NASA TECHNICAL NOTE

NASA TN D-3992

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KINETICS OF THE FLUORINATION OF BERYLLIUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1967

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SUMMARY

The kinetics of the reaction of sheet beryllium and gaseous fluorine to form beryllium fluoride were studied by means of the pressure drop method over the temperature range of 125° to 775° C and at pressures from 20 to 700 torr. The reaction followed the parabolic rate law $y^2 = kt$, where y is the amount of fluorine consumed per unit area of beryllium surface (ml/sq cm), k is the parabolic rate constant, and t is the time (min). Parabolic rate constants were calculated, and activation energies are given. A change of slope in the plot of the rate constant against reciprocal temperature suggests a change in the nature of the reaction near 525° C. Above 525° C the crystal structure of the film changes from α-quartz hexagonal to rhombic tridymite. Beryllium is identified as the diffusing species.

INTRODUCTION

Beryllium, because of its light weight, high-temperature strength, thermal conductivity, and neutron-moderating characteristics, is of interest for application in reactors, satellites, and future supersonic aircraft. The beryllium-oxygen reaction has been extensively studied, and it involves the outward diffusion of beryllium ions (ref. 1). At high temperatures the initially protective oxide film is no longer protective (ref. 2) because of the onset of breakaway oxidation. Several other beryllium-gas reactions have been investigated (ref. 3) including the reactions of beryllium with carbon monoxide and with carbon dioxide (ref. 4). Although data appear in the literature (refs. 5 and 6) concerning the thermodynamic properties of beryllium fluoride (BeF_2), little is reported on the kinetics of the beryllium-fluorine reaction. This report presents the kinetics of the reaction of fluorine with beryllium and the effects of temperature and pressure on the reaction rate.

APPARATUS AND PROCEDURE

The experimental apparatus and the procedure used to measure the rate of fluorina-

tion are described in reference 7. The high-purity-beryllium test pieces were strips measuring 1.27 by 15.24 by 0.012 centimeter with a 0.5-centimeter-diameter hole drilled in one end for handling. The strips were cleaned with a solution of nitric and hydrofluoric acids (HNO_3-HF), with a detergent, with water, and finally with an acetone rinse (ref. 8). The strips were preheated for 0.5 hour at 525° C. After reaction the products were characterized by X-ray diffraction and cross-section metallography.

RESULTS AND DISCUSSION

In figures 1 and 2 the reaction is shown to follow the parabolic rate law $y^2 = kt$, where y is the amount of fluorine consumed (at STP) per unit area of beryllium surface (ml/sq cm), k is the parabolic rate constant, and t is the time (min). All the data over the temperature and pressure ranges studied can be described by this parabolic rate law. A reaction similar to breakaway oxidation was not found with fluorine; the film continued to be protective.

The values of the parabolic rate constants are listed in table I. The parabolic rate constant is plotted as a function of temperature at a pressure of 200 torr in figure 3. In this figure the rate of reaction shows a negative temperature dependence in the low temperature range. This behavior is not unique because in heterogeneous systems where the rate of reaction is determined by diffusion in a solid layer a simple temperature dependence of the net process is not always found. Reactions of this type are complex processes involving the diffusion of at least one ion and electrons across the film through accessible diffusion sites. The number and accessibility of these sites can change at different temperatures; thus, the rate of reaction can decline with rising temperature. A break in the curve appears at 525° C. At this point the activation energy (ΔH_A) changes from -0.8 kilocalorie per mole at the low temperatures to 8 kilocalories per mole at the high temperatures. The following equations define the variation of the rate constant in the two temperature ranges:

$$k = 0.4\times10^{-5}e^{800/RT}\ (\text{ml/sq cm})^2/\text{min} \qquad \text{for } 125^\circ \text{ to } 525^\circ \text{ C} \tag{1}$$

$$k = 1.5\times10^{-2}e^{-8000/RT}\ (\text{ml/sq cm})^2/\text{min} \qquad \text{for } 525^\circ \text{ to } 775^\circ \text{ C} \tag{2}$$

where k is the rate constant, R is the gas constant, and T is the absolute temperature.

