On the Mutual Interaction between Mechanical Stresses and Internal Corrosion during Isothermal and Cyclic Oxidation of Nickel-Base Superalloys

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Abstract. Thermal cycling has been observed to cause a transition from superficial alumina formation to internal oxidation and nitridation, an effect that was shown to depend on the specimen thickness and geometry, which can be described by a spalling-probability model. Once protection by a dense and adherent alumina scale got lost, the internal-corrosion rate is determined by the diffusivity and solubility of nitrogen and oxygen in the alloy. These parameters seem to depend not only on the temperature and the alloy composition but also on the applied mechanical stress. Internal nitridation under a superimposed creep loading was found to follow a higher rate constant than under just isothermal exposure. This effect can probably be attributed to dislocation-pipe diffusion, a mechanism which has been claimed also to be relevant for outward solvent diffusion during internal corrosion, a phenomenon, which was observed as a stress-relief mechanism during various internal-reaction processes

Introduction

Nickel-based superalloys are designed to withstand loading conditions at high temperatures where static or cyclic mechanical stresses are superimposed by corrosive attack from the atmosphere. Structural-integrity concepts for systems that have to survive several ten thousands hours in service, e.g. land-based gas turbines or heat exchangers, require the extrapolation of creep, fatigue and high-temperature corrosion data, which are obtained usually from short-term tests under more severe conditions. Here, the focus is mostly being placed either on the mechanical response or on the surface degradation due to aggressive atmospheres. This may cause a non-conservative design for conditions, where mechanical stresses and the high-temperature-corrosion mechanism interact.

Even though, the general implications of mechanical stresses during the growth of oxide scales are known and reviewed, e.g., by Evans [1], the complex relationships between the phase stability, internal and external corrosion mechanisms and applied mechanical loads are hardly to predict in a quantitative manner. Prediction is made even more difficult, when taking into account that variations in the chronology of the occurrence of mechanical loading and corrosion attack might completely alter the overall damage process. At very high temperatures, solid-state diffusion of both the corrosive species and the metallic alloying elements is the key issue of high-temperature degradation. It was shown by O^{18} tracer measurements on creep-loaded Ni and Zr (Zircaloy 4) [2,3] that tensile stresses lead to an increase in the diffusivities . The consequence is a change in the oxide-scale-growth mechanism as it was shown, e.g., by Calvarin-Almiri et al. [4] for chromia-forming Ni-20Cr foils. On the other hand, high-temperature-corrosion attack strongly deteriorates the mechanical properties of Ni-based superalloys. This was, e.g., shown by Dryepondt et al. [5] for a single-crystalline Ni-base superalloy. They attribute this degradation not only to the reduction in the load-carrying cross section by superficial oxide-scale formation and internal corrosion but also to an enhanced dissolution of the γ' phase and the injection of vacancies into the surface.

Beside the effect of applied creep loading, the mechanical integrity of the oxide scale itself is of substantial significance for the long-term performance of high-temperature components. Often, thermal-cycling loading conditions lead to repeated cracking and/or spalling of superficial oxide scales. This kind of damage may result in a depletion of the oxide-forming element, being particularly pronounced in the case of thin-walled components or cracks [6,7]. Once the concentration of the oxide-forming element has fallen below a critical value, a strong acceleration of high-temperature corrosion can be observed due to the formation of an oxide of higher k_p and the onset of massive internal oxidation and/or nitridation. This process is often referred to as "breakaway oxidation", cf. [8]. As it is also shown in the present paper, the relationship between the high-temperature-corrosion behavior and thermal-cycling conditions depends strongly on the specimen geometry and thickness, the cycle duration, and the kind of oxide being formed. This was the reason why a draft of a standard for cyclic oxidation testing was developed within the framework of the European project COTEST (http://cotest.dechema.de). However, reliable prediction of cyclic oxidation is hardly possible; probably the most promising approaches were suggested by Poquillon and Monceau [9] (probabilistic spalling model) and by Smialek [10] (deterministic interfacial oxidation spalling program, DICOSM) taking partial spalling of the superficial oxide into account. The situation becomes even more complex, if thermal cycling in combination with creep loading occurs. This was recently shown to strongly increase the steady-state creep rate in a superalloy, where a significant dissolution of the γ' precipitates occurred during the high-temperature dwell times [11].

