AFRPL-TR-66-215

HALOGEN PASSIVATION STUDIES

S. K. Asunmaa, W. A. Cannon, W. D. English, and S. M. Toy

Astropower Laboratory, Missile & Space Systems Division
A Division of Douglas Aircraft Company, Inc.

TECHNICAL REPORT AFRPL-TR-66-215

August 1966

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards Air Force Base, California

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

AFRPL-TR-66-215

HALOGEN PASSIVATION STUDIES

S. K. Asunmaa, W. A. Cannon, W. D. English, and S. M. Toy

Astropower Laboratory, Missile & Space Systems Division
A Division of Douglas Aircraft Company, Inc.

TECHNICAL REPORT AFRPL-TR-66-215

August 1966

Preceding Page Blank

FOREWORD

This is the third quarterly progress report prepared under Contract AF04(611)-10932 and covers the period from 1 Many 1966 to July 31, 1966. The program is administered by AFPRL, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California, with Lt. Ralph Fargnoli, Project Monitor.

The report was prepared by Dr. W. D. English, as principal investigator, and by W. A. Cannon, S. K. Asunmaa and S. M. Toy as associate investigators, under the supervision of Dr. N. A. Tiner, Head of Materials Research Department.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

George F. Babits, Lt. Colonel, USAF
Chief, Propellant Division

ii

ABSTRACT

This third quarterly progress report covers research in halogen passivation accomplished during the period from 1 May 1966 to 31 July 1966. Various passivation techniques involving a range of pressures and concentrations of fluorine gas and interhalogens were investigated using stainless steel 316 and Monel 400 powders. The effectiveness of the passivation processes was determined by measuring the additional reaction of the treated powders with fluorine gas. Effects of atmospheric moisture on fluoride films were investigated. Reflection electron diffraction patterns were made of fluoride films formed on copper before and after exposure to atmospheric moisture.

TABLE OF CONTENTS

Preceding Page Blank

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION AND SUMMARY

The objective of the experimental work described in this report has been to obtain detailed information on the properties of passive films formed on metal surfaces by exposure to fluorine and certain interhalogen compounds. The means of obtaining this information has involved investigation of the rates and mechanisms of film formation, of the composition and structure of passive films, and of the environmental factors leading to destruction or alteration of passive films.

The initial experimental work involved determining comparative rates of film formation on various metal and alloy powders in fluorine, chlorine trifluoride, and Compound A. Rates of film growth for periods up to four hours have been evaluated.

Various passivation procedures covering ranges of time, temperature, and pressure have been investigated on certain alloy powders. The efficiency of passivation is interpreted in terms of the amount of additional fluorine taken up when the treated metal surface is exposed to fluorine gas. The effect of water vapor on passive films on stainless steel 316 and Monel has been studied.

composition and structure of fluoride films on copper were investi- by electron diffraction using the reflection method for examining films in situ. A technique for forming fluoride films on metal specimens and introducing them into the electron microscope without exposure to air or moisture has been developed. The electron diffraction method was also used for determining composition changes in the films caused by exposure to moisture in air.

1

SECTION II

EXPERIMENTAL EVALUATIONS

1. REACTION OF GASEOUS COMPOUND A WITH METAL POWDERS

a. Procedure

The gravimetric method described in the first quarterly report[1] was applied to the investigation of the reaction between Compound A vapor and metal powders. As in the experiments with chlorine trifluoride, net weight losses of the sample tubes were observed, and it was necessary to apply corrections to the data to compensate for weight losses of the glass. The modified procedure and method of calculation are described in the last quarterly report.[2]

The following expression is used to determine the mean fluoride film thickness assuming that the weight gain of the metal powder is due exclusively to reaction between metal and Compound A to form a fluoride film of normal composition and density:

$$d = \frac{W_f R}{A \rho} 10^8 \tag{1}$$

where W_f = weight gain of metal powder (g)

     d = fluoride film thickness in angstrom units

     R = ratio of molecular weight of metal fluoride to molecular weight of fluorine in metal fluoride

     A = total area of powder sample (cm^2)

     ρ = density of metal fluoride (g/ml)

For Monel 400 and 316 stainless steel, the film is assumed to be a mixed fluoride of the major alloy constituents of approximately the composition of the alloy. For nickel 200 and aluminum 2024, the fluoride film is assumed to be the fluoride of the main alloy constituent. Calculated densities, molecular weight ratios, and surface areas are given in Table I.

b. Results and Discussion

The results for exposure of four metals and alloys to Compound A vapor at one atmosphere pressure for 60 minutes at 25°C (77°F) are given in Table II. The net weight changes obtained for 316 stainless steel and Monel 400 samples are so small that little significance can be attached to the calculated film thicknesses. Somewhat larger net weight changes were observed for nickel 200 and aluminum 2024. However, the calculated film

Preceding Page Blank   3

TABLE I. DENSITIES, MOLECULAR WEIGHT RATIOS, AND SURFACE AREAS USED IN CALCULATION OF FLUORIDE FILM THICKNESSES

Metal or Alloy	Fluoride Composition	ρ (g/ml)	R	Surface Area (cm^2/g)
Ni 200	NiF_2	4.63	2.54	2330
316 SS	$(17\,CrF_3 + 12\,NiF_2 + 71\,FeF_3)$	3.72	2.01	1040
Monel 400	$(70\,NiF_2 + 30\,CuF_2)$	4.51	2.58	2020
Al 2024	AlF_3	2.88	1.48	4830

4

TABLE II. GRAVIMETRIC FILM THICKNESS MEASUREMENT – COMPOUND A – 25°C (77°F) – ONE HOUR EXPOSURE

Metal or Alloy	Wt. Powder (g)	Total Surface Area (cm²)	Wt. Change Tube & Powder (mg)	Wt. Change Glass Tube (mg)	Wt. Change Powder (mg)	Calculated Film Thickness (Å)
316 SS	39.4595	4.1 x 10⁴	- 7.2	- 6.5	- 0.7	Negative
316 SS	39.5120	4.1 x 10⁴	- 6.5	- 7.9	+ 1.4	1.8
316 SS	39.4997	4.1 x 10⁴	-17.5	- 8.8	- 8.7	Negative
Monel 400	39.6179	8.0 x 10⁴	- 5.1	- 6.4	+ 1.3	0.9
Monel 400	39.6764	8.0 x 10⁴	-13.5	-15.8	+ 2.3	1.6
Monel 400	39.5393	8.0 x 10⁴	-13.5	-12.1	- 1.4	Negative
Nickel 200	39.7704	9.3 x 10⁴	-18.6	-31.0	+12.4	7.4
Nickel 200	39.4840	9.3 x 10⁴	-13.0	-25.9	+12.9	7.7
Al 2024	16.9720	8.2 x 10⁴	-13.5	-23.5	+10.0	6.1

thicknesses are only about half those observed for exposure to chlorine trifluoride vapor under similar conditions.

2. REACTION OF GASEOUS FLUORINE WITH METAL OXIDES

a. Introduction

Most of the metals under study have oxide films onthe surfaces which are probably at least 20 to 50 Å or more in thickness.[3] This is considerably thicker than the apparent fluoride film thickness produced by short exposure to gaseous fluorine[2] and in view of the rapid reaction with fluorine, it is evident that the oxide film is largely, if not exclusively, involved in the reaction. This implies that the method of calculation of fluoride film thickness based on the following reaction is not correct:

$$M + F_2 \longrightarrow MF_2$$

Instead, the following reaction is involved:

$$MO + F_2 \longrightarrow MF_2 + \frac{1}{2}O_2$$

Methods of calculation of fluoride film thickness based on the first equation will yield results which are too low. This applies whether a gravimetric method is employed, or if a pressure change is determined in a closed system, i.e., a volumetric method. If a particular metallic oxide exists in an intermediate oxidation state, for example Cu_2O, another reaction is possible:

$$Cu_2O + 2F_2 \longrightarrow 2CuF_2 + \frac{1}{2}O_2$$
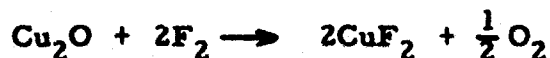
It becomes apparent that detailed knowledge of the nature of reaction of fluorine with surface oxide films is important before any accurate estimation of fluoride film thickness can be made.

Although a large amount of data has been published concerning gas-solid reactions between oxygen and metals, relatively little is known concerning reaction of fluorine with metal oxides. Haendler et al[4] investigated the reaction of CuO with fluorine above 300°C (572°F) and noted extensive reaction. More recently Ritter and Smith[5] noted a detectable reaction between CuO and fluorine at room temperature and above.

b. Experimental Determinations

The relative rates of reaction of fluorine with both thin and thick oxide films on copper and nickel as well as with copper and nickel oxides were determined, using the constant volume passivation apparatus. Samples of copper and nickel powders were used (1) as received, (2) after hydrogen reduction followed by exposure to ambient air, and (3) after air oxidation

at elevated temperature. Reagent grade CuO and NiO were also used. Surface areas of all these materials were measured in order to express the amount of fluorine reacted on an equivalent area basis. The surface areas are given in Table III.

Weighed samples of each of the materials listed in Table III were introduced into the constant volume apparatus, and the amounts of fluorine reacting at approximately one atmosphere initial pressure and 80°F were determined. Figure 1 is a plot of the amount of fluorine in milligrams reacting per 10^5 cm^2 of surface as a function of time on the copper derivatives. A similar plot is given in Figure 2 for the nickel materials.

c. Results and Discussion

The rate of reaction of fluorine with the as-received copper and hydrogen-reduced copper are nearly identical. When expressed in terms of the amount of fluorine reacting for equivalent surface, the curves in Figure 1 are almost superimposable. It may be assumed here that the reacting surface is Cu_2O. There is considerable evidence that the thin oxide on copper is Cu_2O.[3] This film would be expected also to have reformed on the hydrogen-reduced sample when exposed to air.

The MD-301 copper powder which was oxidized in air until a black oxide film of CuO covered the particles, reacts more nearly like the reagent CuO. (Bottom two curves of Figure 1). The reacting oxide, CuO, attains a limiting fluoride film very rapidly which impedes further oxidation. It appears that the reaction between fluorine and CuO nearly ceases after about ten minutes. With a Cu_2O surface, the reaction is still continuing at an appreciable rate for 30 to 60 minutes. Obviously, a different mechanism is involved which is probably related to different diffusion characteristics in the different oxide films.

No simple explanation can be advanced at this time for the widely different reaction rates of fluorine with the nickel oxide surfaces as shown in Figure 2. The similar curve for the nickel powder and NiO lends support to the belief that the reactive film on the nickel is NiO, but this is not supported by the curve for the ignited nickel powder which was obviously covered with a heavy film of NiO (bottom curve of Figure 2). Additional supporting X-ray diffraction or electron diffraction evidence must be sought to establish if the different rates and apparent film thicknesses formed by exposure to fluorine are due to crystal structure or orientation effects, or are due to some other cause.

3. EFFECT OF ATMOSPHERIC MOISTURE ON PASSIVE FILMS

a. Introduction

It is generally conceded that water vapor has a deleterious effect on fluoride films although the exact mechanism is not clearly understood. Many inorganic fluorides are hygroscopic, forming hydrates, hence it is not surprising that small amounts of moisture can alter and affect the protective

TABLE III. SURFACE AREAS OF METALS AND METAL OXIDES

Material and Description	Surface Air (cm^2/g)
1. Copper Powder — MD-301	2500
2. Copper Powder — MD-301 (oxidized at 400°F)	5690
3. Copper Powder — MD-301 (H_2 reduced at 350°F, then exposed to ambient air)	2150
4. Copper Oxide — Reagent Powder	3540
5. Nickel Powder — 112F	2330
6. Nickel Powder — 112F (oxidized at 750°F)	1540
7. Nickel Powder — 112F (H_2 reduced at 650°F, then exposed to ambient air)	1080
8. Nickel Oxide (NiO) — Reagent Powder	4030

