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THERMOGRAVIMETRIC ANALYSIS OF SUPERALLOYS USED FOR BLADE AND VANE APPLICATIONS IN INDUSTRIAL GAS TURBINE
Kinetics and mechanism of thermal degradation

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Abstract

The thermogravimetric analysis is the most suitable technique to study the effect of reactive gas on nickel-base superalloys used in high temperature zone for industrial gas turbines. This work presents the results of behaviour of superalloys IN 738, IN 792 and MA 6000 under environmental conditions simulating those of service in a power plant. The kinetics and the mechanism of environmental degradation on the integrity of turbine blades and vanes are discussed with reference to component performance and lifetime.

Keywords: gas turbines, kinetics, oxidation, superalloys, thermogravimetric analysis

Introduction

The development of gas turbines for power plants is strongly dependent on the use of new materials which can tolerate increasingly more severe service conditions, without suffering a structural degradation [1]. The materials employed for turbine blades are generally Co- or Ni-based alloys whose high temperature mechanical properties are provided by the presence of γ phase with γ' precipitate (Ni_3Al, $Ni_3(Al,Ti,Nb)$) [2–6]. This class of materials is generally called superalloys. A considerable amount of Cr is added to achieve corrosion resistance through the development of a protective Cr_2O_3 surface scale. Generally the presence of Al does not lead to the formation of Al_2O_3 scale even if thermodynamically favoured [7]. The Al_2O_3 scale does not form because the oxidation process is determined by the diffusion laws rather than by chemical potentials.

In the last years greater efforts have been devoted to increase the mechanical properties by adding solid solution strengtheners without particular attentions to

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chemical reactions with the aggressive service atmosphere. This mechanical property improvement has been accompanied generally by a marked decrease in the corrosion resistance, due to a reduced Cr content [8], leading to a marked reduction in the lifetime.

Actual service conditions involve aggressive atmosphere and temperature higher than 900°C; in these conditions the most active degradation process is metal oxidation [9]. This work shows the experimental result of the oxidation behaviour of Ni-base superalloys IN 738, IN 792 and MA 6000 in order to study the lifetime in environmental conditions simulating those of service in a power plant.

Experimental

The materials investigated in this study are superalloys currently used in gas turbine hot zones; in particular they are employed for the fabrication of first stage blades. The IN 738 and IN 792 are conventionally cast superalloys whereas MA 6000 is an oxide dispersion strengthened superalloy (ODS) produced using advanced powder metallurgy production routes.

Samples were obtained from rods in the metallurgical condition whose nominal compositions are reported in Table 1. The surface of all the studied specimens was ground and polished up to 600 papers and then samples were kept in an inert atmosphere before oxidation treatments.

The research has been carried out by studying the oxidation resistance in a temperature range between 900 and 1000°C, in static dry air at ambient pressure, following the evolution of degrading processes up to 1000 h.

Kinetic data were obtained by a thermogravimetric analyzer during the first 50 h of isothermal treatment. For longer time (up to 1000 h) specimens were treated using an electric oven and cooled and weighted at approximately 100 h intervals. The morphology and the distribution of chemical elements of the heat treated samples were studied using Scanning Electron Microscopy (SEM-EPMA), whereas X-ray Diffraction (XRD) was used to follow the growth of oxide phases.

Results and discussion

In Fig. 1a are reported the thermogravimetric curves of specimens isothermally treated at 900°C. The IN 792 superalloy exhibits a continuous weight gain during the first 31 h, with an oxidation rate that follows an exponential law. Subsequently the oxidation rate decreases until about 40 h, and then it increases again. This behaviour is due to the formation, during the initial stage of treatment, of a well adherent oxide scale that covers the metal surface, decreasing the oxidation rate.