Once internal corrosion has set in, additional factors have to be taken into consideration: The higher specific volume of the internal precipitates as compared to the substrate causes the generation of residual compressive stresses in the surface layer. These stresses may (i) induce tensile stresses in the superficial oxide [12] or (ii) act as driving force for outward diffusion of the non-reacting solvent atoms by Nabarro-Herring creep and/or dislocation pipe diffusion [13,14].

For the example of two commercial Ni-base superalloys the present paper illustrates the complexity of mutual interactions between oxide-scale formation, internal corrosion and the occurrence of mechanical stresses and provides a summary of the aspects to be considered for physically-based concepts of service-life assessment.

Experimental

Studies on oxide-scale integrity and internal corrosion were carried out on two commercial Ni-base superalloys, the chromia-forming polycrystalline Alloy 80A and the single-crystalline alumina-forming alloy CMSX-4. The chemical compositions of them are given in Table 1.

Table.1 Chemical composition of the Ni-base superalloys Alloy 80A (Nicrofer 7520 Ti) and CMSX-4 (in wt.%)

	Ni	Cr	Al	Ti	Co	Ta	Mo	W	Re	Hf	S	C
Alloy 80A	(75.2)	20.2	1.6	2.7	0.01	--	--	--	--		20ppm	0.045
CMSX-4	(67.1)	6.0	5.6	1.0	10.0	6.0	0.6	6.0	3.0	0.1	<12ppm	

Both isothermal/cyclic thermogravimetric (TGA) measurements as well as creep tests were carried out in temperature ranges between *T*=850-900°C (creep) and *T*=1000°C-1100°C (TGA) using self-designed systems, which are schematically represented in Fig. 1. To establish a low-$p(O_2)$ nitriding atmosphere an electronically-controlled gas mixture (N_2-45 Vol.-% He-5 Vol.-% H_2) is fed through a package of porous titanium sponge, which acts as an oxygen getter.

The superimposition of thermal cycles during continuous TGA is established by means of a specimen-lift device, by which the specimens (small polished discs or wedge-type specimens) are removed for defined time intervals from the hot furnace area into a cooling zone, and vice versa (cf. Fig. 1a).

Some of the creep tests were carried out on polished specimens with stepwise modified cross sections (cf. Fig. 1b) to allow a correlation between different values of creep strain and the corresponding internal-nitridation attack on one single specimen.

