Surface & Coatings Technology 242 (2014) 118–124

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

A hardness–microstructure correlation study of anodised powder-metallurgical Al–Cu alloy composites

Sissy Nehrkorn, Manja Händel, Dagmar Dietrich *, Harry Podlesak, Daniela Nickel, Bernhard Wielage, Thomas Lampke

Chemnitz University of Technology, Institute of Materials Science and Engineering, 09107 Chemnitz, Germany

ARTICLE INFO

Article history:
Received 27 November 2013
Accepted in revised form 18 January 2014
Available online 31 January 2014

Keywords:
Al–Cu composite
Al_2O_3 particles
SiC particles
Anodic oxidation
Microstructure
Indentation hardness

ABSTRACT

Powder-metallurgical Al–Cu alloy composites with Al_2O_3 and SiC particles have been anodised. The microstructure of the resulting oxide layers with respect to the composition of the matrix and the reinforcing particles has been correlated to nanoindentation results. The reinforcing particles are well-bonded in the conversion layer regardless of remaining stable (Al_2O_3) or being converted to mixed oxides ($SiC \rightarrow Al_xSi_yO_z$). The distinctive pore structure of the matrix conversion layer is known from anodising of bulk Al–Cu alloys and impedes the formation protective coatings on the studied composites. A shell of partly or completely converted aluminium on the Al–Cu composite shows options to improve the hardness of anodised aluminium oxide coatings on Al–Cu alloy composites.

1. Introduction

Strengthening of aluminium alloys by incorporation of inorganic hard particles increases the elastic modulus, the mechanical strength and the creep resistance of the aluminium matrix composites (AMC) at room and higher temperatures in comparison to unreinforced alloys [1,2]. In comparison to technologies comprising the molten state of the matrix as an intermediate, powder metallurgy has the advantage of uniform particle dispersion and control of chemical reactions between the metallic matrix and the reinforcing particles. Thus, during production the degradation of the reinforcing component and the formation of brittle interfaces between particle and matrix are avoided [2] without considering the final compacting and/or thermal treatment step. The reinforcing effect of non-metallic ceramic particles (e.g. Al_2O_3, SiC) in aluminium alloy matrices is influenced by the chemical composition, the size and the volume fraction of the incorporated particles, recently shown for AMCs composed of gas-atomised aluminium powder and non-metallic ceramic particles [3]. However, the higher susceptibility to corrosion in humid and anion-containing atmospheres of AMCs [4] is disadvantageous for any application and requires additional protection. Anodising is an effective and common method to protect aluminium from corrosion. The formation of anodised aluminium oxide (AAO) is influenced by the processing parameters, the composition and the microstructure of the matrix alloy, as well as by the reinforcing components [5]. In particular, anodising of bulk Al–Cu alloys is limited due to an inefficient film growth and an enhanced as well as modified porosity [6,7]. In contrast to the unidirectional (vertical, regular) pores in AAO layers on pure aluminium according to the classical model proposed by Edwards and Keller [8,9] and established by O'Sullivan and Wood [10], the pore structure of AAOs on Al–Cu alloys is characterised by non-unidirectional pores, described as a "reverted sponge structure" by Dasquet [11]. Following Thomson et al. [12], the development of porous AAO layers is related to the solid-state migration of Al^{3+} ions from the substrate and O^{2-} ions from the electrolyte, the field-assisted ejection of Al^{3+} ions to the electrolyte and the field assisted dissolution of the layer. Alloying elements change the ionic transport mechanism in the AAO and influence both the ejection of species to the electrolyte and the solubility of the film material; the porous film formation proceeds with an altered morphology. In particular, the presence of copper is associated with an enhanced film dissolution rate and varying rates of oxidation resulting in a rough alloy/film interface. The development of pores has to accommodate a wide range of pore orientations by branching, merging, and vanishing of pores according to the local conditions [12].

