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KNOLLS ATOMIC POWER LABORATORY

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U.S. ATOMIC ENERGY COMMISSION

THE DIFFUSION OF HYDROGEN THROUGH MATERIALS OF CONSTRUCTION

P. S. Flint

December 14, 1951

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THE DIFFUSION OF HYDROGEN
THROUGH MATERIALS OF CONSTRUCTION

P. S. Flint

December 14, 1951

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ABSTRACT

Results on the investigation of the rate of diffusion of hydrogen through several types of stainless steel and other materials of construction are reported with particular emphasis on Type 347 stainless steel. The use of coatings to reduce the rate is also discussed. Measurements of the diffusion rate were made using an all metal diffuser of new design at temperatures from 100 to 900°C. It was found that the rate of diffusion for Type 347 stainless steel can be represented for the temperature range 200 to 600°C by the equation:

$$\log S = 2.19 - \frac{3.18 \times 10^3}{T}$$

where S , the diffusion constant, is expressed in cc(STP)/cm²/hr/mm at 760 mm of hydrogen pressure, and T is the absolute temperature. Above 600°C, the rate of diffusion is progressively greater than indicated by the equation (at 800°C the rate is 2.7 times the calculated value). Other stainless steels investigated were Types 304, 410, 420, 316, and 321. In addition, low carbon steel, aluminum, and Sylvania Alloy #4 were studied. Variations of as much as 50% under identical conditions were observed in the diffusion rate of different specimens of one type of stainless steel. The small variations of composition of the austenitic stainless steels, including the addition of stabilizers, appeared to produce little change in the rate.

The effects of various coatings on the rate of diffusion of hydrogen through Type 347 stainless steel are reported. Nitriding the surface of the diffuser was found to have little or no effect on its permeability to hydrogen. A low contraction chrome plate was found to reduce the rate 40-fold, but the plate cracked off during thermal cycling in hydrogen. A calorized diffuser (Al clad) had a rate 100-fold lower than clean metal. Ceramic coatings, specially synthesized to have coefficients of expansion compatible with that of stainless steel, reduced the rate as much as 200-fold. A spinel coating, produced by treating Type 347 stainless steel with wet hydrogen at temperatures up to 1000°C, also reduced the rate 200-fold below that of clean metal.

The results of the rate of hydrogen diffusion due to reaction of stainless steel with atmospheric moisture at elevated temperatures are also given. A review of the theory of diffusion and of the permeabilities of a number of common metals and alloys is included, as is a brief review of the solubility of hydrogen in these metals.

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THE DIFFUSION OF HYDROGEN THROUGH MATERIALS OF CONSTRUCTION

P. S. Flint

OBJECTIVE

The object of this work was to determine the rate of diffusion of hydrogen through various materials of construction and to find means of reducing the rate of diffusion at high temperatures, chiefly around 700°C. The materials used were principally stainless steels of various types.

INTRODUCTION

Theories of Diffusion

The term diffusion is used throughout this report to describe the passage of gas through a solid barrier as it is so commonly used throughout the literature. The correct term is permeability; diffusion is the passage of gas through the body of the barrier, while permeability includes adsorption and desorption as well as diffusion.

Diffusion through a solid barrier is a process the mechanism of which is not too well understood. Several aspects of the process have been well established, however. First, it is known that gaseous diffusion through solids takes place through the body of the solid, not along grain boundaries or any other selective paths. This fact has been demonstrated by Edwards⁽⁹⁾ and by Smithells and Ransley⁽¹⁵⁾ by showing that the rate of diffusion of hydrogen through a single crystal of iron remained the same after the specimen was recrystallized into a number of small crystals. Secondly, diffusion through metals is specific; that is, certain gases will diffuse through certain metals, others will not, regardless of molecular weight. Thus hydrogen, nitrogen, and carbon monoxide will diffuse through iron at high temperatures, while helium, whose molecules are considerably smaller than those of either of the latter two, will not diffuse to any measurable extent.⁽²³⁾ Thus, it has been accepted that there must be a chemical affinity between the gas and the metal in order for diffusion to take place. Third, diffusion of diatomic gases through metals takes place in the atomic state. This fact is evidenced by the dependence of the rate of diffusion upon the square root of the gas pressure. Through the more open lattice of ceramic materials diffusion is molecular and depends upon the first power of the pressure. In the case of ceramic materials, helium diffuses more readily than hydrogen; apparently chemical affinity in this case causes blocking, allowing the rare gas to pass through the lattice more readily. Further evidence of atomic diffusion can be seen in the fact that when hydrogen is produced against a metal surface by chemical (acid-metal reaction) or electrochemical (electrolysis) means, the hydrogen will readily diffuse through the metal against several hundred atmospheres of hydrogen pressure on the outlet side. Thus it can be seen that in order for permeation to take place through a metal barrier, a diatomic gas molecule must arrive at the surface of the metal, dissociate

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into atoms, diffuse through the body of the metal in the atomic state, and the atoms must recombine into molecules at the outlet surface and escape as the molecular gas. The surface conditions of the metal, therefore, have much to do with the ability of the gas to dissociate and hence can be controlling factors in the diffusion process. As will be seen, considerable work has been devoted to the effects of various surface conditions on the diffusion rate.

The Diffusion Equation

The General Equation

The equation for expressing the amount of a diatomic gas diffusing through a solid metallic barrier is customarily written as follows:

$$Q = \frac{SDA}{d} (\sqrt{p_1} - \sqrt{p_2}) e^{-\frac{E_0}{RT}} t$$

where

Q = amount of gas diffusing through the barrier (cc(STP))

S = solubility constant

D = diffusion constant

A = area of the barrier (cm²)

d = thickness of the barrier (mm)

p₁ and p₂ = steady state gas pressures on the inlet and outlet sides of the barrier respectively (mm)

E₀ = activation energy for the process

R = the gas constant

T = absolute temperature (°K)

t = time (hr)

This equation indicates that the rate of diffusion through metals varies directly as the area, and as the square root of the pressure at each surface, inversely as the thickness, and exponentially as the reciprocal of absolute temperature. This equation has proved adequate for our purposes as reported in this paper. A brief discussion follows on exceptions to the equation found under certain conditions.

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Effect of Pressure

Experiments in this paper were conducted at atmospheric pressure with a few exceptions. The results of the one run made at a pressure of 592 mm of mercury were in agreement with the $\sqrt{p}$ law. The ratio of the rates S_1 and S_2 at 850°C in cc(STP)/cm²/hr/mm (see page 16) is the same as the ratio of the square roots of the corresponding equilibrium pressures.

$$\frac{S_1}{S_2} = \frac{1.02}{0.90} = 1.13 = \frac{\sqrt{755}}{\sqrt{592}} = \frac{\sqrt{P_1}}{\sqrt{P_2}}$$

In the low pressure region the pressure dependence deviates from a square root relation toward a more linear relationship. No work in this region has been done in the current investigation.

Effect of Temperature

A perceptible deviation from the exponential form of the diffusion equation with respect to temperature dependence of the rate has been found in these experiments. This deviation is illustrated in the case of Type 347 stainless steel in Figure KH-9A1515 (page 37). It is not significant except over a considerable range of temperature. Derivations of the diffusion equation on a thermodynamic basis normally include some power of T, in addition to the exponential terms. The simpler exponential form is quite adequate over a temperature range of a few hundred degrees centigrade.

Effect of Thickness

There is some question as to whether or not the inverse thickness law holds in all cases of gaseous diffusion through solids. The effect of thickness on the rate of diffusion has been observed with the oxygen-silver system by Johnson and Larose,⁽²⁵⁾ with the hydrogen-nickel system by Baukloh and Kayser,⁽⁵⁾ and with the hydrogen-iron system by Baukloh and Lewkonja.⁽⁵⁵⁾ Johnson and Larose investigated the rates through foils of thicknesses from 0.07 to 0.25 mm, and obtained good agreement with the inverse thickness law. Baukloh and his associates used specimens from 1 to 5 mm in thickness, and also found agreement with the inverse law.

It would seem that the inverse thickness law holds only where the diffusion part of the process of permeation is rate controlling. This is probably the case in the above-mentioned systems. In the case where surface adsorption is the controlling factor in the permeation process, one would not expect the inverse thickness law to hold. In such a case, one would expect to find that increased thickness would produce less decrease in the rates than predicted by the inverse thickness law. Also, for a given material and surface conditions, the thicker the specimen, the more controlling the diffusion process becomes, while the thinner the specimen, the more controlling the surface adsorption process becomes. Thus, in the case of the wet hydrogen fired stainless steels

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discussed in this report where the surface is covered with an impermeable oxide layer, it would be expected that an increase in thickness would not reduce the rate too significantly. Such an effect has not yet been determined experimentally, however, because of the difficulty of reproducing oxide coatings.

Application of the Diffusion Equation

If the pressure of gas on the outlet side of the barrier is essentially zero, as in the case of these experiments then the steady state diffusion equation becomes:

$$Q = \frac{SDA}{d} \sqrt{p_1} e^{-\frac{E_0}{RT}} t$$

In the case of a ceramic barrier the dependence of the rate on pressure is linear instead of as the square root because diffusion occurs in the molecular state rather than in the atomic state. In this case the diffusion equation becomes:

$$Q = \frac{SDA}{d} p_1 e^{-\frac{E_0}{RT}} t$$

For the purpose of this work it has been convenient to specify a given temperature and pressure and then combine the constants S , D , p_1 and e^{-E_0/RT_1} into a single constant S_1 . The equation then further simplifies to:

$$QT_1 p_1 = \frac{S_1 A t}{d}$$

The values of S for some of the common materials are given at a number of different temperatures in Table 1 (page 31) at a pressure of 760 mm. To convert to another pressure; for example, 200 mm:

$$S_{200 \text{ mm}} = S_{760 \text{ mm}} \sqrt{\frac{200}{760}}$$

To evaluate S for any particular temperature, one can make use of the conventional exponential expression:

$$\log S = A - B \times 10^3/T$$

where A and B are constants to be evaluated.

Since diffusion rates were obtained over a wide range of temperatures on most materials and since the above equation generally holds only for a limited range of temperature, the data have been plotted so that values between measured temperatures can be read easily.

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Other Factors Affecting Diffusion

Surface Conditions

As has already been mentioned, surface conditions have a marked effect on the rate of diffusion. Surface roughness has a considerable effect on the rate. Smithells and Ransley⁽¹⁵⁾ have shown that an etched iron specimen will show as much as a ten-fold increase in rate over a polished specimen of the same material. Oxide coatings have a marked effect on the diffusion rate. Most active metals when subjected to hydrogen diffusion will poison slowly from traces of oxygen in the diffusing gas. Probably the chief reason for the very low permeability of aluminum to hydrogen is that it readily forms an oxide coating which is stable in hydrogen and which blocks diffusion of the gas. We may think of the oxide coating as a barrier which has a strong affinity for hydrogen molecules or atoms and holds a layer of hydrogen on the surface, blocking further penetration by the gas.

Effect of Structure

The effect of the open lattice of ceramics on the diffusion mechanism as contrasted with the denser lattice of metals has already been discussed. It has also been pointed out that diffusion occurs through the lattice and that grain boundaries and crystal size have negligible effect. Bastien⁽²¹⁾ has shown that cold working of 0.065% carbon steel wire increases the rate of degassing of atomic hydrogen from the wire and hence apparently the rate of diffusion. Darken⁽²²⁾ has shown in the case of low carbon steel that cold working markedly increases the amount and rate of takeup of hydrogen. It is, therefore, probable that cold working will increase the rate of diffusion. The effect of hardness produced by heat treating a 13%-chromium, 0.3%-carbon steel as reported in this paper was hardly noticeable.

Effect of Composition

As would be expected, the addition of elements with a high diffusion rate will normally increase the diffusion rate through an alloy. Baukloh and Kayser⁽⁶⁾ have demonstrated this phenomenon with nickel--copper and nickel--iron alloys. In the case of austenitic 18-8 chrome-nickel steels, the diffusion rate is lower than that for iron or cold rolled steel, probably due both to the high chromium and nickel content and the denser lattice of the face-centered austenitic structure as opposed to the body-centered alpha structure of iron and low carbon steel. In such a case, a structural change must be considered as well as the addition of a different element or elements. Small variations in composition have appeared to give little or no changes in rate of diffusion in the 18-8 stainless steels. The addition of Nb-stabilizer to these steels causes little or no difference in the rate. On the other hand, if a change of structure or of surface conditions is brought about by the addition of a small amount of an element, its presence may affect the rate considerably.

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Relation of Diffusion to Solubility

There is naturally a close relation between diffusion and solubility. If a gas is not soluble in a solid, one would expect, and experiment confirms, that it will not diffuse through the solid. Indeed it is difficult to conceive of one process being possible without the other. A brief table of solubilities of hydrogen in metals is given in Appendix II for convenience. In general, it appears that diffusion rates and solubilities show a close correlation; but there are notable exceptions, such as, for example nickel, which has a high hydrogen solubility compared to that of iron, but a lower diffusion rate. Particularly noticeable are the austenitic stainless steels which have high solubilities in comparison with nickel, but have low rates of diffusion in comparison with those of copper and molybdenum.

The foregoing constitutes a brief introduction to the study of gaseous diffusion through solids. For a more thorough discussion, the reader is referred to the general texts on the subject listed in the bibliography.^(1,2,3,4)

APPARATUS AND METHOD

Apparatus and Methods used by other Investigators

The apparatus used by a number of other investigators to measure the rate of gaseous diffusion through solids are shown in Figure KH-9A1545. A is the type used by Lombard⁽¹²⁾ and by Ham.⁽¹¹⁾ It measures the rate at which gas passes through a thin flat plate of the material to be tested. The chief disadvantages of this design are: (a) vacuum tightness of the apparatus and (b) adsorption from the large area on the low pressure side. This adsorption would be due chiefly to the escape of hydrogen from the high pressure side out into the furnace and from any hydrogen produced from atmospheric moisture reacting with the metal tube on the low pressure side. A modification of this type has been used for diffusion work at high pressures up to 100 atmospheres. B is the type of apparatus used by Richardson⁽¹³⁾ for determining the rate of diffusion of hydrogen through platinum. Similar to it in most respects is apparatus C, used by Metal Hydrides Inc. for work on steels. Both types measure the loss of gas through the tubular membrane rather than the gas evolved on the outlet side. This method can be disadvantageous in certain cases. Both types have a temperature gradient along the length of the diffusion tube, which is quite undesirable as the rate is so strongly temperature dependent. Both types expose the outer surface to air, resulting, particularly in the case of apparatus C, where more active metals are being used, in possible poisoning and reduction of the rate of diffusion. Borelius and Lindblom⁽⁷⁾ used apparatus D in which a uniform temperature can be obtained although with considerable end effects, as it is difficult to find a satisfactory masking material for both ends of the tube at high temperatures. Smithells and Ransley⁽¹⁵⁾ used apparatus E with an exploring thermocouple. The temperature gradient problem is also present in this case, but can be compensated for fairly well.

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DIFFUSION APPARATUS OF OTHER INVESTIGATORS

(A)

(B)

(C)

(D)

(E)

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In each of the above cases, the amount of gas diffusing through the membrane was determined by measuring either the pressure decrease on the high pressure inlet side, or the pressure increase on the low pressure outlet side. The former method was used with apparatus B and C and, of course, is considerably less sensitive than the latter.

Apparatus used in These Experiments

The apparatus used in the following experiments is pictured in Figures KH-9A1543 and KH-9A1544. It consists of a diffuser tube of 1/4 inch OD and 7 1/2 inches long, welded shut with a plug at one end and connected to the measuring section of the vacuum system at the other end. The diffuser tube is enclosed in an outer jacket through which hydrogen flows at atmospheric pressure. The region where the diffuser tube emerges from the jacket and connects to the vacuum system is constructed of heavy stock; hydrogen diffusion through the connection is calculated to be less than 1% of that through the diffuser. The jacket is enclosed in a furnace and two auxiliary heaters are used, one on each end. By controlling the end heaters individually, one can keep the temperature constant over the full length of the diffuser tube within $\pm 2^\circ\text{C}$ up to 600°C and within $\pm 5^\circ\text{C}$ up to 800°C . No trouble has been experienced with leaks as long as the welds are adequately leak tested during fabrication. The disadvantages of this diffuser design are that its fabrication is somewhat tedious--a fault it has in common with a number of the other types mentioned--and that the diffusion rate cannot be determined by measuring the pressure drop since hydrogen loss through the jacket is high. However, by using a metal jacket many of the difficulties attendant to measuring diffusion rates at high temperatures are solved since the entire unit can be heated with no problems in controlling the temperature gradient along the diffuser or in protecting a metal-to-glass seal.

A continually flowing hydrogen stream was used to avoid blanketing of the diffusing surface by impurities in the gas. It has the disadvantage, however, of causing a cumulative poisoning or aging effect on the specimen by trace impurities in the gas which will react with the specimen. This flow system proved to be advantageous when deliberate oxidation of the diffuser was desired, allowing considerable flexibility in exposing the diffuser to various gas atmospheres. If one wishes to use extremely pure hydrogen, a static system using hydrogen passed through a palladium thimble, or evolved from uranium, is most satisfactory. Such a system was used by Smithells and Ransley.^(15,16) They found, however, that with a metal as active as aluminum, poisoning of the diffuser tube could not be prevented even with the precautions mentioned above. They attributed the poisoning to the reduction of oxides on other metallic parts inside the glass jacket by the hydrogen, and to oxidation of the aluminum by the resulting traces of water. For our purposes, the flow stream and the metal jacket have proved adequate.

