

# Influence of pre-oxidation of NiAl intermetallic particles on thermal stability of Al/NiAlp composites at 500 °C

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## Abstract

Thermal stability of PM Al/5%NiAl composites has been studied by exposure at 500 °C up to 24 h. NiAl intermetallic particles were employed as-received and after pre-oxidation at several temperatures. The optimal oxidation condition was determined based on its ability to delay interfacial reactions and prevent debonding at the metal/reinforcement interface.

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## 1. Introduction

Aluminium matrix composites (AMCs) have in general higher specific strength, stiffness and heat resistance than the unreinforced matrix alloy [1]. AMCs reinforced with ceramic particles have already found several applications. However, they suffer from some drawbacks due to the high abrasiveness and brittleness of the ceramics.

Substitution of ceramic reinforcements by intermetallics has appeared as a useful alternative because of their lower abrasiveness and brittleness. Several efforts have already been made to develop and characterize AMCs reinforced with intermetallics [2–10]. Powder metallurgy (PM) has proved to be a very suitable method for their processing [4] because it prevents reactions between matrix and reinforcement. But deleterious reaction products at intermetallic/matrix interfaces may also form during solid solution treatments, giving rise, on the one hand, to brittle interphases and, on the other

hand, to depletion of matrix solute elements; this reduces the age hardening ability of the aluminium alloy, with the corresponding worsening of the mechanical properties of the composite [6,8,10].

Among intermetallics, NiAl emerges as a promising candidate because of its combination of low density and high Young modulus (at stoichiometric composition and room temperature, 5.86 g/cm<sup>3</sup> and 294 GPa, respectively [11]), especially in comparison with Ni<sub>3</sub>Al. Studies on NiAl as reinforcement of Al alloys were carried out by Omura et al. [2]. They employed a casting route, in which partial transformation of NiAl into Al<sub>3</sub>Ni and Al<sub>3</sub>Ni<sub>2</sub> could not be avoided. These phases caused a drastic worsening of the mechanical properties of the composite.

In this work, Al/5 vol.%NiAlp composites were obtained through a PM route that was selected to prevent reactions during the fabrication step. Intermetallic particles were employed in the as-received condition and after pre-oxidation in air at 600–1100 °C. Thermal oxidation promotes a layer of alumina on NiAl that changes its structure from gamma to theta and alpha alumina as temperature increases [12–16]. Reaction

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products that may appear between Al and NiAl at 500 °C up to 24 h have been investigated and the ability of the different oxide layers to act as effective diffusion barriers has been determined. Avoiding or retarding Al atoms from reacting with the intermetallic particles is a *sine qua non* condition for the use of age hardenable Al alloys as matrices. The strength of the bonding between NiAl particle and the matrix has been assessed through tensile tests.

## 2. Experimental procedures

NiAl particles of <350  $\mu\text{m}$  in size were selected for this investigation. The intermetallic powder was produced by self-propagated high-temperature synthesis (SHS) at Fundación INASMET, San Sebastian, Spain, from pure elemental Ni and Al powders followed by jet milling. The aluminium powder used for the matrix was of 99.9% purity with a particle size of <60  $\mu\text{m}$ , which was mechanically blended with 5 vol.% of NiAl. Intermetallic particles were introduced as-received and after pre-oxidation in air at 600, 750, 900, and 1100 °C for 1 and 3 h, followed by slowly cooling to room temperature (1 °C/min) in the furnace.

Cold compacted and extruded specimens of Al/5%NiAl composite were prepared. Cylindrical samples of 10  $\times$  10 $\varnothing$  mm were made by uniaxial cold compaction applying a load of 260 MPa for 900 s. Compacted speci-

mens were heat treated at 500 °C for 24 h. Extruded bars of 12 mm diameter were produced from canned powders at extrusion temperature of 450 °C, extrusion ratio of 14:1, and ram speed of 0.3 mm/s. Extruded samples were heat treated at 500 °C for 0.5–24 h. Microstructural characterization was performed by optical microscopy and a FEG Jeol-6500 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscope (EDS).