A log-log plot of the rate constant as a function of the fluorine pressure is shown in figure 4. The reaction is approximately first order with respect to fluorine pressure.

The low-temperature film is identified as α-quartz hexagonal BeF_2, and the high-temperature film is identified as rhombic tridymite BeF_2 (ref. 9). A study was made

of the reaction of α-quartz BeF_2 with fluorine gas at a temperature of 675° C and a fluorine pressure of 200 torr. No apparent change was observed in that no rhombic tridymite form was found. This observation would lead to the assumption that for the high-temperature reactions the α-quartz hexagonal BeF_2 is not formed first and then converted to the tridymite form but that the tridymite BeF_2 is formed directly. Films formed at low temperatures were dull, nonreflecting surfaces, while those produced at high temperatures resembled shiny mirrors.

When fluorine is first introduced into the system, it contacts bare beryllium metal and reacts with it to form BeF_2. As the time of contact increases, a layer of BeF_2 is built up. For continuation of the reaction either fluorine or beryllium must move across the film barrier. The reacted metal strips are shown in figures 5 and 6. Figure 5 shows a reacted metal strip after fluorine exposure at a temperature of 625° C and a pressure of 630 torr. The mirrorlike characteristics of the surface are evident. Etched cross sections of the strip show that the reaction is not a grain boundary attack but is a transgranular attack. The photomicrograph in figure 6 is a cross section showing the BeF_2 coating. The boundary between the beryllium and the BeF_2 is not well defined but beryllium is seen as light areas extending into the film. This appearance would indicate that outward diffusion of beryllium is taking place. Identification of the diffusing species was determined by the pattern of two BeF_2 surfaces growing towards one another. Fusion of the impinging fluoride layers would indicate beryllium diffusion (ref. 10). Two of the beryllium strips were clamped together along the 1.27-centimeter side with a 0.012-centimeter-thick Monel ribbon inserted between the plates to form a small wedge angle. The sample was then inserted into the apparatus and run at a temperature of 675° C and a fluorine pressure of 400 torr according to standard procedures. After it was removed from the furnace, the sample was set in plastic and dry polished. Figure 7 is a cross section showing that the surfaces have fused together; this figure demonstrates that beryllium is diffusing during fluorination at high temperature.

CONCLUDING REMARKS

The fluorination of beryllium is both temperature and pressure dependent. The pressure dependency is approximately first order with respect to fluorine pressure. The reaction is diffusion controlled and follows a parabolic rate law. The beryllium fluoride layer that is formed on the beryllium substrate is continually protective, and no break-

away oxidation is observed. Cross-section metallography has shown that beryllium is the diffusing species.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 14, 1967,
128-31-04-01-22.

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TABLE I. - SUMMARY OF TEMPERATURE AND PRESSURE CONDITIONS AND CALCULATED PARABOLIC RATE CONSTANTS

Temperature, °C	Pressure, torr	Parabolic rate constant, k, $(ml/sq\ cm)^2/min$
125	200	1.05×10^{-5}
225	200	0.94×10^{-5}
525	60	0.20×10^{-5}
	200	.69
	630	3.77
	700	5.70
575	200	3.30×10^{-5}
625	200	17.0×10^{-5}
	630	41.0
675	20	4.03×10^{-5}
	40	9.70
	60	16.30
	200	69.20
775	60	130×10^{-5}
	200	280

