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High-Temperature Nitridation of Ni-Cr Alloys

A.A. KODENTSOV, J.H. GÜLPEN, C. CSERHÁTI, J.K. KIVILAHTI, and F.J.J. VAN LOO

The nitriding behavior of nickel-chromium alloys was investigated at 1398 K over the range 1 to 6000 bar of external nitrogen pressure. The morphology of the nitrided zone depends on the concentration of chromium in the initial alloy and the N_2 pressure (fugacity) applied upon the system. The transition from CrN to Cr_2N precipitation was observed within the reaction zone after nitriding at 100 to 6000 bar of N_2 when the chromium content in the initial alloys was 28.0 at. pct or higher. It is shown that the ternary phase π ($Cr_{10}Ni_7N_3$) is formed in this system at 1273 K through a peritectoid reaction between Cr_2N and nickel solid solution and becomes unstable above 1373 K. The thermodynamic evaluation of the Ni-Cr-N system was performed and phase equilibria calculated. Evidence for "up hill" diffusion of nitrogen near the reaction front during the internal nitridation of Ni-Cr alloys at 1398 K was found. It was attributed to the relative instability of chromium nitrides and strong Cr-N interaction in the matrix of the Ni-based solid solution within the nitrided zone.

I. INTRODUCTION

WHEN a homogeneous binary alloy A-B is heated in a nitriding atmosphere (e.g., a mixture of $NH_3 + H_2$, N_2 , etc.), selective nitridation may take place if the external activity of nitrogen is sufficient to nitridize B (solute) but not A. Nitrogen can react with the solute to form a surface nitride layer. However, if the permeation of nitrogen into the metal A is appreciable, the precipitation of the solute B (in the form of nitrides) may also occur inside the alloy. Whether exclusive surface nitridation or formation of internal precipitates (or a combination of both) takes place depends on the activity of nitrogen in the surrounding atmosphere, the activity of the solute B in the matrix of solid solution A(B), and the relative diffusivities of nitrogen and the solute element in the solid solution A(B).

Most studies on nitriding behavior have been performed on ferrous alloys. Nitriding of iron-based alloys is a well-known and widely used commercial process. Internal nitridation of nickel-based alloys, however, was first reported by Barnes and Lai only a few years ago.^[1] Later, Rubly and Douglass^[2] studied the nitriding behavior of nickel-chromium alloys in an ammonia-hydrogen mixture over the range of 973 to 1173 K. Internal nitridation rates for different Ni-Cr alloys were found to obey the parabolic time-dependency law and decreased with increasing chromium content. The aims of the present work were as follows:

- (1) to investigate the interaction of Ni-Cr alloys with nitrogen at different external pressures (1 to 6000 bar of N_2) at 1398 K; and
- (2) to evaluate the internal nitriding of Ni-Cr alloys using a thermodynamic assessment of the Ni-Cr-N system.

II. EXPERIMENTAL PROCEDURE

High-purity nickel (99.98) and chromium (99.95) were used as initial materials. Ni-Cr alloys (5.0 to 32.0 at. pct of Cr) were melted in an arc furnace under argon atmosphere using a nonconsumable tungsten electrode. The ingots were cold-rolled to a thickness of 1.5 mm. Slices of 8×8 mm were cut from the sheets and homogenized for 100 hours at 1 bar of gas mixture Ar + 10 vol pct H_2 ($H_2O \leq 5$ ppm) and 1373 K. The grain size in the final materials was in the range of 100 to 150 μm .

Nitriding of the alloys at 1 bar of nitrogen was performed in a vacuum furnace equipped with a gas inlet system which enabled heat treatment in isostatic gas conditions. If quenching of the sample was necessary, a horizontal tube furnace with flowing nitrogen was used. In experiments performed at 1 bar of N_2 pressure, the temperature was controlled within ± 3 deg.

For total gas pressures up to 100 bar, a sintering furnace (KCE, Germany) was used. Temperature control was carried out with an optical pyrometer with an accuracy of ± 5 deg.

Nitridation at 900 to 6000 bar was performed in ultrahigh pressure equipment made by UNIPRESS (Poland). Pressure of N_2 was controlled by using a manganine gauge within ± 10 bar accuracy. Temperature control was carried out within ± 2 deg accuracy. More technical details concerning the ultrahigh pressure equipment can be found elsewhere.^[3]

All nitriding experiments were performed in pure nitrogen ($O_2 \leq 10$ ppm; $H_2O \leq 10$ ppm). Before the nitriding run under isostatic conditions, the furnaces were evacuated up to 10^{-4} mbar, filled with pure nitrogen, and evacuated again. After nitridation under these conditions, no oxide formation was detected with X-ray diffraction (XRD) analysis at the surface of the samples.

