

AGE-HARDENING OF AN ALUMINIUM ALLOY MATRIX COMPOSITE REINFORCED WITH STAINLESS STEEL FIBRES

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SUMMARY: The possibility of reinforcing the age-hardenable aluminium alloy AS9G03 by stainless steel fibres is explored. A first part of the work concerns the composite processing by squeeze casting. Several processing parameters had to be controlled in order to obtain a sound material with optimised microstructure. In a second part, the age-hardening of the composite is considered. The oxide layer on the fibres which was designed to prevent the fibre/matrix reaction during the heat-treatment is showed to strongly affect age-hardening due to the diffusion of Mg towards the oxidic fibre/matrix interface. The paper shows how precipitation hardening can be ensured in the composite by adjustment of solution treatment temperature and time and oxide layer thickness.

KEYWORDS: precipitation hardening, CMM, stainless steel fibres

INTRODUCTION

Aluminium alloys are attractive for applications in the automotive industry because of their low density and high strength at room temperature. However, their mechanical properties rapidly decrease when temperature increases. High strength foundry alloys are often age-hardenable alloys with Si and Mg addition, the precipitates of which are not stable at elevated temperature. Several methods can be used to strengthen Al alloys at high temperature. For example, fine stable precipitates such as nitrides, carbides and oxides can be dispersed in the alloy. An alternative method is proposed in this paper. The idea is to reinforce the alloy by stainless steel fibres, using the squeeze casting method. In contrast to ceramic reinforcement, metallic fibres allow keeping a good ductility of the composite. A problem to be solved is the high reactivity of aluminium with most metals, including Fe. The reaction gives rise to brittle intermetallic compounds at the fibre/matrix interface, which brings about a loss of ductility and toughness of the composite. Former studies [1] have shown that passivation of the fibres by thermal treatment in air before infiltration can help solving the problem.

It is well known that the kinetics and the level of age-hardening are often modified by the presence of a second phase. The currently available literature on this subject concentrates on the effect of ceramic reinforcement (Al_2O_3 and SiC) on the hardening [2-12]. The aim of this

work is to document the effect of the stainless steel oxidised fibres on the aging response of a cast AS9G03 Al matrix composite (9 wt % Si, 0.3 wt % Mg) and to reach, after heat-treatment, at least the same level of hardness in the composite as in the unreinforced alloy.

MATERIALS AND METHODS

The preforms are sintered mats of 12 mm diameter 316L stainless steel fibres. This network of fibres, whose orientation distribution is random planar, presents thus transverse isotropy. The fibre volume fraction in the preforms is about 20 %. They are infiltrated by squeeze casting with alloy AS9G03 which is a currently used alloy for car engine parts. The composition of the alloy is presented in Table 1. Each measurement was made both on the composite and on the unreinforced alloy. These unreinforced pieces were taken in the same cast as the reinforced ones, just above the preform, to ensure the same elaboration conditions.

The age-hardening response of the composites and unreinforced alloys was characterized by Brinell hardness measurements performed under loads of 31.25 and 62.5 kg with a steel ball diameter of 2.5 mm. The Mg and Si content of as-cast and heat-treated materials were determined by electron probe microanalysis.

Table 1 : Weight % composition of AS9G03 69N alloy

	Si	Fe	Cu	Mn	Mg	Ni	Zn	Pb+S n	Na	Ti	Al
Min	9.00	-	-	-	0.3	-	-	-	0.003	0.08	bal.
Max	10.00	0.14	0.02	0.04	0.4	0.02	0.04	0.02	0.012	0.13	

RESULTS

Composite processing

The squeeze casting method allows very high cooling rates and a large variety of parameter adjustments : temperature of the die, of the punch, of the preform, of the casting, pressure on the punch, mass of the alloy... In this work, the pressure was fixed at 25 MPa and some other parameters were determined by the optimisation of the composite. The mold was at room temperature whereas the punch was preheated in order to bring shrinkage voids outside the composite. The micro-porosity was suppressed by bubbling Ar in the liquid alloy. The preform was preheated at a temperature higher than the infiltration temperature of the alloy, so that the heterogeneity of the microstructure could be significantly reduced. Indeed, temperature gradients are present in the preform during the solidification of the alloy (the preform being in contact with the cold bottom of the die). Due to the hypoeutectic nature of alloy AS9G03, these gradients can lead to composition gradients in the composite. Such gradients are minimized when preheating the preform. To completely suppress these gradients, no solidification should occur before complete infiltration of the preform. On the other hand, a grain size gradient can not be suppressed due to different solidification rates near the bottom and near the center of the mold.

