ADVANCES IN THE PRODUCTION OF INFILTRATED ALUMINIUM PARTS USING SELECTIVE LASER SINTERING

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Abstract

Recent advances in a rapid freeform fabrication process for the production of aluminium parts are considered. The methodology involves the formation of an unconstrained, resin bonded aluminium powder part by Selective Laser Sintering, the burnout of the resin, the partial transformation of the aluminium into a rigid aluminium nitride skeleton by reaction with the atmosphere under a magnesium/alumina blanket and the subsequent infiltration with a second aluminium alloy. Here we describe the process and consider potential applications. Strategies for controlling the growth of the aluminium nitride are also to be discussed.

Introduction

The automotive industry is both a major consumer of aluminium and the largest user of Rapid Prototyping (RP) technology (1). However, there is currently no commercialised technique to directly produce aluminium components using RP technology. In a recent paper (2), we described a new technique for producing such parts. It involves the production of a resin-bonded green part using Selective Laser Sintering (SLS), thermal decomposition of the binder, partial transformation of the aluminium particles into a percolating aluminium nitride skeleton by reaction of the aluminium powder with the nitrogen atmosphere, and subsequent infiltration of the preform with a second aluminium alloy. The formation of the skeleton is one of the key factors in the success of the process. It provides an inert rigid skeleton which is critical to maintaining dimensional stability of the preform during infiltration (3). However, the formation of such a skeleton is particularly problematical in aluminium because of the thermodynamic stability of the naturally occurring oxide layer that is present on the surface of the powder particles. The formation of AlN in a N_2 atmosphere will only occur if the oxygen content is exceedingly low, $<10^{-23}$ (4). This is not achievable in conventional atmospheres and therefore the use of an oxygen scavenger is required. Magnesium has a greater affinity for oxygen than Al, and therefore additions of Mg are made to the alumina support powder. This alumina powder provides support to the part for the period between removal of the binder and formation of the nitride skeleton. The Mg reduces the oxygen content below that where the oxide layer is stable, which then facilitates the formation of the AlN.

The AlN skeleton also enhances infiltration by reducing the contact angle of the liquid. It has been reported (5) that the contact angle of molten aluminium on AlN is ~41° at 1100°C, approximately half that of aluminium on alumina. Therefore it is important that AlN forms throughout the entire preform. This is achieved by the addition of Mg to the support powder (6).

The amount of nitride that forms is a critical parameter in the success of the process. Too little and dimensional stability is compromised, too much and cracking can occur (7). Additionally, rapid nitride growth rates makes the process extremely difficult to control, and

dramatically reduces the operational window, increasing manufacturing costs. In this paper, we describe the way in which we control the nitride thickness, thereby increasing the processing window and improving the mechanical properties of the resultant part.

Experimental

The base powder used in this work consisted of pre-alloyed AA6061 powder that was mixed with 2% Mg and 4% (10v%) nylon. All compositions are listed in weight percent unless stated otherwise. To some parts, up to 2% Sn was also added. Selected properties of the powders used in this work are presented in Table 1. Parts were either produced in a SinterStation 2500^{plus} (using a laser power of 32W, part bed and feed temperatures of 120°C and 70°C respectively and a layer thickness of 0.1mm) or heated to ~220°C for 30 min in a small steel mould. This latter technique melted the nylon binder, which resulted in the formation of a resin-bonded green structure that simulated processing by SLS. The green preforms were placed in a crucible with a block of solid infiltrant at one end and covered with an $Al_2O_3 - 1\%$ Mg support blanket. Where only the formation of the skeleton was to be investigated, the infiltrant was omitted. The parts were then heated at 90°C/h in a sealed horizontal furnace to either 540°C or 570°C for up to 24h under flowing high purity N_2.

Table 1. Selected properties of the powders used.

