OXIDATION OF A KANTHAL APM TUBE INITIATED BY NITROGEN DIFFUSION

R. Haubner, S. Strobl
University of Technology Vienna, Institute of Chemical Technologies and Analytics, Vienna, Austria

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Abstract
A Kanthal APM (Fe-22Cr-5.8Al) seamless tube was used in a laboratory setup for sintering PM steel parts under protective nitrogen or under nitrogen-hydrogen atmosphere. Within 12 months of use, oxidation was observed starting from the outside when the tube was held under discontinuous conditions (atmosphere, temperature, time, cooling- and heating rate).
Metallographic investigation shows several morphology gradients. The inner wall of the tube is attacked firstly by diffusion of nitrogen into the steel and aluminium nitride (AlN) is formed, which is observed on the polished cross-section of the sample. The progress of nitriding over time is documented; after formation of AlN, followed by chromium nitride (Cr3N), Braunite (a nitrogen pearlite) is finally formed at the inner side of the tube.
After nitrogen has diffused through the entire tube wall, the exterior of the tube oxidises. In general, the corrosion resistant and non-scaling alumina surface oxide (Al2O3) of Kanthal provides a good protection in most furnace environments, but in our case this protective layer is destroyed.

Keywords: high temperature corrosion, nitrogen diffusion, AlN, Braunite

Introduction

Fig.1 Corroded furnace tube (a) and details from the outside (b and d) and inner surface (c)
A Kanthal APM (Fe-22Cr-5.8Al) [1] seamless tube was used in a laboratory setup for sintering PM steel parts under protective nitrogen atmosphere. Within 12 months of non-continuous use oxidation started on the outer surface and also deformation was observed (Fig. 1). Initial results were published [2]. Kanthal APM is a powder metallurgical steel with high corrosion and temperature stability up to 1250°C. During use in N₂ and H₂+N₂ atmospheres the dew point should be considered and the working temperature should be reduced adequately.

Experimental
Metallographic preparation started with grinding using SiC paper (P 120, 320, 600 and 1200), followed by polishing with 6 µm diamond and 1 µm Al₂O₃ suspension. For etching the V2A reagent was used. The microstructures were examined by light optical microscopy (LOM).

Results and Discussion
Nitrogen diffusion starting from the tube inside and nitride formation
In the original state the furnace tube is covered by a protective dense alumina layer. During use the tube’s protective oxide layer can be destroyed by moving sintering boats. If, in the following, N₂ or N₂+H₂ atmosphere is used, the defects in the oxide layer can not regenerate and N₂ can diffuse into the steel.
Aluminum is the most reactive element in the steel matrix and therefore AlN is formed first. In Fig. 2a the reaction front of AlN formation is shown; the AlN particles can reach sizes up to 100 µm. Figure 2b shows an area near the inner tube surface with smaller AlN crystals. It is expected that this is a spot where nitrogen diffusion starts. The smaller AlN crystals can be explained by faster AlN nucleation caused by the higher N₂ diffusion rates near the tube surface. In Fig. 2c the same region is shown after etching and no other nitrides can be observed. In Fig. 2d the AlN crystals near the outer surface can be seen. They show similar grain size and distribution as those seen in Fig. 2a. These results show clearly that there was continuous N₂ diffusion, which causes homogeneous AlN nucleation and growth over the wall.

Fig.2 Reaction front of AlN formation caused by nitrogen diffusion. (a) overview, (b) source of small AlN crystals at the inner surface, (c) V2A etched, (d) AlN at the outside (V2A etched)
In Fig. 3 a gradient of the various nitrides is shown. AlN is formed first and therefore is present over the whole cross section. At the inner side of the tube globular Fe₃N is observed (Fig. 3b). In regions with less amount of Fe₃N the “Braunite”, a nitrogen pearlite, was observed (Fig. 3c). Further outside a region with Cr₃N precipitation at the grain boundaries (Fig. 3d) is present. At the outside AlN and oxides can be found (Fig. 3e).

Fig. 3 Reaction front of the various nitrides (V2A etched): (a) overview, (b) inside the tube with globular Fe₃N, (c) “Braunite”, (d) Cr₃N at the grain boundaries, (e) oxidation starting at the outside of the tube

Oxide layer formation at the outside of the tube

In Fig. 4 selected places of the tube’s outside are shown. An area where oxidation starts is shown in Fig. 4a and b. Small oxide particles are formed and also AlN is transformed into Al₂O₃. When nitrogen diffusion reaches the outside and Al and Cr are precipitated as nitrides the oxidation of the iron matrix starts. As can be seen in Fig. 4c and d the oxide layer is deep-spread into the steel. At the oxide/metal interface there is a small band in the metallic phase containing less nitrogen. In Fig. 4e and f a thicker oxide layer is shown. It can be seen that the oxide shows a layered structure with changing morphology.

Fig. 4 Oxidation at the outside: (a, b) initial oxide formation, (c, d) first formation of an oxide layer, (e, f) layered structure of the thicker oxide layer
Summary
A Kanthal APM (Fe-22Cr-5.8Al) seamless tube was used in a laboratory setup for sintering PM steel parts under protective nitrogen or under nitrogen-hydrogen atmosphere. Within 12 months of use, oxidation was observed starting from the outside when the tube was held under discontinuous conditions (atmosphere, temperature, time, cooling- and heating rate).
It could be shown by metallographic investigation that nitrogen diffusion starts from inside of the tube and various nitrides are formed. In Fig. 5 the evolution is schematically summarized.
When the nitrogen diffusion reaches the tube’s outside and Al as well as Cr have been converted to nitrides the original corrosion resistance of Kanthal APM gets lost and oxidation from the outside can start.
The inside walls of Kanthal APM should be re-oxidised at certain intervals to ensure the formation of the protective Al₂O₃ and so the probability for corrosive damaging processes and deformation is reduced. Such protective oxide layers will reduce the nitrogen diffusion into the steel. In case of using N₂ or N₂+H₂ it is recommended to decrease the working temperature below 1200°C or 1100°C respectively [1].

![Fig. 5 Stages of nitride formation starting from the inside and oxide formation starting from the outside of the tube](image)

References