Thermodynamic characteristics and numerical modeling of internal nitridation of nickel base alloys

H.-J. Christ*, S.-Y. Chang and U. Krupp

Kinetics and thermodynamics of the process of internal nitridation of various nickel-base alloys have been investigated in oxygen-free nitrogen atmospheres. Furthermore, the influence of formation and spalling of a protective oxide scale on the internal nitridation behavior of the alloys was studied by isothermal and cyclic oxidation tests in air. In general, nitridation kinetics of model nickel-base alloys of the system Ni-Cr-Ti was found to obey a parabolic rate law indicating that the nitridation process is diffusion-controlled. The temperature dependence of the nitridation rate constants is well described by an equation of the Arrhenius type. A thermodynamic calculation of the Ni-Cr-Ti-Al-N system was used to determine the nitrogen solubility in respective alloys as a function of temperature and alloy composition. The results show that a higher chromium content gives rise to an increase in the nitrogen solubility of Ni-Cr-Ti alloys leading to an increased nitridation rate in accordance with the experimental observations. From the calculated values for the nitrogen solubility, the diffusion coefficients of nitrogen were assessed using Wagner’s classical theory of internal oxidation.

A computer model of internal nitridation was developed that combines a commercial thermodynamic software (ChemApp) with a finite-difference diffusion calculation. It was found that this model describes the internal nitridation process in reasonable agreement with the experimental results and allows to treat the case of simultaneous formation of different nitrides. The dependence of internal nitridation behavior on spalling and cracking of the oxide was incorporated into the simulation on the basis of simple assumptions showing that this calculation method successfully applies also to complex internal corrosion processes.

1 Introduction

In many high-temperature applications, alloys are exposed to gaseous environments which contain nitrogen (e.g. air or ammonia). Internal nitridation of nickel-base alloys usually takes place as a consequence of spalling and cracking of a protective oxide scale, which can be considered as impermeable to nitrogen [1, 2]. Nickel-base superalloys usually contain alloying elements such as Ti and Al which can form thermodynamically stable nitrides. In the case of most ‘precipitation-hardened nickel-base superalloys, a near surface depletion of the strengthening γ’-phase (Ni₃(Al,Ti)) may lead to a deterioration of the creep resistance at high temperatures as a consequence of a Ti and Al consumption for nitride formation. Furthermore, due to molar volume difference between the alloying elements and their nitrides, the internal nitride precipitation can give rise to internal stresses and can lead to an embrittlement in the near-surface layer [3, 4].

The phenomenon of internal nitridation has been observed for numerous nickel-base alloys. In oxygen-free atmospheres, where superficial oxide formation is negligible, nitrogen attack was found to follow a parabolic rate law [5–8]. This indicates that the process is controlled by diffusion, i.e., the inward diffusion of the nitride-forming elements are the rate-controlling steps. Following the well-known theory of internal oxidation of C. Wagner [9], the dissolved concentrations of nitrogen c_N and solute element c_B in the alloy as a function of time t and location x is determined by Fick’s second law.

\[
\frac{\partial c_N}{\partial t} = D_N \frac{\partial^2 c_N}{\partial x^2} \quad \text{and} \quad \frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2},
\]

where \(D_N\) and \(D_B\) denote the diffusion coefficients of nitrogen and solute element B in the alloy. If one nitride of type BN, of high thermodynamic stability is formed and the following expression is fulfilled

\[
\frac{D_B}{D_N} \ll \frac{c^0_N}{c^0_B} \ll 1
\]

where \(c^0_N\) is the surface concentration of dissolved nitrogen, and \(c^0_B\) is the initial concentration of solute element B, equation (1) can be solved using some mathematical simplifications. Then, the penetration depth \(\xi\) of the internal nitrides as a function of exposure time \(t\) can analytically be calculated as proposed by Carl Wagner for internal oxidation [9].

\[
\xi^2 = 2k_Nt = 2 \frac{D_Nc^0_N}{v^0_B} t
\]

\(k_N\) denotes the parabolic nitridation rate constant. According to equation (3), nitridation kinetics is determined by the diffusivity and solubility of the interstitially dissolved nitrogen.

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The solubility of nitrogen depends significantly on the composition of the alloy as well as the nitridation temperature [10]. Nitrogen dissolves in metals according to the following reaction [11].

$$\frac{1}{2} \text{N}_2(\text{gas}) = \text{N}_{(\text{dissolved})}$$

The nitrogen solubility in nickel-base alloys is extremely small. Hence, the experimentally determined data show a large scatter [12, 13]. The nitrogen solubility can theoretically be predicted using the CALPHAD (calculation of phase diagrams) method by applying a two-sublattice model. In this study, the calculations were carried out using ChemSage, a software package for Gibbs-energy minimization calculations [14].

