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Isothermal oxidation at high temperature of a nickel-chromium alloy in water vapor-rich air. Part 1: Mass gain rates and kinetic constants

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ABSTRACT

A binary Ni-30Cr alloy, known for its chromia-forming behaviour, previously elaborated by foundry and tested in oxidation at temperatures ranging from 1000 and 1300°C in dry air and in moderately water vapour-enriched air, has been here subjected to hot oxidation at the same temperatures (1000, 1100, 1200 and 1300°C) for 48 hours in a very humidified air, with thermogravimetric measurements. The exploitation of the mass gain files was carried out following several methods. Since chromia volatilization was particularly fast (at 1300°C notably) the treatment was done by applying the $\{m \times dm/$ $dt = Kp - m \times Kv$ }-method. The values of the parabolic constant Kp and of the chromia volatilization constant Kv were specified together. If they both logically increase with temperature the variation with the air humidity rate was less evident. These present kinetic results will be strengthened by metallographic characterization in a second part of this work, for a better interpretation of the effect of water vapor in such high concentration. © 2014 Trade Science Inc. - INDIA

INTRODUCTION

The hot atmospheres in which superalloys are used in high temperature applications often contain gaseous water. This is notably the case of industrial pieces working at high temperature under atmospheric air in which water vapour is necessarily present in more or less contents depending on weather or of turbine blades of jets flying through clouds or just above seas, for instance. There are also other machines in which water vapour is present in high concentrations, as in the power generation field with the vapour turbines. The protective oxide

KEYWORDS

Nickel alloy; Chromium; Water vapour; High temperature; Isothermal oxidation: Oxides XRD characterization.

scales which develop over the pieces made of superalloys (mainly chromia, alumina or silica)[1] may suffer faster deterioration because of the formation of volatile species, phenomena inducing an over-consumption of the element initially added to the alloys to form these protective scales (respectively chromium, aluminium, silicon)^[2]. The influence of vapour present in air as well as in other gases was examined in many previous studies, as the recent works which were carried out in the case of pure metals^[3,4], of intermetallic compounds^[5,6], of metallic coatings^[7], of alloys rich in heavy metals^[8] or of ceramic materials^[9].

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The Ni-30Cr alloy, even if it is a very simple one, is very interesting to study in oxidation in presence of water vapour since – except an eventual small amount of NiO oxide possibly formed in the early stage of oxidation – only chromia develops over this alloy, thanks to its high chromium content and the general good behaviour of a nickel base for Cr diffusion. This is the reason why this alloy was especially prepared by foundry in a two-parts previous work^[10,11] to examine its high temperature oxidation behaviour in air moderately rich in vapour, in terms of oxidation start at heating and of oxide spallation at cooling, and used again in a more recent work with the same purposes (heating and cooling) but in a more humidified air^[12].

In the present work it was wished to analyzed what occurred during the isothermal stage for this same Ni-30Cr alloy in the same air very rich in water, in terms of mass variation kinetic at all the tested temperatures, mass gain (chromia growth) or mass loss (chromia volatilization), this using a method recently developed^[13] to simultaneously extract the parabolic constant Kp and the volatilization constant Kv in case of oxidation in dry air at temperatures higher than 1000°C.

EXPERIMENTAL

The alloy used for this work was previously elaborated by foundry. This was done by melting parts of pure nickel and of pure chromium (Alfa Aesar, >99.9 wt.%), in a high frequency induction furnace under an inert atmosphere made of 300millibars of pure argon. The ingots, of about 40g, were cut in order to obtain parallelepipedic samples of about $10 \times 10 \times 3 \text{ mm}^3$ for the thermogravimetry tests. These samples were polished up to the 1200-grade SiC paper. The thermogravimetry runs were a SETARAM Setsys thermobalance coupled with a SETARAM Wetsys vapor generator. The humidified air was targeted with a relative humidity of RH=90% at 60°C (gas flow of 20mL min⁻¹). The tests' temperatures were 1000, 1100, 1200 and 1300°C and the common test duration was 48 hours. The heating and cooling rates were 20°C min⁻¹ and 5°C min⁻¹ respectively.

The recorded mass gains were plotted in the conventional scheme m versus t (m: mass gain per surface unit area, t: time) to observe the general form of the curves.

They were thereafter according to the $m^2-m_0^2$ versus t-t₀ (t₀: time at which the kinetic begins to be parabolic, m: mass gain at time t, m₀: mass gain at time t₀ including the mass during heating (values taken in ^[10]) and the one during the eventual transient isothermal linear mass gain preceding the parabolic one) in order to specify the parabolic constant with more accuracy.

The mass gains were treated another time, by plotting m × dm/dt versus –m in order to specify the values of the real parabolic constant Kp (real because by taking into account the mass loss by chromia volatilization and then the instantaneous real chromia mass per surface unit area or real chromia thickness). Indeed, the following equation may be verified during the parabolic part of the isothermal oxidation: m × dm/dt = Kp – Kv × m. Thus plotting m × dm/dt versus –m may lead to a straight line the ordinate at the origin is Kp and the slope Kv^[13]. The Kp and Kv values were thereafter tested by plotting mathematical curves and by comparing them to the experimental ones.

RESULTS AND DISCUSSION

Mass gains plotted versus time

All the obtained thermogravimetric curves are presented in Figure 1. They are globally parabolic, except one obtained at 1000°C since it was obviously affected by small jumps probably due to oxide detachment. The three other curves are much more regular and seem parabolic. However one can observe a beginning of stationarity at the end of the curves acquired at the highest temperatures, which is really obvious for 1300°C since the end of the curve is almost horizontal (and even seems starting to decrease). This lets think to a mass loss by volatilization, probably of chromia.

