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Effect of Platinum on the Growth Rate of the Oxide Scale Formed on Cast Nickel Aluminide Intermetallic Alloys

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Thermo-Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) data of the initial stages of oxidation of Ni₅₀Al₅₀ and Ni₄₀Pt₁₀Al₅₀ alloys of low and high sulfur content at 900° C and 1100° C are reported. The results show that the addition of Pt promotes the growth of the transient θ -Al₂O₃ oxide scale. This effect is particularly sensitive in the initial stages of oxidation at 1100° C where Pt considerably increases the total mass gain. It is attenuated in the presence of a high sulfur content in the alloy, indicating a competitive effect of Pt and S on the segregation of Al. The slower θ -to- α transition observed in the presence of Pt leads to an extended lifetime of the θ phase layer, which is proposed to be beneficial to the relaxation of the stresses created by the growth of α -Al₂O₃.

KEY WORDS: nickel aluminide; platinum; sulfur effect; high temperature oxidation; transition alumina.

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INTRODUCTION

Thermal Barrier Coatings (TBC) deposited on high temperature blades in gas turbine applications are of high technological interest since they allow a higher combustion temperature. Their lifetime is often limited by the degradation of the Thermally Grown Oxide (TGO) formed in the interfacial region between the Y_2O_3 -stabilized ZrO_2 ceramic top coat (YSZ) and the β -NiAl intermetallic Bond Coat (BC).¹ Cavities are frequently observed to grow at the interface between the β -NiAl BC and the alumina TGO during oxidation at $900^\circ C$,²⁻⁹ and it was shown by in situ SEM on (Ni, Pd)Al BC that they form in the very early stages of oxidation at $950^\circ C$.¹⁰ The formation of these cavities is quite critical because they decrease the contact area between the intermetallic bond coat (β -NiAl) and the ceramic top coat (YSZ) and can promote the spallation of the TBC. On β -NiAl, it is widely admitted that the alumina scales grow principally by outward diffusion of aluminum at intermediate temperatures (i.e. θ - Al_2O_3 at $\approx 900^\circ C$),^{11,12} or by a combination of inward diffusion of oxygen and outward diffusion of aluminum at higher temperature (i.e. α - Al_2O_3 at $\approx 1100^\circ C$).¹³⁻¹⁵ The interfacial cavities formed at $900^\circ C$ result from the condensation of metallic vacancies injected in the alloy by the growth mechanism of the oxide⁴ or from the non-reciprocal diffusion of the non-oxidized element of the alloy (Kirkendall effect).^{3,16}

The segregation of sulfur impurities present in the alloy at the TGO/BC interface decreases dramatically the oxide adherence.¹⁷⁻²³ It is promoted at the oxide-free surface of the alloy in the interfacial cavities.^{20,21,23} To counteract this detrimental effect, Pt-modified nickel aluminide coatings are commonly used for high temperature oxidation protection of Ni-based superalloys because Pt substantially improves the coating oxidation performance, even in the presence of high level of sulfur impurities.²⁴⁻²⁷ It has been shown recently that the addition of Pt reduces the formation of the interfacial cavities during oxidation at $900^\circ C$ by a factor of 4-5 and decreases drastically the amount of sulfur segregated to the surface of the alloy.²⁸

We report here an investigation of the role of Pt at two temperatures ($900^\circ C$ and $1100^\circ C$) for which the growth mechanisms of the oxide scales differ. The transition between two regimes which occurs in the initial stages of oxidation at $1100^\circ C$ was also investigated. Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) observations performed on single-crystals of $Ni_{40}Pt_{10}Al_{50}$ and $Ni_{50}Al_{50}$ (at.%) containing different levels of sulfur impurities were combined.

EXPERIMENTAL

Materials

Single crystals of $\text{Ni}_{50}\text{Al}_{50}$ and $\text{Ni}_{40}\text{Pt}_{10}\text{Al}_{50}$ (at.%), doped with different sulfur concentrations, were grown at the ONERA in the form of cylindrical rods with a cross section of 8mm. The bulk sulfur content of the samples was measured by Glow Discharge Mass Spectroscopy (Shiva Technology, Toulouse, France). Low sulfur alloys (< 1ppmw) were also produced by annealing under hydrogen during 100hr at 1200° C. The composition and sulfur content of the substrate materials used in this study are summarized in Table I.

After orientation along the [001] direction with a precision of $\pm 1^\circ$ by Laue back-diffraction, the rods were cut by spark erosion in 1mm thick disk samples. Prior to oxidation, their surfaces were mechanically polished down to a final grade of 5 μm and cleaned ultrasonically first in acetone and then in ethanol.

Analysis

The thermogravimetric tests were performed on a "SETARAM™ TAG 24S" thermobalance of sensitivity better than 1 μg . This thermobalance makes use of a double symmetrical furnace designed to compensate all signal perturbations resulting from gas flow, buoyancy and convection. It is well adapted to the accurate measurement of small mass changes occurring during short oxidation tests or induced by very slow-growing oxide scales such as the alumina scales formed on nickel aluminide substrates.