The cooling rate in all experiments was 600 deg/h. Only in experiments carried out at 1 bar of N_2 did this rate vary, from 75 to 600 deg/h.

The surfaces of the alloys after nitriding were examined by XRD analysis with a cylindrical texture camera using nickel-filtered Cu K_α radiation.^[4] The strong intensity modulation of the diffraction lines of the Ni, Cr-substrate are due to the coarse structure of the alloys (grain size $> 100 \mu m$).

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(a)

(b)

Fig. 1—Secondary electron images of the reaction zone after nitriding of various Ni-Cr alloys, (a) Ni-10Cr and (b) Ni-32Cr, at 1398 K and 100 bar of nitrogen for 4 h (A = metal-gas interface).

The formation of the nitride phases on the metal surface was revealed by the continuous lines of cubic CrN (Fm3m) or hexagonal Cr₂N (P31m) in the diffraction pattern.

Then the nitrided samples were cross sectioned and, after standard metallographic preparation, investigated by optical microscopy, scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). The types of internal precipitates which were observed inside the alloys were determined with the aid of transmission electron microscopy (TEM). Samples were prepared by mechanical thinning and dimple grinding; electron-beam transparency was accomplished by 6 kV argon-ion milling.

III. RESULTS

A. Morphology of the Diffusion Zone after Nitriding at 100 Bar of N₂ and 1398 K

After nitriding of the Ni-Cr alloys containing 10.0 to 32.0 at. pct of Cr at 1398 K at 100 bar of nitrogen, the reaction

zone consists of a surface layer of CrN and nitride precipitates inside the alloys. In Figures 1(a) and (b), the microstructures of the nitrided zone in the various Ni-Cr alloys are given. A characteristic feature of the nitrided zone is the presence of a precipitate-free layer of the Ni-Cr solid solution between the surface nitride layer and the zone of internal precipitates.

The type of the internal precipitates (cubic CrN or hexagonal Cr₂N) which can be formed after nitriding under these conditions depends on the concentration of chromium in the initial substrate. Electron diffraction gave positive identification of cubic CrN in the Ni-Cr matrix with an initial chromium content up to 22.0 at. pct and of hexagonal Cr₂N for alloys with a Cr content ≥ 28.0 at. pct when the sample was taken from the central part of the nitrided zone (Figures 2 and 3). However, at the edges of the nitrided sample, the formation of both CrN and Cr₂N precipitates was observed (Figure 4). The average concentration of chromium in the solid solution, which is in equilibrium with both CrN and Cr₂N, was 23.8 ± 0.5 at. pct (point C in Figure 4).

B. Nitriding of Ni-Cr Alloys at 900 Bar of Nitrogen and 1398 K

With increasing external nitrogen pressure (up to 900 bar), the process of internal nitridation becomes more pronounced. Various types of microstructure in the diffusion zone after nitridation at 1398 K and 900 bar of N₂ are given in Figures 5(a) and (b).

Exclusive internal nitridation in the absence of surface nitride layer formation occurs in the alloy with 5.0 at. pct of chromium. The reaction zone consisted of numerous isolated precipitates of CrN with an orientation relationship to the matrix phase (Figure 5(a)).

A surface layer of CrN with internal nitride precipitates was found in the alloys with higher Cr contents. A thin precipitate-free zone of Ni-Cr solid solution was observed between the surface layer and a zone of internal precipitates. Quite large, angular particles of CrN were found near the precipitate-free zone. Deeper in the alloy, the reaction zone consists of particles inside the grains and along grain boundaries of the Ni-Cr matrix. Precipitation along grain boundaries was found even beyond the nitrided front. The reaction front in samples after nitriding at 1398 K and a pressure of 900 bar of nitrogen was nonplanar. Attempts to study the kinetics of the nitrided zone growth were inconclusive.

When the chromium content in the initial alloy was increased to 28.0 at. pct, the formation of both cubic CrN and hexagonal Cr₂N was observed within the reaction zone (Figures 5(b) and 6). Under these experimental conditions, the transition from CrN to Cr₂N precipitation takes place along the whole nitrided zone. The concentrations of chromium in the solid solution, which is in equilibrium with both CrN and Cr₂N precipitates (e.g., point C in Figure 6), are listed in Table I.