Powder	Composition	Particle Size
AA6061	Al-1Mg-0.8Si-0.3Cu-0.1Cr	-53 + 10μm
Mg	99.6% pure	-45μm
Sn	99.8% pure	-45μm
Nylon	co-polyamide 6-12	10μm
Al_2O_3	99.9% pure	-63μm

Infiltration was effected by increasing the temperature at 90°C/h to either 570°C or 700°C for up to 7h. Infiltration was performed either under flowing N_2 or Ar. If Ar was used, the furnace was purged for 1h at 540°C prior to further heating. Composition and melting ranges of the infiltrants used are given in Table 2. The melting ranges were determined using Thermo-Calc and the Al-data database (version 2, 2000) through the Ettan interface supplied by Thermotech Ltd.

Samples for metallographic examination were mounted in epoxy and polished using standard techniques. They were left unetched and examined either optically or in a Phillips XL30 scanning electron microscope (SEM) with a LaB_6 filament and fitted with an Oxford energy dispersive x-ray spectrometer (EDS) and backscatter detector.

Mechanical properties were determined using an Instron 1026 screw machine with a cross-head speed of 0.6mm/min. Strain was measured using an extensometer with a 50mm gauge length. The tensile bars had a parallel length of ~75mm and a cross sectional area of ~85mm^2.

Table 2. The infiltrants used and their melting range.

Infiltrant	Solidus (^{o}C)	Liquidus (^{o}C)	Melting Range (^{o}C)
Al-14.3Si-4.7Mg	557	558	1
Al	660	660	0
Al-1Mg-1Mn	641	654	13
Al-5Mg	580	635	55
Al-2.4Zn	650	656	6
Al-2.9Fe	654	660	6
Al-2.2Zn	639	653	14
Al-2.7Mn	658	677	19
Al-2.3Cu	604	654	50
Al-2.3Si	577	647	70

Results and Discussion

The properties of 6061 - 2%Mg - 4%nylon preforms nitrided for 6h at 540°C and infiltrated with Al - 14.3%Si - 4.7%Mg for 4h at 570°C are presented in Table 3 in the as-cooled and solution treated condition. None of these parts exhibited any significant ductility. The fracture path, shown in Figure 1, indicates that the crack tended to follow the nitride. This suggests that the low ductility is a result of the percolating nitride skeleton providing an easy crack path. In order to improve the properties, it is thus first necessary to control the nitride growth rate, which will allow more accurate formation of a given thickness of nitride layer.

The addition of 2%Sn clearly reduces the rate at which the nitride grows (as measured by weight gain) at both 540°C and 570°C, Figure 2. Without Sn, the nitridation rate increases almost exponentially with time, while the addition of 2% Sn controls the growth to a much slower, linear rate. This reduced growth rate clearly produces a thinner nitride after a given hold time, as illustrated in Figure 3 for a hold of 6h at 540°C. The amount of Sn required to control the nitride is ~0.5wt%, Figure 4, with excess Sn having little effect for these conditions. The mechanism by which the Sn controls the nitride growth rate is not clear. Kondoh *et al* (8, 9) suggest that the Sn forms a physical barrier, isolating the aluminium from the atmosphere. The fact that Sn has a low melting point and low surface tension tends to support this hypothesis. However, in the model proposed by Kondoh *et al*, the Sn formed islands on the particle's surface, which would lead to non-uniform nitride thickness. The micrographs of Figure 3 do not support this. The mechanism by which the Sn controls the nitride is currently under investigation.

Table 3. Mechanical properties of selected alloys. Properties of a common casting alloy is provided for reference.

Base Powder	Infiltrant	Nitride Time	Heat Treatment	Yield (MPa)	UTS (MPa)	Ductility (%)
6061-2Mg-4Nylon	Al-14.3Si-4.7Mg	6	F	-	100	0.4
			T4[@]	-	130	0.5
6061-2Mg-1Sn-4Nylon	Al-14.3Si-4.7Mg	12	F	-	100	0.5
		8	F		117	0.5
		8	24h@540°C		156	0.6
	Al	12	F	61	103	2.0
	Al-5Mg	24	Annealed	121	143	0.6
		12	Annealed	86	155	1.6
		10	Annealed	82	149	2.5
		6	Annealed	77	142	3
	6082	12	T4*	87	118	1.1
		12	T6*	-	184	0.4
		6	T6*	180	209	1.1
	Al-2Cu-1Mg	12	F	91	124	0.95
			T4[#]	126	143	0.72
			T6[#]	-	204	0.52
	Sand Cast 319.0	-	As cast	125	185	2
		-	T6[^]	165	250	2