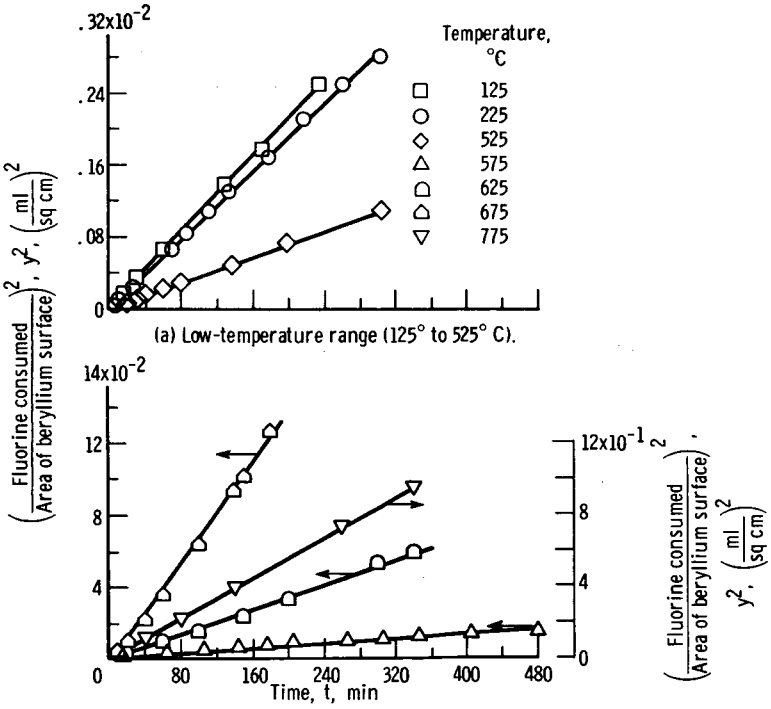


Figure 1. - Effect of temperature on fluorination of beryllium. Pressure, 200 torr.

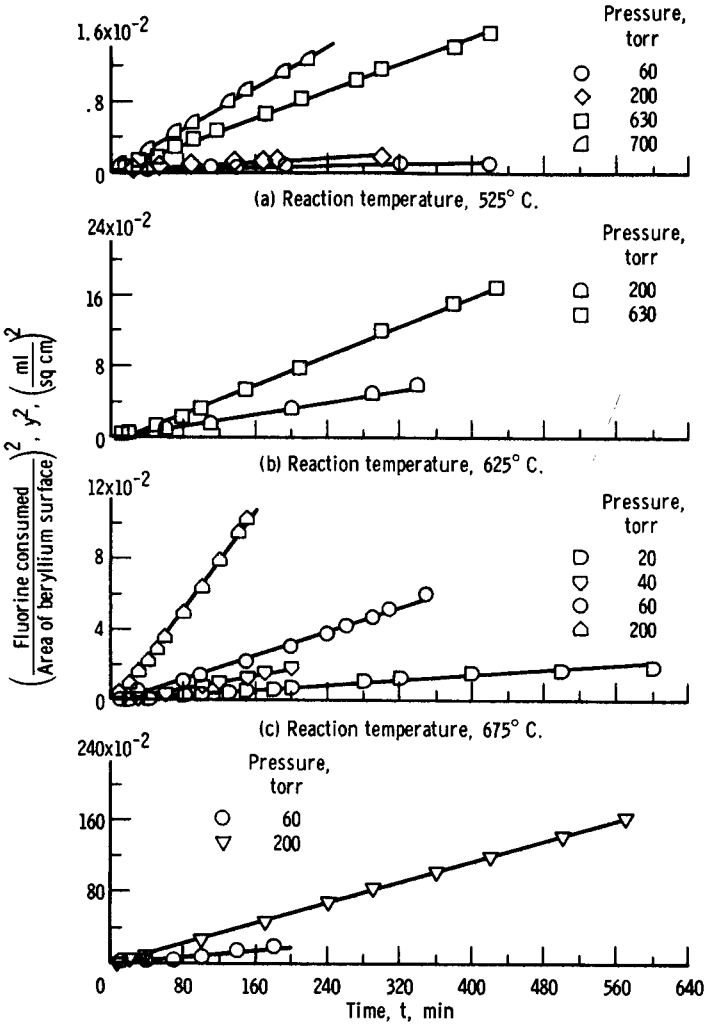


Figure 2. - Effect of pressure on fluorination of beryllium.

