Surface & Coatings Technology 315 (2017) 335–341

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Microstructural evolution of germanium modified AlSi-slurry coatings on alloy 600 at 620 °C in metal dusting environment

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ARTICLE INFO

Article history:
Received 4 November 2016
Revised 20 February 2017
Accepted in revised form 23 February 2017
Available online 24 February 2017

Keywords:
Germanium modified aluminide slurry coatings
Metal dusting
Diffusion barrier

ABSTRACT

Germanium-modified AlSi-slurry coatings were produced via airbrush spraying of two different suspensions on the conventional Ni-base alloy 600, followed by a heat-treatment in Ar at 800 °C. The resulting coatings exhibit a thickness of approximately 130 μm and mainly consist of outer Al-rich β-Ni(Al,Ge) phase followed by inner Ni-rich β-Ni(Al,Ge). In the interdiffusion zone, a continuous layer of $(Cr,Ni)_3Ge$ phase formed. Long term exposure tests in carbonaceous atmosphere at 620 °C showed excellent metal dusting protection. Furthermore, the exposure tests revealed that the $(Cr,Ni)_3Ge$ layer acts as a diffusion barrier, preventing the diffusion of the major coating element aluminum into the substrate. Depletion of aluminum would be detrimental for the lifetime of the coating and consequentially for that of the structural component. Microstructural evolution of the coating during exposure showed inward diffusion of nickel into the coating, resulting in fine Ge_3Ni_5 precipitates, whose formation will be discussed based on the ternary phase diagram of Al-Ge-Ni.

1. Introduction

Iron and nickel aluminides are well-known to be resistant to a wide range of aggressive environments such as oxidizing, carburizing and sulphidizing conditions. Therefore, Al-based intermetallic coatings are used to improve corrosion and oxidation resistance of both Fe and Ni based alloys for industrial applications [1,2]. Even in very low oxygen partial pressures such as in metal dusting promoting, carbonaceous atmospheres, aluminides form dense oxide scales and thus separate the base material from the corrosive environment [3].

With regard to metal dusting protection, a second approach without the use of an oxide barrier has been established. Some elements such as Sn [4] or Cu [5,6] are able to suppress carbon deposition out of the gas phase when being incorporated into a metal dusting susceptible surface. Another candidate that has the potential for catalytic inhibition of the initial step for metal dusting is germanium [7,8]. Besides its catalytic effect, alloying with Ge affects the metal dusting process by destabilizing Fe_3C [8]. Nevertheless, some of the alloys and coatings reported in the literature are prone to oxidizing environments e.g. during start-ups and shut-downs of industrial processes [9]. On this account, a combined coating concept has recently been developed which combines the inhibition approach with an aluminide phase [10]. During operation such coatings develop dense oxide scales. In the case of oxide scale damage, the underlying inhibiting phase suppresses the carbon uptake until re-passivation of the surface. One way to produce such type of coatings is the pack cementation process [11,12]. In the present paper, similar diffusion coatings are accomplished by the well-known slurry technique. To our best knowledge for the first time a germanium modified aluminide coating is reported.

The manufacturing of well-designed slurry aluminide coatings is challenging since there is a wide range of parameters to adjust. Besides the choice of the coating technique (e.g. painting, spraying) or temperature and time of the heat treatment, the components of the slurry have to be carefully chosen. While the use of pure aluminum particles in the suspension leads to high activity coatings, there is also the alternative to lower the aluminum activity by modification of the slurry composition [13]. Addition of elements such as chromium to the slurry is one possibility. Another way is the use of low melting intermetallic aluminides as aluminum source (e.g. eutectic Al-Si intermetallic). Especially when

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http://dx.doi.org/10.1016/j.surfcoat.2017.02.061
0257-8972/

Table 1
Chemical composition of the Ni-base alloy 600.

		Elements [wt.%]										
Alloy	*Alternative notation*	*Fe*	*Ni*	*Cr*	*C*	*Si*	*Al*	*Ti*	*Mn*	*Cu*	*S*	*P*
600	2.4816	6.0–10.0	Bal.	14.0–17.0	0.05–0.1	0.015	0.3	0.3	1.0	0.5	0.015	0.02

Al-Si is used, dissolved Si in the coating can have an additional beneficial effect on the oxidation and corrosion resistance by forming SiO_2 at the surface. The modification of the slurry with other elements has the potential to produce new coating compositions and microstructures [14–16]. Additionally, the corrosion resistance of Sn or Ge containing coatings can be increased for oxidizing environments by the presence of aluminum [10].