As stated above, internal precipitation can be described by Wagner’s theory of internal oxidation [15, 16] in simple cases. However, modeling of more complex internal-precipitation reactions that involve more than one compound or moderate stability of the reaction product and varying boundary conditions (e.g. temperature changes) require a numerical treatment of both the diffusion and the thermochemical processes in the alloy [17, 18]. For this purpose, a computer simulation was developed in which the commercial thermodynamic software ChemApp is combined with a finite-difference diffusion calculation using the explicit method [19]. The calculation of the concentration profiles and the resulting penetration depths of the internal-nitridation zones is based on a simple numerical treatment of the relevant diffusion processes which are the diffusion of nitrogen into the alloy and the counter-diffusion of the alloying elements towards the surface. After each single diffusion step, the precipitated nitride concentration as well as the concentration of nitrogen and the alloying elements are determined assuming local chemical equilibrium. It is shown in this paper that this calculation technique provides a quantitative description of the internal nitridation process of the nickel-base model alloys. Furthermore, this time and location resolved calculation method gives a sound basis for model expansions which aim at a consideration of superimposed effects such as superficial oxide formation and spallation.

### 2 Experimental procedures

The chemical compositions of the alloys studied are listed in Tables 1 and 2. Table 1 contains the compositions of the commercial nickel-base superalloys CMSX-2, CMSX-6 and SRR99 (single-crystalline alloys) and the polycrystalline alloy Nicrofer 7520. These materials were obtained as cylindrical rods of 10 – 12 mm diameter. The model alloys used in this study are listed in Table 2. The alloys were produced by vacuum arc melting and provided as cylindrical rods with a diameter of 10 mm.

For the nitriding experiments, specimens of approximately 1 mm in thickness were cut using a low-speed saw. Their surfaces were wet ground with SiC paper down to grade 1200 and polished with 3 μm and 1 μm diamond suspension. Prior to exposure the specimens were ultrasonically cleaned and degreased in ethanol.

Thermogravimetric measurements were carried out in a thermobalance which has a sensitivity of 10^-6 g. Supplementary long-term nitridation experiments were performed in a vacuum-tight annealing apparatus. As nitriding atmosphere a gas mixture consisting of 45 vol.% He, 5 vol.% H2 and 50 vol.% N2 at a constant flow rate of 6 Nl/h was used. This gas was led through a small package of porous Ti sponge right in front of the specimen. The high oxygen affinity of Ti in combination with the H2 content of the gas mixture reduces the oxygen partial pressure down to a value smaller than $p(O_2) = 10^{-18}$ Pa. The composition, phases and morphology of the products formed as well as nitridation kinetics were investigated applying analytical scanning electron microscopy, transmission electron microscopy and X-ray diffraction (XRD).

### 3 Results and discussion

#### 3.1 Behavior of commercial nickel-base alloys

Exposure to the nitriding atmosphere leads in the case of the commercial alloys, which contain 1.6 – 5.6 wt.% Al and 1.0 – 4.6 wt.% Ti, to an internal reaction zone with precipitates of...
AlN und TiN. SEM micrographs of this nitrided zone are shown in Fig. 1. Needle-shaped precipitates of AlN were formed beneath the surface and are clearly seen as black coarse precipitates in the cross-section. The TiN precipitates show also needle-like shape, but they are smaller and their precipitation zone extends significantly deeper into the alloy. The larger size of the AlN particles is probably a consequence of a higher phase-boundary energy and a smaller thermodynamic stability as compared to TiN. Hence, the critical nucleus size is increased reducing the nucleation rate.

Fig. 2 shows the gravimetrically determined weight gain as a function of time for the alloy Nicrofer 7520 in a representation of the mass gain per surface area versus the square root of time. Results of metallographic examinations of cross-sections are shown in Fig. 3. Both figures confirm that the internal-nitridation process obeys a parabolic rate law justifying the assumption that overall nitridation kinetics is diffusion controlled.

The parabolic nitridation rate constant $k_{\text{par}}$ as defined in equation (3) was calculated from the experimentally determined depths of the internal nitridation. The resulting values of the parabolic nitridation constants of TiN and AlN at 1000 °C for Nicrofer 7520 are $2.1 \cdot 10^{-8}$ and $4.8 \cdot 10^{-9}$ [mm$^2$ s$^{-1}$], respectively.

### 3.2 Behavior of NiCrTi model alloys

Fig. 4 shows the micrographs of cross-sections of Ni-Cr(0-20)-Ti2 alloys after nitridation at 1100 °C for 100 h. In these...
model Ni-Cr-Ti alloys only TiN precipitates were observed which form a well-defined zone of internal nitridation.

