

## MICROSTRUCTURAL CHARACTERIZATION OF OXIDE SCALES FORMED ON $\gamma$ - $\gamma'$ Co-Al-W-BASED SUPERALLOYS

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### Abstract

Cobalt superalloys based on the Co-Al-W system are a new group of heat-resistant materials, which have attracted the interest of researchers in 21<sup>st</sup> century. The advantage of the new materials over conventional cobalt alloys is the strengthening mechanism based on a microstructure of the  $\gamma$ - $\gamma'$  type. This study concerned microstructural study of the oxidation products formed on the Co-9Al-9W (at.%) alloy during isothermal oxidation at different temperatures. Therefore, the alloy was prepared via vacuum induction melting (VIM) and casting to a graphite mold. The alloy was subjected to a two-step heat treatment. In the first step, the alloy was annealed at 1250 °C for 16 h in a tubular furnace and are then water quenched. Afterwards, the ingot was annealed at 900 °C for 100 h.

The oxidation tests were carried out on cylindrical samples, which were ground, polished and degreased. The oxidation oxide scale formation of the alloy was examined under isothermal conditions in the range 500-1000 °C. The morphology of oxides was examined by scanning electron microscopy (SEM), and their composition was analyzed energy dispersive spectroscopy (EDS). The structures of scales formed at different temperatures were compared.

Oxidation at 500 °C results in growth of monolayer scale of Co-oxides, whereas at higher temperatures, multilayer scales are formed. The scales usually consists of outer scale of cobalt oxides, inner oxide layers composed of a mixture of CoO and Co-spinels, and internal oxidation zone.

**Keywords:**  $\gamma$ - $\gamma'$  cobalt-based superalloys, Co-Al-W superalloy, high temperature oxidation, SEM

### 1. INTRODUCTION

The  $\gamma$ - $\gamma'$  Co-based superalloys have begun to be extensively studied due to their promising properties and capability for creating beneficial microstructure. The interest of researchers from around the world is mainly due to high operating temperature and mechanical properties at elevated temperature, which are much higher compared to conventional cobalt superalloys reinforced with carbides [1]. Works related to the development of this group of materials are mainly focused on increasing the operating temperature and mechanical properties [2,3]. Oxidation resistance is one of the most important factors limiting the overall durability of high-temperature components. The oxidation resistance of the alloys is much lower compared to that of nickel-based superalloys [4]. The protective properties against oxidation at high temperatures depend on the scale structure.

The oxide scales formed on Co-Al-W alloys at 800 and 900 °C were described by several authors [5,6]. At these temperatures, the alloys based on Co-Al-W system do not form continuous protective alumina scales. The Al<sub>2</sub>O<sub>3</sub> oxide may be found in the internal oxidation zone in form of oxide islands within  $\gamma$ -Co (at 900 °C) or quasi-continuous alumina layer between the Al-depleted surface and the inner oxide zone (at 800 °C). The outer oxide zone is composed of CoO at 900 °C or a mixture of CoO and Co<sub>3</sub>O<sub>4</sub> at lower temperatures. The inner oxide zone is composed of CoO and Co-Al and Co-W spinel oxides. Such structures of the oxide scales do not provide oxidation protection and are prone of thermal shock [4].

The aim of the study is characterization of the oxidation products formed on Co-9Al-9W (at%) alloy at wider temperature range (500-1000 °C). The study provides the missing data concerning high temperature degradation of Co-Al-W alloys during isothermal oxidation.

## 1. MATERIALS AND METHODS

### 1.1. Material

The alloy with composition Co-9Al-9W (at%) was investigated in the study. The alloy was fabricated via Vacuum Induction Melting (VIM). The pure metals Al, Co, W was melted at 1600-1700 °C under vacuum (~0.13 Pa) and casted under Ar protection to a cold graphite mold. The obtained cylindrical ingots were measured as  $\varnothing 18 \times 150$  mm. The ingots were annealed at 1250 °C for 16 h in a tubular furnace and were then water quenched. The second step of the heat treatment process included annealing at 900 °C for 100 h. The ingots were turned using a lathe up to 15 mm in diameter.

