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A thermogravimetric and metallographic study of the high temperature oxidation of a binary nickel-chromium alloy in humidified air. Part I: Oxidation start at heating

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ABSTRACT

Air humidity may significantly influence the behaviour in oxidation at high temperature of the refractory metallic alloys. To study the effect of water vapour on the oxidation phenomena in thermal cycling conditions in the case of nickel-based alloys a Ni-25Cr binary alloy was considered. It was subjected to oxidation at four high temperatures, 1000, 1100, 1200 and 1300°C for 48 hours in dry air and in a humidified air. The heating parts of the thermogravimetry curves were exploited to specify the temperatures of oxidation start and the amount of oxide mass formed during heating. By comparison with dry air, the water concentration tried in this work induced an earlier oxidation during heating with a good reproducibility of temperature start. © 2012 Trade Science Inc. - INDIA

KEYWORDS

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

INTRODUCTION

Refractory alloys and superalloys used at high temperature are generally exposed in service to aggressive gaseous environments. To resist high temperature oxidation or hot corrosion they are designed to contain sufficient amounts of elements as chromium, aluminum or silicon to develop on their surfaces protective oxides such as chromia, alumina or silica^[1]. In many situations oxygen is not the sole oxidant contained in the hot gases reacting with the metallic surfaces. Water vapor is one of the possible oxidants which are also present in the oxidizing atmospheres with which the alloys are in contact. This

may lead to other mechanisms of hot corrosion^[2]. Gas turbines for power generation is one of the main examples of such situation.

Many studies have been carried out concerning the oxidation behaviour of metals and alloys in presence of water vapor. Among the most recent works one can cite for example articles concerning only pure metals (e.g. Fe, Ti)^[3,4], iron or titanium aluminides^[5,6], molybdenum/tungsten silicides^[7], ceramics^[8], and also MCrAlY coatings^[9]. But most of the studies dealing with the effect of water vapor on the high temperature oxidation behaviors of refractory alloys concern iron-based materials such as FeCrAl alloys^[10,11], highly alloyed steels without^[12]

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or with^[13] coatings, and even carbon-steels^[14]. Many works have been also carried out on simple binary Fe-Cr alloys (for example^[15,16]). Curiously there are not so many recent studies concerning nickel-based alloys. Nevertheless one can cite several works about binary Ni-Cr alloys^[17], conventional commercial superalloys^[18] and even Ni-based single crystal superalloys^[19]. Most of the studies deal with the effect of water vapor on the oxidation rate in isothermal condition, on the oxide characteristics and on the loss of a part of the protective oxide due to the formation of volatile oxy-hydroxides. In contrast the start of oxidation during the heating before reaching the targeted temperature at which the oxidation kinetics are specified by thermogravimetry, is less frequently studied. This is also true for the spallation of oxide during cooling after the isothermal stage.

The purpose of this work is precisely to focus attention on the influence of the presence of water vapour on both the oxidation start during heating and the occurrence and frequency of oxide detachment during the post-isothermal stage cooling, in the case of a simple Ni-25Cr alloy, by exploiting the heating and cooling parts of the thermogravimetric results which are commonly not considered but which however led earlier to interesting investigations^[20,21].

EXPERIMENTAL

Preparation of the alloy samples and thermogravimetry tests

The alloys were synthesized by foundry from parts of pure nickel and of pure chromium (Alfa Aesar, > 99.9 wt.%), by using a CELES high frequency induction furnace under a pure argon atmosphere (pressure about 400mbar). Each of the four obtained ingots (all of about 40g) was cut in order to prepare samples for the thermogravimetry tests at one of the four considered temperatures. The samples, all of about $10 \times 10 \times 3$ mm³, were polished up to the 1200-grade SiC paper, with smoothing of edges and corners.

The same apparatus was used to perform the oxidation tests in dry air and in wet air: a SETARAM Setsys thermo-balance coupled with a humidity generator SETARAM Wetsys. For the tests in dry air the air com-

ing from a bottle of Alphagaz 1 passed through the humidity generator with as settings: Relative Humidity of 0% at 30°C, while these settings were RH=80% at 40°C for the test in wet air. The gas flow was 20mL min⁻¹ in both cases.