Cylindrical tensile specimens of 3 mm diameter and 20 mm gauge length were machined from the extruded bars while maintaining the tensile axis parallel to the extrusion direction. To investigate the quality of interfacial bonding between matrix and intermetallic particles, tensile tests were carried out at a strain rate of  $5 \times 10^{-4} \text{ s}^{-1}$  and fracture surfaces were analysed by SEM.

## 3. Results and discussion

Fig. 1a shows typical cross-sections of SHS NiAl particles. As can be seen, unlike small particles, larger ones contain defects such as pores and cracks. Fig. 1b shows the surface of an as-received NiAl particle, and Fig. 1c and d shows surfaces after oxidation for 1 h at 750 and at 1100 °C, respectively. The smooth surface of the as-received particles changes to a rough surface with increasing oxidation temperature. According to the

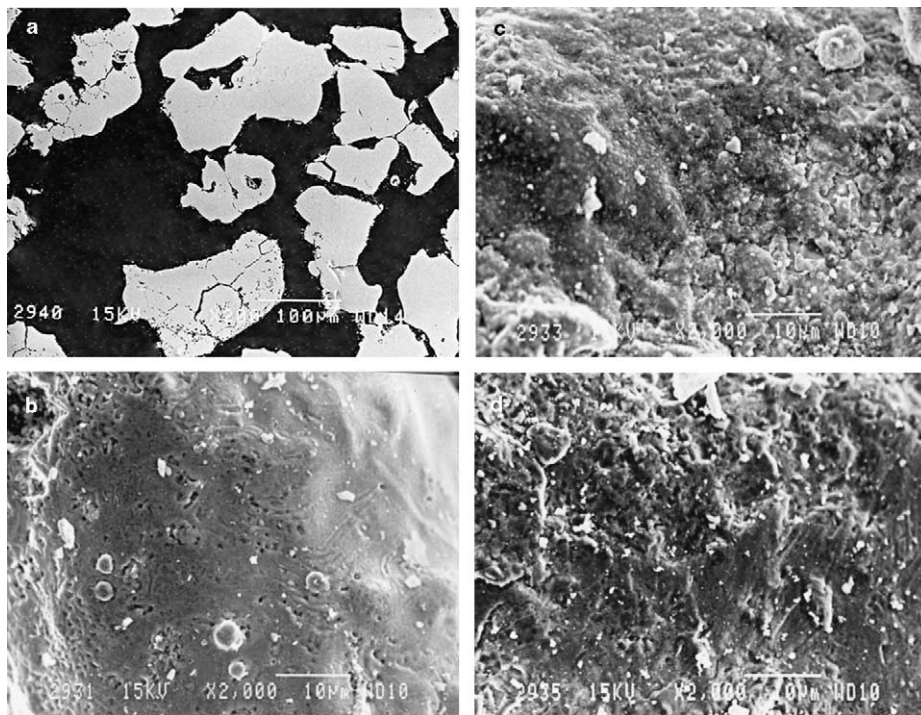


Fig. 1. (a) Cross-section of NiAl powder in as-received condition, and surfaces of NiAl particles, (b) as-received, (c) oxidized for 1 h at 750 °C and (d) oxidized for 1 h at 1100 °C.

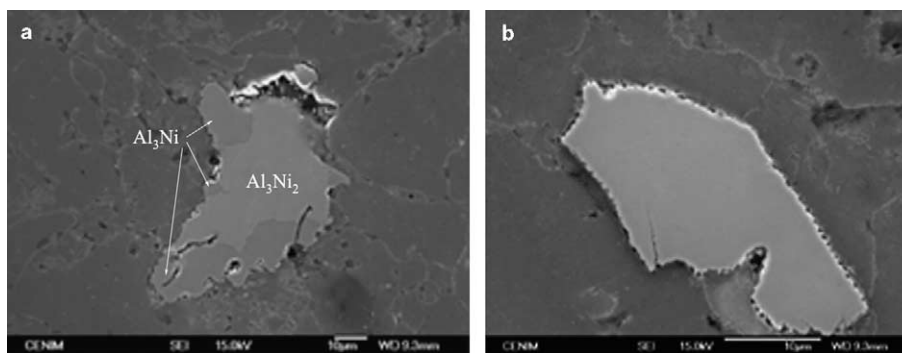


Fig. 2. Cold compacted Al/NiAl composite after heat treatment at 500 °C for 24 h: (a) unoxidized NiAl particles and (b) NiAl particles oxidized at 900 °C.