Method Used in These Experiments

The rate of diffusion is determined by measuring the pressure increase in the calibrated measuring volume (normally under vacuum) over a given period of time. Mercury cutoffs are used to isolate the measuring volume. The pressure is measured with a double McLeod gauge with a combined range of 0.001μ to $3,000 \mu$. The measuring volume was calibrated by the expansion of hydrogen from a calibrated bulb. Upon installation each diffuser was leak tested in situ at room temperature. At first, leak tests were made before each rate determination at elevated temperatures by substituting helium for hydrogen in the outer jacket; but since no trouble was encountered with leaks, leak tests during operation were later made only when there was a suspicion that a leak might have developed. Rate measurements were made normally by approaching the measuring temperature from a lower temperature. The diffusion process is not completely reversible and a different rate will be obtained by approaching the measuring temperature from a higher temperature. The time necessary to establish steady state at which point the diffusion rate becomes constant at a given temperature varies greatly with the temperature. At 100°C the equilibrium time is at least 24 hours, while at 700°C it is less than 5 minutes.

The hydrogen used was electrolytic tank hydrogen purified by passing over copper at 750°C and through a liquid nitrogen trap to remove oxygen and water vapor. The analysis of the hydrogen before purification is:

0.06% CH_4

0.18% H_2O

0.52% N_2

< 0.01% CO_2

< 0.01% He

The water content was reduced to the order of 0.01% by trapping at -184°C . The helium used was U. S. Bureau of Mines tank helium; the impurities by mass spectrometer analysis are:

< 0.01% H_2

~ 0.01% N_2

~ 0.02% H_2O

Wet hydrogen was produced by simply bubbling the hydrogen through water at 25°C (giving about 80% saturation or about 20 mm of water vapor). Steam was produced by boiling water in a small flask connected to the jacket by lagged glass tubing. When applying the steam, hydrogen was swept through the steam generator and diffuser jacket until the boiling point was reached, at which time the hydrogen was turned off.

18 DIFFUSER (LONG. SECT.)

DIFFUSION SYSTEM

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Analyses have been made on all specimens tested except in certain cases where oxidation treatments of the specimens were carried out and the exact composition of the base metal was unimportant. Analytical results have been included in the tables along with the diffusion rates.

Reverse diffusion runs were accomplished by filling the system, including the measuring volume, with pure hydrogen evolved from a uranium bed and sweeping the outer jacket with dry helium (passed through a liquid nitrogen trap). The helium carried any hydrogen diffusing through the diffuser tube into a copper oxide furnace, where it was converted to water, and thence into an Anhydron drying tower where the water was absorbed and weighed.

ACCURACY AND LIMITATIONS

The accuracy in measuring thickness of the diffuser, temperature control, the method of calibration of the measuring volume, and the method of measuring pressure of the diffused gas limit the over-all accuracy of the system to within 1 to 2%. Precision of measurement is good; values were reproducible to well within 1%.

The fact remains that the diffusion process is a very sensitive one and affected by many variables some of which are not understood. It is possible to obtain good precision in results of diffusion rates on a single specimen; but in comparing different specimens of the same material, differences of rate of 50% are not uncommon. Thus, in diffusion work one must consider more often the order of magnitude of the rate and consider only marked changes in the rate under various conditions. For example, the rate of diffusion of hydrogen through a piece of clean Type 347 stainless steel, cold drawn tubing (as received from stock) will decrease or "age" about ten-fold from being exposed to dry hydrogen, purified in the manner mentioned above, for 100 hours at 620°C. The diffusion rate is very sensitive to surface conditions as has already been mentioned. In the following work the diffusion rates through the clean metals were determined as rapidly as possible to avoid the "aging" effect just mentioned. Rates obtained on clean specimens should, generally, be accurate to within 1 to 2%. In further work done on specimens to determine the effect of oxidation, etc., the rates are treated more according to their order of magnitude, although, generally, they are accurate to within a few per cent.

DATA

Brief Summary of Experimental Data Available

General

A tabulation of data on most of the important materials of construction is given in Table 1. Figure MH-9A8068 contains a plot of most of these data. The data available from the literature are plotted in solid lines and those obtained by this project in dotted lines. The data of Smithells and Ransley^(15,16) have been taken as representing some of the best values

available. They have been extended by the work of others to cover as much of the temperature range as possible. Included are the most important findings with regard to oxide and ceramic coatings. The data are given only to two significant figures as additional figures would be meaningless when comparing different specimens. A brief look at the data and plot will disclose the following facts.

In general, with metals one observes a great increase in diffusion rates with increase in temperature. Also there is a noticeable tendency for the diffusion curves to spread at the low temperatures and to converge at the high temperatures. Thus, for example, the rate of iron is about 1000 times that of Type 347 stainless steel at 100°C, but only about 5 times that of stainless steel at 700°C.

Reduction of Diffusion at Low Temperatures

In the low temperature range (up to 500°C) aluminum is the most impervious of the common elements (probably because of its adherent stable oxide coating). Copper and molybdenum are also quite resistant to hydrogen diffusion. Iron, nickel, and low carbon steel have relatively high rates of diffusion. Among the alloy steels, the austenitic groups (Types 304, 316, 321, 347) show rates close to those of copper and molybdenum. Ceramic materials, of course, are quite effective at holding hydrogen at low temperatures. They are also very effective at high temperatures but, of course, have mechanical disadvantages for construction purposes. A brief survey of diffusion through ceramic materials is included in a later section.

Reduction of Diffusion at High Temperatures

In the high temperature range (above 500°C) aluminum becomes useless because it melts at 660°C, and the rates through all metals become high. Molybdenum has a relatively low rate but is not too common a material. The rate curves for the steels converge above 700°C; at 700°C the rate for low carbon steel is only five-fold that of Type 347 stainless steel, as previously mentioned. However, as will be explained later, the stainless steels, for example Type 347, will "age" (oxidize), that is, the diffusion rate will decrease with time at elevated temperatures in hydrogen. Furthermore, such aging can be accelerated and the rate further decreased by artificial aging in controlled oxidizing atmospheres at higher temperatures, as, for example, with wet hydrogen. A modification of this procedure is to caloricize the base metal, that is, to alloy a thin layer of aluminum into the surface and to oxidize the surface. A third means of reducing the diffusion rate at high temperatures is to coat the base metal with a glass, essentially, therefore, putting an oxide layer on the surface as in the other methods. By such methods, one can reduce the rate of diffusion through Type 347 stainless steel 100-fold or more below that of the clean metal at 700°C.

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Rebutle 5%

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Table 1
Diffusion of Hydrogen Through Metals
Diffusion Rate D (cc(STP)cm²/hr/mm) for H₂ at 760 mm

Material	Treatment	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	Ref.
Aluminum Analysis: Cu 0.03% Fe 0.90% Mn 0.03% Si 0.4% Zn 0.17%	-	-	-	-	-	4.6 x 10 ⁻⁴	4.5 x 10 ⁻³	(M.P. 660°)	-	-	(16)
51-S Aluminum Analysis: 0.25% Cu 0.6% Si 1.0% Mg 0.025% Cr	-	-	-	1.2 x 10 ⁻⁴	1.7 x 10 ⁻³	2.6 x 10 ⁻³ 4.2 x 10 ⁻⁴	2.1 x 10 ⁻³ 5.6 x 10 ⁻⁴	-	-	-	KAPL
Copper O.F.H.C. Copper	treated for several hours at 500°C in H ₂ cold drawn	2.7 x 10 ⁻⁷	1.5 x 10 ⁻⁶	8.0 x 10 ⁻⁵	9.0 x 10 ⁻⁴	6.0 x 10 ⁻³	-	-	-	-	(15)
no spec.	-	-	-	-	-	-	4 x 10 ⁻²	6 x 10 ⁻²	1.2 x 10 ⁻¹	2.1 x 10 ⁻¹	(8) (5,6)
Inconel Nominal Comp. Ni 77% Cr 15% Fe 7%	-	3.7 x 10 ⁻⁵	1.7 x 10 ⁻⁴	2.0 x 10 ⁻³	-	-	-	-	-	-	(56)
aged six days	-	-	-	-	-	-	2.2 x 10 ⁻¹	-	-	-	(17)
Iron mild steel	decarburized for 4 hr at 870°C in wet H ₂ , and etched with acid	-	1.2 x 10 ⁻²	3.5 x 10 ⁻²	1.2 x 10 ⁻¹	3.0 x 10 ⁻¹	6.2 x 10 ⁻¹	1.10	-	-	(15)
Niobium Analysis: <0.02% Si Spect. traces of Ca, Cu, Fe	-	-	-	-	-	3.5 x 10 ⁻³	1.2 x 10 ⁻²	3.3 x 10 ⁻²	6.4 x 10 ⁻²	-	(15)
Nichrome (standard) Nominal Comp. Ni 80% Cr 20%	-	-	-	-	-	-	1.3 x 10 ⁻¹ 1.6 x 10 ⁻²	-	-	-	(17)
aged 14 days	-	-	-	-	-	-	-	-	-	-	
Nichrome V Nominal Comp.	-	-	-	-	-	-	1.3 x 10 ⁻¹ 3 x 10 ⁻³	-	-	-	(17)
aged 14 days	-	-	-	-	-	-	-	-	-	-	
Nickel Analysis: Chief impurity 0.02% Mg	-	-	-	-	-	1.2 x 10 ⁻¹	3.4 x 10 ⁻¹	8.5 x 10 ⁻¹	-	-	(15)
Steel, low carbon Analysis: C 0.12% (KAPL) C 0.1% (57)	-	5.6 x 10 ⁻⁵	9.8 x 10 ⁻⁴	8.2 x 10 ⁻³	5.2 x 10 ⁻²	3.0 x 10 ⁻¹ 2.4 x 10 ⁻¹	5.4 x 10 ⁻¹	8.7 x 10 ⁻¹	-	-	KAPL (57)
S.S. Type 304 Analysis: Fe bal Cr 18.6% Ni 10.2% Mn 0.3% C 0.075%	wet H ₂ + steam (stable coating)	-	-	-	4.1 x 10 ⁻³	2.0 x 10 ⁻²	6.6 x 10 ⁻²	1.8 x 10 ⁻¹ 2.6 x 10 ⁻³	4.0 x 10 ⁻¹	7.4 x 10 ⁻¹	KAPL
S.S. Type 316 Analysis: Fe bal Cr 17.4% Ni 13.8% Mn 1.65% Mo 2.4% C 0.044%	-	-	-	-	1.0 x 10 ⁻²	4.0 x 10 ⁻²	1.2 x 10 ⁻¹	3.1 x 10 ⁻¹	7.4 x 10 ⁻¹	-	KAPL
S.S. Type 321 Analysis: Fe bal Cr 17.8% Ni 10.9% Mn 0.6% C 0.078%	-	-	-	-	1.0 x 10 ⁻²	4.5 x 10 ⁻²	1.3 x 10 ⁻¹	3.3 x 10 ⁻¹	7.0 x 10 ⁻¹	-	KAPL
S.S. Type 347 Analysis: (High Cr) Fe bal Cr 18.4% Ni 13.3% Mn 0.4% Cb 0.08% Ta 0.1% C 0.06%	wet H ₂ (unstable coating) wet H ₂ + steam (stable coating) glass coated calorized and oxidized	8.6 x 10 ⁻⁷	3 x 10 ⁻⁵	4.3 x 10 ⁻⁴	2.6 x 10 ⁻³	1.1 x 10 ⁻²	3.9 x 10 ⁻²	1.6 x 10 ⁻¹ 6.1 x 10 ⁻⁴ 2 x 10 ⁻³ 4.0 x 10 ⁻³ 3.0 x 10 ⁻³	5 x 10 ⁻¹	1.4	KAPL
S.S. Type 410 Analysis: Fe bal Cr 12.6% C 0.13%	-	-	8.0 x 10 ⁻³	-	3.1 x 10 ⁻²	8.6 x 10 ⁻²	1.9 x 10 ⁻¹	3.6 x 10 ⁻¹	5.8 x 10 ⁻¹	-	KAPL
S.S. Type 420 Analysis: Fe bal Cr 12.8% C 0.36%	-	-	-	3.5 x 10 ⁻³	1.1 x 10 ⁻²	3.5 x 10 ⁻²	1.0 x 10 ⁻¹	2.5 x 10 ⁻¹	5.2 x 10 ⁻¹	-	KAPL
Wrought Alloy #4 Analysis: Fe 49% Ni 44% Cr 7%	-	-	-	-	-	2.5 x 10 ⁻²	7.2 x 10 ⁻²	1.8 x 10 ⁻¹	-	-	KAPL

*clean surface
**oxidized surface

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Problems Encountered with Coatings

The main difficulty with coatings at high temperatures is their resistance to thermal shock. The general theory of producing coatings that are thermally shockproof is well understood. This problem has been solved in regard to glass coatings on steel, and for the most part in regard to oxidation treatments such as wet hydrogen firing. In the presence of hydrogen, an additional problem exists with coatings. The evolution of hydrogen from a metal under certain conditions can be detrimental to a surface coating. This problem applies to certain glass coatings at high temperatures and to some extent to the oxide coatings.

The data as presented in this report are organized according to the various metals tested and include artificial aging tests (chiefly the so-called "wet hydrogen firing" method) for each particular type of metal. A second section covers the calorizing procedure and a third section covers the glass coatings.

TYPE 347 STAINLESS STEEL

The initial work was done on Type 347 stainless steel and results are given in Table 2a and plotted in Figure KH-9A1503. Figure KH-9A1515 contains a plot of $\log S$ vs. $10^3/T$. The values in the temperature range 200° to 550°C give a straight line plot $S = 2.19 - 3.18 \times 10^3/T$. However, as can be seen, the curve falls above the straight line at both high and low temperatures. Generally it is true that such a plot will produce a slight curve over a wide temperature range.

General

The results were obtained, starting at 621°C and working down the temperature scale. As was already explained under Method, the value at each temperature was normally obtained by approaching the temperature from below and waiting for steady state to be reached. The diffusion rates found at various temperatures are listed in Table 2a in cubic centimeters of hydrogen (at standard temperature and pressure) diffusing through one square centimeter of metal one millimeter thick in one hour from a pressure of one atmosphere to vacuum. At 100°C the value was 8.6×10^{-7} after eight hours, and 9.6×10^{-7} after 16 hours. Upon approaching the temperature from 300°C the value at 100°C was 1.8×10^{-6} after eight hours. Thus it appeared that as other investigators had found, the diffusion rate is different if the temperature of measurement is approached from above rather than from below.

Following this work, the rate of diffusion was again ascertained at 621°C and found to be 3.63×10^{-2} rather than 5.04×10^{-2} as found previously. This reduction in rate with time was similar to that observed by Metal Hydrides, Inc. (11) in their work with stainless steels, and has been termed "aging". It was estimated that the diffuser had been operated at this point for about 300 hours, most of which had been at temperatures well below 621°C . Table 2b shows

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Table 2a

Hydrogen Diffusion through Type 347 Stainless Steel

(Diffuser No. 1 - 0.011 inch thick)

Analysis: Fe - 68.1% Cr - 18.4% Ni - 13.3% Mn - 0.4%
Cb - 0.8% Ta - <0.1% C - 0.08%

<u>T (°C)</u>	<u>S (cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
100	$8.6 \times 10^{-7} - 1.8 \times 10^{-6}$
215	4.82×10^{-5}
317	6.18×10^{-4}
410	3.43×10^{-3}
539	1.96×10^{-2}
621	5.04×10^{-2}
731	1.40×10^{-1} (aged)

Table 2b

Aging of 347 Stainless Steel in Dry Hydrogen

<u>No. of Hours of Operation</u>	<u>Aged at</u>	<u>Temp. of Diffusion</u>	<u>S (cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
8	~ 620°C	620°C	5.04×10^{-2}
250 estimated	620°C	620°C	4.65×10^{-2}
300 estimated	620°C	620°C	3.63×10^{-2}
325	732°C	732°C	1.40×10^{-1}
371	732°C	732°C	7.8×10^{-2}
404	854°C	854°C	2.45×10^{-1}
424	854°C	854°C	1.19×10^{-1}
421	854°C	620°C	6.05×10^{-3}

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further aging at several temperatures. The value at 620°C shows almost a 10-fold decrease from 5.04×10^{-2} at the start to 6.05×10^{-3} after 421 hours. The value of 1.40×10^{-1} given for 731°C in Table 2a is low and indicates the effect of aging since later work has shown the correct value for unaged metal to be about 2.5×10^{-1} .

Aging

Work was continued on a second specimen of Type 347 stainless steel to check reproducibility of results and to investigate the aging process further. The specimen had a thickness of 0.019 inch, almost double that of the first specimen. Measurements were made on its rate at 620° as soon as the furnace was up to temperature in order to trace the early part of the aging curve. Aging data on this specimen are given in Table 2c and plotted in Figure KH-9A1516. The initial rate was high but dropped rapidly, until after eight hours the rate was identical with that for the first specimen at eight hours. Both rates levelled off to nearly constant values after 100 to 200 hours of aging at 620°C. The rate of the second specimen after 273 hours at 614°C was 8.2×10^{-3} , as compared with 6.05×10^{-3} for the first specimen after 421 hours at about 620°C.

The aging curve was interrupted to obtain a temperature curve on the partly aged specimen. The plot in Figure KH-9A1503 shows clearly the parallelism of the slopes of the curves of the two diffusers. Thus, in all cases except where extremely pure hydrogen is being used, one observes an aging effect with Type 347 stainless steel. Considering this effect, one may say that the rate of diffusion is fairly reproducible.

