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Kinetics and mechanism of high temperature internal oxidation of Ni-14wt%W alloy at 1000°C

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Abstract. Ni-14wt%W model-alloy has been used to study the kinetics and the mechanism of high temperature internal oxidation in presence of an external oxide scale. Oxidations have been done in air at 1000°C for different oxidation times and have allowed the evaluation of the oxidation kinetic from mass gain and from oxide thickness measurements. The oxidation kinetic which follows a parabolic oxidation rate indicates a diffusive behaviour of species during the oxide formation. Cross-section observations by Scanning Electron Microscopy (SEM) and analysis by Grazing Incidence X-Rays Diffraction (GIXRD) show a multi-layered structure of the oxide. Starting from the surface towards the bulk alloy, the scale is layered as follows : (i) a pure nickel oxide (NiO) in the outer part (ii) a porous NiO matrix containing NiWO₄ second phase and (iii) an internal oxidation zone of tungsten, first forming WO₃ sub-micrometer oxides that progressively transform into NiWO₄ oxide precipitates in the alloy.

Introduction

Nickel-Tungsten (Ni-W) alloys are encountered in the development of superconductor substrates (for YBCO deposition) [1,2] as well as in the conception of new Ni-based super-alloys for the Generation IV nuclear plants, where tungsten is introduced in order to improve creep properties [3]. Although in the former, the high temperature oxidation is a benefit for the technological improvement of superconductor devices, in the latter, high temperature oxidation might result in internal oxidation that is known to occur in binary Ni-W alloys without chromium. Such a situation can be envisaged in case of oxide spallation where chromium depleted area would be exposed to the oxidising environment and consequently result in the embrittlement of the substrate [4]. Thus, understanding high temperature oxidation of a binary Ni-W model-alloy is necessary to predict the kinetics of degradation during aging.

Internal oxidation of Ni-W alloys during high temperature oxidation has already been observed by El-Dahshan et al. [5]. In the present study, we propose to update their results in a complementary composition window, corresponding to tungsten content typical of high temperature structural materials, like Haynes 230, for longer oxidation times. Thus, a systematic study of a model-alloy of composition Ni-14wt%W oxidized for different oxidation times at 1000°C in air, have been realized. From the oxidation kinetics and the characterization of the oxide micro-structure evolution, we propose a scenario of the oxide formation based on the diffusive behaviour of species and on the stability of phases formed during the high temperature oxidation.

Materials and experimental procedure

Sample's preparation. The Ni-14wt%W model-alloy rod was prepared from high purity Ni and W by multistep inductive melting under hydrogen containing atmosphere and subsequent hot working at Ecole des Mines de Saint-Etienne. Chemical analysis of this model-alloy have resulted in less

than 6 ppm of C, 5 ppm of S, and 10 ppm of O. X-ray analysis confirmed that there is no phase precipitation in the alloy and that the small amount of W (7 at%) is fully solved in the Ni matrix. Samples were prepared as platelets of 3 mm thickness and 16 mm diameter. Metallographic observations revealed grain sizes in the range 100-300 microns diameter. Before high temperature oxidation, the samples are entirely polished : the circular edge down to P4000 SiC paper and the faces down to 1 micron diamond suspension.

Oxidation's procedure. Oxidations were realized in standard furnaces with temperature fixed to 1000°C for duration of respectively 6 min, 15 min, 1 hour, 3 hours and 120 hours. Weight measurements were done before and after oxidation, in order to establish the oxidation kinetics. Microstructure and phase analysis were done on cross-sections of the oxidized samples using scanning electron microscopy (SEM) with backscattered electrons and energy dispersive X-Ray spectroscopy (EDX). For the shortest oxidation time, Grazing Incident X-Ray Diffraction (GIXRD) analysis was used.

Results and Discussions

Oxidation kinetics. The oxidization kinetics was evaluated from weight measurements realized before and after different oxidation times. The result presented in the Fig. 1 shows that the oxidation process strictly follows a parabolic rate law being thus diffusion controlled. The global rate constant

k_w evaluated as $\left(\frac{\Delta W}{A}\right)^2 = 2k_w t$ is $1.7 \times 10^{-10} \text{ g}^2 \text{ cm}^{-4} \cdot \text{s}^{-1}$. This value is slightly lower than the thermo-

balance based measurements of El-Dahshan *et al.* for similar compositions [5]. This small discrepancy can be attributed either to our experimental procedure where a part of the samples in contact with the alumina support is less oxidized or to the partial evaporation of WO_3 through NiO oxide, as supposed to occur at high temperature [5].