C. Internal Nitridation at 6000 Bar of Nitrogen and 1398 K

When an extremely high pressure of nitrogen of 6000 bar was applied upon the system, the exclusive internal nitridation in the absence of the surface nitride layer was

(a)

(b)

(c)

Fig. 2—(a) Bright-field image and selected area diffraction patterns taken from the nitride particle formed inside the Ni-22Cr alloy upon nitriding at 100 bar of N_2 (1398 K, 4 h) indexed as (b) [110] and (c) [211] directions in the cubic lattice of CrN ($Fm\bar{3}m$, $a = 0.4148$ nm).

observed in the alloys with the chromium content up to 15.0 at. pct (Figures 7(a) and (b)). The morphology of the nitrided zone was somewhat similar to that described by Douglass for the case of nitriding Ni-Cr alloys from a mixture of $NH_3 + H_2$ in the temperature range 973 to 1173 K.^[2] Internal precipitates near the metal-gas interface were small and generally rounded, becoming coarser with increasing depth.

With increasing chromium content in the initial alloy up to 22.0 at. pct, the formation of the surface layer of CrN and internal nitride precipitates was found. Relatively

small, rounded precipitates of CrN were formed close to the surface nitride layer. Deeper in the alloy, precipitates became coarser and transformed to a "Widmanstätten"-type structure of relatively large, angular precipitates. In some areas of the diffusion zone, precipitates had a blocky morphology, especially in the matrix with a high initial Cr content (Figure 8(a)). Deeper into the alloy, intergranular nitride formation with plate-type particles inside of grains was observed. The internal nitridation boundary was not sharp, which made it difficult to get reliable kinetic data.

The transition from CrN to Cr_2N precipitation within the

Fig. 3—(a) Bright-field image and selected area diffraction patterns taken from the nitride particles formed inside the Ni-28Cr alloy after nitriding at 100 bar of N_2 (1398 K, 4 h) indexed as (b) $[0001]$ and (c) $[1213]$ direction in the hexagonal lattice of Cr_2N ($P\bar{3}1m$, $a = 0.481\ \text{nm}$, $c = 0.4484\ \text{nm}$). Sample for TEM was prepared from the central part of the nitrided zone.

diffusion zone was again clearly visible at a Cr content in the initial alloys of 28.0 at. pct and higher (Figures 8(a) and (b)). The average composition of the Ni-Cr solid solution which is in equilibrium with CrN and Cr_2N precipitates (point C in Figure 8(b)) was found as 24.3 ± 0.3 and 24.6 ± 0.5 at. pct of Cr for Ni-Cr alloys with 28.0 and 32.0 at. pct of chromium, respectively.

D. Phase Formation in the System Ni-Cr Alloy—Nitrogen at External Pressure of 1 Bar

Only the hexagonal nitride Cr_2N was detected at the surface and inside the Ni-Cr alloys with a chromium content more than 28.0 at. pct after annealing at 1398 K and 1 bar of N_2 when samples were cooled down quite fast (about

Fig. 4—Backscattered electron image of a Ni alloy with 32.0 at. pct of Cr nitrided at 100 bar of N_2 and 1398 K for 4 h showing the formation of CrN precipitates at the edge of the sample (A = metal-gas interface). Point C indicates alloy in equilibrium with CrN and Cr_2N .

(a)

(b)

Fig. 5—Backscattered electron images of the nitrided zone in different Ni-Cr alloys after annealing at 1398 K and 900 bar of N_2 for 4 h: (a) Ni-5Cr and (b) Ni-28Cr (A = metal-gas interface).

Fig. 6—Backscattered electron image showing the transition from CrN to Cr_2N precipitates within the nitrided zone. Micrograph represents the magnified area B in Fig. 5(b).

Table I. Composition of the Ni-Cr Solid Solution in Equilibrium with CrN and Cr_2N Precipitates in the Nitrided Zone after Annealing at 1398 K at 900 Bar of N_2

Initial Alloy (At. Pct)	Annealing Time (Hours)	Average Chromium Content in Ni-Cr Solid Solution (At. Pct)
Ni-28Cr	4	24.0 ± 0.4
	9	24.2 ± 0.5
	16	24.4 ± 0.5
Ni-32Cr	4	24.3 ± 0.4
	9	24.1 ± 0.3
	16	24.5 ± 0.5

500 to 600 deg/h). Grain boundary precipitation of Cr_2N and plate-type precipitates inside the grains was observed. A typical microstructure of the diffusion zone in the samples after heat treatment under these conditions is shown in Figure 9.