8
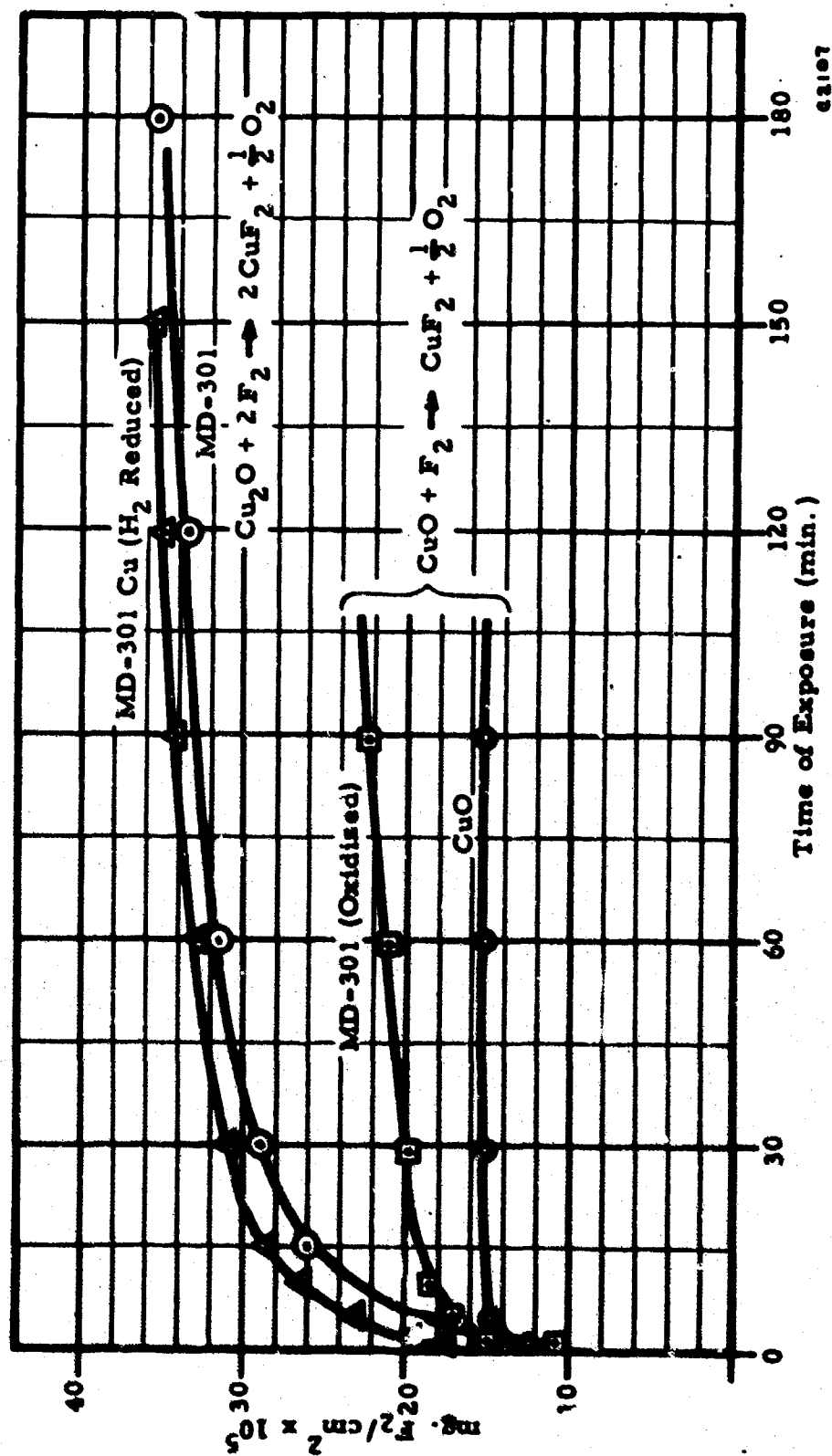
Figure 1. Reaction of Fluorine With Copper Oxides — One Atmosphere F_2 Pressure — 27°C (80°F)

$$Cu_2O + 2F_2 \longrightarrow 2CuF_2 + \tfrac{1}{2}O_2$$

$$CuO + F_2 \longrightarrow CuF_2 + \tfrac{1}{2}O_2$$

MD-301 Cu (H$_2$ Reduced)

MD-301

MD-301 (Oxidized)

CuO

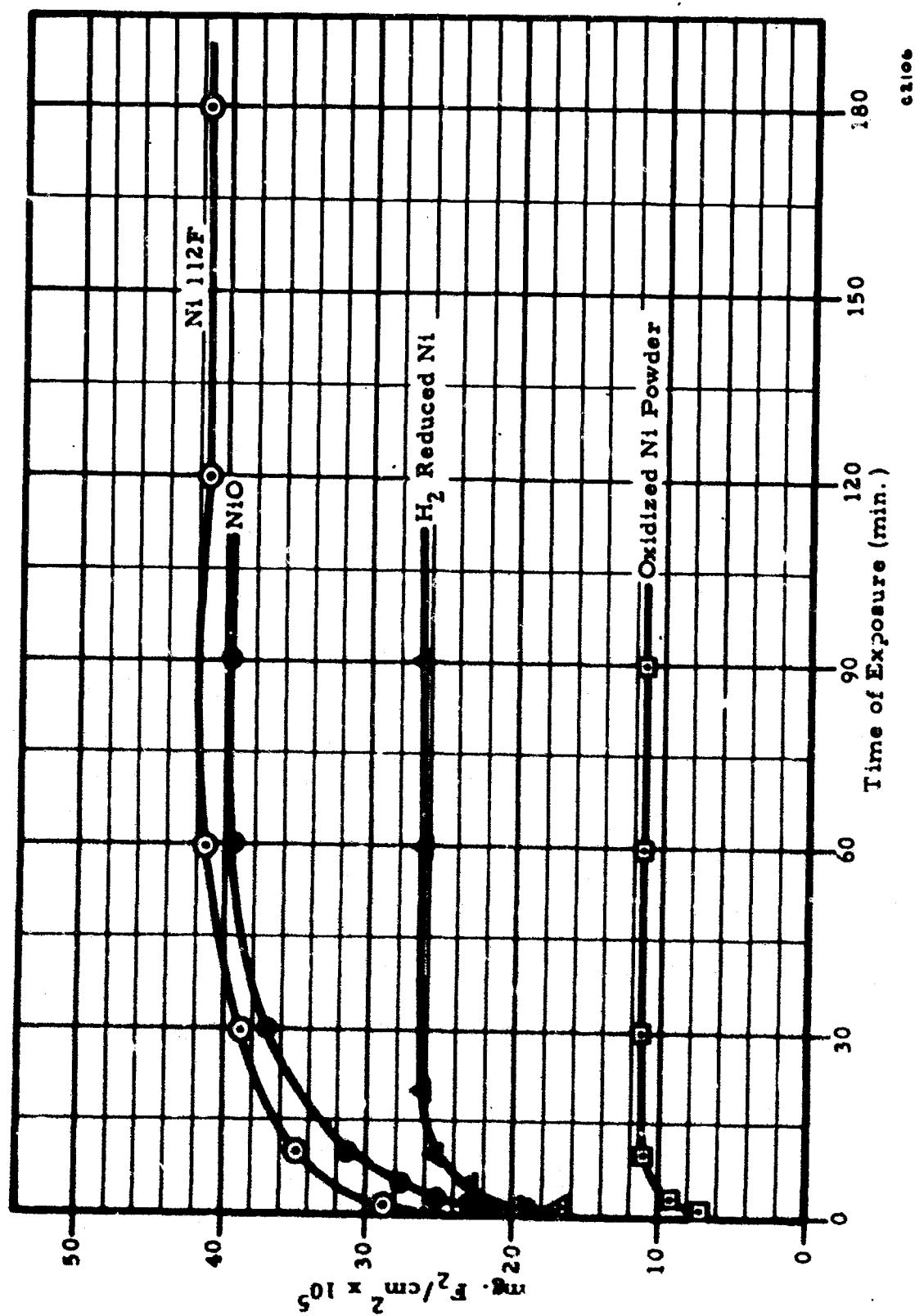Time of Exposure (min.)

mg. F_2/cm^2 x 10^5

6

Figure 2. Reaction of Fluorine With Nickel Oxide Surfaces — One Atmosphere F_2 Pressure — 27°C (80°F)

character of a fluoride film. In addition to the possible loss of film integrity, the subsequent reaction of fluorine with adsorbed moisture or with hydrates can result in formation of HF which may be excessively corrosive to certain metals and alloys in a system.

Very few quantitative data are available concerning interaction of water vapor and fluoride films. A few preliminary experiments with passive films on nickel and Monel were reported in the last quarterly report.[2] Kleinberg and Tompkins[6] reported on the amount of fluorine reacting with samples of fresh and passivated metal powders. The passivated powders were exposed to atmospheric moisture (condition and time of exposure were not stated) prior to a second passivation with fluorine at one atmosphere. The amount of fluorine taken up in the second passivation ranged from a low of 4 per cent of the first passivation (nickel powder) to 95 per cent of the first passivation (Monel). The results were somewhat erratic. Replicate analyses of Monel ranged from 30 to 95 per cent comparing the second passivation to the first.

The approach which has been used in this investigation is as follows: Samples of metal powders are passivated by various methods described below, then exposed to fluorine gas at near one atmosphere pressure and the pressure of fluorine gas observed as a function of time in an isothermal closed system of constant volume. This procedure is repeated on a fresh sample of powder which has been passivated, then exposed to 50% relative humidity in air at room temperature. The pressure dependence is compared with that of an identical charge of fresh powder which has received no passivation treatment. These experiments were carried out in the constant volume passivation system described in detail in previous reports.[1,2]

In interpreting the results of the various experiments, the simple assumption is made that if a sample of metal powder does not take up any additional fluorine upon exposure to fluorine gas at one atmosphere and 80°F, it is completely passivated in the sense employed herein. On the other hand, if a sample of powder, following some specified pre-treatment, takes up an appreciable amount of fluorine when exposed, the passivation is not complete. Expressing the data as a pressure change, rather than a fluoride film thickness or weight of fluorine, does not require one to make any assumption as to the nature of the reaction.

b. Experimental Determinations

Three distinct operations were required to determine the efficacy of the various passivation procedures and the effect of moisture on them. These are described as follows.

(1) A 100 gram sample of metal powder was charged to the sample bomb of the constant volume passivation apparatus.[1] The apparatus was evacuated for a minimum of 30 minutes, a volume calibration carried out with helium gas and the system again evacuated. Fluorine was then introduced to the system and the system pressure was measured as a function of time

11

as fluorine reacted with the metal powder. The initial fluorine gas pressure was near one atmosphere and the sample bomb was thermostatted at $27^{\circ}C$ $(80^{\circ}F)$.

(2) A fresh 100 gram sample of metal powder was charged to the bomb. After evacuation for a minimum of 30 minutes, the metal powder was subjected to one of the passivation treatments described in the later sections. The sample bomb is equipped with valve and coupling so that the passivation treatment can be conducted outside the constant volume apparatus. After completion of the prescribed passivation, the bomb was evacuated and introduced into the constant volume apparatus. The procedure under paragraph (1) above was repeated and the pressure change due to additional reaction of fluorine, if any, was recorded as a function of time.

(3) The operations under paragraph (2) were repeated using a fresh 100 gram charge of powder, except that before the sample bomb containing the passivated powder was placed in the constant volume apparatus, it was opened up to expose the bomb contents and placed in a constant humidity chamber at 50% relative humidity at $25^{\circ}C$ $(77^{\circ}F)$ for 48 hours. After the exposure, the sample was evacuated in the constant volume system for 30 minutes before continuing the experiment.

The pressure changes plotted for the various experiments are directly comparable because the same sample size, viz 100 gram, was always used and the system volume was always constant (430 ml total). Corrections to ΔP were applied for large variations in temperature of the unthermostatted parts of the constant volume apparatus. (It is impractical to thermostat the entire system, for example the gauge volume, hence minor corrections need to be applied for ambient temperature variations.)

c. Results and Discussion — Stainless Steel 316

The following results were obtained for stainless steel 316 alloy (Plasmadyne Plasmalloy No. 215-F, Lot No. Q10495). A 100 gram sample has a total surface area of 1.04×10^5 cm^2. Previous data indicate that a fluoride film of 7.1 Å thickness is formed in one hour exposure to fluorine at one atmosphere and at $27^{\circ}C$ $(80^{\circ}F)$, assuming the reaction to take place between metal and fluorine without evolution of gaseous reaction products.

(1) Fluorine Passivation at One Atmosphere — The data are plotted in Figure 3. Curve 1 shows the change in pressure in the system due to uptake of fluorine by a fresh, unpassivated sample. Curve 2 is obtained after prior passivation for one hour at one atmosphere fluorine pressure at $27^{\circ}C$ $(80^{\circ}F)$. On the basis of the criterion set forth in paragraph 3(a) above, the sample is completely passive by virtue of its lack of any further reaction with fluorine. After the same passivation followed by exposure to 50% relative humidity in air, Curve 3 is obtained. The pressure change after one hour is approximately 45% that of the unpassivated sample (Curve 1). The rate of reaction appears to be slower in the early stages as evidenced by the initially different negative slope of Curve 3 compared to Curve 1.

