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EFFECT OF TRANSIENT COMBUSTION SPECIES ON 4340 STEEL.(U)

MAY 79 G N KRISHNAN, A C SCOTT, B J WOOD

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May 1979

Final Report

By: G. N. Krishnan, A. C. Scott,
B. J. Wood, and D. Cubicciotti

Prepared for:

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Research Triangle Park, North Carolina 27709

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The erosion of gun barrels results from combined chemical-thermal-mechanical action of propellant gases on the gun bore. The rate of the erosion is too great for corrosion by normal gaseous species. It is likely that transient, energetic species including free radicals, such as atomic hydrogen, atomic nitrogen, and carbon- or oxygen containing radicals, are the active species that chemically alter the gun bore. A study of the effects of such species on gun barrel steel was undertaken.		

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Partially dissociated (by a microwave discharge) hydrogen, nitrogen, and methane were allowed to react with 4340 steel strips heated to 400-900°C. While undissociated gases at low pressures (~ 1 torr) were found to have negligible effect other than those due to heat treatment, atomic free radicals were highly reactive at steel temperatures ranging from 600 to 900°C. At 600°C atomic hydrogen removed carbon from surface layers and at 900°C bulk decarburization was rapid. The product of decarburization was found to be mainly methane. The extent of carbon removal was proportional to the square root of exposure time so that the rate was controlled by diffusion of carbon from the bulk of the specimen. Surface hardness decreased with carbon removal and the microstructure was observed to change from martensite to ferrite with increasing decarburization.

Microwave dissociation of a 3% CH₄-helium mixture was found to case-carburize the steel strips. Similarly, dissociated nitrogen nitrided the steel. The hardness after exposure to dissociated methane or nitrogen were substantially higher than that of the original material.

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1. INTRODUCTION

Gun barrel erosion is a complex process involving high temperature chemical and mechanical interactions between barrel, propellant combustion gas, and projectile. The interior surface of a typical used gun barrel has several layers that show the effects of temperature, mechanical stresses, and chemical attack.¹ In addition, part of the surface has been removed by melting, abrasion, or evaporation and cannot be observed directly. The remaining surface layers have been found to contain carbon, nitrogen, and oxygen in compounds with iron.

Objective

The objective of the present study is to understand the role of transient chemical species in combustion gases in the erosion of steel. Such chemical interactions between propellant gases and the steel surface can change the chemical nature of the surface or can lead to higher metal surface temperature due to exothermic reactions.

Atomic Free Radicals in Propellant Gas

Ahmad¹ has pointed out that during its life a gun barrel is exposed to the propellant environment for a total of only about 10 to 20 sec. The reactions of steel with molecular gases are not fast enough to account for the extent of reaction observed on gun barrels after such short exposure. Therefore, it appears that reaction of free radicals or other excited gaseous species with steel must play a major role in incorporating interstitial elements into the steel from the propellant gas.

Equilibrium calculations of propellant gas compositions show that gaseous free radicals must be present. For example, calculations made for gun propellant IMR 4198 show that hydrogen atoms constitute a few tenths of a percent of the equilibrium gas. Because the pressure inside

a gun barrel reach thousands of atmospheres, the equilibrium hydrogen atom pressures exceed one atmosphere. Other free radicals such as N, OH, O, etc., have smaller concentrations in the equilibrium gas.

The surface of a burning particle of propellant, however, is far from equilibrium. The conditions there are probably like those in a flame, where the concentrations of free radicals are high.² In fact, the propagation of the very rapid chemical reactions that result in a flame occur by free radical mechanisms. Therefore, in the vicinity of the burning front of a propellant particle there must be larger-than-equilibrium concentrations of atomic free radicals. These radicals recombine as they diffuse away from the flame; however, the recombination of two atomic radicals requires the involvement of a third body to remove the reaction heat. Metal surfaces are generally good catalysts for gaseous atom recombinations, and the reactions of gaseous atoms on metal surfaces have been studied extensively.³ However, most of these studies have emphasized the reaction between gaseous substances, that is, radical combinations, rather than the effects of radicals on the metal surface.

Free radicals are expected to react at metal surfaces in two ways. They can recombine to form stable gaseous products. In that case, the metal surface acts as a catalyst for the recombination. The heat of recombination is transferred mainly to the metal, causing a significant temperature increase. (This is the basis for the atomic hydrogen torch). Alternatively, the free radicals can react with the substrate metal and penetrate into the bulk of the metal. The elements in those free radicals all can form interstitial compounds and solutions with metals, and the reactions would form a surface layer of metal with altered properties. Reduction of the thermal conductivity of the layer by the reaction would lead to increased surface temperatures and possibly melting. Wear-reducing additives might be expected to influence the surface reactions of free radicals. The additives may provide catalytic surfaces for recombination and so decrease the concentrations of radicals reaching the metal; or they may poison active sites on the metal surfaces and

thereby reduce the rate of reaction of the radicals that lead to penetration into the metal.

Methodology

We studied the effects of atomic free radicals on specimens of AISI 4340 steel, a type similar to gun barrel steel. Steel strips, maintained at a constant temperature in the range of 400° to 900°C, were allowed to react with hydrogen, nitrogen, carbon monoxide, and methane that were partially dissociated by microwave discharge. Parallel control experiments with undissociated gases were also performed. By heating strips of steel in a helium atmosphere, we determined how heat treatment alone affected the properties of steel specimens. Steels plated with chromium and titanium dioxide were also used to study the behavior of such coatings in the presence of atomic free radicals.