However, with a decreasing cooling rate up to 300 deg/h, the formation of a ternary phase of the Ni-Cr-N system inside the Ni-Cr alloy was found (Figure 10). Probably, this ternary phase is the same nitride phase that was reported by Kikuchi and designated as a π phase.^[5,6] He made a conclusion that the π phase in Ni-Cr-N system has the metal-atom arrangement of β -manganese and may be formed at 1273 K through a peritectoid reaction between dichromium nitride Cr_2N and the nickel solid solution. This possibility seems to be confirmed by the morphology of the reaction zone after nitridation of nickel alloy with 32.0 at. pct of Cr at 1 bar of N_2 and slow cooling (75 to 300 deg/h) (Figure 10). A rim of the π phase around nitride particles indicates that a peritectoid reaction between the Ni-Cr solid solution and chromium nitride may occur upon cooling. After subsequent annealing of such a sample at 1398 K and 1 bar of nitrogen and quenching, the π phase has disappeared completely. However, the π phase was still detected in the nitrided zone of the samples quenched after a heat treatment at 1273 K and 1 bar of N_2 . In general, the present results are consistent with the experimental data of Kikuchi and co-workers^[5,6] and the thermodynamic assessments of the Ni-Cr-N system performed by Frisk.^[7] They agreed that

Ni15Cr

(a)

(b)

Fig. 7—Backscattered electron images of the reaction zone after nitriding a Ni alloy with 15.0 at. pct of chromium at 1398 K and 6000 bar of N_2 for 4 h: (a) general view and (b) variation in precipitate morphology (A = metal-gas interface).

the π phase exists as an equilibrium phase at temperatures below 1273 K and becomes unstable at higher temperature.

The chemical composition of the π phase was determined by Kikuchi using EPMA to be $Cr_{13}Ni_7N_4$.^[5] However, microprobe measurements performed in the present study gave slightly different results. The composition of the π phase formed inside the Ni-Cr alloy with 32.0 at. pct of Cr after nitridation at 1398 K (1 bar of N_2), subsequent annealing at 1273 K and 1 bar of nitrogen, and quenching was found to be $Cr_{10}Ni_7N_3$. Most likely, such a difference can be attributed to the existence of a certain homogeneity range of the ternary π phase in the Ni-Cr-N system.

IV. DISCUSSION

A. Surface Nitridation of Ni-Cr Alloys at 1398 K

Phase equilibria in the Ni-Cr-N system were calculated using the latest thermodynamic evaluations of the pure components.^[8] The binary Ni-Cr, Ni-N, and Cr-N systems were calculated using primarily the data of Frisk.^[7] The

Ni28Cr

(a)

(b)

Fig. 8—Backscattered electron image of the diffusion zone after nitriding a Ni alloy with 28.0 at. pct of Cr at 1398 K and a pressure of 6000 bar of N_2 for 4 h: (a) general view and (b) magnified area B in showing the transition from CrN to Cr_2N precipitates (A = metal-gas interface).

Ni32Cr

Fig. 9—Typical microstructure of the diffusion zone in the Ni-32Cr alloy after nitriding at 1398 K and 1 bar of N_2 for 16 h and fast cooling (600 deg/h) in the furnace at 1 bar of N_2 . Secondary electron image (A = metal-gas interface).

Fig. 10—The formation of the ternary π phase of the Ni-Cr-N system in a Ni alloy with 32.0 at. pct of Cr after nitriding at 1398 K and 1 bar of N_2 for 16 h and slow cooling (75 to 300 deg/h) at 1 bar of nitrogen. Backscattered electron image (A = metal-gas interface).

Fig. 11—Calculated stability diagram of chromium nitrides at 1398 K in various Ni-Cr alloys as a function of the nitrogen fugacity together with experimental data (●—chromium nitride was detected at the surface of alloy with XRD; ○—no nitride formation).

interstitial solution model containing two sublattices was applied to all solid solution phases in which nitrogen is dissolved.^[9] The magnetic contribution is taken into account using Hillert and Jarl's^[10] modification of the model for the magnetic Gibbs energy proposed by Indén.^[11] The magnetic contribution used herein is the one evaluated by Frisk.^[12]

The Ni-Cr-N system was reassessed in the present work by introducing a new binary parameter which takes into account the interaction between Ni and N atoms in the face-centered cubic (fcc) solution and describes the excess Gibbs energy of the fcc phase. In order to reach the best agreement between the experimental and calculated values, the binary parameter was chosen to be equal to -10.5 kJ/mol.