Mass gains plotted as m²-m₀² versus t-t₀

The same mass gain files plotted as $m^2-m_0^2$ versus t-t₀, displayed in Figure 2 for the tests done at 1000°C and 1100°C, and in Figure 3 for the tests done at 1200°C and 1300°C. If the curve obtained in this scheme is not straight for the test performed at 1000°C (because of the irregularities already shown in the m=f(t) representation for this temperature) the curve corre-

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Figure 1 : The four thermogravimetric curves obtained, plotted as m versus t

sponding to the test at 1100°C is on the contrary much more straight (except at the beginning of the curve), this allowing an accurate determination of the parabolic constant.

This is not the same with the $\{m^2-m_0^2 \text{ versus t-t}_0\}$ curves corresponding to 1200°C and 1300°C (Figure 3) for which a curvature appears. This one, which is especially strong for 1300°C, clearly shows that the

Materials Science An Indian Journal mass gain did not increase according to a parabolic law but significantly slower. This confirms that chromia volatilization exists and even induces significant mass losses, able to balance the oxidation-due mass gain. It appears thus compulsory to analyze the mass gains files by taking into account the chromia volatilization in order to specify realistic values of the parabolic constant Kp (and also to value the volatilization constant Kv).



Figure 2: The two thermogravimetric curves obtained at the two lowest temperatures (top : 1000°C, bottom : 1100°C), plotted as $m^2-m_0^2$ versus t-t₀



Figure 3 : The two thermogravimetric curves obtained at the two highest temperatures (left: 1200°C, right: 1300°C), plotted as m²-m₀² versus t-t₀

Mass gains plotted as m × dm/dt versus -m

The same mass gain files were thus treated according to the $\{m \times dm/dt = Kp - m \times Kv\}$ -method to assess simultaneously the volatilization constant Kv data as important as the parabolic constant since it also describes an aspect of the high temperature oxidation behavior of the alloy – and the not underestimated value of the parabolic constant Kp. Two examples of such $\{m \times dm/dt \text{ versus } -m\}$ plots are given in the top parts of Figure 4 (1000°C) and Figure 5 (1200°C), the bottom parts of the same figures illustrating the test of the Kp and Kv values obtained by comparison of the mathematical curve with the experimental one.



Figure 4 : The {m \times dm/dt versus -m} plot of the mass gain files acquired at 1000°C for the Ni-30Cr alloy (top) and the tests of comparison to the experimental {m=f(t)} curve of the classically determined Kp value (red curve, "math1" and of the {Kp, Kv} couple of values determined above (green curve, "math2")



Figure 5 : The {m \times dm/dt versus -m} plot of the mass gain files acquired at 1200°C for the Ni-30Cr alloy (top) and the tests of comparison to the experimental {m=f(t)} curve of the classically determined Kp value (red curve, "math1" and of the {Kp, Kv} couple of values determined above (green curve, "math2")

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In the two cases the values obtained for Kp by taking into account chromia volatilization are much better than the classically determined Kp since the green curves fit very correctly the experimental curves while it is absolutely not the case for the red curves. This is also true for the constants' values determined for the two other temperatures (1100 and 1300°C).

The values of Kp and Kv determined by applying the {m × dm/dt = Kp – m × Kv}–method are graphically given in Figure 6 for Kp and Figure 7 for Kv, for the four temperatures and this "very wet" air (90% of relative humidity at 60°C), with the recalled values of the constant earlier obtained for the same alloy at the same temperatures but in "dry" air (no water vapor) and in "wet" air (80% of relative humidity at 40°C)^[14]. One can see first that the two constants logically increase with temperature but second that Kp and Kv do not follow a systematic variation (the differences due to humidity depend on temperature).



Figure 6 : Plot versus temperature of the values of Kp derived from the $\{m \times dm/dt = Kp - m \times Kv\}$ -plot for the Ni-30Cr alloy oxidized in the "very wet" air (90% of relative humidity at 60°C, this work); comparison with earlier values obtained for the same alloy in "dry air" (no humidity) and in "wet air" (only 80% of relative humidity at 40°C)

General commentaries

Thus, by enriching again air in water vapour the high temperature oxidation behaviour of the Ni-30Cr alloy goes on changing, by comparison with what was previously observed between dry air and moderately humidified air^[14]. However the parabolic constant Kp does not continue to decrease with the water vapour enrich-



Figure 7 : Plot versus temperature of the values of Kv derived from the {m × dm/dt = Kp – m × Kv}–plot for the Ni-30Cr alloy oxidized in the "very wet" air (90% of relative humidity at 60°C, this work); comparison with earlier values obtained for the same alloy in "dry air" (no humidity) and in "wet air" (only 80% of relative humidity at 40°C)

ment while the chromia volatilization constant Kv becomes higher only for 1300°C (with as result a remarkable stationarity of the mass variation near the end of the 48 hours stage).

CONCLUSIONS

Thus, the evolutions of the general kinetic of isothermal mass gain with the humidity rate of air previously seen are not really found again with this new especially high water vapour content. The oxidized samples will be characterized in the second part^[15] of this work (XRD diffraction, metallography of cross-sections...) in order to try interpreting the present observations done here in the mass variation kinetic field only.

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