The oxidation tests were performed at 1000, 1100, 1200 and 1300°C for 48 hours in the two atmospheres. For all tests the applied heating rate was 20°C min⁻¹.

Exploitation of the heating parts of the thermogravimetric curves

During heating the volume mass of air decreases, with as consequence an artificial mass gain for the heating sample hanged by a platinum wire to the microbalance. This is only due to the decrease in Archimede's thrust and a correction must be applied for allowing the detection of the real mass gain by starting oxidation. The mass gain results were then first corrected from air buoyancy variation by applying a method, involving the perfect gas law, which was described earlier^[20]. One can summarize it practically here by first reminding that there is an almost linear part of mass gain which is progressively established after a first more rapid increase in mass gain at lower temperatures. The practical treatment consists in revealing this linear mass gain in the heating part of the thermogravimetry curve, in determining the related linear equation, then subtracting this linear expression to the mass gain file.

The temperature of real start of oxidation can then be read on the corrected mass gain curve, as well as the total mass gain obtained at the end of heating. For each atmosphere (dry air and wet air) the four oxidation tests (four stage temperatures) lead to four values of this temperature of oxidation start, this allowing studying the reproducibility or dispersion of the oxidation start temperature, and then a better comparison between the two atmosphere conditions. Concerning the mass gain by oxidation during heating four results can be obtained for the heating up to 1000°C (the test at 1000°C but also the tests at the three higher temperatures by noting the mass gain when the temperature reaches 1000°C before continuing increasing up to the stage temperature 1100, 1200 and 1300°C). Similarly three results can be obtained for 1100°C, two for 1200°C, but only one for 1300°C.

RESULTS AND DISCUSSION

The conventional plot ($\Delta m/S = f(t)$) of the obtained thermogravimetric curves shows that the isothermal parts are all parabolic or almost parabolic, as illustrated in Figure 1(a) with the example of the Ni-25Cr oxidized at 1100°C in wet air. Plotting the whole curves in the $\Delta m/S = f(T)$ scheme as shown in Figure 1(b) with the same alloy in the same temperature and air humidity conditions, allows seeing that the artificial mass variation due to air buoyancy follows the same variation versus temperature as earlier encountered^[22], during the heating as well as during the cooling (visible in this latter case because of the absence of any oxide spallation). One can remind that this type of variation, which can be interpreted using the $\{P.V = n.R.T\}$ – law, can be described by a hyperbolic (low temperature) to almost linear (high temperature) law. The treatment of the thermogravimetric results, explained above in the experimental part and illustrated in Figure 2 with the example of the Ni25Cr alloy oxidized at 1100°C in dry air, leads first to the {air buoyancy variation}-corrected curves presented in Figure 3. These ones allow observing the start of detectable mass gain due to exclusively oxidation. One can first remark that the corrected heating mass gain curves obtained for the four temperatures in dry air and plotted together in the same graph (Figure 3(a)) display some differences for their common parts (up to 1000°C for all curves, up to 1100°C for three of them, up to 1200°C for two of them) which are not really partly superposed. In contrast the corresponding heating curves obtained in wet air, for the four temperatures too, are much more close to one another (Figure 3(b)). After enlargement of the bottom parts of these curves (Figure 3(c) for dry air and 3(d) for wet air), these differences become enhanced and additionally one can see that the temperatures of oxidation start are rather dispersed for the four oxidation tests in dry air and really close to one another for the tests in wet air. Their values, presented in TABLE 1, confirm the preceding qualitative observations: in dry air the temperature of oxidation start varies between 860 and 930°C while these oxidation start temperature are much more closer to one another (around 865°C).