Aging a Surface Effect

The nature of the aging process has not been thoroughly investigated, but it is probably due chiefly to a surface poisoning effect which we attribute to the presence of traces of oxygen in the dry hydrogen. The surface of the aged specimen is covered with a greenish film similar in appearance to that obtained by artificial aging in wet hydrogen at higher temperatures, discussed in a later section. The effects of cleaning up the surface of the metal by pickling are shown in Table 2d. The results of the first pickling, following a rate determination on the piece as received, show that this type of pickle removes the film formed on aging and restores the hydrogen permeability of the metal to that corresponding to as received metal. After the oxidation treatment the rate was definitely low, 5.0×10^{-2} at 708°. Pickling following this rate determination returned the rate to that obtained initially with the clean metal. This fact indicates that the aging process is a surface effect. If aging were caused by some change in the body of the metal, as for example, stress annealing, the rate should be lowered permanently. The austenitic stainless steels are not heat-treatable, and it was found that cooling and heating between runs gave only very slight changes in rate. Photomicrographs, (1104454) indicate no noticeable change in the structure of the metal after diffusion for 500 hours except for the normal amount of grain growth expected at the operating temperature. The effect of reducing the rate by artificial aging is carried on further in a later section.

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Table 2cAging of Type 347 Stainless Steel in Dry Hydrogen

(Diffuser No. 2 - 0.019 inch thick)

Analysis: Fe - 67.4% Cr - 18.6% Ni - 12.0% Mn - 1.2%
Cb - 0.8% Ta - <0.1% C - 0.08%

<u>No. of Hours of Operation</u>	<u>Aged at</u>	<u>Temp. of Diffusion</u>	<u>S (cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
2	620°C	620°C	9.8 x 10 ⁻²
4 1/2	620°C	620°C	7.3 x 10 ⁻²
7 1/2	620°C	620°C	5.0 x 10 ⁻²
12	620°C	620°C	4.46 x 10 ⁻²
15	620°C	620°C	3.82 x 10 ⁻²
18	620°C	620°C	3.79 x 10 ⁻²
18	620°C	614°C	1.88 x 10 ⁻²
18	620°C	528°C	5.0 x 10 ⁻³
18	620°C	403°C	8.1 x 10 ⁻⁴
18	620°C	310°C	1.74 x 10 ⁻⁴
87	614°C	614°C	1.88 x 10 ⁻²
172	614°C	614°C	1.15 x 10 ⁻²
273	614°C	614°C	8.2 x 10 ⁻³

FIGURE 8
PHOTOMICROGRAPHS OF TYPE 347 STAINLESS STEEL
AGED AND NITRIDED

347 stainless steel as received, longitudinal section. 250X

Type 347 stainless steel after 500 hr aging at 620°C, longitudinal section. 250X

Type 347 stainless steel, longitudinal section, showing localization of welded area at plug end. 50X

Type 347 stainless steel nitrided to a depth of 0.005" on the outside, longitudinal section. 50X

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Table 2dEffect of Pickling Type 347 Stainless Steel

(Diffuser No. 7 - 0.010 inch thick)

Analysis: Fe - bal Cr - 18.4% Ni - 10.9% Mn - 1.5%
 Cb - 0.8% Ta - <0.1% C - 0.09%

Pickling Mixture: HNO₃ - 14% HCL - 5% HF - 2%
 (% by volume)

Pickled for 5 minutes at 110°F (43°C)

<u>T (°C)</u>	<u>Treatment of Material</u>	<u>S (cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
639	Cold drawn tubing as received	1.02×10^{-1}
621	Pickled	9.5×10^{-2}
708	Cold drawn tubing as received	1.9×10^{-1}
708	After various oxidation treatments	5.0×10^{-2}
626	Pickled	1.09×10^{-1}

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Surface Effects of Various Gas Atmospheres

Some rough experiments were conducted on the effects of various gas atmospheres on the surface of the diffuser. These were conducted on an aged specimen of stainless steel and listed in Table 3a. The effects noted were that oxidation of the outer surface by air followed by partial reduction by hydrogen (this is necessary in order to measure the diffusion rate) tends to etch the surface and increase the rate as observed by Smithells and Ransley.⁽¹⁵⁾ This is very strikingly noticed in the later oxidation treatments. As one might expect, oxidation alone of the inside surface of the diffuser gave a decrease in rate. The attempted reduction with hydrogen on the inner surface gave anomalous results possibly because of a water vapor blanket which could have been formed in the static system or because of aging of the outside surface. Nitriding the inside at 620° further reduced the rate, but at 850° the rate increased. This increase may have been due to cleanup of the outer surface with dry hydrogen at the elevated temperature.

Surface Nitriding

To test the effect of nitriding further, a specimen of Type 347 stainless steel was treated by the Drever Co. of Philadelphia. The nitride coating was put on the outside to a depth of about 0.005 inch (see Photograph 1104454). The coating was hard, brittle, and porous. The results are shown in Table 3b. The nitride coating did not block diffusion at all and the rate at 620°C was almost identical to the initial rate on Diffuser No. 2 (Table 2c). A striking effect was that no aging occurred after 122 hours even after increasing the temperature to 871°C. This fact is probably due to the ability of hydrogen to penetrate the nitrided layer easily, and to the inability of water vapor and oxygen to penetrate the layer readily. The fact that aging does not occur in this case is further evidence that no changes are occurring with time in the body of the metal which will affect diffusion.

CONTROLLED OXIDATION OF TYPE 347 STAINLESS STEEL

The aging of Type 347 stainless steel suggested that the application of the proper type of oxide coating might yield a barrier highly impermeable to hydrogen. For example, the importance of the oxide coating on aluminum in reducing diffusion as demonstrated by Smithells and Ransley is described in a later section. Therefore, an investigation was made of methods of producing oxide coatings.

General Discussion of Oxide Coatings

General

It was not known at the beginning of this investigation what oxides would reduce hydrogen diffusion most. It was natural, of course, to try to improve and accelerate the formation of the coating obtained in the aging process. Initial experiments with a wet hydrogen atmosphere on stainless steel at high

Table 3aSurface Effects on Type 347 Stainless Steel

(Diffuser No. 1 - 0.011 inch thick)

<u>Treatment*</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
As received	5.04×10^{-2}
After aging for 421 hours	6.05×10^{-3}
<u>Oxidation + Reduction</u> high pressure side oxidized by air for 1/2 hour followed by H ₂	1.17×10^{-2}
<u>Oxidation + Reduction</u> high pressure side oxidized by air for 1/2 hour followed by H ₂	2.12×10^{-2}
<u>Oxidation</u> - low pressure side oxidized by 760 mm air for 1/2 hour	1.09×10^{-2}
<u>Oxidation</u> - low pressure side oxidized by 160 mm O ₂ for 15 minutes	6.7×10^{-3}
<u>Reduction</u> - low pressure side reduced by 760 mm H ₂ for 1/2 hour	6.0×10^{-3}
<u>Nitriding</u> - low pressure side nitrided by 760 mm N ₂ for 1/2 hour	4.2×10^{-3}
<u>Nitriding</u> - low pressure side nitrided by 760 mm N ₂ at 850°C for 16 hours	1.1×10^{-2}

*All treatments and diffusion measurements were carried out at 620°C unless otherwise indicated.

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Table 3bNitrided Specimen of Type 347 Stainless Steel - 0.005 inch
of External Surface

(Diffuser No. 4 - 0.022 inch thick)

<u>No. of Hours of Operation</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
64	626	1.03 x 10 ⁻¹
72	871	6.4 x 10 ⁻¹
92	618	9.8 x 10 ⁻²
122	619	9.6 x 10 ⁻²

temperatures showed that oxide coatings could have a striking effect in reducing the diffusion of hydrogen through metals. It is worthwhile to include a brief general discussion of oxide coatings; for further information the reader's attention is directed to Metals Handbook⁽²⁹⁾ which contains a general discussion of the problem.

Protective Oxides

There are two classes of oxide coatings, protective and nonprotective, depending chiefly on their tendency to scale off the surface and on their porosity. Only the protective class need interest us here. In general, an oxide coating is protective when the specific volume of the oxide $\geq$ specific volume of the metal or when

$$\frac{(M)(d)}{(m)(D)} \geq 1$$

where M and D are the molecular weight and density, respectively, of the oxide and m and d are the molecular weight and density, respectively, of the metal. On this basis the following common metals have protective oxides: aluminum, silicon, chromium, manganese, iron, cobalt, nickel, copper, zinc, palladium, cerium, and lead.

Effect of Chromium

The stainless steels form protective oxides, of course, which accounts for their stainless character, at least at low temperatures. At high temperatures, the oxides often are not nearly so protective. It appears that the principal criterion for reducing the rate of oxidation is that the oxide be refractory, indicating a low conductivity-diffusivity oxide. It is the low diffusion rate of metallic atoms through the oxide layer which gives this type of oxide its low rate of oxidation. In the alloy steels, chromium has proved to have the most refractory oxide of the alloying elements and is

the principal constituent of high temperature steels. The addition of 6 to 8% of chromium to a low carbon steel reduces scaling enormously even at 800°C. Aluminum probably is the next most important element and additions in excess of 2% have considerable additional effect on reducing scaling. Chromium added to nickel helps considerably. In alloys containing up to 10% chromium, NiO predominates in the coating; at higher concentrations, Cr₂O₃ is the major constituent, thereby improving the scale. At 20% chromium, the spinel NiO·Cr₂O₃ is formed, giving optimum results. Spinels, i.e., combined oxides, provide some of the most stable and protective oxides known.⁽³⁸⁾ Above 25%, the limit of solubility, further additions of Cr have little or no effect. In the three-component system Fe-Ni-Cr, the chromium is the chief anti-scaling constituent. Considerable work has been done on oxide coatings of metals over a wide range of temperatures, particularly by Gulbransen and other co-workers.^(31-36,39,40)

Stratified Coatings

If the base metal forms more than one oxide, a stratified layer of oxides will normally form with the highest oxide on the surface, the lowest oxide next to the metal. Thus, in the case of iron on low carbon steel treated with air or oxygen at 1 atm at 550°C, three layers are formed:

outer layer	0.5 to 2% of thickness	Fe ₂ O ₃
middle layer	10 to 15% of thickness	Fe ₃ O ₄
inner layer	85 to 90% of thickness	FeO

The FeO layer is thickest because the rate of diffusion of iron atoms through FeO is the fastest of the three oxides, the iron atoms tending to reduce the next higher oxide Fe₃O₄. In general, metallic particles of the more noble metallic constituents are found in the scale. There will generally be a layer of the oxide enriched with metallic atoms next to the base metal.

Oxidizing Gas Atmosphere

One of the best ways of applying oxide coatings is, of course, by using a gas atmosphere of the proper composition, temperature, and pressure. Some of the more common constituents used are CO, CO₂, air, oxygen, SO₂, all with or without water vapor present, and steam. Hydrogen is sometimes added to reduce certain oxides in order to obtain preferential oxidation. Steel is oxidized by the following gases in order of increasing effectiveness: CO₂, dry air, oxygen, and steam. The effect of small percentages of water vapor is very pronounced. In some cases, a cycling treatment of alternately one gas atmosphere followed by a different gas appears to give the best results. The following data show the effect of certain oxidizing gases and of water vapor mixed with air:

The oxidation of mild steel in air increased 3-fold with 5% SO₂ + 5% H₂O.

The oxidation of 18-8 stainless steel in air increased 10-fold with 5% CO₂ + 5% H₂O.

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The oxidation of 18-8 stainless steel in air increased 8-fold with 5% SO_2 + 5% H_2O .

The oxidation of 18-8 stainless steel in air increased 7-fold with 5% H_2O .

Effect of Thermal Cycling

The rates of heating and cooling are important, particularly after the coating is formed. Rapid temperature cycling naturally has a deleterious effect on any coating. This is not entirely due to thermal stresses. Dissolved gases in the metal, particularly hydrogen, can cause considerable damage to coatings when they are evolved from the metal, or when they react with constituents of the coating. The ideal coating from the standpoint of thermal stress is one which is under slight compression upon cooling, that is, the oxide has a slightly smaller coefficient of expansion than the base metal. The effect here is simply that oxides generally have greater compressive strength than tensile strength. The fact that the layer may be under tension at high temperatures causes little trouble as stresses can be relieved at the higher temperatures. This principle is the one used in preparing glass coatings to be applied to metals, discussed in a later section.

Wet Hydrogen Treatment of Type 347 Stainless Steel

General

The use of wet hydrogen (hydrogen bubbled through water at room temperature) at high temperatures to produce oxide coatings on alloy steels for glass-to-metal seals had already been in practice at the start of these experiments. Also, since the wet hydrogen atmosphere is an extension of the dry hydrogen atmosphere containing traces of oxygen (present as water in hydrogen at elevated temperatures), and since aging was attributed to this atmosphere, the use of a wet hydrogen atmosphere was considered as the logical starting point in these studies. The results were immediately very striking as can be seen in Table 4a. There was no observable effect on the rate with wet hydrogen or tank hydrogen as compared to dry hydrogen at 630°C. However, upon raising the temperature to 984°C for three hours as in Example 1 (Table 4a) the rate at 984°C was only 7.8×10^{-3} or about 30-fold smaller than the rate at 730°C for the clean metal. Apparently a very marked reduction in the diffusion rate had been brought about. After cooling to room temperature in an inert atmosphere, the rate at 603°C was 1.56×10^{-3} . Normally one would expect the rate to drop at least about 20-fold between 984°C and 603°C; it therefore appeared that some disintegration of the coating might have taken place. Thus, in essence the wet hydrogen treatment produces an oxide coating at high temperatures which is chemically stable to hydrogen at low temperatures (700°C and below) and effectively blocks the diffusion of hydrogen. This coating shows some instability upon cooling.

Example 2 (Table 4a) shows the best results obtained so far with wet hydrogen on Type 347 stainless steel. Treatment at 979°C for three hours gave a rate of 2.94×10^{-3} at 979°C. After cooling to 700°C in wet hydrogen, the

Table 4aWet Hydrogen Firing of Type 347 Stainless Steel

(Diffuser No. 7 - 0.010 inch thick)

Analysis: Fe - bal Cr - 18.4% Ni - 10.9% Mn - 1.5%
 Cb - 0.8% Ta - <0.1% C - 0.09%

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Dry H ₂ received	639	1.02×10^{-1}
Dry H ₂ received	730	2.52×10^{-1}
Wet H ₂ at 640° for about 15 min	640	1.03×10^{-1}
Tank H ₂ at 630° for about 15 min	630	9.9×10^{-2}
Dry H ₂ at 619° for about 15 min	619	9.3×10^{-2}

Example 1

Wet H ₂ at 984° for 3 hours*	984	7.8×10^{-3}
(Cooled to room temperature in helium)		
Dry H ₂	603 ca	1.56×10^{-3}

Example 2

Wet H ₂ at 979° for 3 hours	979	2.94×10^{-3}
(Cooled to 700° in wet H ₂)		
Wet H ₂	728	6.1×10^{-4}
(Cooled to room temperature in helium)		
Dry H ₂	724	3.88×10^{-3}

*Times given in this and other tables on oxidation treatments include the warm-up time, normally from 700°C which is about 1/2 hour.

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rate at 728° was 6.1×10^{-4} . This five-fold drop in rate going from 979°C to 728°C is about what one would normally observe for the clean metal and suggests that probably little of the coating disintegrated. The rate of 3.88×10^{-3} at 724°C after cooling to room temperature in helium indicates that some disintegration had taken place. In general, cooling in the range 700°C to 25°C has caused some deterioration of the coating.

Physical Stability of the Coating

The lack of physical stability of the coating formed has posed a considerable problem. The problem is probably not so serious as it would appear at first sight, however, for it should be remembered that all coatings must show some sealing under severe temperature cycling, and the diffusion process is a particularly sensitive method for detecting this effect in situ. In spite of this problem, definite progress has been made in reducing the rate of diffusion. The exact causes of the instability are not fully understood, but the evidence cited in Table 4b gives strong indication that essentially two forces are at work: (1) thermal stressing, and (2) the disruptive force of evolved hydrogen from the stainless steel. As has been previously mentioned, the presence of hydrogen at high temperatures in metals can have a pronounced effect on coatings.

It appears that under the normal conditions of firing in wet hydrogen, the first factor, thermal stressing, is the chief cause of deterioration of the coating. In Table 4b, Example 1 already discussed in the preceding paragraph shows that most of the disintegration almost certainly takes place in the low temperature part of the cooling range, i.e., below 700°C. This effect indicates that thermal stressing is the probable cause of deterioration as the stresses would be greatest in the low temperature range.

In some cases the second factor, the hydrogen evolved from the base metal underneath the protective layer, may be the chief cause of deterioration, particularly at high temperatures where there is a sudden drop in the gaseous partial pressure of hydrogen as in evacuation or by the introduction of some other gases, for example, helium. Such abrupt changes in hydrogen pressure at high temperatures should be avoided if possible when using these coatings. This effect is not serious over most of the temperature range, at least up to 700°C; however Example 3 (Table 4b) shows that helium at 700°C had little effect on the coating, and Example 2 shows that cooling from 700° to room temperature in wet hydrogen rather than in helium, even at a slower rate, produced about the same effect. In general, however, it is considered preferable to allow the treated piece to cool in the same oxidizing atmosphere in which it was treated. There is probably no advantage to cooling in an inert gas, as it is doubtful that the oxide layer changes while cooling due to the oxidizing atmosphere.

