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ARGONNE NATIONAL LABORATORY
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THE MECHANISM AND KINETICS OF THE REACTION
BETWEEN NICKEL AND FLUORINE

by

R. L. Jarry, W. H. Gunther,
and J. Fischer

Chemical Engineering Division

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THE MECHANISM AND KINETICS OF THE REACTION BETWEEN NICKEL AND FLUORINE

by

R. L. Jarry, W. H. Gunther, and J. Fischer

ABSTRACT

The mechanism and kinetics of the nickel-fluorine reaction have been studied. Marker (isotopic tracer) experiments, in which radioactive nickel-63 was used, and scale-impingement experiments, in which two scales formed during the reaction were forced to impinge upon each other, were carried out to determine whether nickel or fluorine migrates through the nickel fluoride scale formed during the fluorination of nickel. Similar experiments were performed with the nickel-oxygen system to verify the experimental results obtained in the nickel-fluorine study with those obtained in a reaction of known mechanism. The radioactive tracer experiments indicated that fluorine migrates through the growing fluoride scale. This was shown by the lack of movement of the radioactive tracer, which was found at the nickel fluoride scale-fluorine gas interface. In the nickel-oxygen experiments, the radioactivity was found to be distributed through the oxide scale in a manner predicted from the known mechanism. This result was in accord with the accepted mechanism for that reaction, namely, that nickel migrates through the nickel oxide scale to the nickel oxide-gas interface. In the fluoride scale-impingement experiments, the existence of an interface between the two scales growing from opposing surfaces indicated that fluorine is the migrating species. In the oxide scale-impingement experiments, a continuous scale was formed, thereby indicating that nickel is the migrating species in this case.

The kinetics of the nickel-fluorine reaction have been studied between 300 and 600 C using high-purity and commercial nickel. The parabolic rate constants for the reaction with high-purity nickel were found to be 9.8, 81, 461, and 1860 ($\mu\text{g F}_2/\text{sq cm}$)² per minute at 300, 400, 500, and 600 C, respectively.

No significant difference in reaction rates for the two types of nickel was noted except in the initial portion (less than 500 min) of the reaction period. The parabolic rate was found to be independent of the pressure of fluorine over the range of 100 to 700 mm Hg when the thickness of the nickel fluoride scale was 10^4 Å or less. After a scale having a thickness of about 10^5 Å had been deposited, the rate of scale formation was found to vary with the one-half power of the fluorine pressure.

I. INTRODUCTION

Fluorine is used in fluoride volatility processing of spent nuclear reactor fuels to convert uranium and plutonium to their respective hexafluorides. The best material of construction for use with fluorine at elevated temperatures, say 500 to 600 C, is nickel. Fluorine reacts with nickel to form a coherent, adherent scale of nickel fluoride which acts protectively by diminishing the rate of reaction. Several investigations of the corrosion of nickel have been reported,⁽¹⁻³⁾ and a recent publication summarizes the data available at the present time.⁽⁴⁾ No description of the mechanism of the nickel-fluorine reaction has been reported.

Oxidation reactions of metals and alloys which result in protective scales, that is, a scale which controls the reaction rate in some manner proportional to its thickness, have been treated according to the theory developed by Wagner.⁽⁵⁾ According to this theory, metal or nonmetal ions

are considered to be transported across the growing scale to a reaction interface. Concurrently with the ion transport, vacancies, representing vacant lattice sites, and electrons travel through the scale, thereby maintaining electrical neutrality across the scale. This scheme is shown diagrammatically in Figure 1. It follows from this consideration that in the case for which metal-ion migration predominates the reaction occurs at the scale-gas interface. When nonmetal-ion migration predominates, the reaction occurs at the metal-scale interface.

The classical example of the use of

(A) Outward Migration of Positively Charged Metal Ions and Electrons, Reaction Occurs at ①

(B) Inward Migration of Negatively Charged Nonmetal Ions and Outward Migration of Electrons. Reaction Occurs at ②

this mechanistic approach has been the study of the oxidation of copper⁽⁵⁾ in which it was shown that the copper ions migrated to the oxide-gas interface.

The Wagner Theory further states that reactions producing protective scales follow a parabolic reaction rate law. The oxidation of nickel has also been shown to follow the parabolic rate law,⁽⁶⁾ and measurements of the diffusion of nickel and oxygen in nickel oxide⁽⁷⁾ have shown that the diffusion rate of nickel is greater by several orders of magnitude than that of oxygen.