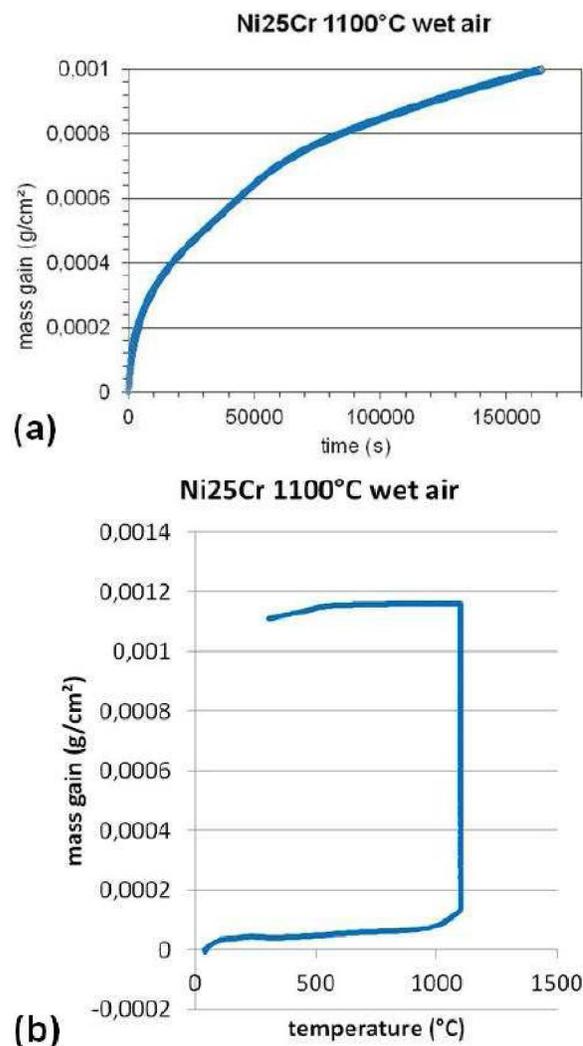


Figure 1 : Example of the mass gain curves obtained: (a) conventionally plotted (isothermal part only), and (b) plotted versus temperature (whole file: heating, isothermal and cooling parts)

When reaching the targeted temperature the total mass gains resulting from early oxidation during heating logically increase with the stage temperature (1000, 1100, 1200 and 1300°C). This is clearly shown in Figure 4 in which the average values (e.g. for $T = 1000^\circ\text{C}$: average of the mass gain values obtained at the end of heating for the test at 1000°C and of the three other mass gain values recorded at 1000°C during the heating up to 1100, 1200 or 1300°C). For the two atmospheres (dry air and wet air) the mass average mass gains are almost equal when reaching 1000°C (0.0169 ± 0.0118 and 0.0166 ± 0.0023 mg/cm² in dry air and wet air respectively) and when reaching 1100°C (0.0670 ± 0.0329 and 0.0672 ± 0.0050 mg/cm²). In contrast small differences arise for 1200°C

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(0.162 ± 0.014 (dry) and $0.170 \pm 0.002 \text{ mg/cm}^2$ (wet)) and for 1300°C (0.410 (dry) and 0.378 (wet)).

However there are no significant differences between the two atmospheres.

