Effect of heat treatments at 520°C on an aluminium alloy matrix composite reinforced with Ni₃Al powder particles

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Abstract

The effect of heat treatment at 520°C on Si and Mg in 6061/5% volume Ni₃Alp composite was investigated. Si atoms diffused through the Al₃Ni reaction product to form a Si-containing Al₃Ni₂ phase with variable amounts of Si, whereas Mg accumulated at matrix-Al₃Ni interphases. As a consequence, the 6061 alloy lost its age harden ability.

Keywords: Composites; aluminium alloys; nickel aluminides; diffusion; powder processing.

1. Introduction

Al-base composites (AMC) reinforced with Ni-aluminides have been proposed as substitutes for ceramic reinforced composites [1-2] especially in applications where friction is involved [3-4]. To control interfacial reactions that appeared during processing by casting routes, a powder metallurgy (PM) route was developed [5] in which Ni-aluminide and Al powder particles were blended, encapsulated and finally consolidated by extrusion. The PM route demonstrated its capability of producing as-consolidated materials that did not present any reaction product between particulate reinforcement and matrix. This happens because the intimate union between them occurred only when the blend of powders passed through the extrusion die, and this lasts only a few seconds at normal extrusion speeds. However, if the matrix is an age hardening Al alloy, the AMC should be submitted to a solid solution treatment in order to get maximum mechanical properties through subsequent precipitation of small particles from the supersaturated solid solution. This ageing treatment, typically at around 500°C, may promote reactions between matrix atoms and the Ni-aluminide reinforcement.

Thermal stability studies performed on PM unalloyed Al blended with 5 vol.% Ni₃Al [6] showed that this composite was thermally stable at 300°C up to 1000 h. Above this temperature, dissolution of Ni₃Al occurred with formation of an outer Al₃Ni layer and an intermediate Al₃Ni₂ phase. More particularly, at 500°C, the Al₃Ni and Al₃Ni₂ phases were detected already after 1 hour, with layer thickness of 9 µm and 7 µm, respectively.

In the present paper, an age hardening 6061 Al alloy matrix was employed, which is more attractive from a technological point of view than an unalloyed Al matrix. The alloy powder was blended with 5% volume of Ni₃Al particles, cold compacted and then submitted to heat treatments at 520°C, which is a typical solution temperature for this alloy. The main aim of this work was to establish the behaviour of matrix solute elements, Mg and Si, during high temperature heat treatments, with special attention to their interaction with the Ni-aluminide particles. Finally, the age hardening response of this composite was investigated at 175°C for extruded Al/5 vol.% Ni₃Al material.

2. Experimental procedure

Gas atomised powder particulate of 6061 aluminium alloy was supplied by ALPOCO, Sutton Coldfield, UK, with $< 50\ \mu\text{m}$ in particle size and composition in mass % of 0.45 Si, 0.96 Mg, 0.27 Cu, 0.16 Cr, 0.15 Fe and balance Al. These particles were blended with 5% volume of Ni_3Al powder particles of irregular morphology and $< 54\ \mu\text{m}$ in size, produced at Fundación INASMET, San Sebastian, Spain, by self-propagated high-temperature synthesis (SHS), followed by grinding of the porous product. The blends of powders were uniaxially cold compacted by applying 240 MPa for 3 minutes to form cylinders 10 mm diameter and about 10 mm high. The apparent density of the 6061/ Ni_3Al compacts was $2.3\ \text{g/cm}^3$, which corresponds to 85% of theoretical density. Cold compacts were submitted to solution heat treatments in air at 520°C for 15 minutes, 24, 500 and 1000 hours. Specimens for microstructural characterisation were prepared by conventional metallographic techniques. Microstructural observations were made by scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDS) analysis.