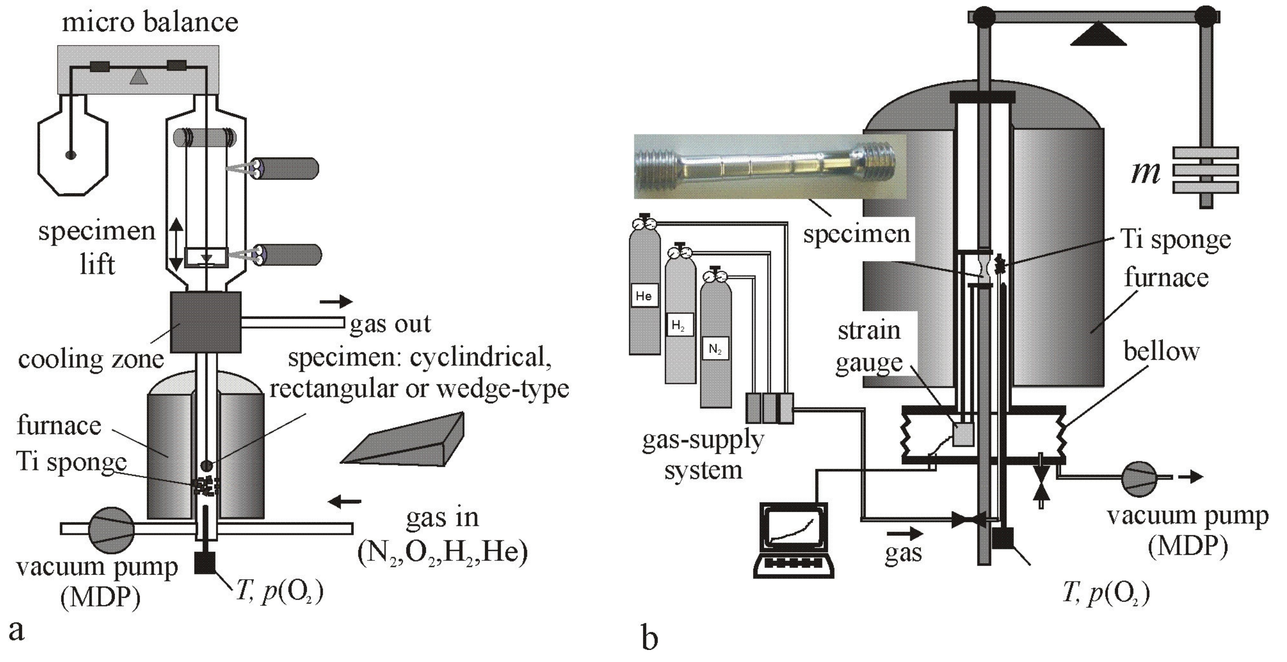

Fig. 1. Schematic representation of (a) the thermobalance used for TGA under isothermal and thermal cycling conditions on cylindrical and wedge-type specimens and (b) the creep machine for creep tests in defined gas atmospheres.

Internal Nitridation and Mechanical Stresses during Isothermal Exposure with and without Applied Creep Loading

Exposure of Ti- and/or Al-containing Ni-base superalloys in nitrogen-based atmospheres (air or at very low $p(O_2)$) results in the formation of internal nitrides. The introduction of additional phases with new interfaces gives rise to changes in the diffusion kinetics. Due to the higher specific volume of the nitrides as compared to the Ni-base matrix, compressive stresses are generated within the surface layer acting as driving force for an outward diffusive flux of the non-reacting matrix atoms. This kind of diffusion manifests itself in the formation of surface protrusions with the chemical composition of the non-reacting solvent on top of the surface, as it is shown in Fig. 2, and as it was observed in several studies on internal oxidation and nitridation, e.g. [13,14]. Nabarro-Herring creep, dislocation-pipe diffusion and grain-boundary sliding were suggested to be most relevant for the diffusive flux but it turned out to be extremely difficult to distinguish between the contributions of bulk, interfacial or pipe diffusion and to estimate the flux-blocking effect of the precipitates themselves.

The stresses generated by the internal precipitation process can be superimposed by applied creep loading. For the case of internal nitridation it was shown that the higher the creep strain or stress the higher is the internal nitridation depth (cf. Fig. 3) [15,16]. A pronounced coverage of the specimens by surface protrusions was never observed, hinting to the fact that the residual compressive stresses are compensated by the tensile creep stress. With respect to creep damage, so far no beneficial effect of the nitrides was observed. Rather, the preferential precipitation of nitrides along the alloy grain boundaries promotes the occurrence of brittle intergranular cracking.

It is worth mentioning that a specimen of Alloy 80A crept under vacuum conditions at *T*=900°C at 30MPa reached a strain value of 14.6%, while the specimen crept under the same conditions but in nitriding atmosphere failed in a more brittle manner (N_2-45 Vol.-% He-5 Vol.-% H_2 + Ti sponge) at a strain value of 8.6%. In agreement with Pieraggi [17] it can be concluded that the deteriorating effect of high-temperature corrosion attack (in this case internal nitridation) is not restricted to the corrosion-affected surface layer.

