1005
SAND78-1078

Unlimited Release

MASTER

Thermodesorption of Gases From Various Vacuum Materials

Leonard C. Beavis

Sandia Laboratories

THERMODESORPTION OF GASES FROM VARIOUS
VACUUM MATERIALS

Printed June 1979

Leonard C. Beavis

Tube Development Division 2354
Sandia Laboratories, Albuquerque, New Mexico 87185

ABSTRACT

A number of materials are commonly used as vacuum system walls. The desorption of gases from these materials may contribute significantly to the internal pressure of an unpumped device or to the gas load which a pump must handle in a dynamic system. This report describes the thermodesorption measurements made on a number of metals (molybdenum, nickel, Kovar alloy, copper, copper-2% beryllium alloy) and two insulators (molybdenum sealing glass ceramic and high alumina ceramic). All of the materials after typical cleaning and air exposure contain considerable gas. With a long 400°-500°C vacuum bake, however, all can be cleaned sufficiently so that they will not contribute appreciable gas to their surrounding when vacuum stored at room temperature for many years. Most materials display desorption kinetics which are first order (a single bond or trap energy must be overcome for desorption). It appears that the desorption of CO from Kovar is rate limited by carbon diffusion ($D_0 \approx .4 \text{ cm}^2/\text{s}$ and $E_d \approx 27,000 \text{ cal/mol}$). The desorption of hydrogen from glass ceramic also appears to be diffusion rate limited ($D_0 \approx 1 \times 10^{-3} \text{ cm}^2/\text{s}$ and $E_d \approx 11,000 \text{ cal/mol}$). Carbon monoxide is the major gas desorbed from metals, except copper for which hydrogen is the major desorbing species. The insulators desorb hydrogen primarily.

DISCLAIMER

This document contains information which is proprietary to Sandia Corporation. It is loaned to you for your information only and is not to be distributed outside your organization. It is to be destroyed when it is no longer needed. It is not to be used for any purpose other than that for which it was loaned. It is not to be used for any purpose other than that for which it was loaned.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION - - - - -	5
EXPERIMENTAL - - - - -	7
DATA INTERPRETATION- - - - -	10
DISCUSSION OF DATA - - - - -	20
Kovar - - - - -	20
Molybdenum - - - - -	23
Nickel - - - - -	23
Copper - - - - -	27
Copper 2% Beryllium Alloy - - - - -	27
Molybdenum Sealing Glass Ceramic (Mexim)- -	32
Alumina Ceramic - - - - -	32
Predicted Outgassing Rates - - - - -	38
CONCLUSIONS - - - - -	38
REFERENCES - - - - -	40

THIS PAGE INTENTIONALLY LEFT BLANK

INTRODUCTION

Vacuum workers have long known that all materials they use have at least some gases both in and on them. The purpose of an actively pumping vacuum system is to remove these gases from the experiment or process of interest in the system.

In the case of a static (nonpumped) vacuum envelope, gases from wall materials or materials mounted internally can destroy the vacuum. If we wish to predict the long-term (days or years) gas-up characteristics of a vacuum device, we have the choice of measuring the outgassing rates and permeabilities of materials directly, e.g., under use conditions¹, or the parameters which go into determining these rates. The rate of gas-up is dependent upon a number of factors. These include mobility of gas in the solids (diffusivity), quantity of gas in (solubility) or adsorbed on the materials, how well the gas is bound to its initial position, the environment (e.g., presence of external gases, temperature) and whether or not sinks for any molecules which reach the gas phase exist.

This report will be confined to outgassing and will not discuss gettering or permeation further, although their importance in long-term predictions cannot be ignored.

Measuring outgassing rates directly is complicated by the dynamic interaction between the samples being measured and the apparatus in which the measurements are made. That is, gases which are being desorbed from the specimen under test react with the walls of the vacuum chamber and may be either sorbed directly or sorbed with displacement of species initially resident. A lower measured rate of desorption is the net effect of such phenomena.² As the specimen outgassing rate decreases, the interaction of the desorbed gases with the measurement system causes increased errors in the estimate of the actual outgassing of the specimen. Because of this and our interest in maintaining low pressures in small sealed volumes for periods of years (implying rates of 10^{-19} mol/s cm² or less), we decided to make measurements of the factors which contribute to outgassing.

Thermodesorption measurements have been made for about the past 20 years, although the technique was first described in 1948 by Apker.³ The mathematical description of thermodesorption by first- and second-order kinetics was first given in 1958 by Smith and Aranoff.⁴ Redhead⁵ gives the most complete description

Fig. 1. Photograph of thermodesorption apparatus
(Note the QRGAs mounted directly over the sample.)

of simple first- and second-order surface desorption kinetics. Most early works concern themselves with the relationship between the temperature of maximum outgassing rate and the energy required to desorb surface gas (binding energy). Typically, thermodesorption experiments^{6,7} were run by heating a filament or ribbon of the material to be studied to very high temperature in order to thoroughly outgas it while the gases were pumped away. The material was then cooled to room temperature. Next, it was exposed to a metered quantity of gas, e.g., 1 Langmuir/cm² of CO or H₂. The filament was then rapidly heated, either temperature varying linearly with or the reciprocal of temperature time. The pressure profile was measured in either a sealed or rapidly pumped system using a total pressure gauge. The peak or peaks in outgas rate were related to the binding energy by relations given in References 3 or 4. The materials studied were restricted to refractory conductors, e.g., molybdenum, tungsten, and tantalum.