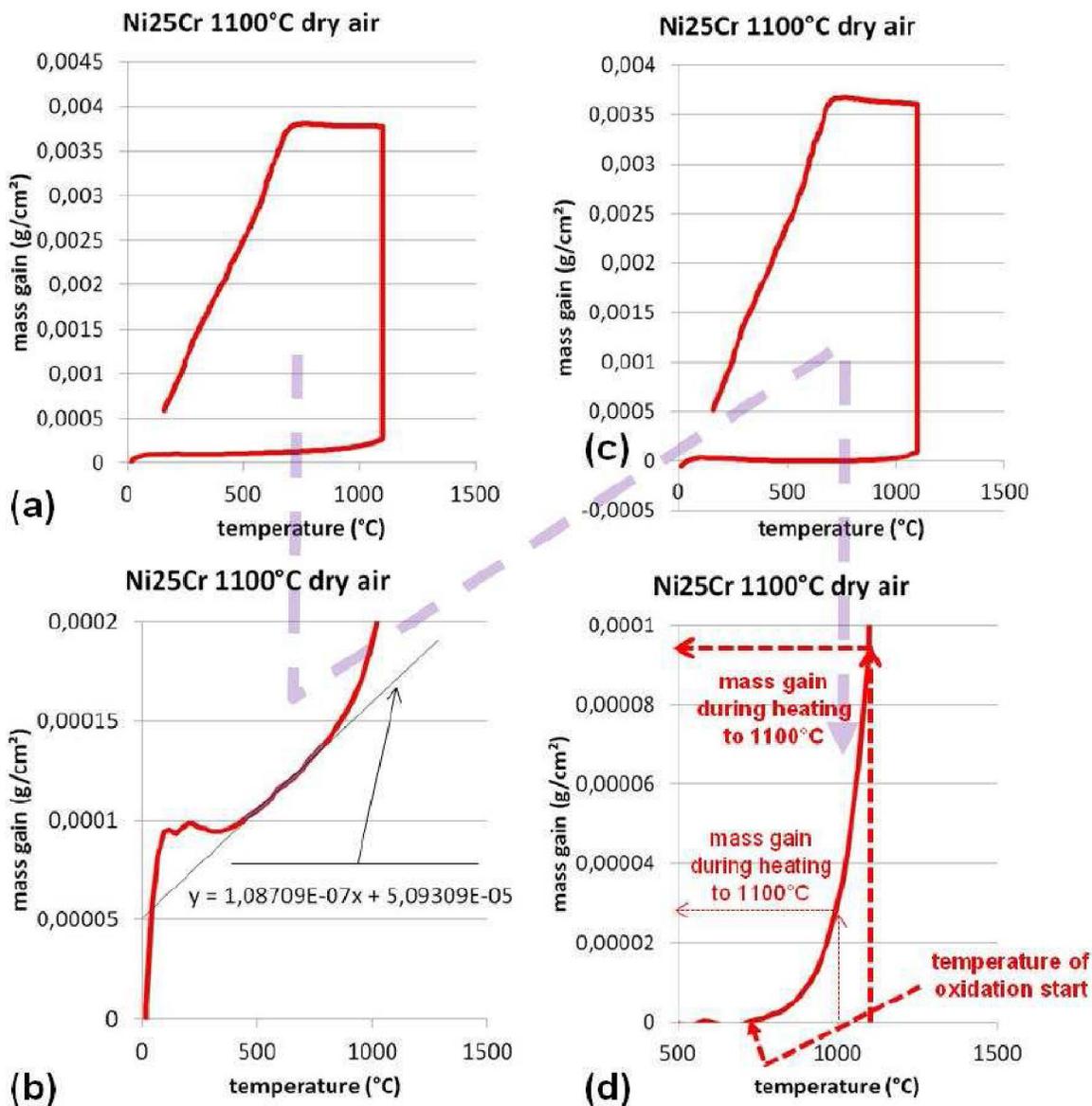


Figure 2 : Treatment of the thermogravimetric curve to correct the mass variation from the Archimede's thrust (air buoyancy): (a) initial curve plotted in the mass gain versus temperature representation, (b) determination of the equation of the high temperature linear part of apparent mass gain due to air density decrease, (c) correction of the whole curve using the previous equation and (d) determination of the temperature of oxidation start and of the final mass gain when reaching 1100°C (and also 1000°C)

After these first results it can be interesting to examine how varies the instantaneously linear oxidation rate during the heating. At each step of heating, i.e. for each temperature, the elemental increase in mass gain was divided by the time step of mass record (50s) and the obtained rate plotted versus the running temperature, which may give additional data about oxidation during heating^[22]. It appears that it unsurprisingly increased with

temperature. Further, the neperian logarithm of the $K_1(T)$ kinetic mass gain constants were plotted versus the reciprocal temperature $1/T_{\text{absolute}}$ (K^{-1}). The obtained graphs, presented in Figure 5 for the oxidation tests performed in dry air and in Figure 6 for the ones in wet air, show that these curves are composed of two successive straight lines in most cases. The temperatures at which the slope of these $\ln(K_1)=f(1/T)$ curves