After the steel specimens were exposed to the reactive gases, they were analyzed by various techniques. Scanning electron microscopy (SEM) was used to observe surface morphology. X-ray fluorescence in SEM was used to estimate the elemental composition of the specimens in the 1- μ m-thick region near the surface. Auger electron spectroscopy (AES), in conjunction with argon ion-sputtering, was used to determine the composition profile within this 1- μ m-thick layer. A Vickers microhardness tester with a 200-g load was used to measure changes in hardness after various treatments. Optical metallography revealed the microstructure on the surface and in the interior of the specimen after the specimen was taper polished 15°. Chemical analyses indicated bulk composition changes.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

A microwave discharge is an established⁴ and convenient means to generate a flux of atoms in a stream of diatomic gas at subatmospheric pressure. The technique can produce steady-state concentrations of hydrogen, nitrogen, or oxygen atoms in the range of 1% to 10% of the total pressure of the respective diatomic gas at pressures near one torr. Atoms of these gases are highly reactive, and they are lost rapidly through recombination, both in the gas phase by way of three-body collisions and on surfaces in processes that involve at least one chemisorbed atom. Consequently, to obtain a reasonable atomic flux incident on a steel surface of interest, the steel specimen must be relatively close to the atom source.

Figure 1 shows a schematic of the apparatus used in our experiments. The main chamber is a section of 10-cm-ID Pyrex pipe with an integral flange that accommodates a cap with five O-ring-sealed, 0.6-cm-tube fittings. These fittings provide access for electrical feedthroughs, mechanical supports, and chemical titrants, depending on the needs of the experiment. The chamber is connected through a liquid nitrogen trap to a 2-liter-sec⁻¹ mechanical pump. At one end of the chamber the mixture of atomic and molecular gas enters through a fused silica tube 1.2 cm in diameter. The silica tube passes through a microwave cavity where a discharge is excited within the tube. The cavity is a foreshortened 1/4-wave coaxial type, and its characteristics are described by Fehsenfeld et al.⁴ Microwave power at 2450 MHz is supplied to the cavity by a magnetron driven from a regulated power supply. The discharge region, located approximately 10 cm upstream from the outlet of the quartz tube, is the atom source. Gas enters the system through a needle valve at the inlet of the quartz tube. The steady state pressure in the chamber is monitored by a Validyne pressure transducer, calibrated against a Wallace and Tiernan aneroid dial gauge.