For hardness evaluation, a composite bar was obtained by extrusion at 520°C , with an extrusion ratio of 18:1 and at a ram speed of 1 mm/s. A PM 6061 unreinforced bar was also obtained by the same route for comparison purposes. Extruded specimens were submitted to solution treatment at 520°C for 90 minutes and heat treated at 175°C for times varying between 15 minutes and 24 hours. Vickers hardness values were the average of at least 10 indentations applying 5 kg load for 15 seconds. The extruded composite bar was also observed by transmission electron microscopy (TEM) equipped with EDS, after a heat treatment of 120 hours at 520°C followed by 8 hours at 175°C .

3. Results

The cold compacted 6061/ Ni_3Al composite submitted to a 15 minute exposure at 520°C already presented signs of reaction between the matrix and the intermetallic particles. This reaction consisted on the formation of the Al_3Ni phase at matrix/intermetallic interfaces. Fig. 1a shows a backscattered image of this composite, where the 6061 matrix appears black, the Ni_3Al appears white and the dark grey phase corresponds to the Al_3Ni reaction product, as determined by EDS, Fig. 1b. It must be noted that cold compaction did not promote complete contact between particles and matrix, as is evident from the fact that its density was only about 0.85 of the density of the fully consolidated material. This resulted in a lack of bonding at some matrix/particle interfaces, which together with the presence of some porosity, resulted in reactions occurring asymmetrically, i.e. only at those matrix/particle areas that were really well bonded.

Fig. 1. (a) Backscattered image of a 6061/ Ni_3Al cold compact, heated for 15 minutes at 520°C and (b) EDS of the Al_3Ni interphase.

After 24 hours at 520°C , a new phase containing Ni, Al and Si was formed between the Ni_3Al original particles and the outer Al_3Ni reaction product. This is illustrated in the backscattered image of Fig. 2a, where the new intermediate phase has a bright grey contrast. Concentration analysis of Si and Mg were measured each two micrometers starting at point A in the micrograph and ending at point B, and results are presented in the diagram of Fig. 2d. As can be seen, the intermediate phase contains a variable amount of Si that increases to more than 3% in the region close to the interface with the Al_3Ni reaction product and drops to almost zero in the region close to the interface with Ni_3Al . Furthermore, Si content is negligible in the matrix and in the Al_3Ni phase and undetectable in the Ni_3Al phase. With

regards to the behaviour of Mg, the other solute element that takes part in the age hardening of 6061 alloys, it appears concentrated at the matrix/particle interface, Fig. 2d. This microstructure changed after 500 hours of heat treatment, Fig. 2b, as no presence of the original Ni_3Al particles could be observed. This indicates that transformation of Ni_3Al into Al_3Ni and Al-Ni-Si phases was total during that duration of exposure. According to the EDS analysis, Fig. 2e, in this case Si concentration increases towards the centre of the Al-Ni-Si phase to more than 4% and is negligible in the Al_3Ni phase and in the matrix. On the other hand, concentration of Mg increases at the matrix/ Al_3Ni interface, Fig. 2e. Finally, the sample heated for 1000 h at 520°C, Fig. 2c, presented only Al_3Ni particles, indicating a total transformation of the intermetallic reinforcement. In this case, no significant amount of Si was detected in the particles, Fig. 2f, and only a gradient of Mg remained at the interfaces.

Fig. 2. Backscattered images of 6061/ Ni_3Al cold compacts, heated at 520°C for a) 24 h, b) 500 h and c) 1000 h, and their corresponding Si and Mg EDS analysis: d), e) and f).

In order to determine the final evolution of Si when the 6061/5 vol. % Ni_3Al composite was wholly transformed, i.e. in the equilibrium state, TEM samples were prepared from the extruded bar, that was previously submitted to a heat treatment of 120 h at 520°C. This gave enough time to achieve the desired condition, as extrusion promotes efficient bonding between matrix and reinforcing particles, and thus, diffusion reactions occurred much more quickly than in cold compacted specimens. The micrograph of Fig. 3a shows a bright field image with an Al_3Ni particle, as indicated by the EDS of Fig. 3b. At the matrix/particle interface, a white phase is observed, that is rich in magnesium and oxygen, Fig. 3c. Apart from this, the matrix presents some dark precipitates less than 20 nm in size. These dispersoids, which contain Si, Fe and Cr, Fig. 3d, can be identified with the $\text{Al}_{12}(\text{Fe,Cr})_3\text{Si}$ phase, which precipitates during homogenisation of 6061 alloys that contain some Cr [7, 8]. As the alloy employed in the present work contains 0.16% of chromium, it is assumed that this element acted to stabilize the formation of this quaternary phase.