F: as infiltrated; [@] T4: 2h @ 500°C, water quench; * T4: 2h at 530°C, water quench. T6: T4 + 18h at 160°C; [#] T4: 2h at 540°C, water quench. T6: T4 + 18h at 200°C; Annealed: 2h at 410°C, water quench. [^] 12h @ 500°C, water quench, 2-5h @ 150°C.
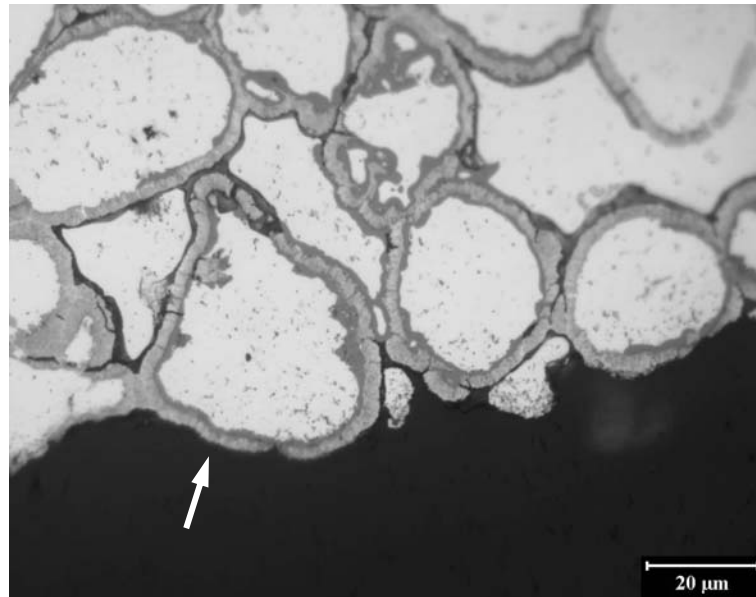

Figure 1. Fracture path for a 6061-2% Mg-4nylon preform infiltrated with Al-14.3% Si-4.7% Mg. This specimen was nitrided for 6 at 540°C and infiltrated at 570°C for 6h. The crack has tended to follow the nitride layer (arrowed) [from (2)].
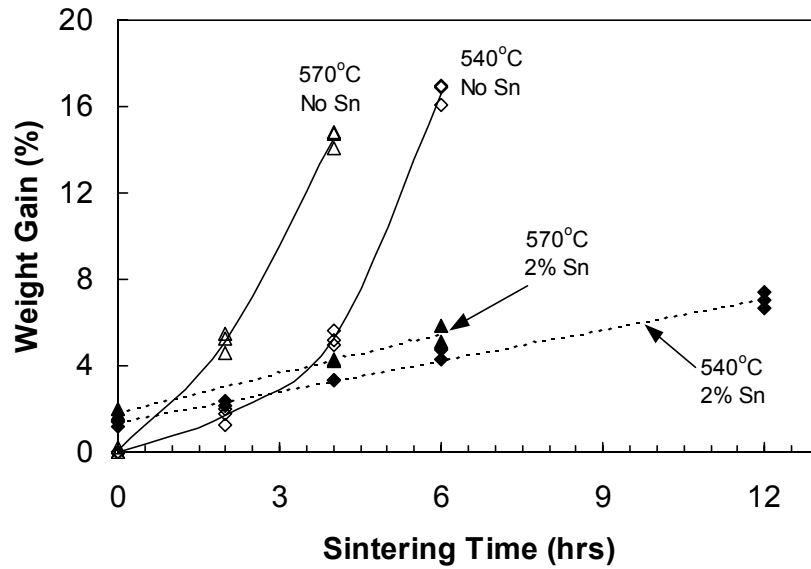
Figure 2. The effect of 2%Sn addition on the nitride growth rate (weight gain) of 6061 - 2%Mg - 4%nylon at 540°C and 570°C. The addition of Sn clearly reduces the rate at which the nitride forms.