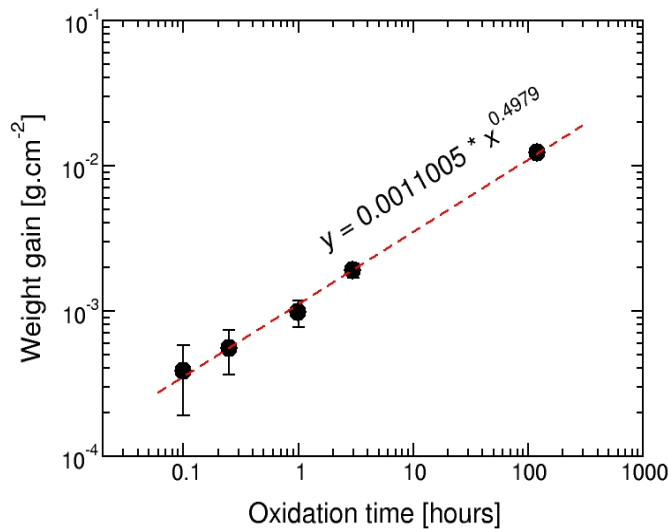


Figure 1: Weight gain during oxidation at 1000°C in air versus the oxidation time of Ni14%wtW model-alloy.

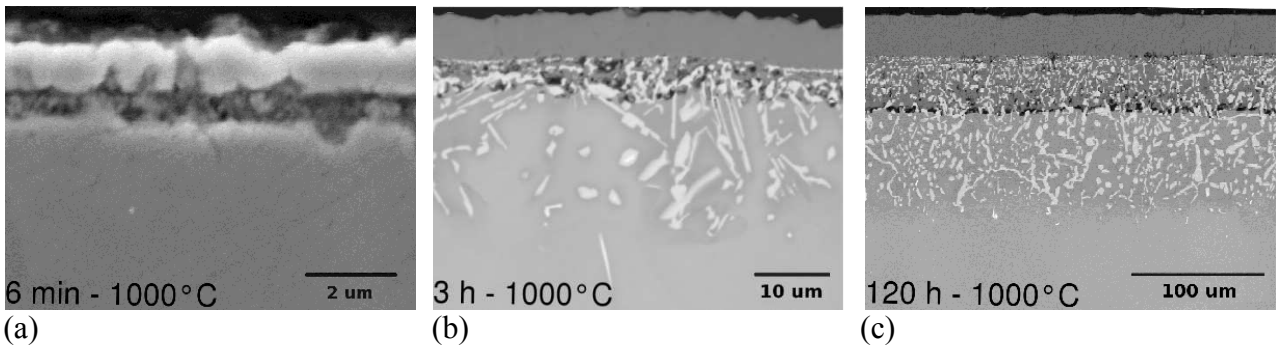


Figure 2: SEM cross-section micrographs of Ni-14wt%W alloy oxidized for 0.1, 3 and 120 hours at 1000°C in air.

Nature of the oxide layers. Fig. 2 presents SEM cross-section views of samples oxidized at 1000°C for 0.1, 3 and 120 hours. For 6 min oxidation time, EDX measurements showed that the surface is covered by a uniform, 1 μm thick NiO film with the underlying, non-uniform and porous sub-layer. The nature of this sub-layer was determined using GIXRD measurements. Fig. 3 presents the corresponding GIXRD diffractograms for 0.75°, 1.5°, 2.5° and Bragg-Brentano incident angles (pie chart on the right corresponds to a quantitative analysis). The smallest incidence angle, corresponding to the lowest X-ray penetration depth, confirms that the upper dense layer is composed of pure NiO oxide. At larger incident angles (deeper X-ray penetration depths), new peaks appearing in the diffractograms indicate the presence of NiWO₄ oxide in the observed sub-layer.