From SEM observations, no reaction between the matrix and the fibres was observed, even in the absence of passivation layer on the fibres. This low reactivity can be attributed to the significant Si content of the alloy. Indeed, Si reduces the activity of Al and the melting temperature of the alloy and increases the solubility of iron in the Al alloy.

Thermal treatment

Suppression of the reaction

The heat-treatment conditions recommended for the peak hardening of alloy AS9G03 (T6 treatment) consists in a solution treatment at 530°C in air during 5 hours, followed immediately by a quench in water at 50°C and by an aging treatment at 180°C during 6 hours. Without passivation of the fibres, some reaction appears between the fibres and the matrix during the solution treatment at 530°C. The preform was thus passivated by heat-treatment in air at 650°C before infiltration so that the oxide layer formed on the fibres acts as a diffusion barrier at the fibre/matrix interface. Isothermal study by differential thermal analysis (DTA) was performed on composites processed with different fibre oxidation times in order to determine the time/temperature conditions allowing the solution treatment to be completed before the beginning of interface reaction. Composite samples were heated in argon at a heating rate $l = 15^\circ\text{C}/\text{min}$ to a dwell temperature T_d . They were maintained at T_d until the exothermal peak corresponding to the fibre/matrix reaction has leveled off. Fig. 1 shows an example of 3 thermograms obtained for the same composite at 3 different T_d . For each dwell temperature (508, 518, 528, 538, 548, 558°C) and each oxidation condition of the preform (5, 10 and 30 min at 650°C), we recorded the dwell time t_d necessary for the beginning of the reaction.

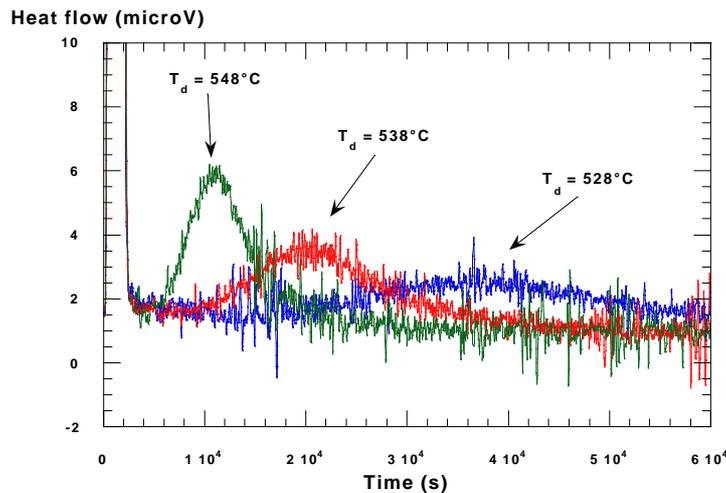


Fig.1 : DTA thermograms of an AS9G03/ss composite (oxidation : 10 min at 650°C) for 3 dwell temperatures : 528, 538 and 548°C

If the process of destabilisation of the oxide layer leading to the initiation of the reaction is thermally activated and is linked to only one mechanism in the studied temperature range, the results of the DTA can be fitted by straight lines according to ¹ :

$$\ln t_d = (E_a/R) \cdot 1/T_d + C \quad (1)$$

where E_a is the activation energy for the destabilisation of the oxide layer and t_d is evaluated in minutes. Fig. 2 shows all the results for 3 preform oxidation conditions : 5, 10 and 30 min at 650°C. Plotting $\ln(t_d)$ as a function of $1/T_d$, we can see that the activation energy seems to remain about 470 kJmol^{-1} independently of the oxidation conditions. This DTA study allows

¹This relation is valid when the isothermal time equivalent to the heating can be neglected in comparison with t_d

defining the range of conditions in which the solution treatment can be completed without reaction. It also shows that, without passivation of the fibres, the reaction begins before 500°C, thus preventing any solution treatment.