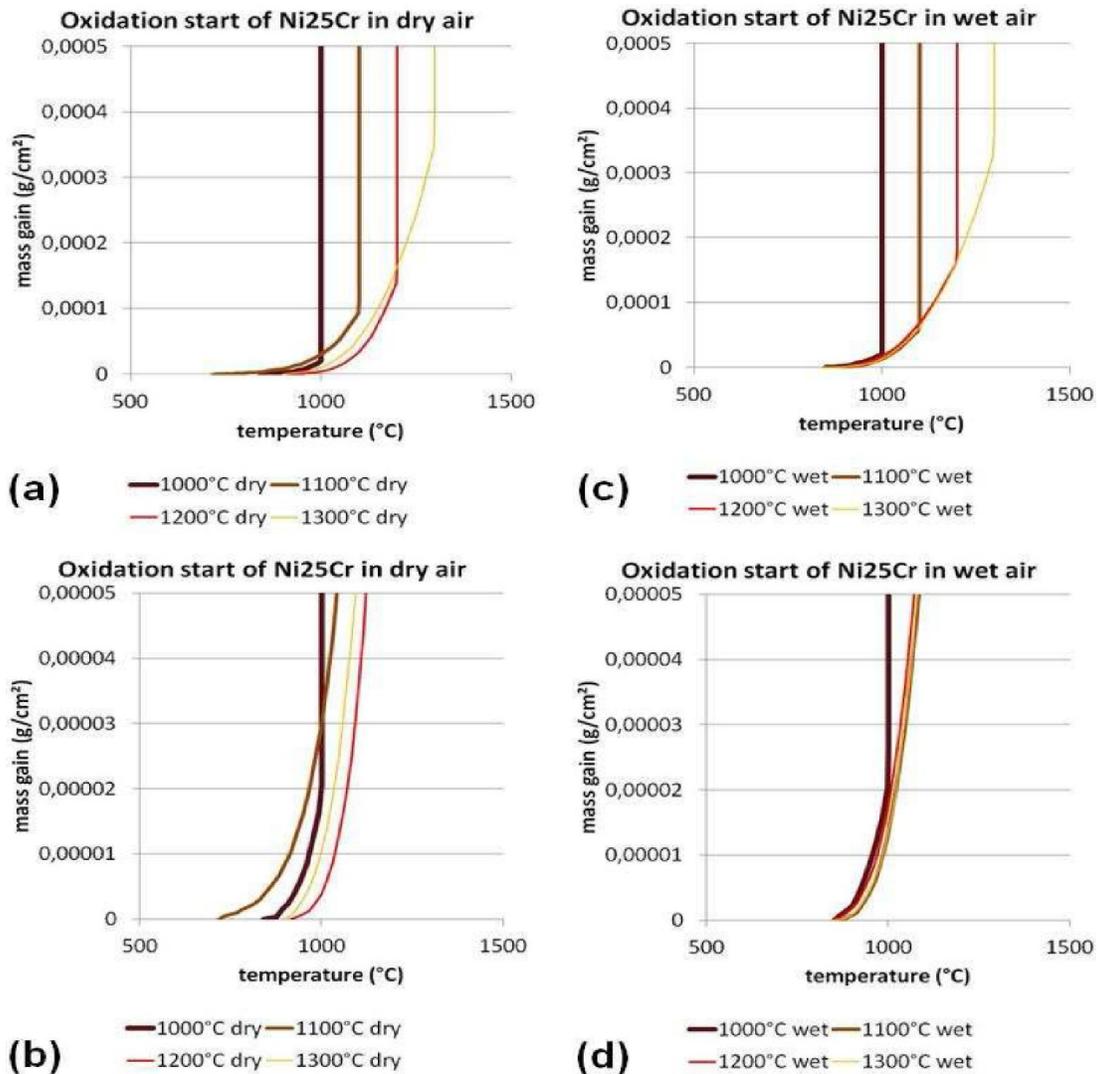


Figure 3 : End of the heating parts of the thermogravimetry curves corrected from air buoyancy for the determination of the temperatures of oxidation start: (a) (enlarged in (b)) Ni₂₅Cr oxidized in dry air, and (c) (enlarged in (d)) Ni₂₅Cr oxidized in wet air

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

Temperature of oxidation start (°C)	Air humidity	
	dry	Wet
Stage temperature		
1300°C	915	863
1200°C	932	863
1100°C	732	863
1000°C	858	868
Average ± Std dev.	859 ± 91	864 ± 3

suddenly varies, as well as the activation energies which may correspond to these successive straight lines, are given in TABLE 2. For the oxidation tests done in dry air the temperature of transition is not reproducible. The reproducibility is much better, but not perfect, for the

