affected by variations in processing conditions. Any degradation of whiskers and reactions with the matrix alloy are not observed in the scanning electron microscope.

3) The composites strength was more than twice the unreinforced alloy, and was found independent of processing conditions. This confirms good stability of the aluminiumborate whiskers toward pure Al and Al alloyed with Si and/or Cu when squeeze casting at temperatures up to 800°C.

4) When exposed to 700°C for 30 minutes, the whiskers were strongly attacked, and Al_2O_3 was identified on the whisker surface. With 7.5 minute exposure the attack was significantly reduced. The whiskers were more heavily attacked in an AlSiCu-matrix, than in pure Al.

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