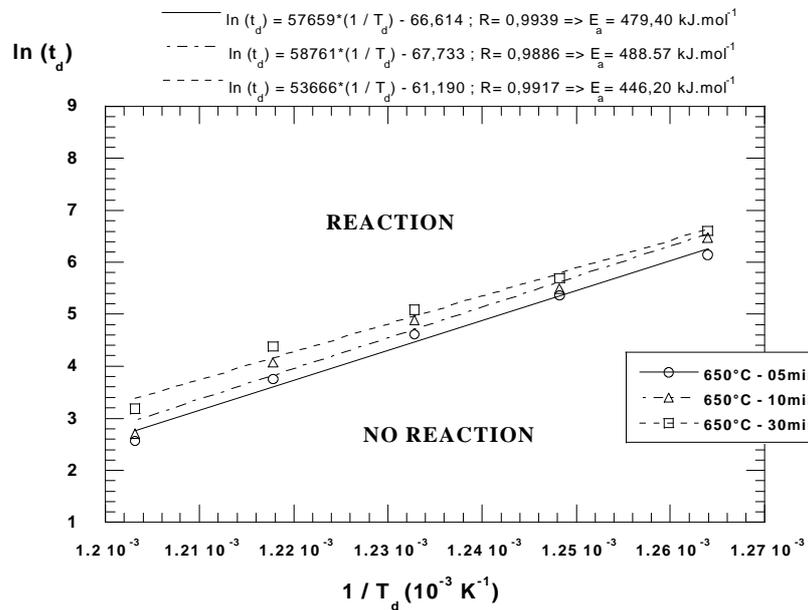


Fig.2 : Evolution of $\ln(t_d)$ as a function of $1/T_d$ for 3 oxidation conditions of the fibres

The micrographs of Fig. 3 present the microstructure of an AS9G03/ss composite, (a) as cast and (b) treated during 3 h at 510°C in air. The needles of Si have globularised during the treatment and no reaction has appeared.

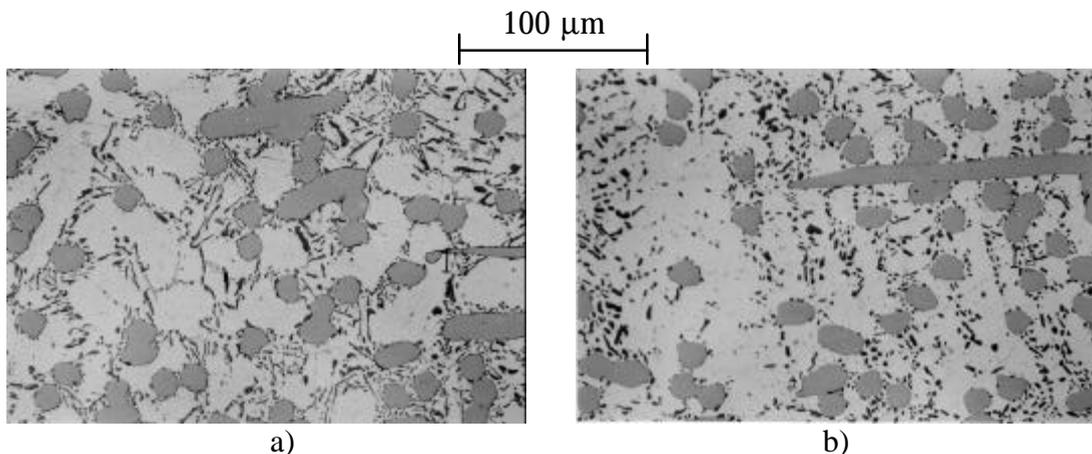


Fig.3 : Micrographs of an AS9G03/ss composite a) as-cast b) treated during 3 h at 510°C

Age-hardening

Fig.4 presents the hardness evolution as a function of the aging time at 180°C for three materials :

- AS9G03 alloy - solution treatment = 3 h, 510°C
- AS9G03/stainless steel - fibre oxidation treatment = 10 min, 650°C - solution treatment = 3 h, 510°C
- AS9G03/stainless steel - fibre oxidation treatment = 60 min, 650°C - solution treatment = 5 h, 510°C

We can see that precipitation hardening at 180°C allows the unreinforced alloy to reach 105 HB after 6 hours. The hardening is a little less important (99 HB) in the composite made after fibre oxidation treatment of 10 min and we can see nearly no hardening at all in the composite made after fibre oxidation treatment of 60 min.