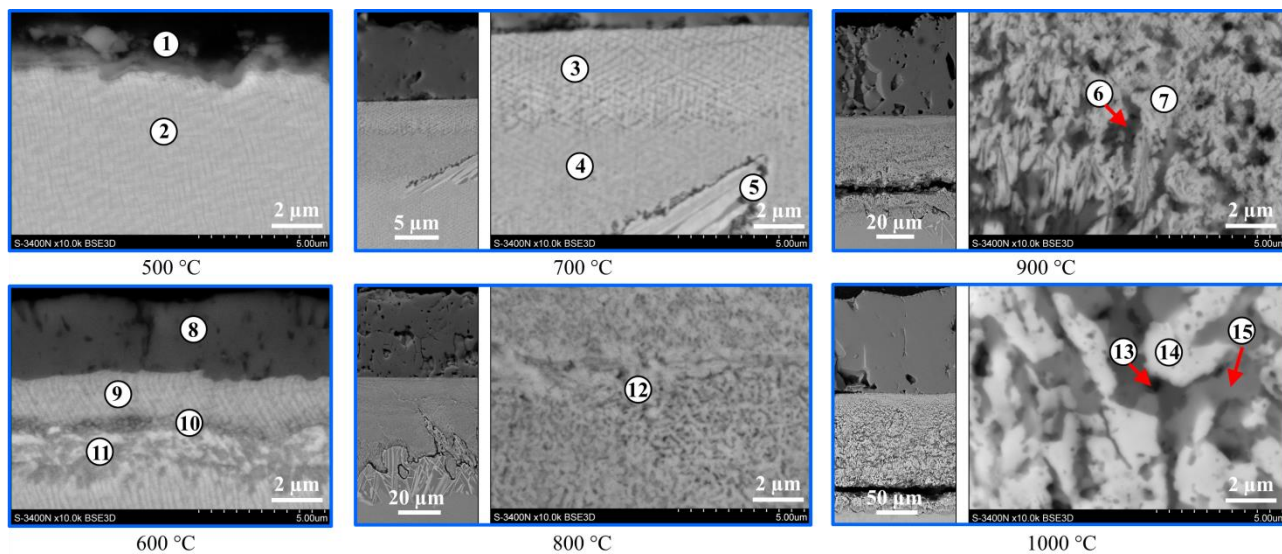
### 1.2. Characterization methods

The cylindrical samples with a dimension of  $\varnothing 15 \times 2$  mm were electro-discharge machined from the annealed rods. The acquired samples were isothermally oxidized at 500-1000 °C for 100 h in a chamber furnace. After each oxidation test, the cross-section samples were prepared. The oxide scales were characterized using scanning electron microscope (SEM, Hitachi S-3400 N) equipped with an energy dispersion spectrometer (EDS, Thermo Noran System Seven).

## 2. RESULTS AND DISCUSSION

The SEM micrographs revealing microstructure of the oxidized scales are shown in **Figure 1**. The results of the scale thickness measurements are presented in **Table 1**. The results of EDS analysis in micro areas are shown in **Table 2**. The layer of oxidation products which grown on the substrate was thin and monolayer. The ca. 2  $\mu\text{m}$  thick layer was mostly composed of Co, which implies presence of Co oxides on the surface. Below the oxide layer, the  $\gamma$ - $\gamma'$  microstructure may be seen (p. 2). The average thickness of the oxidized layer grown at 600 °C was over 7  $\mu\text{m}$ . The outer layer (p. 8) was composed of only Co and O, similarly to oxide scale at 500 °C. Such external layer may be formed as a result of outward diffusion of Co cations [7]. Below, an inner oxide layer (p. 9) O, Co, Al, and W may be observed. Between this layer and a substrate, an intermediate zone (p. 11) can be found. This area also contains O, however, the concentration of Al and W is substantially lower compared to that of inner oxide zone. Therefore, an internal oxidation zone may occur.