In the mid-1960s interest developed in the study of nonmetallic materials which exhibited diffusion-controlled desorption of implanted inert gases.^{8,9} Finally, during the 1970s the importance of peak shape in the analysis of thermodesorption data has been recognized.^{10,11,12} Also, the influence of multisteped processes on desorption peak shape has been studied.^{13,14,15}

By using all of the information available in thermodesorption peaks, it is sometimes possible to infer the desorption-limiting mechanisms, as well as the activation energies for desorption. As will be pointed out later, it is this information which is required to make outgassing rate calculations for vacuum devices.

The materials for which we have measured thermodesorption spectra include molybdenum, nickel, iron-nickel-cobalt glass sealing alloy hereafter referred to as Kovar, copper, copper 2% beryllium, molybdenum sealing glass ceramic (referred to as Mexim), and high-alumina ceramic. All these materials are likely to be found in long shelf-life, high-vacuum devices.

EXPERIMENTAL

The thermodesorption experimental apparatus consists of a bakeable ultra-high vacuum chamber, associated pumps, a quadrupole gas analyzer which was used because we were interested in the gas species being emitted in addition to the total amount, which was more typical of earlier work, a thermocouple, a programmable high-current source, a Data Trac motor-driven variable resistance to drive

the current source, a Digital Equipment PDP 11/40 computer which was used to collect temperature data, drive the gas analyzer, and collect gas species quantity information, and the heater which in some instances is the sample. Figure 1 is a photograph of the apparatus.

There are several precautions which were taken to minimize errors in and simplify data interpretation. Ideally, one wishes to measure only the gases being desorbed by the specimen. In most instances, the desorbed gases interact with the vacuum system in some ill-defined fashion which includes substitution of one species for another on the interior of the vacuum system. The impact of these processes is minimized by using a mercury diffusion pump during measurements. The ion pump on the system was found to regurgitate gases when subjected to even small loads of active gases. This pump is used to maintain the system in a relatively clean condition during periods when measurements are not being made. A small volume-to-chamber pumping speed (exit conductance) ratio (V/C) also helps reduce extraneous interaction in addition to improving the time/temperature vs outgas rate resolution. Our system has a V/C of ≈ 0.1 s for mass = 28 AMU. The gas analyzer is located directly over the sample so that most gases measured have not collided with a cold wall.

The temperature ramp is made linear by empirically adjusting the motor-driven resistor (Research Inc. Data Trac) which controls the programmable current source. Ramp rates of 1 K/s - 100 K/s were achieved; most measurements were made with a 5 K/s - 10 K/s ramp.

Two types of samples have been measured. The first class included those which could be fabricated into thin conducting foils less than 0.1 mm thick, i.e., molybdenum, nickel, and Kovar. These samples were heated by passing a current directly through them. The measurement thermocouple was attached to the center of the foil. Foils were Kovar, 0.075 mm x 6.4 mm x 89 mm; nickel, 0.05 mm x 6.4 mm x 50 mm; and molybdenum, 0.025 mm x 6.4 mm x 50 mm. They were attached to heavy copper electrodes (6.4 mm diameter). A disadvantage of measuring foils by this method was that a zone near each heavy copper conductor was not at the same temperature as the remaining foil when it was heated. This deviation becomes greater the higher the temperature of the center. At high temperature ($>1000^{\circ}\text{C}$), we estimated the non-uniform zone may have accounted for 10-15% of the sample length. The second class of samples included copper, molybdenum, alumina ceramic, copper 2% beryllium alloy, and glass ceramic. These were heated in a furnace as

described by Patrick.¹⁶ The heater was capable of accepting samples of about 10 mm on a side. Typical samples were discs 10 mm in diameter by 1/2 mm thick. The temperature was monitored with a thermocouple mounted to the bottom cover of the heater. The sample was initially mounted for a desorption measurement in a tubular holder away from the heater. After pumpdown, the empty heater was ramped. This preliminary outgassing was followed 30 minutes later by a second temperature ramp during which mass spectra were obtained. These two runs produced the background spectra. Finally, after an additional 30-minute wait, the sample was dropped into the heater; it was ramped to the maximum temperature for which data were desired. Mass spectra were again obtained. To analyze the data, the background values were subtracted from the sample values in order to obtain sample only mass spectra. For samples which needed to be heated above 1200°C, the walls of the chamber were cooled with liquid nitrogen in order to reduce outgassing from them. The main limitations of this desorption technique were: samples did not always fall to the bottom of the heater where the thermocouple was located. Temperature gradients in the sample introduced uncertainties in its temperature. We compared the desorption spectra for molybdenum using directly heated foils and a disc sample. They were in close agreement (peaks occurred within 20 K for the two samples).

Detection and quantification of desorbed gas species were accomplished using a computer-controlled quadrupole mass spectrometer (QRGA UTI Model 100B). The programmed computer put out voltages to the QRGA sweep control circuit which tuned the mass-to-charge ratio (mass number) of the QRGA. Any mass number from 1 to 100 could be tuned. Typically, mass numbers 2(H_2), 15(CH_3^+), 16(CH_4^+ , O^+), 18(H_2O^+), 28(CO^+), 32(O_2^+), 40(Ar^+), and 44(CO_2^+) were measured at least once for each sample type. Then the list of peaks scanned was reduced to the 4 or 5 which had the largest signal on the first sample. The electron multiplier current for each peak was fed through a 7-decade (1V/decade) logarithmic amplifier to an analog-to-digital converter and then to the computer. Thermocouple readings were sent through a similar channel to the computer. Data were stored on a 1-million-word disk. Because of the slow response of the log amplifier in the 10^{-11} - 10^{-12} ampere ranges, the scan rate of the QRGA was limited to about 10 mass peaks/s. Typical sampling times were 150-200 ms on most spectra. On the fastest ramps (50 K/s - 100 K/s), only one species was monitored per sample in order that shorter sampling

times could be used. A large dynamic range was not required of the log amplifier under single-mass-peak monitoring. The system was calibrated by the use of a standard leak for each of the gases (except H_2O) we expected to see desorbed. Figure 2 shows a block diagram of the system and its interconnection.

