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Thermogravimetric study of the effect of the vapour concentration in wet air on the oxidation start at heating and on the oxide spallation at cooling of a nickel-chromium alloy exposed at high temperature

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ABSTRACT

The high temperature oxidation behaviour of alloys in air may be influenced by the presence of water vapour. In this work this is more precisely the effect of the water concentration which was investigated. Four thermogravimetry runs were performed for a nickel-chromium alloy, at temperature ranging from 1000 to 1300°C, in air especially enriched in water vapour by comparison with previous studies. The heating parts and the cooling parts of the mass gain curves were characterized with comparison with previous results obtained in dry air and in moderately humidified air. The supplementary addition of water vapour to air already wet led to another reduction in oxidation rate during heating and in total mass gain achieved before the isothermal stage. This new vapour concentration also improves the adherence of the oxide scale during cooling by comparison with dry air, but not so efficiently as the more moderate water concentration earlier tested. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Nickel alloy;
Chromium;
Water vapour;
High temperature;
Oxidation start at heating;
Spallation at cooling.

INTRODUCTION

Water vapour is often present in the hot atmospheres in which many refractory alloys and superalloys are working as pieces thermally and mechanically solicited, such as turbine blades. In such cases the protective oxides formed on surface from elements as chromium, aluminium or silicon[1] may be faster damaged by comparison to dry air, with notably the acceleration of the volatilization of chromia or silica into oxy-hydroxides species, and the appearance of a volatilization phenomenon for alumina. Thus, the presence of water is known to induce additional mechanisms of hot corrosion[2]. The effect of gaseous water mixed with air or with other gases has been the subject of many studies, as - among the most recent ones – works carried out for pure metals[3,4], intermetallics[5,6], alloys based on heavy metals[7], ceramics[8], metallic coatings[9], ... Most of these recent studies and also of the older ones concern the effect of water vapour on the oxidation rate in isothermal conditions (including the volatilization into oxy-hydroxides) or on the oxide natures or morphologies.

The influence of the vapour content in the oxidizing air on the transient oxidation and the adherence behaviour of the oxides isothermally formed on surface were seemingly less studied. This was what encouraged the recent works previously carried out[10,11]. In addition, since a same superalloy can be used at high temperature in contact with air containing few vapour or with air much richer in vapour – this depending on the context (aeronautic turbines, gas turbines, ...) – it appeared important to test a same material in another atmosphere of the same type but with a higher water concentration.

EXPERIMENTAL

Preparation of the alloy samples and thermogravimetry tests

One can remind that the alloy used for the study was elaborated by foundry, by melting together parts of pure nickel and parts of pure chromium (Alfa Aesar, > 99.9 wt.%), using a high frequency induction furnace under inert atmosphere. The ingots (weighing about 40g) were cut in order to obtain parallelepipedic thermogravimetry samples of about $10 \times 10 \times 3$ mm^3, which were polished up to the 1200-grade SiC paper.

The thermogravimetry tests were carried out using the same apparatus as previously[10,11]: a SETARAM Setsys thermobalance coupled with a SETARAM Wetsys device to generate humidified air at relative humidity of RH=90% at 60°C ("very wet air", instead the settings previously used: 80% at 40°C[10,11], "wet air") with a gas flow of 20mL min^{-1}. The oxidation tests were performed at 1000, 1100, 1200 and 1300°C for 48 hours. In all cases the applied heating rate was 20°C min^{-1} and the cooling rate was 5°C min^{-1}.

Exploitation of the heating parts of the mass gain curves

During the heating the air present in the hot part of the thermobalance becomes less and less dense. This results in a decrease of the Archimede's thrust, and then in an artificial mass gain despite the real mass of the sample does not change (at least during the low temperature part of the heating when oxidation is still inexistent or very slow). A correction, earlier described[12], was applied to the mass gain files to take into account the air buoyancy variation. After this preliminary treatment, the {medium to high temperature} part of the heating curve becomes linear and horizontal, allowing reading both the temperature of real start of oxidation (beginning of the mass gain rise) and the real total mass gain existing at the end of heating. Since there were four oxidation tests (because four stage temperatures) one can determine four times the value of the temperature of oxidation start. This allowed to assess the reproducibility or dispersion of the oxidation start temperature, and then a more realist comparison between the present atmosphere and the two other atmospheres tried in the previous studies carried out on the same binary alloy[10]. Concerning the mass gain resulting from the oxidation progress during the heating, four values can be obtained for the [R.T.; 1000°C] range (the test at 1000°C but also the tests at 1100, 1200 and 1300°C for which the sample temperature also reached 1000°C before continuing to increase). Three values are similarly available for 1100°C, two values for 1200°C, but only a single value for 1300°C.