The external layer of Co-oxides may be found also in the case of oxide scale formed at 700, 800, 900, and 1000 °C. Below the external layer of alloy oxidized at 700 °C, an inner oxide zone (p. 3) is observable. This zone contains oxidation products, mainly oxides rich in Al and W (contents over 20 at%). The morphology of oxides in the inner oxide zone is similar to that of  $\gamma$ - $\gamma'$ . Underneath, an oxide zone may be found. The concentration of Al and W was below 20 at%. Within this layer, some multiphase zones (p. 5), rich in Al, were found. Oxides of such morphology are characteristic for internal oxidation zone [4]. The inner oxide zones of the alloy oxidized at 800, 900, and 1000 °C are also rich in O, Co, Al, and W. However, their morphology is not similar to that of  $\gamma$ - $\gamma'$ . The appearance of the inner oxidze zone suggest presence of an oxide mixture. Within the inner oxide zone which grown at 800 °C, a mixture of very fine oxides can be observed. However, at higher temperatures, a coalescence of the oxide phases may be seen. Within the inner oxide zone formed at 1000 °C, the characteristic zones corresponding to different oxides may be easily distinguished. The bright ones (p. 14) are rich in W and are corresponding to Co-W spinels (e.g.  $\text{CoWO}_4$ ). The gray areas (p. 15) are composed mostly of Co, which implies presence of CoO. The dark zones (p. 13) are rich in Al and are corresponding to Co-Al spinels ( $\text{Co}_2\text{AlO}_4$  or  $\text{CoAl}_2\text{O}_4$ ).



**Figure 1** SEM micrographs of oxide scales formed on Co-9Al-9W alloy after 100 h oxidation at 500-1000 °C

**Table 1** Thickness of oxide scales on Co-9Al-9W alloy oxidized for 100 h at 500-1000 °C

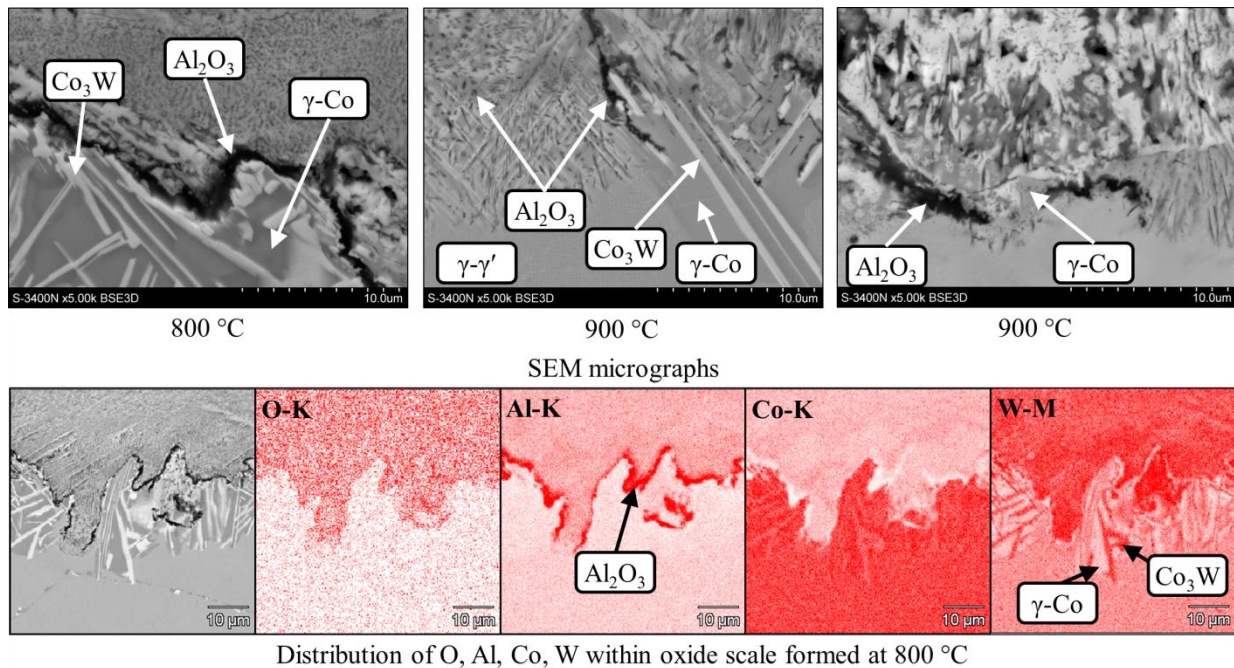
Scale thickness	Oxidation temperature					
	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C
Mean thickness (μm)	1.91	7.34	16.41	78.71	127.64	281.73
Standard deviation (μm)	0.25	0.21	0.61	5.06	5.55	7.08
variation coefficient (%)	13.06	2.79	3.70	6.43	4.35	2.51