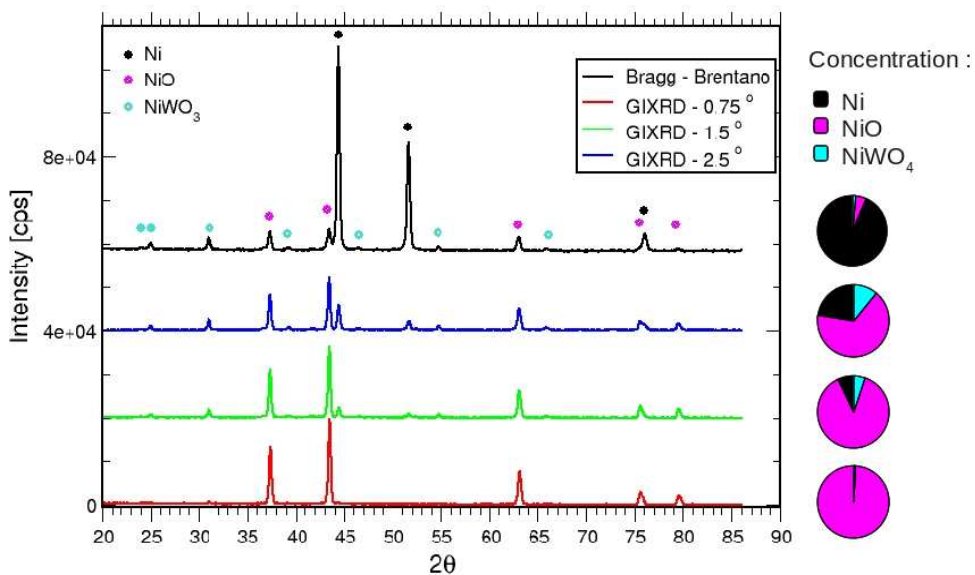


Figure 3: GIXRD diffractograms and quantitative analysis (pie charts) of Ni-14wt%W model-alloy oxidized during 6 min at 1000°C

For longer oxidation times, a multi-layered scale develops on the surface of the Ni-W alloy. Fig. 2b and Fig. 2c present the cross-section observations by SEM for 3 hours and 120 hours oxidation times at 1000°C. Using EDX measurements, different phases formed in the scale, have been characterised. Starting from the surface towards the bulk alloy, the scale is layered as follows : (i) a pure nickel oxide (NiO) in the outer part, (ii) a porous NiO matrix containing NiWO₄ second phases and (iii) a layer of internal oxidation where WO₃ precipitates form at the oxidation front

(white precipitates) and progressively transform into NiWO₄ oxide precipitates in the alloy. In the internal oxidation layer, a tungsten depletion resulting from the formation of the above mentioned precipitates is observed, as evidenced by the SEM cross-sections where a darker contrast in the alloy is associated with less tungsten (Figs. 2b and 2c). These last results were confirmed by Auger Electron Spectroscopy (AES) measurements. In fact AES measurements with 100 nm spot size are not subject to the relatively high beam-matter interaction volume as this is the case for EDX analysis. Consequently, lines scans starting from the Ni-14wt%W matrix indicate a progressive decrease of W content, while approaching oxide precipitates. Moreover, measurement on small, white precipitates at the oxidation front have clearly shown the presence of oxygen and tungsten only, implying the formation of WO₃, as stated above.

Scenario of oxides formation. In order to explain the multi-layered structure of the scale, the relative stability of the formed oxides as well as the diffusion behaviour of Ni, W and O species in the alloy have to be considered. Based on ref. [6], the interdiffusion coefficient of the Ni-W couple in our model-alloy is estimated to be $2.2 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 1000°C where Ni atoms are the fastest diffusing ones resulting in the Kirkendal effect in the structure.