In this paper, alloy 600 is aluminized in a germanium modified slurry process. The use of intermetallic Al-Si powder in the slurry enabled the formation of β-phase in the coating. The influence of further modification with germanium on the coating composition and microstructure was investigated. During application of coated components at high temperatures, the aluminum reservoir of pure aluminide coatings depletes either by oxide formation at the surface, but often more severely by inward diffusion of aluminum into the substrate. Modification of the slurry with other elements can overcome this disadvantage by the formation of intermetallic diffusion barriers with insignificant aluminum solubility.

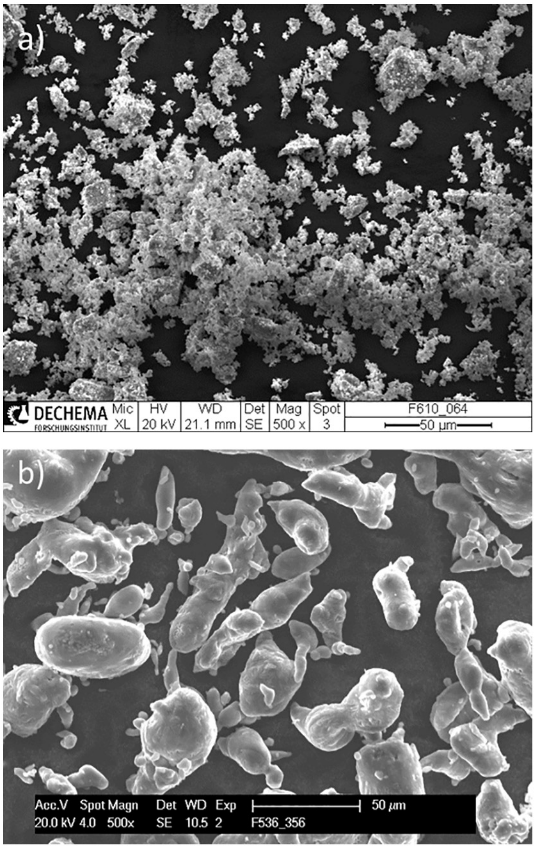

Fig. 1. Metallic powders used for slurry suspensions. Germanium particles (a) and Al-Si-particles (b).

2. Materials and methods

A conventional Ni-base alloy 600 was used as substrate. The chemical composition is given in Table 1. Coupon samples with the dimensions (15 × 10 × 3) mm^3 were cut from the alloy. Oxide layers and organic deposits were removed by etching the samples in nitric acid for 30 s.

Two types of suspensions were produced with a ratio of 1:1.3 of metal powder:binder. The binder consisted of one part of polyvinyl alcohol and ten parts of distilled water. Germanium (Haines & Maassen) was crushed and afterwards ball milled for two hours in order to receive fine powder flakes in the range of 10–20 μm. Al-Si particles (eutectic composition with approximately 12 wt.% Si, $T_m = 577$ °C) produced by Poudres Hermillon with a particle size of 20–50 μm were used for the second suspension. SEM images of the metal powders are shown in Fig. 1.

The coatings were produced by airbrush spraying of 3 layers Al-Si-suspension and 2 layers of Ge-suspension with a drying step between each deposition. The coated samples were heat-treated in argon at 800 °C for 5 h to obtain a diffusion layer and suppress oxidation.

Discontinuous isothermal metal dusting tests were carried out at 620 °C in a tube furnace (*Carbolite TZF 12/100/900*). The gas mixture consisted of 68% H_2, 22% CO and 10% steam corresponding to a carbon activity $a_C = 7.4$ calculated as described in [17]. The gas flow of hydrogen and carbon monoxide was regulated by mass flow controllers (*NATEC MC-100SCCM-D*) and mixed before moisturizing. The H_2O content was supplied by conveying the gas through a membrane tube (*Permapure MH 110-12F-4*) with a continuous flow of water equivalent to 10% relative humidity on the outside. The samples were exposed under carburizing conditions for 1000 h. Two steps were integrated in the exposure after 100 h and 500 h in order to evaluate the samples condition and determine mass changes.

The microstructure and the composition of the as-coated and exposed samples were characterized using metallographic and microanalytical methods, such as optical light microscopy (*LOM; Leica DLMA*) and electron probe microanalysis (*EPMA; Jeol JXA-8100*). The spatial resolution of the obtained elemental distribution maps and concentration profiles is 1 μm. XRD measurements of cross sections were conducted using a *Bruker D8 Advance* and CuK_α radiation. The adjustment of the spatial measuring point was supported by an x-ray-fluorescence sample and two laser-beams. The measuring time for each angle was set to 5 s in order to obtain high intensities.

3. Results and discussion

3.1. Coating microstructure

A cross section image of the coated sample and the corresponding elemental distribution maps are shown in Fig. 2. The coating has a thickness of approximately 130 μm and exhibits large porosity in a depth of 50 μm. The position of the large pores can be attributed to