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Surface oxidation of heating resistors made from Kanthal AF: Increasing the lifetime of glow plugs

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ABSTRACT

Glow plugs in the automotive industry are based on heating resistors made from FeCrAl alloys, often referred to as Kanthal. Metals and alloys exposed to high temperatures tend to react with the surrounding atmosphere, often resulting in high-temperature corrosion. Some high-temperature alloys use aluminium to form an Al_2O_3 protective layer in order to improve the oxidation resistance. In the temperature range above 1200 °C, SiO_2 and Al_2O_3 are the two oxides capable of forming an efficient, protective barrier against further oxidation. The alloy nominally requires more than 4 wt % Al to form a continuous protective layer. In this paper we have investigated the Al_2O_3 formation and growth on the surface of iron aluminides prepared using different heat-treatment parameters to achieve a continuous protective layer on the surface of the heating resistors. SEM/EDX mapping analyses were performed to confirm the elemental distribution on the cross-section of the resistors heat treated in air or pure oxygen, or in a humid H_2/Ar atmosphere, for different times and temperatures to achieve a continuous coverage of the oxide layer. The results of different heat treatments and their influences on the oxide growth are compared.

1. Introduction

By using stop-start technology the automotive industry is reducing fuel consumption and lowering CO_2 emissions. The implementation of this technology, however, requires heating elements with an extended lifetime for glow plugs and glow plugs with integrated pressure-sensor grooves.

The resistance-heating wire in a glow plug is made of an FeCrAl alloy. Such a composition in theory means a continuous protective layer of Al_2O_3 is formed. In the temperature range above 1200 °C, SiO_2 and Al_2O_3 are the two oxides capable of forming an efficient, protective barrier against further oxidation. The alloy nominally requires about 4 wt % Al to form a continuous protective layer. But there is a problem with porosity and the continuity of the protective oxide layer that is, at high temperatures, permeable for the oxygen diffusion into the interior of the wire, which means that the oxide degradation usually continues. Oxidation is the most important high-temperature corrosion reaction.

The main cause of failure for glow plugs, leading to a shorter lifetime, is the high-temperature degradation in the tip of the filament heater. Our aim is to improve the ignition resistance and the resistance to corrosion at high temperatures and thus to extend the lifetime of glow plugs. Material improvements and SEM/EDX characterizations were performed to understand the mechanism for a better corrosion resistance of the heating wire.

The aim of the research is to prevent the high-temperature degradation of the ferritic FeCrAl alloy. A protective oxide layer grows on the surface of the heating resistors and this growth depends on several parameters, such as the temperature and time of the exposure to heat, the atmosphere of the heat treatment (i.e., the partial pressure of oxygen), the content of Al in the matrix material, etc. For the heating resistors we used FeCrAl alloys, known as Kanthal AF.

The growth of Al_2O_3 on the surface of the heating resistors is based on the diffusion of the Al from the bulk material onto the surface. This diffusion is not constant during the oxidation process due to the oxide's growth on the surface. Thermodynamically, an oxide is likely to form on a metal surface when the oxygen potential in the environment is higher than the oxygen partial pressure in equilibrium with the oxide.

The theory of FeCrAl-alloy oxidation has been studied to better understand the protective role of the surface oxide. Oxidation of Fe-

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based aluminides at low and intermediate temperatures was studied by Brito et al. [2], where they claim that Fe (and/or Cr) reacts with the O before the Al to form a precursor oxide (α-Fe_2O_3 and/or α-Cr_2O_3) with the same crystal structure as α-Al_2O_3 [3,4]. The isostructural oxide, which may also be an Al-containing solid solution [5], acts as a template for the nucleation of stable α-Al_2O_3, accelerating the formation of the protective layer. When the metal is heated to 1200 °C or higher, the Cr_2O_3 scale, which exhibits high growth rates as well as forming volatile CrO_3, becomes largely non-protective. Under these very-high-temperature conditions, an Al_2O_3 scale provides excellent protection against oxidation. While Al_2O_3 grows extremely slowly at low and intermediate temperatures, and so should provide less protection at these temperatures, Cr_2O_3 is a protector and a substrate for Al_2O_3 growth at these temperatures [6]. Some studies were performed using XPS, TEM and XRD, and the procedure for forming α-Al_2O_3 on the FeCrAl ferritic steel has been explained [7].

The formation of the protective oxide layer has a lot of steps and parameters that influence the protective layer's formation. Although many researchers have reported on the effect of water vapour on the oxidation of FeCrAl alloys, their explanations of the oxidation mechanism remain a subject of controversy. Some researchers state that water vapour accelerates oxidation [8–10]; others claim that it has little or no effect on the reaction [11–13]. All the authors have confirmed the growth of the protective Al_2O_3 on the substrate of Cr_2O_3 and/or Fe_2O_3 [6,11–14]. Based on those previous studies, the oxidation of FeCrAl alloys at high temperature is expected to depend on the phase and microstructure of the Al_2O_3 scale formed on the surface. The corrosion protection is provided by a slowly growing α-Al_2O_3 (corundum) phase [15,16]. On the other hand, transient alumina such as Υ-Al_2O_3 (cubic), δ-Al_2O_3 (tetragonal) and θ-Al_2O_3 (monoclinic) results in rapid oxidation owing to the high defect concentration [5,6,8,17]. Scale spallation caused by mechanical stress is another reason for the lack of protection [18]. Onal et al. [11] investigated cyclic oxidation for a number of alumina formers in both dry air and air containing 30% H_2O at temperatures from 700 to 1000 °C. The authors proposed that water vapour reduced the adhesion of the aluminium oxide scale, thus causing oxide spallation [6]. The main influencing parameters on the protective oxide layer of the FeCrAl alloys are studied in this paper.