Since reaction sites for the migrating metal and nonmetal ions are different (the former reacts at the scale-gas interface, the latter reacts at the metal-scale interface), the determination of the reaction site can serve as a means of elucidating the mechanism of a reaction. Two different approaches were used to indicate the location of the reaction site in this study of the nickel-fluorine reaction. To check the experimental methods with a reaction of known mechanism similar experiments were performed with the nickel-oxygen system. In the first experimental approach, a radioactive tracer, nickel-63, was used as a self-marker. Nickel-63 was plated on the specimens to be fluorinated or oxidized and the radioactivity in the reacted specimens was located by autoradiographic means.

It is possible to predict the position of the activity in the resulting scale on the basis of the work carried out by Bardeen and associates.⁽⁸⁾ In this work, the expected distribution of the radioactive self-marker was calculated according to the Wagner theory and verified experimentally for the copper-oxygen system. Additional verification of the expected distribution of the activity was obtained by Castellan and Moore.⁽⁹⁾

The solid curve of Figure 2 shows the expected distribution when metal-ion migration predominates. In this case, there is a diminution of the radioactive tracer from the oxide-gas interface to the metal-scale interface. For the case in which nonmetal-ion migration through the scale predominates, the isotopic tracer would not be involved and the activity would appear in a narrow band at the scale-gas interface as shown by the dotted line in Figure 2. In the investigation of the oxidation of uranium by Schnizlein *et al.*,⁽¹⁰⁾ the isotope uranium-235 was used as a self-marker. The concentration of the alpha activity of the uranium-235 at the oxide-gas interface showed that migration of the nonmetal, oxygen, predominated in this reaction.

Figure 2
CALCULATED CONCENTRATION OF
RADIOACTIVITY IN OXIDE LAYER
BASED ON THE CATIONIC
VACANCY MECHANISM

The second technique used an experiment in which the character of the interface, at the point at which two scales of the same material, nickel fluoride or nickel oxide, growing toward each other from nearly parallel nickel surfaces would meet, as an indication of the mechanism. (This technique will be referred to hereafter as the "impinging scale" technique.) If metal atoms were the principal species migrating through the scale to react at the scale-gas interface, the two scale surfaces growing toward one another would fuse into one scale as the metal ions from one scale surface migrated into the other. If the mechanism were dependent on the movement of the nonmetal across the forming scales, the two scales would not fuse upon coming together, and an interface would be present. This technique was used by Schnizlein⁽¹⁰⁾ to identify the diffusing species in the oxidation of uranium.

The kinetics of the nickel-fluorine reaction were studied over the temperature range from 300 to 600 C by a manometric technique.

II. MECHANISM OF THE NICKEL-FLUORINE REACTION

A. Materials, Apparatus, and Experimental Procedure

The fluorine used in this work was procured from the General Chemical Company. The purity of the fluorine was assayed to be 98.2 v/o by the mercury reaction method.⁽¹¹⁾ Hydrogen fluoride was removed from the fluorine by passing the gas through a sodium fluoride trap kept at about 100 C.

The nickel used was commercial A-nickel which had a purity of 99.4 percent. Analyses by chemical and spectrographic means showed that the principal impurities, expressed in parts per million, were as follows: manganese, 2800; carbon, 700; iron, 1000; silicon, 800; and copper, 500.

The nickel-63 tracer was obtained from Oak Ridge National Laboratory in 5-mc lots as an acid chloride solution. Nickel-63 is a pure beta emitter with an energy of 63 kev. A small amount of nickel-59, with a K-capture X ray of 1.07 Mev, was present as a contaminant to the extent of about 0.01 percent. This gamma activity was not objectionable as it did not interfere with the autoradiographic process.

Two types of stripping film were used in this work: Kodak Experimental Permeable Base Stripping Film, which consisted of 5- μ emulsion overload with 5 μ of gelatin on a roll-film backing, and Kodak Autoradiographic Film AR-10, which consisted of a 5- μ -thick emulsion overlaid with 10 μ of gelatin on a glass-plate backing. Because of the greater thickness of the AR-10 film, it was found to be easier to handle for this type of use.

The fluorination and oxidation experiments were carried out in electrically heated tube reactors. The tube reactor for the fluorinations was a 2-ft section of 2-in. nickel pipe with a welded plate at one end and a flange closure at the other. A thermocouple tube made of $\frac{1}{4}$ -in. nickel tubing was welded through the top flange and extended to the midpoint of the reaction tube. Hooks welded to the thermocouple tube were used to support the sample specimens. A second $\frac{1}{4}$ -in. nickel tube, which was also welded through the top flange, and which extended to within one inch of the bottom of the reaction tube, served as an inlet for fluorine gas. The tube reactor for the oxidation experiments was a 10-in. section of 2-in.-diameter nickel tubing with a welded cap at one end and a flange closure at the other.

