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Influence of Water Vapour on the Rate of Oxidation of a Ni-25wt.%Cr Alloy at High Temperature

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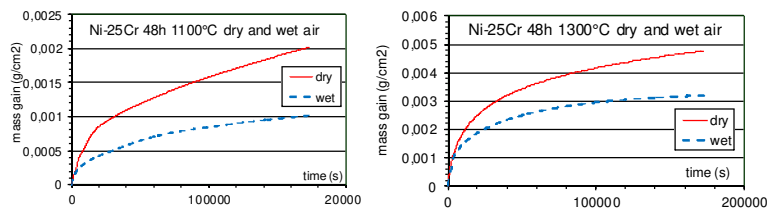
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In many industrial applications water is present in the hot oxidant gases to which the metallic components can be exposed in service. The presence of vapor may influence the progress of high temperature oxidation by modifying the structural characteristics of the growing external oxide scales and the kinetics of mass gain as well as of mass loss. The chromia-forming refractory alloys or superalloys are especially concerned since, in vapor-containing hot gases, the volatilization of their protective oxide scale is enhanced by the formation of oxy-hydroxides according to the equation $\frac{1}{2} Cr_2O_3(s) + H_2O(g) + \frac{1}{2} O_2(g) = CrO_2(OH)_2(g)$, with as result a minimization of the mass gain rate when the oxidation progress is followed by thermogravimetry. When the temperature is very high the volatilization of the platinum wire to which the sample is hung may also contribute to this linear mass loss by volatilization, while, on the contrary, a linear mass gain may occur in case of redeposition of a part of the previous volatilized species on the suspension in colder places of the thermobalance. It is thus important, in the mass variations recorded by the thermobalance, to separate on the one hand the parabolic contribution of the oxidation of the alloy, and on the other hand all of the linear mass losses (volatilization) or linear mass gains (recondensation), in order to better characterize the resistance of the alloy to high temperature oxidation. This uncoupling can be done for example by exploiting the mass gain curves according to a method previously adapted to the assessment of both the parabolic and volatilization constants from the mass gain curves recorded during oxidation in dry air.

The aim of the present study is to test Ni25Cr-type samples cut in the same ingot obtained by equiaxed solidification, in dry air and in a humidified air with the same thermo-balance and with the same parameters (heating and cooling rates, temperature and duration of the isothermal stage), in order to clearly reveal the differences of mass variation kinetic and of characteristics of the oxides formed (composition, external morphology, ...), induced by the presence of water vapor.

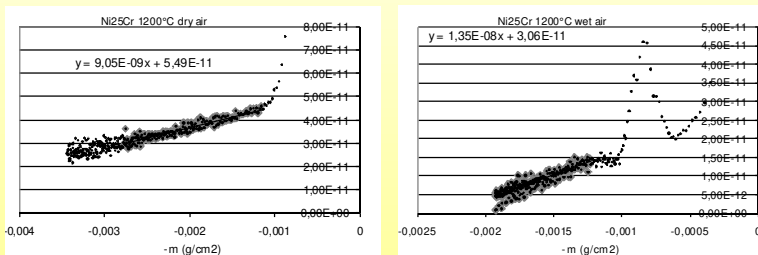
Kinetic study of the H.T. oxidation progress of a cast Ni-25Cr alloy in dry and wet air



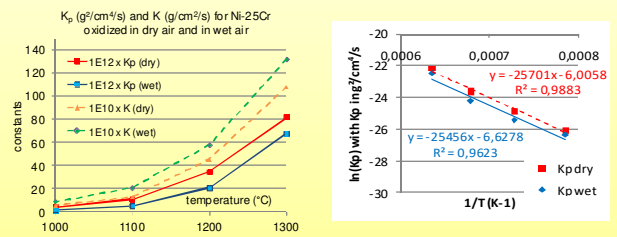
Thermogravimetry curves obtained at 1100°C (left) and at 1300°C (right) for the Ni-25Cr alloy in dry air and in wet air, showing the dependence of mass gain on the presence or not of water

Values of the parabolic constant K_p and of the constant K including all the linear mass gain variations (chromia volatilization, Pt volatilization, re-deposition), issued from the $m \times dm/dt = f(-m)$ plots

