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Innovative slurry coating concepts for aluminizing of an austenitic steel in chlorine and sulfur containing atmosphere

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ABSTRACT

Three new concepts for AlSi-slurry diffusion coatings manufactured in air and in aggressive, chlorine and sulfur containing atmosphere on alloy 800 H have been studied. These concepts were: an oxygen getter concept with fine Al-powder, a eutectic concept with Ge and a barrier concept with a glass-ceramic. Particularly the oxygen getter concept is based on the high reactivity of the fine Al-powder to form a dense and stable oxide layer. The eutectic concept is established via the facilitated diffusion of Al in the liquid phase. The barrier concept aims at the formation of a dense glass-ceramic layer. All three studied concepts were based on the idea of reducing the partial pressure of oxygen and other critical gases (Cl, S) within the Al-containing slurry near the substrate surface via a protective second layer. For the heat treatment several hold times were intentionally chosen to simulate the heating up process of waste to energy plants. Due to the slow heating up, an extended time is allowed for the oxidation or corrosion of the underlying substrate as well as the aluminum powder of the slurry before the diffusion occurs. The application of slurry manufacturing route in air with all three studied concepts leads to homogeneous diffusion coatings. The barrier concept provides the best results in aggressive atmosphere, whereas both other concepts lead to inhomogeneous coating structures. The presence of Ge changes the coating microstructure due to the fast diffusion of Ge into the base material. A model of the microstructural evolution of the coating in Cl- and S-containing atmosphere is proposed.

1. Introduction

In a large number of high temperature industrial processes, metallic components encounter aggressive gases and deposits. The most critical are atmospheres containing chlorine, sulfur, alkalis, and heavy metal compounds, all of which cause severe corrosion damage [1–4]. These atmospheres arise for example in waste-to-energy, biomass or cement plants. Aluminide diffusion coatings are well established to improve the corrosion resistance of base materials via the formation of Al_2O_3 [5–8]. In such diffusion coatings the substrate is enriched with aluminum close to the surface. An aluminum containing intermetallic is formed, which acts as a reservoir. A typical application of such coatings is the oxidation protection of gas turbine components.

There are several methods to manufacture aluminum diffusion coatings. By the classical CVD-process or the powder pack cementation process [for example [9,10]] aluminum is transported as a halide to the substrate surface, on which it decomposes producing aluminum, which reacts and diffuses into the metal substrate subsurface zone. The gaseous aluminum halide reacts with the solid substrate and Al diffuses via bulk diffusion into the metal subsurface zone. Another possibility to deposit aluminum even at temperatures below the melting point of aluminum is the MOCVD-process, in which organic phases are used for the aluminum transport [11]. The above stated methods have the transport via gaseous species in common. In contrast, manufacturing of aluminide coatings by a reaction between liquid aluminum and the solid substrate is also possible. In comparison to the chemical vapor deposition processes, such reactions occur in very short times. The reason for this is the so called “combustion synthesis”, which was described for nickel in detail [12,13]. Initially, aluminum melts and dissolves some substrate metal from the alloy. In the case of nickel base alloys an intermetallic $NiAl_3$ is formed as a result. Due to the exothermic reactions of dissolution and local $NiAl_3$ formation, the temperature increases. This triggers the further dissolution of nickel and thereby the further formation of more Ni-rich intermetallic phase, which becomes self-propagating (combustion synthesis). After these reactions, solid-state diffusion determines the rates of phase transformations and interdiffusion.

To yield this liquid–solid reaction, aluminum has to be delivered directly onto the substrate. Different techniques exist, for example non-aqueous electrochemical plating, wrapping with aluminum foil or slurry coating. Depending on the application for the latter several deposition methods can be used — dip coating, screen printing, air brush or simply painting are the most common ones.

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The generation of diffusion coatings by the slurry route is a well established low cost process technique, which uses Argon as an inert gas environment to protect the diffusion and the base metal from oxidation during the manufacturing process. Commercially available sealants were already used on top of a deposited slurry to manufacture coatings in steam environment on a ferritic steel. No previous diffusion heat treatment under argon or air was required [14]. Furthermore, the formation of slurry diffusion coatings, prepared without environmentally critical additions – such as chromates – and in air, has also been achieved at the laboratory scale [15–17]. The base materials of the coated samples in air had very high nickel contents (>60 wt.%) or were even nickel-plated to get continuous diffusion layers.