Fig. 3. Extruded 6061/ Ni_3Al composite treated for 120 h at 520°C. (a) Bright field TEM image, (b) EDS of the Al_3Ni particle, (c) EDS of the bright phase at the reinforcement/matrix interface, and (d) EDS of the small dark particles in the matrix.

Fig. 4 shows hardness evolution of the extruded 6061/ Ni_3Al composite and 6061 alloy at 175°C. After a solution treatment of 1.5 hour at 520°C, hardness of the composite was 85 Hv, which is 30% higher than that of the unreinforced alloy. With increasing time of ageing at 175°C, the matrix alloy behaved as expected, i.e. reaching a peak hardness of about 105 Hv at around 8 hours of ageing. On the contrary, hardness of the composite remained quite constant during the whole treatment, which indicates a lost of hardening ability of the matrix in the 6061/ Ni_3Al composite material.

Fig. 4. Vickers hardness versus time of ageing at 175°C of extruded 6061/ Ni_3Al composite and 6061 alloy.

4. Discussion

The age hardening curves of the composite and matrix alloy, Fig. 4, show that 6061/ Ni_3Al composite did not age harden. This behaviour is contrary to what is expected from a 6061 matrix. More typically, AMCs maximum hardness is higher and occurs earlier than in monolith alloys [9-13] due to the difference in coefficients of thermal expansion (CTE)

between composite components. In the present case, CTE are $22 \times 10^{-6}/\text{K}$ and $12.5 \times 10^{-6}/\text{K}$ for 6061 and Ni_3Al , respectively, which would promote an increase in dislocation density during quenching from solid solution temperature, which in turn would promote diffusion of Si and Mg solute elements and nucleation of β'' and β' precipitates. The anomalous behaviour of the 6061/5 vol.% Ni_3Al composite should be attributed to the reactions that took place during the solution treatments.

During heating of the 6061/ Ni_3Al composite at 520°C , two reaction phases appeared between the matrix and the Ni_3Al particles. The first phase to form was Al_3Ni , which is the same intermetallic as reported to appear first when the matrix was Al [6, 14] or Al-Mg [15]. The second reaction phase, which formed after an incubation time, contained Ni, Al and Si, instead of being simply Al_3Ni_2 , as was the case for Al and Al-Mg matrices. The ternary Al-Ni-Si equilibrium diagram [16] establishes that up to 25 at.% Al can be substituted by Si in the Al_3Ni_2 phase at 600°C giving rise to an Al_3Ni_2 phase with Si. More recently [17], a solid solubility of 11.5 at.% has been reported at 550°C . The existence of Si in the intermediate reaction interphase between Al-Mg-Si and Ni_3Al indicates that Si atoms, originally in solid solution in the Al-Mg-Si matrix, diffused through the Al_3Ni phase, reached the Al_3Ni_2 phase and became trapped in it as substitutional atoms for Al. The small amount of Si detected in the Al_3Ni phase is also in agreement with the Al-Ni-Si phase diagram that establishes a solid solubility of 0.7 at. % Si in Al_3Ni . The absence of Si in Ni_3Al is again consistent with the ternary Al-Ni-Si phase diagram, as no solubility of Si is expected in it. Whereas the Si concentration throughout the Al_3Ni phase is constant, the Al_3Ni_2 phase presents variable amounts of Si. As Al_3Ni_2 is only an intermediate phase, its volume fraction in the composite increases initially during heat treatment and afterwards decreases. It is interesting to calculate the maximum amount of Si that could be consumed by the Al_3Ni_2 phase, for which the maximum possible volume fraction of Al_3Ni_2 has been estimated from a Al/5 vol. % Ni_3Al composite [6] and resulted in about 3.4 vol. %. This amount of Al_3Ni_2 phase would be able to consume as much as 3 to 4 times the amount of Si present in the alloy matrix (0.45 mass %). This indicates that a way to avoid a depletion of Si in solid solution in the matrix during solution treatments would be to use an Al alloy with more than 1.5 mass % Si.