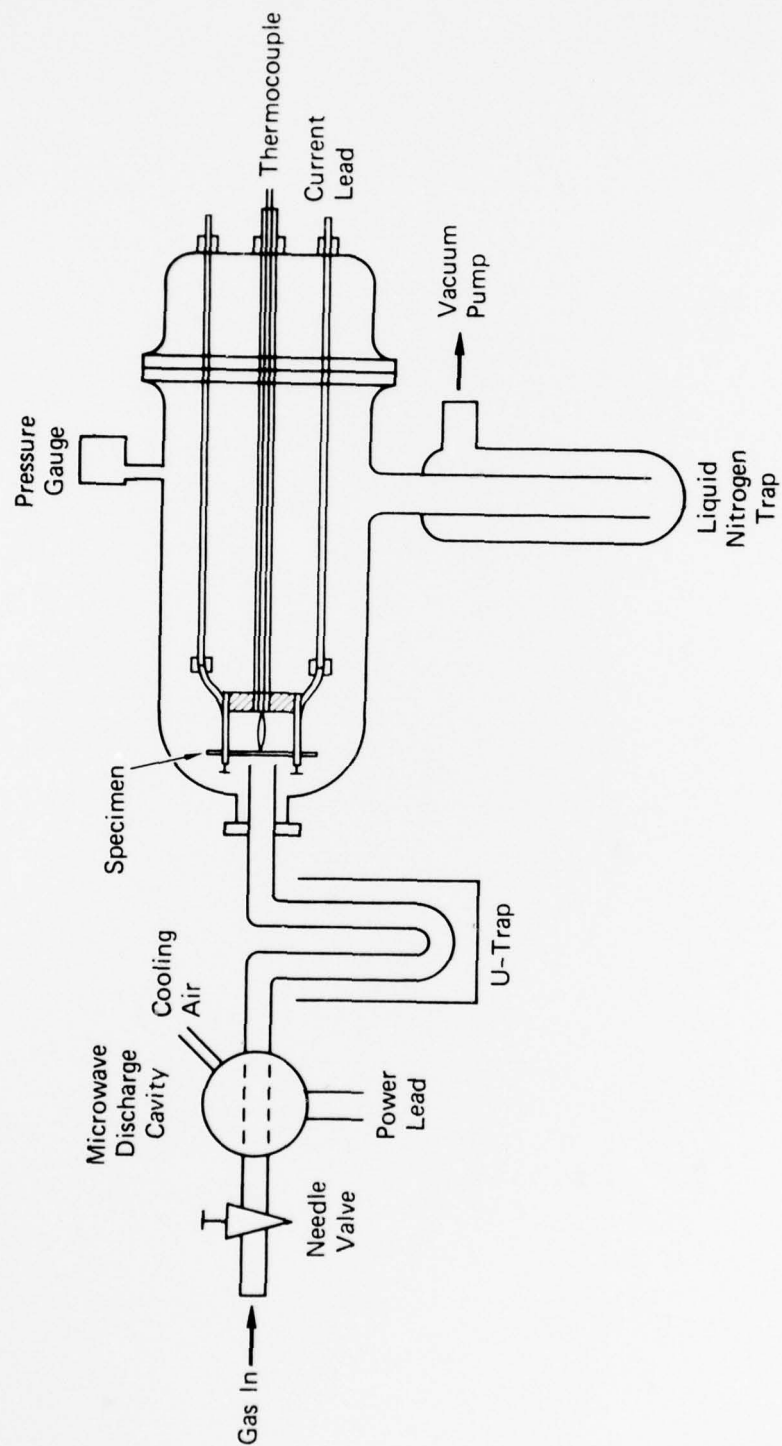


FIGURE 1 SCHEMATIC OF THE MICROWAVE DISCHARGE APPARATUS

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Diagnostic measurements were performed to estimate the concentration and distribution of gaseous hydrogen atoms. Two techniques were used. The first employed a calorimetric principle in which the heat of atom recombination on a metal filament is used as a measure of the local atom flux Φ , in accordance with the following heat balance:

$$\Phi = \Delta H \gamma \beta / Q$$

The exothermic heat of recombination ΔH for hydrogen is well known.⁵ Values of the recombination efficiency γ and the recombination energy accommodation efficiency β have been evaluated⁶ for hydrogen atoms recombining on tungsten. Hence, the atom flux can be evaluated from the measured heat input Q to a tungsten filament. In our experiments, the heat input was estimated from the electrical current changes necessary to maintain steady state temperature of a tungsten filament. The maximum value of hydrogen atom flux observed at the location of the specimen corresponded to a partial pressure of 0.1 torr in a total pressure of 1 torr. In the range of 0.25 to 1 torr of hydrogen, the partial pressure of hydrogen atoms decreased linearly. Between 3 to 25 watts, the power applied to the microwave discharge did not change the atom concentration significantly, and below 3 watts the atom flux diminished rapidly. The atom concentration decreased only slightly along the length of the fused silica tube but the atom density decreased sharply in the main chamber as the gas expanded.

The second technique for measuring hydrogen atom concentration involved titration with NO_2 .⁷ For this measurement, a multiport gas nozzle was situated in the chamber so that NO_2 from a tank could be metered into the apparatus. The chemiluminescence produced by decay of activated HNO species at 6200–800 Å was monitored by a photomultiplier tube (EMI 9558B with Wratten Filter No. 29). The end point is denoted by the cessation of light emission, which is indicative of the complete consumption of hydrogen atoms by NO_2 . From the reaction sequences, it can be shown that at the end point, the mass flow rate of

hydrogen atoms ($\dot{m}_H$) and nitrogen dioxide molecules ($\dot{m}_{NO_2}$) corresponds to the ratio

$$\dot{m}_{NO_2} / \dot{m}_H = 3/2$$

The results of such a titration indicated a hydrogen atom partial pressure of 0.08 torr for a total pressure of 1 torr at the normal sample location. These results are in good agreement with the calorimetric measurement reported above.

In subsequent experiments, minor modifications to the fused silica inlet section of the apparatus were made to (1) enhance the fractional concentration of hydrogen atoms in the gas stream and (2) to eliminate the transport into the chamber of a silicon oxide species that apparently is reactively sputtered off of the silica wall in the discharge region.

The atom generation rate is enhanced by the addition of a small amount of water vapor to the hydrogen supply stream. Although the mechanism of enhancement is not established, the technique has been by many investigators. To prevent water vapor from entering the main chamber of the apparatus, a U-bend was incorporated in the silica tube between the discharge and the outlet. The U-bend increased the distance between discharge and specimen to 30 cm. The U-bend was refrigerated by immersion in a dry ice-acetone mixture to condense nonpermanent gaseous impurities in the flow stream. Among the impurities removed by this method were the silicon oxide species originating in the discharge region. Hydrogen atom loss in the cold section was minimal, because the recombination efficiency of hydrogen on silica diminishes at subambient temperatures in accordance with an activation energy of about 2 kcal mole⁻¹. At 200 K, the rate of recombination of hydrogen atoms on fused silica is only one-fifth its value at room temperature.⁸ For gases other than hydrogen, the U-tube trap was not used. The discharge was located in a straight silica tube approximately 10 cm upstream from the location of the sample.

Samples of Type 4340 steel were exposed to atomic free radicals in this apparatus for various periods of time and at various temperatures. The steel specimens were 4.4-cm by 0.32-cm strips cut from 0.1 cm sheet that had been rolled from 0.635 cm-thick billets tempered to Rockwell C 40 hardness. The specimens were polished, then mounted in a fixture that permitted them to be heated by passage of an ac current (up to 40 A) and that held them in the chamber so the center region of the specimen intercepted the gas stream from the silica tube at a distance of approximately 10 cm from the atom source (30 cm with the U-tube trap). The temperature of the specimen was monitored by an iron-constantan thermocouple spot-welded to its back side midway between the ends. A 1-cm region in the center of the specimen had a uniform temperature ($\pm 15^\circ\text{C}$) when the specimen was heated to 900°C . At the end of the exposure period, the microwave discharge was extinguished, and the specimen was allowed to cool in the ambient, undissociated gas. The chamber was then back-filled with air, and the specimen was removed for examination by various physical and chemical techniques.