12

Figure 3. Exposure of Stainless Steel 316 Powder (100 g) to Fluorine — 27°C (80°F)
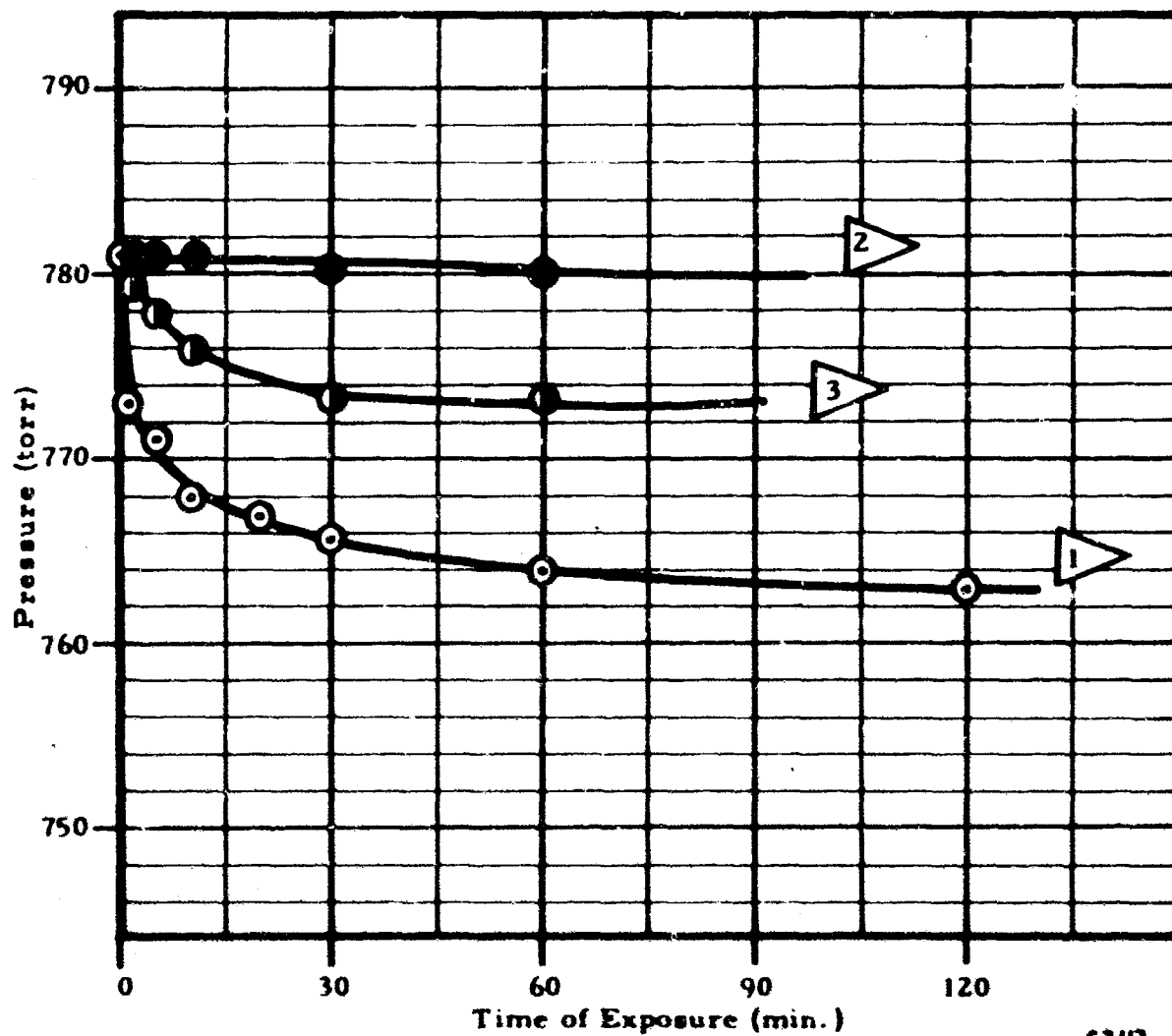
1 ▷ No prior passivation

2 ▷ Passivated in F_2 — 1 atm. — 1 hr. — 27°C (80°F)

3 ▷ Same as 2 ▷ plus exposure to 50% relative humidity at 25°C (77°F) for 48 hours

This is a general observation for most of the later experiments and its significance will be discussed later.

(2)   Fluorine Passivation at One Atmosphere with Incremental Build-Up of Pressure — This experiment is very similar to the one described in paragraph (1) above except that instead of abruptly exposing the sample to fluorine at one atmosphere, the pressure is gradually built up in stages with evacuations between pressure increases. This is a common method of fluorine passivation. The technique is applied probably for two reasons: (1) it helps avoid runaway reaction caused by burning of organic contaminants, and (2) it helps avoid diffusion blocks in dead ends of systems or long runs of pipe or tubing. It is not known whether a better or more effective passive film is produced per se. The incremental pressure build-up was accomplished as follows:

> Pump sample for 30 minutes
>
> Pressurize with fluorine at 1 psia for 5 minutes — pump down
>
> Pressurize with fluorine at 2 psia for 5 minutes — pump down
>
> Pressurize with fluorine at 4 psia for 5 minutes — pump down
>
> Pressurize with fluorine at 8 psia for 5 minutes — pump down
>
> Pressurize with fluorine at 1 atmosphere for 60 minutes — pump down for 30 minutes.

The results shown in Figure 4, Curve 2, indicate that the procedure results in complete passivation. Curve 3 shows a pressure change amounting to 65% of the first passivation after one hour. The somewhat greater sensitivity to moisture shown here perhaps reflects a slightly thicker fluoride film formed although this is conjecture.

(3)   Fluorine Passivation at Low Temperature — The data are plotted in Figure 5. The sample passivated at liquid nitrogen temperature (~195°C) in fluorine at 0. 1 atmosphere for four hours continued to take up a small amount of fluorine as indicated by Curve 2. It is not conclusive that the passivation to the extent indicated took place at the low temperature. Adsorption of fluorine is expected to take place at liquid nitrogen temperature. The adsorbed fluorine may not have been completely removed by pumping, and as the sample warmed up, the adsorbed fluorine could have reacted with the metal surface. Curve 3 for the moisture exposed sample generally falls in line with the two previous experiments.

(4)   Passivation in Fluorine at High Pressure — Data for the samples passivated at 60 atmospheres (900 psi) in fluorine for one hour at 25°C (77°F) are presented in Figure 6. Curve 2 shows complete passivation and Curve 3 shows a relatively large pressure change for the humidity exposed sample. The pressure change amounts to 75% of that for a fresh sample after one hour exposure. This observation is in line with the belief that a much thicker film would be formed at the high pressure. If the high root

14
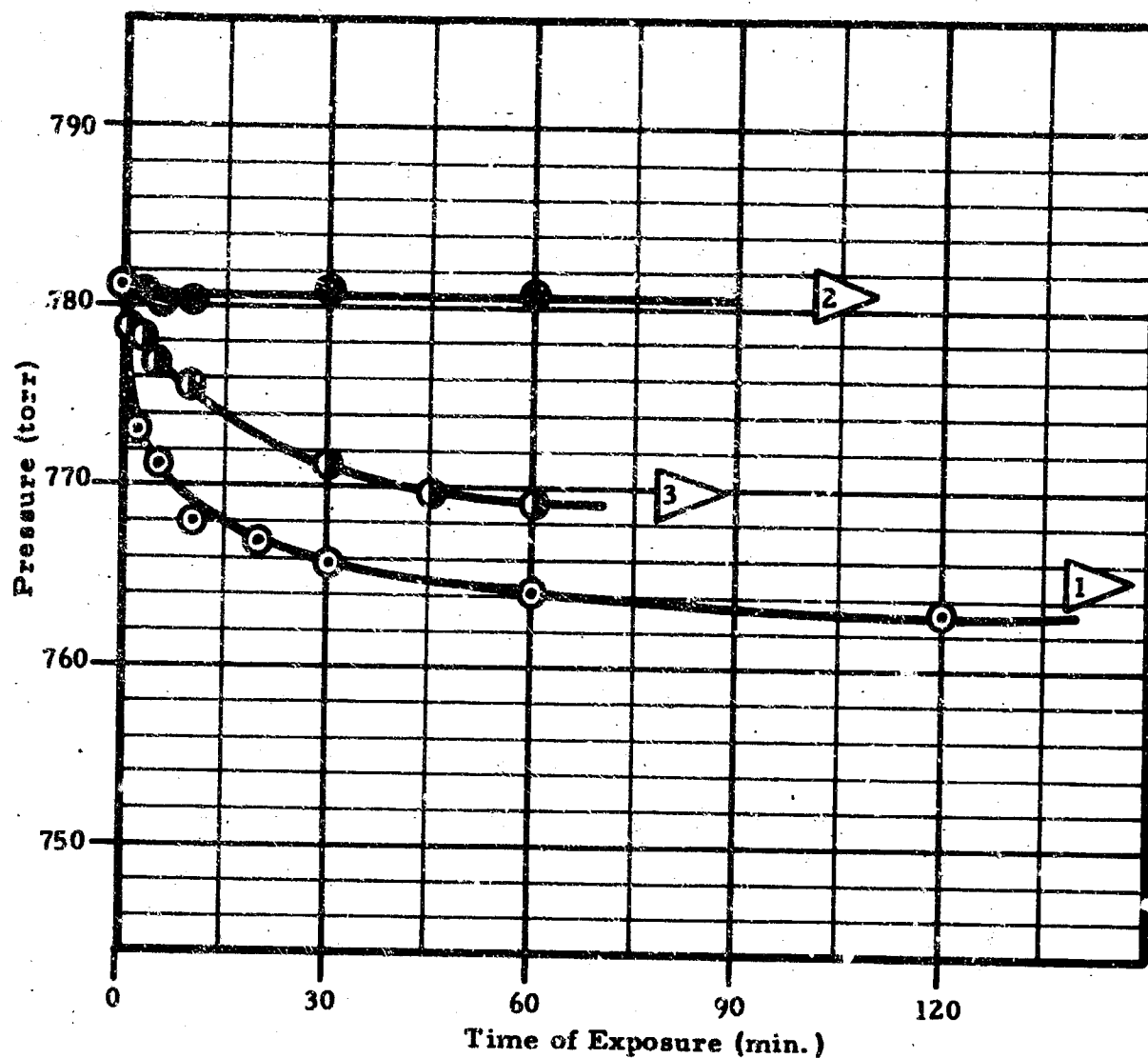
C 2109

▷1▷ No prior passivation

▷2▷ Passivated in F_2 — 1 atm. — 1 hr. — 27°C (80°F) following
incremental build-up of pressure (see text)

▷3▷ Same as ▷2▷ plus exposure to 50% relative humidity in air
at 25°C (77°F) for 48 hours

Figure 4. Exposure of Stainless Steel 316 Powder (100 g)
to Fluorine — 27°C (80°F)

15

Figure 5. Exposure of Stainless Steel 316 Powder (100 g)
to Fluorine — 27°C (80°F)
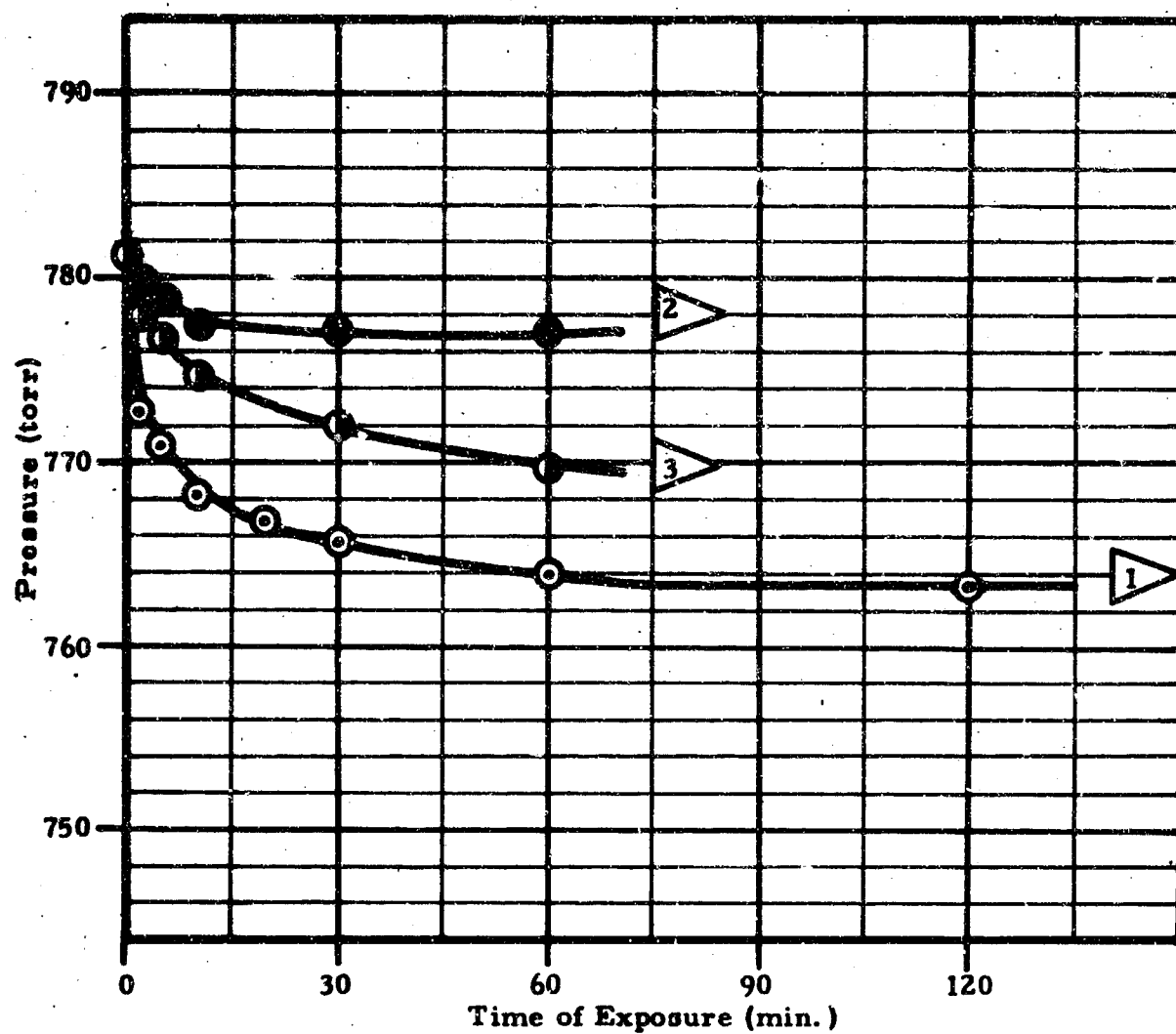
⟐1⟐ No prior passivation

⟐2⟐ Passivated in F_2 — 0.1 atm. — 4 hrs. — -195°C (-320°F)

⟐3⟐ Same as ⟐2⟐ except exposed to 50% relative humidity in
air at 25°C (77°F) for 48 hours