Exploitation of the cooling parts of the mass gain curves

At the end of the isothermal stage, the oxide scale which formed over the sample is subjected to increasing compression stresses, due to the difference of thermal contraction amplitude existing between the metallic substrate and the oxide scale. These stresses promote the local detachment of the oxide which may result in its partial loss by spallation, phenomenon leading to irregularities in the cooling parts of the thermogravimetry curves. Examining these parts of the mass gain curves allows determining if there was spallation or not during cooling, and therefore to characterize the adherence of the oxide formed. This good or bad adherence can be thereafter confirmed by the surface examination of the oxidized sample after its return to room temperature.

RESULTS AND DISCUSSION

Oxidation during the heating

The end of the heating parts of the thermogravimetric curves are presented in Figure 1(a), with an enlarged view in (b). The start of oxidation seems having occurred to temperatures which are seemingly close together. The four temperatures of detectable mass gain

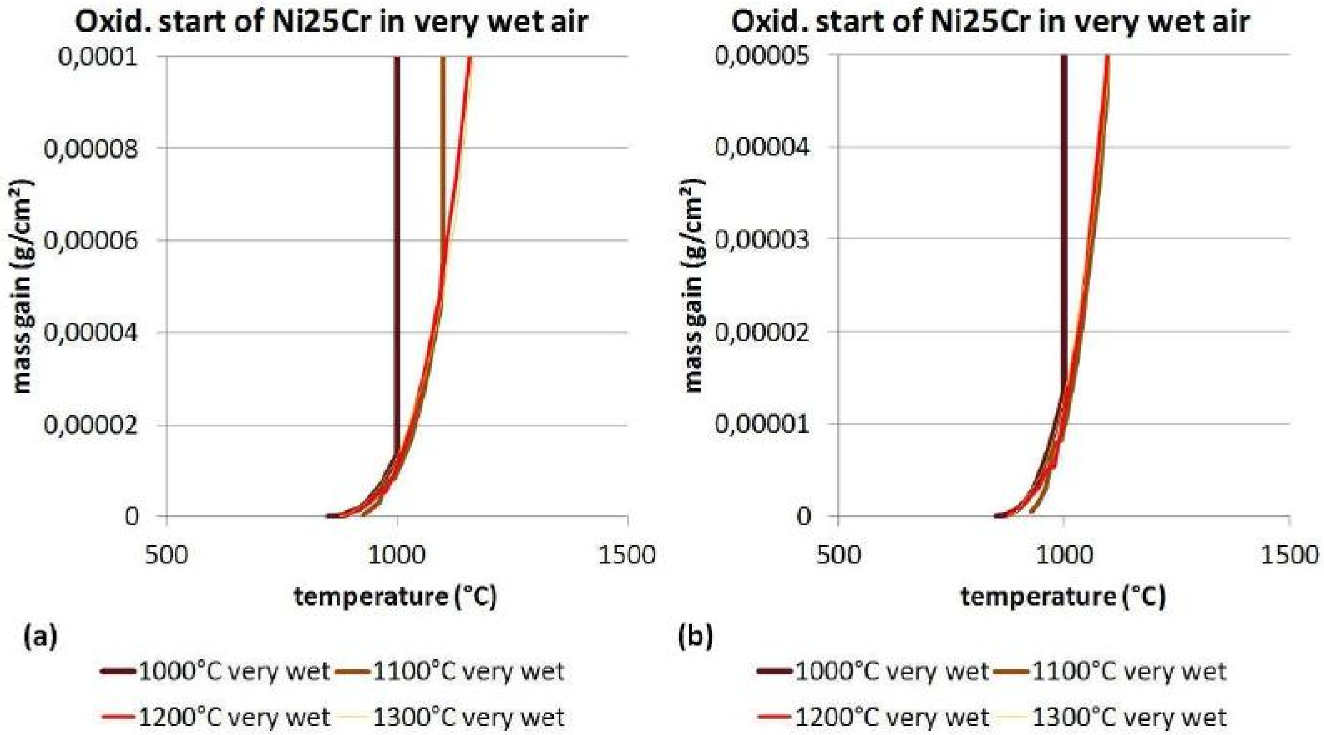

Figure 1 : End of the heating parts of the mass gain curves corrected from air buoyancy for the determination of the temperatures of oxidation start (less (a) or more (b) enlarged view)

due to oxidation are given in TABLE 1 ("very wet air"), in which the values earlier obtained for dry air and "wet air" (RH 80% at 40°C) are also reminded to facilitate the comparisons. It appears that the average temperature of oxidation start tends to be slightly higher than previously determined in "wet air", which was itself slightly higher than in dry air. The reproducibility is ten times worse than for "wet air" but three times better than for dry air.