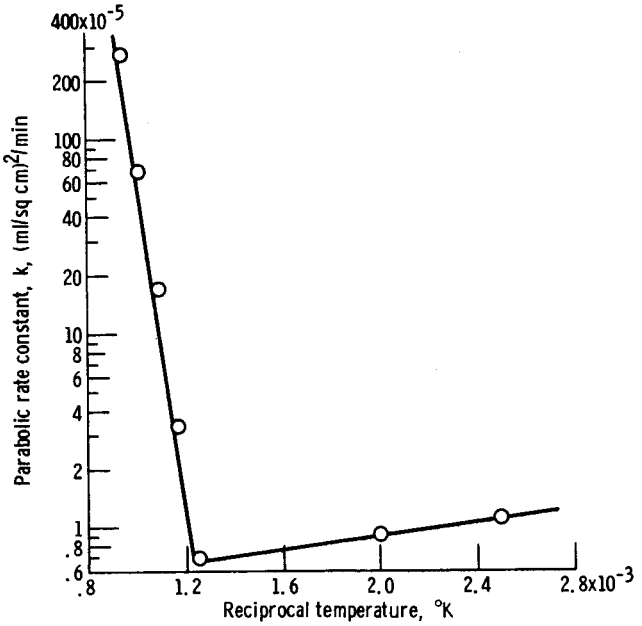


Figure 3. - Effect of temperature on parabolic rate constant. Pressure, 200 torr.

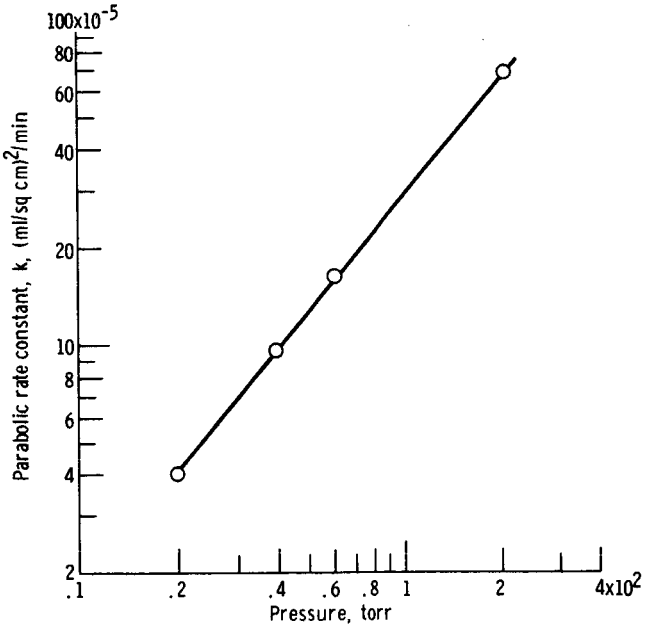
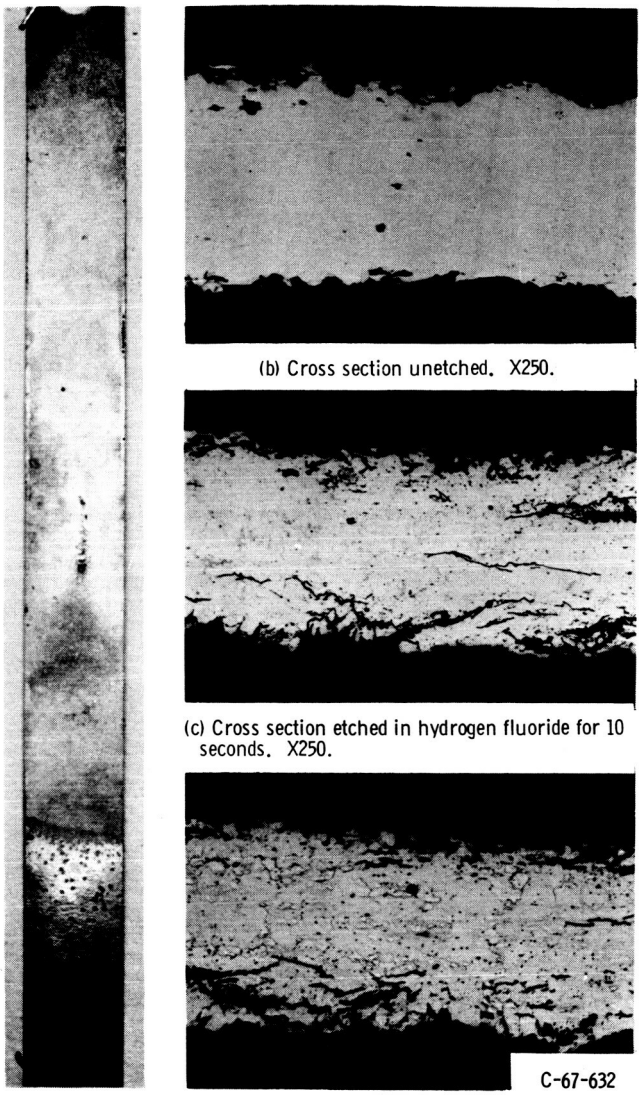