3. RESULTS AND DISCUSSION

Interaction of 4340 Steel with Nonexcited Gases

Helium

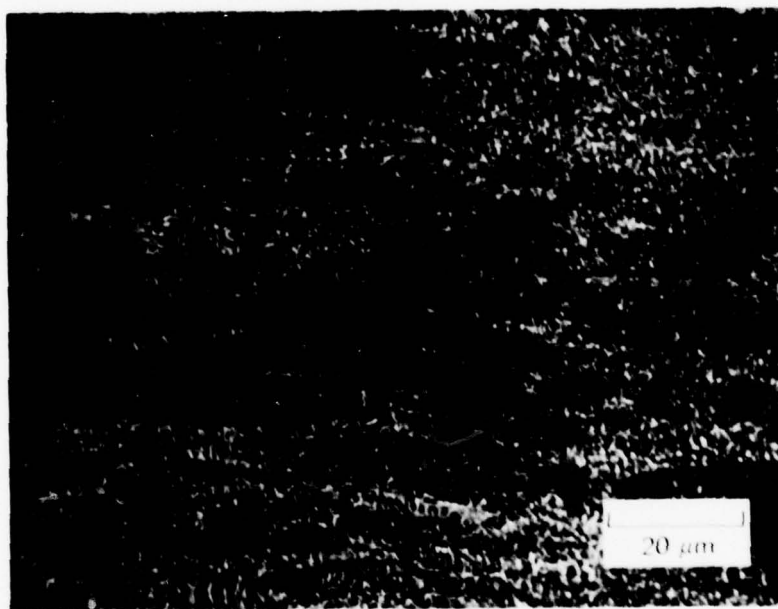
The mechanical properties of steel depend heavily on previous heat treatment. The unreacted steel specimens had a hardness 430 ± 40 VPHN* (R_c 52),† and the microstructure was that of tempered martensite (see Figure 2). Specimens treated in helium atmosphere will indicate the effects of heat treatment in the absence of any chemical interactions. A two-hour treatment in helium at 400°C did not considerably change either the hardness or the microstructure of the specimens. Specimens heated at 600°C, for two hours in helium were softened, i.e., the hardness decreased to 285 VPHN (R_c 28). However, in the specimens heated to 900°C in helium for two hours and subsequently cooled to room temperature, the hardness increased to 550 VPHN (R_c 52), and the microstructure was that of fine martensite. This result is due to heating the specimen above the austenizing temperature followed by rapid quenching ($\sim 8^\circ\text{C sec}^{-1}$) to form martensite. Table 1 summarizes the effects of heat treatment, and Figure 3 illustrates the microstructure changes.

Hydrogen

Because molecular hydrogen constitutes the bulk of microwave excited gas, experiments with undissociated hydrogen were performed to determine the effect of molecular hydrogen on the steel. As with helium, at 400°C no significant changes were observed (see Table 2). When the specimens were exposed at 600°C for two hours, the hardness was reduced to 260 VPHN

* Vickers Pyramid hardness number.

† Rockwell C hardness number converted from VPHN.



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FIGURE 2 MICROSTRUCTURE OF UNREACTED SPECIMEN

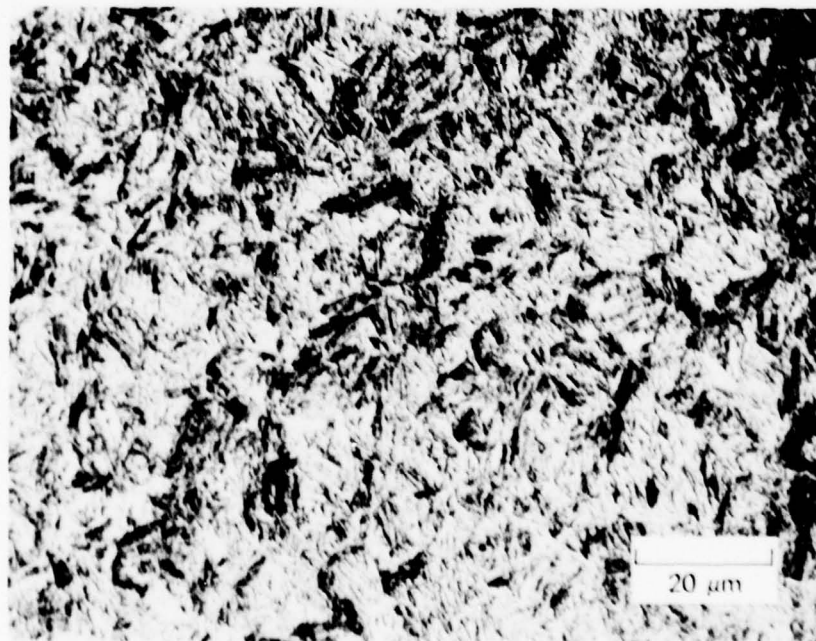
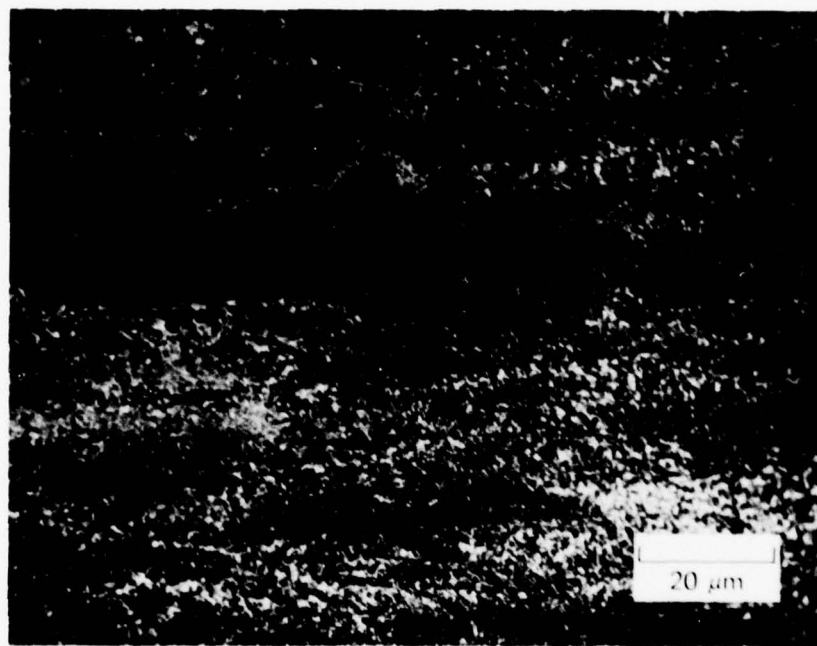
Table 1