After that, at about 40 h, there is an increase in the oxidation rate probably due to cracking of the oxide scale. Afterwards this phenomenon tends to extinguish. Figure 1b shows the oxidation rate of the other two tested superalloys on a higher weight gain scale. Even if the weight gain is ten times lower, changes

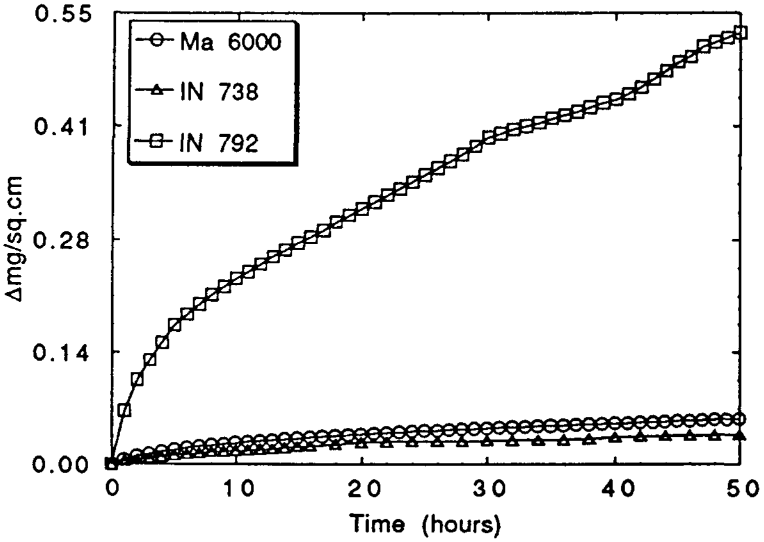

Fig. 1a Oxidation rate at 900°C

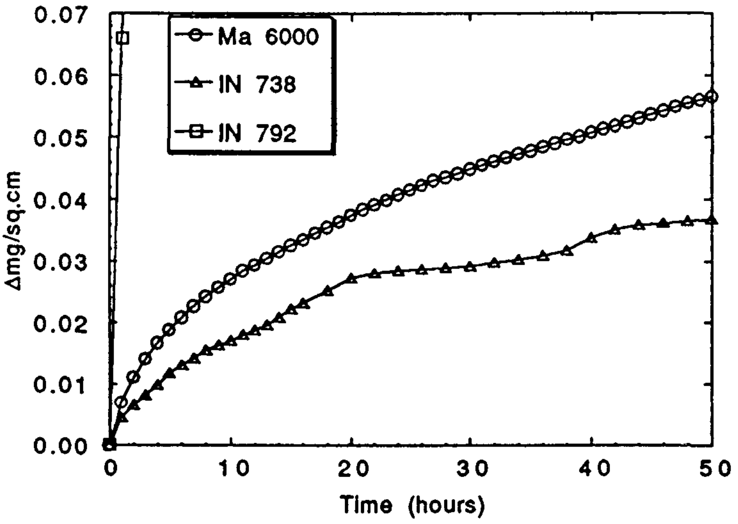

Fig. 1b Oxidation rate at 900°C

Table 1 Compositions of superalloys, wt% (Bal.=balance)

Alloy	C	Cr	Ni	Co	Mo	W	Nb	Ta	Ti	Y_2O_3	Al	Zr
IN 738	0.17	16.00	Bal.	8.50	1.70	2.60	0.90	1.70	3.40	0.00	3.40	0.10
IN 792	0.10	12.00	Bal.	8.50	1.65	3.85	0.50	3.85	3.75	0.00	3.15	0.01
MA 6000	0.04	15.10	Bal.	0.02	1.99	3.97	0.00	2.07	2.54	1.06	4.50	0.16