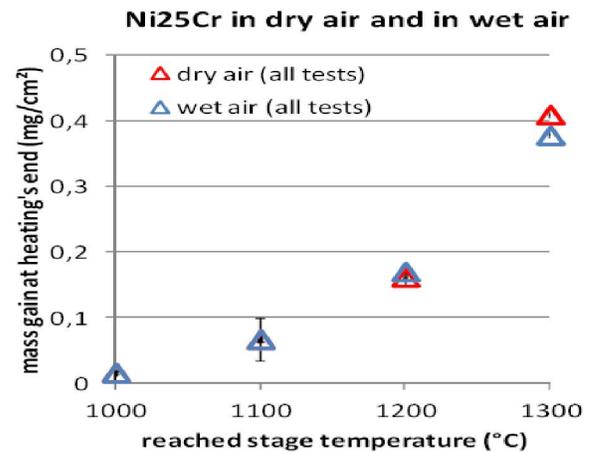


Figure 4 : Total mass gains obtained during heating for the Ni₂₅Cr alloy in dry air and in wet air (average ± standard deviation calculated on 4 values for 1000°C, 3 values for 1100°C and 2 values for 1200°C)

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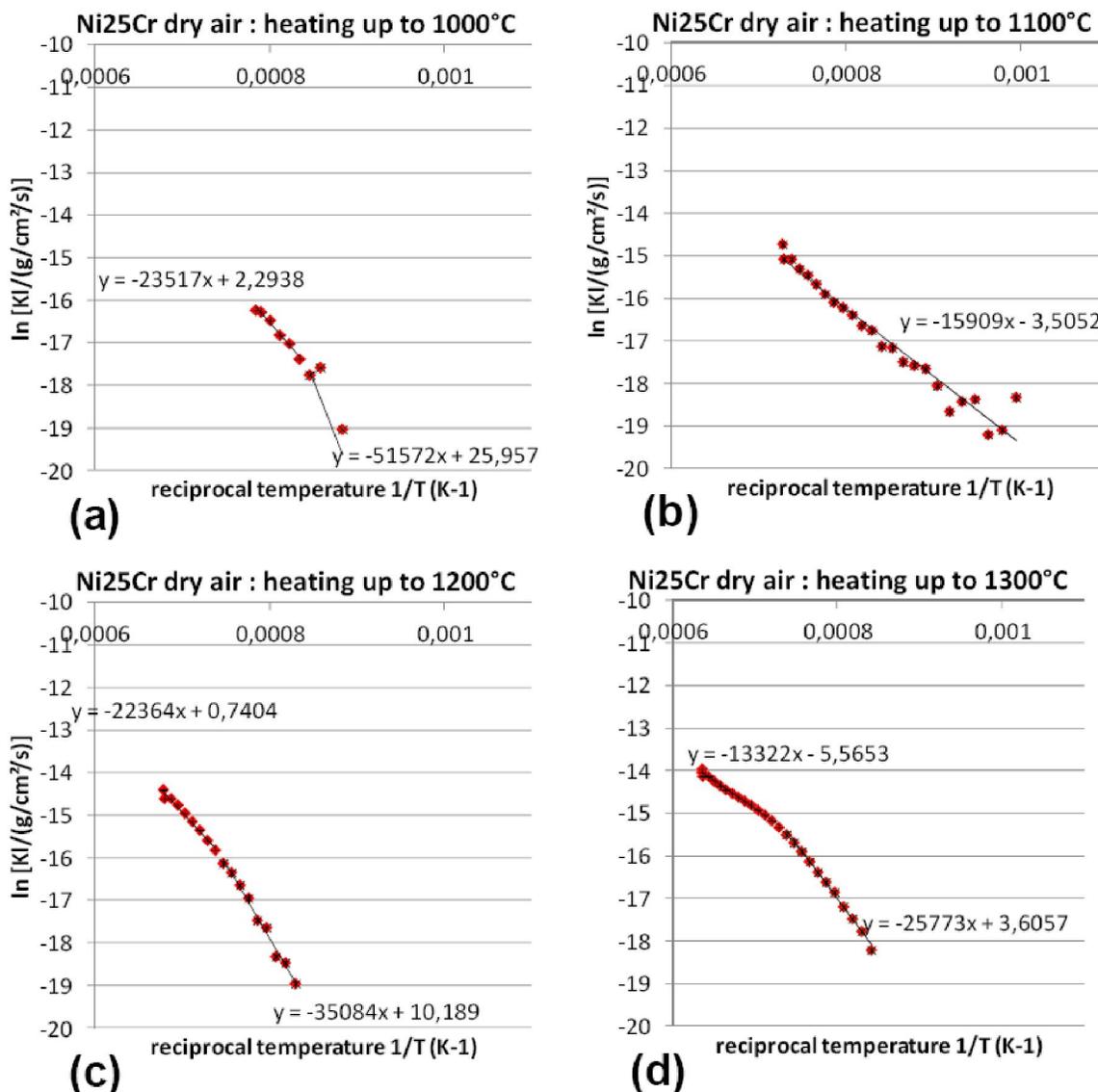


