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Influence of water vapour in air and of TaC carbides in alloy on the high temperature oxidation of cobalt-based refractory alloys. Part 2: Kinetic results in oxidation in wet air and comparison with dry air

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It is widely recognized that water vapour plays an important role, but not necessarily unfavourable for the sustainability of the metallic component. If it is true that the presence of water vapour in air tends to provoke the volatilization of SiO₂ and Al₂O₃ protecting the silica or alumina-forming alloys, and to accelerate of Cr₂O₃ covering for the chromia-forming ones, some advantages were also noticed: sometimes a slow-down in speed for the oxidation rate and frequently an improvement of the scale adherence when temperature varies.

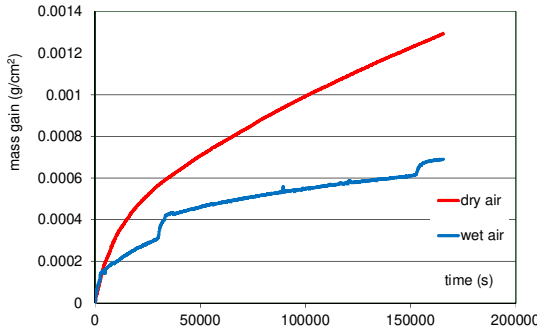
In the case of the Cr₂O₃-forming superalloys many studies dealing with the effect of water vapour on the high temperature oxidation concern nickel-based alloys. In contrast, the cobalt-based alloys, although they constitute also an important family of cast and wrought chromia-forming high temperature alloys, were curiously less studied in this field. Since such alloys are also used in the hottest parts of aeroengines and in the hottest pieces involved in various industrial processes (such glass working), with in both cases the possible presence of water vapour even in little concentration, it appears interesting to better know the effect of water vapour on the behaviour in oxidation at high temperature for this family of alloys.

In this work, a model Co-10Ni-30Cr-0.5C-7.5Ta was considered (all contents in wt.%). This rather simple alloy, which is however close to commercial Co-based superalloys as MarM-509 and others, was subjected, in a thermo-balance, to oxidation at high temperature in synthetic air humidified with a special apparatus. The mass gain files were analysed according to the $(m \times dm/dt = K_p - K_v \times m)$ method [1] to determine the oxidation rate and the chromia-volatilization one, simultaneously. The heating part and the cooling parts of the mass gain files were also exploited to specify the oxidation start temperature and the parameters characterizing the resistance of the scale to spallation. The results were compared to the ones presented last year [2] and to others presented this year [3], to evidence the effects of the presence of water vapour and of the presence of tantalum carbides. The results of the metallographic characterization of the oxidized samples will be presented next year [4].

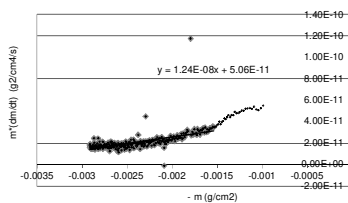
The Co-10Ni-30Cr-0.5C-7.5Ta alloy (wt.%) was elaborated by high frequency induction melting from pure elements, in inert gas. Parallelepiped samples were prepared and subjected to thermogravimetry runs carried out in humidified air (temperatures of test: synthetic air 80%N₂ – 20%O₂ with addition of 180mbars H₂O (air with 90% of relative humidity at 60°C), temperatures: 1000 and 1200°C, duration: 46 hours.

Isothermal mass gain kinetic

Oxidation of the Co-10Ni-30Cr-0.5C-7.5Ta alloy at 1000°C

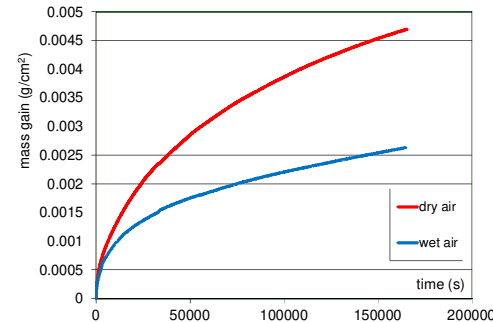


Example of $(m \times dm/dt = K_p - K_v \times m)$ treatment for specifying the parabolic and chromia volatilization constants (case of Co-10Ni-30Cr-0.5C-7.5Ta at 1200°C in wet air)



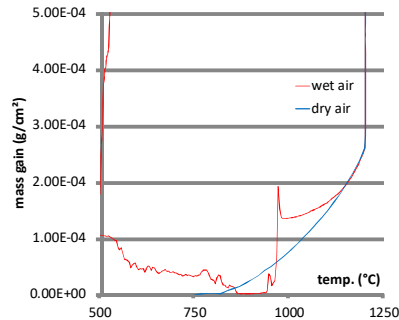
	$10^{-12} \times K_p$ (g ² /cm ² s ⁻¹)		$10^{-10} \times K_v$ (g/cm ² s ⁻¹)	
	1000°C	1200°C	1000°C	1200°C
dry	5.15	132	/	156
wet	1.04	50.6	1.63	124