EFFECT OF HEATING AND COOLING A 4340 STEEL STRIP

<u>Temperature</u> (°C)	<u>Time</u> (Min)	<u>Hardness</u> (VPHN)	<u>Microstructure</u> <u>Microstructure</u>
Unreacted	0	420	Tempered martensite
400	120	420	Tempered martensite
600	120	290	Tempered martensite
600 ^b	120	540	Fine martensite

^a200-g load; VPHN: Vickers Pyramid hardness number.

^bCooling rate $\sim 8^{\circ}\text{C sec}^{-1}$



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FIGURE 3 MICROSTRUCTURES OF SPECIMENS HEATED IN 1 TORR OF HELIUM AT 600° C (top) AND AT 900° C (bottom) FOR TWO HOURS

Table 2

EFFECT OF HEATING 4340 IN MOLECULAR HYDROGEN

<u>Temperature</u> (°C)	<u>Time</u> (Min)	<u>Hardness^a</u> (VPHN)	<u>Microstructure</u>	<u>Carbon Content^b</u> (wt%)
Unreacted	0	420	Tempered martensite	0.4
400	120	426	Tempered martensite	NM ^c
600	120	260	Tempered martensite	NM
900	120	590	Fine martensite	NM
900	420	590	Coarse martensite	0.4

^a200-g load.

^bChemical analyses performed by Metallurgical Laboratories, Inc.
1142 Howard Street, San Francisco, California

^cNot measured.

(R_c 24). At 900°C and after seven hours of exposure to hydrogen gas at 1 torr pressure, the specimens showed no significant change in carbon content and had a hardness value of about 595 VPHN (R_c 55). These results are very similar to those obtained with helium.

The absence of decarburization under our experimental conditions at 900°C is not surprising. Turkdogan and Martonik⁹ have investigated the decarburization of plain carbon steels from 800°C to 1140°C in hydrogen atmosphere. They concluded that the kinetics were controlled by the surface chemical reaction and that the rate of reaction was proportional to $p_{H_2}^{3/2}$. From the extrapolation of their data, we estimate that with 1 torr pressure of hydrogen an exposure of about 4000 hours would be required to reduce the carbon content of a 0.4% carbon steel by 0.05%.

Interaction of 4340 Steel With Gaseous Free Radicals

Hydrogen Atoms

A major portion of our investigation was devoted to studying the effect of hydrogen atoms on steel because thermodynamic calculations indicated that, in the propellant gas mixture, hydrogen atoms would be the most abundant free radical. We calculated that in the combustion gas from propellant IMR 4198, hydrogen atoms constitute a few tenths of a percent of equilibrium gas, and the total pressure of hydrogen atoms could exceed one atmosphere for a total pressure of 50,000 psi in a gun barrel.

When hydrogen atoms impinge on a specimen, about 10% to 20% of the atoms recombine on the surface, liberating a large amount of heat³ (104 kcal mole⁻¹). This recombination heat was found to be ~ 10% of the electrical power applied to the specimen at 900°C. When the electrical current was not reduced, the temperature of the specimen increased by ~ 65°C.

Table 3 summarizes the results of the effects of hydrogen atoms on steel. At 400°C, the effect of hydrogen atoms at low pressure on steel seems to be negligible, and the steel specimen showed no change