The phenomena associated with extending the lifetime of glow plugs have been researched. The protective oxide layer on the surface of the heating resistors is, however, not the only very important factor for the prolongation of the lifetime of glow plugs. Another essential point is the manipulation of the mounting of the treated resistors into the glow plug. This is due to extending the spiral of the resistors (spiral wire) when mounting into the casing. The oxide layer on the surface of the resistor is harder towards bulk resistor and therefore fragile. The extension should not be too high though the oxide layer can crake and thus the protection is aggravate.

2. Materials and methods

Kanthal AF alloy, which is a ferritic FeCrAl alloy, was used in this study. This alloy consists of the main alloying elements and small amounts of additional elements such as Si, Mn and C. The nominal chemical composition of the alloy is 22 wt % Cr, 5.3 wt % Al and Fe balance. The investigated material was wire, average 1.5-mm in diameter, which was twisted into a spiral and prepared as a "heating resistor – spiral wire", as used in glow plugs. The heating resistors were prepared in Hidria AET Company, Slovenia. The resistors were differently heat treated in lab retort furnace to achieve an oxide surface layer. Some were heat treated in atmospheric air, some in pure oxygen (Messer, O_2 purity 5.0) and some in a humid H_2/Ar atmosphere (controlled atmosphere Ar + 4% H_2 + $H_2O_{(g)}$, where the Ar and 4% H_2 gas were saturated with water vapour by flowing the gases through water at fixed temperatures, 0 °C/273 K in our cases). The flow of the gasses was approximately 200 ml/min. The heat treatments were performed at different temperatures and times, exposed to different concentrations of the oxygen and vapour to achieve the optimum coverage of the oxide layer on the surface. The temperatures, times and atmospheres of the treatments are presented in Table 1.

The as-treated heating resistors were prepared as standard cross-section metallographic specimens by grinding and polishing. The SEM analyses (SEM JEOL 6500F coupled with EDX Oxford INCA 450) were performed to see the morphology and the thickness of the oxide layer, and EDX mappings and line analyses were performed to see the elements' distributions after the diffusion. The EDX analyses were performed at a 15-keV acceleration voltage, where the approximate depth of the analysed material is 2 μm. The results of the high-temperature oxidation on the surface of the heating resistors were compared.

In addition, the heating resistors with the optimal protection layer were built into the glow plugs and the mechanical influences (because of the manipulation) of the building-in were observed in the cross-section metallographic sample. Additional investigations were performed to oxidise the interior of the potential cracks that appeared during the extending of the spiral before welding the tip of the filament heater. The glow plug was flushed with inert gas to decrease the oxygen in the filler. With an appropriate surrounding atmosphere the crack in the protective surface layer can be self-healed using a high-temperature self-healing mechanism [19–21].

3. Results and discussion

The first set of samples was heat treated in atmospheric air at 950 °C for 1 h and 7 h and the other set of samples in pure O_2 for 1 h and 7 h. All samples were put into the furnace at the temperature and left there for 1 or 7 h, then taken out from the furnace. The cross-sections of the samples revealed that there are not many differences in the thickness or in the morphology of the oxide layer grown in 1 h or in 7 h for samples heat treated in the air. The differences were observed for the samples oxidising in the pure O_2. The layer of oxide is thinner than the layer formed in the air (see Fig. 1).

In all the sets of samples, the oxide layer has approximately the same morphology, i.e., there is a spallation structure that is not homogeneous and it is full of cracks. The same morphology of the oxide layer was also formed on the surface of the samples heat treated in the air at higher temperature (Fig. 2). The differences were only observed in the thickness of the layer, but not in its morphology.

The EDX elemental distribution of the surface oxidation was performed to see the diffusion of the Al on the surface of the material (Fig. 3). The elements Cr and Fe stay homogeneously distributed in the ferritic steel, but Al diffuses on the surface, were the oxide is formed.

The differences between the Al_2O_3 layer on the surface of the heating resistors oxidized in air or in pure O_2 are not great. In both cases the layer is not continuous but has areas of spallation morphology, as seen in Fig. 2. There is also the fact that 1 h or 7 h of the material's exposure at high temperature in the same atmosphere has no great influence on the thickness of the layer. The differences in the Al_2O_3 layers were noticed only when the oxidation was performed at higher temperature. Nevertheless, the same atmosphere, air or pure O_2, have the same influence on the morphology of the layer. Higher temperatures of the surface's

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