One reason for feeling that evolution of gas from the metal can have an adverse effect on the coating is shown in Example 3 (Table 4b). It was desired to compare the diffusion rate in one direction through a barrier with the rate in the other direction, particularly when a coating is present. The

Table 4b

Stability of Wet Hydrogen Fired Coating on Type 347 Stainless SteelExample 1 (Cooling in helium)

(Diffuser No. 7 - 0.010 inch thick)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 980°C for 3 hr	979	2.94×10^{-3}
*1 (Cooled to 700° in wet H ₂)		
Dry H ₂	728	6.1×10^{-4}
*2 (Cooled to room temperature in He)		
Dry H ₂	724	3.88×10^{-3}

Example 2 (Slow cooling in wet hydrogen)

(Diffuser No. 10 - 0.020 inch thick)

Wet H ₂ at 960°C for 2 hr	-	-
(Cooled slowly over a 2-hr period to 700° in wet H ₂)		
Wet H ₂	721	1.16×10^{-3}
(Cooled slowly over a 4-hr period to room temperature and heated slowly over same period to 700° in wet H ₂)		
Wet H ₂	716	4.05×10^{-3}

*1 - Normally requiring 1/2 hour

*2 - Normally requiring 2 hours

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Table 4b (continued)Example 3 (Effect of Reverse Diffusion)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Rate in after wet hydrogen	713	2.77×10^{-3}
Rate out	726	4×10^{-2}
Rate in after reverse diffusion	726	5.0×10^{-2}
Rate in after wet H ₂	724	3.88×10^{-3}
Rate in after He treatment at 728° for 15 min	723	4.31×10^{-3}

Example 4 (Chemical Stability to Hydrogen)

Wet H ₂	721	1.59×10^{-3}
Dry H ₂ (after 20 min)	726	2.02×10^{-3}
Wet H ₂	979	2.94×10^{-3}
Dry H ₂ (after 1 1/2 hr)	981	6.1×10^{-1}

method used to measure the rate of reverse diffusion was discussed under the section APPARATUS AND METHOD. This method was not fully developed and its results should be considered correct only to within about 20%; hence it can only give indications. Example 3 shows that the rate out (reverse diffusion) immediately rose some 15-fold over the rate in. This higher rate out remained quite constant. When the rate in was checked again, it was found to be almost the same as the rate out, within the limit of error. A number of runs confirmed this effect. The coating apparently deteriorates quite rapidly and approaches the rate 5×10^{-2} at 726°C. The helium check was made to ascertain whether or not it might cause any deterioration of the coating as the reverse rate method requires helium in the outer jacket. Thus it appears that gas evolved from the metal, at least when it is evolved under steady state diffusion conditions, can cause serious deterioration of such a coating.

Chemical Stability to Hydrogen

The chemical stability of the coating to dry hydrogen is important for long term applications. No long-range tests have been conducted, but a brief test is shown in Example 4. The coating is quite stable to dry hydrogen at 700°C. At higher temperatures it is reduced more rapidly and is almost completely removed at 980°C. Thus, by using wet hydrogen at 1000°C we are able to produce an oxide coating which is relatively stable to dry hydrogen at 700°C.

Optimum Conditions for Wet Hydrogen Firing

The original conditions of firing at 1000°C for three hours, in hydrogen bubbled through water at 25°C, have been found to be optimal, allowing for the fact that our limiting furnace temperature is 1000°C. Firing at higher temperatures may give even better results. A discussion of the tests made follows below and data appear in Table 4c.

Results have shown that the higher the temperature of wet hydrogen firing the better the coating, at least up to 1000°C. It has already been shown in Table 4a that wet hydrogen has little or no effect at 600°C. In Example 1 of Table 4c, the effect obtained at 840°C is compared with that at 974°C. The higher temperature gave better results, but it is apparent that quite good results can be obtained even at 840°C.

Examples 2 and 3 show the effect of decreasing the water vapor concentration by various amounts at high temperature. As illustrated in Example 2, tank hydrogen increases the rate noticeably and dry hydrogen increases it drastically as was previously mentioned. Example 3 shows the effect of intermediate concentrations of water vapor. With the bubbler at 25°C (3% H₂O (v)) the rate was decreasing somewhat faster than with the bubbler at 0°C (0.7% H₂O (v)).

Initial Surface Conditions

Another effect which has been noticed in these experiments is that at times it has proved difficult to apply a good coating. This effect has been noted after etching the coating with air as shown in Example 4, Table 4c. In selective oxidation processes, such as wet hydrogen firing, a surface enrichment of the more noble constituents of the alloys tends to occur. This reduces diffusion. Surface etching by air removes this layer, depleting the surface of the enriched elements. Time is required for more of the same elements to diffuse to the surface. We are not yet certain of the composition of the surface oxide layer. It appears to be chiefly composed of a spinel lattice of the form X₃O₄ in which the oxides of chromium and possibly of nickel play an important part. Experimentally it has been found that new specimens of the steel as received (cold drawn tubing) give good results. This is in accordance with the findings of Vernon, Wormwell, and Nurse⁽⁴¹⁾ who found surface enrichment of chromium in stainless steels as received from the mill. Polishing accentuates the effect. A specimen whose surface has been etched as in Example 4 will generally require treatment for a longer period of time to obtain equivalent reductions in rate.

Effects of Air

As is indicated in Example 1, Table 4d, air treatment at 740°C followed by hydrogen etches the coating and virtually removes it. The rate after such treatment is usually about 6×10^{-2} at 735°C. Example 2 shows the effect of air on the exit surface of the diffuser. Normally helium is used in the outer jacket in reverse diffusion measurements, but substitution of air produced no change in rate. It would be advisable to try this experiment with a clean specimen.

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Table 4cOptimum Conditions for Wet Hydrogen Firing of Type 347 Stainless SteelExample 1 (Temperature)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 840° for 2 hr (Cooled to 700° in wet H ₂)	842	4.59 x 10 ⁻³
Dry H ₂	716	2.05 x 10 ⁻³
Wet H ₂ at 974° for 1 1/2 hr (Cooled to 700° in wet H ₂)	974	6.1 x 10 ⁻³
Dry H ₂	704	8.8 x 10 ⁻⁴

Example 2 (Water Vapor Concentration)

Wet H ₂ at 950° for 1 hr	948	4.09 x 10 ⁻³
Tank H ₂ (after 25 min)	974	1.34 x 10 ⁻²
Wet H ₂	974	6.1 x 10 ⁻³
Dry H ₂ at 980° for 3 hr	981	6.4 x 10 ⁻¹

Example 3 (Water Vapor Concentration)

Wet H ₂ at 980° for 2 1/2 hr	979	5.8 x 10 ⁻³
Wet H ₂ (after 15 min)	979	4.38 x 10 ⁻³

Bubbler temperature changed from 25°C to 0°C - % H₂O (v) changed from about 3% to about 0.7%

Wet H ₂ (after 10 more min)	979	3.82 x 10 ⁻³
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Example 4 (Surface Conditions)

Dry H ₂	730	2.52 x 10 ⁻¹
Wet H ₂ at 980° for 3 hr	984	7.8 x 10 ⁻³
Etched with air at 740°C for 35 min followed by H ₂	734	6.3 x 10 ⁻²
Wet H ₂ at 975° for 3 hr	974	2.49 x 10 ⁻²

Table 4dEffect of Air on Coating and on the Clean MetalExample 1 (Effect on Coating)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ fired at 975° for 2 hr	-	-
Dry H ₂	704	8.8 x 10 ⁻⁴
Treated with air at 740° for 35 min followed by H ₂	-	-
Dry H ₂	734	6.3 x 10 ⁻²

Example 2 (Effect on Exit Surface)

Diffuser partially oxidized by wet H ₂ firing	-	-
Rate out (helium at exit surface)	726	4.0 x 10 ⁻²
Rate out (air at exit surface)	726	4.0 x 10 ⁻²

Other Oxidation EffectsWet Helium

The effect of wet helium firing was investigated to determine whether or not a coating could be produced in the absence of hydrogen. This would avoid the disruptive forces of evolved hydrogen at least during the application of the coating. As can be seen in Example 1, Table 5a, the wet helium gave no effect.

Steam

The effect of steam alone was briefly tested as shown in Example 2. As can be seen, the results are comparable to those of wet hydrogen. Example 3 shows the effect of following the wet hydrogen treatment with a steam treatment. The rate of 1.34×10^{-2} at 754°C after the reverse diffusion test indicates that the coating is more stable than that obtained by wet hydrogen alone. The rate following reverse diffusion through a wet hydrogen-fired coating was 5.0×10^{-2} at 726°C. This is particularly true of Type 304 stainless steel as reported in a later section.

Carbon Monoxide

It was desired to place an oxide directly into the lattice of the metal where it could not be readily removed as at the surface. Carbon monoxide was used for this purpose since it diffuses through iron slowly and is known to form carbonyls with iron and metal. The specimen was treated with carbon monoxide under 18 cm pressure gauge at 975°C for 35 minutes. The rate of diffusion of carbon monoxide in Type 347 stainless steel is about 15-fold lower than that through iron, 7.19×10^{-2} at 993°C. (26) The permanent reduction in rate produced by the carbon monoxide was only about 7-fold lower than that of the clean metal. The dry hydrogen treatment at 975°C flushed out most of the CO in one half hour, so that the rate of diffusion became once more close to that for the clean metal. Thus it appears that there is little tendency for the CO to form sufficiently stable bonding with the metal to produce any pronounced or permanent blocking effect.

Coating both Surfaces of the Diffusing Barrier

Considerable work had been done on producing coatings on only one side of the diffusing barrier; it was desired to test also the effect of coating both sides. Doing this properly required modification of the system and the process had to be carried out where there was no opportunity to measure the rate during treatment. The diffuser had to be cooled and installed in the vacuum system before measurements could be made. The reduction in rate was only about 18-fold that of the clean metal, the rates being 1.06×10^{-2} at 704°C for the oxidized steel and 1.8×10^{-1} at 700°C for the clean metal as shown in Table 5b. More satisfactory results were obtained by applying the coating to one side only. It is quite possible that leaving one side of the barrier uncoated permits free evolution of the dissolved hydrogen and protects the coating from disintegration.

Nature of the Oxide Coatings - Electron and X-ray Diffraction Studies

Appearance

Visual inspection has shown the coatings obtained to assume various colors and they have also shown varying amounts of roughness. In general the coatings are greenish, wet hydrogen firing producing a coating varying in hue from blue to green to brown, generally quite smooth but superficially scaly in spots. Steam alone gave a dark somewhat iridescent appearance, while steam with wet hydrogen gave a glossy green to grey appearance. Aging of this type of steel has given a coating very similar to that obtained by wet hydrogen firing. The color of oxide films can be very deceiving as it may often be due to interference effects.

Thickness

These coatings must have an appreciable thickness since they are not penetrated by a 40 kv electron beam with a penetration of 500 Å. They are probably considerably less than 1 mil thick as continued treatment of a 10-mil

Table 5a

Other Oxidation Effects on Type 347 Stainless Steel

(Diffuser No. 10 - 0.020 inch well)

Analysis: Fe - bal Cr - 18.7% Ni - 10.4% Mn - 1.4%
 Cb - 1.0% Ta - <0.1% C - 0.07%

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Dry H ₂ (as received)	730	2.54×10^{-1}
Treated with wet He at 962° for 1 hr	-	-
Dry H ₂	718	1.90×10^{-1}

Example 2 (Steam)

Diffuser partially oxidized	733	6.3×10^{-2}
Steam at 950° for 40 min (Cooled to 750° in steam)	-	-
Dry H ₂ (Cooled to room temperature in H ₂)	750 (estimated)	2.12×10^{-3}
Dry H ₂	735 (estimated)	8.8×10^{-3}

Example 3 (Steam and Wet Hydrogen)

Treated with wet H ₂ at 954° for 2 hr	-	-
Dry H ₂	735	5.5×10^{-3}
Treated with steam at 975° for 1 1/2 hr (Cooled to 700° in steam)	753	3.39×10^{-3}
Reverse Diffusion for 1 hr		
Rate in (dry H ₂)	754	1.34×10^{-2}

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Table 5a (Continued)Example 4 (Carbon Monoxide)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Diffuser pickled	730	2.5×10^{-1}
Treated with CO at 975° for 35 min		
CO (Cooled to 756° in He)	975 (estimated)	5.03×10^{-3}
Dry H ₂	756	4.60×10^{-2}
Treated with dry H ₂ at 975° for 1/2 hr		
Dry H ₂	793	2.75×10^{-1}

Table 5bCoating Both Surfaces of the Diffusing Barrier

Treated with wet H₂ at 1000° for 1 1/2 hr
followed by steam at 1000° for 1/2 hr -
both surfaces -
(Cooled in steam to room temperature)

Dry H ₂	704	1.06×10^{-2}
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diffuser in which the coating was fractured from the surface a number of times produced almost no noticeable change in the outside diameter. The coating shows no stratification in the electron beam.

Structure

An X-ray powder pattern of the surface layer of a wet hydrogen fired specimen of Type 347 stainless steel showed Fe₃O₄* with a small amount of elementary chromium interspersed. An electron diffraction pattern of another specimen of wet hydrogen fired Type 347 stainless steel showed Fe₃O₄ with a small amount of Cr₂O₃. An electron diffraction pattern of Type 304 stainless

*As is mentioned later, the Fe₃O₄ lattice is almost identical to that of the various spinels (mixed oxides). The thermodynamic stability of the spinels and evidence from investigations of oxide coatings indicate strongly that they are the main constituents of these coatings.

steel treated with wet hydrogen and steam showed only Fe_3O_4 . Thus, the results definitely indicate that Fe_3O_4 is the major constituent of these coatings. From thermodynamic considerations, however, Fe_3O_4 should not be stable to dry hydrogen at 700°C .

Production of Magnetite

It was considered desirable to produce a layer of pure magnetite (Fe_3O_4) on a diffusing barrier and to test its effect on hydrogen diffusion. Stainless steel did not appear to be the best material on which to produce such a layer because of the alloying elements present. Ephraim⁽³⁰⁾ mentions the reaction of steam on red hot iron as the common means of producing the magnetic oxide. On this basis a rough test was conducted with steam on low carbon steel as reported in a later section. This test was unsuccessful in producing pure magnetite and the effect of this oxide on hydrogen diffusion is yet to be determined.

Work by Other Investigators on Oxide Coatings

Oxides of Iron, Nickel and Chromium. The extensive work of Gulbransen, Hickman, and Phelps^(31-36,39,40) on oxide coatings on metals should be cited at this point. They have investigated the oxides of iron, nickel, chromium and other metals formed under a pressure of 1 mm of oxygen at temperatures from 25°C to 700°C by electron diffraction techniques in situ, at the given temperature.⁽³³⁾ In general, they found that with iron chiefly $\alpha\text{-Fe}_2\text{O}_3$ was formed below 250°C , Fe_3O_4 in the range 250 to 450°C , and FeO above 450°C , that is, at 700°C the lowest and most stable oxide of iron is predominant. The oxide layer underwent a conversion to Fe_3O_4 upon cooling from 700°C to 25°C in vacuum. Upon cooling in like manner in 1 mm of oxygen, some $\alpha\text{-Fe}_2\text{O}_3$ was present with the Fe_3O_4 , and in 0.05 atm hydrogen part of the Fe_3O_4 was reduced to Fe . These results are also in accord with those of Jackson and Quarrell.⁽³⁷⁾ Nickel metal in 1 mm of oxygen gave NiO over the entire temperature range. Cooling in hydrogen from 700° gave some reduction of the oxide. Chromium metal in 1 mm of oxygen gave Cr_2O_3 over the entire temperature range. Cooling in hydrogen from 700° appeared to have no effect on the oxide. These results are in accordance with thermodynamic data which indicate that Cr_2O_3 is stable to hydrogen at 700°C while iron and nickel oxides are not.

Oxides of the Stainless Steels. Similar investigations were carried out on stainless steels and various alloys.⁽³⁵⁾ The results on 18-8 stainless steel are particularly pertinent. They found a spinel + $\alpha\text{-Fe}_2\text{O}_3$ (or Cr_2O_3) structure over the temperature range 400 to 700°C in 1 mm of oxygen. The spinel was designated by them as Fe_3O_4 , but could well be a true spinel such as $\text{NiO} \cdot \text{Cr}_2\text{O}_3$, $\text{NiO} \cdot \text{Fe}_2\text{O}_3$, or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The lattice constants of these cubic structures are too similar to allow resolution. Similarly the rhombohedral structure of $\alpha\text{-Fe}_2\text{O}_3$ is indistinguishable from that of Cr_2O_3 .

Upon cooling to 25°C in 0.05 atm hydrogen, they found all Fe_3O_4 (spinel) on specimens treated at 400°C and 700°C, and Fe_3O_4 (spinel) + $\alpha\text{-Fe}_2\text{O}_3$ (or Cr_2O_3) on specimens treated at 500°C and 600°C. It is difficult to understand why a conversion of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 should occur at both 400° and 700°, but not at the intermediate temperatures of 500° and 600°. It is also difficult to explain how $\alpha\text{-Fe}_2\text{O}_3$ can exist at these temperatures. Furthermore, the conversion indicated that the oxide can hardly be Cr_2O_3 . Thus the X_2O_3 part of the lattice is in question. The stability of the coating to dry hydrogen obtained in their work as well as in ours, would indicate that the Fe_3O_4 portion of the lattice is most likely one of the spinels, perhaps, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ or a structure close to it in composition, because of the proportions of the various elements present and the stability of their oxides to dry hydrogen.

Spinel Coatings on Stainless Steels. It can hardly be denied that the spinels play a most important part in the oxidation resistance of stainless and other alloy steels. The spinel structure has been observed by Gulbransen and Hickman on practically all alloys containing Fe-Ni, Ni-Cr, or Fe-Cr combinations. A 13% chromium stainless steel gave identical oxide coatings to those obtained with the 18-8 stainless steel. Mahla and Nielsen⁽³⁸⁾ have shown that 18-8 and 13% chromium stainless steels form a spinel-type oxide at room temperature in air. The thickness of the oxide layer may be increased by passivation. Such films almost certainly account for the stainless character of the metal. The films have been stripped and analyzed chemically, and the primary constituents are iron and chromium in each case.