DATA INTERPRETATION

There are a number of potential mechanisms which would allow gas to be released into a vacuum envelope. These mechanisms, because of difference in their fundamental nature, can lead to differences in the amount of gas seen in the vacuum as a function of time and temperature. There are three simple mechanisms with which we will be concerned. In addition, combinations of these could also be considered but will not be here. The three simple mechanisms are illustrated in Figure 3. The samples in the figure deal with (or use) CO but are applicable to other polyatomic molecules (e.g., H_2 , CO_2). For first-order desorption, imagine that the surface is covered with molecules (CO in Figure 3.a). These may be migrating or stationary on the surface. Through random thermal processes, as molecules receive enough energy, they leave the surface and appear in the gas phase. In this case, release to the gas phase is considered to be first-order rate limited because only the single bond to the surface need be broken in order for the molecule to appear as gas. In the case of second-order kinetics, imagine the surface to be randomly covered with the constituent atoms of a diatomic molecule (carbon and oxygen in Figure 3.b). If the rate of appearance of molecules in the gas phase is limited by the combination of the different atoms to form the molecules, then the rate is second order. Finally, consider the mechanism of bulk diffusion. In Figure 3.c, the bulk is shown to contain carbon atoms. It is also possible that the surface may contain these atoms. The rate of desorption is limited by the rate at which one or both of the reactants move through the bulk to the surface to be desorbed.

The mathematical descriptions for these desorption mechanisms, first order, second order, or diffusion, are well known.^{4,10} The first- or second-order desorption rate equation is

$$-N = v_i N^i \exp(-E/RT) \quad (1)$$

Fig. 2. Block diagram of the thermodesorption apparatus with illustrations of the various input and output signals associated with a measurement

(a)

(b)

(c)

Fig. 3. Illustration of first order, second order, and diffusion limited desorption.

where

i = order of reaction, 1 for first order, 2 for second order;

ν_i = frequency term for the reaction;

N = coverage of the surface (particles/cm²);

E = binding energy of the species (kcal/mol);

R = gas constant (1.99×10^{-3} kcal/mol K);

T = absolute temperature (K).

For diffusion-controlled desorption, the rate equation is

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial x^2} \quad (\text{Fick's Law}). \quad (2)$$

In this equation, τ is a pseudotime defined in Ref. 10.

$$\tau = \int_0^t D(t) dt \quad \text{and} \quad D(t) = D_0 \exp \{-E_d/RT\} \quad (3)$$

where

E_d = the activation energy for diffusion (kcal/mol);

t = time (seconds).

In the experiments we performed, the temporal dependence of temperature was

$$T = T_0 + \beta t \quad (4)$$

where

T_0 = initial temperature;

β = heating rate (K/s).

Equations (1) and (2) are derived assuming that gas is removed from the system at a high rate compared to the heating rate (i.e., $\frac{V}{C} < \frac{1}{\beta}$).

It is worth emphasizing here that our desorption experiments were quite different from those described in the earlier literature.²⁻⁸ In our measurements,

we looked at gases which were desorbed from materials exposed to air after cleaning and low temperature bake (500-700°C). In the referenced experiments, the first step is a high-temperature flash (>2000 K), normally followed by the introduction of the gas to be studied, then another high-temperature ramp during which the desorption is measured. We measured various desorbed species by mass spectrometry, whereas the earlier experimenters measured a total pressure and assumed it was the gas which they tried to introduce in a controlled fashion. Additionally, investigators which doped samples with specific gases usually had some preconceived idea of the rate-limiting mechanism for desorption. It was normally assumed to be first-order (occasionally second-order) rate limited. These investigators then easily analyzed their thermal desorption peaks. The thermal desorption peak(s) may be easily analyzed by solving equation (1) for the temperature at the peak desorption rate (T_p);⁴

$$\frac{E}{RT_p^2} = \frac{\nu_1}{\beta} \exp\left(\frac{-E}{RT_p}\right) \quad \text{for first order,} \quad (5)$$

or

$$\frac{E}{RT_p^2} = \frac{\nu_2 N_0}{\beta} \exp\left(\frac{-E}{RT_p}\right) \quad \text{for second order.} \quad (6)$$

In equation (6), the initial surface coverage N_0 has been substituted for $2N(T_p)$, which is valid only if $\left(\frac{E}{T_0}\right) > 4\left(\frac{E}{T_p}\right)$. From equations 5 and 6, the binding energy of the rate-limiting step may be found. If diffusion is the rate-controlling mechanism, the temperature at which the peak outgas rate occurs depends not only on the geometry of the sample, the activation energy of diffusion, the initial bulk concentration, and the concentration profile of the species controlling desorption, but also upon D_0 , which unlike ν_1 or ν_2 , can vary over many orders of magnitude. Thus, data analysis of diffusion-controlled desorption is much more complex.

If the mechanism of the rate-limiting step is known with certainty, even if it is diffusion controlled and D_0 must be estimated, then the energetics for the

mechanism can be found. In our desorption measurement, we are not certain what the rate-limiting mechanism was and this complicated data analysis. From the outgassing versus temperature data (peak shape) in Figure 4, it was possible to determine whether diffusive first- or second-order kinetics control desorption (for example, see refs. 6 and 10). Typically, first-order desorption exhibits a narrow asymmetric peak. The second-order peak will be somewhat broader with diffusion-controlled kinetics having the broadest peak for any but extremely thin samples. The rate-controlling mechanism can be found in a number of ways. All of these methods depend upon knowing peak shape in addition to the temperature where the peak outgassing rate occurs.