literature [12–16], the oxide formed at 750 °C should be mainly  $\gamma\text{-Al}_2\text{O}_3$ , whereas at 1100 °C,  $\alpha\text{-Al}_2\text{O}_3$  should have been formed. X-ray diffraction patterns obtained from the oxidized NiAl particles were unable to show the type of oxide that was actually formed due to the low volume of the alumina layer expected at these temperatures and times [16] in comparison with the volume of the NiAl particles (less than 2% in all cases).

Cold compacts of Al/NiAl powder were prepared to perform a first evaluation of thermal stability of the Al–NiAl system. It must be noted that contact between particles and matrix after cold compaction is not complete so the severity of reactions in this case is just a foresight of the behaviour of the extruded composite. In all samples, except in that with NiAl oxidized at 750 °C, diffusion reaction products were evident. The compact with unoxidized NiAl shows large amounts of reaction products, which were identified through EDS as  $\text{Al}_3\text{Ni}$ , and  $\text{Al}_3\text{Ni}_2$ , Fig. 2a. Particles oxidized at 600 °C also exhibit a substantial amount of interfacial products, which indicates that the oxide layer formed during the heat treatment at 600 °C did not act as effective barrier at 500 °C against diffusion of Al atoms across the Al–NiAl interface. Extrapolating from Uran et al. [16], oxidation of NiAl for 1 h at this temperature causes a  $\gamma\text{-Al}_2\text{O}_3$  layer of about 12 nm in thickness. In the sample obtained with NiAl particles oxidized at 750 °C, only a few particles underwent some transformation. In this case,  $\gamma\text{-Al}_2\text{O}_3$  was also formed with an estimated thickness of 65 nm [16]. Cold compacted samples with NiAl particles oxidized at 900 °C presented a  $\theta\text{-Al}_2\text{O}_3$  oxide layer of about 0.3 µm in thickness [16] with visible cavities underneath, Fig. 2b. These cavities are a consequence of vacancy condensation [12]. In this case, bonding to Al was almost non-existent and only a few NiAl particles showed  $\text{Al}_3\text{Ni}$  or  $\text{Al}_3\text{Ni}_2$  phases as diffusion reaction products. A similar aspect was shown with particles oxidized at 1100 °C, where NiAl was surrounded by a thick  $\alpha\text{-Al}_2\text{O}_3$  layer.

Extruded bars were prepared with NiAl as-received and NiAl particles oxidized at 750 °C for 1 and 3 h

and at 1100 °C for 1 h. In spite of the high temperature employed during the extrusion process, as-extruded composites did not present any reaction product. This is because intimate contact between matrix and intermetallic particles only occurred when the powder passed through the extrusion die and, therefore, the consolidated composite remained at high temperature only for few seconds [4].

Heat treatments at 500 °C of as-extruded samples promoted nucleation and growth of interphases between NiAl and Al that depended on the oxidized state of the intermetallic particles. Fig. 3 shows composite samples prepared with as-received NiAl. The composite was heat treated for 0.5, 1 and 24 h at 500 °C. The shortest heat treatment produced reactions at only the sharp parts of a few particles, Fig. 3a. This lack of symmetry is probably due to the fact that transformation kinetics is favoured at protuberances that have high curvature angles [17]. Treatment for 1 and 24 h, Fig. 3b and c, gave rise to the formation of two concentric layers around each NiAl particle. Analysis by EDS indicated that the outer layer corresponds to the  $\text{Al}_3\text{Ni}$  phase and the intermediate one to  $\text{Al}_3\text{Ni}_2$ . Both phases are the same as those formed in Al/5%Ni<sub>3</sub>Al composite at similar time and temperature [6]. Once transformation started, local volume changes due to the different densities of the forming layers may produce cracks that help the reaction to proceed [18]. This would explain the morphology of the particle shown in Fig. 3c, where the possible cracks are arrowed. It is difficult to deduce from these specimens the transformation sequence and kinetics of NiAl in Al/5%NiAl composites, and a more complete study at other temperatures and with intermetallic particles of more regular shape will be the subject of further research.