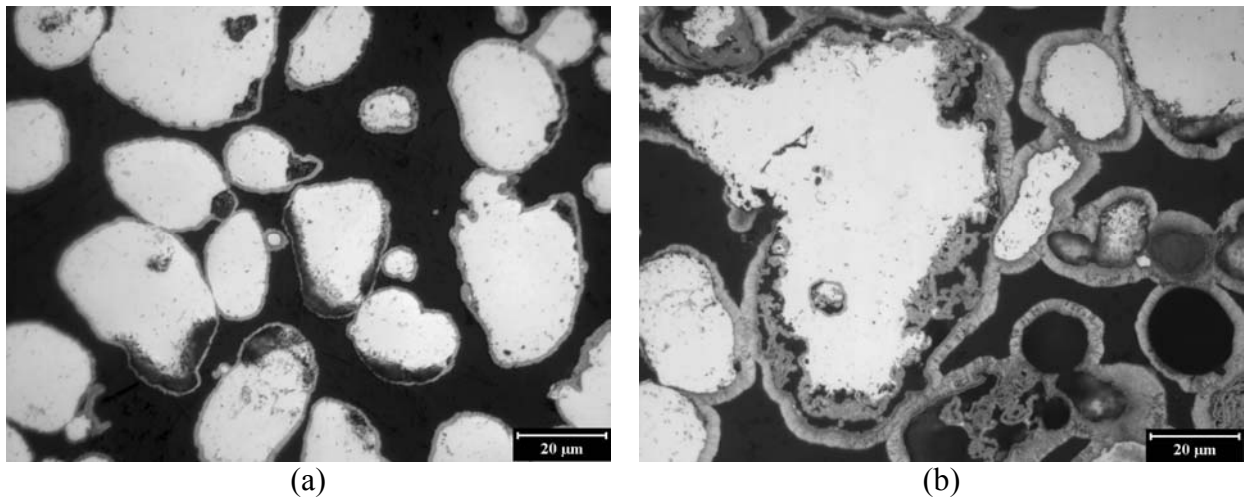(a)   (b)

Figure 3. Microstructure of 6061 - 2%Mg - 4%nylon (a) with Sn and (b) without 2% Sn after 6h at 540°C. The addition of Sn has clearly resulted in a much thinner nitride layer [from (10)].
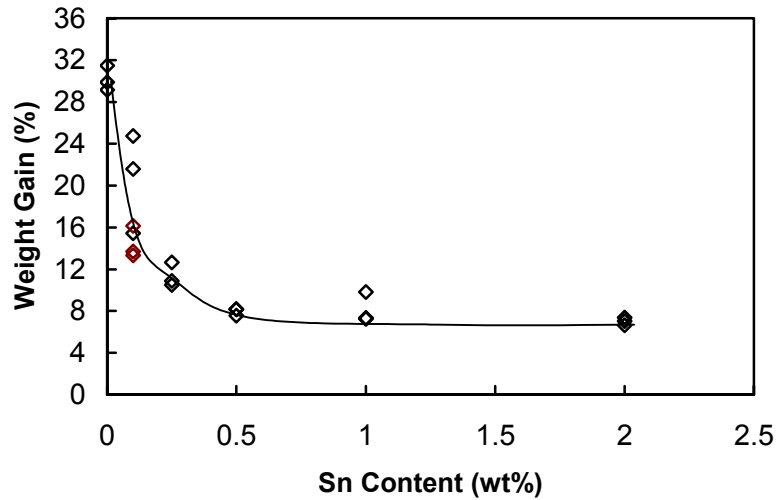
Figure 4. The effect of Sn content on the nitride growth of 6061-2% Mg-4% nylon after 12h at 540°C. As little as 0.5%Sn is sufficient to significantly reduce the nitride thickness.