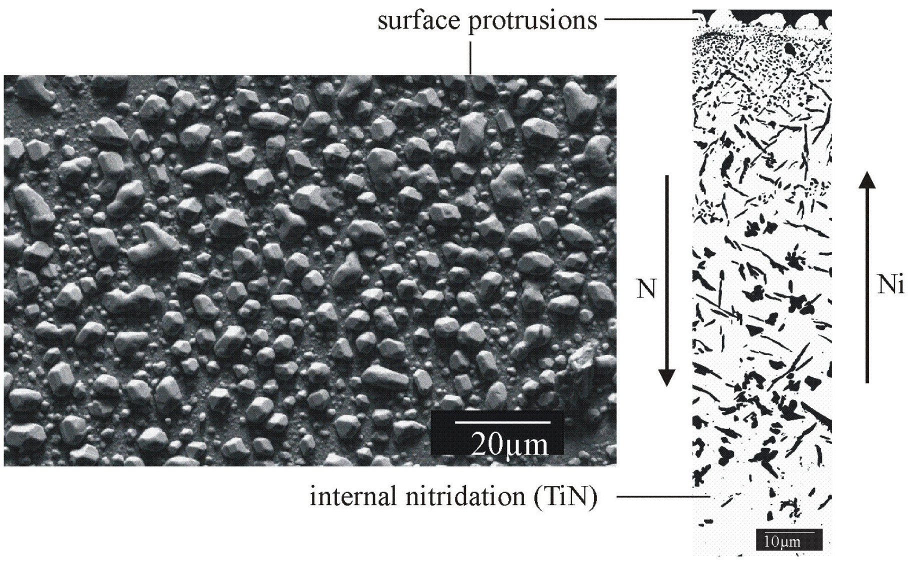

Fig. 2. Formation of surface protrusions as a consequence of internal precipitation of TiN in Ni-10Cr-2Ti during exposure to nitriding atmosphere for 150h at 1100°C (ref. [13]).

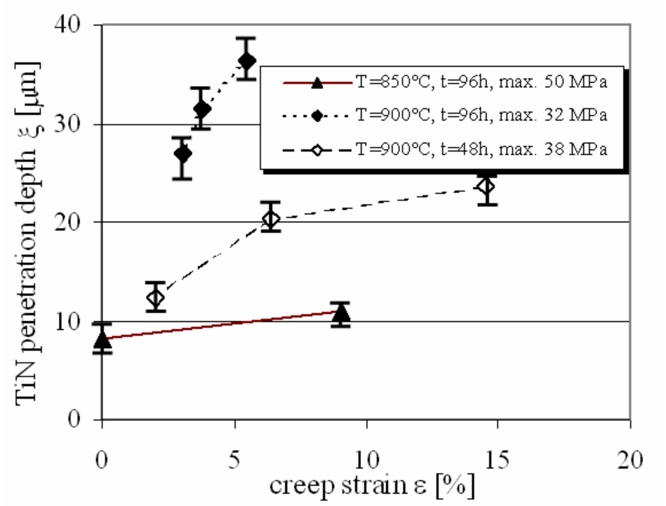

Fig. 3. TiN penetration depth vs. creep strain after creep testing of alloy 80A (Nicrofer 7520 Ti) in oxygen-free nitrogen atmosphere (ref. [15]).