Constants	K_p ($\times 10^{-13} g^2 cm^{-4} s^{-1}$)		K ($=K_p + K_{vol} + K_{red}$) ($\times 10^{-10} g cm^{-2} s^{-1}$)	
	dry	wet	dry	wet
1300°C	236	170	418	460
1200°C	54.9	30.6	90.5	135
1100°C	16.0	9.09	33.9	67.7
1000°C	4.82	3.51	23.5	33.5

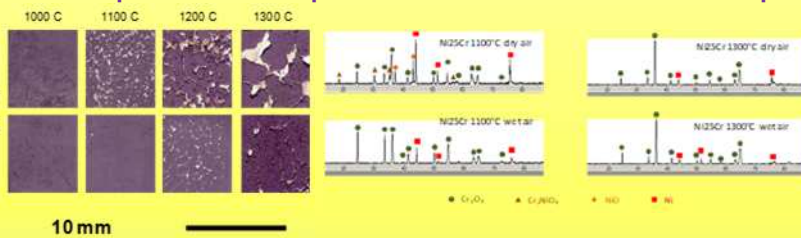


Treatment of the mass gain results according to the $(m \times dm/dt = K_p - K \times m)$ method



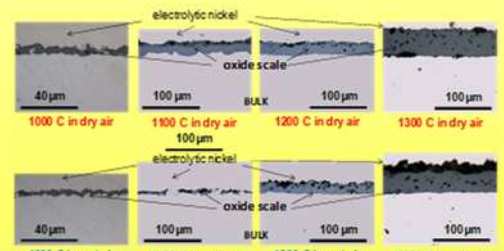
Arrhenius plot of the K_p values obtained at the four temperatures in the two atmospheres

Macroscopic and microscopic characterization of the oxidized samples

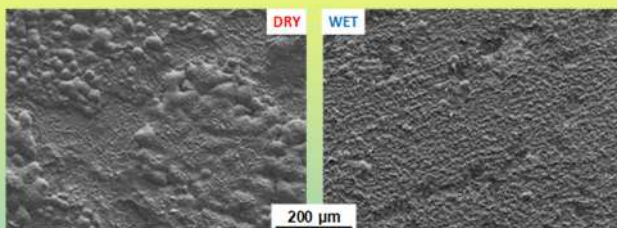


Surface states after the oxidation tests, revealing denuded alloy caused by oxide spallation

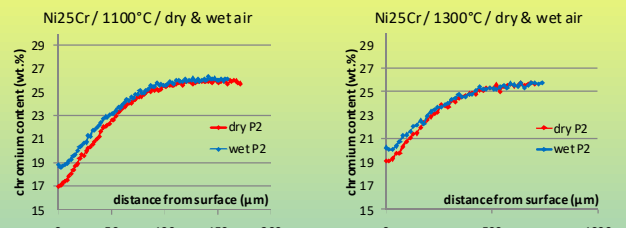
Examples of the diffraction spectra obtained on the surfaces of the external oxides



Oxide scales formed after 48 hours at the four temperatures in the two atmospheres



SEM micrographs of the external oxide scales after 48 hours of oxidation at 1100°C of the Ni-25Cr alloy in dry air (left) and in wet air (right)



WDS chromium profiles across the sub-surfaces of the Ni-25Cr samples after 48 hours of oxidation at 1100°C (left) and at 1300°C (right)

The presence of water vapor in hot air, which is generally known to have a great importance on the high temperature oxidation behavior of the alloys, generally in the bad way, obviously had rather a good influence in the present case, for the studied cast Ni-25Cr alloy and for the water concentration. Indeed the oxidation rate was slowed (but the chromia-volatilization rate probably accelerated), as shown by the thermogravimetry records, oxides thicknesses and quantifications of alloy's chromium consumption. Furthermore the oxides were of pure chromia, displayed a greater fineness, and a significantly better adherence on the substrate (at least better resistance against spallation which can be also due to a better plasticity of the oxide as often reported), an important point for alloys which are exposed to thermal cycling. After these observations one can imagine that it can be interesting to artificially enrich hot air with a precise quantity of water to improve both the isothermal oxidation resistance of such alloy and its resistance against cycling oxidation. However these observations need to be confirmed by additional investigations, including for example in situ XRD measurements during certain periods of oxidation or technical improvements of the thermogravimetric device for avoiding the lack of precision due to the re-deposition of volatile species.