Fig. 12—Concentration profiles (schematically) for solute atoms (N_B) and penetrating atoms (N_F) through the reaction zone during internal precipitation in the case of a low solubility product of the precipitated compound: (a) solute atoms are relatively immobile and (b) solute diffuses appreciably (A = initial gas-metal interface, F = reaction front, and ξ = the thickness of the zone of internal precipitates).

This is in the range of $+20$ to -30 kJ/mol which has been recently evaluated for the fcc phase in other 3d transition metal-nitrogen systems.^[13] The calculated stability diagram of chromium nitrides at 1398 K in various Ni-Cr alloys as a function of the nitrogen fugacity is given in Figure 11. The values of the nitrogen fugacity as a function of metal ratio $U(Cr) = N_{Cr} / (N_{Cr} + N_{Ni})$ were calculated assuming that the molar volumes of the condensed phases are independent of the external gas pressure applied upon the system. In fact, using this graph, it is possible to predict which nitride phase will be formed at the metal-gas interface under a certain external pressure (fugacity) of nitrogen. For example, the curve AB in Fig. 11 represents three-phase equilibria when CrN is in equilibrium with the fcc Ni-Cr solid solution with a specified concentration of Cr and N_2 gas pressure (fugacity). Similarly, the curve BC shows three-phase equilibria $Cr_2N + fcc + N_2$ gas. Point B in this diagram displays a four-phase (invariant) equilibrium in the ternary Ni-Cr-N system at 1398 K.

Fig. 13—Concentration profiles (schematically) for solute (N_B) and penetrating elements (N_F) across the diffusion zone in the case of moderate stability of the precipitated compound during internal precipitation (A = initial gas-metal interface, F = reaction front, and ξ = the thickness of the zone of internal precipitates).

Results of the thermodynamic calculations were verified experimentally by nitriding various Ni-Cr alloys at 1 to 40 bar of nitrogen pressure at 1398 K assuming ideal behavior of the nitrogen gas under these conditions.

According to our calculations, a nitrogen pressure of ~ 27 bar is needed to produce CrN at the surface of the Ni-Cr alloy containing 10.4 at. pct of chromium at 1398 K. Experimentally, a fragmented layer of cubic CrN was detected at the surface of such an alloy after annealing at this temperature and a N_2 pressure equal or higher than 30 bar. An external nitrogen pressure of 8 bar was already enough to produce a detectable layer of CrN at the surface of a Ni-Cr substrate with a Cr content of 17.3 at. pct but not for an alloy with only 15.0 at. pct of chromium. When using a nitrogen pressure of 4 bar at 1398 K, the formation of cubic CrN was observed at the surface of the alloy with 22.0 at. pct of chromium. However, no positive indications of the reaction products at the interface gas-Ni-Cr substrate with 17.3 at. pct of Cr were found after nitriding under the same conditions.

In order to check the calculated equilibrium line $\text{fcc} + \text{Cr}_2\text{N}$ (Figure 11, curve BC), a number of Ni-Cr alloys with relatively high (22.0 to 32.0 at. pct) concentrations of Cr were exposed to 1 bar pressure of nitrogen at 1398 K for 9 hours. Under these conditions, hexagonal Cr_2N was formed at the metal surface when the chromium content was 25.5 at. pct or higher. The results of the nitridation of the Ni-Cr alloys are depicted in Figure 11.

The correctness of the thermodynamic description used can be checked indirectly at a higher value of nitrogen fugacity as well. As was mentioned previously, exclusively internal nitrides were found inside the Ni-Cr alloy with 5.0 at. pct of Cr after nitriding at 1398 K and 900 bar of N_2 . However, in some places of the reaction zone, the particles of CrN are in equilibrium with Ni-Cr solid solution and N_2 gas (Figure 5(a)). Composition of the Ni-Cr solution, which is in equilibrium with CrN particles and N_2 gas after nitriding under these conditions, can be estimated by extrapolation of the concentration profile of chromium across the diffusion zone to the metal-gas in-