16

Figure 6. Exposure of Stainless Steel 316 Powder (100 g) to Fluorine — $27^{\circ}C$ ($80^{\circ}F$)
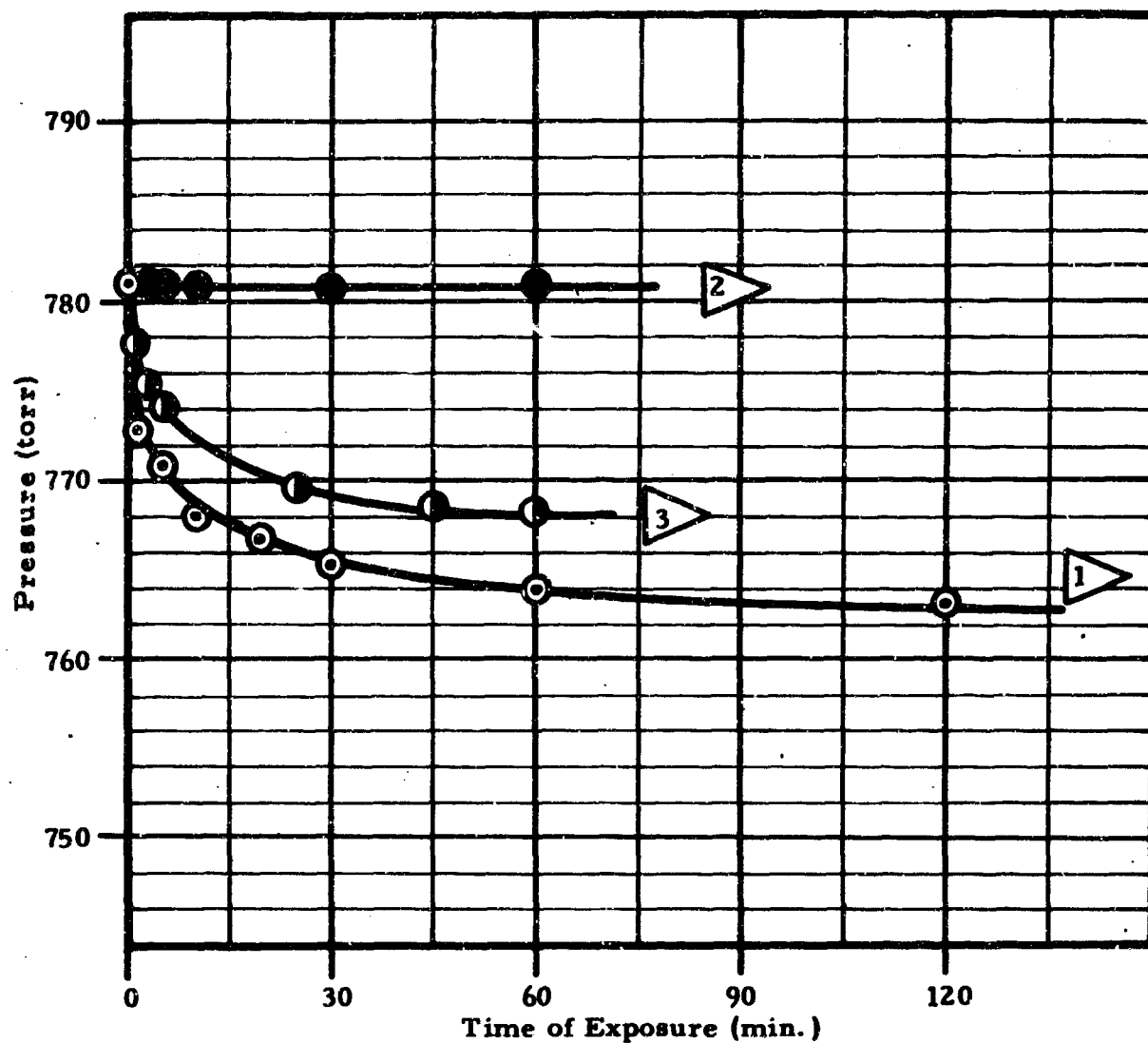
1 ▷ No prior passivation

2 ▷ Passivated in F_2 — 60 atm. — 1 hr. — $25^{\circ}C$ ($77^{\circ}F$)

3 ▷ Same as 2 ▷ except after passivation exposed to 50% relative humidity in air at $25^{\circ}C$ ($77^{\circ}F$) for 48 hours

17

dependence (5th to 7th root) between pressure and apparent fluoride film thickness, as established for nickel,[2] holds for stainless steel 316, approximately twice as thick a film should be found at 60 atmospheres than at one atmosphere.

(5)   Passivation by Compound A — Figure 7 gives data for samples passivated in Compound A vapor at one atmosphere for one hour at 27°C (80°F). Curve 2 reveals that a sample so passivated takes up a small amount of fluorine but in a very peculiar manner. There is almost a linear decrease of pressure with time rather than the usual curve convex to the abscissa. Curve 3 is similar to Curve 2, indicating relatively little sensitivity of the passive film to moisture. It is unfortunate that technical difficulties prevented carrying these curves to longer intervals of time.

(6)   Passivation by Compound A at Higher Temperature — In this set of experiments the Compound A passivation was carried out at 71°C (160°F). As the plots in Figure 8 show, the character of the passive film is completely changed. Complete passivation is indicated by Curve 2 while great sensitivity to moisture is revealed by Curve 3. The uptake of fluorine exceeds that for a fresh sample (Curve 1) by 50%.

(7)   Passivation by Chlorine Trifluoride — The sample passivated in chlorine trifluoride vapor at one atmosphere for one hour at 27°C (80°F), appeared to be completely passivated as evidenced by the horizontal Curve 2 of Figure 9. The sample exposed to water vapor took up over 85% as much fluorine as a fresh sample indicating considerable sensitivity to water vapor. The passivation in chlorine trifluoride was in each case followed by pumping while the sample was heated to 71°C (160°F); therefore, retention of adsorbed chlorine trifluoride on the sample should not be excessive.

(8)   Passivation in Bromine Pentafluoride — Passivation in bromine pentafluoride vapor was investigated. The data are presented in Figure 10. The rather unexpected observation was that the samples took up very large quantities of fluorine, both before and after exposure to humidity. Approximately three times as much fluorine is consumed as for the unpassivated sample. There is a strong implication that by reaction with metal, or by dissociation, a relatively large amount of bromine trifluoride is left in the sample which subsequently reacts with fluorine. Bromine trifluoride, if present, would not be readily removed by pumping at 71°C (160°F) — the temperature employed here.

d.   Results and Discussion — Monel

The results described in the following paragraphs were obtained with Plasmadyne Monel 206F -- Lot No. Q-10435. A 100 gram sample has a surface area of 2.02×10^5 cm^2. Previous results have shown that a fluoride film thickness of 6.7 Å is formed in one hour in fluorine at one atmosphere at 27°C (80°F) assuming that the reaction is between metal and fluorine and that no volatile reaction products are formed.
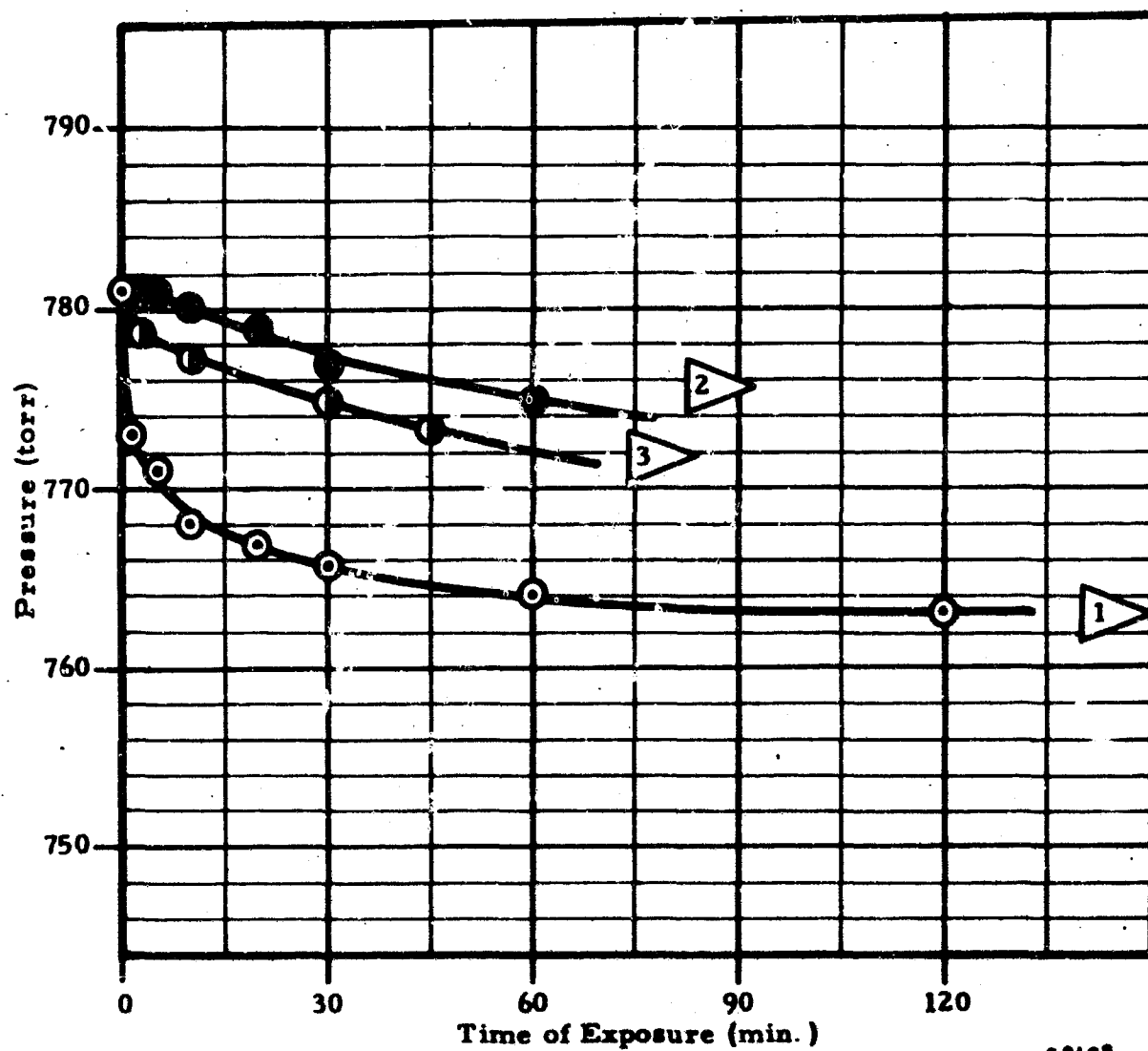
Figure 7. Exposure of Stainless Steel 316 Powders (100 g) to Fluorine — 27°C (80°F)

Figure 8. Exposure of Stainless Steel 316 Powder (100 g)
to Fluorine — 27°C (80°F)

1▷ No prior passivation

2▷ Passivated in Compound A vapor — 1 atm. — 1 hr. — 71°C
(160°F)

3▷ Same as 2▷ except followed by exposure to 50% relative
humidity in air at 25°C (77°F) for 48 hours

20

c2117

1 ▷ No prior passivation

2 ▷ Passivated in chlorine trifluoride vapor — 1 atm. — 1 hr. — 27°C (80°F)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

Figure 9. Exposure of Stainless Steel 316 Powder (100 g) to Fluorine — 27°C (80°F)

21

c2105

1 ▷ No prior passivation

2 ▷ Passivation in bromine pentafluoride vapor — 0.4 atm. — 1 hr. — 27°C (80°F)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

Figure 10. Exposure of Stainless Steel 316 Powder (100 g) to Fluorine — 27°C (80°F)

22

(1)   Fluorine Passivation at One Atmosphere — The curves are given in Figure 11   Curve 1 is the pressure change as a function of time for a fresh sample.   After passivation in fluorine for one hour at one atmosphere, Curve 2 is obtained.   There is a gradual, almost linear decrease in pressure with time but this seems to be normal for Monel.   All previous work with Monel reveals that it continues to react with fluorine almost indefinitely so far as known.   Unlike stainless steels and nickel, the pressure changes continuously with time.   A fairly large moisture sensitivity is indicated by Curve 3.

(2)   Fluorine Passivation With Incremental Build-Up of Pressure — The data are given in Figure 12 and are virtually identical to the results given in paragraph (1) above.

(3)   Fluorine Passivation at Low Pressure — Passivation was carried out in fluorine at 0.1 atmosphere for one hour at 27^OC (80^OF).   This was the first time a low pressure passivation was attempted near room temperature.   In view of the apparent complete passivation obtained (see Curve 2, Figure 13) and the lower sensitivity to moisture revealed by Curve 3, this passivation technique deserves further investigation.

(4)   Passivation in Compound A Vapor — Passivation in Compound A vapor at one atmosphere for one hour at 27^OC (80^OF) yielded results shown in Figure 14.   The results were very similar to those obtained by fluorine passivation under similar conditions.

(5)   Passivation in Chlorine Trifluoride Vapor — The data are given in Figure 15.   Somewhat lower moisture sensitivity was observed than for Compound A and fluorine under similar conditions of passivation.

e.   General Comments

From the experiments completed to date, it is evident that passive fluoride films can be formed on stainless steel 316 and Monel by exposure to fluorine, Compound A, and chlorine trifluoride.   This conclusion is based on the observation that exposure to these compounds results in a surface film which is resistant to further attack by fluorine at a pressure of one atmosphere at a near room temperature.   The use of bromine pentafluoride to form passive fluoride films seems to be inadviseable; even if a passive fluoride film is formed, a reaction product is evidently left on the surface which reacts further with fluorine.   Low temperature passivation with fluorine (-195^OC) appears to be incomplete.