Heat treated samples prepared with NiAl oxidized at 750 °C for 1 h presented much higher thermal stability, as only a few transformed particles were visible after 1 h at 500 °C. Increasing the oxidation time to 3 h reduced even more the reaction between the matrix and the oxidized particles, Fig. 4a. Increasing the time

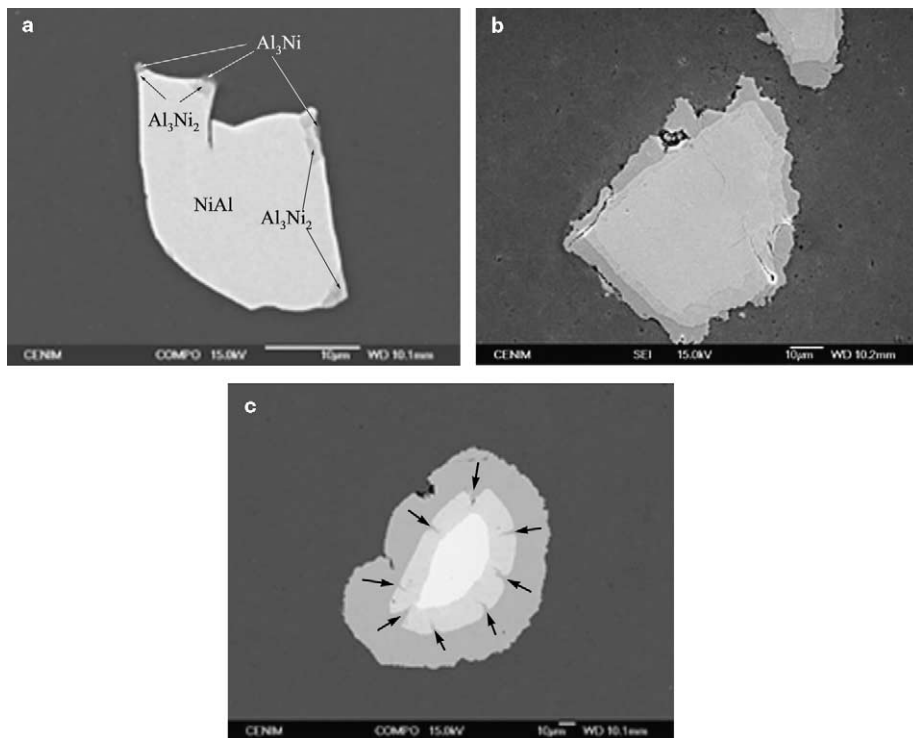


Fig. 3. Al/as-received NiAl composite after heat treatment at 500 °C for (a) 0.5 h, (b) 1 h and (c) 24 h.

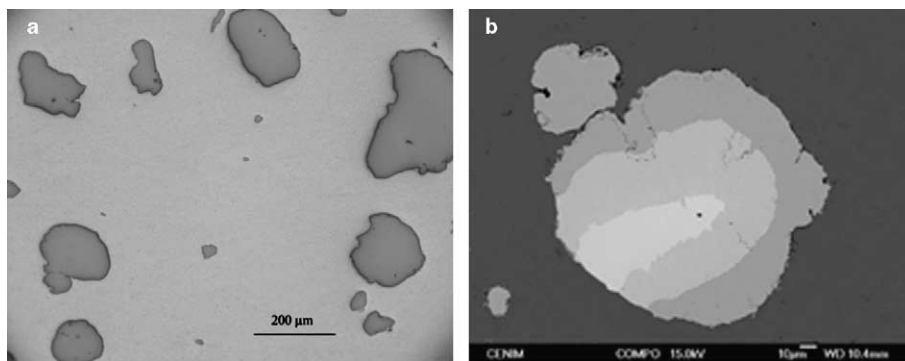


Fig. 4. Al/NiAl composite with NiAl particles oxidized at 750 °C for 3 h, after heat treatment at 500 °C for (a) 1 h and (b) 24 h.