Table 2 Crystalline phases produced by thermal treatments

Alloy	Test	Oxide thickness	Main developed phases
IN 738	50 h at 900°C	3 micron	Cr_2O_3, TiO_2, $(Cr, Ti, Ta, Nb)O_2$
IN 792	50 h at 900°C	9 micron	Cr_2O_3, TiO_2, TaO_2, NbO_2
MA 6000	50 h at 900°C	6 micron	Cr_2O_3, TiO_2, $(Cr, Ti, Ta, Nb)O_2$
IN 738	50 h at 1000°C	12 micron	Cr_2O_3, TiO_2, $(Cr, Ti, Ta, Nb)O_2$
IN 792	50 h at 1000°C	13 micron	Cr_2O_3, TiO_2, TaO_2, NbO_2
MA 6000	50 h at 1000°C	13 micron	Al_2O_3, Cr_2O_3, $(Cr, Ti, Ta, Nb)O_2$
IN 738	1000 h at 1000°C	88 micron	Cr_2O_3, $Cr(Ta, Nb)O_4$, $(Cr, Ti)O_2$
IN 792	1000 h at 1000°C	58 micron*	Cr_2O_3, $CoNiO_4$, TiO_2, $NiTiO_3$
MA 6000	1000 h at 1000°C	40 micron	Al_2O_3, $Cr(Ta, Nb)O_4$, $(Cr, Ti, Ta, Nb)O_2$

*Loss of scale due to evaporation.

in the trends are still present due to the same mechanism described before. Results of the thermogravimetric analysis of the superalloys isothermally treated at 1000°C are reported in Fig. 2. In this case the oxidation rate is similar for the three studied materials.

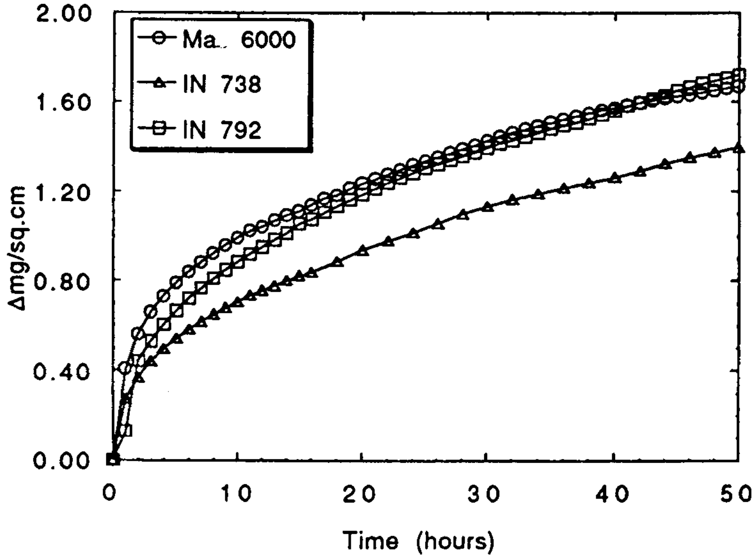

Fig. 2 Oxidation rate at 1000°C

To obtain a comprehensive understanding of the high temperature degradation process it was useful to evaluate the reaction mechanism and the activation energy from the thermogravimetric data for a wide temperature range. Several analytical curves were tested to model the data; finally, the best result, for all samples and treatments, was achieved fitting the following equation:

$$\frac{dx}{dt}=\frac{K_p'}{x}$$

where x is the weight gain (mg/cm^2), t is time and K_p' is a rate constant. After integration, the following parabolic relation results

$$x^2=2K_p't+C=K_p\,t+C$$

where K_p and C are constants. Following the Wagner's theory [10], high temperature parabolic oxidation means that the rate is controlled by a thermal diffusion process. Such a process may include a uniform diffusion of one or both of the reactants through a growing compact scale, or a uniform diffusion of the gaseous reactant into the superalloy.

In order to check the proposed model, the gravimetric data obtained at 800, 900, 950, and 1000°C were plotted using an x^2 *vs.* time representation, to verify that data lie on a straight line, whose slope is K_p. As shown in Fig. 3, the activation energy of the oxidation process can be obtained from K_p values calculated at different temperatures of thermal treatment, using an Arrhenius equation:

$$K = K_o \exp(-E_a/RT)$$

The following values were obtained for the activation energy of the oxidation process during the first 50 h: E_a = 260.1 kJ/mol (IN 792); E_a = 251.1 kJ/mol (IN 738); E_a = 298.3 kJ/mol (MA 6000).