The addition of 1%Sn also increases the infiltration rate, as shown Figure 5. These curves were produced by removing parts from the furnace after various times at 570°C, removing and weighing the remaining infiltrant, and converting this to a percentage infiltrated, assuming that the part is 100% infiltrated when all the infiltrant has been consumed.
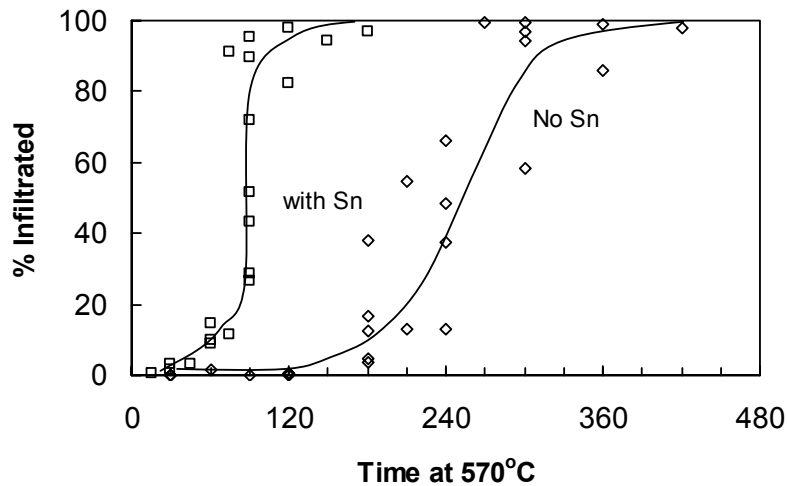

Figure 5. The effect of hold time on the infiltration rate of 6061 - 2%Mg - 4%nylon preforms with and without 1%Sn. The presence of Sn clearly increases the rate of infiltration. There is also a rapid increase in the infiltration rate of the Sn-containing alloys after ~15% has infiltrated [from (10)].

Figure 5 shows that without Sn, there is an incubation period of ~2h, prior to the onset of infiltration. The rate of infiltration (slope of the line) then increases and remains fairly constant, and the part is fully infiltrated after ~5h. In contrast, only a very short incubation period exists in

the presence of Sn, with noticeable infiltration occurring after as little as 30 minutes. After approximately 15% has been infiltrated, the rate increases sharply, producing a large amount of scatter at 90 minutes. Full infiltration has occurred after 2h. The enhanced infiltration may be attributed to the segregation of the Sn to the liquid interface, as illustrated in Figure 6. This figure shows a section through the advancing liquid, and the corresponding backscattered electron images from the liquid front as well as from the fully infiltrated zone behind the front. It shows that the infiltrated area has become depleted in Sn (the white phase), which appears to be concentrated at the advancing liquid interface.
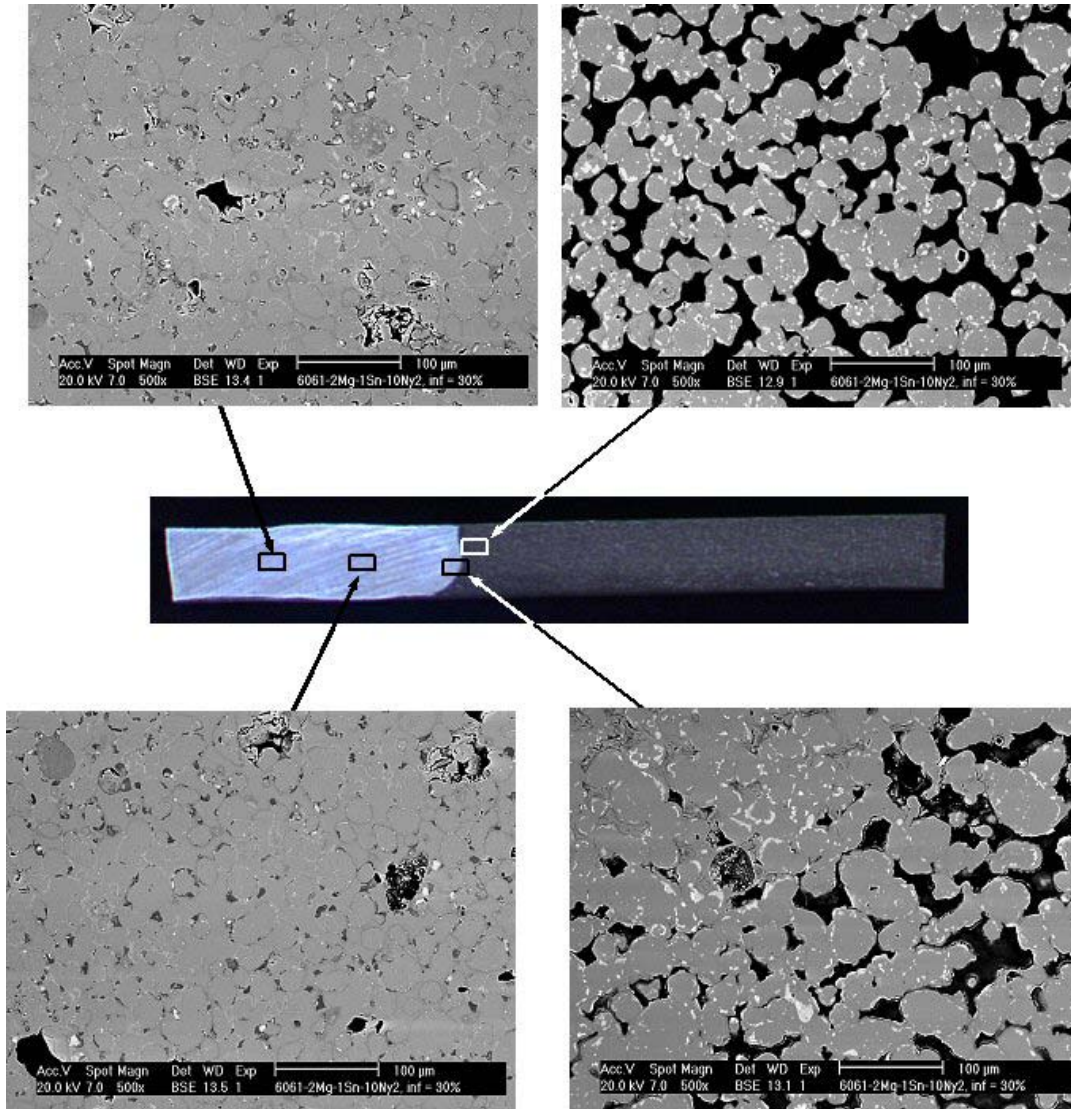