We have used two methods primarily in obtaining and analyzing desorption data (see Figure 5). The first method compared the upper half of actual thermal desorption peak with those shapes predicted by the various rate limiting mechanisms. The upper portion of Figure 5 illustrates the regions where data were compared to the single theoretical models. If instead of carrying the temperature ramp through the entire thermal desorption peak, the ramp was stopped ($T = \text{constant with time}$), see Figure 5.b, at some point on the rising edge of the desorption peak, then the outgassing decays with characteristics which were dependent upon the rate limiting step. This was the second method of obtaining information on the rate limiting mechanism. Using either of the general methods it was possible to discern the rate controlling mechanism because the peak shape of the desorption as a function of temperature (method 1) or time (method 2) is unique to the kinetics. A more complete description of these methods is given below.

The thermal desorption peak shape for first- and second-order rate-limiting mechanisms may be defined in terms of the ratio $\dot{N}_j/\dot{N}_p$ of the rate outgassing at any temperature T_j to the maximum rate observed at T_p . Equation (1) gives both rates. Their ratio is

$$\frac{\dot{N}_j}{\dot{N}_p} = \left(\frac{N_j}{N_p} \right)^i \exp \left[\frac{E}{R} \left(\frac{1}{T_p} - \frac{1}{T_j} \right) \right]. \quad (7)$$

Fig. 4. Typical peak shapes for desorption controlled by 1st order, 2nd order, and diffusion mechanisms.

Fig. 5. Illustration of the portion of data analyzed to determine the rate controlling mechanism.

(a)

(b)

Determination of the ratio N_j/N_p requires integration of equation (1). A new function is defined; $i = 1$ or 2 for first-order or second-order kinetics, respectively.

$$f_{k,j} = \frac{\nu_i E}{3} \int_{T_k}^{T_j} \exp\left(\frac{-E}{RT}\right) dT. \quad (8)$$

Then, for first-order desorption

$$\frac{\dot{N}_j}{\dot{N}_p} = \exp\left[\frac{E}{R}\left(\frac{1}{T_p} - \frac{1}{T_j}\right) + f_{j,p}\right], \quad (9)$$

and for second-order desorption

$$\frac{\dot{N}_j}{\dot{N}_p} = \exp\left[\frac{E}{R}\left(\frac{1}{T_p} - \frac{1}{T_j}\right)\right] \left(1 + N_p f_{p,j}\right)^2, \quad (10)$$

where N_p , the coverage at the desorption rate maximum, is related to the initial coverage N_0 by

$$\left(\frac{1}{N_p}\right) = \left(\frac{1}{N_0}\right) + f_{0,p}.$$

The integrals $f_{k,j}$ are evaluated as follows: (1) For $E/RT > 9$, convergence is best for the series

$$f_{k,j} = \frac{\nu_i E}{3R} \left[\frac{\exp\left(\frac{-E}{RT}\right)}{\left(\frac{E}{RT}\right)^2} \left(1 + \frac{2!}{\frac{-E}{RT}} + \frac{3!}{\left(\frac{-E}{RT}\right)^2} + \frac{4!}{\left(\frac{-E}{RT}\right)^3} + \frac{5!}{\left(\frac{-E}{RT}\right)^4}\right) \right]; \quad (11)$$

(2) for $E/RT < 9$, the following expression is easier to use.

$$f_{k,j} = \frac{\nu_j E}{\beta R} \left[\frac{\exp\left(\frac{-E}{RT}\right)}{\frac{E}{RT}} + E_1\left(\frac{-E}{RT}\right) \right] \quad (12)$$

where E_1 is the exponential integral.¹⁸

For diffusion-controlled desorption, assume the desorbing membrane to have thickness 2ℓ and to contain C_0 atoms cm^{-3} of the diffusing species, uniformly distributed through the sample. With these assumptions, Carslaw and Jaeger¹⁹ give the desorption rate per unit areas as

$$\dot{N}_j = \frac{2D(T_j)C_0}{\ell} \sum_{i=0}^{\infty} \exp \left[-\left(2i+1\right)^2 \pi^2 \left(\frac{\tau_j}{4\ell^2}\right) \right] \quad (13)$$

$$\text{where} \quad \tau_j = \frac{1}{\beta} \int_{T_0}^{T_j} D_0 \exp\left(\frac{-E}{RT}\right) dT \quad \text{from equations (3) and (4).}$$

The pseudotime, τ_j , is evaluated similar to $f_{k,j}$ in equations (11) and (12).

A simple and commonly used method of desorbing gas is through isothermal annealing. The sample is rapidly raised to some temperature T where desorption is known to occur and held at that temperature. The time to achieve T must be such that appreciable desorption does not take place before measurements can be made. The desorption rates versus time are given by

$$\dot{N}(t) = -\gamma_1 N_0 \exp(-\gamma_1 t) \quad \text{first order} \quad (14)$$

$$\dot{N}(t) = -\gamma_2 / \left(\gamma_2 t + \frac{1}{N_0} \right)^2 \quad \text{second order} \quad (15)$$

Fig. 6. Comparison of various theoretical desorption spectra with data from a single Kovar desorption of carbon monoxide.

$$\dot{N}(t) = \frac{DC_0}{(\pi Dt)^{1/2}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \ell^2}{Dt}\right) \right] \quad \text{diffusion} \quad (16)$$

where

$$\gamma_i = v_i \exp\left(\frac{-E_i}{RT}\right), \text{ and} \quad (17)$$

C_0 = initial bulk concentration of diffusing atoms.

It should be noted that equation (16) is used where $Dt/\ell^2 < 0.1$ because of its rapid convergence. Dt/ℓ^2 will be small for reasonable times at any temperature on the rising side of a desorption peak.