XRD and SEM/EPMA were used to study structure, morphology and spatial distribution of the crystalline phases developed during the thermal treatments. The results are summarized in Table 2.

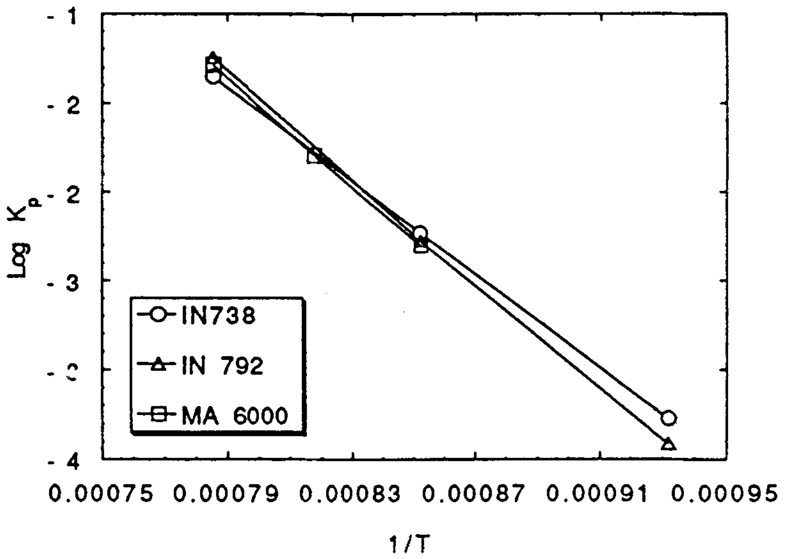

Fig. 3 Arrhenius plot

The heat treated superalloys produce different thickness oxide due to different oxidation rate, but in all cases the surface scale was made up of three different layers. The outer one was thin and rich of Titanium and Tantalum oxides, whereas the layer below was thick, mainly composed of Chromium oxide, with traces of Niobium, Iron and Titanium oxides. The third, innermost layer was close to the interface between metallic matrix and oxide scale; Titanium and Tantalum oxides were found inside it. Underneath the oxide scale and inside the metal matrix an internal oxidation is also present with development of Al and Ti-oxide rich clusters. As an example Fig. 4 shows the cross section of a MA 6000 sample heat treated 50 h at 1000°C and Fig. 5 the relative XRD analysis.

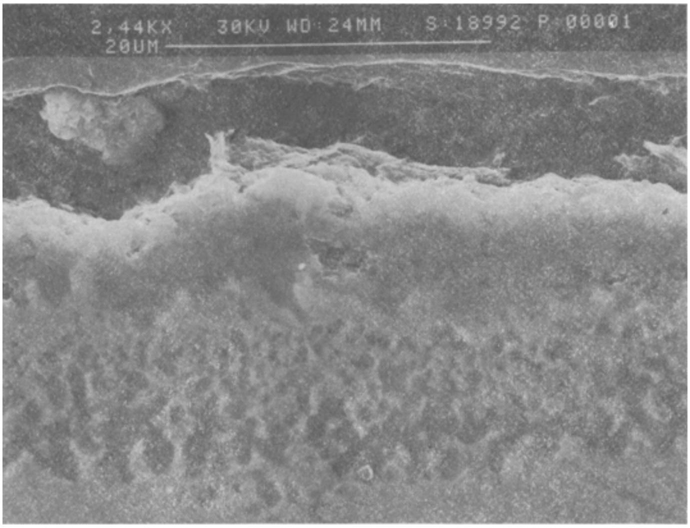

Fig. 4 Cross section of MA 6000 treated 50 h at 1000°C

As demonstrated by XRD measurements, the main difference among the three superalloys concerns the formation of pure oxides: IN 792 formed pure oxides, whereas IN 738 and MA 6000 formed mixed oxides, with rutile- and spinel-like structures. Inside the metallic matrix, near the metal-oxide interface, several clusters were observed in all the studied materials. This occurrence is associated both with an impoverishment in the interfacial region of chemical elements that diffused toward the surface, and with an internal oxidation. These structural modifications are highly detrimental, because they lead to a lowering of the mechanical strength of the superalloys.