A nickel manifold connected to the reactor systems provided access for vacuum, fluorine and oxygen sources, and pressure-measuring devices. Both Bourdon-type gages and a Booth-Cromer null-point gage were used for pressure measurements.

Temperature was maintained by tube furnaces through a proportionally circuited Variac controlled by a pyrometer controller. The pyrometer was activated by a chromel-alumel thermocouple in the thermocouple well of the reactor. A second chromel-alumel thermocouple in the reactor was used in conjunction with a Brown potentiometer for measuring and recording the reaction temperature.

Figure 3
NICKEL-63 PLATING
CELL

Nickel containing the nickel-63 tracer was plated on the nickel coupons with the plating cell shown diagrammatically in Figure 3. The cell was constructed of 30-mm Pyrex tubing, 80 mm in length, capped with a 24/40 standard taper joint. The platinum leads were sealed through the Pyrex for support without attempting to produce gas-tight seals.

The coupons to be plated with nickel-63 were one cm by five cm by 0.16 cm, and were polished with one-micron diamond paste and then degreased using acetone. The acid chloride solution containing the nickel-63 was made basic with ammonia to form the tetraammine complex. A plating time of about 15 min at 10 ma and 2.2 v was required to obtain a $2\frac{1}{2}$ - μ -thick plate of nickel. Only the lower 1-2 cm of the coupon

was plated, the remainder of the coupon being masked with paraffin. The thickness of the plate was calculated from the weight gain of the coupon, the geometric area, and the theoretical crystal density of nickel.

Coupons used for the impinging scale experiments were one cm by three cm by 0.16 cm. A reaction specimen was prepared by welding two coupons together along the one-cm edges so as to make an angle of about one degree between surfaces, as shown in Figure 4.

Figure 4
WEDGE SPECIMEN FOR IMPINGING
SCALE EXPERIMENT

The plated coupons and welded impinging scale specimens were reacted with fluorine or oxygen in the following manner. The prepared coupons were placed in the reactor, and the system was evacuated and tested for leaks. Following this step, the reactant gas was admitted and the heating period was begun. This procedure was followed because it was found that starting the heating cycle after the fluorine was admitted to the reactor produced a more adherent scale. Fluorinations were carried out at 600 to 700 C for periods of 24 to 36 hr. The oxidations were run at about 1000 C for periods of 48 to 72 hr. After the reaction period, the reactor was evacuated and allowed to cool slowly for a period of about 12 to 24 hr before the samples were removed.

In order to examine the specimens metallographically or apply the autoradiographic emulsion, the coupons were mounted in Bakelite. The mounts were then sectioned normally to the short axis of the coupon for the nickel-63 specimens and normally to the long axis for the impinging scale specimens.

The autoradiographic technique described by Gomberg⁽¹²⁾ was used in these experiments. The specimen, mounted in Bakelite, was prepared by polishing with 600 grit metallographic paper. The mount was then cleaned in an ultrasonic bath to ensure the removal of residual activity spread over the surface during the polishing.

The emulsion, which was about 5- μ in thickness, plus the 5- or 10- μ -thick gelatin layer, was removed from the film backing. The emulsion, active side down, was floated onto the surface of the specimen using a drop of water containing a trace of wetting agent. An exposure time of five days was used, after which the emulsion was developed. After development the emulsion was removed from the mount and mounted on a standard microscope slide. Removal of the developed emulsion from the specimen was found desirable because the background made it difficult to observe the details of the exposed emulsion. The activity and replication of the surface could easily be observed when the emulsion was mounted on the glass slide. From the replicated surface it was possible to identify the interface regions without ambiguity.

B. Results and Discussion

The results of the impinging scale experiments are shown in Figures 5 and 6 which are micrographs of samples which have been reacted with fluorine and oxygen, respectively. It is apparent from Figure 5, that the impinging fluoride scales are separated by an interface, which indicates that fluorine migrated from the gas-solid interface through the fluoride scale to the nickel-nickelfluoride interface and that metal migration was negligible.

Figure 5
MICROGRAPH OF IMPINGING NICKEL FLUORIDE SCALES

A and A', nickel substrates; B and B', nickel fluoride scales; C, interface between nickel fluoride scales.

Figure 6
MICROGRAPH OF IMPINGING NICKEL OXIDE SCALES

A and A', nickel substrates; B, continuous nickel oxide scale.

In Figure 6, a continuous oxide scale is seen between the two metal surfaces. This confirms the fact that the metal migrates through the metal oxide scale, and reacts at the metal oxide-gas interface to produce a continuous oxide film.