Figure 5 : Arrhenius plot of the linear constant K_1 estimated at each step of temperature increase during the heating: (a) up to 1000°C, (b) up to 1100°C, (c) up to 1200°C and (d) up to 1300°C, all for the Ni₂₅Cr heated in dry air

oxidation tests performed in wet air. Indeed the transition temperature is about 1030°C for the four tests done in wet air and it seems separating the curve in a low temperature part for which the activation energy tends to be rather high (between 182 to 281 kJ/Mol) and a high temperature part for which the activation energy is lower (100 to 127 kJ/Mol).

General commentaries

The exploitation of the heating parts of the thermogravimetry curves, which are often ignored by comparison to the isothermal parts, may be interesting to consider since they can bring useful results. Some of these ones concern the start of oxidation and amount of oxide formed before reaching the isothermal stage, the

latter being for example of great importance for the determination of a parabolic constant. However this needs a prior correction from the consequences on mass variation of the Archimede's thrust evolution. In this work this allowed seeing that the temperature of oxidation start seems to be more reproducible in wet air than in dry air. Furthermore, the presence of water vapor in the oxidizing air obviously promotes an earlier detectable oxidation, as is to say mass gain is detected for lower temperature than in dry air. The phenomena appear then to be not the same between the two cases (dry air and wet air) and reactions may be more complex in wet air as revealed by the two activation energies determined on both sides of a constant temperature of about