As shown by the thermogravimetric results reported in Fig. 6, the behaviour of the three superalloys during 1000 h heat treatment at 1000°C is completely different. After an initial weight gain due to oxidation, IN 792 exhibits a marked weight loss. This behaviour is due to the growth of pure Cr_2O_3, that tends to oxidize and vaporize above 950°C [11], following the reaction:

$$1/2Cr_2O_3(s) + 3/4\ O_2 = CrO_3(g)$$

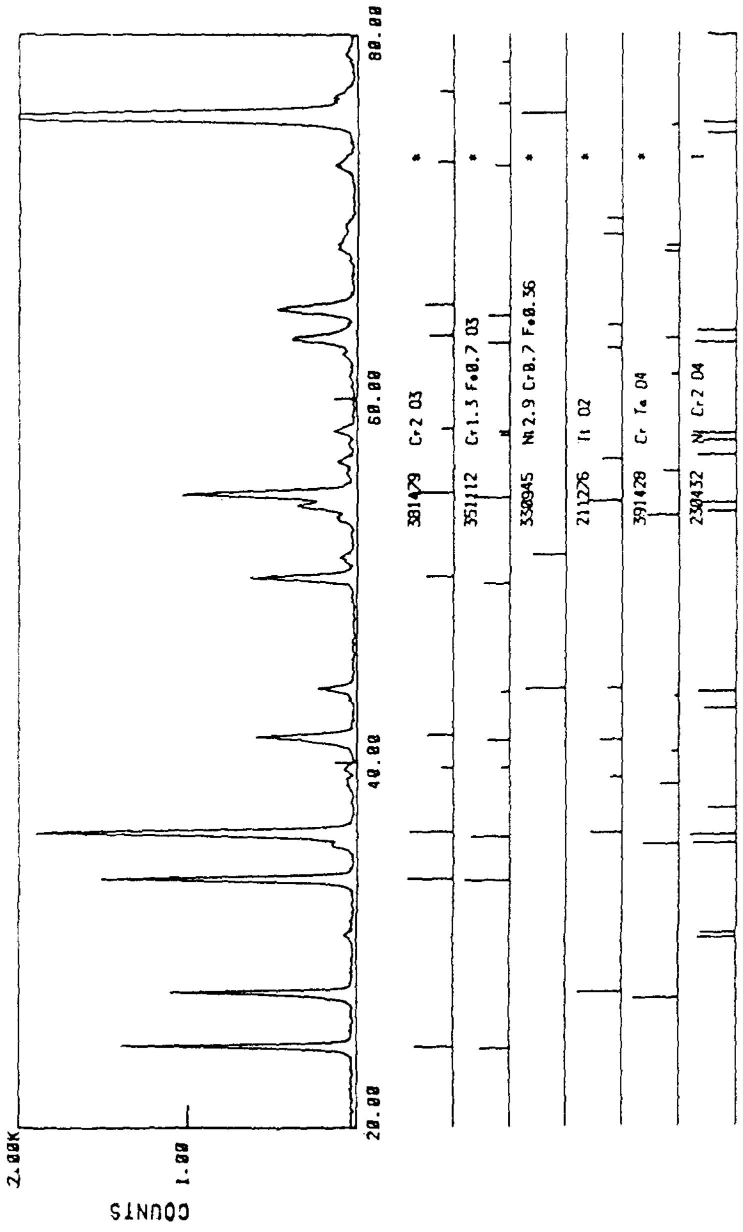

Fig. 5 XRD pattern of MA 6000 treated 50 h at 1000°C

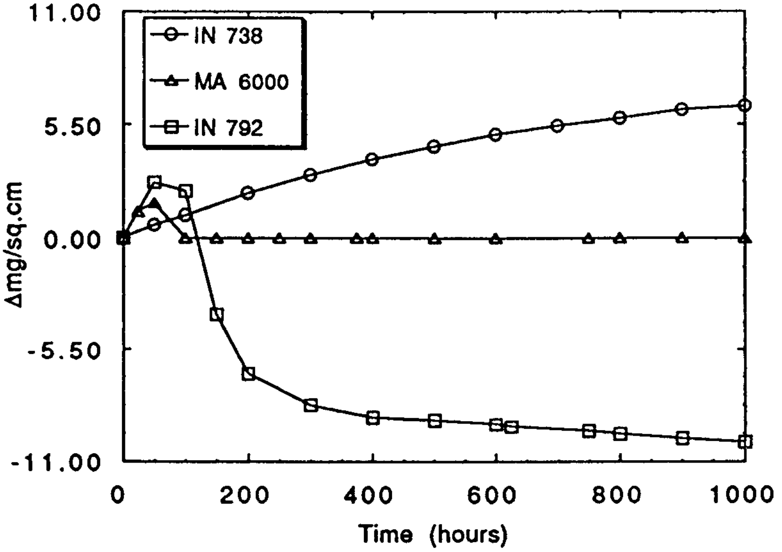

Fig. 6 Oxidation rate at 1000°C

The progressive evaporation of the surface scale leads to a remarkable internal oxidation of the metallic matrix, with a consequent structural degradation.

On the contrary, IN 738 forms a more stable oxide scale because of the formation on the surface of mixed oxides with spinel-like structure, whose evaporation temperature is beyond 1800°C. In spite of the fast oxidation kinetic, the structural damage is reduced by the protective scale that works as a diffusion barrier.

The oxide scale grown onto MA 6000 is even more effective: after an initial growth of external Cr_2O_3 that tends to evaporate, the metal matrix internal oxidation develops a well compact and effective Al_2O_3 scale that is very stable and active as a barrier against the diffusion of anions and cations. This behaviour is attributable at the effective role of Y_2O_3, that diffuses at grain boundary and reduces the Cr^{3+} outward diffusion allowing only an inward O^{2-} diffusion with formation of the more chemically stable Al_2O_3.

Conclusions

The thermogravimetric analysis during the first 50 h at 1000°C showed that the kinetic of the initial stage of oxidation follows a parabolic law for all the studied superalloys. This suggests that the diffusion of anions and cations through the surface scale formed during the initial stage of heat treatment is rate determining.