Fig. 14—Concentration profiles of chromium across the zone of internal precipitates after nitriding various Ni-Cr alloys at 1398 K and 900 bar of N_2 : (a) 1—Ni-10Cr, 2—Ni-15Cr, and 3—Ni-22Cr for 9 h; and (b) 1—Ni-28Cr and 2—Ni-32Cr for 4 h. The experimental curves represent portions of the profiles where no interference with nitride particles was encountered. (F = reaction front, and T = plane in the diffusion zone where transition from CrN to Cr_2N precipitation takes place).

terface. It was determined as 2.8 at. pct of Cr. A corresponding value of ~ 1000 bar for the fugacity of N_2 gas, which is in equilibrium with CrN and an fcc Ni solid solution with a Cr content of 2.8 at. pct, was found using the calculated stability diagram. On the other hand, the fugacity of nitrogen at 1398 K and 900 bar pressure can be calculated using, for instance, the Peng-Robinson equation of state.^[12] It gives the value ~ 1070 bar. Generally, the thermodynamic predictions are in good agreement with the experimental results.

B. On the Diffusion of Nitrogen during the Internal Nitridation of Ni-Cr Alloys

The nitriding behavior of Ni-Cr alloys at 1398 K depends on the concentration of chromium in the initial alloy and the N_2 pressure (fugacity) applied upon the system. One might expect a large gradient of nitrogen activity in the nitrided zone, especially in the possibly present surface nitride layer. Once formed, the surface layer grows slowly by the combination of outward diffusion of chromium from the matrix of the alloy and inward diffusion of nitrogen

Fig. 15—Isothermal cross sections through the Ni-Cr-N system at 1398 K and various external pressure of N_2 : (a) 1 bar, (b) 10 bar, (c) 100 bar, and (d) 1000 bar.

through the surface nitride. In the latter case, a nitrogen activity inside the alloy is determined by its equilibrium value at the alloy/external nitride interface, rather than at the external surface. Such a reduction of the flux of nitrogen into the material can cause a difference in the precipitation process. For instance, the formation of CrN precipitates in the “corner” of the sample containing 32.0 at. pct of Cr after nitriding at 100 bar of nitrogen (Figure 4) is a result of the overlapping of fluxes of nitrogen atoms arriving from the two gas-metal interfaces which lead to an increasing nitrogen activity inside the alloy.

In general, the activity of nitrogen is decreased gradually toward the precipitation front. Grain boundary precipitation beyond the reaction front can be attributed to the fact that grain boundaries are preferred nucleation sites and chromium might be present in higher concentrations at grain boundaries due to segregation.

Two limiting cases of the formation of a zone of internal precipitates were identified.^[13] The first one is the classical internal precipitation process that can be associated with high stability (low solubility product) of the precipitating compounds. The theory of this phenomenon

Fig. 16—Nitrogen concentration profiles through the matrix of the Ni-Cr solid solution within a zone of internal precipitates after nitriding various Ni-Cr alloys at 1398 K and 900 bar of N_2 . (a) Diffusion zone consists of only CrN precipitates (1—Ni-10Cr, 2—Ni-15Cr, and 3—Ni-22Cr). (b) Transition from CrN to Cr₂N precipitates takes place within the nitrided zone (plane T) (1—Ni-28Cr, 2—Ni-32Cr, and F = reaction front).

was developed by Wagner initially for internal oxidation,^[14] and the present status was given by Rapp^[15] and Meijering.^[16]

In the case of "classical Wagnerian behavior," the amount of precipitates across the reaction zone is constant and precipitation exclusively occurs at the reaction front. The very low solubility product of the precipitated compound implies that practically all solute is precipitated out in the precipitation zone. The activity of the penetrating element drops to a near-zero value at the reaction front. Depending on the relative mobility of the solute atoms, two types of concentration profiles through the diffusion zone can be derived (Figures 12(a) and (b)).

The second limiting case implies that the precipitated compound has a "moderate" stability. In this case, precipitation occurs continuously through the reaction zone. The activity of the penetrating element does not approach a near-zero value at the reaction front and diffusion of this element continues beyond the zone of internal precipitates. Furthermore, the solute is not precipitated completely in the reaction zone. Recently, Christ *et al.*^[17] made a computer simulation of the process of penetration of an element into an alloy connected with internal precipitation. Computed

concentration profiles for internal precipitation-type reactions with a moderate stability of precipitated compound were indeed somewhat similar to those supposed for the second limiting case by Laflamme and Morral^[13] (Figure 13).