Geometrically-Induced Mechanical Stresses during Cyclic Oxidation

High temperature exposure under cyclic-loading conditions causes the formation of thermal stresses in the oxide scale/substrate surface layer system due to strongly different coefficients of thermal expansion (CTE). The response of the system depends on (i) the scale adherence on the substrate surface, (ii) the scale coherence, and (iii) the ability of the scale/substrate to accommodate the stresses by creep. Furthermore, the component geometry and thickness as well as the cycle duration and the cooling rate are of high significance for the long-term behaviour of the oxide scale. Figure 4a shows that in the case of Cr_2O_3-scale formation on Alloy 80A thermal cycling leads to an increased mass gain, which corresponds to an oxidation process that is accelerated by the presence of a crack network [18]. The situation is different in the case of Al_2O_3 formation on CMSX-4 (Fig. 4b): Here, strong cyclic spalling was observed. One would expect that the extent of spalled oxide depends strongly on the cycle duration; the longer the high-temperature dwell time the thicker is the oxide scale and the higher are the stresses within the scale/substrate interface. Surprisingly, the spalled gross mass is more or less a function of the number of cycles, the mass change for 20 cycles with 1h dwell at 1100°C is almost the same than for 20 cycles with 5h dwell at 1100°C (Fig. 4b). Finally, Fig. 4c shows the effect of the specimen geometry. TGA under thermal-cycling conditions on wedge-type specimens (cf. Fig. 1a and [19,20]) results in an enhanced spalling behaviour as compared to a conventional rectangular specimen.