Stripped Oxide Films from Iron, Nickel, and Chromium. Phelps, Gulbransen, and Hickman⁽³⁹⁾ have made additional studies on the oxide coatings of elementary metals and alloys in which they obtain electron diffraction patterns before oxidation, after oxidation at temperature, after cooling in a vacuum to room temperature, and by transmission after stripping the film. Oxidation was carried out chiefly at 500 to 600°C with 0.1 atm of oxygen for from 5 to 40 minutes. The results on iron, nickel, and chromium alone were essentially the same as found using 1 mm oxygen, discussed earlier. The transmission pattern showed no change, indicating that the oxide layer was of uniform composition. The stripped film showed considerable variation in thickness. Chromium and nickel formed small crystals; iron formed large crystals, with crystal sizes varying from 100 Å to 2500 Å. Small crystals appear to be more protective and tend to give a more uniform layer.

Stripped Oxide Films from Stainless Steels. The same studies, applied to 18-8 and 13% chromium stainless steels,⁽⁴⁰⁾ showed some stratification of the oxide layers. The 18-8 specimen showed Fe_3O_4 (spinel) + $\alpha\text{-Fe}_2\text{O}_3$ by a reflection pattern as found previously in 1 mm of oxygen. However, the transmission pattern of the stripped film showed only Cr_2O_3 . There is again some question here as to whether the X_2O_3 lattice is $\alpha\text{-Fe}_2\text{O}_3$ or Cr_2O_3 . No spectrographic analysis was made of the film. No cubic spinel lattice was observed, however by transmission, indicating that probably the bulk of the undercoating was an oxide of the form X_2O_3 . A 13% chromium stainless steel showed Cr_2O_3

by reflection, and Cr_2O_3 with a trace of Fe_3O_4 (spinel) by transmission. Spectrographic analysis of the stripped film showed iron and chromium.

Oxide Conversion on 18-8 Steel at 700°C. Gulbransen⁽³³⁾ has also done work on the rate of oxidation of various metals, using a quartz microbalance enclosed in an all glass vacuum system inside a furnace. He compared the oxidation rate of 18-8 and 13% chromium stainless steels in 0.1 atm of oxygen at 700°C and found the latter to be more protective. At 700°C the 18-8 stainless steel showed a decided increase in rate of oxidation over the rate at 650°C or lower, and the oxide coating appeared to be cracking after about 60 min at this temperature. In the previous electron diffraction work with 18-8 stainless steel in 1 mm of oxygen, a marked change in the lattice parameter of the oxide coating was noticed at 700°C. Below this temperature $a = 8.42 \text{ \AA}$ and the structure was identified as Fe_3O_4 (spinel). At 700°C the lattice expanded to $8.66 \text{ \AA}$ and the pattern became diffuse, indicating that the film was highly stressed or that a chemical change occurred. It is also noteworthy that the lattice parameters of most of these oxides, notably the cubic spinel form, show no change over the temperature range 25°C to 700°C, indicating their small coefficients of thermal expansion. This fact almost certainly indicates considerable stressing of these coatings upon cooling.

Other Properties of Wet Hydrogen Fired Coatings

Properties of these coatings other than permeability to diffusion are proving to be very interesting. Only very rough tests have been made with respect to electrical resistivity, corrosion resistance to acids, and resistance to oxidizing atmospheres at high temperatures.

Electrical Resistivity. The electrical resistivity has been determined at room temperature on several specimens and found to be exceedingly high for oxide layers (of the order of 10^6 ohms/cm^2 or more). This high resistivity is to be expected in view of the slow rate of corrosion of stainless steel in these oxidizing atmospheres at high temperatures, since resistivity or conductivity accompanies diffusivity of metallic atoms.

Chemical Corrosion Resistance. A rough test on chemical stability to acids was conducted on a specimen treated with wet hydrogen and steam by pickling with a mixture of 13% HNO_3 , 5% HCl and 2% HF at 122°F for ten minutes. This specimen initially appeared gray, but pickling rapidly exposed a green underlayer which appeared to be relatively unaffected by the acid. The coating had to be removed by abrasion with emery cloth and was very adherent.

High Temperature Corrosion Resistance. A test of resistance to high temperature oxidation was conducted on Type 304 stainless steel treated with wet hydrogen and steam; data are presented in the section on Type 304 stainless steel. The coating was subjected to air at 750° for 40 minutes, and at 1000° for 10 minutes; each exposure was followed by hydrogen with almost no damage to the coating. Such a treatment had extremely drastic effects on the coating produced by wet hydrogen alone on Type 347 stainless steel.

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OTHER TYPES OF STEEL INVESTIGATEDGeneralComposition

Besides Type 347 stainless steel, Types 304, 316, 321, 410, and 420 stainless steel, low carbon steel, and 44% nickel, 7% chromium alloy steel were investigated. The nominal composition of these steels is given below:

Low carbon steel - 0.1% C

Type 304 stainless steel - 18% Cr, 8% Ni, 0.08% C

Type 316 stainless steel - 18% Cr, 8% Ni, 0.08% C, 3% Mo (stabilized)

Type 321 stainless steel - 18% Cr, 8% Ni, 0.08% C, 0.6% Ti (stabilized)

Type 347 stainless steel - 18% Cr, 8% Ni, 0.08% C, 0.8% Cb (stabilized)

Type 410 stainless steel - 13% Cr, <0.15% C

Type 420 stainless steel - 13% Cr, >0.15% C

Sylvania Alloy #4 - 7% Cr, 44% Ni

Properties

The 18-8 stainless steels are all austenitic and therefore not heat-treatable. The stabilized austenitic stainless steels lend themselves more readily to welding, of course. Types 410 and 420 combine stainlessness with hardenability, the former type being used in the manufacture of turbine blades, the latter for cutlery. They were investigated chiefly because of their heat treating properties and because it was expected they would give oxide coatings of low permeability under controlled oxidation. Sylvania Alloy #4 is used for making vacuum-tight glass-to-metal seals, and was investigated for its oxidation properties.

Permeabilities to Hydrogen

Briefly, the diffusion rates on these steels at 700°C compare as follows: Type 347, Type 304 and Sylvania Alloy #4 showed almost identical rates of 1.8×10^{-1} . The two former gave a marked response to wet hydrogen firing. Type 316 and Type 321 gave higher rates of 3.2×10^{-1} . As will be discussed later, these higher rates could be due to a thickness effect, since unlike the other specimens used these specimens were about 40 mils thick rather than 20 mils. Type 316 responded to wet hydrogen treatment while Type 321 did not. Type 410 gave erratic results until given a high temperature etch after which it gave a high rate of 4.0×10^{-1} ; Type 420 (annealed) gave a

rate of 2.7×10^{-1} . Type 410 responded to wet hydrogen firing; Type 420 was given no oxidation treatments. The rate for low carbon steel was 8.6×10^{-1} or about five times that of Type 347 stainless steel.

Work of Metal Hydrides, Inc.

The work that Metal Hydrides, Inc. (17) has done on the diffusion of hydrogen through steels gives good general agreement with the above results. Their rates were determined chiefly at 650°C and covered stainless steel of Types 304, 316, 347, as well as some nichromes and one Inconel. The initial rates for these metals were all about 1.2×10^{-1} to 1.5×10^{-1} at 650°C as compared to our rate of 1.0×10^{-1} at 650°C for stainless steel of Types 304 and 347. In general, Metal Hydrides used specimens thicker than those used in our experiments. The wall thickness varied between about 40 and about 80 mils. Thus it would be expected that Metal Hydrides' initial results might be somewhat higher than ours. The aging observed by them at 650°C was pronounced. They found that all the metals tested aged noticeably at this temperature, giving reductions of rate after some 300 hours of from about 10 to 50-fold that of the clean metal. This large aging effect at a relatively low temperature is very likely due, partly to oxidation of the outer surface of the diffusing membrane by air, and perhaps partly to the purity of the hydrogen used. The fact that a static hydrogen supply was used may also help to account for the large effect noticed.

The following sections give details of the experiments conducted at this laboratory on each type of steel.

Low Carbon Steel

General

The rate of diffusion of hydrogen through low carbon steel was determined over a limited temperature range as shown in Table 6a and plotted in Figure KH-9A1517. The rate at 745° is about five times that of Type 347 stainless steel. The rate at 770° shows a small amount of aging after 2 hours. The same specimen was treated with steam in an attempt to produce a layer of pure magnetite on the surface as explained in an earlier section.

Production of Magnetite

The first steam treatment was at 770° for 1 hour. The steam reacted with the metal to form the oxide, releasing hydrogen which diffused at a substantial rate through the metal. The same type of reaction of water vapor with metals with the accompanying release of hydrogen is discussed in Appendix I concerning the reaction of atmospheric moisture with stainless steels at high temperatures. Dry hydrogen following steam treatment at 770°C gave almost exactly the same rate as before steam treatment. A further treatment was carried out with steam at 950° for 2 hours in order to observe the effect at elevated temperatures.

Table 6aHydrogen Diffusion Through Low Carbon Steel

(Diffuser No. 25 - 0.037 inch thick)

Analysis: C - 0.121%

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
501	3.00×10^{-1}
631	6.4×10^{-1}
745	1.00
770 after 2 hr	9.9×10^{-1}

Table 6bSteam Treatment of Low Carbon Steel

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Treated with steam at 770° for 1 hr	770	5.3×10^{-1}
Dry H ₂	770	1.03
Treated with steam at 950° for 2 hr	950	1.80

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The rate of diffusion with steam was high and gave no indication of the formation of an impermeable layer. The effect of the steam on the steel at this temperature was drastic and produced a leak in the diffuser so that no further measurements could be made.

Effects of Steam on Low Carbon Steel

The diffuser tube was sectioned and the following effects were noted. The tube swelled so that the outer radius of the tube was increased about 20 mils, increasing the wall thickness from about 40 mils to about 60 mils. The oxide layer was stratified as mentioned in the general discussion on Oxide Coatings and appeared as annular rings each about 20 mils thick. The outer layer was extremely porous, containing large gas bubbles, and had the reddish appearance of Fe_2O_3 . The inner layer consisted of a mixture of oxides and metal, the oxides being probably Fe_3O_4 and FeO . The base metal remaining was 20 mils thick, half the thickness of the tube having been destroyed. The production of magnetite alone would require much more closely controlled conditions.

Type 410 Stainless Steel

General

Type 410 stainless steel was tested in view of the results Armbruster⁽²⁰⁾ obtained with a 13% chromium, 0.3% carbon steel, which she found came to equilibrium very slowly in solubility tests. She attributed this effect to the formation of an oxide coating which was impermeable to the passage of hydrogen. The rate obtained for this type of steel in dry hydrogen was erratic and the initial value of 1.58×10^{-1} at 725°C was low compared to 2.3×10^{-1} at 725°C for Type 347 stainless steel. The results of the first run with this specimen are shown in Figure KH-9A1518. The reasons for the erratic behavior are not entirely clear, but it appears that this type of steel may be very readily etched by small amounts of oxygen followed by hydrogen. With trace amounts of oxygen as found in dry hydrogen, it appears to age in the same way as Type 347. By etching the specimen with air followed by a dry hydrogen treatment at 900 to 1000°C and making rate determination with an uninterrupted flow of hydrogen, we were able to get a consistent temperature curve as shown in Run No. 2, Figure KH-9A1518 and tabulated in Table 7a. This series of rates may be somewhat high and probably represents the maximum obtainable with this type of steel; the average rate under most conditions probably is lower. The rate at 716°C was 4.33×10^{-1} as compared with 2.1×10^{-1} at 716°C for Type 347 stainless steel. The rates at 842° and 992° show the effects of aging usually observed when determining rates at these high temperatures.

Effects of Wet Hydrogen and Steam

Oxidation effects carried out with controlled atmospheres showed this type of steel to be similar, but inferior, to Type 347 stainless steel in

reducing the rate of diffusion. Example 1, Table 7b indicates that steam reduces the rate more than wet hydrogen does, and the combination of the two produced a coating quite stable to temperature cycling and air oxidation, in agreement with the results obtained with Type 347 stainless steel. Some experiments were made with this specimen to determine whether or not concentrations of water vapor in hydrogen, intermediate between those of wet hydrogen (3% water vapor) and steam, would improve the coating. Example 2 shows that results with wet hydrogen firing were better with the bubbler at 25°C than at 100°C. Thus it appears that with this type of steel at least 3% of water vapor in hydrogen gives better results than higher concentrations of water vapor.

Effects of Carbon Dioxide

Carbon dioxide was tried in an effort to test its oxidizing effect and also to determine the effect of a thin layer of carbon on the surface. The gas was used both wet and dry at 500°C, 750°C, and 1000°C. No marked effect was observed; dry CO₂ lowers the rate most, about 10-fold, as indicated in Example 3. The effect of a layer of carbon on the surface should have been more prominent in the CO treatment mentioned earlier in which, however, it exhibited no marked reduction of the rate.

Type 420 Stainless Steel - Hardness Effects

Preparation

It was desired to observe the effect of hardness upon the diffusion rate, and for this purpose several specimens of Type 420 stainless steel were heat treated to various hardnesses and tested. The ranges of hardness obtained were determined with a Vickers Hardness Tester and values were converted to the Rockwell C Scale. The three specimens were pickled in a mixture of 14% HNO₃, 5% HCL, and 2% HF for 5 minutes at 50°C. All specimens were heated in dry hydrogen at the same rate, and measurements were taken at the same temperatures. The runs were conducted without interruption to avoid any etching effects as observed with Type 410 stainless steel. The results appear in Table 8 and are plotted in Figure KH-9A1520.

Heat Treating Ranges

Types 410 and 420 stainless steels are both heat-treatable, 13% chromium steels, Type 420 having >0.15% carbon, Type 410 having <0.15% carbon. A greater degree of hardenability can be achieved, therefore, with Type 420. Type 420 is normally heat treated in the range 1775° to 1850°F (969° to 1010°C), annealed in the range 1450° to 1100°F (788° to 594°C), and tempered in the range 350° to 800°F (177° to 427°C).

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Diffusion of H₂ through Type 420
Stainless Steel of Various Hardnesses
produced by Heat Treating

Table 7aHydrogen Diffusion Through Type 410 Stainless Steel

(Diffuser No. 12 - 0.020 inch thick)

Analysis: Fe - bal

Cr - 12.6%

C - 0.13%

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
309	9.9×10^{-3}
410	3.65×10^{-2}
528	1.18×10^{-1}
630	2.52×10^{-1}
716	4.33×10^{-1}
842	5.6×10^{-1}
992	8.7×10^{-1}

Table 7bVarious Oxidation Effects on Type 410 Stainless SteelExample 1 (Wet Hydrogen and Steam)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 940° for 2 hr	940	9.6×10^{-2}
Wet H ₂	700	1.08×10^{-2}
Followed by steam at 1000°C for 40 min		
Dry H ₂	730	6.9×10^{-3}

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Table 7b (continued)Example 1 (continued)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
(Cooled to 250°C and heated to 730° in H ₂)	730	9.8 x 10 ⁻³
(Cooled to 200°C in H ₂)		
(Heated to 730° in O ₂)		
Dry H ₂	730	1.08 x 10 ⁻²

Example 2 (Water Vapor Concentration)

Wet H ₂ at 910° for 1 hr (Bubbler at 25°C)	910	3.93 x 10 ⁻²
Followed by wet H ₂ at 910° for 1 hr (Bubbler at 100°C)	910	2.37 x 10 ⁻¹

Example 3 (Effect of CO₂)

Treated with dry CO₂ at 750°C
for 20 min

Dry H ₂	750	4.24 x 10 ⁻²
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Table 8

Effect of Hardness on Hydrogen Diffusion Through Type 420 Stainless Steel

(Diffusers No. 20 to 22 - 0.020 inch thick)

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
<u>Rockwell C 58-61</u>	
300	4.70×10^{-3}
518	4.85×10^{-2}
703	5.6×10^{-1}
860	8.0×10^{-1}
<u>Rockwell C 30-33</u>	
300	8.8×10^{-3}
512	5.3×10^{-2}
713	3.42×10^{-1}
866	7.4×10^{-1}
<u>Rockwell C 22-28</u>	
300	3.53×10^{-3}
520	4.20×10^{-2}
703	2.70×10^{-1}
866	7.4×10^{-1}

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Effect of Hardness on Rate of Diffusion - Expected and Observed Results

The results show no marked effect on the rate of diffusion produced by heat treating. One would expect to observe a difference in rates between the three specimens below the annealing temperature with the specimens of increasing hardness showing increasing rates of diffusion. The effect was observed above 400°C, but the difference in rates was quite small. One would also expect to observe partial convergence of the rates in the tempering range and complete convergence of the rates above the annealing temperature to that of the annealed metal. Neither of these effects is particularly evident. The high value obtained with Diffuser No. 21 at 300°C is unexpected and may be due to degassing, although degassing is normally over well below this temperature. The high value obtained with Diffuser No. 20 at 703° may be due to some residual hardness showing a more noticeable effect on the rate in the high temperature range than at lower temperatures.

Precautions Used

Considerable care was taken to make measurements at the same temperature, to heat each specimen at the same rate, and to make each run without interruption of the gas flow to avoid any surface etching effects. It is impossible to say whether or not the surface conditions of the three specimens were the same, as the hardness may affect the pickling of the surface. Pickling all three specimens alike was considered the best available criterion for obtaining a standard surface. The rate at 700°C for the three specimens ranged between 2.7×10^{-1} and 5.6×10^{-1} as compared with 1.8×10^{-1} for Type 347 stainless steel. The rates used in Table 1 for this type of steel were taken from Diffuser No. 22.

Type 304 Stainless Steel

General

The rate of diffusion of hydrogen through Type 304 stainless steel was determined as shown in Table 9a and plotted in Figure KH-9A1519. The rate is very close to that of Type 347 stainless steel at 700°. The oxidation effects on this steel appeared to give more stable coatings than on Type 347 stainless steel as outlined below.