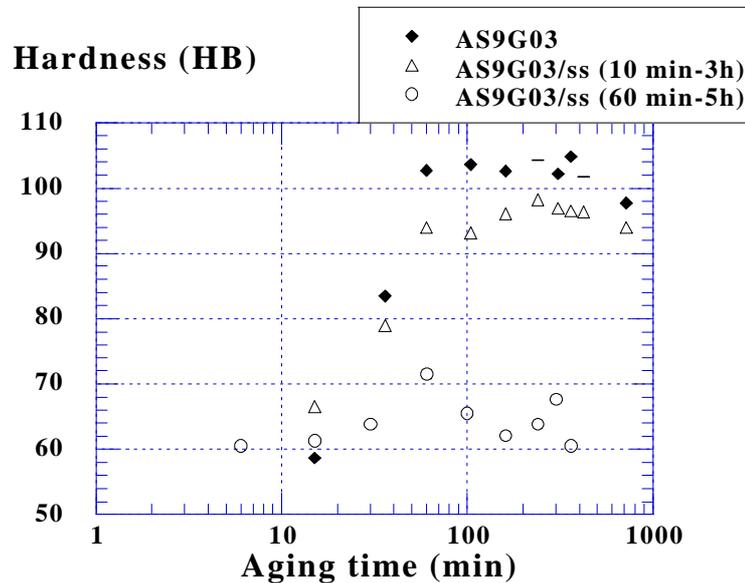


Fig.4 : Evolution of the hardness as a function of the aging time at 180°C for AS9G03, AS9G03/ss oxidized 10 min at 650°C and treated 3 h at 510°C, AS9G03/ss oxidized 60 min at 650°C and treated 5 h at 510°C

The cause of this absence of age-hardening is the migration of Mg towards the fibre/matrix interface. Mg tends to oxidize while reducing the oxides on the fibres. This can help wetting the fibres by the alloy [8] but Mg is then not any more available for precipitation hardening. Mapping by electron probe microanalysis has proven this segregation of Mg. Fig. 5 shows 3 microanalysis profiles recorded (a) on the as-cast composite, (b) on the unreinforced alloy after heat treatment and (c) on the composite after heat-treatment. In the as-cast composite, Mg is found in the Al dendrites, in the eutectic and, particularly, in some areas also enriched in Fe and Mn. After heat-treatment, an homogeneous concentration of about 0.4 at % Mg is present in the different phases of the unreinforced alloy. This concentration allows the age-hardening. After the same treatment on the composite, we see that all the Mg of the matrix has migrated around the fibres so that no matrix age-hardening is ever possible. No or little diffusion of the Mg towards the fibre/matrix interface had occurred during the squeeze casting of the composite due to the very high cooling rates obtained with this method.