When time of heat treatment increased, the system continued to move towards the equilibrium condition: the Ni_3Al and the Al_3Ni_2 with Si phases reacted with Al to be finally transformed into Al_3Ni . In the completely transformed state no Si remained in the intermetallic particle (Fig. 2f). This indicates that Si should have diffused outwards through the Al_3Ni phase, returning to the matrix. In this new situation, one could expect to find the Si atoms in solid solution in α -Al. Instead of this, some of them became trapped by Cr and Fe to form $\text{Al}_{12}(\text{Fe,Cr})_3\text{Si}$ precipitates. This causes a depletion of Si atoms in the solid solution, that are otherwise supposed to react with Mg in solid solution, if there is any, to form Mg_2Si precipitates.

The other solute element that plays a crucial role in the age hardening behaviour of 6061 alloys is Mg. As is shown in Fig.2, after heat treatments of the composite at 520°C , Mg appeared concentrated at the matrix/particle interface. Two effects contribute to this accumulation: the first one is that the Al_3Ni and $(\text{Al,Si})_3\text{Ni}_2$ phases consume Al, leaving the matrix around the intermetallic particle enriched in Mg [15]. The second one is related to the tendency of Mg to segregate at interfaces and grain boundaries, as was already reported to occur in AMCs reinforced with Al_2O_3 , SiO_2 and SiC [18-20]. This segregation can result in the formation of MgAlO_3 spinel [21] when Mg content in the matrix is less than 4 mass %. In addition, Wang et al. [22] observed that the oxygen needed for this phase is supplied by any oxide that is present in the material. In our case, this oxygen may come from the Al_2O_3 layer that always surrounds each 6061 powder particle. Similarly to what occurred with silicon, the depletion of Mg could be compensated by adding a larger amount of Mg to the alloy matrix.

A different way to avoid depletion of solute elements from the matrix and thus to avoid loss of age hardening would be to previously oxidize the reinforcing particles. This strategy has proven to be successful in a great deal of composites and, more specifically, in a NiAl reinforced Al composite [23]. NiAl powder exposed to oxidation treatments between 600 and 1100°C produced alumina layers that delayed nucleation of interphases, whereas particles oxidized for 3 hours at 750°C presented the best combination of effective diffusion barrier and sound bonding to the matrix. In the present material it is expected that an oxide layer on the Ni₃Al particles would also act as a diffusion barrier for Al and Si atoms, therefore creating an effective protective coating.

5. Conclusions

A PM 6061/5 vol. % Ni₃Al cold compacted composite was heated at 520°C and the evolution of Si and Mg solute elements investigated, together with its age hardening response.

During heat treatments, two reaction phases appeared between the matrix and Ni₃Al: i) Al₃Ni, and ii) Al₃Ni₂ with variable amounts of Si, the latter after an incubation time. Simultaneously, Mg accumulated at the matrix-Al₃Ni interface.

When transformation was completed, Ni-aluminide particles were wholly transformed into Al₃Ni. In this condition, Si appeared precipitated in the matrix in small Al₁₂(Fe,Cr)₃Si particles.

Hardness of 6061/Ni₃Al in its solutionized condition was higher than that of the monolithic alloy. However, it lost its age harden ability after long solution treatments because of a drastic depletion of Si and Mg solute elements in the matrix.

Two solutions have been proposed in order to improve composite behaviour: i) to increase the Si and Mg content in the matrix alloy to avoid drastic depletion of solute elements, and ii) to create a protective coating on reinforcement to avoid composite degradation, which appears more suitable as a general guidance for composite processing. In the present case this would be achieved by previously oxidizing the Ni₃Al reinforcement, which would result in the formation of a diffusion barrier for Al and Si atoms.

Acknowledgements

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