The reactivity of passive fluoride films to water vapor appears to vary greatly.   In general, the reaction takes place at a slower rate than the initial passivation.   The fluoride films formed by chlorine trifluoride or Compound A are most reactive to water vapor.   Whether this is due to the film thickness or composition is not known.   There is some evidence that the thinner the film formed by fluorine passivation, the less additional fluorine is taken up following exposure to moisture.   It appears that fluorine

Figure 11. Exposure of Monel Powder (100 g) to Fluorine — 27°C (80°F)
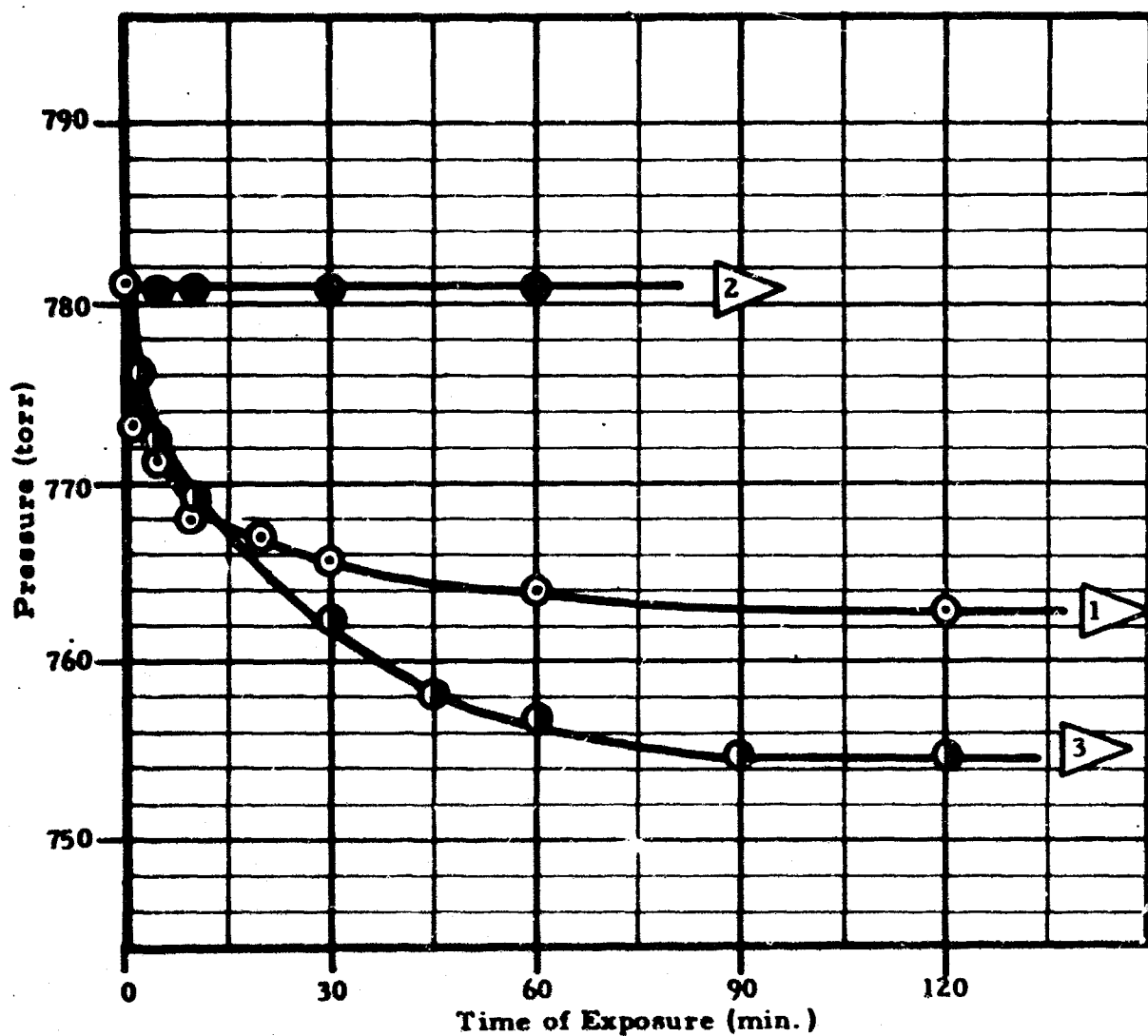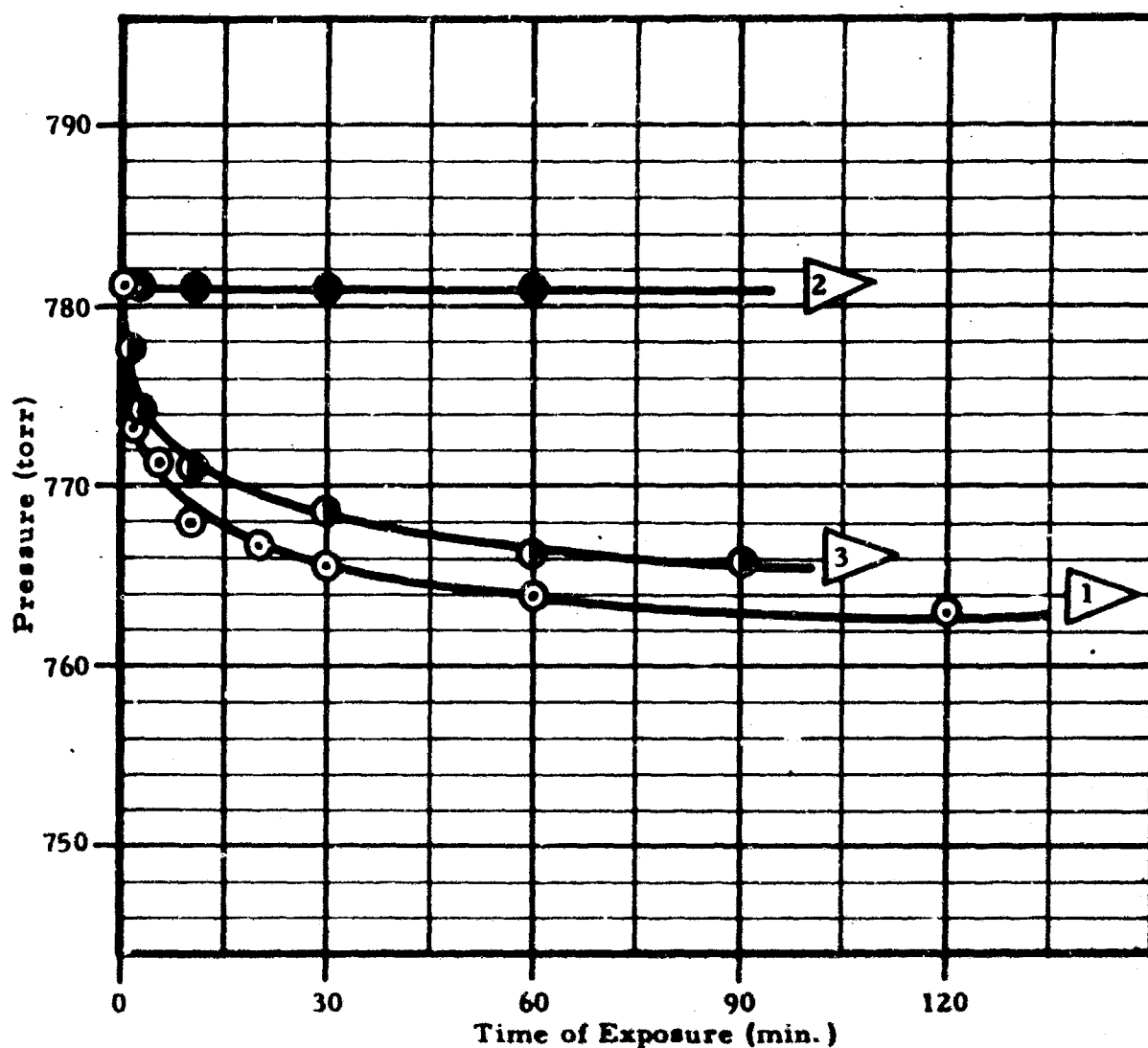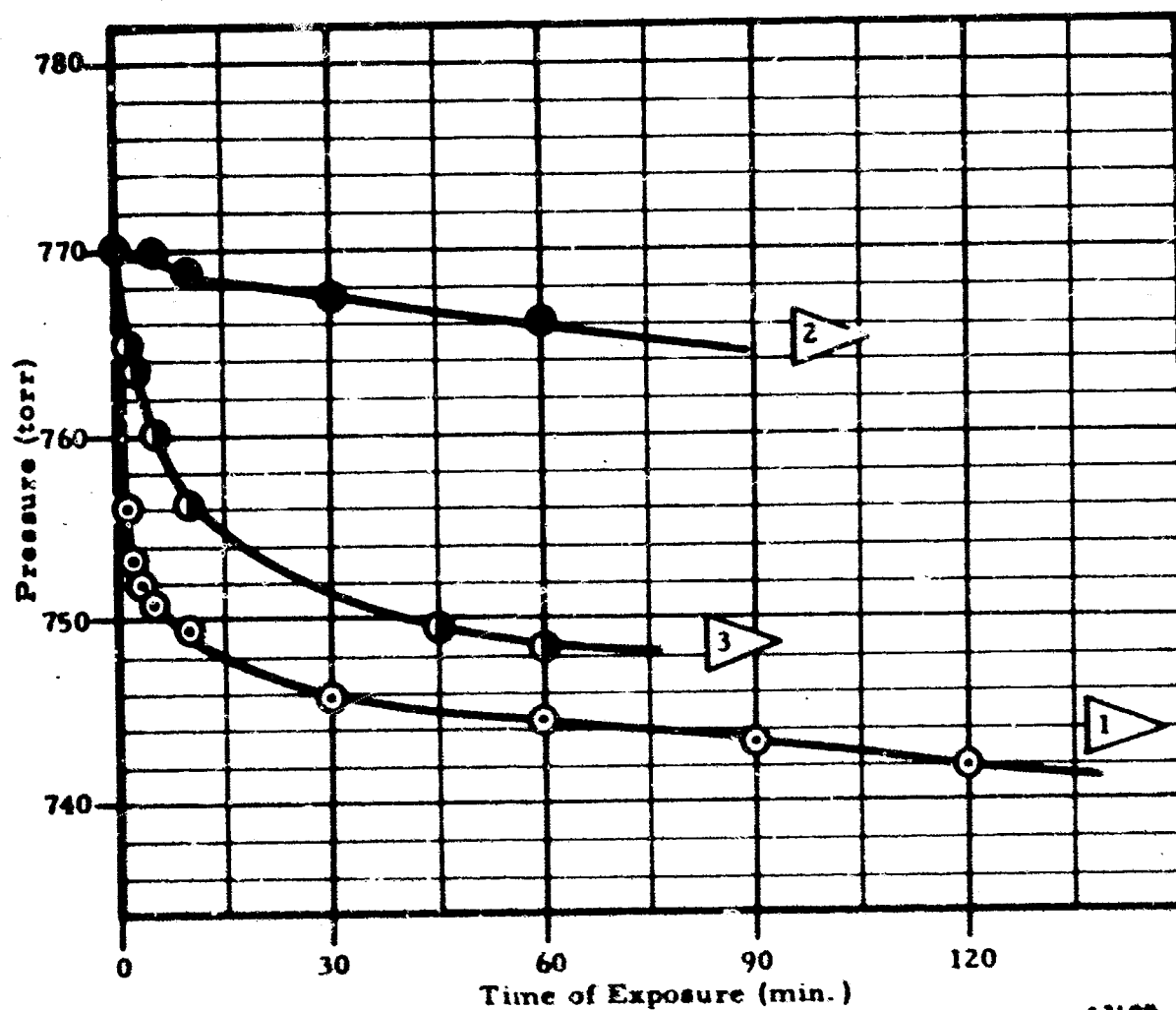
1 ▷ No prior passivation

2 ▷ Passivation in fluorine gas — 1 atm. — 1 hr. — 27°C (80°F)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