Considerable porosity in the nickel oxide scale is evident in the micrograph reproduced in Figure 6. The adjacent metal surfaces, which were etched to provide more contrast with the scale, also exhibit porosity. The porosity of the oxide scale can be attributed to the removal of cation vacancies by condensation and precipitation within the oxide phase. This mechanism for the removal of cation vacancies from the metal oxidation system was proposed by Birchenall.⁽¹³⁾ The vacancies are present in the system as a result of cation diffusion during the reaction. The presence of what appear to be voids in the metal substrate may be the result of the production of vacancies at the metal-oxide interface and their subsequent migration to the growing voids within the metal. This, according to Vermilyea,⁽¹⁴⁾ results from the movement of atoms from the metal into the oxide from positions other than preferred sites, e.g., lattice-step positions.

The results obtained for the radioactivity tracer experiments are shown in Figures 7 and 8. Figure 7 is a micrograph of the autoradiograph of the nickel fluoride scale. This micrograph clearly shows a narrow band

Figure 7

MICROGRAPH OF AUTORADIOGRAPHIC EMULSION
SHOWING NICKEL-63 ACTIVITY IN NICKEL
FLUORIDE SCALE

A, original location of nickel substrate; B, nickel-nickel fluoride interface; C, nickel fluoride scale; D, darken zone in emulsion due to radioactivity; E, location of nickel fluoride-fluorine gas interface; F, original location of dental rubber mounting.

Figure 8

MICROGRAPH OF AUTORADIOGRAPHIC EMULSION
SHOWING NICKEL-63 ACTIVITY IN NICKEL
OXIDE SCALE

A, original location of nickel substrate; B, nickel-nickel oxide interface; C, nickel oxide scale; D, darkened area of emulsion due to radioactivity; E, location of nickel oxide-oxygen gas interface; F, original location of Bakelite mounting.

of activity at the position of the scale-fluorine interface. The line, indicated by arrow E in Figure 7, locates the position of the scale-gas interface. The width of the darkened portion of the emulsion is greater than the thickness of the portion of the nickel fluoride film occupied by the radioactive nickel because of the dispersion of the beta rays in the 5- μ -thick emulsion. From the location and distribution of the radioactivity, it can be deduced that fluorine is the migrating species in this reaction and that it migrates through the nickel fluoride film to the metal surface where it reacts with the nickel.

Figure 8 is a micrograph of an autoradiograph of the nickel oxide scale. The nickel activity is seen to penetrate into the nickel oxide scale. The linear penetration normal to the surface of the film is as much as 70 percent of the thickness of the oxide film.

Bardeen⁽⁸⁾ predicted that the activity would extend to the nickel-nickel oxide interface. However, the diminution of the activity close to the interface may not be resolved in the autoradiograph. In addition, Birchenall⁽¹³⁾ has pointed out that the expected distribution of radioactive tracer has been found by other workers to drop off rapidly in the region near the metal-oxide interface. He has postulated that this effect is due to an abrupt change in the diffusion coefficient owing to the porosity in the scale near the metal-oxide interface. Porosity has been observed in the nickel oxide scales produced in these experiments and could therefore account for the activity distribution found in Figure 8.

The results obtained in both types of marker experiments indicate that fluorine, rather than nickel, migrates through the fluoride scale during the course of the reaction. Fluorine could reach the metal surface by gross movement through pores and cracks in the fluoride scale or by some transport process through the bulk of the scale. Since the kinetics of the reaction have been shown to follow a parabolic rate,* it is more likely that the mechanism involves the transport of fluorine through the bulk of the nickel fluoride scale. Resolution of the mode of transfer of fluorine from the gas phase through the fluoride scale requires further experimental work. The evidence obtained from the marker experiments for the nickel-oxygen reaction is in accord with the accepted metal-ion diffusion mechanism for that reaction.

*See Section III of this report.

III. THE KINETICS OF THE REACTION OF NICKEL WITH FLUORINE

A. Materials, Apparatus, and Experimental Procedure

Both high-purity nickel and commercial A-nickel were used in these experiments. The high-purity nickel, designated by the name Nivac, was obtained from the Crucible Steel Company and was prepared by vacuum melting. Analyses of the Nivac nickel by chemical and spectrographic means indicated 99.92 percent nickel. The principal impurities, in parts per million, were as follows: cobalt, 300; iron, 400; carbon, 82; oxygen, 28; and nitrogen, 31. The properties of the A-nickel are described in Section II.A.

The fluorine used in these experiments was purified by distillation and was assayed by reaction with mercury.⁽¹¹⁾ It was found to be 99.93 v/o percent fluorine. The impurities in parts per million as determined by mass spectrographic analysis of the residual gas were as follows: oxygen, 396; water, 117; nitrogen, 78; carbon dioxide, 30; silicon tetrafluoride, 30; and argon, 12.