DISCUSSION OF DATA

Kovar

Kovar primarily desorbs carbon monoxide. Some carbon dioxide is desorbed in the 400-600°C range. Because carbon monoxide ions are fragments of carbon dioxide in the QMG, the low-temperature portion of the CO desorption peak is somewhat overestimated. The amount of water desorbed is typically small; when it does appear, it desorbs at 200°C or less. Occasionally, hydrogen and water were noted in the system at sample temperatures over 1000°C. This was ascribed to desorption from the vacuum system walls due to the radiant energy from the sample. In comparing chemically cleaned Kovar with that as received from the manufacturer and degreased, an order of magnitude more gas was desorbed from the "as received" material than from the cleaned material. Chemical cleaning consists of a 900°C one-hour wet hydrogen firing to remove carbon followed by an 800°C one-hour vacuum fire to remove hydrogen. From the cleaned Kovar, it appears that approximately one monolayer ($9 \times 10^{14}/\text{cm}^2$) of carbon monoxide was desorbed at temperatures up to about 1000°C. Most of this gas comes in one large peak which, depending on the temperature ramp rate, occurs at 700°C to 850°C, Figure 6. The data indicate that this large peak is much too broad to be caused by either a single first-order or second-order desorption rate-limiting step, which are plotted on Figure 6 along with the diffusion calculation and the actual data.

Isothermal anneals indicate $t^{-1/2}$ time dependence of the peak decay. Therefore, it appears that this peak could best be explained on the basis of a diffusion rate-limiting mechanism. Carbon monoxide probably does not diffuse as a molecule in Kovar, but it can diffuse as its constituents; i.e., carbon and oxygen. The measurements indicate on the basis of diffusion-limited desorption an activation energy for diffusion of 27.5 kcal/mol with a D_0 of approximately $0.4 \text{ cm}^2/\text{s}$. The diffusion parameters reported for carbon diffusion in gamma iron are²⁰ activation energy, 27 to 40 kcal/mol; and D_0 , .04 to $0.6 \text{ cm}^2/\text{s}$. Kovar is face-centered cubic (gamma phase at room temperature and above). Notis²¹ studied the decarbonization of a Kovar-like alloy in wet hydrogen. He reported a diffusion activation energy for carbon of 25.6 kcal/mol with a D_0 of $.0085 \text{ cm}^2/\text{s}$. The data from our experiments were toward the low end of the range of reported values for the energy of diffusion and mid-range for D_0 .

Kovar always shows two desorption peaks; the second one could not be totally measured because of possible melting of the alloy. The outgassing spectra from Kovar can be explained as two diffusion-limited processes (see Figure 7). At low temperatures, the layer on the surface is probably primarily oxygen from air exposure. As the Kovar is heated, eventually the carbon inside the alloy becomes mobile. It comes to the surface, reacts with the oxygen, and then desorbs as CO. In this temperature regime, the rate-limiting step is that of carbon diffusion through the bulk of the Kovar. As the temperature is raised, the surface oxygen is finally completely depleted and the amount of CO desorbing decreases due to oxygen starvation. At this temperature, $\approx 800^\circ\text{C}$ on a slow ramp, there is probably still oxygen dissolved in the bulk, and there is certainly carbon. The oxygen at this point is not mobile enough to move within the solid. As the temperature continues to increase to 1100°C , the bulk oxygen becomes mobile. It diffuses to the surface where it combines with already-mobile carbon and desorbs. This then makes up the high-temperature CO desorption peak observed from Kovar. This explanation, although not unique in explaining the observed behavior of Kovar, is the simplest explanation.

Finally, it should be noted that it is possible that carbon monoxide may be bound to the Kovar surface with energy greater than the activation energy for diffusion. Although the diffusion process was measured at high temperatures ($>700^\circ\text{C}$), it is possible that at room temperature or somewhat higher temperatures,

Room Temp
O on surface

700°C
C - mobile
O - immobile
Surface O deficient

800°C
C - mobile
O - immobile
Surface O deficient

1100°C
C - mobile
O - mobile

Fig. 7. Illustration of carbon and oxygen diffusion in Kovar and how they might account for the CO desorption spectra observed.

the rate-limiting step might be due to first-order or second-order desorption. For example, if the first-order binding energy is about 50 kcal/mol, then at room temperature the desorption rate will be controlled by the 50 kcal bonds and not the diffusion process.

Molybdenum

Molybdenum primarily desorbs carbon monoxide. Figure 8 compares first-order and second-order desorption of carbon monoxide with the measured desorption spectra. Typically, the amount of gas desorbed is $8-9 \times 10^{15}/\text{cm}^2$. Most of this appears at temperatures over 1000°C (see Figure 9). A few percent (1-6%) appears at somewhat lower temperatures ($\approx 700^\circ\text{C}$). This desorption was apparently one or more first-order desorption peaks (determined by e^{-t} relationship of isothermal treatment). The energy of desorption for this peak is 61-64 kcal/mol. Most of the CO desorbs at about 1100°C . This is a first-order desorption peak whose binding energy is 91 kcal/mol. It was interesting to observe that as molybdenum was thermally ramped several times, the desorption peaks moved to slightly lower temperatures after the first bakeout. Undoubtedly, this phenomenon has something to do with molybdenum recrystallization which becomes quite rapid at temperatures over 900°C . The binding energies appear to be reduced about 5% after the first desorption.