In this study, a possible solution has been investigated in order to manufacture aluminum diffusion coatings in air or aggressive environments using a two layer system (Fig. 1). On the substrate, a first layer consisting of a slurry containing the diffusion metal was applied. The second layer, also being a slurry, was placed on top of both, the first layer and the base material, for their protection from oxidation and corrosion. The idea behind all these concepts is to reduce the partial pressure of oxygen (and other corrosive elements) significantly at the substrate surface and within the aluminum slurry. The formation of a dense and stable oxide by the second layer before and during the diffusion heat treatment is required. Thereby the impact of the environment and its critical elements is limited. Three concepts are suggested for the protective layer 2, and described in the following:

1.1. Oxygen getter concept

For the oxygen getter concept a slurry with fine aluminum particles (in the particle size range of 2–5 μm) is used in order to provide a large surface area, which is highly reactive and thus oxidizes easily. A dense and stable Al_2O_3-layer can form on top and the diffusion of the critical elements below is limited.

1.2. Eutectic concept

In this case, a slurry with germanium powder particles is used as the second layer to form a eutectic with a low melting point of about 420 °C. The idea is to form a liquid phase on top, wherein Al can diffuse fast. Thus the aluminum in the eutectic composition can easily be transformed to aluminum oxide on top, which protects the underlying aluminum till the diffusion into the substrate has taken place. Furthermore, owing to the lower melting point of the eutectic system, the wetting of the surface is facilitated and hence the combustion synthesis can be initiated at lower temperatures. Zinc was deliberately not used for the eutectic concept, since it is well known to initiate liquid metal embrittlement at high temperatures (hot cracking) [for example [18]].

1.3. Barrier concept

The barrier concept is based on the slower diffusion of oxygen in oxides like SiO_2. With a dense glass/ceramic layer, only a small amount of oxygen can reach the aluminum, thus the diffusion of oxygen is limited until the diffusion of the underlying aluminum occurs. In order to achieve a dense and protective layer in the early stage at low temperatures, very fine SiO_2-particles with a high sintering activity are used.

The present paper describes slurry coating systems, which can be directly manufactured in air and even in aggressive atmosphere containing chlorine and sulfur on austenitic steel with only 33 wt.% nickel content. Therefore, the application of in-situ coatings for plant components using the inherent energy of the plant process may become possible as a low cost method to enhance the corrosion resistance in the future. Although the formation of diffusion coatings via the slurry route is fast, other aspects have to be considered, when it comes to direct application of slurry coatings in plants. For the alloys with high nickel-content, the coating process can be performed in air, however the amount of the oxidized aluminum plays an important role. For instance, if the particles are oxidized to a large extent, there will not be enough liquid aluminum for the formation of aluminides. Furthermore, a high aluminum oxide content hinders the combustion synthesis. In addition to the oxidation of aluminum particles, the oxidation of the base material has to be considered. Fast growing iron oxides as well as the formation of nickel and chromium oxides prevent the development of the diffusion coating. The heating up in process plants (first time or after an inspection) is done very slowly in order to minimize the induced stress in the plant components and to cure refractory linings. Various dwell times for several hours at relatively low temperatures (below 600 °C) are required, which means significant time for the oxidation of the base material and aluminum particles of the slurry. Even though the heating up of process plants is often performed with uncritical synthesis gas or similar fuels, chlorine and sulfur compounds can still be present

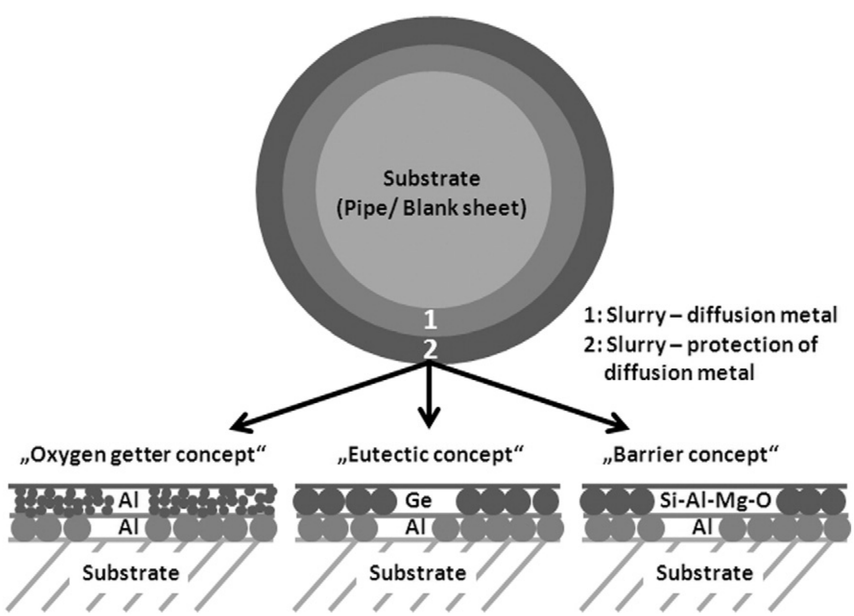

Fig. 1. Schematic two layer system for a slurry diffusion coating in aggressive environment with three different concepts.