**Table 2** Chemical composition in micro areas (EDS) marked in **Figure 1**

Point	Oxidation temperature (°C)			
	O-K	Al-K	Co-K	W-M
1	+	2	96.7	1.3
2	-	9.2	81.7	9.1
3	+	24.9	50.8	24.3
4	+	17.6	65.3	17.1
5	+	38.7	50.4	10.9
6	+	13.5	66.6	19.9
7	+	13.5	66.6	19.9
8	+	-	100	-
9	+	23.8	53.1	23.1
10	+	24.4	52.5	23.1
11	+	14.1	72.1	13.8
12	+	15.8	62.3	21.9
13	+	35	63.3	1.7
14	+	-	51.9	48.1
15	+	7.8	91.8	0.4

The presence of such phases in the inner oxide zone is consisted with thermodynamics and literature data [8]. Although the thickness of the oxide scales is relatively low up to 700 °C, the oxidized layer on the alloys after annealing at 800-1000 °C are very thick.

**Figure 2** shows internal oxidation zones formed at 800, 900, and 1000 °C. Between a substrate and an inner oxide zone of the alloy oxidized at 800 °C, an layer of Al<sub>2</sub>O<sub>3</sub> can be observed. Such oxide zone act as a diffusion barrier, which improves oxidation resistance. However, the layer is not continuous, therefore, does not provide the sufficient protection [5]. Below the Al<sub>2</sub>O<sub>3</sub>, double-phase microstructure composed of gray and bright areas may be seen (γ/Co<sub>3</sub>W). The gray areas are corresponding to γ-Co<sub>ss</sub>, whereas the bright ones are connected with Co<sub>3</sub>W phase. Such phases are known to occur in Co-Al-W alloys due to Al-depletion [4, 5]. In the oxide scale which grown at 900 °C. Al<sub>2</sub>O<sub>3</sub> may be observed as well, but does not form any layer. Al oxides can be found as fine spots within γ-Co, or as elongated oxides. At 900 °C, Al-depletion and formation of γ/Co<sub>3</sub>W areas may be observed. The morphology of Al<sub>2</sub>O<sub>3</sub> at 1000 °C is similar to that of 900 °C. However, no Co<sub>3</sub>W phases were observed in this case. The morphology of internal oxidation zone formed at 700 °C was similar to that of 800 °C, however, γ/Co<sub>3</sub>W areas surrounded by Al<sub>2</sub>O<sub>3</sub> occurred only locally.



**Figure 2** SEM micrographs of internal oxidation zones formed at 800, 900, 1000 °C; distribution of O, Al, Co, and W in the oxide scale formed at 800 °C

The oxidation products formed on Co-9Al-9W alloy at different temperatures were characterized. At temperatures above 500 °C, multiphase oxide scales are formed. Taking into consideration the present oxides and literature data, during the oxidation of Co-Al-W alloys, the following reactions may take place:



### 3. CONCLUSION

Co-9Al-9W alloy does not form protective oxide scales at temperatures over 500 °C. The multilayer oxide scales are formed on Co-Al-W alloys after oxidation at 600 °C and higher temperatures. The composition on inner oxide layer in the range 600-1000 °C is similar, whereas the oxides morphology is different. Oxidation at lower temperatures results in finer oxides in a mixture. The formation of internal oxidation zone rich in Al oxides and Co<sub>3</sub>W phase was noticed at 700, 800, and 900 °C. Formation of inner alumina layer was detected only at 800 °C.

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