Figure 9

APPARATUS FOR THE STUDY OF THE
KINETICS OF THE NICKEL-
FLUORINE REACTION

The system used for these measurements is shown schematically in Figure 9. It consists of (1) a reaction vessel and tube furnace, (2) a manifold with outlets for vacuum, fluorine supply, and the pressure-measuring devices, and (3) a thermostatted section containing calibrated vessels of different volumes. The volumes of appropriate portions of the manifold, the thermostatted vessels, and the pressure transmitter section were determined by PVT measurements, using a water-calibrated standard volume.

The internal surfaces of the reaction vessels served as the nickel reactant. The vessels were fabricated from either Nivac sheet or A-nickel tubing and sheet by helium-shielded arc welding. The vessels were about 4 in. in length and one inch in diameter; each vessel had a volume of about 47 cc and an area of about 95 sq cm. The Nivac nickel sheet was about 20 mils in thickness and had been vacuum annealed; the A-nickel was used as received. During the forming and welding of the vessels, special care was taken to prevent contamination of the metal, and the fabrication was broken up into steps between which the subassemblies were cleaned and degreased. A length of $\frac{1}{8}$ -in.-diameter A-nickel tubing was welded through the top plate of each vessel to serve as the connection to the manifold.

The reaction vessels were held in a 10-in.-long nickel cylinder which in turn fitted snugly into a $2\frac{1}{2}$ -in. tubular furnace. This section of the apparatus is shown schematically in Figure 10. In addition to the hole drilled to hold the reaction vessels, two thermocouple wells were drilled in the block, one terminating at the level of the midpoint and the other at the bottom of the reaction vessel. The temperature of the tube furnace was controlled by means of a pyrometer-indicator-controller through a proportional circuited Variac. The pyrometer was actuated by the output of a chromel-alumel thermocouple placed near the resistance winding of the tubular furnace.

Figure 10
REACTION VESSEL AND NICKEL BLOCK

Platinum-90 percent platinum, 10 percent rhodium thermocouples were used to sense the temperature of the reaction vessel. A Rubicon type B potentiometer and associated standard cell and galvanometer were utilized to measure the output of the thermocouples. Temperature control during a reaction period was within $\pm$ one degree C.

The pressures on the inert side of the nickel diaphragms of the Booth-Cromer electrical pressure transmitters were measured with either a well-type mercury manometer or a U-tube manometer filled with Octoil-S.

At the start of an experiment the nickel vessel was attached to the manifold, evacuated, and tested for leaks. The evacuated vessel was then heated to the reaction temperature and fluorine was admitted to a pressure of 700 mm of Hg. At this point, pressure and time recordings were started. The changes in pressure were recorded at suitable time intervals: at $\frac{1}{2}$ -min intervals for the first 1-2 min, at 1-min intervals for the first half hour, and then at gradually lengthening time intervals as the reaction slowed down. The pressure in the system was kept within ± 25 mm of the initial pressure by intermittent additions of fluorine as the pressure dropped. Pressure readings during the initial rapid portion of the reaction were made with a mercury manometer. Subsequent readings were made using an Octoil-S-filled manometer to utilize its greater sensitivity.

For overnight periods, when the apparatus was left unattended, one of the ballast volumes was included in the reaction system so that the pressure in the system would not drop below the specified value. The quantity of fluorine in the reaction volume was calculated from values of the pressure, volumes, and temperatures of the various sections of the apparatus involved.

B. Results and Discussion

The results obtained in the nickel-fluorine kinetic experiments with Nivac nickel over the temperature range from 300 to 600 C are shown in Figure 11, in which micrograms of fluorine consumed per sq cm of nickel surface are plotted versus the reaction time in minutes. The experiments were run for about 2000 min at each temperature.

In Figure 12 the data are presented as a log-log function of the same coordinates used in Figure 11. In the construction of these plots the data for the first minute of reaction time were discarded, because the reaction is initially governed by a random selection of reaction sites due to activity differences over the nickel surface. The reaction proceeds rapidly on these sites in the manner of a nucleation process which, by subsequent outgrowth and coalescence of growth sites, results in a continuous fluoride scale over the entire nickel surface. In the initial phase, the reaction is not controlled by the transport of fluorine through a nickel fluoride barrier, as is the case once a continuous fluoride scale is present over the entire nickel surface.