The mass gains achieved at the end of heating for the four temperatures are graphically presented in Figure 2 (average value ± standard deviation). In the same graph the corresponding results previously obtained in wet air are added for comparison. The mass gain logically increases with the [Tstart of oxidation; stage temperature] range. Furthermore one can see that these mass gains obtained during heating tend to be all a little

TABLE 1 : Temperatures of detectable mass gain during heating versus the air humidity

Temperature of oxidation start (°C)	Air humidity		
Stage temperature	**Dry[10]**	**Wet[10]**	**Very wet**
1300°C	915	863	851
1200°C	932	863	928
1100°C	732	863	878
1000°C	858	868	878
Average ± Std dev.	859 ± 91	864 ± 3	884 ± 32

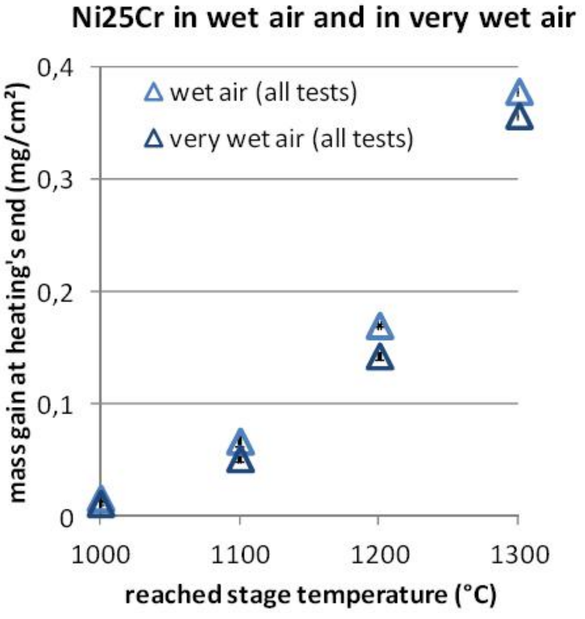

Figure 2 : Total mass gains obtained during heating in the very wet air (average ± standard deviation calculated on 4 values for 1000°C, 3 values for 1100°C and 2 values for 1200°C); comparison with the results earlier obtained in wet air (RH80% at 40°C)[10]

lower than earlier in “wet air”, which were themselves a little lower than in dry air [10].

For the high temperature parts of the four heating curves the instantaneous mass gain rate K_l was determined and plotted versus temperature according to the Arrhenius representation. The four ln (K_l)=f (1/T) curves which were obtained, displayed in Figure 3, tend to be all almost linear, although two out of them (T_{stage} = 1200 and 1300°C) seem perhaps to be composed of two successive linear parts but with slopes which are close to one another. The slopes of these linear curves were multiplied by R = -8.314 J/Mol to express the corresponding activation energies, the values of which are given in TABLE 2, in comparison with the ones earlier obtained for the two other atmospheres (dry or “wet”). The separation of the curves in two parts found here for the two highest stage temperatures is similar to what was previously observed in dry air and in wet air, with in addition a transition at a similar temperature level. However the values of activation energy are generally different, even if the ones determined in “very wet air” are often similar to the ones determined in “wet” air.