AAO layers formed on particle strengthened Al–Cu alloy composites like AMC(SiC_p) or AMC(Al_2O_{3p}) are suggested to be subjected to further modifications. To the knowledge of the authors, the behaviour of submicron-sized ceramic particles during the anodisation process and their effect on the microstructure of AAO layers as well as the mechanical behaviour have not been examined in detail, but are highly interesting. For instance, the size of SiC particles reinforcing an Al–Li alloy exerts

* Corresponding author. Tel.: +49 371 531 38128; fax: +49 371 531 35392.
E-mail addresses: sissy.nehrkorn@mb.tu-chemnitz.de (S. Nehrkorn), manja.haendel@mb.tu-chemnitz.de (M. Händel), dagmar.dietrich@mb.tu-chemnitz.de (D. Dietrich), harry.podlesak@mb.tu-chemnitz.de (H. Podlesak), daniela.nickel@mb.tu-chemnitz.de (D. Nickel), bernhard.wielage@mb.tu-chemnitz.de (B. Wielage), thomas.lampke@mb.tu-chemnitz.de (T. Lampke).

0257-8972/$ – see front matter
http://dx.doi.org/10.1016/j.surfcoat.2014.01.028

a strong influence on the formation rate of the anodised film and the uniformity of the film–substrate interface if the particle diameter is about some micrometers or more [13].

Nanoindentation tests provide the determination of local mechanical properties. They are suspected to give an insight into the different mechanical behaviour of the components of an AMC. Applied to a composite consisting of alumina particles with a size of some micrometers and a matrix containing magnesium and silicon as its major elements, the difference of the hardness of the incorporated particles and the matrix was clearly resolved [14,15]. Furthermore a reinforcement of the matrix by such large particles could be excluded, but some controversy arose regarding the enhanced hardness in the vicinity of the embedded particles [15]. Nevertheless, nanoindentation seems to be the method of choice for hardness evaluation of thin coatings or multilayer in comparison to their substrate. For example, the hardness of barrier-type AAO films with a thickness of about 0.5 μm could be determined provided that film thickness and applied experimental parameters, e.g. load, are appropriate [16]. The mechanical behaviour of porous AAO layers was mostly examined by Vickers microhardness measurements indicating a dependence on the occurrence of the alloying elements in the substrate [17]. The local mechanical behaviour of AAO layers formed on AMCs has not been examined by nanoindentation, so far.

The focus of this paper is to correlate indentation hardness profiles of AAO layers on Al–Cu alloy composites with their microstructure. The microstructure of such AAO films with submicrometer-sized SiC and Al_2O_3 particles has been studied by transmission electron microscopy (TEM). Nanoindentation testing has been applied for the observation of the local variation of mechanical properties of AAO films on AMCs. In addition, a specific sample configuration with the composite powder placed in an aluminium shell actually designed for the production of semi-finished AMCs was examined to show the feasibility of the formation of AAO coatings on Al–Cu alloy composites with enhanced wear-protective properties.

2. Materials and methods

A gas-atomised powder of an Al–Cu alloy similar to EN AW-2017 with a composition according to Table 1 was used as the basic material for the metal matrix. Silicon carbide (SiC, ESK-SIC GmbH) and aluminium oxide (Al_2O_3, Alfa Aesar GmbH & Co KG) were used as the reinforcement component. Particle sizes are given in Table 2 according to the producer's specifications. Aluminium alloy powder and particles were mixed in volume percentages of 85% alloy and 15% particles by high-energy ball-milling (HEM, Zoz GmbH Simoloyer). The composite powder was encapsulated in a commercially pure aluminium cylinder (cp Al, Al 99.5), hot degassed, hot-isostatically pressed (HIP) and extruded. Subsequently, a T4 heat treatment (solution annealing, natural aging) of the compacted composite was carried out. The process conditions, the microstructure formation of the powder in the HEM process, and the microstructure of the extruded material are described in detail in [3].

The powder was placed in a cp Al cylinder for tool protection from abrasive and adhesive load. The semi-finished bar after extrusion is shown schematically in Fig. 1a. Before anodising and depending on further applications, the remaining aluminium layer was removed completely or partially. By subsequent anodising, the remaining cp aluminium on the AMC provides the possibility to form an AAO layer by conversion of both cp Al and Al–Cu AMC (Fig. 1b).