Figure 11

LINEAR PLOT OF RATE OF REACTION OF NICKEL WITH FLUORINE
IN THE TEMPERATURE RANGE FROM 300 TO 600 C

Fluorine Pressure: 700 ± 25 mm

Material: Nivac nickel

Figure 12

LOGARITHMIC PLOT OF RATE OF REACTION OF NICKEL WITH
FLUORINE IN THE TEMPERATURE RANGE FROM 300 TO 600 C

Fluorine Pressure: 700 ± 25 mm

Material:

Nivac Nickel: 99.92%

Fluorine: 99.93%

For these log-log plots the reciprocals of the slopes are the values of n in the equation $w^n = kt$, in which w is the fluorine consumed per sq cm of nickel surface, k is the reaction rate constant, and t is the time. Values of n determined graphically from the plots of Figure 12 are listed above the appropriate linear sections. These values indicate that the reaction initially follows a parabolic rate law, but that after a period of time the reaction slows down, conforming to a cubic or slower rate. The parabolic rate constants are listed in Table 1, and the logarithms of these rate constants are plotted versus $1/T$ in Figure 13. The slope of this plot yields an activation energy of 17 kcal/mole.

Table 1

PARABOLIC RATE CONSTANTS FOR THE NICKEL-
FLUORINE REACTION OVER THE TEMPERATURE
RANGE FROM 300 TO 600 C

Material: Nickel, Nivac 99.92%
Fluorine, 99.93%

Temperature (C)	Value of n	Parabolic Rate Constant $(\mu\text{g F}_2/\text{sq cm})^2/\text{min}$
300	1.9	9.8
400	1.9	81.0
500	2.2	461
600	1.9	1860

Figure 13

ARRHENIUS PLOT OF PARABOLIC RATE
CONSTANTS FOR THE REACTION
 $\text{Ni} + \text{F}_2 \rightarrow \text{NiF}_2$ IN THE TEM-
PERATURE RANGE FROM
300 TO 600 C

Results obtained in experiments with A-nickel at 400, 500, and 600 C are shown in Figure 14; included on the plot are the data for Nivac nickel at the same temperatures. From these data, it is apparent that the reaction between fluorine and A-nickel is slower at a given temperature than that between fluorine and Nivac nickel. This difference is greatest during the initial periods of the reactions, and becomes less pronounced with time and at higher temperatures. This is illustrated by the fluorine consumption and scale thickness data at various reaction times. The scale thicknesses were calculated by use of the theoretical density for nickel fluoride: 4.63 g/cm^3 based on X-ray data.

Figure 14

COMPARISON OF THE REACTION BETWEEN FLUORINE
AND NIVAC AND A-NICKEL IN THE TEMPERATURE
RANGE FROM 400 TO 600 C

Pressure: $700 \pm 25 \text{ mm}$

Material: NV - Nivac, 99.92% purity

AN - A-nickel, ~99.4% purity

The data show that the rate of formation of nickel fluoride scale at 600 C becomes identical for the two nickel samples at reaction times greater than 500 min. At 500 C this leveling off of the rate of scale formation does not occur until 1000 min of reaction time have elapsed. At 400 C it would apparently require a longer reaction period than that used in these experiments to reach the leveling-off period. From these data it can be concluded that, after a certain scale thickness has been formed the continuing fluorine consumption of the system will be constant and independent of the purity of the nickel.

At the present time an explanation for the difference in reactivity can be attributed to two variables: (1) the differences in purity and (2) the grain size of the two types of nickel. Differences in the amounts of

the main impurities in the two types of nickel, in parts per million, are iron, 400 versus 1000; carbon, 80 versus 700; silicon, 100 versus 800; and copper, 100 versus 500, for Nivac and A-nickel, respectively. Estimation of the average grain size was made using the ASTM method designated E91-51T (ASTM Standards 1952, Part 2, Nonferrous Metals). In this method, micrographs (magnification 100X) of polished and etched samples are compared with micrographs of a standard grain size series. By this method, it was determined that the average grain size of the A-nickel was 0.11 mm and that of the Nivac nickel was 0.03 mm. It is possible, therefore, that the higher initial reactivity of the Nivac nickel could be due to the small grain size of the Nivac nickel and the consequent greater grain-boundary area.

A comparison of the rate constants at various temperatures could not be made for the A-nickel because of a change in the order of the reaction with temperature. This variation is shown in the log-log plots of Figure 15. At 400 and 500 C, the reaction appears to follow a logarithmic rate law; at 600 C the reaction approaches a parabolic rate law behavior. This change in order was also noted by Steunenberg *et al.*⁽¹⁵⁾ in a previous study of the kinetics of the nickel-fluorine reaction. The results obtained in that work and in the present study are in good agreement, as is shown in Table 2, in which the nickel fluoride scale thicknesses formed after a reaction time of 1000 min at various temperatures are compared. In the previous study by Steunenberg, A-nickel and commercial tank fluorine of greater than 99 percent purity were used.