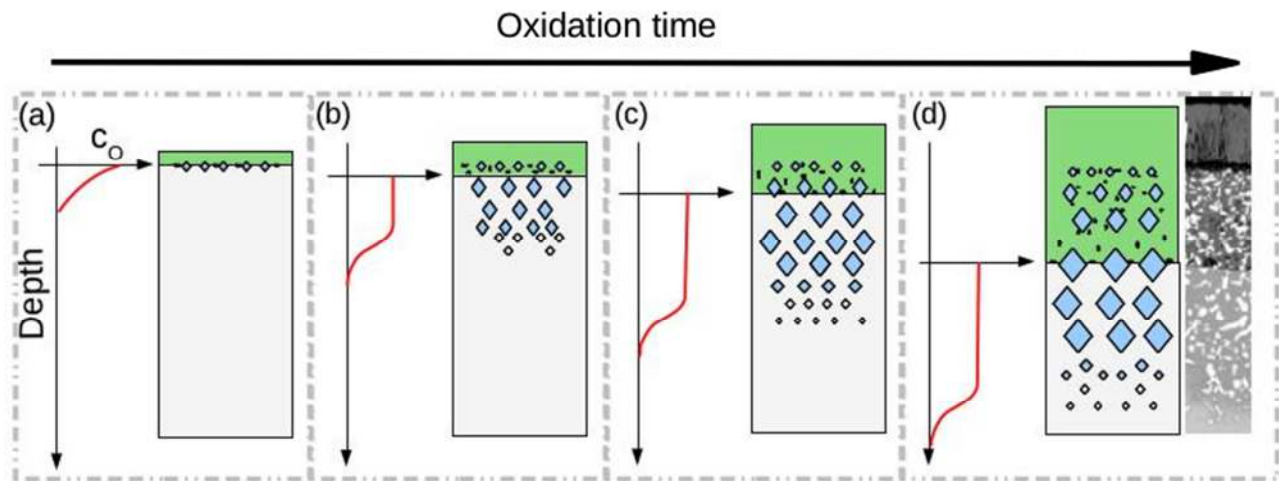


Figure 4: Schematic representation of the oxygen concentration profile in the alloy and scale morphology versus the oxidation time. Green layer corresponds to NiO oxide, white and blue diamond shapes represents the WO₃ and NiWO₄ precipitates forming in the alloy, respectively. The dark blobs surrounding confined precipitates in the NiO oxide represents the porosity. The picture in (d) shows SEM cross-section of a sample oxidized for 120 hours.

The presence of internal oxidation area in the alloy indicates that the oxygen atoms diffuse in the alloy. In our Ni-rich alloy, the oxygen diffusion coefficient can be reasonably estimated by the one corresponding to the diffusion in pure Ni which is equal to $8.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 1000°C [7]. This large difference between the diffusion coefficient of oxygen on the one hand and Ni and W on the other hand implies that the oxygen atoms diffuse in a frozen-like Ni-W matrix. The inward diffusion of oxygen results in the formation of WO₃ oxide precipitates that progressively transform into NiWO₄. According to the Ellingham diagram giving the standard free energy of formation for WO₃, NiWO₄ and NiO oxides, the WO₃ oxide is the most stable one, followed by NiWO₄ and NiO oxides, respectively [8]. Consequently, real Ni and W activities have to be taken into account in order to demonstrate the observed transformation from WO₃ to NiWO₄.

Taking into account all these considerations, the following scenario is proposed for the scale formation. Fig. 4 schematically presents the chronological evolution of the scale formation. At short oxidation times (Fig. 4a), the large amount of Ni (93at%) and its relatively high mobility in

comparison to W imply the formation of an initial NiO oxide layer on the top of the substrate followed by a highly concentrated NiWO₄ sub-layer. The presence of this latter layer is justified by the fact that the mechanism of the NiO oxide formation is cationic-like, i.e. the formation of the dense NiO oxide is dominated by Ni⁺⁺ cations migrating towards the surface to react with oxygen. Note that at short oxidation time, we do not observe WO₃ precipitates : either they are too small to be observed or they are already transformed into NiWO₄. In case of long oxidation times, WO₃ precipitates are only found at the internal oxidation front (Figs 4b to 4d). The internal oxidation layer that is observed at longer oxidation times requires a source of oxygen which dissolves in the alloy. This oxygen source may come from asperities in the NiO oxide which is supposed not perfectly dense as it presents a columnar grain structure (Fig. 2c and ref. [5]). El-Dahshan *et al.* suggest that this columnar-like oxide may result from the evaporation of WO₃ oxide in NiW alloys [5]. Our analysis has shown that WO₃ oxide is not present in the intermediary NiO layer which contains NiWO₄ precipitates. Consequently, the columnar grains structure observed in the upper NiO oxide is not due to the evaporation of a constituent but it more likely results from strain relaxations of this oxide layer during its formation. Such columnar arrangement of the grains in NiO oxide is also observed in the case of high temperature oxidation of pure Ni [9].