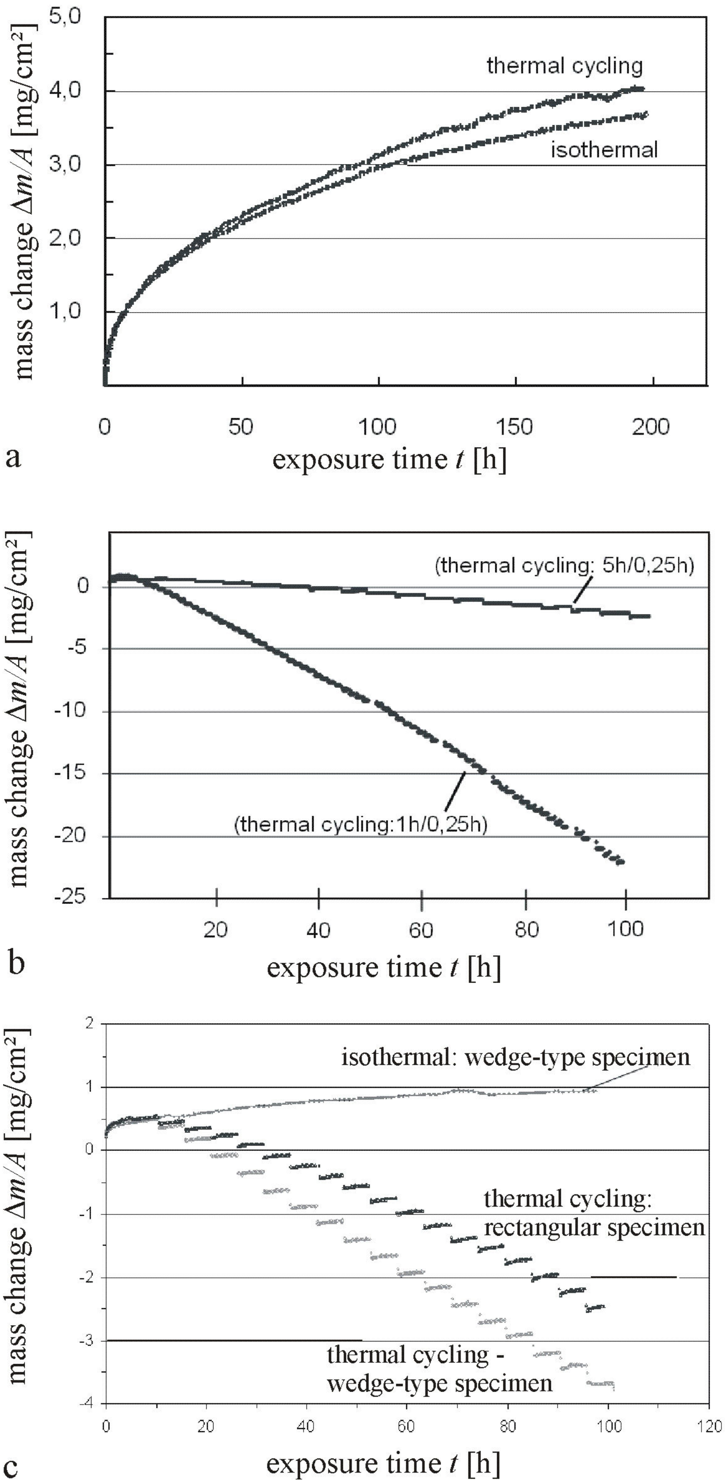

Fig. 4. Thermogravimetrically measured mass change vs. exposure time for (a) oxidation of Alloy 80A in air at 1000°C (b) oxidation of CMSX-4 in air at 1100°C and (c) oxidation of rectangular and wedge-type specimens of CMSX-4 in air at 1100°C (thermal cycling: intervals of 1h/5h dwell at high temperature followed by 15min. cooling at 50°C).

The effect of the geometry on the extent of cyclic spalling behaviour becomes obvious from the cross section micrographs in Fig. 5. Isothermal exposure results in the formation of an adherent alumina scale without showing any indication of spalling, cracking, Al depletion, and internal oxidation, even at the very sharp tip of the wedge-type specimen (Fig. 5a). However, exposure under thermal-cycling conditions causes a transition from external to internal oxidation and nitridation. Obviously, cyclic spalling leads to a depletion in the Al concentration in the specimen tip below the critical value required for superficial scale formation. Eventually, the formation of internal oxides and nitrides causes stresses in the thin-walled area which are accommodated by cracking.

The results show clearly that components or materials of low wall thickness and/or sharp edges exhibit a particular susceptibility to "breakaway oxidation" in combination with massive internal attack.

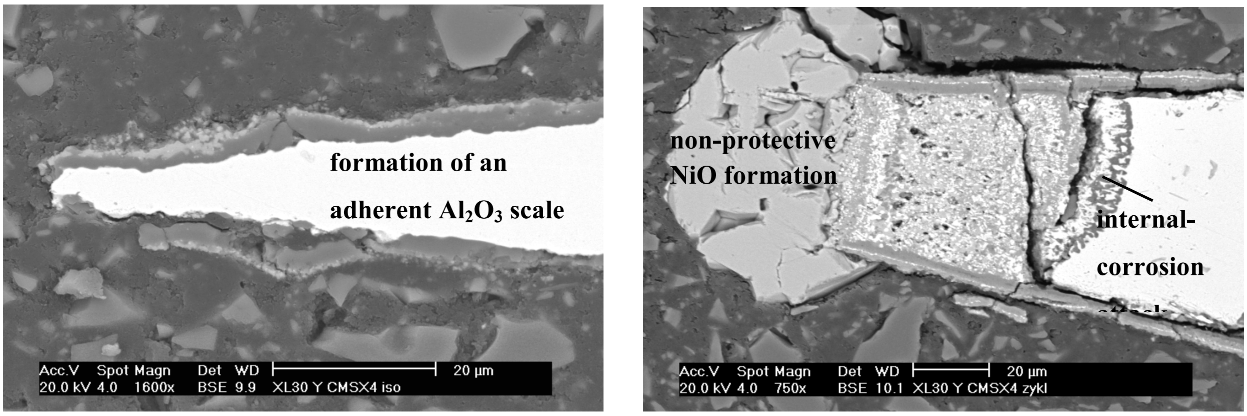

Fig. 5. Sharp tip of wedge-type specimens of CMSX-4: (a) after 100h isothermal exposure at 1100°C to air and (b) after 100h exposure under thermal-cycling conditions at 1100°C to air.

A further set of thermogravimetric experiments were carried out on specimens with different thicknesses ranging from t=100µm to t=500µm (cf. [21]). The results are summarized in Fig. 6. There is a clear trend for thick specimens to exhibit stronger oxide spallation (Al_2O_3). Any kind of "breakaway oxidation" or massive internal corrosion could not be identified. Also, the depth of the dissolution of the γ' phase (Ni_3Al) due to oxidation-induced Al consumption was more or less the same for all specimens. Hence, the thickness effect on the spalling behaviour must be attributed to changes in the stress-state within the scale-substrate system. In agreement to [22], thin specimens can accommodate stress peaks in the oxide substrate interface by creep with the consequence that the spalling rate is strongly reduced.