Figure 15

THE FLUORINATION OF A-NICKEL IN THE
TEMPERATURE RANGE FROM 400 TO 600 C

Table 2

NICKEL FLUORIDE SCALE THICKNESSES AFTER
1000 MIN OF REACTION TIME FOR A-NICKEL

Temperature (C)	Nickel Fluoride Scale Thickness, Å	
	This Study	Steunenber <i>et al.</i> ⁽¹⁵⁾
400	4,400	3,800
500	8,200	9,200
600	29,000	30,000

Gas-metal reactions in which the rates are controlled by a diffusion process and are dependent on the thickness of the scale formed sometimes show a pressure dependence of a fractional order. Two experiments at each of the following pressures of fluorine: 100, 350, and 700 mm Hg, were made at 500 C with Nivac nickel. Ultimate fluoride scale thicknesses obtained in these experiments after 1500 to 2000 min of reaction time were approximately 17,000 Å. The results of these reactions did not indicate a pressure dependence of the reaction rate beyond the reproducibility of the data, approximately ± 10 percent. Parabolic rate constants obtained from these data are listed in Table 3, along with the average values at each pressure and the average of the six rate constants. It is apparent from these rate constants that the effect of pressure on the reaction over the range covered in this work must be less than the magnitude of the deviation between runs.

Table 3

PARABOLIC RATE CONSTANTS FOR THE NICKEL-FLUORINE
REACTION AT 500 C AND FLUORINE PRESSURES OF
100, 350, AND 700 mm

Material: Nivac nickel, 99.92%
Fluorine, 99.93%
Final Scale Thickness: $\sim 1.7 \times 10^4$ Å

Pressure (mm)	Parabolic Rate Constants	
	$(\mu\text{g F}_2/\text{sq cm})^2/\text{min}$	Average Values
700	461	424 $\pm$ 37
700	387	
350	370	346 $\pm$ 23
350	322	
100	355	396 $\pm$ 41
100	438	

Average of 6 Constants = 388 $\pm$ 40

Work performed at the Gaseous Diffusion Plant at Oak Ridge by Hale and coworkers⁽²⁾ showed the rate for the nickel-fluorine reaction to be pressure dependent in the case of samples having initial nickel fluoride scales of about $2.5 \times 10^5 \text{ \AA}$ in thickness. The data were used to derive the constants in the following equation:

$$dx/dt = kp^n ,$$

in which dx/dt is the rate of growth of the fluoride scale, k is the rate constant, and p is the pressure. From the slope of a log-log plot of dx/dt versus p for their data at 600 C, a value of n of 0.87 was obtained.

These measurements were repeated by us with both A-nickel and Nivac nickel samples having initial nickel fluoride scales of about $2.5 \times 10^5 \text{ \AA}$ in thickness. Our data along with values obtained from the Oak Ridge data by interpolation are listed in Table 4. The data obtained for A-nickel are plotted in Figure 16. From the data listed in Table 4, it can be seen that our results for A-nickel compare closely with those obtained at Oak Ridge. However, the Nivac nickel results are higher than those obtained for A-nickel. In Figure 17, the rate of change in the thickness of the film is plotted versus the pressure of fluorine in atmospheres as a log-log plot of the data from this study for Nivac nickel and for interpolated points obtained from the Oak Ridge work. From the slopes of these curves, a value of n of 0.55 was obtained for this work and a value of n of 0.87 was obtained for the Oak Ridge work.

Table 4

THE EFFECT OF PRESSURE ON THE RATE OF BUILDUP
OF A NICKEL FLUORIDE SCALE AT 600 C

Initial Scale Thickness: $\sim 2.5 \times 10^5 \text{ \AA}$

Equation: $dx/dt = kp^n$

Rate of Increase of Scale Thickness,
 $dx/dt, (\mu\text{g F}_2/\text{sq cm})/\text{min}$

Pressure (atm)	This Study		Oak Ridge, A-Nickel ⁽²⁾
	Nivac	A-Nickel	
0.96	1.20	0.13	0.17
0.46	0.78	0.082	0.085
0.13	0.11	0.038	0.030

Figure 16

PRESSURE DEPENDENCE OF NICKEL-FLUORINE REACTION

Temperature: 600 C
 Initial NiF_2
 Scale Thickness: $\sim 2.5 \times 10^5 \text{ \AA}$

Figure 17

RATE OF CHANGE OF SCALE THICKNESS AS A
FUNCTION OF FLUORINE PRESSURE

Temperature: 600 C
 Initial Scale
 Thickness: $2.5 \times 10^5 \text{ \AA}$
 Equation
 $\log dx/dt = \log k + n \log p$