Oxide adherence or spallation during the cooling

The cooling parts of the curves (Figure 4) remain

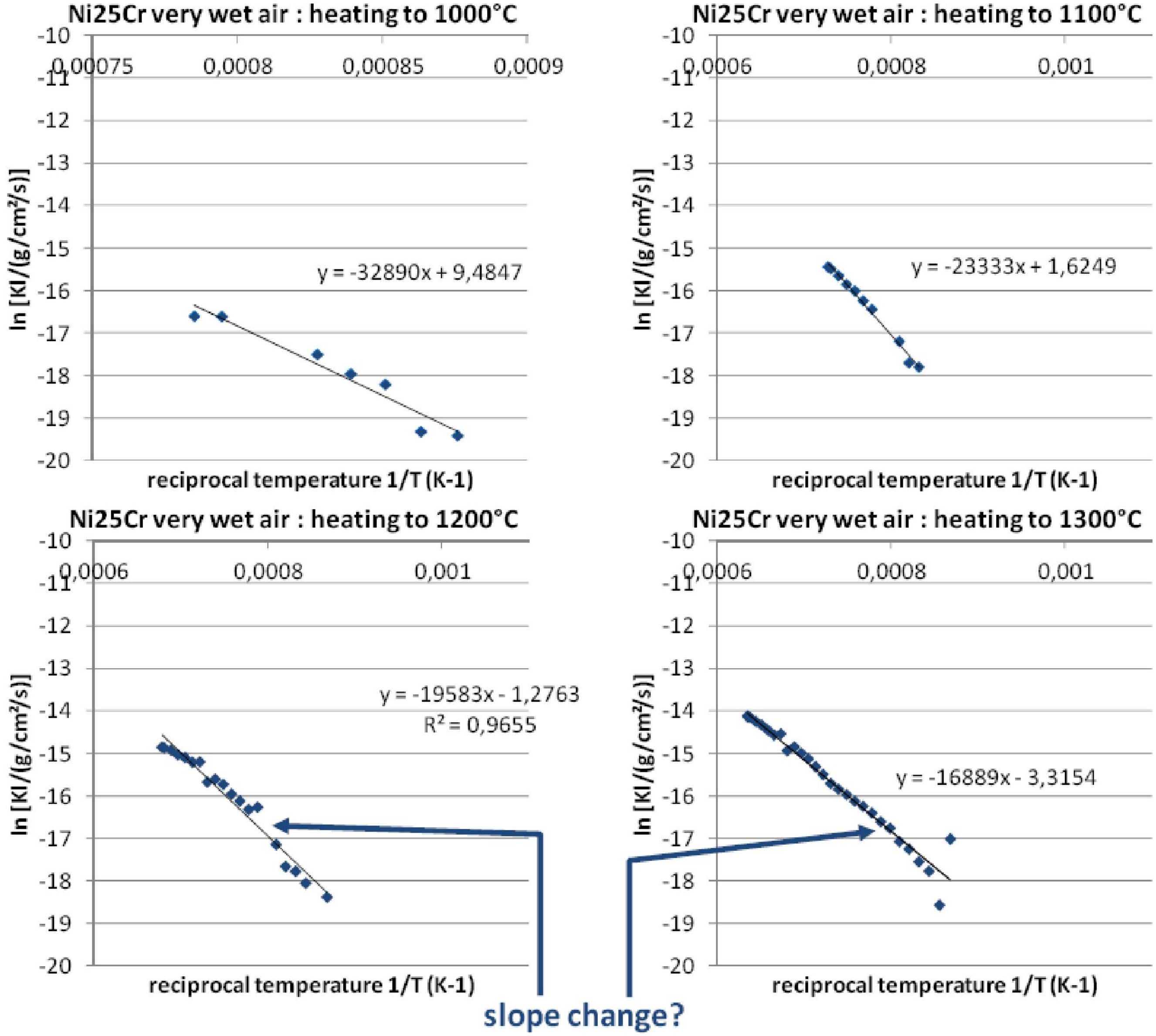

Figure 3 : Arrhenius plot of the linear constant K_l estimated at each step of temperature increase during the heating: up to 1000°C, up to 1100°C, up to 1200°C and up to 1300°C