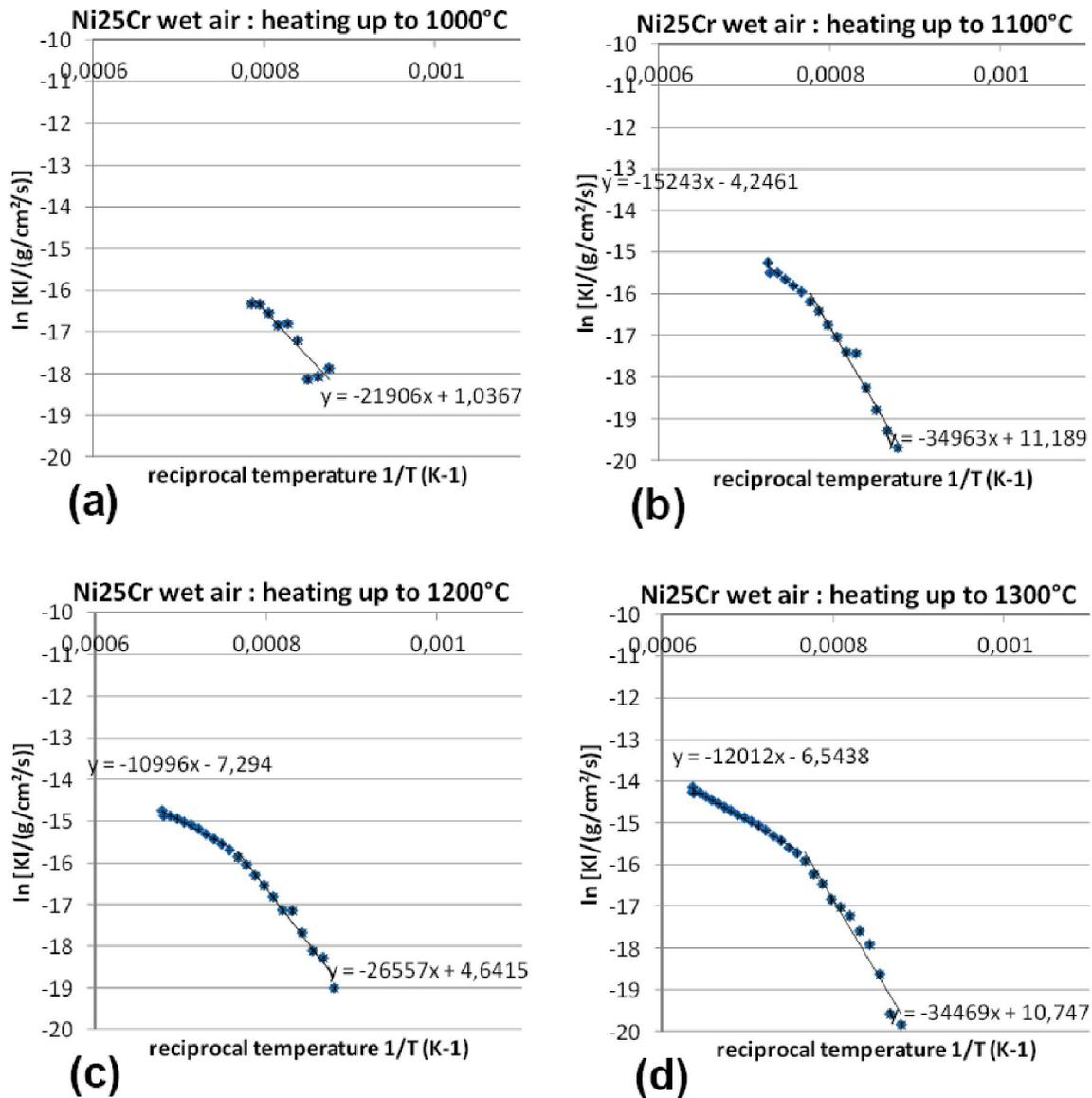


Figure 6 : Arrhenius plot of the linear constant K_1 estimated at each step of temperature increase during the heating: (a) up to 1000°C, (b) up to 1100°C, (c) up to 1200°C and (d) up to 1300°C, all for the Ni25Cr heated in wet air

TABLE 2 : Activation energies describing the Arrhenius dependence on temperature of the K_1 value during heating; temperature range of transition from a low activation energy to a high activation energy

Linear oxidation during heating	dry air		wet air	
	Stage temperature	temperature range (°C)	temperature range (°C)	activation energy
1300°C		1098 to 1300:	1048 to 1300:	100 kJ/mol
		915 to 1082:	863 to 1030:	287 kJ/mol
1200°C		1081 to 1200:	1046 to 1200:	91 kJ/mol
		932 to 1065:	863 to 1030:	221 kJ/mol
1100°C		/	1030 to 1100	127 kJ/mol
		732 to 1100:	863 to 1013	291 kJ/mol
1000°C		not applicable	/	/
			868 to 1000°C:	182 kJ/mol

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1030°C. Further investigation may imply in situ XRD-measurements during heating to better understand what occurs in these two temperature ranges. New oxidation tests with lower heating rates can be also of interest to amplify the mass gains in heating situation, for these temperature domains. It can be also interesting to perform new thermogravimetric tests with the same parameters but with other water concentrations in air.

CONCLUSIONS

Since the hot oxidizing atmospheres often contain a more or less small quantity of water, or in contrast very high levels of water as for some gas turbines, the effect of water on the high temperature oxidation behavior of the alloys is of great importance. The presence of water vapor leads to differences in oxidation rate at constant temperature, by a difference of reaction kinetic and an accelerated volatilization of the protective oxides by forming volatile hydroxides. But the presence of water obviously also influences the oxidation phenomena and rates of mass gain during heating, which is maybe less well-known.

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