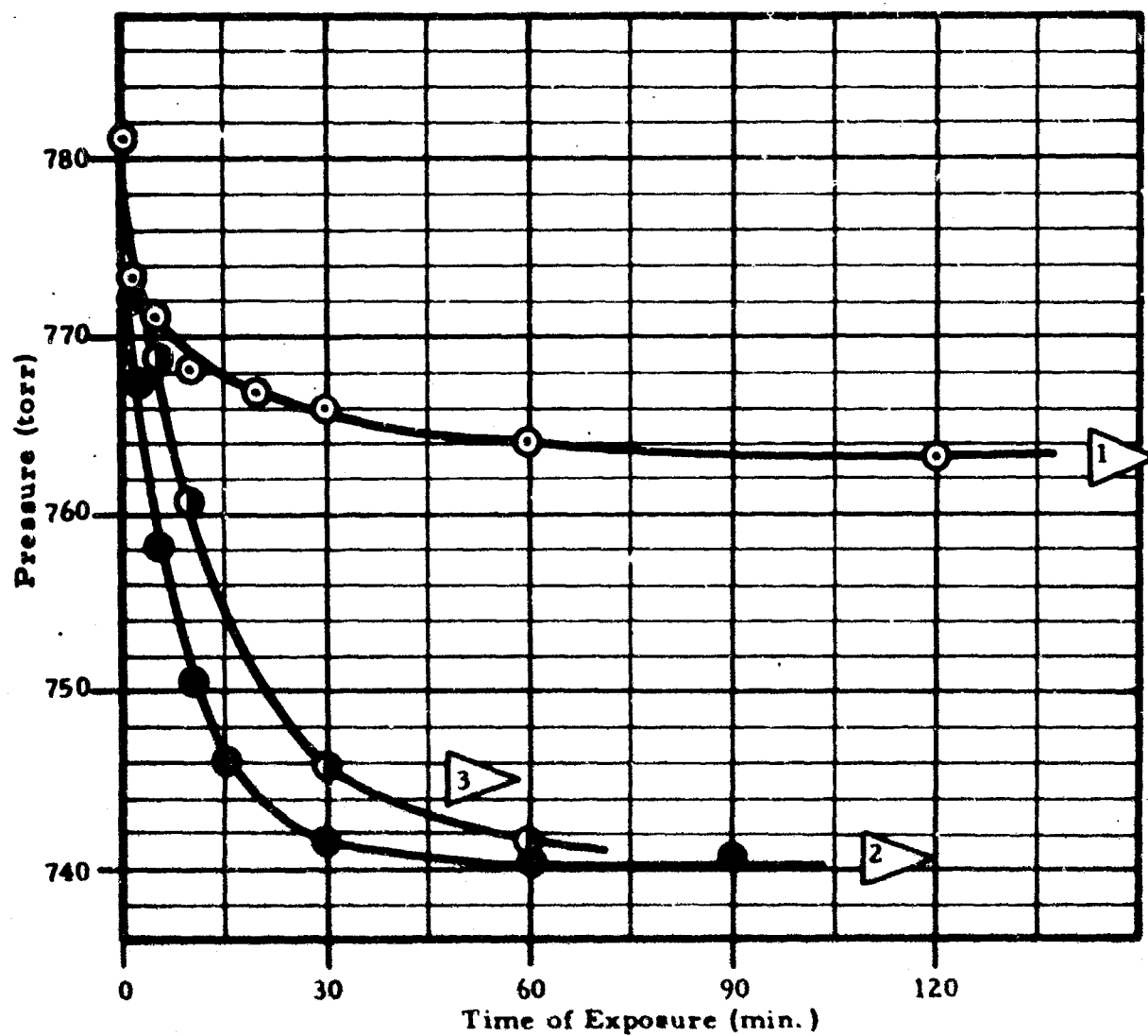Figure 12. Exposure of Monel Powder (100 g) to
Fluorine — 27°C (80°F)
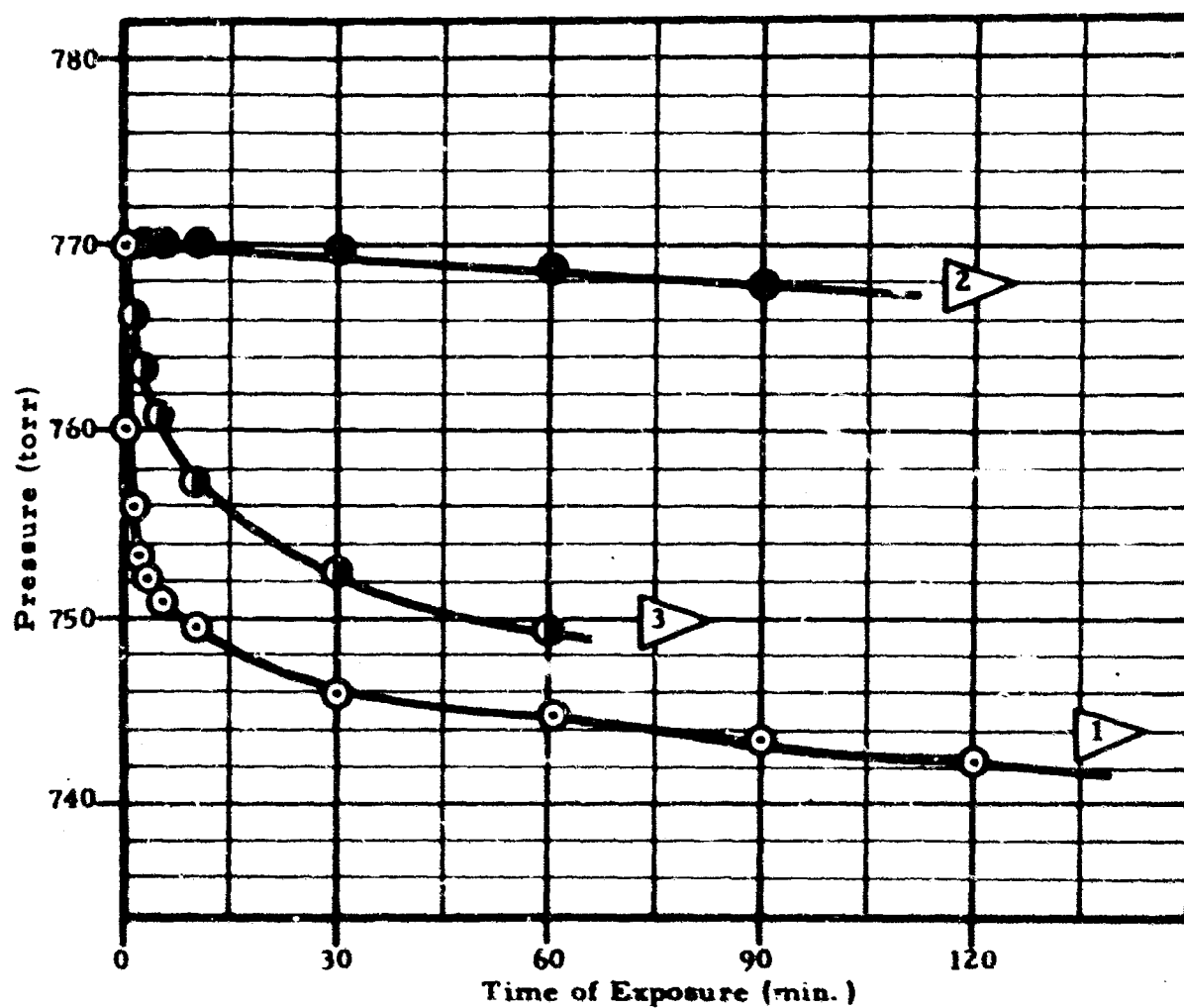
1 ▷ No prior passivation

2 ▷ Passivated in fluorine gas — 1 atm. — 1 hr. — following incre-
mental build-up of pressure (see text for details)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative
humidity in air at 25°C (77°F) for 48 hours
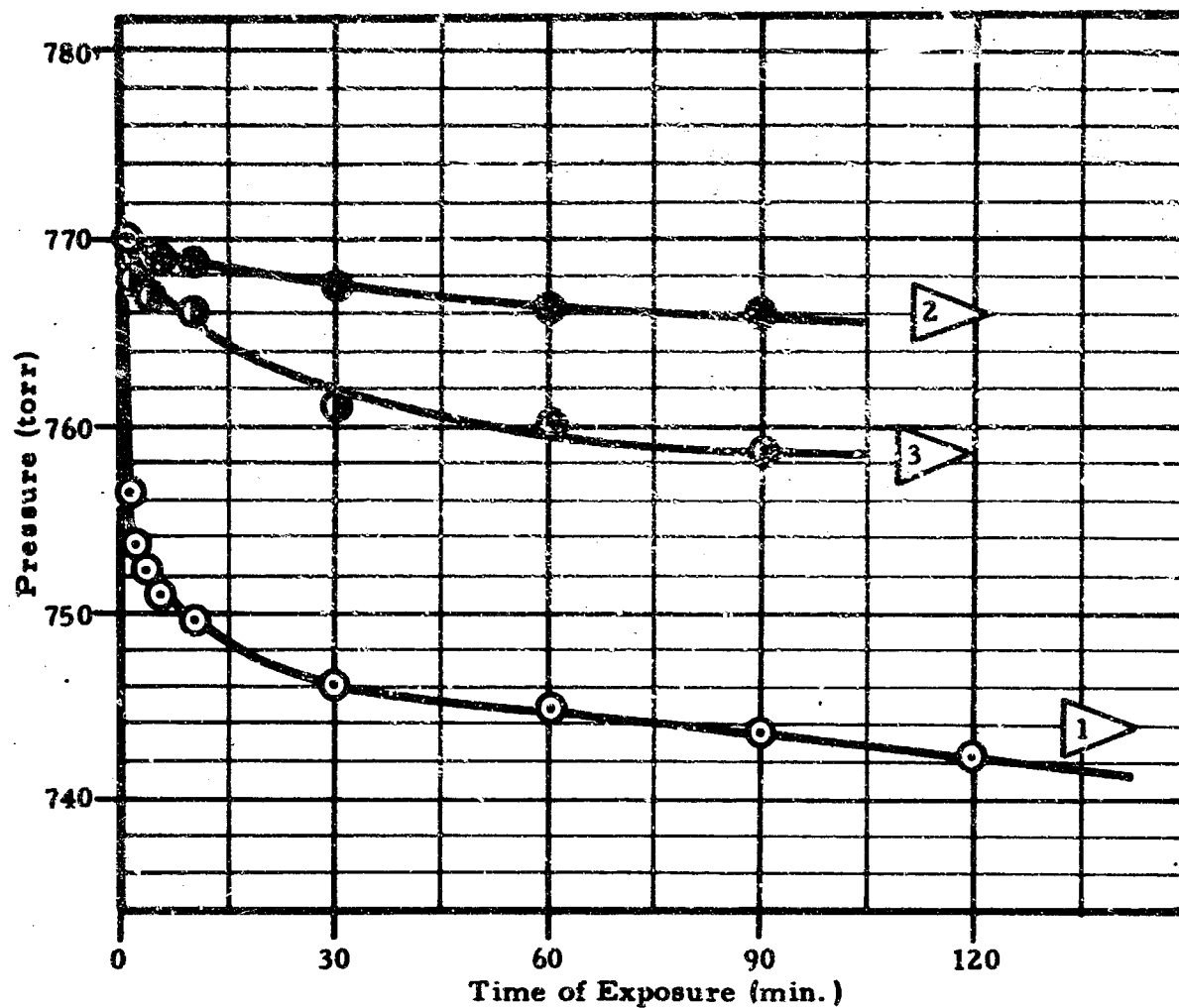
≈2116

1 ▷ No prior passivation

2 ▷ Passivated in fluorine gas — 0.1 atm. — 1 hr. — 27°C (80°F)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

Figure 13. Exposure of Monel Powder (100 g) to Fluorine — 27°C (80°F)

c 2115

1 ▷ No prior passivation

2 ▷ Passivated in Compound A vapor – 1 atm. – 1 hr. – 27°C (80°F)

3 ▷ Same as 2 ▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

Figure 14.   Exposure of Monel Powder (100 g) to Fluorine – 27°C (80°F)

27

c2114

1▷ No prior passivation

2▷ Passivated in chlorine trifluoride vapor — 1 atm. — 1 hr. — 27°C (80°F)

3▷ Same as 2▷ except followed by exposure to 50% relative humidity in air at 25°C (77°F) for 48 hours

Figure 15.   Exposure of Monel Powder (100 g) to Fluorine — 27°C (80°F)