Oxidation Effects

Example 1, Table 9b, shows the effect of wet hydrogen at 1000°C on this type of steel. The rate at 778° after firing was 7.2×10^{-3} as compared with 5×10^{-1} at 778°C for the clean metal, corresponding to an approximately 70-fold reduction. Temperature cycling to room temperature changed the rate only to 8.7×10^{-3} at 778°C. Wet hydrogen followed by steam treatment as shown in Example 2 gave a rate of 3.55×10^{-3} at 720° after cooling to room temperature, comparable to the rate of 3.39×10^{-3} at 753°C obtained with Type 347 stainless steel as recorded in Table 5a, Example 3. A rapid cooling to room temperature and reheating had no serious effect on the coating. The

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Table 9aHydrogen Diffusion Through Type 304 Stainless Steel

(Diffuser No. 13 - 0.020 inch thick)

Analysis: Fe - bal Cr - 18.6% Ni - 10.2% Mn - 0.3%
 C - 0.075%

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
378	3.37×10^{-3}
562	4.28×10^{-2}
650	1.12×10^{-1}
756	3.16×10^{-1}
900	7.5×10^{-1}

Table 9bVarious Oxidation Effects on Type 304 Stainless Steel

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
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Example 1 (Wet Hydrogen Firing)Wet H₂ at 1000°C for 1 1/2 hr

Wet H ₂	778	7.2×10^{-3}
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(Cooled to room temperature and heated to 780° in H₂)

Dry H ₂	778	8.7×10^{-3}
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Example 2 (Wet Hydrogen and Steam)Wet H₂ at 1000°C for 1 hr followed by steam at 930° for 25 min(Cooled slowly to room temperature in wet H₂)

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Table 9b (continued)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
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Example 2 (continued)

Wet H ₂	720	2.55 x 10 ⁻³
(Cooled rapidly to 150° in H ₂) (Heated rapidly to 700° in H ₂)	735	5.6 x 10 ⁻³
Air at 750° for 40 min		
Dry H ₂	785	9.5 x 10 ⁻³
Air at 1000° for 10 min		
Dry H ₂	771	1.22 x 10 ⁻²

Table 9cCoating Both Surfaces of Type 304 Stainless Steel

Wet H₂ at 1000° for 2 hr
followed by steam at 1000°
for 1/2 hr

Dry H ₂	781	6.7 x 10 ⁻²
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striking effect noticed was the stability of this coating to air followed by treatment with hydrogen, both at 750°C and at 1000°C. The rate subsequent to these treatments was noticeably low, 1.22 x 10⁻² at 771°C. These effects indicate that the coatings obtained on Type 304 stainless steel are equal to, or superior to those obtained on Type 347.

Coating Both Surfaces

A specimen of Type 304 stainless steel was treated on both surfaces with wet hydrogen followed by steam and attached to the measuring volume. Its rate of diffusion in dry hydrogen was then determined as shown in Table 9c. This experiment parallels the one conducted on Type 347 stainless steel reported in Table 5b. In this case, Type 347 gave better results, but in each case the coating was poor compared to that obtained on one surface alone.

Nature of the Oxide Coating

The nature of the coating formed has already been discussed in the section on CONTROLLED OXIDATION OF TYPE 347 STAINLESS STEEL. The reason why Type 304 stainless steel gives a more stable coating than Type 347 is not clear. Ostensibly the difference should be due to the presence of the columbium - tantalum stabilizer in the latter. It is not entirely unreasonable that such a small amount of alloying material might cause the difference. With Type 321 stainless steel wet hydrogen had almost no effect, perhaps due to the titanium stabilizer, while Type 316 stabilized with molybdenum reacted similarly to Type 347. These two steels are reported on in the following sections.

Type 316 Stainless Steel

The rate of hydrogen diffusion through Type 316 stainless steel was determined approximately (only three values obtained) as shown in Table 10a and plotted in Figure KH-9A1521. The rate was high, being 4.2×10^{-1} at 735° as compared to 2.5×10^{-1} at 735° for Type 347 stainless steel. The difference in rates here is a bit surprising and might be due to the thickness effect mentioned in the Introduction. Treatment with wet hydrogen, as shown in Table 10b, gave an approximately 100-fold decrease in rate before cooling, and an approximately 70-fold decrease after cooling to room temperature. This effect is comparable to that obtained with Type 347 stainless steel.

Type 321 Stainless Steel

The rate of diffusion for hydrogen through Type 321 stainless steel was determined approximately (at three points only) as shown in Table 11a and plotted in Figure KH-9A1521. The rate over the entire temperature range was almost identical with that of Type 316 stainless steel (3.1×10^{-1} at 700°C), and was well above that of Type 347 stainless steel, indicating that again there may be a thickness effect present as discussed in the Introduction. Wet hydrogen had almost no effect on this steel as can be seen from Table 11b.

Sylvania Alloy No. 4

Sylvania Alloy No. 4, a 49% Fe, 44% Ni, 7% Cr alloy, was investigated for its oxidation properties. Sylvania Electric Products, Inc. has used it for glass-to-metal seals, producing the necessary oxide coating by firing in wet hydrogen at 1100°C for several hours. The green oxide coating formed has shown exceptional craze resistance to mechanical bending. The alloy contains several tenths of a per cent of aluminum to increase the adherence of the coating. All these facts indicated that such an alloy might produce a coating which would be extremely adherent, although its permeability to hydrogen was yet to be determined. The results in dry hydrogen are shown in Table 12a (only two points measured). The rate at 726°C is 2.37×10^{-1} , almost identical to that of Type 347 stainless steel 2.3×10^{-1} at 726°C . Wet hydrogen had little if any effect on the alloy as shown in Table 12b. Electron diffraction studies on this coating showed predominately Fe_3O_4 or spinel with some Cr_2O_3 (or $\alpha\text{-Fe}_2\text{O}_3$).

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Table 10aHydrogen Diffusion Through Type 316 Stainless Steel

(Diffuser No. 18 - 0.036 inch thick)

Analysis: Fe - bal Cr - 17.4% Ni - 13.8% Mn - 1.65%
 Mo - 2.4% C - 0.044%

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
396	9.9 x 10 ⁻³
614	1.48 x 10 ⁻¹
842	9.7 x 10 ⁻¹

Table 10bOxidation Effects on Type 316 Stainless Steel

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 1000°C for 3 hr (Cooled to room temperature in wet H ₂)	1000	2.86 x 10 ⁻²
Dry H ₂	785	1.22 x 10 ⁻²

Table 11aHydrogen Diffusion Through Type 321 Stainless Steel

(Diffuser No. 19 - 0.034 inch thick)

Analysis: Fe - bal Cr - 17.8% Ni - 10.9% Mn - 0.6 %
 Ti - 0.58% C - 0.078%

<u>T (°C)</u>	<u>S(cc(STP)cm²/hr/mm) at 760 mm H₂</u>
386	7.6 x 10 ⁻³
590	1.20 x 10 ⁻¹
792	7.0 x 10 ⁻¹

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Table 11bOxidation Effects on Type 321 Stainless Steel

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 940° for 1/2 hr	940	1.90

Table 12aHydrogen Diffusion Through Sylvania Alloy No. 4

(Diffuser No. 28 - 0.020 inch thick)

Analysis: Fe - 53% Ni - 42.4% Cr - 5.47% C - 0.058%
 Al - 0.092%

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
530	3.63×10^{-2}
726	2.37×10^{-1}

Table 12bOxidation Effects on Sylvania Alloy No. 4

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Wet H ₂ at 1000° for 2 hr	990	1.40

EFFECT OF METAL PLATINGChrome Plated Type 347 Stainless Steel

A specimen of chrome plated Type 347 stainless steel was tested in order to investigate the effects of chromium and Cr₂O₃ on the rate of diffusion of hydrogen. The exact role of chromium or Cr₂O₃ in the oxide coatings on stainless steels is still undetermined as discussed previously.

The test was not too successful inasmuch as part of the plating scaled off. It is unlikely that the scaling occurred because of faulty plating, as this type of plating had previously been carried out successfully on this type of steel, and the photomicrograph, Figure 1104453 (page 95) shows a good bond between the plating and the base metal. The type of plating process used was the so-called "low contraction chrome" plating process. The plating bath

consisted of 400 grams of CrO_3 per liter and 49 grams of sulfuric acid per liter; the plating was carried out at 185°F with a current density of 750 amperes per square foot. This process gives a layer of relatively soft chrome of around 450 Brinell hardness with few cracks in the surface.

Several noteworthy effects were observed in treating this chrome-plated specimen, and results are shown in Table 13. The rate through the plated specimen was 2.52×10^{-1} at 708°C in dry hydrogen. Wet hydrogen at 735°C gave an approximately 40-fold immediate reduction in the rate, while it gave no effect on Type 347 stainless steel at this temperature. At the higher temperature one would expect an improved oxide coating, however, the rate of diffusion at 966°C shows an 18-fold increase over that at 735°C , indicating a deterioration of the coating. Normally the coating would exhibit a six-fold increase in rate over this temperature range if the coating remained unchanged. Treatment in air at 987°C gave almost no change. Cooling to room temperature, however, had a noticeably disruptive effect on the coating, giving a final rate of 2.27×10^{-1} at 728°C .

It appears, therefore, that temperature cycling has a considerably disruptive effect on the plating; and it is probable that hydrogen at high temperatures is also deleterious. However, a decided reduction in the rate of diffusion was observed with wet hydrogen at 735°C . On the evidence of the work of Gulbransen and Hickman⁽³⁴⁾ it appears that the resulting oxide is Cr_2O_3 .

USE OF ALUMINUM IN RETARDING HYDROGEN DIFFUSION

General

Since aluminum is very effective against the diffusion of hydrogen below 600°C , an investigation was made of the application of aluminum onto Type 347 stainless steel at temperatures above 600°C (mp of aluminum is 660°C) to determine the effect on the rate of diffusion. The surface application of aluminum at high temperatures to other metals is called calorizing and is an old art. As a preliminary to calorizing, a test was made on 61-S aluminum to determine the rate of diffusion of hydrogen through 61-S aluminum and the effect of oxidation of the elementary metal.

Diffusion of Hydrogen Through 61-S Aluminum

Table 14 and Figure KH-9A1522 show the results obtained with 61-S aluminum. The rate of diffusion of hydrogen at 500°C was 1.7×10^{-3} , four-fold that at 500°C (4.6×10^{-4}) found by Smithells and Ransley.⁽¹⁶⁾ This difference in rates could be due to the larger amount of impurities in the 61-S sample, or perhaps to different initial conditions of the surface oxide layer.

Smithells and Ransley found that by deliberate oxidation of the specimen, they could reduce the rate from 2.6×10^{-3} to 4.2×10^{-4} at 580°C , or about seven-fold. The oxide coating could be removed by mechanical abrasion in situ in hydrogen, in which case the rate of diffusion returned to its initial value

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Cr - 0.25%

T (°C)

S (cc(STP) / cm² / hr / mm) at 760 mm H₂

396

1.29 x 10⁻⁴

515

2.10 x 10⁻³

525

3.37 x 10⁻³Accidentally oxidized by air at 500°C

513

5.6 x 10⁻⁴

295

9.5 x 10⁻⁵

386

9.3 x 10⁻⁵

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DIFFUSION OF H_2 AND He
Through SiO_2

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KH-9A1693

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Table 15a

Calorizing of Type 347 Stainless Steel by Metal Spraying

(Diffuser No. 6 - 0.010 inch 347 stainless steel coated
with 0.005 inch aluminum)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Heated to 700°C for 1 hr in He		
Dry H ₂	702	1.72×10^{-2}
Wet H ₂ at 700°C for 1/2 hr	700	1.17×10^{-2}
Dry H ₂	460	3.61×10^{-4}
Air at 460° for 2 1/2 hr		
Dry H ₂	462	2.10×10^{-4}
Dry H ₂	700	1.56×10^{-2}
Air at 700°C for 1/2 hr		
Dry H ₂	700	5.3×10^{-3}
Air at 860°C for 40 min		
Dry H ₂	860	8.8×10^{-3}
N ₂ at 860° for 20 min		
Dry H ₂	860	8.8×10^{-3}
O ₂ at 860°C for 2 hr		
Dry H ₂	867	1.06×10^{-2}
Dry H ₂	713	3.46×10^{-3}
Dry H ₂	602	3.96×10^{-3}

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Table 15bCalorizing Type 347 Stainless Steel with Aluminum Paint

(Diffuser No. 17b - 0.020 inch 347 stainless steel coated with 0.001 inch aluminum)

<u>Treatment</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Heated in dry H ₂ from room temperature to 900°C over a period of 1 hr		
Wet H ₂	900	2.08×10^{-1}
Wet H ₂ (after 25 min)	990	3.11×10^{-1}
Dry H ₂	766	4.70×10^{-2}
Air at 950° for 15 min		
Dry H ₂	~980	2.77×10^{-1}
Dry H ₂ (8 min later)	980	4.15×10^{-1}
Dry H ₂ (16 min later)	980	5.2×10^{-1}
Dry H ₂	~720	1.04×10^{-1}

Comparison of Helium and Hydrogen Diffusion Through Ceramics

Most work on diffusion of gases through ceramics has been done with helium. Therefore, it is worth while to consider how the rates of diffusion of hydrogen and helium through ceramics compare. Data on the rate of diffusion of helium through fused silica are at variance with each other. The data of Barrer⁽⁴⁶⁾ and of Williams and Ferguson⁽⁴⁷⁾ on helium diffusion are plotted in Figure KH-9A1693. It is surprising that their data show good agreement for hydrogen, but disagree markedly for helium. Barrer observed an approximately two-fold difference in rate at 500°C, and no difference at 900°C. Williams and Ferguson observed a 22-fold difference in rate at 500°C. Norton⁽⁴⁹⁾ reports an approximately ten-fold difference in the low temperature range, below 500°C. The hydrogen and helium curves are reasonably parallel, indicating that the difference in rate is fairly constant over a considerable temperature range. Thus it appears that the rate of diffusion of hydrogen through fused silica is lower than that of helium, and probably averages about ten times slower. Norton⁽⁴⁹⁾ has observed that the rate of diffusion of hydrogen through Corning No. 1720 pyrex glass is about one sixtieth that of helium at 685°C. It appears, therefore, that in general hydrogen diffuses more slowly through ceramics than helium does.

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Table 16aDiffusion Rates of Various Gases Through Fused Quartz at 900°C⁽³⁾

<u>Gas</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
He	9.9 x 10 ⁻³
H ₂	1.76 x 10 ⁻³
Ne	3.24 x 10 ⁻⁴
N ₂	2.62 x 10 ⁻⁴
A	1.59 x 10 ⁻⁴

Table 16bDiffusion Rates of Helium Through Various Glasses and Quartz at about 300°C⁽³⁾

<u>Material</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
SiO ₂	300	8.6 x 10 ⁻⁴
Pyrex	300	1.04 x 10 ⁻⁴
Soda-glass	283	2.69 x 10 ⁻⁶
Lead-glass	283	1.01 x 10 ⁻⁶

Barrer⁽³⁾ gives a comparison of the rates of diffusion of various gases through fused silica at 900°C, shown in Table 16a, in which he uses data of T'sai and Hogness⁽⁵⁸⁾ instead of his own for the rate of diffusion of helium.

Diffusion of Helium through Various Types of Glass and the Effect of Temperature

In general, it appears to be true that the soft glasses give low rates of helium diffusion and the hard glasses give relatively high rates. Table 16b shows Barrer's⁽³⁾ comparison of rates of diffusion of helium through various glasses at around 300°C. Norton⁽⁴⁹⁾ has investigated the rate of diffusion of helium through glasses of various known compositions in the low temperature range. His data are plotted in Figure KH-9A1702, and show an increase in rate with increased silica content in accord with Barrer's results. It is apparent that at low temperatures the rate of diffusion of helium through glasses changes rapidly with temperature. As one approaches the softening point of the glass, the rate of change with temperature is less rapid. Thus, in the

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case of the hard glasses, an increase in rate of only about ten-fold for both hydrogen and helium is observed when the glass is heated from 500°C to 900°C. As a result of this fact, the hard glasses show considerably lower rates of diffusion for hydrogen at high temperatures than the least permeable of the metals. Thus, the rate of diffusion of hydrogen through fused silica is about 7×10^{-4} at 700°C as compared to 1.8×10^{-1} for Type 347 stainless steel at the same temperature.

Work done at the University of Illinois in Applying Glass Coatings to Metals

General

The poor mechanical properties of ceramics prompted our investigation of their application to metals to combine good mechanical properties with high impermeability to gaseous diffusion. Considerable work of this nature has been done at the Ceramics Department of the University of Illinois. The application has been chiefly to various steels to increase high temperature oxidation resistance. These investigators have had considerable success in applying glass coatings to most types of steel, including Type 347 stainless steel. They have also made measurements of the rate of diffusion of helium through the glasses alone in connection with their work.

Effects of Various Oxides in Glass on the Permeability to Gases

A study was made at the University of Illinois of the effect of various oxides in glass on the rate of diffusion of helium.⁽⁵⁰⁾ The glasses studied were mostly of the hard type to permit work at high temperatures. A brief resume of results obtained at the University is shown in Table 16c. It was found that alkali metal oxides reduce the rate of diffusion noticeably. Of the oxides tried, the following appear to reduce the rate of diffusion, in order of increasing effectiveness: Al_2O_3 , K_2O , Na_2O , Li_2O .

Expansion Characteristics of the Coating

In attempting to coat metal surfaces with glass, one must adjust the composition of the glass to match the coefficient of expansion of the base metal as discussed in the section on Oxide Coatings. At the same time, one must use a glass of satisfactory diffusion characteristics. The fact that the glass may have a low softening point does not necessarily indicate that it will be unsatisfactory in blocking diffusion when coated onto a metal surface. On the basis of experience the Department of Ceramics of the University of Illinois has glass coated some specimens of Type 347 stainless steel for measurement of the rate of diffusion of hydrogen at this Laboratory. The coefficient of thermal expansion of the austenitic stainless steels is high and limits the types of glass that can be applied. The results of this work are included in the following section.