of heat treatment of the composite at 500 °C produced an increasing degree of transformation and after 24 h most particles presented asymmetrical transformation, Fig. 4b, which would indicate that reactions started only at specific areas of the interfaces, where the oxide layer was thinner or damaged during processing. Once transformation started, local volume changes due to the different densities of the forming layers, contributed to the breaking of the oxide layer and help diffusion to proceed.

Heat treated samples prepared with NiAl oxidized at 1100 °C showed only a few transformed particles. In this case the oxide layer was very thick and cavities were formed beneath it, also preventing diffusion. When the

oxide layer broke, diffusion proceeded as in unoxidized particles.

Another feature that is worthy of remark is that oxygen content at particle/matrix interface clearly increased with oxidation temperature and time from around 6% in as-received NiAl particles, to 9% in particles oxidized at 750 °C for 1 h, 14% in particles oxidized at 750 °C for 3 h, and 46% in particles oxidized at 1100 °C, as was semi-quantitatively measured by EDS. This is a consequence of the larger oxide layer formed as oxidation temperature and time increased.

Tensile tests were performed to investigate the quality of the bonding between the Al matrix and NiAl particles as a function of the oxidation condition of the reinforce-



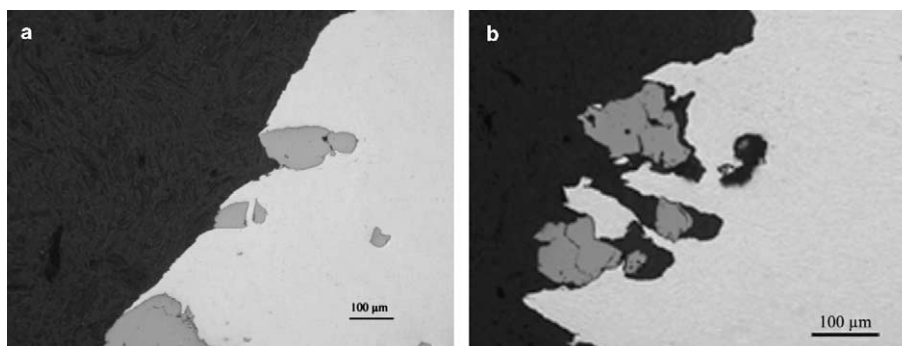


Fig. 5. Longitudinal section at the fracture surface of the composite with NiAl particles preoxidized at (a) 750 °C for 3 h and (b) 1100 °C for 1 h.

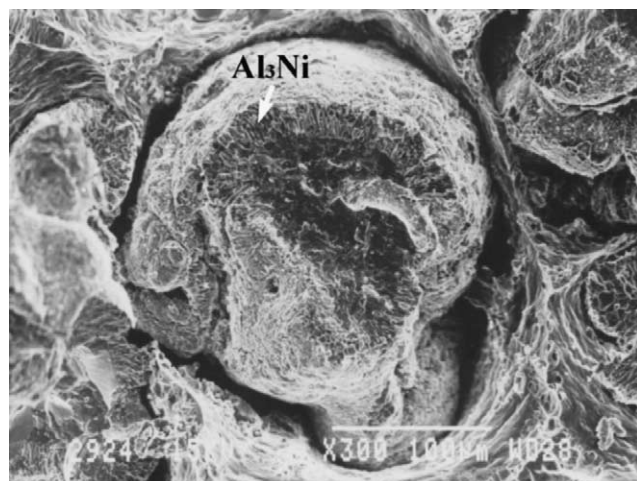


Fig. 6. Fracture surface of the Al/NiAl composite with NiAl particles preoxidized at 1100 °C for 1 h, heat treated at 500 °C for 24 h.