Table 3

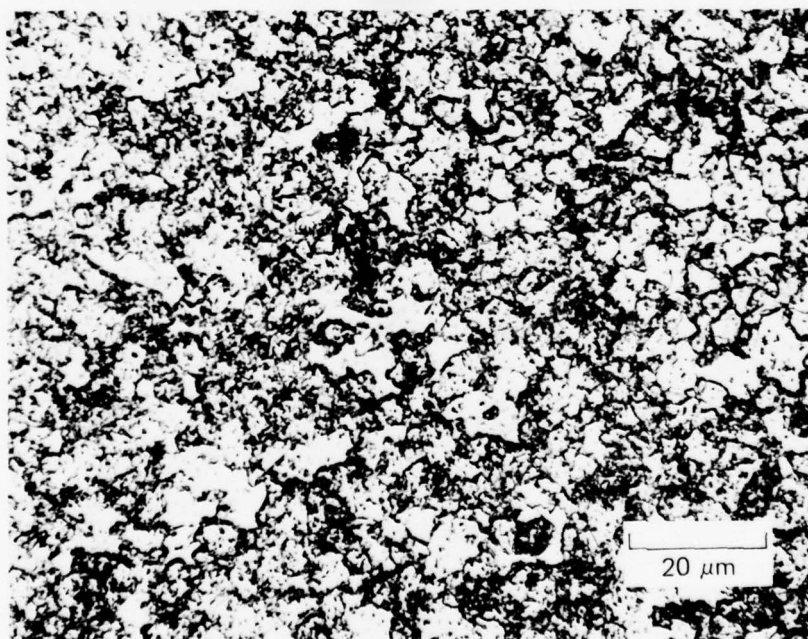
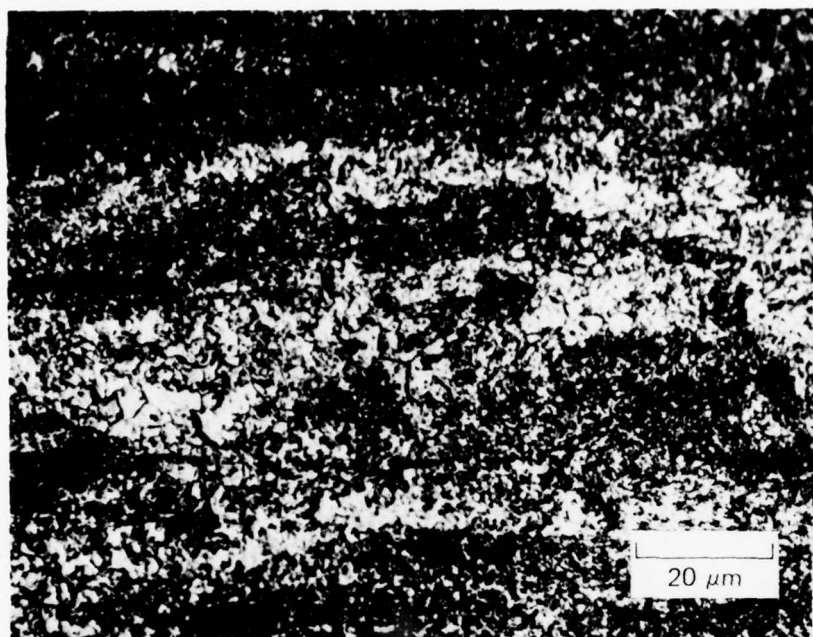
EFFECT OF HEATING 4340 STEEL IN HYDROGEN ATOMS^a

Temperature (°C)	Time (Min)	Hardness ^b (VPHN)	Microstructure (VPHN)	Carbon Content ^c (wt%)
400	120	450	Tempered martensite	NM ^d
600	30	270	Tempered martensite	NM
600	45	270	Ferrite + tempered martensite	NM
600	60	260	Ferrite + tempered martensite	0.4
600	120	220	Ferrite on the sur- face, tempered mar- tensite below	0.4
900	10	505	Fine martensite	NM
900	30	250	Ferrite + martensite	0.28
900	60	200	Mostly Ferrite, martensite below the surface	0.19
900	120	210	Ferrite up to 50 μ m deep	0.16
900	420	150	Mostly ferrite throughout the specimen	0.05

^a0.1 torr atomic hydrogen in 0.9 torr molecular hydrogen.^b200-g load.^cChemical analyses were performed by Metallurgical Labs, Inc.,
1142 Howard Street, San Francisco, California.^dNot measured.

in either microhardness or in microstructure. At 600°C, the specimen softened considerably after being exposed to hydrogen atoms. The softening was partly due to the tempering similar to that observed in hydrogen or helium. A certain amount of surface decarburization was also observed and contributed to the loss of hardness. Microscopic observation of the specimen surface revealed the presence of ferrite, and the amount of ferrite on the surface increased with increasing exposure (see Figure 4). Samples heated in helium or undissociated hydrogen at 600°C did not exhibit any ferrite on the surface. We interpret the presence of ferrite grains on specimens exposed to hydrogen atoms to indicate decarburization of the surface. Even though there was evidence of decarburization at 600°C, bulk chemical analyses did not indicate any loss of carbon; therefore, the decarburization was apparently limited to a thin layer near the surface. On the other hand, the carbon may have reacted with dissolved hydrogen to form methane and may have become trapped in microvoids. The formation of such voids with high pressure hydrogen gas¹⁰ has been reported. Methane trapped in such microvoids would have been reported as dissolved carbon in the standard metallurgical analyses.

At 900°C, in the austenite phase region, decarburization by hydrogen atoms was rapid. As shown in Table 3, the carbon content of the specimen decreased substantially with time of exposure to hydrogen after 30 minutes or more. At the end of 420 minutes, the carbon content had decreased to approximately 0.05%. The microhardnesses of the specimens decreased monotonically with exposure time. The high hardness value of the specimen exposed to hydrogen atoms for 10 minutes was due to martensite formation. The microstructure of the specimen exposed to hydrogen atoms for one hour consisted of a mixture of ferrite and martensite. At the end of a two-hour exposure, the microstructure consisted mainly of ferrite to a depth of 60 μm . A seven-hour exposure resulted in ferrite throughout the specimen. Figures 5 and 6 illustrate the changes in microstructures of 15° taper cut specimens after various reaction periods.