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Table 16c

Effect of Composition of Glasses on Rate of Diffusion of Helium⁽⁵⁰⁾

<u>Type of Glass</u>	<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
Pyrex	600	1.69×10^{-3}
Pyrex	300	2.56×10^{-4}
Na ₂ O(25%)-SiO ₂	300	6.3×10^{-6}
Na ₂ O(30%)-SiO ₂	300	2.8×10^{-6}
K ₂ O(30%)-SiO ₂	300	5.8×10^{-6}
Li ₂ O(5%)-Na ₂ O(25%)-SiO ₂	300	7.1×10^{-7}
Al ₂ O ₃ (13%)-B ₂ O ₃ (9%) -Na ₂ O(12%)-SiO ₂	300	4.8×10^{-6}
Al ₂ O ₃ (5%)-B ₂ O ₃ (9%) -Na ₂ O(12%)-SiO ₂	300	8.2×10^{-6}

Application of Glass Coatings to Type 347 Stainless SteelEffect on the Diffusion Rate

Table 17a and Figure KH-9A1523 show the results of measurements of the rate of diffusion of hydrogen through glass coated Type 347 stainless steel. The composition of the glasses is given in Table 17b except for base coat No. 418-4. This coat was formulated with 25% Cr₂O₃ to test the effect of this oxide on diffusion. The rate with coating No. 327-1 was about 60 times lower than that of the clean metal at 740°C. As would be expected the glass-coated specimen shows less variation in rate with temperature than the base metal does in the high temperature range. Coating No. 32-21 flaked off slightly on the end of the diffuser; the specimen was therefore fired in wet hydrogen to reduce diffusion through the bare spots. The rate at 732°C was then almost 200 times lower than that of the base metal. After cooling to room temperature, however, the rates obtained showed a decided increase, indicating some deterioration of the coating. Visual inspection showed the coating had flaked off the surface in places and was generally full of bubble holes. Inspection of Coating No. 327-1 showed some bubble holes but no evidence of flaking. Coating No. 418-4 showed a reduction in rate of only about 15 fold from that of the clean metal. Cooling to room temperature appeared to have no deleterious effects on the coating. Inspection afterward showed the coating to be dark and rough although not pitted. Originally its appearance had been light green and glossy as was the case with the other coatings.

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Table 17aHydrogen Diffusion Through Glass Coated Type 347 Stainless Steel(1) Base Coat No. 327-1(Diffuser No. 14 - 0.010 inch 347 stainless steel -
0.002-inch glass fired at 2050°F)

<u>T (°C)</u>	<u>S(cc(STP)/cm²/hr/mm) at 760 mm H₂</u>
516	2.69×10^{-4}
642	1.67×10^{-3}
725	4.02×10^{-3}
827	8.0×10^{-3}

(2) Base Coat No. 32-21

(Diffuser No. 15 - 0.020 inch 347 stainless steel - 0.007 inch glass fired at 1650°F)

725	4.03×10^{-3}
-----	-----------------------

Treated with wet H₂ at 1000°C
for 1 hr

732	1.51×10^{-3}
-----	-----------------------

(Cooled to room temperature in H₂)

387	6.2×10^{-4}
541	7.1×10^{-3}
607	1.18×10^{-2}
744	3.94×10^{-2}

(3) Base Coat No. 418-4(Diffuser No. 24 - 0.020 inch 347 stainless steel-
glass coated approximately 1-2 mils thick)

718	1.44×10^{-2}
760	1.90×10^{-2}

(Cooled slowly to room temperature in H₂)

815	3.89×10^{-2}
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Table 17bComposition of Base Coat Glasses

<u>Frit No. 32</u>		<u>Frit No. 327</u>	
Quartz	24.25%	Keystone Feldspar	83%
Potash Feldspar	34.80	Sodium Carbonate	5
Borax	23.80	Soda Niter	5
Soda ash	6.44	Vanadium Pentoxide (92.25% V ₂ O ₅)	5
Soda Niter	4.13		
Fluorspar	<u>3.17</u>	Iron Oxide (Fe ₂ O ₃)	<u>2</u>
	99.59		100

<u>Oxide Composition</u>		<u>Oxide Composition</u>	
SiO ₂	56.50%	SiO ₂	57.4%
Al ₂ O ₃	8.38	Al ₂ O ₃	17.6
Na ₂ O	12.06	Na ₂ O	7.3
K ₂ O	5.15	K ₂ O	10.9
CoO	0.56	V ₂ O ₅	4.9
NiO	0.60	FeO	1.9
MnO ₂	1.81	<u>Mill Addition to make Coat No. 327-1</u>	
B ₂ O ₃	10.55	Frit	100 parts
CaF ₂	4.48	"X" clay	7%
<u>Mill Addition to make Coat No. 32-21</u>		Borax	0.75
Frit	100 parts	Water	50
"X" clay	7%		
Borax	0.75		
Water	40-50		

Base Coat 418-4 contained 25% Cr₂O₃

Reboiling Phenomenon with Ceramic Coatings on Metals

Considerable work on the reboiling of enamels (evolution of gas in the coating upon second or subsequent firings) on steels has been done by Keeler, Chu, and Davis^(51,52,53,54) They found that reboiling occurs upon heating to 600°C and subsides after a few minutes at around 700°C. Rapid heating of the specimen is always accompanied by reboiling, especially if preceded by rapid cooling. It appears that the enamel coating itself is the source of supply of the gas and that the gas is principally hydrogen. In the case of specimens used in hydrogen diffusion work such as ours, the additional dissolved hydrogen may intensify the effect.

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DISCUSSION AND CONCLUSIONS

Effect of Temperature, Pressure, Thickness, and Structure

The rate of diffusion of hydrogen was determined with a number of metals at various temperatures, chiefly at a pressure of one atmosphere. The rate of diffusion deviates slightly from exponential dependence on the temperature, but gives very close agreement over a range of several hundred centigrade degrees, as generally observed by others. Only one run was made at a pressure other than atmospheric; this run showed very close agreement with the $\sqrt{p}$ law in the pressure range 500 to 800 mm of mercury. It is generally recognized that grain size has little or no effect on the rate of diffusion, at least through iron. Small variations in the composition of the austenitic stainless steels, including the addition of stabilizers, appear to produce little if any change in the rate. According to other observers, cold working of low carbon steel appears to increase the rate of diffusion. The effect of hardening by heat treatment on the rate of diffusion was observed in a 13% chromium, 0.3% carbon steel and found to be small, if observable at all.

Accuracy of Results

The diffusion apparatus was designed for high sensitivity and close temperature control. As a result, it was possible to measure the rate of diffusion from near 25°C up to 1000°C with a probably accuracy of several per cent.

Diffusion Rates Through the Clean Metals

In general, metals show a wide divergence in diffusion rates at low temperatures with considerably less difference at high temperatures (700°C and above). Of the common materials of construction, iron shows a relatively high rate, copper, molybdenum, aluminum, and the stainless steels show low rates. Aluminum metal has the lowest rate of diffusion for hydrogen of this group, below 600°C. Above this temperature, molybdenum and copper give the lowest rates except for the special treatment of stainless steels mentioned below.

Among the stainless and alloy steels almost identical rates were found at 700°C for Types 304 and 347 stainless steel and for a 44% nickel, 7% chromium, 0.1% aluminum steel. Types 316 and 321 stainless steel had almost double the rate of Type 347 at 700°C. Type 410 stainless steel gave erratic results and appeared to be susceptible to etching by small amounts of oxygen present in the hydrogen. It gave double the rate of Type 347 after a high temperature etch. Type 420 stainless steel gave a rate close to that of Type 347 at 700°C. The rate through 0.1% carbon steel at 700°C was 5 times that of Type 347 stainless steel.

The stainless steels show an aging effect at high temperatures from traces of oxygen present in hydrogen. Type 347 stainless steel shows an approximately ten-fold reduction in rate after aging in dry hydrogen for 100 to 200 hours at 620°C. The dry hydrogen is produced by passing tank hydrogen over copper turnings at 750°C and through a liquid nitrogen trap. Increasing the temperature will, of course, accelerate the aging process. Aluminum metal also shows a reduction in rate by oxidation. Direct oxidation of aluminum with air at around 500°C produced an approximately four-fold reduction in rate.

Reduction of Hydrogen Diffusion Through Stainless Steels by the Wet Hydrogen Firing Method

The aging of stainless steel can be promoted by increasing the oxygen content of the hydrogen atmosphere and also by increasing the temperature. The oxygen content is not critical and an optimum concentration can be obtained by bubbling the hydrogen through water at room temperature, hence introducing the oxygen in the form of water vapor. Such a procedure constitutes the Wet Hydrogen Firing Method. The optimum temperature is 1000°C or possibly higher and the time required is about 3 hours. The treatment produces a green oxide coating which markedly reduces the rate of hydrogen diffusion through stainless steel at high temperatures. Reductions of rate, as much as 400-fold, at 700°C have been obtained with Type 347 stainless steel. Types 304, 316, and 410 showed similar results. Type 321 stainless steel showed little reduction in rate with wet hydrogen.

The effect noticed, therefore, is that a wet hydrogen atmosphere at 1000°C will oxidize certain stainless steels selectively to form an oxide coating which is relatively stable to dry hydrogen at 700°C and below, and which markedly reduces the rate of diffusion of hydrogen through the metal. This coating is not completely stable to temperature cycling, especially while cooling to room temperature, and may also be disrupted by rapid evolution of dissolved hydrogen from the metal such as that which would be produced by degassing the metal at high temperatures. It appears that following wet hydrogen treatment with steam for 30 minutes, both at 1000°C before cooling helps considerably to stabilize the coating. Type 304 stainless steel appears to respond especially well to this additional steam treatment. Relatively stable coatings have been obtained by the method on both Type 347 and Type 304 stainless steels showing reductions in rate of 50 to 100-fold at 700°C.

Following the treatment specified above, the specimen should be allowed to cool to room temperature in the firing atmosphere that was last used (wet hydrogen or steam). The oxide coating formed appears to be a spinel, perhaps $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. It is reduced in dry hydrogen at 1000°C. The effect of steam alone was about the same as that of wet hydrogen alone, the combination of the two seeming to impart more stability to the coating. The effect of wet helium and wet and dry CO_2 was not nearly so pronounced as that of the wet hydrogen. Carbon monoxide introduced into the metal lattice at 1000°C produced a small permanent blocking effect against hydrogen at 700°C. Coating

one side of the diffusing barrier gave a greater reduction in rate than coating both sides, probably because, in the former, dissolved gases are freer to escape from the metal without damaging the coating.

Other Possible Applications of the Wet Hydrogen Firing Method

The electrical resistivity of these coatings is very high, of the order of 10^6 ohms/cm² or higher. The coating produced by wet hydrogen and steam on Type 347 stainless steel was relatively unaffected by a pickling mixture of 13% HNO₃, 5% HCl, and 2% HF at 122°F for 10 minutes, indicating considerable resistance to acid corrosion. The coating had to be removed by abrasion and was very adherent. A similar coating on Type 304 stainless steel when subjected to air at 750°C for 40 minutes and air at 1000°C for 10 minutes, each treatment followed by hydrogen, showed remarkable stability, the rate subsequently still being some 50-fold lower than that of the clean metal at 735°C. Such exposure to air followed by hydrogen at these high temperatures constitutes an extremely drastic treatment and would completely disrupt the coating obtained by wet hydrogen firing alone on Type 347 stainless steel. Thus it appears that this coating may have exceptional oxidation resistance at high temperatures.

Reduction of Hydrogen Diffusion Through Metals by the Calorizing-Oxidation Method

Preliminary tests on the calorizing and oxidizing of Type 347 stainless steel indicate that this method is quite satisfactory. Inasmuch as aluminum alloys with most metals to form an adherent surface coating, the application of the method to metals should be quite general. The aluminum can be applied by a number of methods, principally by (1) tumbling in flake aluminum in an inert atmosphere in a rotating furnace, (2) hot dipping, (3) metal spraying. The second method is generally convenient for coating outside and inside surfaces; the third method is most convenient for coating outside surfaces. A coating of about 0.005-inch thickness is quite adequate. The conditions for the alloying-oxidation process do not have to be very exact. Treatment at 850°C for one half hour in an inert atmosphere to initiate alloying followed by oxidation by air at 850°C for an hour gives an approximately 100-fold reduction in rate at 860°C. Oxidation must be carried out at fairly high temperatures with a reasonably high oxygen concentration. Air at 460°C for several hours gave little reduction in the rate and selective oxidation at 700°C with wet hydrogen produced almost no effect at all.

These coatings have not been tested for stability to thermal shock as have the wet hydrogen fired coatings. There is no question about the chemical stability of the aluminum oxide coating to hydrogen even at 1000°C. In general, aluminum oxide coatings show excellent adherence and should stand thermal shock better than the wet hydrogen fired coatings.

One condition which must be avoided is too great a penetration of the aluminum into the base metal. In the case of Type 347 stainless steel, the aluminum definitely renders the metal porous if penetration is too deep.

Continued operation at high temperatures, of course, will increase the depth of the aluminum diffusion. It will also change the composition of the surface oxide layer by diffusion of the base metal outward and the aluminum oxide inward. These two effects brought about by solid diffusion will be the main factors limiting long operation.

Gaseous Diffusion Through Ceramic Materials

In general, ceramic materials have low rates of diffusion. The rate of diffusion of hydrogen through fused silica is about 300-fold lower than that through Type 347 stainless steel at 700°C. At lower temperatures, there is less difference in the rates. It is generally true of glasses that the rate of diffusion shows a small increase with increasing temperature near the softening point. Thus, even the hard glasses show only a ten-fold increase in rate going from about 500°C to 900°C. In the low temperature range the glasses show steep temperature curves similar to the metals. Most of the work on gaseous diffusion through glasses has been done with helium. Of the common gases, helium and hydrogen are the fastest diffusing through ceramic materials. The difference in rates of diffusion of the two gases appears to vary among different glasses, but it can be said generally that hydrogen diffuses at a slower rate than helium. For example, the hydrogen rate is about ten-fold lower than that of helium through fused silica over the temperature range 300°C to 600°C, while it is about 60-fold lower through Corning No. 1720 pyrex glass at 685°C. Hydrogen apparently is retarded by chemical attraction in the lattice of the ceramic materials. Other inert gases, such as neon, nitrogen, and krypton diffuse inversely as their molecular weights.

Results of diffusion of helium through various types of glass show a direct correlation to the amount of silica present. In general, the harder the glass, that is, the higher the silica content, the higher the rate of diffusion at a given temperature. At 300°C the rate of diffusion of helium through silica is approximately 1000-fold that through lead glass. One exception to this is Corning No. 1720 pyrex, mentioned above, which has a rate about 2,000-fold lower than that of fused silica at 760°C. The effects of various oxides in glass on the rate of helium diffusion have been studied at the Ceramic Department of the University of Illinois. It was found that the alkali oxides were particularly effective in reducing the rate of diffusion even in the hard glasses. The oxides tested reduced the rate of diffusion of helium in order of increasing effectiveness as follows: Al_2O_3 , K_2O , Na_2O , Li_2O . A glass of composition 5% Li_2O , 25% Na_2O , 70% SiO_2 gave a rate 1000-fold below that for fused silica at 300°C.

Reduction of Hydrogen Diffusion Through Metals by the Glass Coating Method

Considerable work in applying glass coatings to metals has been done at the University of Illinois. Glass coatings can generally be applied successfully to metals if the expansion coefficient of the glass is controlled so as to be slightly less than that of the base metal. If at the same time the composition of the glass is adjusted to give low permeability to gaseous diffusion, the

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glass can be applied to metal and the low permeability of the glass can be combined with the mechanical strength of the metal. Sufficient variation in the expansion coefficient of the glass can be effected to match most of the available metals. Several coatings have been successfully applied to Type 347 stainless steel. A coating of 0.002 inch of a glass of composition 18% Al_2O_3 , 11% K_2O , 7% Na_2O , 57% SiO_2 gave a reduction in rate of hydrogen diffusion 60 times lower than that of the clean metal at 740°C . A 0.007-inch coating of composition 12% Na_2O , 11% B_2O_3 , 8% Al_2O_3 , 5% K_2O , 57% SiO_2 reduced the rate to 200 times below that of the clean metal at 732°C . A third coating containing 25% Cr_2O_3 gave only a 15-fold reduction in rate at 718°C .

APPENDIX I

HYDROGEN DIFFUSION FROM ATTACK OF ATMOSPHERIC MOISTURE ON STAINLESS STEELS AT HIGH TEMPERATURES

Introduction

In vacuum systems made of metal parts operating at high temperatures, there is the problem of what gases may be picked up from the atmosphere. The only gas that can diffuse through the metal parts of the system at other than high temperatures (around 700°C and above) is hydrogen. Hydrogen may come from two sources in the atmosphere. (1) the hydrogen already present in the atmosphere, and (2) hydrogen produced by the reaction of moisture in the atmosphere with the metal forming an oxide and releasing hydrogen into the metal. Data on (1) vary, but the hydrogen content is almost certainly less than 0.01%. By applying the $\sqrt{p}$ law we can say that the diffusion rate from this component should not exceed 1% of that of hydrogen at one atmosphere through the clean metal. The determination of (2) was the object of these experiments. Data were obtained on three kinds of stainless steel, Types 410, 347, and 304. Analyses of these steels follow:

<u>Steel</u>	<u>Fe</u>	<u>Cr</u>	<u>Ni</u>	<u>Mn</u>	<u>Cb</u>	<u>C</u>
Type 410 SS	bal	12.6	-	-	-	0.13
Type 347 SS	bal	18.5	10.5	1.4	0.9	0.08
Type 304 SS	bal	18.6	10.2	0.3	-	0.08

The method used in these experiments is exactly the same as that used previously for measuring rates of diffusion of hydrogen. The desired gas atmosphere was circulated through the outer jacket of the diffuser over the diffuser tube and the pressure of the gas diffusing through the tube was measured. The diffusion rate S is given throughout this report in cc(STP)/hr/cm²/mm at 760 mm H₂.