Figure 6. An optical cross section through a partially infiltrated bar. The bar is 100 mm in length. The backscattered SEM micrographs are from the areas indicated. The Sn (white contrast) is concentrated predominantly at the advancing liquid interface.

Tin has a low surface tension and is known to improve the wetting characteristics of a number of pressed and sintered aluminium alloys (11-13) . It is possible that Sn is having a

similar effect during infiltration. Once a critical Sn level has been reached in the advancing melt, wetting will be enhanced and rapid infiltration will follow. The result of this enhanced infiltration is that the time to fully infiltrate is halved.

Despite the control of the nitride thickness due to the addition of Sn, the ductility of alloys infiltrated with the Al - 14.3%Si - 4.7%Mg eutectic remains low, Table 3. Even the thinner nitride formed after a shorter hold at 540°C (8h as opposed to 12h) had minimal effect on properties. A long term heat treatment aimed at spheroidising the Si improved the strength, but not the ductility. Investigation of the crack path, Figure 7, shows that failure is accompanied by cracking of the primary Si particles (arrowed). Thus it seems that the inherent brittleness of the Al-Si-Mg infiltrant causes premature failure of the infiltrated parts.
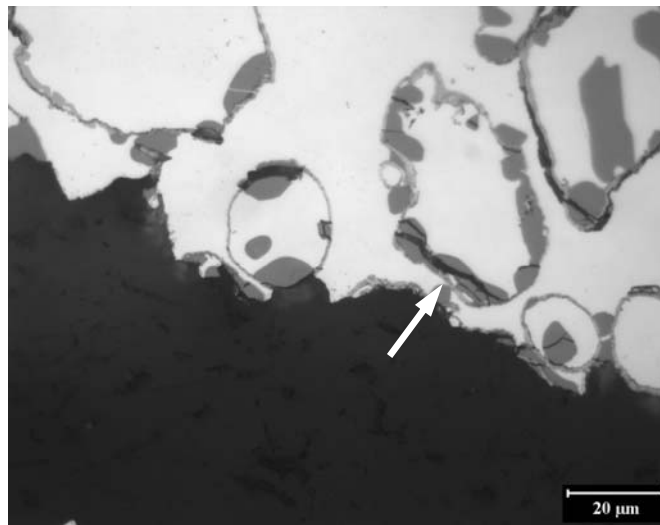