Nickel

Carbon monoxide is the primary gas desorbed from nickel. Typically, three desorption peaks were seen (see Figure 10). The apparent total coverage was about $4 \times 10^{15}/\text{cm}^2$. The lowest temperature peak occurs at about 400°C and is first-order. Its binding energy is 40-42 kcal/mol. The second peak occurs at about $800-1000^\circ\text{C}$ and may be several first-order peaks or a diffusive peak. The third peak, which occurs at $1000-1100^\circ\text{C}$, is either first or second order. Because the first- and second-order peaks are very nearly the same shape, the mechanism was not determined unequivocally. In either event, the binding energy is about 90 kcal/mol.

Fig. 8. Comparison of various theoretical desorption spectra with data from a single molybdenum desorption of carbon monoxide.

Fig. 9. Typical outgassing spectra from molybdenum foil heated at 1.2 K/s. The constant level at low temperatures and the rise at the very highest temperatures are vacuum system artifacts.

Fig. 10. Comparison of various theoretical desorption spectra with data from a single nickel desorption of carbon monoxide.

Copper

Copper was the only metal studied which showed hydrogen to be a major desorbing species. All of the samples did not display the first-order peak(s) as seen in Figure 11. The peak when observed, occurs at 640°C, 57 kcal/mol first-order desorption and contains about 2×10^{15} molecules of hydrogen/cm². At temperatures over 800°C, the rising edge of a broad peak is observed but not portrayed on Figure 11. The entire peak was not observed because the ramp was terminated at 900-950°C to forestall the sample sticking to the heater. This peak may be due to hydrogen diffusing from the bulk. Oxygen, carbon dioxide, and carbon monoxide are also noted to desorb. Figure 12 shows the oxygen desorption; at least 3 peaks are apparent. These appear to be first order. The first occurs at 365°C, 33 kcal/mol; the second at 520°C, 49 kcal/mol; the third at 575°C, 53 kcal/mol. They contain in total 10^{13} molecules/cm². The carbon dioxide and carbon monoxide desorption have the same general shape differing only in amplitude which reflects the thermodynamic equilibrium partition of the two species at the desorption temperature. The spectra are quite complex (Figure 13). The first peak occurs at 400°C, 42 kcal/mol if first order; the major peak occurs at 590°C, 54 kcal/mol and appears to be first order. The total gas desorbed was 1×10^{14} /cm² and 7×10^{13} /cm² for carbon dioxide and carbon monoxide, respectively.

Copper 2% Beryllium Alloy

Copper 2% beryllium alloy (CuBe) behaves somewhat like copper. Hydrogen is desorbed only at the highest temperatures, with no peaks below 850°C, i.e., ≈20°C below the melting temperature. Carbon monoxide is the major gas desorbed. Figure 14 shows the carbon monoxide desorption spectra after various treatments of the CuBe. Carbon monoxide amounts to 6×10^{14} molecules/cm² under the largest peak. The temperatures of the peaks and corresponding binding energies are 450°C, 45 kcal/mol; 675°C, 59.4 kcal/mol; 775°C, 66 kcal/mol. Approximately 1 and 10%, respectively, of oxygen and carbon dioxide are desorbed at the same temperatures as the carbon monoxide.

Fig. 11. Low temperature hydrogen desorption peak from copper.

Fig. 12. Oxygen desorption spectra from copper.

Fig. 13. Carbon dioxide desorption from copper.

Figure 14

Molybdenum Sealing Glass Ceramic (Mexim)

Hydrogen was the principal gas desorbed from the glass ceramic we measured. The material was in its fired (crystallized) form. Figure 15 shows the hydrogen desorption spectra. The upper curve was measured after the ceramic had been abraded with silica and cleaned. The lower curve is after cleaning only. The peaks are broad. They can be explained on the basis of hydrogen diffusion from the bulk (actually a layer ≈ 0.1 cm thick), with $D_0 = 1 \times 10^{-3}$ cm²/s and $E_d = 11$ kcal/mol. This compares to Perkins' and Begeal's²² reported values for deuterium diffusion in vitreous silica of $D_0 = 5.1 \times 10^{-4}$ cm²/s and $E_d = 10.5$ kcal/mol. The agreement is probably fortuitous in light of the many simplifying assumptions made in the calculations based upon the measured desorption. The apparent gas quantities were 1.4×10^{16} /cm² lower curve, 3.0×10^{16} /cm² upper curve. The difference in the quantity of water desorbed depending upon whether or not it received abrasive treatment is even greater. Figure 16 shows the water desorption spectra from glass ceramic. The upper curve was from an abraded sample and contains 2×10^{15} molecules/cm². It peaks at about 250°C. The first-order binding energy is 32 kcal/mol. The lower curve is a non-abraded but cleaned sample containing 1.1×10^{14} molecules/cm². The 450°C peak has 48 kcal/mol binding energy. The only other appreciable gas observed was methane. It was not observed from all samples. A spectrum from an abraded sample is shown in Figure 17. The lower temperature peak contains about 2×10^{13} molecules, the upper about 2×10^{14} molecules. The peaks occur at about 185°C and 520°C with first-order binding energies of 28 and 49 kcal/mol, respectively.

Alumina Ceramic

Alumina ceramic desorbs primarily hydrogen. It comes off as several first-order peaks followed by a broad peak which may be diffusive (Figure 18). The first peak occurs at about 600°C and contains $\sim 1 \times 10^{15}$ molecules/cm² with a binding energy of 55 kcal/mol. The total, including the apparent diffusive peak, hydrogen may be as much as 5×10^{16} /cm². Typically, the total hydrogen desorbed is less than 1×10^{16} , with the first-order peaks accounting for $2-3 \times 10^{15}$ /cm². The only other gas emitted from alumina up to 1600°C is methane. Methane is emitted as a first-order peak at $\sim 760^\circ\text{C}$ (Figure 19), 65 kcal/mol, and amounts to 10^{14} to 10^{15} molecules/cm².