Two types of experiments were performed in this study. In the first one, the four samples were oxidized directly at 1100° C, with a heating rate of 60° C. min^{-1} . In the other one, the four samples were oxidized first at 900° C until a 500nm thick alumina scale was formed, and then at 1100° C during 15hr (heating rate of 60° C. min^{-1}). All oxidation experiments were conducted under 1atm of pure oxygen with a gas flow of 30 $\text{cm}^3 \text{min}^{-1}$. Since most of the experimental data did not follow simple

Table I. Composition and Sulfur Content of the Single-crystalline Cast Nickel Aluminide Alloys Used in this Study

Composition (%at.)	Sulfur concentration (ppm weight)	Polishing	Orientation
$\text{Ni}_{50}\text{Al}_{50}$	< 1(0.7)		
	57	4000-grit SiC (□ 5 μm)	(001)
$\text{Ni}_{40}\text{Pt}_{10}\text{Al}_{50}$	< 1(0.4)		
	90		

parabolic kinetics but included a transient oxidation stage at the beginning of the test, the parabolic constant k_p was extracted from the mass gain data using the local fitting of the general parabolic law.²⁹ This ensures the accurate determination of the instantaneous parabolic rate constant (k_p), once parabolic kinetics is established after a transient stage of oxidation.

The SEM analysis was performed on a GEMINI982 operated at 5kV with a secondary electron detector. Measurements were performed on the oxide scales and on the alloy surface revealed in microscopic local areas spalled during sample cooling.

Results

Isothermal Oxidation at 900° C

Figure 1 shows the time dependence of the parabolic rate constant k_p measured during isothermal oxidation at 900° C. After formation of a 500nm thick oxide scale, the temperature was set to 1100° C. The corresponding results are reported further on. All samples, except $Ni_{50}Al_{50}$ ($S = 57$ ppmw), show a rather constant k_p value, which is indicative of a stationary oxidation regime. In the case of the $Ni_{50}Al_{50}$ ($S = 57$ ppmw) alloy, peaks are observed after 3hr of oxidation. They are assigned to the spallation and reformation of the oxide scale. Table II reports the average values of the k_p measured at 900° C during the growth of 0.5 μ m

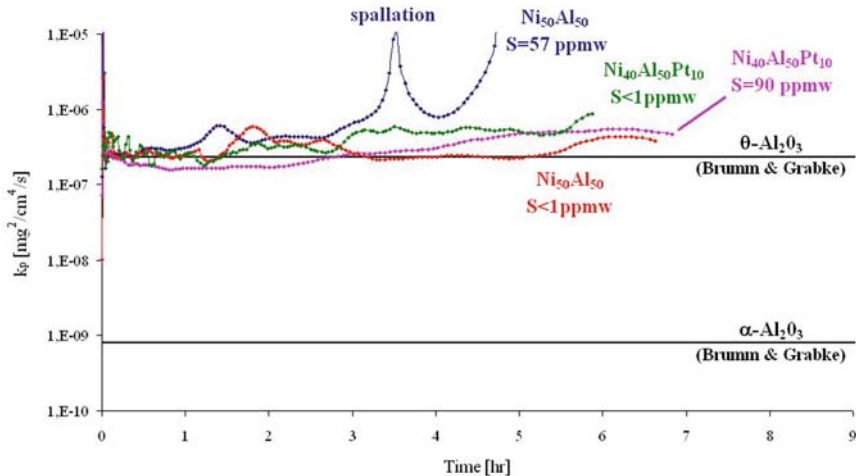


Fig. 1. Time dependence of the parabolic rate constant k_p during isothermal oxidation at 900° C. Values from Brumm & Grabke³⁹ are shown for comparison.

Table II. Average Values of the Parabolic Rate Constant k_p Measured During Isothermal Oxidation at 900° C

Composition (% at.)	Sulfur content	k_p ($\text{mg}^2/\text{cm}^4/\text{s}^1$)
Ni ₅₀ Al ₅₀	S< 1ppmw	2.8×10^{-7}
Ni ₄₀ Pt ₁₀ Al ₅₀	S< 1ppmw	5.1×10^{-7}
Ni ₅₀ Al ₅₀	S= 57ppmw	3.0×10^{-7}
Ni ₄₀ Pt ₁₀ Al ₅₀	S= 90ppmw	4.4×10^{-7}

thick oxide. The calculated parabolic constant k_p are similar for all samples (before spallation for the Ni₅₀Al₅₀ with S= 57ppmw sample). The obtained values are in good agreement with literature data from Brumm and Grabke³⁹ for the growth of θ -Al₂O₃ (see also Fig. 1). Note that the two alloys containing platinum have a slightly faster (by a factor of 1.5–1.8) oxidation kinetics.