Clearly, the TiN precipitation zone depth increases strongly with increasing Cr content. For each temperature, again a parabolic rate law holds true indicating that the nitridation process is diffusion-controlled. An Arrhenius diagram of the logarithm of the parabolic rate constant versus the reciprocal temperature for the internal nitridation of NiCrTi2 alloys is given in Fig. 5.

In order to reveal the effect of chromium on the nitridation rate, thermodynamic equilibrium calculations were carried out using the computer program ChemSage in combination with a thermodynamic data base for the system Ni-Cr-Al-Ti-N. According to the calculated results, the nitrogen solubility in pure nickel can be expressed by the following equation:

\[ c_N = 0.039 \exp \left( \frac{-45645 \text{ [J/mol]}}{RT} \right) \sqrt{p(N_2) \text{ [bar]} \left[ \text{at.} \% \right]} \]  

(5)

The effect of chromium on the internal nitrogen behavior can be attributed to its influence on the activity coefficient of nitrogen in solid solution. Following the formalism of Wagner and Chipman, the logarithm of the nitrogen activity coefficient \( f_N \) can be expressed as [20]

\[ \log f_N = \epsilon_N^c \epsilon_{Cr} + \gamma_N^c \epsilon_{Cr}^2 \]  

(16)

where \( \epsilon_N^c \) and \( \gamma_N^c \) are the first and second order interaction coefficients between nitrogen and chromium. The nitrogen concentration \( c_N \) can be calculated according to the equation

\[ c_N = 0.039 \exp \left( \frac{-45645 \text{ [J/mol]}}{RT} \right) \sqrt{p(N_2) \text{ [bar]} \left[ \text{at.} \% \right]} \]  

(5)
Experimental values for the parabolic nitridation rate constant, thermodynamically calculated nitrogen solubilities (at a nitrogen pressure of 0.5 bar), and nitrogen diffusion coefficients (as derived from C. Wagner’s parabolic rate law) are listed in Table 3. The calculation results document clearly that the nitrogen solubility increases strongly with increasing temperature as well as with increasing Cr concentration.

Table 3. Experimentally observed values for the parabolic nitridation rate constant, thermodynamically calculated nitrogen solubilities (at a nitrogen pressure of 0.5 bar) and nitrogen diffusion coefficients (as derived from C. Wagner’s parabolic rate law)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T$ [°C]</th>
<th>$k_N$ [mm²/s]</th>
<th>$c_N$ [at.%]</th>
<th>$D_N$ [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCr5Ti2</td>
<td>900</td>
<td>6.84 $\times$ 10$^{-10}$</td>
<td>5.08 $\times$ 10$^{-4}$</td>
<td>3.27 $\times$ 10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2.68 $\times$ 10$^{-9}$</td>
<td>6.98 $\times$ 10$^{-4}$</td>
<td>9.30 $\times$ 10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>9.66 $\times$ 10$^{-9}$</td>
<td>9.15 $\times$ 10$^{-4}$</td>
<td>2.57 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td>NiCr10Ti2</td>
<td>900</td>
<td>1.66 $\times$ 10$^{-9}$</td>
<td>9.46 $\times$ 10$^{-4}$</td>
<td>4.24 $\times$ 10$^{-8}$</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.06 $\times$ 10$^{-8}$</td>
<td>1.33 $\times$ 10$^{-3}$</td>
<td>1.93 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>3.11 $\times$ 10$^{-8}$</td>
<td>1.66 $\times$ 10$^{-3}$</td>
<td>4.52 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>3.74 $\times$ 10$^{-9}$</td>
<td>1.01 $\times$ 10$^{-3}$</td>
<td>8.81 $\times$ 10$^{-8}$</td>
</tr>
<tr>
<td>NiCr20Ti2</td>
<td>1000</td>
<td>3.80 $\times$ 10$^{-8}$</td>
<td>2.86 $\times$ 10$^{-3}$</td>
<td>3.16 $\times$ 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1.38 $\times$ 10$^{-7}$</td>
<td>5.56 $\times$ 10$^{-3}$</td>
<td>5.91 $\times$ 10$^{-7}$</td>
</tr>
</tbody>
</table>
tify a sound conclusion. As an average value of the activation energy \( Q = 135 \pm 12 \text{ [kJ/mol]} \) can be derived.

The calculation of \( D_N \) shows that the concentration of Cr in the Ni-Cr-Ti alloys affects not only the nitrogen solubility but also the nitrogen diffusion. Hence, the observed change of nitridation kinetics with Cr concentration results from both an increased solubility and an enhanced diffusivity at increased chromium concentration.