Figure 7. Fracture path for a 6061 – 2%Mg – 1%Sn – 4%nylon preform infiltrated with Al – 14.7%Si – 4%Mg. This specimen was nitrided 8h at 540°C, infiltrated at 570°C for 6h, cooled to room temperature and then spherodised for 24h at 540°C. The crack has tended to follow the nitride layer, and is accompanied by cracking of the primary Si particle (arrowed).

The usual requirement (3) of selecting an infiltrant with a melting point below that of the base powders (~580°C in this case) means that only highly alloyed infiltrants, based on the Al-Si-Mg ternary eutectic were able to be used. Since a percolating AlN skeleton has formed and AlN has a melting point in excess of 2000°C, the requirement for selecting an infiltrant with a melting point below that of the base powders is no longer applicable. However, since the nitride reaction will continue to occur until the infiltrant has covered the particles, variable nitride thickness is likely to result, with thicker nitride occurring in regions furthest from the infiltrant site. This problem is exacerbated by the fact that the nitridation rate will be accelerated at the higher infiltration temperature. However, the nitridation reaction can be halted if the process gas is switched to Ar at the end of the 540°C hold. The difference in nitride thickness for 6061 – 2%Mg – 1%Sn – 4%nylon specimens that have been infiltrated in either N_2 or Ar, thickness is illustrated in Figure 8. Both samples were nitrided for 12h at 540°C in N_2. For the alloy shown in Figure 8(b), the process gas was then switched to Ar and the parts infiltrated for 6h at 570°C. Clearly, the sample infiltrated in Ar has resulted in a thinner nitride layer.

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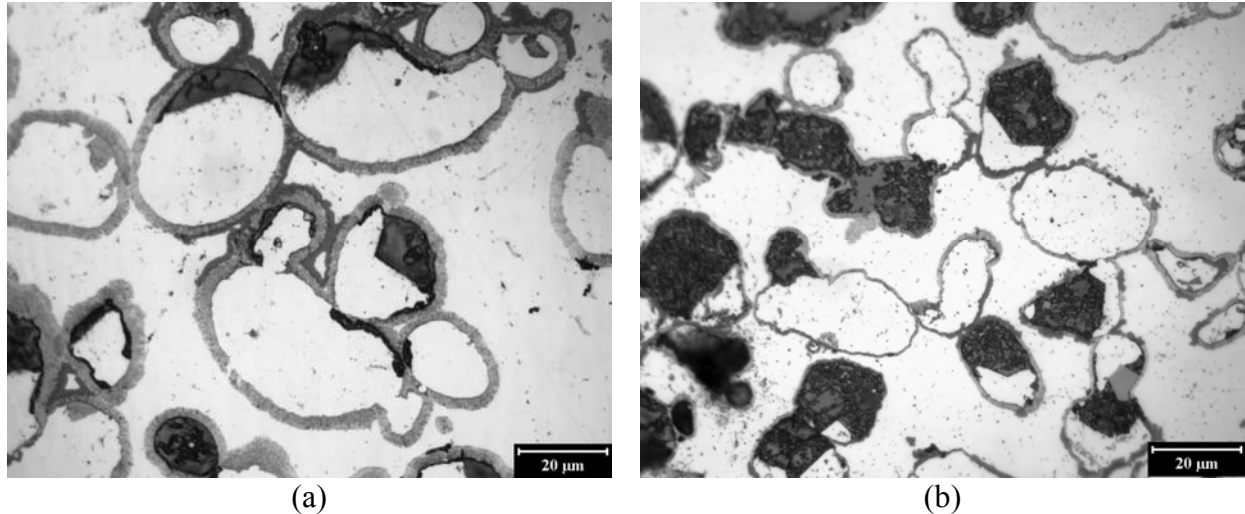<center>(a)   (b)</center>

Figure 8. Microstructure of the 6061 – 2%Mg – 1%Sn – 4%nylon preforms infiltrated with Al – 14.3%Si – 4.7%Mg. Parts were nitride for 12h at 540°C and then infiltrated for 6h at 570°C in either (a) N_2 or (b) Ar. Clearly the nitride skeleton is thinner when infiltration occurs in Ar.