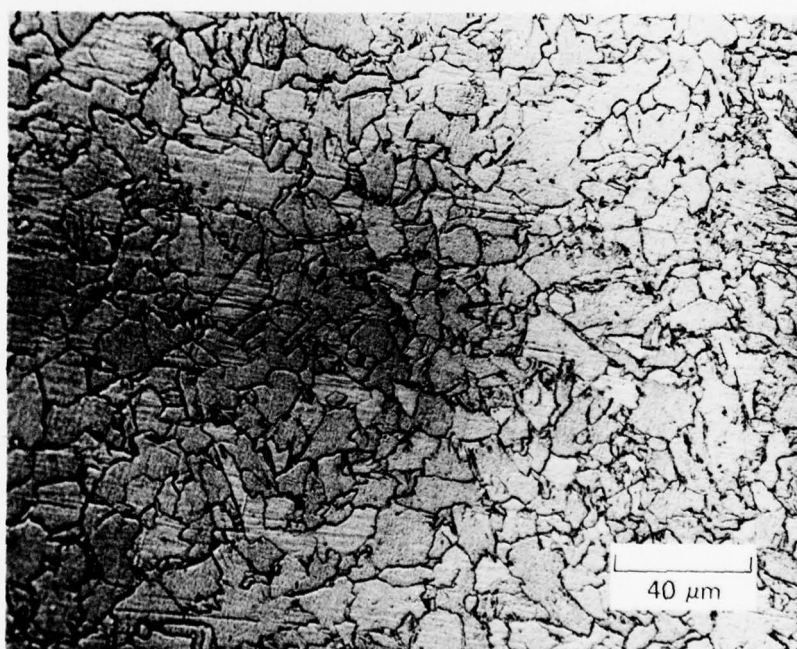
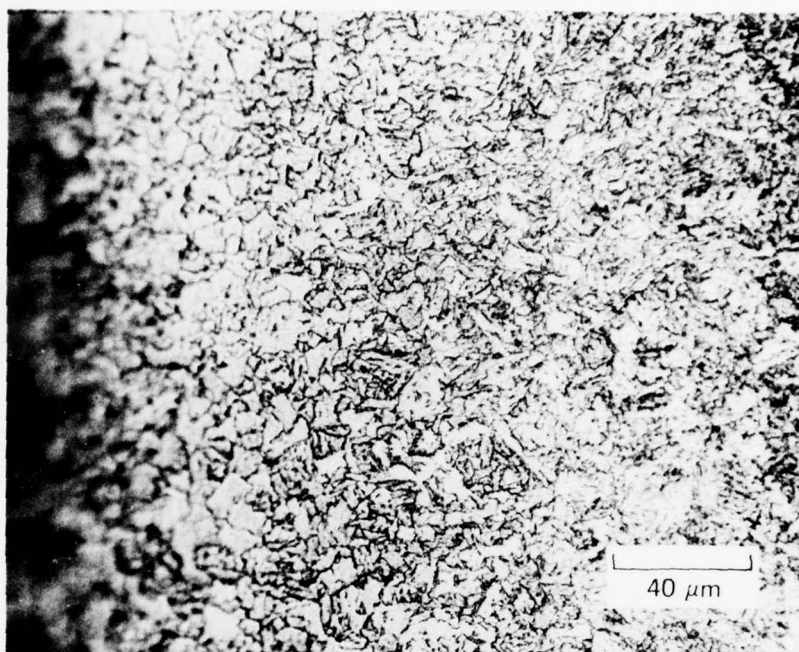
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FIGURE 4 MICROSTRUCTURES OF SPECIMENS EXPOSED TO HYDROGEN ATOMS AT 600°C FOR 45 MINUTES (top) AND 120 MINUTES (bottom)



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FIGURE 5 MICROSTRUCTURES OF 15° TAPER CUT SPECIMENS EXPOSED TO HYDROGEN ATOMS AT 900°C FOR 10 MINUTES (top) AND FOR 60 MINUTES (bottom). The left-hand side is near the surface.



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FIGURE 6 MICROSTRUCTURES OF 15° TAPER CUT SPECIMENS EXPOSED TO HYDROGEN ATOMS AT 900°C FOR 120 MINUTES (top) AND 420 MINUTES (bottom). The left-hand edge is near the surface.