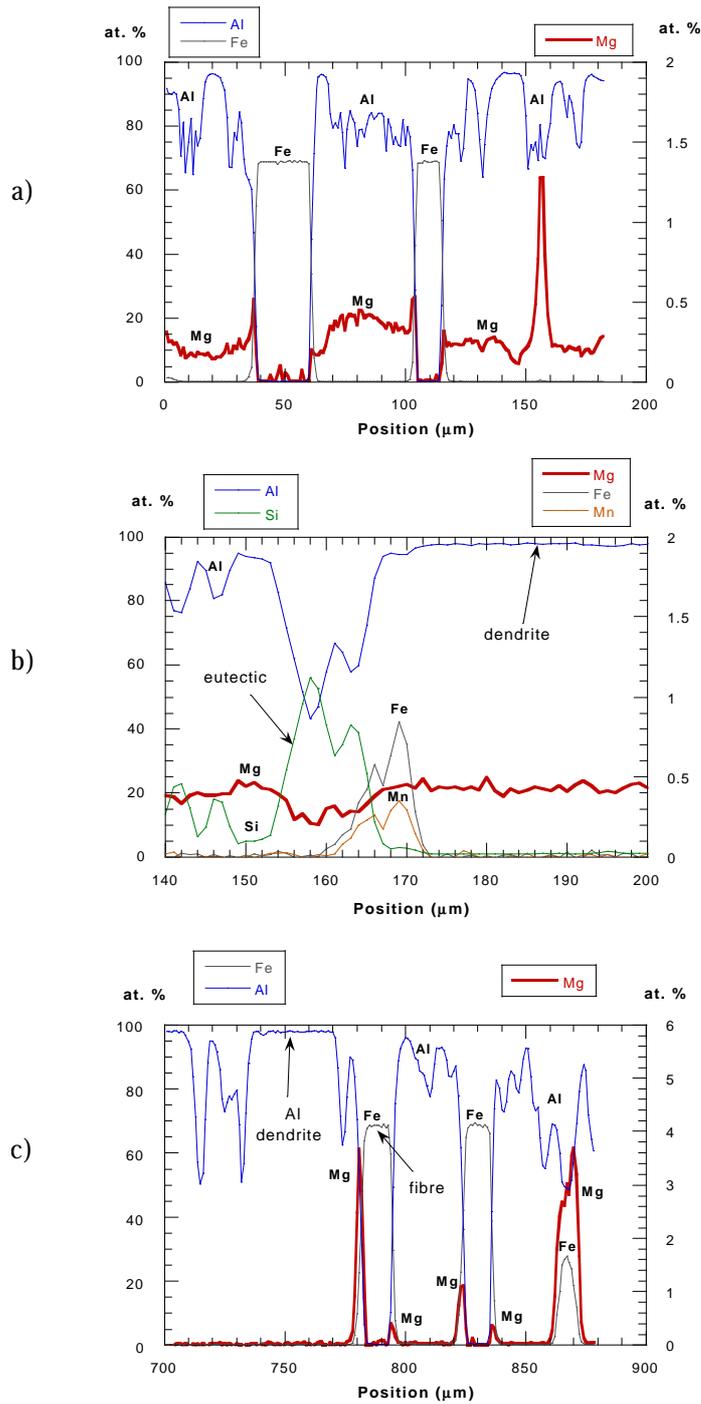


Fig.5 : Microanalysis profiles of a) AS9G03/ss as cast, b) unreinforced AS9G03 treated (5h at 510°C and 6h at 180°C) and c) AS9G03/ss treated (5h at 510°C and 6h at 180°C)

The parameters that influence the diffusion of Mg are the temperature and time of solution treatment and the thickness of the oxide layer on the fibres. The evolution of the hardness of the treated composite as a function of the thickness of the oxide layer is presented in Fig.6. It shows that the combination of (i) a short time and (ii) a relatively low temperature for the solution treatment and (iii) a thin oxide layer can lead to satisfactory age-hardening. That confirms also the results presented in Fig. 4.

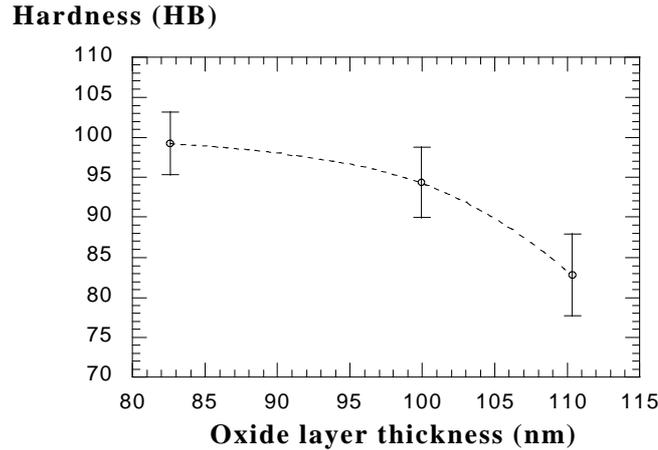


Fig.6 : Evolution of AS9G03/ss composites hardness as a function of the oxide layer thickness on the fibres (Heat-treatment : 3h at 510°C and 6h at 180°C)