28

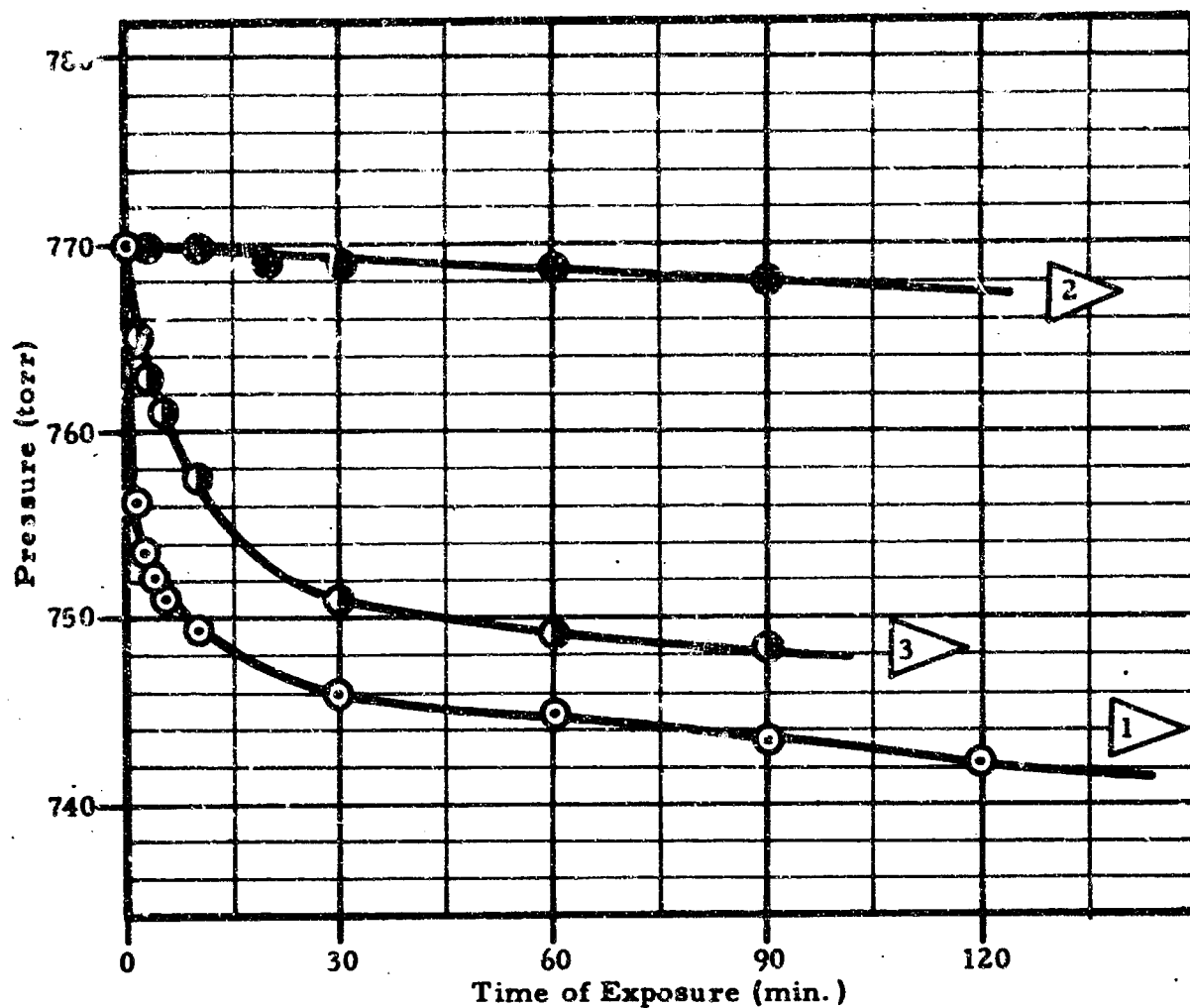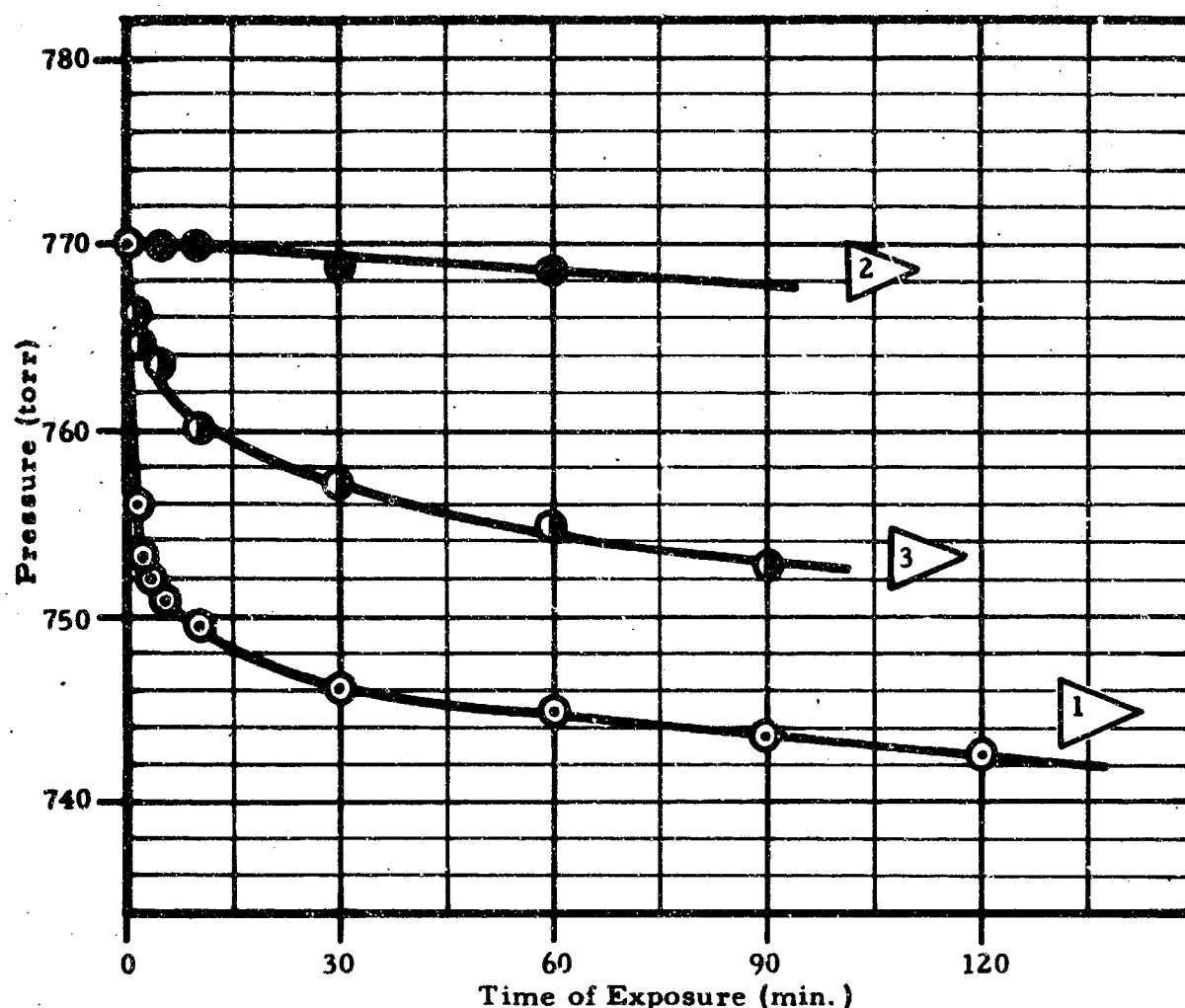passivation at low pressure is the most advantageous passivation procedure from both an economical point of view, and from the point of view of obtaining films less sensitive to moisture attack.

4. CHARACTERIZATION OF FLUORINE PASSIVATION FILMS ON COPPER SAMPLES

Attempts were made to characterize surface films formed by passivation on copper samples by means of reflection diffraction techniques. The copper samples were cut from 0.037 inch annealed sheet stock (American Brass Company, 99.46 Cu, 0.01 Fe) in the form of rectangular coupons, 7 x 8 mm in size. Surface preparation before passivating in fluorine consisted of wet grinding on 600 silicon carbide paper followed by etching in cold concentrated HCl. This was followed by rinsing, drying and final degreasing in Freon 11. Samples were then subjected to the following treatment:

1. Sample A: Exposed to fluorine gas at one atmosphere pressure for one hour (80°F), stored in vacuum, never exposed to air before diffraction analysis.

2. Sample B: Sample A after exposure to dry air for 15 minutes in the microscope.

3. Sample C: Sample A after exposure to air (80°F), 50% relative humidity for two days.

4. Sample D: Exposed to fluorine at 200°F, stored in vacuum.

5. Sample E: Sample A after exposure to air (80°F), 50% relative humidity, for 48 hours, and re-exposed to fluorine gas at 80°F, one atmosphere pressure for one hour.

Copper powder samples were prepared and exposed to the same five reaction conditions.

a. Technique of Reflection Diffraction

An Hitachi HU-11 electron microscope with a reflection diffraction attachment RDA was used with 75kv acceleration voltage and a charge neutralizer Type SG-B electron spray gun. The purpose of the charge neutralizer is to produce a low voltage electron spray from a helicoidal filament, and to eliminate surface charge in the specimen area. A collected surface charge, particularly in insulating and semiconducting materials may cause a distortion or instability of the diffraction pattern.

A dry box (see Figure 16) was attached to the reflection diffraction stage for specimen manipulation in a dry argon atmosphere. The microscope column was purged by dry argon and maintained under positive pressure during change of specimens and introduction of the diffraction stage. The reflection diffraction attachment (RDA) also carried a reference sample: deposited aluminum film on a specimen grid. The known d-spacings, (d) of the reference sample, were used for determining the camera length (L) and thus for calculating the crystallographic d-spacings of the specimen under examination. The distances R (in millimeters) of observed electron diffraction spots from the non-diffracted beam o. the radii of the diffraction

29
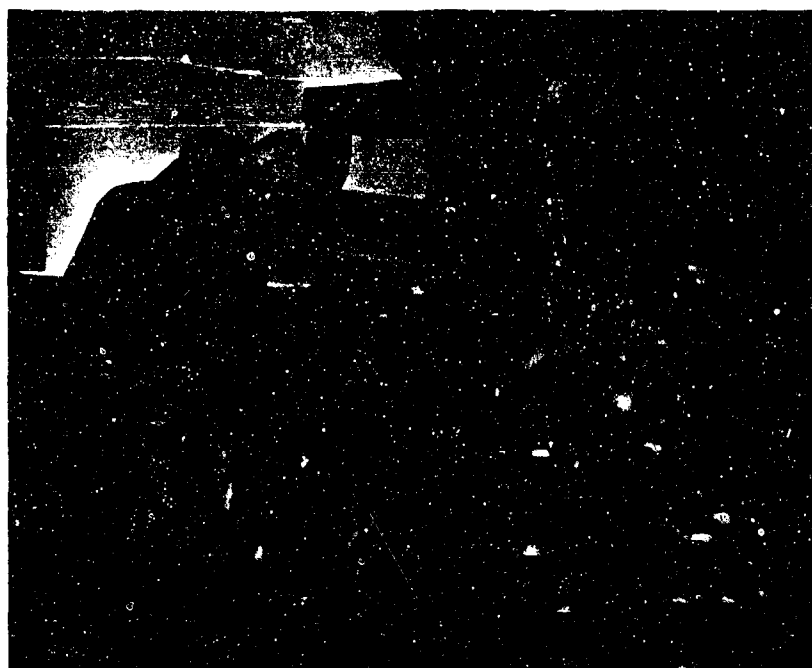
C2093

Figure 16. Argon Filled Dry Box Attached to the Hitachi HU-11 Electron Microscope for Introduction of Specimens into the Reflection Diffraction Stage Without Exposing Them to Air. (Note charge neutralizer E)

rings were measured and converted to d-values (in Angstroms) using the calibrated camera constant $L\lambda$ (λ = wave length) by means of the relation

$$d = \frac{L\lambda}{R}$$

From d-values so obtained, an identification may be made using the ASTM X-ray standard card file.

b. Results of Diffraction Analysis

When metal samples were exposed to fluorine and never exposed to air (Sample A), a rather thin crystallized fluoride coating was found, as inferred from the fact that diffraction patterns of the copper substrate predominated and overshadowed the fluoride patterns. The prominence of the copper patterns increased during electron beam irradiation indicating that a non-crystalline fraction of the fluoride film was gradually decomposed or evaporated during the beam treatment. Diffraction of copper oxides, hydroxides, and the following fluorides was observed: $Cu(OH)F \cdot CuF_2$, $CuF_2 \cdot 2H_2O$ and occasionally CuF_2 (see Table IV and Figure 17). Insignificant changes were noted after exposure to dry air for 15 minutes (Sample B). After two days exposure to air of 50% relative humidity (Sample C), fluoride patterns became less prominent and two additional diffraction rings were noted, indicating small crystals (less than 100 $\text{\AA}$ diameter) of Cu_2O and CuO (see Table V and Figure 18). In certain samples exposed to moisture, thicker and non-uniform chemical films were noted as inferred by less prominent copper lines.

When the exposure to fluorine occurs at higher temperatures ($200^\circ F$, Sample D), the fluoride diffraction patterns consist of spotty rings indicating a uniformly distributed copious amount of small crystals (see Figure 19). The major fraction of fluoride was identified as $Cu(OH)F \cdot CuF_2$. Some CuF_2 and also $Cu(OH)_2$ were found in certain areas (Table VI).

When the samples exposed to fluorine and moist air are re-exposed to fluorine (Sample E), a thicker fluoride coating was formed, as inferred by disappearance of the copper substrate diffraction patterns and appearance of $CuF_2 \cdot 2H_2O$ and $Cu(OH)F \cdot CuF_2$ patterns with higher intensity (Figure 20 and Table VII).

It was also found that sheet samples and powder samples exposed to fluorine and moist air exhibited diffraction patterns of similar composition. The copper sheet samples studied in detail showed that the formation of a passive film by fluorination of surface oxide and hydroxide coatings had not been completed in the period of exposure to fluorine. This is in agreement with the observations previously reported[2], in which it was noted that fluorine uptake by copper was not complete after one hour at room temperature and one atmosphere pressure of GF_2.

