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Influence of the Water Vapor Presence on the High Temperature Oxidation Behavior of two Chromium-Rich Cobalt-Based Alloys

Patrice Berthod, Lionel Aranda, Thierry Schweitzer

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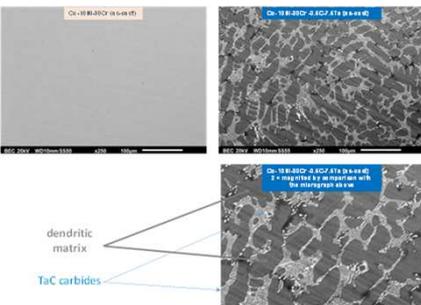
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Besides nitrogen and oxygen, water vapor is often present in the hot air in which refractory alloys are working, and its presence influences the behavior of superalloys in high temperature oxidation [1]. Notably, it is widely recognized that water vapor plays an important role, but not necessarily detrimental for the metallic component. The presence of water vapor in air tends enhancing the volatilization of Cr₂O₃ covering the chromia-forming alloys, but it is also true that a slow-down in oxidation speed is sometimes induced by water vapor as well as an improvement of the scale adherence when temperature varies.

For many studies dealing with the effect of water vapor on the high temperature oxidation, this is the nickel-based alloys family which is considered, notably aluminum-rich Ni alloys solidified in order to be single-crystalline finally. However one of the latest works concerning Ni-based alloys but polycrystalline and equi-axed, concerned an alloy which contained no aluminum but only chromium for its oxidation and corrosion resistance at high temperature [3]. In contrast, although they also represent an important family of high temperature alloys [2], the cobalt-based alloys were less studied in this field. Since such alloys are also used in the hottest parts of aero-engines and in the hottest pieces involved of various industrial processes (such glass working), with in both cases the possible presence of water vapor, it appears interesting to better know the effect of water vapor on the behavior in oxidation at high temperature for this second important family of alloys. Recently a few studies were devoted to the effect of water vapor on the high temperature oxidation resistance of chromium-rich cobalt-based superalloys, models or commercial [4, 5].

In this work, two model Co-10Ni-30Cr and Co-10Ni-30Cr-0.5C-7.5Ta alloys were considered (all contents in wt.%). They were elaborated by melting pure elements with a high frequency induction furnace under pure argon. The thermogravimetry tests were carried out at 1000, 1100 and 1200°C in a synthetic air humidified with a specific device.



SEM/BSE micrographs illustrating the alloys' as-cast microstructures

Microstructures of the alloys, the apparatus used for the high temperature oxidation tests in dry and wet air



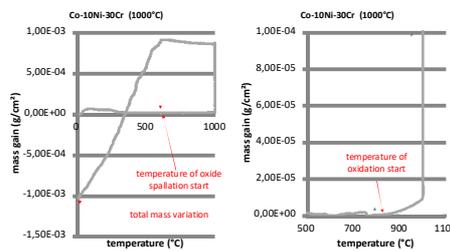
Photograph of the apparatus used for the thermogravimetry tests, without or with water vapor in air

Oxidation during the +20K/min heating and oxide scale behavior during the -5K/min cooling

Co-10Ni-30Cr (T alloy)	1200°C - dry	1200°C - wet
Temp. of oxidation start	825 °C	851 °C
Total mass gain at heating	151 µg cm ⁻²	113 µg cm ⁻²
Temp. of spallation start	890 °C	954 °C
Mass loss by spallation	-13 µg cm ⁻²	-11 µg cm ⁻²

Co-10Ni-30Cr (T alloy)	1100°C - dry	1100°C - wet
Temp. of oxidation start	851 °C	1091 °C
Total mass gain at heating	45 µg cm ⁻²	9 µg cm ⁻²
Temp. of spallation start	721 °C	719 °C
Mass loss by spallation	-6 µg cm ⁻²	-5 µg cm ⁻²

Co-10Ni-30Cr (T alloy)	1000°C - dry	1000°C - wet
Temp. of oxidation start	844 °C	851 °C
Total mass gain at heating	9 µg cm ⁻²	13 µg cm ⁻²
Temp. of spallation start	636 °C	629 °C
Mass loss by spallation	-2 µg cm ⁻²	-3 µg cm ⁻²



Example of plot of the mass gain versus temperature (here: T alloy oxidized at 1000°C in dry air)