Fig. 15. Desorption of hydrogen from Mexim.
Upper curve silica abraded; lower curve un-
abraded; both had been cleaned.

Fig. 16. Desorption of water from Mexim.
Upper curve silica abraded; lower curve unabraded;
both had been cleaned.

Figure 17

Fig. 18. Desorption of hydrogen from alumina ceramic.

Figure 19

Predicted Outgassing Rates

The table gives rates of outgassing based upon the measurements reported in this paper for materials, stored at 300 K and 350 K, before bakeout and after a 675 K, 10^4 s bakeout.

CONCLUSIONS

The value of a high-temperature bakeout becomes apparent when the several orders of magnitude reduction in moderate outgas rates occurs after such a bakeout. If the outgas rate is very small (a high desorption energy), then the bakeout has little impact, but the low flow should be no problem in either case. It can also be seen that desorption kinetics controlled by bulk diffusion have a much larger and long lasting impact on desorption. Raising the bakeout temperature will improve the long-term desorption characteristics. Therefore, it would seem prudent to subject materials which may desorb by diffusion to a thorough high temperature vacuum firing before they are assembled into the final vacuum device but after they are to be exposed to high temperatures in the presence of gaseous atmospheres, e.g., H_2 .

Acknowledgements

I wish to thank D. Begeal and R. Patrick for taking much of the data. W. G. Perkins and G. W. McClure for many interesting and helpful discussions on the data and its manipulation, and L. Bustard for his critical reading and comments on the manuscript.

TABLE OF PREDICTED OUTGAS RATES (molecules/s cm²)

Material and Treatment	t = 0		10 ⁵ s ≈ 1 day		10 ⁶ s ≈ 12 days		10 ⁷ s ≈ 4 mos.		10 ⁸ s ≈ 3 yrs.	
	300K	350K	300K	350K	300K	350K	300K	350K	300K	350K
1. Kovar Co desorption $C_0 = 10^{13}/\text{cc}$ $\Delta = .05 \text{ cm}^3/\text{g}$, $E_d = 27,500 \text{ cal/mol}$, $D_0 = 4 \text{ cm}^2/\text{s}$	4×10^8	1.1×10^{10}	1.3×10^8	3.3×10^7	4×10^5	1.1×10^7	1.3×10^5	3.3×10^6	4×10^4	1.1×10^6
2. As 1 after 675K, 10 ⁴ s bakeout	7	4.7×10^3	7	4.7×10^3	7	4.7×10^3	7	4.7×10^3	7	4.7×10^3
3. Molybdenum CO desorption $E = 61,000 \text{ cal/mol}$ $H_0 = 8 \times 10^{14}/\text{cm}^2$	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}
4. As 3 after 675K, 10 ⁴ s bakeout	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}	3.5×10^{-17}	7.1×10^{-11}
5. Nickel CO desorption $E = 40,000 \text{ cal/mol}$ $H_0 = 2 \times 10^{14}/\text{cm}^2$	2.2×10^{-2}	305	2.2×10^{-2}	305	2.2×10^{-2}	305	2.2×10^{-2}	305	2.2×10^{-2}	305
6. As 5 after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
7. Nickel CO desorption $E = 47,000 \text{ cal/mol}$ $H_0 = 2 \times 10^{15}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	6.4×10^{-21}	5.4×10^{-14}	6.4×10^{-21}	5.4×10^{-14}	6.4×10^{-21}	5.4×10^{-14}	6.4×10^{-21}	5.4×10^{-14}	6.4×10^{-21}	5.4×10^{-14}
8. Copper H ₂ desorption $E = 57,000 \text{ cal/mol}$ $H_0 = 2 \times 10^{15}/\text{cm}^2$	1.1×10^{-13}	8.6×10^{-8}	1.1×10^{-13}	8.6×10^{-8}	1.1×10^{-13}	8.6×10^{-8}	1.1×10^{-13}	8.6×10^{-8}	1.1×10^{-13}	8.6×10^{-8}
9. As 8 after 675K, 10 ⁴ s bakeout	1.1×10^{-13}	8.2×10^{-8}	1.1×10^{-13}	8.2×10^{-8}	1.1×10^{-13}	8.2×10^{-8}	1.1×10^{-13}	8.2×10^{-8}	1.1×10^{-13}	8.2×10^{-8}
10. Copper O ₂ desorption $E = 33,000 \text{ cal/mol}$ $H_0 = 3 \times 10^{12}/\text{cm}^2$	39	1×10^5	39	1×10^5	39	9.7×10^4	39	7.2×10^4	39	3.5×10^1
11. As 10 after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
12. Copper O ₂ desorption $E = 49,000 \text{ cal/mol}$ $H_0 = 2 \times 10^{12}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	2.2×10^{-18}	2.6×10^{-13}	2.2×10^{-18}	2.6×10^{-13}	2.2×10^{-18}	2.6×10^{-13}	2.2×10^{-18}	2.6×10^{-13}	2.2×10^{-18}	2.6×10^{-13}
13. Copper O ₂ desorption $E = 53,000 \text{ cal/mol}$ $H_0 = 5 \times 10^{12}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	8.9×10^{-14}	2.7×10^{-8}	8.9×10^{-14}	2.7×10^{-8}	8.9×10^{-14}	2.7×10^{-8}	8.9×10^{-14}	2.7×10^{-8}	8.9×10^{-14}	2.7×10^{-8}
14. Copper CO ₂ desorption $E = 42,000 \text{ cal/mol}$ $H_0 = 1 \times 10^{13}/\text{cm}^2$	3.9×10^{-5}	.88	3.9×10^{-5}	.88	3.9×10^{-5}	.88	3.9×10^{-5}	.88	3.9×10^{-5}	.88
15. As 14 after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
16. Copper CO ₂ desorption $E = 56,000 \text{ cal/mol}$ $H_0 = 1 \times 10^{13}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	3.5×10^{-13}	1.3×10^{-7}	3.5×10^{-13}	1.3×10^{-7}	3.5×10^{-13}	1.3×10^{-7}	3.5×10^{-13}	1.3×10^{-7}	3.5×10^{-13}	1.3×10^{-7}
17. CuBe CO desorption $E = 45,000 \text{ cal/mol}$ $H_0 = 10^{13}/\text{cm}^2$	2.7×10^{-7}	1.2×10^{-2}	2.7×10^{-7}	1.2×10^{-2}	2.7×10^{-7}	1.2×10^{-2}	2.7×10^{-7}	1.2×10^{-2}	2.7×10^{-7}	1.2×10^{-2}
18. As 17 after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
19. CuBe CO desorption $E = 59,400 \text{ cal/mol}$ $H_0 = 2 \times 10^{13}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	2×10^{-16}	3×10^{-10}	2×10^{-16}	3×10^{-10}	2×10^{-16}	3×10^{-10}	2×10^{-16}	3×10^{-10}	2×10^{-16}	3×10^{-10}
20. Maxfm H ₂ desorption, $C_0 = 10^{18}/\text{cc}$ $\Delta = .1 \text{ cm}^3/\text{g}$, $E_d = 10,500 \text{ cal/mol}$, $D_0 = 5 \times 10^{-11} \text{ cm}^2/\text{s}$	2×10^{12}	7×10^{12}	6.3×10^9	2.2×10^{10}	2×10^9	7×10^9	6.3×10^8	1.4×10^9	1.5×10^8	1.4×10^9
21. As 20 after 675K, 10 ⁴ s bakeout	3×10^7	3.7×10^8	3×10^7	3.7×10^8	3×10^7	3.6×10^8	3×10^7	1×10^8	1.1×10^4	130
22. Maxfm H ₂ O desorption $E = 32 \text{ kcal/mol}$ $H_0 = 2 \times 10^{13}/\text{cm}^2$	1×10^5	2.8×10^8	1.4×10^5	2.8×10^8	1.4×10^5	2.4×10^8	1.4×10^5	7×10^7	1.4×10^5	230
23. As 22 after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
24. Maxfm H ₂ O desorption $E = 45,000 \text{ cal/mol}$ $H_0 = 2 \times 10^{14}/\text{cm}^2$ after 675K, 10 ⁴ s bakeout	0	0	0	0	0	0	0	0	0	0
25. Alumina H ₂ desorption $E = 55 \text{ kcal/mol}$ $H_0 = 1 \times 10^{15}/\text{cm}^2$	1.5×10^{-12}	7.5×10^{-7}	1.5×10^{-12}	7.5×10^{-7}	1.5×10^{-12}	7.5×10^{-7}	1.5×10^{-12}	7.5×10^{-7}	1.5×10^{-12}	7.5×10^{-7}
26. As 25 after 675K, 10 ⁴ s bakeout	1.3×10^{-12}	6.2×10^{-7}	1.3×10^{-12}	6.2×10^{-7}	1.3×10^{-12}	6.2×10^{-7}	1.3×10^{-12}	6.2×10^{-7}	1.3×10^{-12}	6.2×10^{-7}