The use of Ar to control the nitride thickness increases the range of possible infiltrants that can be employed, as well as the temperature at which infiltration can occur. A list of the different infiltrants that have been tested is given in Table 1, along with their melting range. Successful infiltration has been possible for all of these infiltrants using a 12h hold at 540°C in N_2 to form the skeleton, a 1h purge with Ar and then infiltrating for 2h at 700°C in Ar. The mechanical properties of preforms infiltrated with selected alloys are listed in Table 3. Clearly, the use of lower alloy content infiltrants has resulted in the recovery of some tensile ductility. Nonetheless, the ductility is generally <3%. The infiltrated strength is also largely dependant on the properties of the infiltrant. Thus, since Mg is the most effective solid solution hardening element for aluminium (14), properties are highest when infiltrating with the Al-5Mg. For infiltrants that are heat treatable, a standard heat treatment cycle provides an increase in strength, but to the detriment of the ductility.

Once a ductile infiltrant is used, the embrittling effect of the nitride is more apparent. Figure 9 plots the ductility as a function of nitride thickness (as measured by weight gain) for 6061 – 2%Mg – 1%Sn – 4%nylon preforms nitrided for various times at 540°C. These were subsequently infiltrated with Al – 5%Mg for 2h at 700°C in Ar. Clearly, excessive nitride results in poor tensile ductility and therefore a balance is required between parts containing sufficient nitride to maintain dimensional stability and excessive nitride which degrades the mechanical properties. The addition of Sn and the associated reduction of nitride growth rate makes this balance easier to achieve. When the optimum balance is made between the two, complex parts can be produced with properties equivalent to a common casting alloy, Table 3. Examples of such parts are shown in Figure 10.
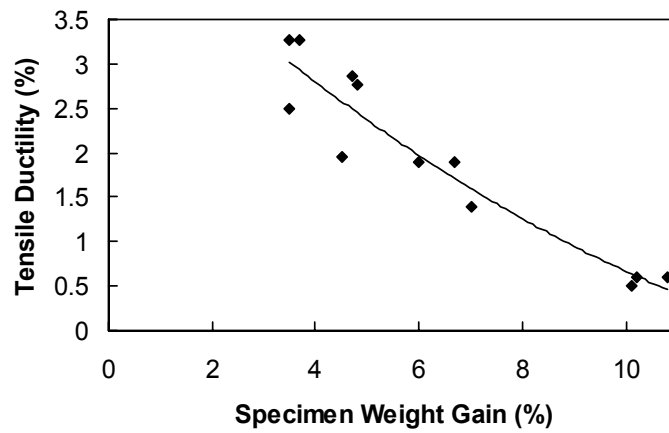
Figure 9. Effect of amount of nitride (weight gain) on the tensile ductility for 6061 - 2%Mg - 1%Sn - 4%nylon preforms infiltrated with Al - 5%Mg for 2h at 700°C. The embrittling effect of excessive nitride thickness is evident.

(a)

(b)

(c)

Figure 10. Some example parts made by SLS and infiltration, (a) pump body, (b) heat sink, bracket and sculpture and (c) hollow tubes of diameter 35mm (photo courtesy of K. Newall, 3D Systems, Inc).

Conclusions

In this paper, we have highlighted some of the recent advancements made in the production of infiltrated aluminium components via Selective Laser Sintering. The addition of Sn controls the nitride growth rate. This allows more accurate control of the nitride thickness, which is critical in maintaining ductility and mechanical properties. Tin also improves the infiltration rate, due to the reduction of the surface tension of the liquid as it dissolves the Sn. Finally, switching the process gas to Ar at the end of the nitriding stage not only arrests the nitride growth, but also permits the use of much higher infiltration temperatures, which in turn permits the use of more ductile infiltrants. In this way, complex parts with properties comparable to conventional casting alloys can be produced.

Acknowledgements.

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