Figure 4. - Effect of pressure on parabolic rate constant. Temperature, 675° C.



(a) Corrosion strip. X1.5.

(b) Cross section unetched. X250.

(c) Cross section etched in hydrogen fluoride for 10 seconds. X250.

(d) Cross section etched in hydrogen fluoride for 20 seconds. X250.

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Figure 5. - Reacted metal strip after fluorine exposure. Temperature, 625° C; pressure, 630 torr. (Reduced 40 percent in printing.)

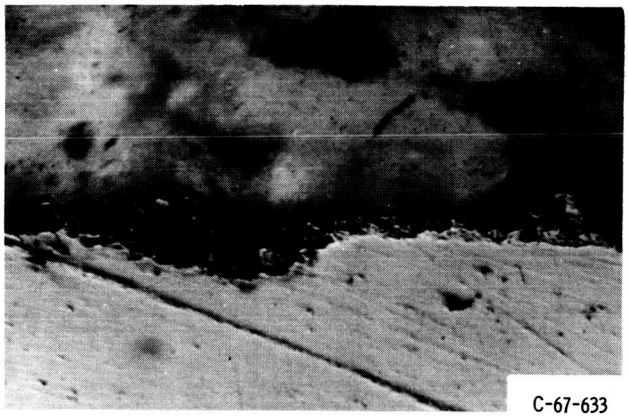

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Figure 6. - Cross section showing beryllium fluoride coating. X500. (Reduced 25 percent in printing.)

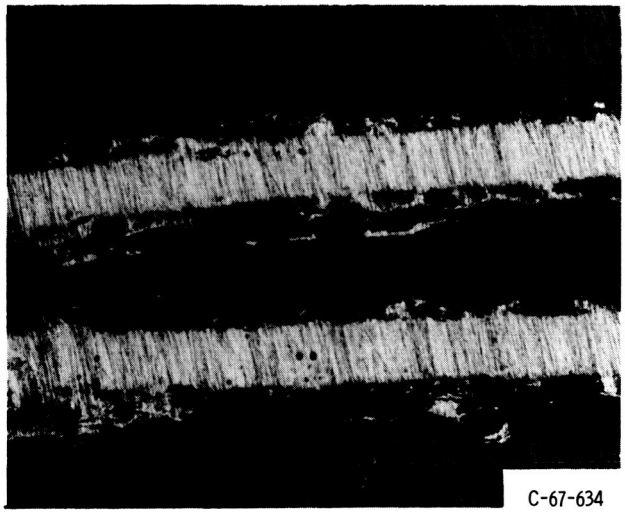

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Figure 7. - Cross section showing that surfaces have fused together. X75. (Reduced 25 percent in printing.)