31

TABLE IV.   COMPUTED DIFFRACTION PATTERN OF SAMPLE A AND REFERENCE LINES
FOR THE COMPOUNDS IDENTIFIED (Principal Lines are Underlined)

Specimen 1	2	3	Cu	ASTM Reference Patterns $CuF_2 \cdot 2H_2O$	$Cu(OH)F \cdot CuF_2$	$Cu(OH)_2$	CuF_2	$6CuO \cdot Cu_2O$
5.14	5.14					**5.30**		
4.75	4.53	4.75		**4.78**				
4.32	4.32							
					4.22			
4.05	4.05							**4.04**
3.93	3.92							
	3.71	3.80		**3.71**	**3.54**	**3.75**		
3.50	3.47				**3.45**			
3.24	3.24			3.15			**3.22**	3.13
		2.95		2.98				2.90
2.71	2.71	2.71		**2.71**	2.71	**2.64**	**2.82**	
2.64					2.61		**2.66**	
	2.58	2.59		2.55	2.58	2.51	**2.53**	**2.50**
	2.49	2.43			2.47			**2.47**
2.36	2.40			2.35	2.34	2.36	2.39	
	2.21			2.29	2.25	2.26		
2.16	2.16	2.16		2.18	2.20		2.21	
2.00	2.09	2.02	2.09	2.02	2.10	2.08	2.04	2.05
1.83	1.89	1.88	1.81	1.85	1.87		1.82	1.88
1.73	1.70	1.63		1.70	1.72	1.73	1.77	
		1.58					1.69	**1.58**
1.54	1.45	1.43		1.43	1.43	1.45	1.51	
1.12	1.32		1.27			1.29	1.20	**1.25**
	0.90		0.90					
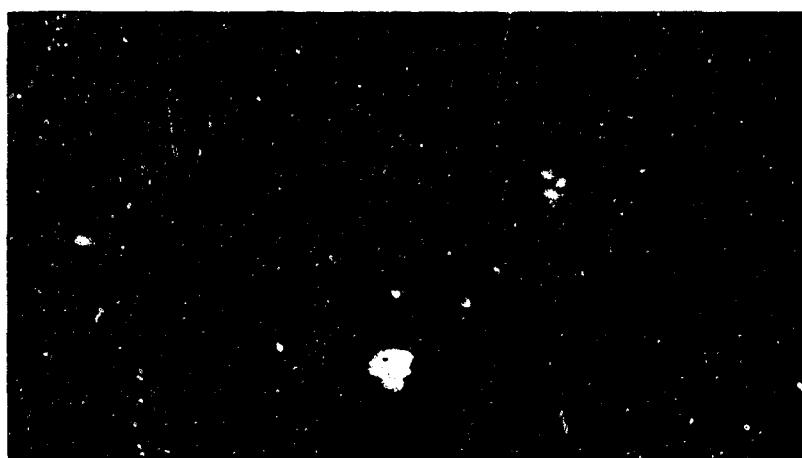
C2094

Figure 17. Reflection Diffraction Pattern of Sample A.
Note specimen shadow at the lower part of the
Figure.   Distinct rings originate from copper
substrate. Spot pattern (marked by commas)
inside the smallest circle show d-spacings
characteristic of CuF_2 . $2H_2O$.

TABLE V. COMPUTED DIFFRACTION PATTERN OF SAMPLE C AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED

(Principal Lines are Underlined)

Specimen	ASTM Reference Patterns				
	Cu	Cu(OH)F	6CuO·Cu$_2$O	Cu$_2$O	CuO
4.58		4.68			
3.07			3.13	3.02	
2.88			2.90		2.75
2.50		2.55	2.50	2.47	2.53
2.42		2.43	2.47		
2.09	2.09	1.97	2.05	2.13	1.96
1.83	1.81	1.83			
1.50		1.51	1.58	1.51	1.50

c3095
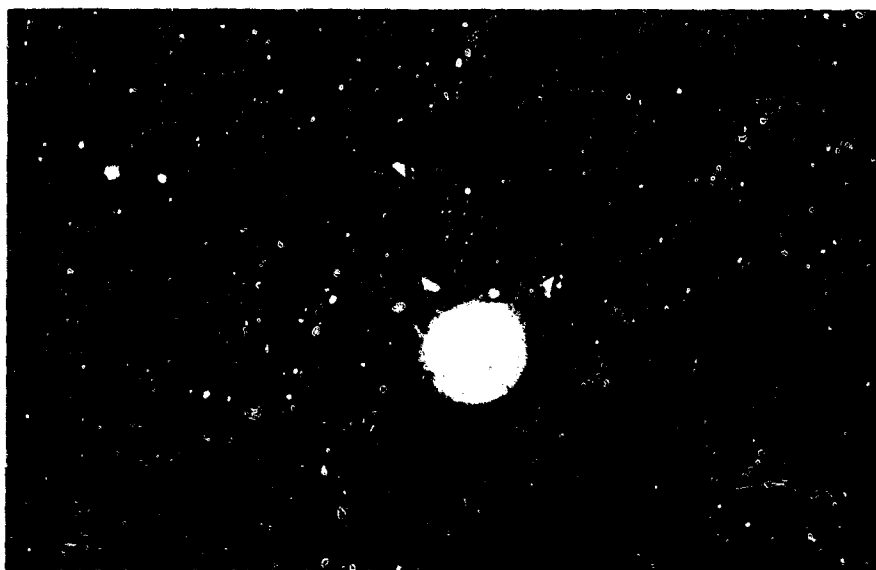
Figure 18. Reflection Diffraction From the Surface of Sample C.
Note less prominent copper rings. Hydrolytic oxida-
tion products of the copper fluorides are identified
mainly as two new CuO and Cu_2O rings, pointed out
by arrows, and disappearance of the $Cu(OH)F$. CuF_2
pattern.
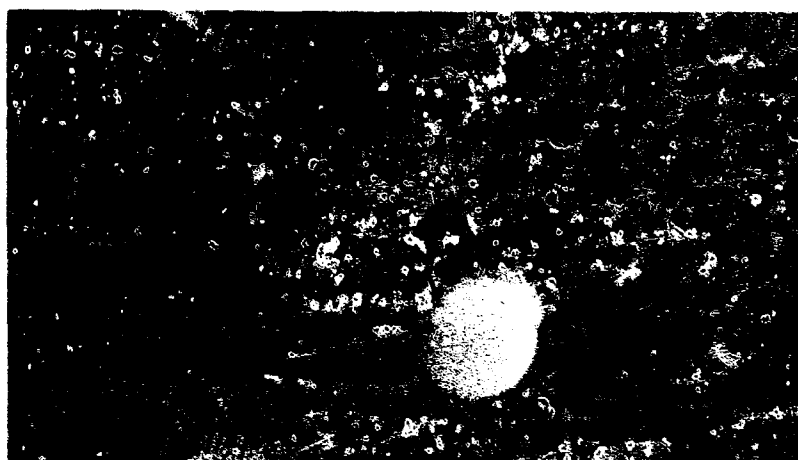
c2696

Figure 19. Reflection Diffraction From the Surface of Sample D, Fluorinated at 200°C. A prominent ring (marked by arrows) appears close to the center. The computed d-spacing indicates $Cu(OH)F$, CuF_2; the intensity of the diffracted beam indicates copious amounts of the crystalline fraction.

TABLE VI. COMPUTED DIFFRACTION PATTERNS OF SAMPLE D AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (Principal Lines are Underlined)

Specimen			ASTM Reference Patterns			
1	2	3	Cu	$CuF_2 \cdot 2H_2O$	$Cu(OH)F \cdot CuF_2$	$Cu(OH)_2$
4.80	4.75	4.70		4.78		
4.20	4.17	4.17			4.22	
		4.00				
		3.93				
3.65	3.76	3.70		3.71		3.75
3.50	3.50	3.50			3.54	
2.92				2.98		
2.70	2.73	2.88				2.86
	2.54	2.64		2.71	2.71	2.64
2.19	2.18	2.18		2.18	2.20	2.26
		2.06	2.09	2.02	2.10	2.08
	1.74	1.75	1.81	1.75	1.77	1.73
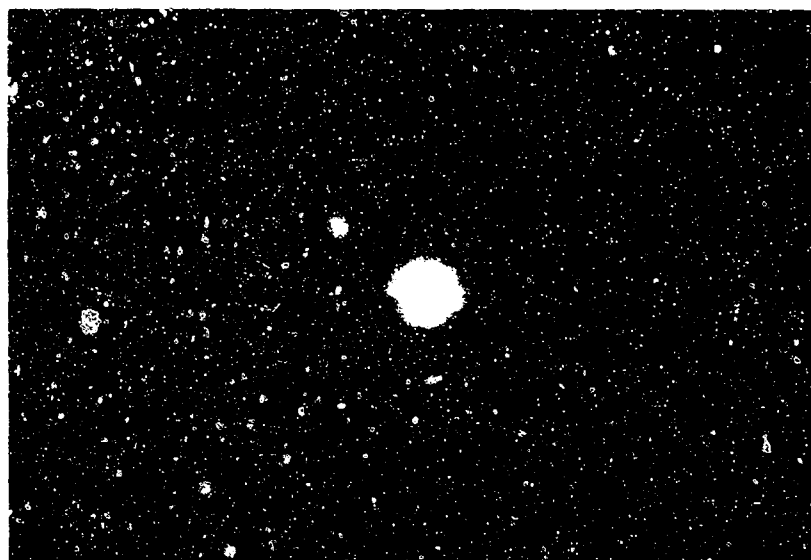
c 2097

Figure 20. Reflection Diffraction of Sample E. Note the
disappearance of Copper Patterns and the
prominence of spot patterns of CuF_2 . $2H_2O$
and $Cu(OH)F$. CuF_2.

TABLE VII. COMPUTED DIFFRACTION PATTERNS OF SAMPLE E AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (Principal Lines are Underlined)

Underlined (principal) lines are shown in **bold**.

Specimen 1	Specimen 2	ASTM Reference Patterns CuF₂·2H₂O	Cu(OH)F	CuF₂	Cu(OH)F	5CuO·Cu₂O	Cu₂O	CuO
		4.78						
4.75								
4.32								
			4.22					
4.17								
4.05								
						4.04		
3.90								
		3.71						
			2.58					
	2.56							
		2.55			**2.55**			
2.53								**2.53**
						2.50		
	2.47		2.47			**2.47**		
2.46								
2.40								
		2.35						
			2.34		**2.34**			
								2.32
	2.20		2.20					
		2.18						
2.16								
					2.14			
							2.12	
2.10	2.10							
					1.88	1.88		
	1.87		1.87					1.87
1.85		1.85						
	1.72							
								1.71
		1.70	1.70					
1.69								
1.66								
			1.63					
						1.58		1.58
1.56								
		1.55	1.55					
		1.52						
	1.51		1.51				1.51	
1.50								1.50
					1.49			
1.48								
						1.45		
					1.44			
	1.43	1.43	1.43			1.43		
	1.41		1.41					1.41
1.39								
								1.37
					1.36			
1.35								
					1.26			1.26
						1.25		
						1.24		
1.23							1.23	
					1.21			
1.16								1.16
								1.07
						1.06	1.06	
1.02						1.02		
								0.90
0.89								
							0.87	

39

The increase in Cu_2O and CuO after exposure to humid air is in accord with the data from fluorine uptake experiments. It is interesting that the $Cu(OH)F$ pattern decreases as much or more than the $CuF_2 \cdot 2H_2O$.

A

SECTION III

FUTURE WORK

During the next reporting period work will be completed on the determination of the effects of water vapor and other environmental factors on fluoride films. The determination by electron diffraction of composition and structure of fluoride films will be continued. Work will be extended to their metal and alloy materials, and fluoride films produced by reaction with interhalogen will be investigated.

Various passivation procedures utilizing different ranges of time, temperature, and pressure will continue to be investigated. The efficiencies of the passivation procedures will be determined by measuring the addition reaction with fluorine before and after exposure to atmospheric moisture. The influence of flexing of the passivated metal upon stability of the passive films will be checked.

REFERENCES

1. W. D. English, S. M. Toy, and W. A. Cannon, Halogen Passivation Studies, AFRPL-TR-66-63, Astropower Laboratory, Douglas Aircraft Co., Inc., January 1966.

2. W. A. Cannon, S. M. Toy, and W. D. English, Halogen Passivation Studies, AFRPL-TR-66-110, Astropower Laboratory, Douglas Aircraft Co., Inc., May 1966.

3. O. Kubaschewski and B. E. Hopkins, Oxidation of Metal and Alloys, Academic Press, Inc., New York, 2nd ed., 1962, pp. 37-38.

4. H. M. Haendler et al, J. Am. Chemical Society, 76, 2178 (1954).

5. R. L. Ritter and H. A. Smith, Journ. Phys. Chem., 70, 805 (1966).

6. S. Kleinberg and J. F. Tompkins, The Compatibility of Various Metals With Liquid Fluorine, ASD-TRD-62-250, Air Products and Chemicals, Inc., March 1962.

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Astropower Laboratory Missile and Space Systems Division A Division of Douglas Aircraft Company, Inc. Newport Beach, California	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

Halogen Passivation Studies

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Quarterly Report - May 1966 through July 1966

5. AUTHOR(S) (Last name, first name, initial)

English, W.D., Cannon, W. A., Asunmaa, S.K., and Toy, S.M.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
August 1966	42	6

8a. CONTRACT OR GRANT NO. AF04(611)-10932	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 3148	AFRPL-TR-66-215
c. BPSN 623148	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. Program Structure No. 750G	

10. AVAILABILITY/LIMITATION NOTICES

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPPR-STINFO), Edwards, California 93523.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command Edwards Air Force Base, California 93523

13. ABSTRACT

This third quarterly progress report covers research in halogen passivation accomplished during the period from 1 May 1966 to 31 July 1966. Various passivation techniques involving a range of pressures and concentrations of fluorine gas and interhalogens were investigated using stainless steel 316 and Monel 400 powders. The effectiveness of the passivation processes was determined by measuring the additional reaction of the treated powders with fluorine gas. Effects of atmospheric moisture on fluoride films were investigated. Reflection electron diffraction patterns were made of fluoride films formed on copper before and after exposure to atmospheric moisture.

DD FORM 1473

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluorine						
Passivation						
Fluorinating Agents						
Fluoride Films, formation						
Fluoride Films, characteristics						
Structural Materials						
Halogen Fluorides						
Aluminum Alloys						
Stainless Steel						
Nickel Alloys						
Copper						
Metal Powders, surface area						
Aluminum Foil, impurities						
Electrode Polarization, bromine trifluoride						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.