TABLE 2 : Activation energies describing the Arrhenius dependence on temperature of the K_l value during the heating in "very wet air"; in some cases: temperature range of transition from a high activation energy to a lower one; comparison with the corresponding results earlier obtained in dry air and in "wet air"[10]

Linear oxidation during heating	dry air[10]		wet air[10]		very wet air	
Stage temperature	temperature range (°C)	energy (kJ/mol)	temperature range (°C)	energy (kJ/mol)	temperature range (°C)	energy (kJ/mol)
1300°C	1098 to 1300:	111	1048 to 1300:	100	1062 to 1300:	136
	915 to 1082:	214	863 to1030:	287	851 to1045:	138
1200°C	1081 to 1200:	186	1046 to1200:	91	995 to 1200:	120
	932 to 1065:	292	863 to 1030:	221	928 to 978:	164
1100°C	732 to 1100:	132	1030 to 1100:	127	878 to 1100:	194
			863 to 1013:	291		
1000°C	not applicable	not applicable	/	/	878 to 1000:	273
			868 to 1000:	182		

regular until reaching the ambient temperature for the samples cooled from 1000°C or from 1100°C. A tendency for little irregularities appear for the cooling from 1200, while the cooling part of the mass gain curves

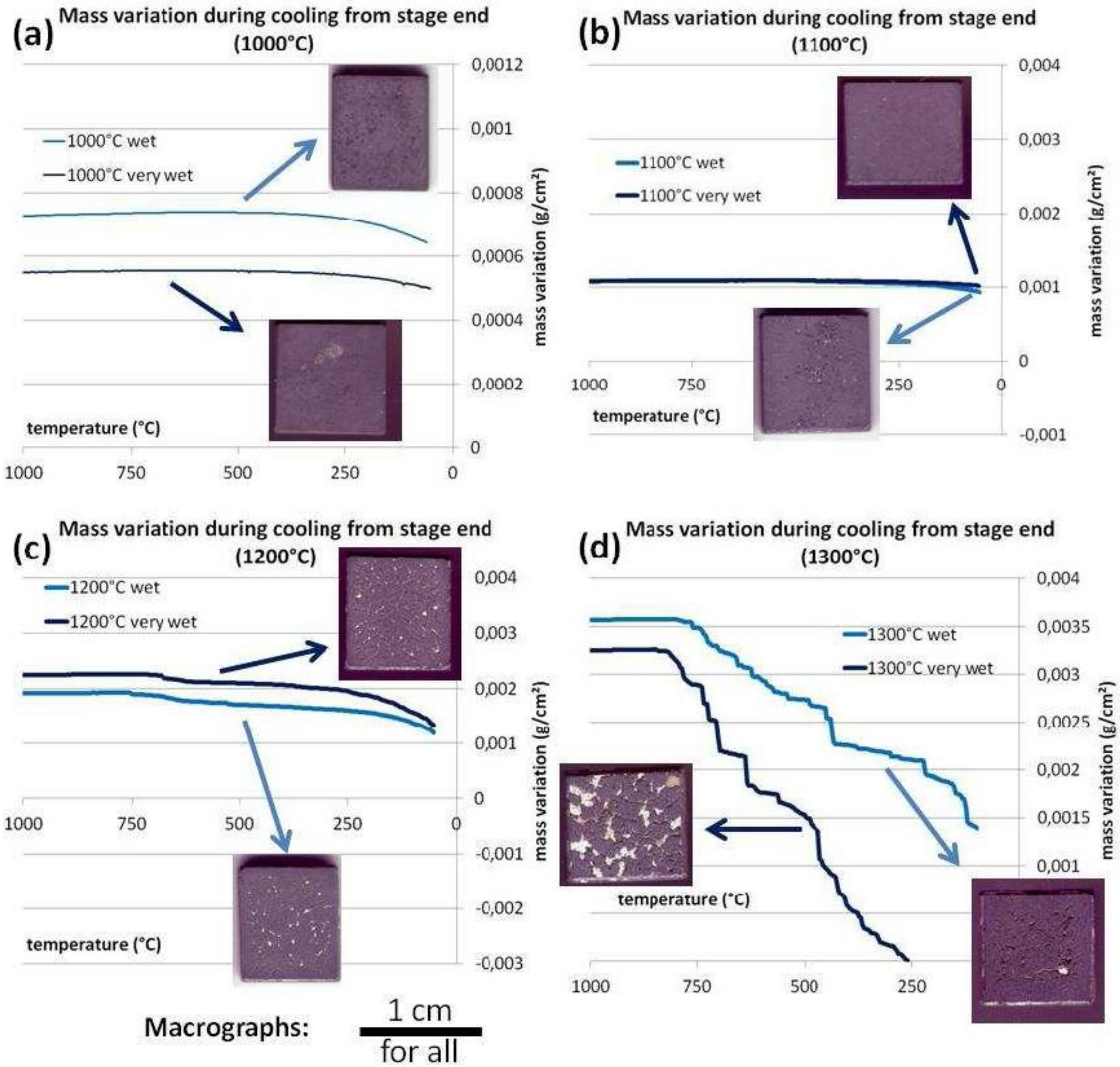

Figure 4 : Curves of mass variation during cooling after oxidation in the "very wet air" atmosphere, in comparison with the corresponding ones earlier obtained in "wet air"[11]

have become very irregular for the cooling from 1300°C. When one compares the cooling curves obtained here after hot oxidation in "very wet air" to the ones earlier obtained in "wet air" only, it appears that the curves are very similar for a given temperature.

When one looks at the surface states of the oxidized samples after return to room temperature (macrographs inserted in Figure 4), it appears that the oxide remained adherent to the substrate for the cooling from the stage at 1000°C as well as after the stage at 1100°C. In contrast, limited spallation seemingly occurred during the cooling from 1200°C, and much more oxide was obviously lost during the cooling from 1300°C. These qualitative observations can be strengthened by quantitative surface fractions, measured by image analysis using Adobe Photoshop CS (TABLE 3). It appears that, if the introduction of water in the oxidizing air earlier led to an improvement of the oxide adherence, a further water enrichment did not change anymore this effect for cooling from 1000 or 1100°C, slightly continued this effect for 1200°C, but led to a partial loss of this beneficial effect for 1300°C (although the adherence is still better than in dry air).