In the case of internal nitridation of Ni-Cr alloys at 1398 K from a N_2 gas atmosphere, a significant concentration of chromium in the fcc matrix within the zone of precipitates was found. As an example, the concentration profiles for chromium through the zone of internal precipitates formed during nitriding various Ni-Cr alloys at 1398 K and 900 bar of N_2 are given in Figures 14(a) and (b). These experimental curves represent portions of the concentration profiles across the nitrided zone where no interference with nitride particles was encountered.

Since chromium is not precipitated out entirely at the reaction front, the nitrogen atoms diffuse in the nitrided zone not through a nearly pure Ni lattice but through the solid solution with certain concentration of chromium having a relatively high affinity for nitrogen. For diffusion, as well as for the estimated chemical activities, the interaction between Cr and nitrogen atoms in the Ni-based matrix has to be taken into consideration.

The effect of the presence of chromium in the Ni-based matrix on the thermodynamic behavior of nitrogen can be derived from the phase diagram. Using the same thermodynamic assessments as in the previous case, a number of isothermal cross sections through the Ni-Cr-N system can be calculated. In Figures 15(a) through (d), such diagrams at 1398 K and an external nitrogen pressure of 1, 10, 100, and 1000 bar are given. Unfortunately, it was impossible to verify these calculated diagrams experimentally, because the concentration of nitrogen in the fcc solid solution was below the limit of detection in our analytical technique. However, the calculated concentration of chromium in fcc solid solution in equilibrium with CrN and Cr₂N (point B in Figures 15(b) through (d)) is 24.1 at. pct. This value is very close to that which was determined for the "triple" point within a reaction zone of a nitrided sample, where the Ni-Cr solid solution was in equilibrium with both CrN and Cr₂N precipitates (Figures 4, 6, and 8(b)).

When the fcc Ni-Cr solid solution is in equilibrium with CrN or Cr₂N precipitates, the values for x_N^{fcc} and x_{Cr}^{fcc} are independent of the external N_2 pressure applied upon the system (Figures 15(b) through (d)). The relations between x_N^{fcc} and x_{Cr}^{fcc} in equilibrium with CrN precipitates at 1398 K were found as

$$\ln x_N = 12.66 x_{Cr} - 7.71 \quad (\text{for } 0.06 < x_{Cr} < 0.241) \quad [1]$$

The similar relations for the equilibrium fcc + Cr₂N precipitates were determined as

$$\ln x_N = 7.46 x_{Cr} - 6.47 \quad (\text{for } x_{Cr} > 0.241) \quad [2]$$

Now, the experimental penetration curves for chromium (Figures 14(a) and (b)) across the internal nitrided precipitation zone can be converted into a nitrogen concentration profile through the matrix of Ni-Cr solid solution within a reaction zone using the preceding equations (Figures 16(a) and (b)). This implies that in the Ni-based matrix, within the nitrided zone, nitrogen diffuses "up hill" its own concentration gradient toward the precipitation front, although the activity of nitrogen decreases in that direction. Behind

the precipitation front, the mole fraction of nitrogen must fall back to (in principle) a zero value at a large ("infinite") distance from the external surface.

Swisher^[18] also mentioned a somewhat similar behavior of a penetrating element forming internal precipitates. He found evidence for up hill diffusion of sulfur near the reaction front during the internal sulfidation of an Fe alloy with 0.38 wt pct of titanium at 1573 K in a $H_2S + H_2$ mixture. It was attributed to the relative instability of titanium sulfide and strong Ti-S interaction in the iron-based solid solution within the sulfidized zone.

V. CONCLUSIONS

When relatively unstable phases are precipitated out during internal precipitation reactions, the distribution of the various atoms within the diffusion zone can be predicted based on thermodynamic considerations of the respective systems. In this case, not only is a relative stability of the precipitated compound of importance but also the interaction between solute and penetrating atoms in the matrix of the solid solution within the precipitated zone must be taken into account.

In particular, attractive Cr-N interaction in the fcc Ni-Cr solid solution results in up hill diffusion of nitrogen through the Ni-based matrix toward the precipitation front. Such a behavior of nitrogen is opposite to the boundary conditions in Wagner's description of internal oxidation.

The experimental data on the equilibrium compositions of coexisting phases turned out to be consistent with the thermodynamic assessment of the Ni-Cr-N system.

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