The activation energies for IN 738 and IN 792 superalloys were comparable, because the values are strongly influenced by the initial oxide growth, which was similar for the two materials, whereas the activation energy for MA 6000 was higher due to its better oxidation resistance.

The structural and thermogravimetric study of treatments up to 1000 h suggests that the chemical composition of the oxide scale formed during the early hours plays an important role. IN 738 formed a surface scale composed of mixed chromium, niobium and tantalum oxides with spinel-like structure which are thermally stable. On the contrary, IN 792 formed a pure Chromia layer that evaporated at the treatment temperature; without a surface diffusion barrier the material suffered a remarkable internal oxidation, with a consequent structural damage. MA 6000 gave the best result because, after an initial evaporation of Chromium oxide, a stable Alumina scale formed, which was effective in reducing the degradation process caused by oxidation.

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Zusammenfassung — Die TG ist die am besten geeignetste Technik zur Untersuchung des Einflusses reaktiver Gase auf Nickel-Superlegierungen, wie sie in der Hochtemperaturregion von Industrie-Gasturbinen verwendet werden. Vorliegend werden die Resultate einer Untersuchung des Verhaltens der Superlegierungen IN 738, IN 792 und MA 6000 unter Umweltbedingungen dargelegt, welche den Betrieb in einem Kraftwerk simulieren. Hinsichtlich Leistung und Lebensdauer werden Kinetik und Mechanismus der auf diese Weise verursachten Herabsetzung von Integrität der Turbinenschaufeln und -flügel diskutiert.