REFERENCES

1. Yale Strausser, Review of Outgassing Results, Varian Associate Publication VR-51, Palo Alto, Calif. undated.
2. J. P. Hobson, Proc. of the 1975 Isabelle Summer-Study, Brookhaven National Laboratory, New York.
3. L. R. Apker, Industrial and Engineering Chemistry, 40, #5, p.846-847 (1948).
4. A. W. Smith and S. Aranoff, Journal of Physical Chemistry, 62, p.684-686 (1958).
5. P. A. Redhead, Vacuum, 12, p.203-211 (1962).
6. Gert Ehrlich, Journal of Applied Physics, 32, p.4-15 (1961).
7. P. W. Tamm and L. D. Schmidt, Journal of Chemical Physics, 54, #11, p.4775-4787 (1971).
8. G. Farrell, W. A. Grant, K. E. Rents, and G. Carter, Vacuum, 16, #6, p.295-298 (1966).
9. W. A. Grant and G. Carter, Physics and Chemistry of Glasses, 8, #1, p.35-37 (1967).
10. W. W. Brandt, International Journal of Heat and Mass Transfer, 13, p.1559-1570 (1970).
11. D. A. King, Surface Science, 47, p.384-402 (1975).
12. D. Edwards, Jr., Surface Science, 54, p.1-5 (1976).
13. G. Carter, B. J. Evans, and G. Farrell, Vacuum, 25, #5, p.197-199 (1975).
14. S. E. Donnelly and D. G. Armour, Vacuum, 27, #1, p.21-25 (1976).
15. K. L. Wilson and M. I. Baskes, "Deuterium Trapping in Irradiated 316 Stainless Steel," SAND77-8756, April 1978.
16. R. C. Patrick, J. Vac. Science and Tech., 15, #1, p.133-134 (1978).
17. S. M. Ko and L. D. Schmidt, Surface Science, 42, p.508-524 (1974).
18. M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions," p.223 and p.242-243, AMS-55, National Bureau of Standards, June 1964.
19. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," p.97, 2nd Edition, Oxford-Clarendon Press, 1959.
20. J. D. Fast, "Interaction of Metals and Gases, Kinetics and Mechanisms," p.126-127, Barnes and Noble, 1972.
21. M. R. Notis, J. of the American Ceramic Society, 45, #9, p.412-416 (1962).
22. W. G. Perkins and D. R. Begeal, J. of Chem. Phys., 54, #4, p.1683-1694 (1971)