The thickness effect can be extrapolated by means of the probabilistic spalling model (p-k_p model) suggested by Poquillon and Monceau [9]. The results are shown by the solid lines in Fig. 6. The model accounts for a change in the amount of spalled oxide volume, which was also found experimentally by evaluating the specimen surfaces after certain thermal-cycling intervals, assuming that the nature of the oxide scale remains unaffected.

The results summarized in the preceding sections illustrate strong interactions between mechanical stresses and the external and internal high-temperature corrosion behaviour. To implement these effects into service-life assessment methods, it is required to use (i) stress terms in the diffusion differential equations to account for superimposed creep loading and for residual stresses arising from internal precipitation, (ii) quantitative failure criteria for the different types of superficial oxide (cracking/spalling), (iii) the mechanical-stress and the alloying-element distributions in thin walled or sharp-edged specimens to account for depletion or stress-relief effects, and (iv) a quantitative description of phase stability within the complete system (substrate and corrosion products) by means of the CALPHAD approach in combination with a numerical treatment of multi-element diffusion.

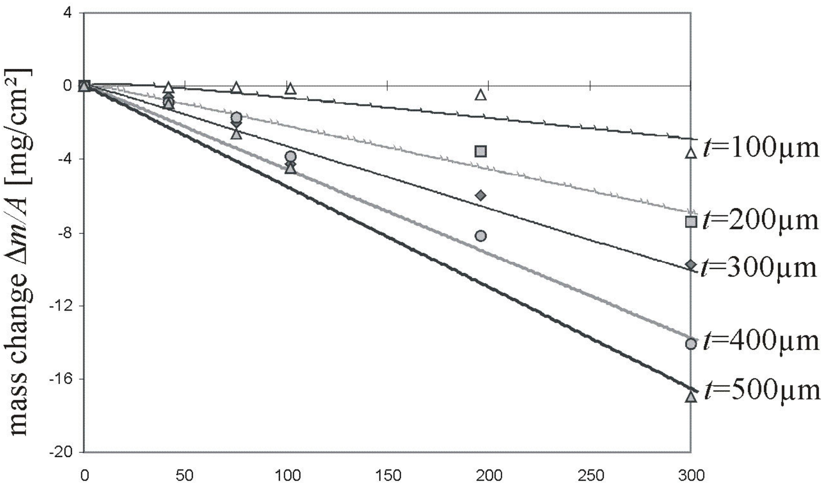

Fig 6. Measured (data points) and simulated (solid lines, p-k_p model [9]) net mass change vs. number of thermal cycles for exposure of CMSX-4 specimens of different thickness in air at 1100°C (1h dwell times, 15min cooling at 50°C).

Summary

High-temperature exposure of the Nickel-base superalloys Alloy 80A (chromia former) and CMSX-4 (alumina former) in air and a hydrogenated nitrogen/helium gas mixture of low $p(O_2)$ under thermal-cycling conditions and with superimposed creep loading revealed a strong alteration in the oxidation mechanism under the influence of mechanical stresses: Depending on the kind of oxide, cracking (Cr_2O_3) or spalling (Al_2O_3) decreases the integrity of the superficial oxide scale. The worst case was shown for wedge-shaped specimens: In the area of the sharp tip of the wedge, a transition from external to massive internal oxidation and nitridation in combination with cracks was observed. The occurrence of cracks in the internal-corrosion zone can be correlated with results on internal-nitridation experiments, where the high specific volume of the internal nitrides causes residual stresses acting as driving force for outward diffusion of solvent atoms. These residual stresses can be accommodated by a superimposed creep loading, which was shown to increase the depth of internal nitridation attack. Creep seems also to play a role during cyclic oxidation of thin specimens. It was shown that with decreasing specimen thickness the spalling susceptibility is reduced, which can be attributed to stress relief due to specimen creep.

Acknowledgments

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