Type 410 Stainless Steel

The data on Type 410 stainless steel are given in Table I. As can be seen, the rate of diffusion with air containing atmospheric moisture in the outer jacket at 720° is appreciable, about 5% of that for the clean metal at 1 atmosphere of hydrogen. The substitution of dry air brought about a further marked drop in rate to about 0.25% that for the clean metal at 1 atmosphere. Upon returning to air containing atmospheric moisture, the original rate was again obtained. Atmospheric moisture, therefore, appears to produce a perceptible amount of hydrogen by the reaction of water with the steel. The rate of reaction appears to maintain itself at a certain level, so that the oxide coating is apparently not completely protective at this temperature. The rate of reaction is considerably lower at 380°C.

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95Type 347 Stainless Steel

Data on Type 347 stainless steel appear in Table II. Measurements in this case were made starting at low temperatures. The initial rate of diffusion at 350° was high. As the temperature was increased, the rate kept at about the same level, indicating considerable self-poisoning of the reaction. Further treatment at 815°C for three hours reduced the rate further to less than 0.1% that of hydrogen at 1 atmosphere through the clean metal. At this point, dry air produced no difference in the rate as compared to atmospheric air. Thus with Type 347 stainless steel it appears that under the above conditions the oxide layer is very protective. The rate of diffusion is very low and appears to be produced chiefly by hydrogen already present in the atmosphere.

Table IHydrogen Diffusion from the Atmosphere Through Type 410 Stainless Steel

<u>Gas Atmosphere</u>	<u>T (°C)</u>	<u>S</u>
H ₂	~730	2.71×10^{-1}
Atmospheric air*	~730	2.37×10^{-2}
Atmospheric air after 15 minutes	~720	1.38×10^{-2}
Atmospheric air after 50 minutes	~720	1.15×10^{-2}
Dry air	~720	4.9×10^{-4}
Atmospheric air	~720	1.23×10^{-2}
Atmospheric air	~380	4.9×10^{-4}

*Relative humidity 75% at 23°C

Table IIDiffusion of Hydrogen from the Atmosphere Through Type 347 Stainless Steel

Atmospheric air*	350	1.55×10^{-3}
Dry air	350	8.8×10^{-4}
Atmospheric air	350	6.0×10^{-4}
Atmospheric air	497	1.02×10^{-3}
Atmospheric air	650	1.14×10^{-3}

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Table II (continued)

<u>Gas Atmosphere</u>	<u>T (°C)</u>	<u>S</u>
Atmospheric air	800	1.34×10^{-3}
H ₂	800	4.60×10^{-1}
Atmospheric air	800	1.45×10^{-3}
Atmospheric air after 3 hours	815	3.2×10^{-4}
Dry air	815	2.9×10^{-4}
Atmospheric air	815	2.9×10^{-4}

*Relative humidity 68% at 25°C

Type 304 Stainless Steel

Data on Type 304 stainless steel are given in Table III. This type of steel appears to act like Type 410 rather than like Type 347, a fact which seems somewhat surprising. The reaction appears to maintain itself at around 2.6×10^{-3} at 750°C and a noticeable decrease in rate is observed with dry air. Subsequent application of atmospheric air returns the rate to the original level of 2.6×10^{-3} which is about 1% of the rate of hydrogen at one atmosphere through the clean metal. That Type 304 should act differently from Type 347 stainless steel is not entirely unreasonable. It appears, however, that there is some difference in the oxide coating formed by wet hydrogen firing as compared to that formed by reaction with wet air. In the former case Type 304 stainless steel proved superior.

Table IIIDiffusion of Hydrogen from the Atmosphere Through Type 304 Stainless Steel

<u>Gas Atmosphere</u>	<u>T (°C)</u>	<u>S</u>
Atmospheric air*	316	2.8×10^{-4}
Atmospheric air	~ 560	2.1×10^{-3}
Atmospheric air	~ 750	2.9×10^{-3}
Dry air	~ 750	5.6×10^{-4}
Atmospheric air	~ 750	2.6×10^{-3}

*Relative humidity 68% at 25°C

Conclusions

1. Hydrogen will diffuse into vacuum systems through metal parts at high temperature due to (1) hydrogen already present in the atmosphere, and (2) the reaction of atmospheric moisture on the metal to form oxides, liberating hydrogen in the metal.

2. Type 410 stainless steel shows an appreciable rate of reaction with atmospheric moisture at 720°C which does not appear to be self-poisoning. Type 304 stainless steel shows the same characteristics, however with a lower rate. Type 347 stainless steel shows a very low rate at 815° which is apparently due only to hydrogen already present in the atmosphere.

An interesting paper on this subject by F. J. Norton - J. of App. Phys., Vol 11, No. 4, pp. 262-267 (1940) covers the diffusion of hydrogen into a metal vacuum tube at 25°C from water in the atmosphere due to the corrosion process.

THE SOLUBILITY OF HYDROGEN IN METALS

For the convenience of the reader, the following data on solubility of hydrogen in metals are included. Data on elementary metals in Table I are taken from Dushman.* The most complete work on solubility of hydrogen in steels has been done by Armbruster.** Table II contains data from this paper on pertinent steels. The solubility equation for diatomic gases is normally written:

$$s = S \sqrt{p} e^{-Q_s/2 R_0 T}$$

where s = solubility (usually expressed in micromoles/100 g or in cc(STP)/100 g).

S = solubility constant

p = gas pressure

Q_s = activation energy

R_0 = gas constant

T = absolute temperature.

The increase of solubility with increasing temperature is small compared to that of the diffusion rate. The $\sqrt{p}$ law holds from very low pressures in the micron range up to at least one atmosphere. Table III contains solubilities of hydrogen in 18-8 stainless steel at various pressures calculated from Armbruster's data using the $\sqrt{p}$ law. Data in both Tables II and III were calculated from solubility measurements at 1.0 mm pressure.

*S. Dushman - Vacuum Technique, John Wiley and Sons; (page 572 and following).

**M. H. Armbruster, J. Am. Chem. Soc., 65, 1043 (1943).

Table IThe Solubility (cc(STP)/100 g) of Hydrogen at 1 atm in Elementary Metals

(Dushman)

<u>T (°C)</u>	<u>Element</u>					
	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>	<u>Cu</u>	<u>Al</u>	<u>Mo</u>
200	1.70					
300	2.35	0.16				
400	3.15	0.35		0.06		0.165
500	4.10	0.75		0.16		0.175
600	5.25	1.20	0.5	0.30		0.185
700	6.50	1.85		0.49	(m.p. 660°) 0.15	0.21
800	7.75	2.45	1.0	0.72	0.49	0.25
900	9.10	3.0 (α)* 4.7 (γ)	2.0	1.08	1.48	0.29
1000	9.80	5.50	3.0	1.58	3.0	0.50

*Phase Change

Table IIThe Solubility of Hydrogen (cc(STP)/100 g) at 1 atm in Various Steels

(Armbruster)

<u>Type of Steel</u>	<u>400°C</u>	<u>500°C</u>	<u>600°C</u>
0.4% C Steel	0.28	0.60	0.98
13% Cr 0.3% C Steel (ferritic)	0.20	0.45	0.90
13% Cr 0.3% C Steel (austenitic)	2.70	3.22	3.82
18% Cr 8% Ni Steel	3.24	3.94	4.67

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Table III

The Solubility of Hydrogen (cc(STP)/100 g)
at Various Pressures in 18-8 Stainless Steel

(Armbruster)

<u>T (°C)</u>	<u>Pressure (mm of Hg)</u>				
	<u>1</u>	<u>10</u>	<u>100</u>	<u>200</u>	<u>760</u>
400	0.117	0.370	1.17	1.65	3.24
500	0.142	0.450	1.42	2.02	3.94
600	0.169	0.532	1.69	2.38	4.67
700	0.205*	0.648*	2.05*	2.90*	5.68*

*Extrapolated

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BIBLIOGRAPHY

The reader is referred to the General Texts below for a thorough coverage of the theoretical basis of diffusion. Reference No. 4 contains a very complete bibliography on hydrogen in metals.

GENERAL TEXTS

1. Scientific Foundations of Vacuum Technique - S. Dushman, John Wiley and Sons (1949), pp. 396-416, 531-538, 547-653.
2. Gases and Metals - C. J. Smithells.
3. Diffusion in and Through Solids - R. M. Barrer, The Macmillan Co. (1941).
4. Hydrogen in Metals - D. P. Smith, the University of Chicago Press (1948).

HYDROGEN DIFFUSION THROUGH METALS

5. Baukloh, W. and Kayser, H. - Z. Metallkunde, 26, 156 (1934).
Cu, Ni, Cr-Ni, Cu-Ni and armco iron; effect of thickness H₂-Ni system.
6. Baukloh, W. and Kayser, H. - Z. Metallkunde, 27, 281, (1935).
Cu, Fe, Ni, Al; effect of varying composition in Fe-Ni and Cu-Ni systems.
7. Borelius, G., and Lindblom, J. - Ann. Physik. 82, 201 (1927).
Fe, Ni, monel, Pd-Pt.
8. Bratten, E. O. and Clark, G. F. - Proc. Roy. Soc. (Lond.), A, 153, 504 (1936).
Cu.
9. Edwards, C. A., - J. Iron Steel Inst., 110, 9 (1924).
Effect of grain size.
10. Fast, J. D. - Phillips Technical Review, 7, 73 (1942).
Fe, Cu, Pd; surface effects on atomic and molecular H₂.
11. Ham, W. R. - J. Chem. Phys., 1, 476 (1932).
Pt, Ni, apparatus.
12. Lombard, V. - Compt. rend. 177, 116 (1923).
Ni, apparatus.
13. Richardson, O. W.; Nicol, J. and Parnell, T. - Phil. Mag. (6), 8, 1 (1904).
Pt, apparatus; Discussion of Diffusion Equation.
14. Russell, A. S. - Metal Progress, 55, 827 (1949).
Al; effect of ionization of the gas.

15. Smithells, C. J., and Ransley, C. E. - Proc. Roy. Soc. (Lond.), A, 150, 172 (1935). Mo, Cu, Fe, Ni, apparatus; effect of grain size in iron.
16. Smithells, C. J. and Ransley, C. E. - Proc. Roy. Soc. (Lond.), A, 152, 706, (1935) Al, effect of oxidation, spontaneous aging.

HYDROGEN DIFFUSION THROUGH STAINLESS STEELS

17. Metal Hydrides, Inc. Progress Reports - NEPA Nos. 836, 855, 891, 914, 969, 1005, 1031, 1060, 1085, 1123, 1221 (1948) CONFIDENTIAL
Stainless steel Types 304, 316, 347, Nichrome I, Nichrome V, Inconel, aging effect.
18. Norton, F. J. - Diffusion of Hydrogen through Cr-Fe Alloy (Allegheny 55) - Private communication (General Electric Research Laboratory) November, 1951.
19. Wiskind, H. K. and Sibbitt, W. L. - Diffusion of gases through metals with emphasis on the system hydrogen - stainless steel (Type 347) ANL 4693 Feb. 15, (1951) UNCLASSIFIED

MISCELLANEOUS PAPERS ON GASES IN METALS

20. Armbruster, M. H. - J. Am. Chem. Soc., 65, 1043 (1943).
Solubility of H₂ in various steels, H₂ impermeability of 13% Cr steel.
21. Bastien, P. - Genie civil, 118, 9.
Compt. rend., 212, 788 (1941).
Chem. Zentr., 1942, II, 1547.
Effect of cold working on H₂ diffusion in 0.065% C steel.
22. Darken, L. S. - Corrosion, 5, 1 (1949).
Effect of cold working on H₂ solubility and rate of takeup in 0.15% C steel.
23. Norton, F. J. - Non-Diffusibility of He and Kr through Iron (1947)
Private communication (General Electric Research Laboratory)
November, 1951.
24. Norton, F. J., and Marshall, A. L. - Diffusion of nitrogen through steel - General Electric Research Laboratory Data Folder 55620.
25. Johnson, F. M. G., and Larose, P. - J. Am. Chem. Soc., 46, 1377 (1924).
Diffusion of O₂ through Ag, effect of thickness.
26. Ryder, H. M. - Elec. J., 17, 161 (1920).
Diffusion of CO through Fe.

METALLURGY AND HIGH TEMPERATURE OXIDATION OF METALS

27. Stainless Steels - C. A. Zapffe, American Society for Metals (1949).
28. High Temperature Properties of Metals, pp. 93-132 (High Temperature Oxidation Testing) American Society for Metals (1951).
29. Metals Handbook, pp. 223 (The Resistance of Metals to Oxidation at Elevated Temperature) - American Society for Metals (1948).
30. Inorganic Chemistry - pp. 441-450 (Basic Oxides of the Heavy Metals) Fritz Ephraim, Interscience Publishers (4th Edition, 1943).
31. Gulbransen, E. A. - J. App. Physics, 16, 718 (1945).
High temperature electron diffraction camera.
32. Gulbransen, E. A. - Ind. and Eng. Chem., 41, 1385 (1949)
Kinetic and structural factors involved in oxidation of metals.
33. Gulbransen, E. A. - Trans. Electrochem Soc., 91, 573 (1947)
Kinetics of oxide film formation on metals and alloys. Film cracking on 18-8 stainless steel.
34. Gulbransen, E. A. and Hickman, J. W. - Metals Tech., 13, 7 (1946), T.P. 2068
Electron diffraction studies of oxides on various elementary metals including Fe, Ni, and Cr.
35. Gulbransen, E. A. and Hickman, J. W. - Metals Tech., 13, 7 (1946) T.P. 2069
Electron diffraction studies of oxides on various alloys including 18-8 and 13% Cr stainless steels.
36. Gulbransen, E. A. and Hickman, J. W. - Trans. Electrochem. Soc., 91, 605 (1947)
Electron diffraction studies of various alloy steels including stainless steel Types 301 and 446.
37. Jackson, R., and Quarrell, A. G. - Iron and Steel Inst. Spec. Report No. 24, 65 (1939). Electron diffraction study of oxides of Fe.
38. Mahla, E. M. and Nielsen, N. A. - Trans. Electrochem. Soc., 93, (1948)
Study of films from passivated stainless steels.
39. Phelps, R. T., Gulbransen, E. A. and Hickman, J. W. - Ind. and Eng. Chem., 18, 391 (1946) Anal. Ed. Electron diffraction transmission studies of films stripped from elementary metals including Fe, Ni, and Cr.
40. Phelps, R. T., Gulbransen E. A. and Hickman, J. W. - Ind. and Eng. Chem. Anal. Ed. 18, 640 (1946) Electron diffraction transmission studies of films stripped from various alloys including 18-8 and 13% Cr stainless steels.

41. Vernon, W. H. J., Wormwell, F., and Nurse, T. J. - J. Iron and Steel Inst., 150, 81 Specific formation of Cr_2O_3 at surfaces of 18-8 steels.

METAL PLATING

42. Gardam, G. E. - J. Electrodepositors' Tech. Soc., 20, 19 (1946)
Low contraction chrome plating.

CALORIZING

43. Metals Handbook, pp. 703 (Aluminum Impregnation) - American Society for Metals (1948).
44. Metals Handbook, pp. 704 (Hot Dipped Aluminum Coatings on Steel) - American Society for Metals (1948).
45. Bulletin of the General Committee on Metallurgy of the General Electric Co., Vol 4, No. 4 (Aug., 1943).

DIFFUSION THROUGH CERAMICS AND THE ENAMELING OF STEELS

46. Barrer, R. M. - J. Chem. Soc., 378, (1934).
Diffusion of H_2 and He through SiO_2
47. Williams, G. A. and Ferguson, J. B. - J. Am. Chem. Soc., 44, 2160 (1922); 46, 635 (1924). Diffusion of H_2 and He through SiO_2 .
48. Johnston, J. and Burt, J. - J. Optical Soc. Am., 6, 734 (1922).
Diffusion of H_2 through fused quartz.
49. Norton, F. J. - Diffusion of He through various glasses - Private communication (General Electric Research Laboratory) Nov., 1951.
50. Bennett, D. G. - An Investigation of the Gas Permeability of Base Coat Glasses; Reports No. 27, 35, and 40, Oct. 1, 1948, May 14, 1949 and June 3, 1949 - Submitted to the Wright-Patterson Air Force Base by the University of Illinois.
51. Keeler, J. H., Chu, P. K., and Davis, H. M. - Classification and Definition of Delayed Defects in Porcelain Enamels - Finish, 7, 37, (1950).
52. Davis, H. M., Keeler, J. H. and Chu, P. K. - Distribution of Hydrogen in the Steel - Enamel System - Better Enameling, 21, 6 (1950).
53. Chu, P. K., Keeler, J. H. and Davis, H. M. - A Study of Gases in Porcelain Enameling - Better Enameling, 21, 8 (1950).
54. Keeler, J. H., Chu, P. K., and Davis, H. M. - An Examination of Reboiling - Better Enameling, 21, 12 (1950).

ADDENDA

55. Lewkonja, G., and Baukloh, W. - Z. Metallkunde, 1933, 25, 309.
56. Bousman, H. W. - Hydrogen Permeation through Materials of Construction; Private communication (General Engineering Laboratory), March 10, 1951.
57. Norton, F. J. - Diffusion of Hydrogen through 0.1% Carbon Steel; Private communication (General Electric Research Laboratory) November 1951.
58. T'sai, L. S., and Hogness, T. - J. Phys. Chem., 36, 2595 (1935).