The samples were etched in 3 wt.% sodium hydroxide (NaOH) for 60 s at 50 °C and de-smutted in 10 vol% nitric acid (HNO_3) for 20 s at room temperature. Subsequently, the samples were anodised at 5 °C in 10 vol% sulphuric acid (H_2SO_4) with a current density of 2 A/dm^2. The anodising process lasted some hours to produce a thickness of the AAO layer on the AMC in a range of 10 μm. Every process step was terminated by thorough water rinsing.

Table 1
Composition of the matrix powder in wt.% [3].

Al	Cu	Mg	Mn
Balance	3.9	0.7	0.6

Table 2
Particle size.

Particle	D10 NMT	D50 NMT	D90 NMT
SiC	0.4 μm	0.6–0.9 μm	2 μm
Al_2O_3	0.25 μm	0.37 μm	1.12 μm

Metallographic cross-sections were prepared for instrumented indentation tests, nanoindentation tests and scanning electron microscopy (SEM, Zeiss NEON 40). Electron transparent cross-sections were prepared by grinding and Ar ion polishing (GATAN PIPS) and studied by transmission electron microscopy (TEM, Hitachi H8100) at 200 kV. Energy-dispersive X-ray spectroscopy (EDS, Ametek EDAX Genesis) was used for local chemical analysis, which was carried out on cross-sections with a remaining thickness of about 100 nm. Due to contamination effects, carbon has not been considered for evaluation. The concentration specifications are normalised to 100% and rounded off. The detection limit is about 0.5 wt.%.

Evaluation of the Martens hardness was done according to DIN EN ISO 14577 by means of an HM2000 XYp FISCHERSCOPE using a Vickers indenter with a load of 50 mN. Nanoindentation was realised using a universal nanomechanical tester (UNAT, Asmec) with a Berkovich tip. The applied measuring routine was a fast hardness measurement according to DIN EN ISO 14577 (loading–creep–unloading time: 10 s–5 s–4 s or 10 s–30 s–4 s) with a maximum load of 50 mN. The indentation hardness was derived from the load–displacement curves by means of the method of Oliver and Pharr [18]. Using silica and sapphire for references, the indenter tip was calibrated with respect to projected area and stiffness. The choice of test points provided adequate distances for eliminating the influence of neighbouring measurement points or interfaces.

3. Results

3.1. Microstructure of AAO layers on Al–Cu composites with reinforcing Al_2O_3 and SiC particles

The appearance of AAO layers on the cp Al and the Al–Cu alloy is shown on cross-sections in schematic diagrams (Fig. 2a, b), in SEM studies (published in [19]) and in TEM bright-field images (Fig. 3a, b). The microstructure of the oxide layer on Al 99.5 is typical for pure aluminium and aluminium alloys of the 3000, 4000, 5000 and 6000 series, with efficient film growth according to Keller et al. [9], O'Sullivan and Wood

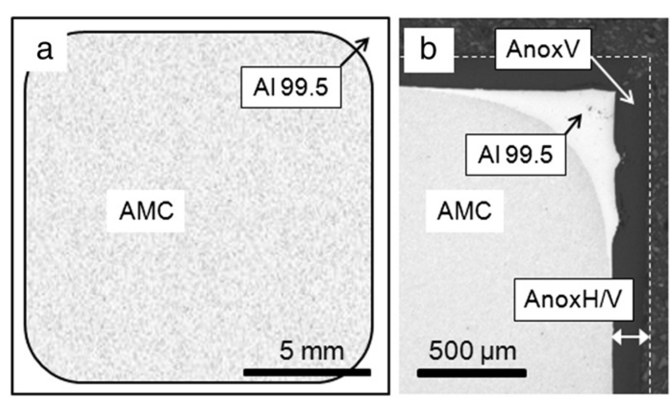

Fig. 1. Cross-section of the semi-finished AMC bar after extrusion; a) schematic diagram showing the remaining encapsulation and b) optical micrograph of the anodised composite showing the upper right corner.