IV. SUMMARY

Evidence obtained from two experimental approaches has been presented for the mechanism of the nickel-fluorine reaction. In one approach the isotope nickel-63 was used as a self-marker, and the distribution of the beta activity of the nickel-63 in the scale indicated the species, nickel or fluorine, that migrated during the reaction. In the second or impinging scale technique, the character of the interface formed when scales from opposing nickel surfaces are made to grow against one another indicated the migrating species. The validity of the method was checked by performing similar experiments with the nickel-oxygen system, a system for which the reaction mechanism is known. In this system, the reaction proceeds via migration of nickel ions through the oxide scale to the oxide-scale interface.

In the isotopic tracer experiments, nickel-63 was plated on the surfaces of nickel coupons which were then fluorinated or oxidized. The reacted specimens were then mounted in Bakelite and sectioned normal to the surface of the scale. An autoradiograph was then taken and, after development, was mounted on a microscope slide. The autoradiograph replicated the surface of the specimen so that an unambiguous identification of the metal-scale and scale-gas interfaces could be made. In the nickel-fluorine experiments, the nickel-63 activity was found concentrated at the fluoride scale-fluorine interface, thus indicating that the reaction mechanism involved the migration of the fluorine through the nickel fluoride scale to the scale-gas interface. A similar experiment with the nickel-oxygen system showed a distribution of the nickel-63 activity such as would be expected for a mechanism in which nickel migrated through the growing oxide scale to the nickel-nickel oxide interface. The results obtained in the nickel-oxygen experiment are in accord with the accepted mechanism for this reaction.

In the impinging scale experiments, reaction specimens were prepared by welding together two nickel coupons along a common edge, so that the opposing surfaces were separated by only a fraction of a millimeter. The specimens, after reaction, were mounted in Bakelite and sectioned to expose the scales held between the opposing nickel faces. If the two opposing scales are fused into a single, continuous scale, metal migration is indicated with reaction occurring at the scale-gas interface. If, however, the two scales are not fused into a single, continuous scale and a definite interface exists between them, nonmetal migration is indicated, with reaction occurring at the scale-metal interface. In the fluoride impingement experiments, the presence of an interface between the two fluoride scales indicated the migration of the nonmetal, fluorine. In the nickel oxide impingement experiments, the fusion of the two scales into one continuous scale indicated migration of the metal, nickel.

Although these experiments showed that the mechanism of the nickel-fluorine reaction involves the migration of fluorine through the growing fluoride scale to the metal-scale interface, they did not indicate the mode of transport of the fluorine. Two possibilities exist: the fluorine migrates to the metal-scale interface by gross movement through pores and cracks in the fluoride scale, or by some transport process through the bulk of the scale. Since the kinetics of the reaction have been shown to follow a parabolic rate law, it is more likely that the mechanism involves the transport of fluorine through the bulk of the nickel fluoride scale.

The kinetics of the nickel-fluorine reaction were measured over the temperature range from 300 to 600 C with Nivac, a high-purity nickel, and commercial A-nickel. A manometric technique was employed and the reactions were performed under isobaric conditions. The kinetics of the reaction between Nivac nickel and fluorine were found to obey a parabolic rate law, with reaction rate constants of 9.8, 81.0, 461, and 1860 ($\mu\text{gF}_2/\text{sq cm Ni})^2/\text{min}$ at 300, 400, 500, and 600 C, respectively. An activation energy for the reaction of 17 kcal/mole was calculated from the value of the slope of an Arrhenius plot of the data. Comparison of the temperature dependence of the rate constants obtained for the reaction between A-nickel and fluorine with those for the reaction between Nivac nickel and fluorine could not be made as the rate law compliance in the case of A-nickel changed with temperature, from logarithmic at 400 and 500 C to parabolic at 600 C. The rate of reaction was, however, higher for Nivac than it was for A-nickel. A smaller crystal grain size for the Nivac nickel might account for its higher reactivity. The parabolic reaction rate constants for the Nivac nickel did not show a pressure dependence greater than the uncertainty for an individual constant, which was ± 10 percent, over the pressure range from 100 to 700 mm of Hg. However, for samples having an initial fluoride scale of about 10^5 Å in thickness the rates obtained were found to be dependent on a fractional power of the pressure of fluorine. The reaction rate of Nivac nickel was found to be dependent on the 0.55 power of the pressure, whereas that for A-nickel was about 0.87 power of the pressure which was confirmatory of the pressure dependence found for A-nickel by workers at Oak Ridge.⁽²⁾

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