Thus, the formation of the multi-layered scale results from two phenomena occurring in the same time: first, the growth of the NiO oxide scale and second, the formation of WO₃, NiWO₄ precipitates due to oxygen diffusion within the alloy. Progressively, the growth of NiO layer consumes Ni from the alloy implying the displacement of the NiO interface that induces trapping of the stable NiWO₄ particles that have previously formed within the alloy. Consequently, the NiWO₄ precipitates trapped in the NiO oxide are larger and larger from the outer to the inner part of the scale. The porosity observed in the NiO layer containing NiWO₄ particles might be due either to the cationic behaviour of the NiO oxide growth and/or to the Kirkendal effect in the Ni-W alloy.

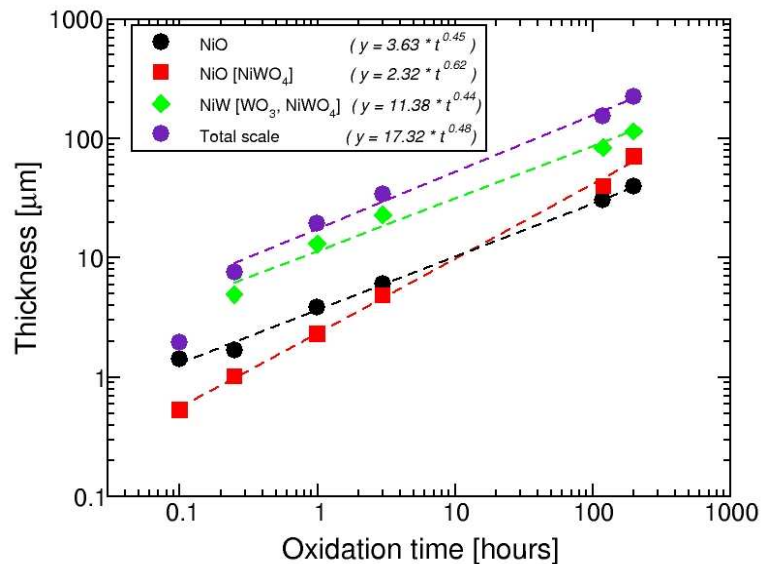


Figure 5: Thickness of the layers during oxidation at 1000^oC in air versus the oxidation time of Ni14%wtW model-alloy.

Evaluation of oxygen diffusion coefficient in the alloy. Fig. 5 presents the evaluation from SEM observations of the thickness of the oxide layers as a function of the oxidation time. Although, the evolution of the total scale thickness strictly follows a parabolic law comforting the fact that the growth is governed by diffusion, the kinetics of the individual layers growth do not follow a parabolic-like law. The NiO layer with NiWO₄ precipitates has a slightly faster kinetics growth than the others that may indicate an anionic contribution in the growth of the former. From the evolution of the internal oxidation layer thickness, which is nearly parabolic, we have evaluated the O

diffusion coefficient in the alloy. Assuming that oxygen is the fastest diffusive species and that the precipitates formation is not a limiting process, the penetration depth of oxygen (internal oxidation) is approximated as $d_0 \approx \sqrt{D_0 t}$. From this assumption, the oxygen diffusion coefficient in the alloy is estimated to $8.7 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$. This result is in good agreement with electrochemical measurements by Park et al. [7] who found $9.14 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ in pure nickel. It justifies the assumption that interdiffusion in the Ni-W alloy is negligible as compared to oxygen diffusion in the alloy.

Summary

High temperature oxidation of Ni-14wt%W model-alloy at 1000°C for different oxidation times has allowed to determine the kinetics and the morphological evolution of the scale formed on the alloy surface. SEM, EDX and GIXRD analysis together with weight increase show that the oxidation kinetics follows a parabolic law. A three layers structure composed of an outer NiO layer, intermediate NiO/NiWO₄ layer and inner internal oxidation layer has been evidenced. The evolution of the micro-structure as a function of the oxidation time is explained on the basis of the internal oxidation process within the alloy. The inward oxygen diffusion results in the formation of WO₃ precipitates that progressively transform into NiWO₄ precipitates. Continuous thickening of the outer NiO oxide results in trapping NiWO₄ precipitates. Oxygen diffusion coefficient within the Ni-W alloy has been determined to be $8.7 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$.

Acknowledgements

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