The SEM micrographs recorded after 10 hr of isothermal oxidation at 900° C (for a different oxidation test than that shown in Figure 1) are shown in Figure 2. The growth of short and thin whiskers or platelets is observed at the surface of the oxide. This is typical for an oxide growing predominantly at the oxide/gas interface as the result of an outward cation diffusion process, as expected for the growth of the transient alumina θ -Al₂O₃ in this temperature regime^{11,12,30,31}. It can be seen that the oxide morphology is essentially the same for the Pt-modified nickel aluminide alloy, even in the presence of a high sulfur content.

Figure 3 shows the morphology of the alloy surface in microscopic local spalled areas. Spallation in these isothermal experiments results from the development, during sample cooling, of stresses induced by the thermal expansion mismatch between metal ($15.6 \times 10^{-6}/^\circ\text{C}$ for NiAl at 1100° C³²) and oxide ($10 \times 10^{-6}/^\circ\text{C}$ for Al₂O₃ at 1100° C³³) that have been shown to be a crucial cause of spallation of the alumina scale.³⁴

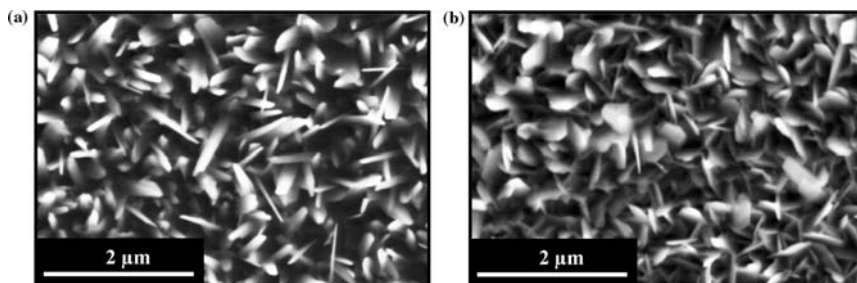


Fig. 2. SEM images of the oxide scale after 10 hr of oxidation at 900° C. (a) Ni₅₀Al₅₀ (S< 1 ppmw), (b) Ni₄₀Pt₁₀Al₅₀ (S= 90ppmw).

Such spalled areas reveal the morphology of the alloy surface underneath the oxide scale. Cavities are observed, in agreement with previous observations for this oxidation temperature.²⁻⁹ Less stress is expected in the oxide scale during the growth by outward cationic diffusion because the new oxide has enough space to grow at the oxide/gas interface. For an oxide scale growing by cationic diffusion, the formation of the observed interfacial cavities may result from the injection and condensation of the metallic vacancies in the alloy surface underneath the oxide.^{4,35} This is consistent with the growth of θ -Al₂O₃ on β -NiAl at 900° C. The observed effect of Pt is to reduce the volume of the cavities formed underneath the oxide. This result has been described in more details previously.²⁸

These isothermal oxidation experiments performed at 900° C confirm the growth, by cationic outward diffusion, of a transient alumina scale assigned to θ -Al₂O₃. The k_p measurements indicate that the scale grows faster than the stable α -Al₂O₃ polymorph (see Fig. 1) and is promoted by the presence of Pt in the alloy. At first sight, the formation of this faster growing oxide does not seem particularly advantageous because this metastable alumina is less protective than the final α -alumina polymorph formed at 1100° C. Moreover, the formation of the interfacial cavities during the growth of θ -Al₂O₃ is known to promote the segregation of sulfur impurities on the metallic surface,^{4,22,23} which is expected to be detrimental to the oxide scale adhesion. However, we have shown previously that the total volume of cavities is lower in the presence of Pt.²⁸

Isothermal Oxidation at 1100° C

The net mass gain curves obtained at 1100° C for the two alloys containing a low level of sulfur ($S < 1$ ppmw) are shown in Fig. 4. They clearly show that the addition of Pt increases the scale growth rate, since

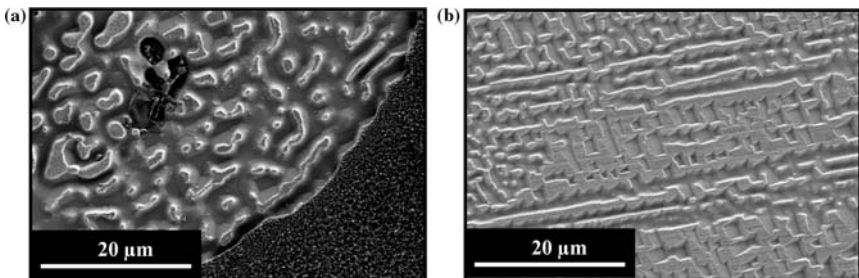


Fig. 3. SEM images of locally spalled areas after 10 hr of oxidation at 900° C. (a) Ni₅₀Al₅₀ ($S < 1$ ppmw), (b) Ni₄₀Pt₁₀Al₅₀ ($S = 90$ ppmw).