ment and the heat treatment of composite. Specimens with as-received NiAl particles and oxidized at 750 °C for 1 and 3 h showed evidence of strong adherence between matrix and particles even after 1 h of heat treatment at 500 °C, as can be seen in the longitudinal section at the fracture surface in Fig. 5a. When oxidation temperature was increased to 1100 °C, clear signs of particle detachment were observed even when no interphases were present, Fig. 5b, which indicates that debonding is mainly due to a weak cohesion between the thick oxide layer and the Al matrix. After 24 h of heat treatment at 500 °C, particles that suffered phase transformation appeared almost detached from the matrix due to the presence of a thick layer of  $\text{Al}_3\text{Ni}$  at the interfaces, Fig. 6.

#### 4. Conclusions

The influence of pre-oxidation of NiAl particles on the thermal stability of Al/5%NiAlp composite at 500 °C has been investigated. The reaction phases that appeared at 500 °C between Al and NiAl intermetallic

particles were  $\text{Al}_3\text{Ni}$  and  $\text{Al}_3\text{Ni}_2$ . NiAl powder exposed to oxidation treatments between 600 and 1100 °C produced alumina layers that delayed nucleation of interphases. Particles oxidized for 3 h at 750 °C presented the best combination of an effective diffusion barrier and sound bonding to the matrix. Lower oxidation times and temperatures reduced thermal stability whereas higher oxidation temperatures resulted in severe detachments of intermetallic particles from the surrounding Al matrix under tensile requirements.

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#### References

- [1] Clyne TW, Withers PT. An introduction to metal matrix composites. Cambridge: Cambridge University Press; 1993.
- [2] Omura H, Miyoshi T, Takahashi Y, Conley CG, Yodogawa M. In: Kim Y-M, Griffith WM, editors. Dispersion strengthened aluminium alloys. Warrendale, PA: The Minerals, Metals, and Materials Society; 1988. p. 421.
- [3] Varin RA, Metelnic M, Wronski Z. Metall Trans A 1989;20A:1153.
- [4] González-Carrasco JL, García-Cano F, Caruana G, Lieblisch M. Mater Sci Eng 1994;183A:L5.
- [5] Díaz C, González-Carrasco JL, Caruana G, Lieblisch M. Metall Mater Trans A 1996;27A:3259.
- [6] Lieblisch M, González-Carrasco JL, Caruana G. Intermetallics 1997;5:515.
- [7] da Costa CE, Velasco F, Varez A, Badía JM, Ruiz Prieto JM, Torralba JM. Actas del II Congreso Nacional de Materiales Compuestos, Madrid, 1997, 542.
- [8] Torres B, Wang Y, Lieblisch M, Ibáñez J, Rainforth WM, Jones H. Z Metallkd 2001;92:604.
- [9] Wang Y, Rainforth WM, Jones H, Lieblisch M. Wear 2001;251:1421.

- [10] Torres B, Lieblich M, Ibáñez J, García-Escorial A. *Scripta Mater* 2002;47:45.
- [11] Liu CT, Stiegler JO, (Sam) Froes FH. *ASM handbook*, vol. 2. 10th ed. Materials Park, OH: ASM International; 1990. p. 913.
- [12] Grabke HJ. *Intermetallics* 1997;7:1153.
- [13] Yang JC, Schumann E, Levin I, Ruhle M. *Acta Mater* 1998;46:2195.
- [14] Saltykov P, Fabrichnaya O, Golczewski J, Aldinger F. *J Alloys Compd* 2004;381:99.
- [15] Rivoaland L, Maurice V, Josso P, Bacos M-P, Marcus P. *Oxid Met* 2003;60:159.
- [16] Uran S, Grimsditch M, Veal BW, Paulikas AP. *Oxid Met* 2001;56:551.
- [17] Philibert J. *Atom movements diffusion, mass transport in solids* [Translated version]. Les Éditions de Physique, Les Ulis Cedex A, 1991, 293 [France].
- [18] Klinger L, Levin L. *Scripta Metall Mater* 1994;31:769–73.