T + 0.5C-7.5Ta (Q alloy)	1200°C - dry	1200°C - wet
Temp. of oxidation start	903 °C	817 °C
Total mass gain at heating	292 µg cm ⁻²	281 µg cm ⁻²
Temp. of spallation start	885 °C	371 °C
Mass loss by spallation	-9 µg cm ⁻²	-1 µg cm ⁻²

T + 0.5C-7.5Ta (Q alloy)	1100°C - dry	1100°C - wet
Temp. of oxidation start	859 °C	681 °C
Total mass gain at heating	80 µg cm ⁻²	78 µg cm ⁻²
Temp. of spallation start	791 °C	no
Mass loss by spallation	-5 µg cm ⁻²	spallation

T + 0.5C-7.5Ta (Q alloy)	1000°C - dry	1000°C - wet
Temp. of oxidation start	816 °C	697 °C
Total mass gain at heating	28 µg cm ⁻²	57 µg cm ⁻²
Temp. of spallation start	584 °C	no
Mass loss by spallation	1 µg cm ⁻²	spallation

"T alloy"

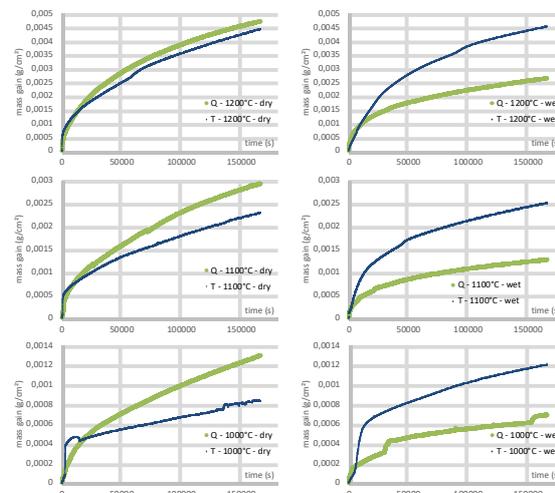
(Co-10Ni-30Cr)

Co-10Ni-30Cr (T alloy)	1200°C - dry	1200°C - wet
classical k _p	61.5 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	65.5 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	76.9 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	100.0 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	45.9 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	129.0 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

Co-10Ni-30Cr (T alloy)	1100°C - dry	1100°C - wet
classical k _p	15.8 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	17.1 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	15.8 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	63.7 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	3.44 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	169.0 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

Co-10Ni-30Cr (T alloy)	1000°C - dry	1000°C - wet
classical k _p	1.71 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	1.71 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	1.40 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	8.97 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	-2.10 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	52.0 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

Isothermal oxidation kinetics: obtained values for the different constants



"Q alloy"

(Co-10Ni-30Cr-0.5C-7.5Ta)

T + 0.5C-7.5Ta (Q alloy)	1200°C - dry	1200°C - wet
classical k _p	73.5 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	21.5 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	132.0 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	50.6 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	156.0 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	124.0 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

T + 0.5C-7.5Ta (Q alloy)	1100°C - dry	1100°C - wet
classical k _p	27.5 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	4.90 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	41.3 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	11.0 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	59.7 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	59.6 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

T + 0.5C-7.5Ta (Q alloy)	1000°C - dry	1000°C - wet
classical k _p	5.15 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	1.36 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _p corr. from volatilization	4.24 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹	1.04 × 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹
k _v	-0.60 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹	1.63 × 10 ⁻¹⁰ g cm ⁻³ s ⁻¹

In this work the different results obtained concerning isothermal oxidation but also oxidation during the heating phase and the oxide spallation phenomena showed that water vapor imposed modification to the general behavior of these two cobalt-based alloys. This allows announcing that consequences of steam presence in the oxidizing air may be expected for cobalt alloys as more extensively studied for other refractory alloys based on nickel or iron. But this influence also depends on the chemical composition and/or the microstructure of the cobalt alloys, as evidenced with the presence or not of tantalum carbides in a same base. Further work remains now to be done in order to explain the effect of water vapor on the ternary alloy (base of many cobalt-based superalloys) and to understand the role of the TaC carbides. The oxidized will be characterized using different means: X-ray diffraction and topological observation in Scanning Electron Microscopy before cutting, SEM observation in cross-section, concentration profiles by Castaing microprobe.

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