DISCUSSION

The diffusion of Mg towards the fibre/matrix interface occurs principally during the solution treatment and not during the squeeze casting because of very short contact times between liquid matrix and reinforcement allowed by this method. The diffusion happening during the solution treatment is explained by the thermodynamic tendency of Mg to reduce the oxides present on the fibres (principally Fe₂O₃ and Cr₂O₃ for the oxidation conditions considered here). Reactions between the Mg present in the alloy matrix and the reinforcement phase have often been mentioned in the literature [2, 3, 4, 5, 6, 7, 8] in MMCs containing Al₂O₃, SiO₂ or oxides coatings on SiC particles. If limited, this reaction could be beneficial because it enhances the interfacial wetting [8]. However, it must of course be kept under control because Mg is necessary for the age-hardening of the matrix.

It has been shown in Fig. 4 that, even in the optimised conditions of thermal treatment and oxidation, the hardness of the composite still stays a little under the hardness of the unreinforced alloy. One might have anticipated that it should actually be a little higher due to the higher hardness of the fibres. The hardening potential of the alloy is thus modified by the presence of the second phase. Either this is entirely due to a slight reduction of the Mg content in the matrix (even for a very thin oxide layer on the fibres), or some other microstructural phenomenon should be considered, as suggested by some authors. Friend et al. [9] have attributed the reduced level of hardening obtained in δ -alumina-fibre reinforced Al-matrix composites to the decreased vacancy concentration in the MMC, due to the availability of a large number of vacancy sinks at the fibre/matrix interfaces. This low vacancy concentration modifies the kinetics of formation of the precipitates and reduces the volume fraction of the GP zones formed in the composite [10]. Dutta et al. [11] confirm that addition of alumina in 6061 Al alloy affects the relative amounts of the various precipitates present. They suggest that, because of the high dislocation density in the composite, the early precipitates, which are coherent with the matrix, can orient themselves relative to the dislocations so as to reduce the associated strain energy. This would stabilize these coherent precipitates and reduce the volume fraction of the semi-coherent β' and incoherent β phase. The β' precipitates are the most efficient as far as the hardening is concerned.

Many papers also mention a significant acceleration of the aging kinetics in the composite as compared to the unreinforced matrix alloy [3, 10, 11, 12] : the high dislocation density in the composites reduces the incubation time for heterogeneous nucleation of the precipitates and enhances the diffusion rate of Mg in the matrix. Such phenomena have not been observed in our Al alloy/stainless steel composite : the peak hardness is reached quite at the same time in the composite and in the unreinforced alloy (Fig.4). A probable cause of this is the relatively small difference between the thermal expansion coefficient (CTE) of Al (24.10^{-6}K^{-1}) and the CTE of stainless steel (18.10^{-6}K^{-1}). Until now, all published results deal with composites with ceramic reinforcement, where the CTEs of the matrix and of the fibres are much more different, and thus the dislocation density is higher.

CONCLUSIONS

1. MMCs consisting of stainless steel fibre-reinforced AS9G03 are produced by squeeze casting. An optimisation of the processing parameters allows us to produce sound composite, without reaction between Al alloy and stainless steel, with a quite homogeneous microstructure.
2. The subsequent age-hardening treatment of the material required to proceed to an oxidising treatment of the fibres before infiltration in order to prevent the Al/stainless steel reaction from appearing during the solution treatment.
3. The age-hardening of AS9G03 alloy can be considerably altered by the presence of oxidised stainless steel fibres, because of the diffusion of Mg towards the fibre/matrix interface. Some conditions of oxidation of the fibres lead to complete annihilation of the hardening process.
4. By adjustment of parameters such as solution treatment temperature and time and oxide layer thickness, it is possible to ensure precipitation hardening in the composite to a level comparable to the unreinforced alloy. In contrast to some authors, no acceleration of the kinetics of precipitation has been observed.

ACKNOWLEDGEMENTS

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