### 3.3 Thermodynamic prediction of the range of stability of \( \pi \) phase

The predictive capacity of the numerical thermodynamic calculation becomes evident, when alloys with even higher Cr content are considered. As an example, the nitridation of NiCr30Ti2 at temperatures below 1100 °C leads to the formation of further phases in the zone of internal nitridation. Needle-shaped \( \text{Cr}_2\text{N} \) precipitates as well as the so-called \( \pi \)-phase [10, 21] precipitate and form a clearly visible nitridation zone close to the surface which is embedded in the deep TiN zone (Fig. 8).

Using the thermodynamic program ChemSage isothermal Ni-Cr-N equilibrium diagrams were calculated. Fig. 9 shows such a diagram for the temperature of 1000 °C. Taking into account that the nitrogen partial pressure was limited to 0.5 bar in this work, the thermodynamic calculation predicts the experimentally observed phases very accurately. As an example, the stability diagram shows that \( \pi \)-phase formation is confined to high Cr contents above 22.8 wt.% at 1000 °C.

### 3.4 Simulation of internal nitridation

The numerical simulation of the internal nitridation process is based on a calculation of the diffusion of nitrogen into the alloy and the counter-diffusion of the alloying elements. Fick’s second law is solved applying an explicit finite-difference method [19]. For this purpose, time and location are subdivided in intervals and after each time step the concentrations resulting from diffusion are calculated for all positions. Before the diffusion calculation is continued by increasing time by one time interval, the precipitated nitride concentrations are determined assuming local thermodynamic equilibrium. A detailed description of the calculation method is presented in ref. [6].

Fig. 10 depicts the calculated concentration profiles of the reacting elements for the internal nitridation reaction of a NiCr20Ti2 alloy. In Fig. 11, the experimentally observed
As a first step towards an extension of the simulation in such a way that the superficial processes can be taken into account, a two-dimensional simulation model was developed. One application of this model is the calculation of internal nitridation as a consequence of a cracked oxide scale. For an experimental verification of the calculated results (Fig. 12a), a crack in the oxide scale of a pre-oxidized specimen of NiCr20Ti6 was generated using a diamond wire saw. Then the specimen was exposed for 100 h at 1000 °C to oxygen-free nitrogen atmosphere. Fig. 12b shows that the TiN precipitation depth underneath the crack is obviously larger than the depth below the oxide scale. A comparison of the nitridation depth underneath the crack and the numerical prediction shows a reasonable agreement between experimental and calculated data.

Fig. 10. Calculated concentration profiles of the internal nitridation of NiCr20Ti2 for an exposure time of 100 h at (a) 900 °C, (b) 1000 °C and (d) 1100 °C

Fig. 11. Comparison of the prediction (solid line) with the experimentally determined internal nitridation depths (data points) for NiCr20Ti2 at 1000 °C and a nitrogen pressure of 0.5 bar

Fig. 12. Internal nitridation of NiCr20Ti6 as a consequence of a crack in the oxide scale after 100 h at 1000 °C in 0.5 bar N2-atmosphere: (a) calculated TiN concentration profile and (b) cross-section of a sample, the oxide scale of which was locally removed after pre-oxidation (1000 °C, 100 h, air)
4 Conclusions

- The growth rate of the internal-precipitation zone obeys a parabolic rate law in all cases studied. Hence, the internal nitridation of nickel-base alloys is diffusion-controlled. A detailed analysis proved that the process can be described by the classical theory of internal oxidation by C. Wagner.

- The diffusivity and solubility of nitrogen in nickel-base alloys was found to depend strongly on alloy composition. In Ni-Cr-Ti model alloys the influence of Cr content on the maximum dissolved concentration of nitrogen was confirmed theoretically by means of thermodynamic calculations. Using this data of the nitrogen solubility, the simple C. Wagner equation for internal oxidation yields an increase of the nitrogen diffusion coefficient with increasing Cr concentration.

- At a Cr content higher than 20 wt.%, a peritectic reaction of Cr₂N with Ni can lead to the formation of the ternary π phase. The occurrence of Cr₂N and the π phase is in accordance with the prediction of thermodynamic equilibrium calculations.

- A numerical simulation model was developed and used to quantitatively describe the internal nitridation process. The distribution of the various elements within the diffusion zone during internal precipitation can reasonably be predicted based on a combination of kinetic and thermodynamic considerations.

- An extension to a two-dimensional calculation was carried out, in order to take oxide scale failure into account. First results indicate the close correlation of internal nitridation and oxide scale integrity.

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6 References


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