TABLE 3 : Surface fraction of denuded alloy after oxide spallation during cooling (versus oxidation temperature and air humidity)

% air	dry air Average ±std dev.	wet air Average ±std dev.	very wet air Average ±std dev.
1300°C	18.3 ±4.5	1.8* ±1.5*	12.7 ±5.5
1200°C	18.1 ±2.2	3.5 ±1.6	1.8 ±0.5
1100°C	8.5 ±09	0.6 ±0.4	0.6 ±0.1
1000°C	0.5 ±0.2	0.4 ±0.2	0.6 ±0.2

***: measurements not accurate because shadow effect (the real value are much higher than the present ones)**

General commentaries

With these new thermogravimetry tests performed on the same binary Ni-25Cr chromia-forming alloy, in the same conditions of stage temperature and heating and cooling rates, but for a higher concentration in water vapour in air, it appeared that the oxidation goes on to start at slightly higher temperature and also to lead to a slightly lower mass gain when reaching the stage temperature. During the cooling the beneficial effect of the presence of water in air for the resistance of the oxide against spallation during the cooling is also kept, even if a deterioration of the oxide scale can be noted when the cooling occurs after 48 hours of oxidation at 1300°C (but without reaching the spallation earlier observed in dry air for a cooling from this temperature). Thus, the effects of the presence of water vapour in air, previously observed for a first water concentration, were confirmed here and they seem to be valuable over a more or less broad range of water concentration.

CONCLUSIONS

By enriching the previous studies[10,11] with these new results, one obtains a better knowledge about the behaviour of this alloy, and probably for real more complex alloys with chemical compositions based on Ni-25Cr, in a range of water concentration but, it is true, for given values of the duration of the isothermal stage, of the heating rate and of the cooling rate. The influence of the heating rate on the oxidation during heating should be further investigated with additional tests while the high temperature duration (which notably influences the oxide thickness just before cooling) and the cooling rate would be changed to investigate their influences in association to the vapour concentration. Much more work remains to be done at given alloy.

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