Oxidation of the Co-10Ni-30Cr-0.5C-7.5Ta alloy at 1200°C

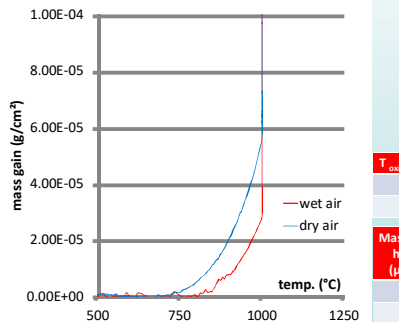


Oxidation at heating

Co-10Ni-30Cr-0.5C-7.5Ta oxidized at 1200°C

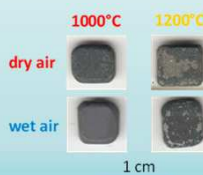


Co-10Ni-30Cr-0.5C-7.5Ta oxidized at 1000°C



	T _{oxid start} (°C)	
	1000°C	1200°C
dry	816	not available
wet	697	817

	Mass gain at heating (µg/cm²)	
	1000°C	1200°C
dry	28.4	not available
wet	56.5	281



	T _{spall start} (°C)	
	1000°C	1200°C
dry	604	884
wet	497	475

	Final mass variation (mg/cm²)	
	1000°C	1200°C
dry	+0.50	not available
wet	+0.67	+1.39

The isothermal mass gains by oxidation kinetic of the studied TaC-containing cobalt-based alloy globally follows a parabolic law. In contrast with the ternary Co-10Ni-30Cr alloy [3], the water vapour significantly decreases the oxidation (much lower K_p) while the volatilization of chromia (into CrO₂(OH)₂) seems to be curiously a little lower.

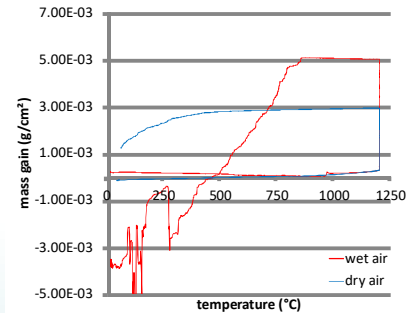
Because a not successful test at 1000°C in dry air it is not possible to specify the role of water vapour for the oxidation during the +20°C/min-heating up to the stage temperature. A new test is required.

Contrarily to the ternary Co-10Ni-30Cr alloy [3], and consistent with what is generally expected when there is significant concentration in water vapour in the oxidizing atmosphere, the adherence of the oxide scale on the substrate and then the spallation behaviour at cooling are improved by the present content in water vapour by comparison with what occurs in dry air.

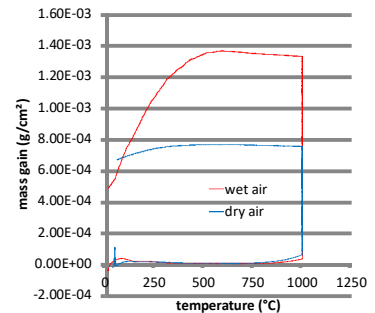
Obviously, the presence of tantalum (in solid solution in the matrix) and/or of the TaC carbides influences the oxidation behaviour in the good direction: lower mass gains resistance against spallation... The formation of tantalum-chromium oxides, as films immersed in the external oxide scale and as islands at the alloy/scale, is possibly at the origin of a slowing down of ionic diffusion through the scales, of partial protection against chromia volatilization and of a better adherence of these ones on the substrates. This may inhibit the aggressivity of humidified air and allowing taking benefit the better plasticity given by vapour to the scale. The post-mortem metallographic investigations will help to clarify the reasons of the observed differences.

Scale behaviour at cooling

Co-10Ni-30Cr-0.5C-7.5Ta oxidized at 1200°C



Co-10Ni-30Cr-0.5C-7.5Ta oxidized at 1000°C



[1] Berthod, P., "Kinetics of high temperature oxidation and chromia volatilization for a binary Ni-Cr alloy", Oxidation of Metals, Vol. 64, No. 3-4 (2005), pp. 235-252.
 [2] Aranda, L., Schweitzer, T., Berthod, P., Navet A., Leroy, A., "Influence of water vapour in air and of TaC carbides in alloy on the high temperature oxidation of cobalt-based refractory alloys. Part 1: Results in oxidation in dry air", Eurocorr 2014, Pisa.
 [3] Schweitzer, T., Aranda, L., Villeger P., Berthod, P., Conrath, E., "Effect of the presence of water vapour on the high temperature oxidation of a Co-10Ni-30Cr alloy. Part 2: Kinetic results in oxidation in wet air and comparison with dry air", Eurocorr 2015, Graz.
 [4] Next communication at Eurocorr 2016, Montpellier.