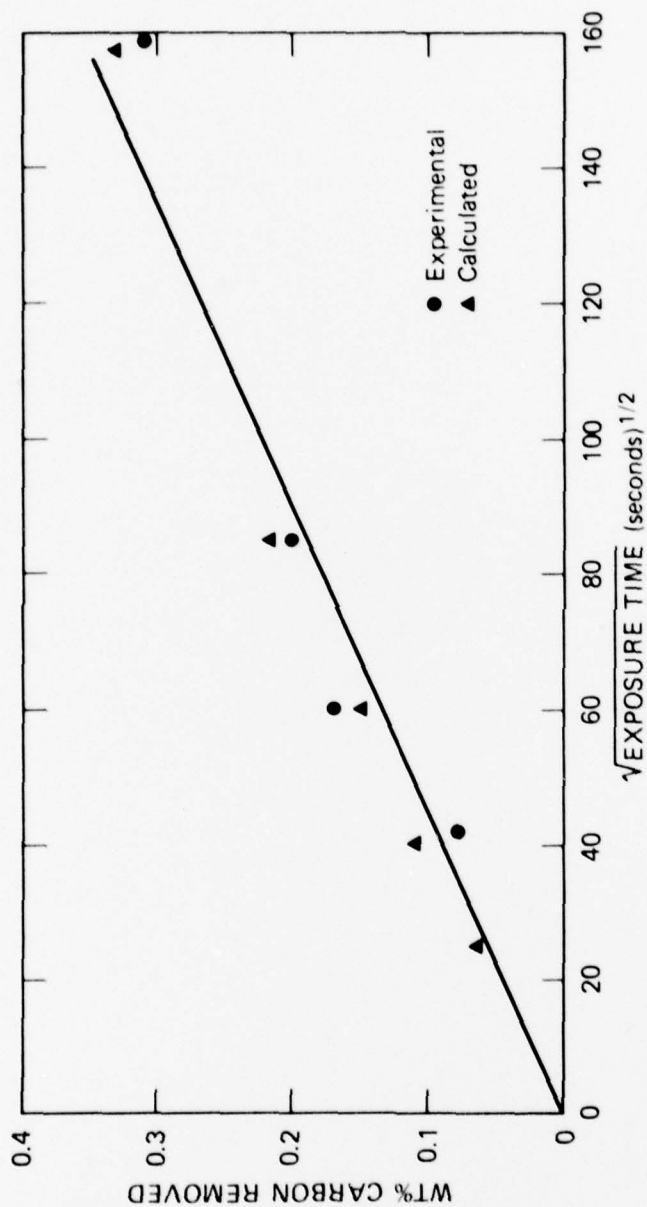
The amount of carbon removed from a specimen at 900°C in the presence of hydrogen atoms is plotted in Figure 7 as a function of the square root of the exposure time. A linear relationship was obtained. Because the geometry of the specimens is planar, this square root of time relationship indicates that decarburization was controlled by diffusion through the solid. Diffusion through a gas boundary layer or other gaseous transport processes could not account for the observed time dependence of the reaction. There are two processes whose rates could follow the observed time dependence and hence could be the rate controlling:

- (1) Diffusion of carbon through the steel to the surface
- (2) Diffusion of hydrogen into the steel.

The diffusion of hydrogen in steel is rapid¹¹ ($D = 2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 600°C). Process (2) is too rapid to account for the observed decarburization rates. Moreover, for Process (2) to be viable, methane produced within the specimen must diffuse through cracks or be trapped in voids in the specimen. No such cracks or voids were observed in our specimens after the reaction. If methane was trapped in microvoids too small to be observed, it would have been included in the analyses for dissolved carbon.

To determine the nature of gaseous reaction products, we collected the reactor effluent. The gaseous products from a specimen maintained at 900°C for 420 minutes were collected in a molecular sieve bed (Linde 13X) kept at 77 K. Then the molecular sieve trap was removed and taken to a gas chromatograph.* The sieve was heated, and the evolved gases were analyzed. After the sieve warmed to room temperature, only hydrogen was detected. When the sieve was further heated to 150°C, a significant amount of methane and additional hydrogen were found in the evolved gases.

* Hewlett-Packard 5750 Research chromatograph equipped with Linda 5A Molecular sieve column and thermal conductivity detector.



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FIGURE 7 PLOT OF PERCENT CARBON REMOVED AS A FUNCTION OF EXPOSURE TIME

The quantity of methane evolved was not measured because the apparatus was not equipped for a quantitative determination.

Thus, diffusion of carbon from bulk to the surface, appears to be rate controlling. The diffusion coefficient of carbon¹² in austenite at 900°C is $1 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$. Because the specimens in our study were 0.1 cm thick, they could not be considered as semi-infinite solids for the purpose of estimating the diffusion rate of carbon from bulk to the surface. The transition from the semi-infinite slab model to the thin slab model occurs when the thickness l (thin slab) $< 3.2 \sqrt{Dt} < l$ (semi-infinite slab). The thin slab approximation is valid when the exposure time t is greater than one hour, as was the case in most of our experiments.

The amount of carbon diffusing out of a thin slab as a function of time is given by the following equation¹³

$$\frac{Q_c}{Q_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp -D(2n+1)^2 \pi^2 t / l^2$$

where Q_c = amount of carbon diffused after time t

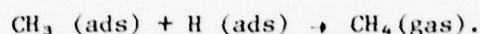
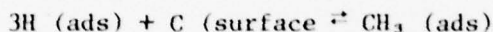
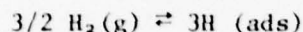
Q_∞ = maximum amount that can be extracted

D = diffusion coefficient of carbon in steel at 900°C.

Assuming all the carbon in steel can be removed in infinite time, we calculated the amount of decarburization as a function of exposure time. The results of the calculation are shown in Figure 7. The extremely good agreement between the calculation and the observed values provides strong evidence that the reaction rate is governed by outward carbon diffusion in the steel (Process 1).

It is of interest to contrast the kinetics of decarburization of steel by gaseous atomic hydrogen with those reported for gaseous molecular hydrogen.^{9,14} For molecular hydrogen the rate of decarburization was

found to depend on the 3/2 power of the hydrogen pressure, which suggested the following reaction sequence:



The second reaction is presumably the rate limiting step. When atomic hydrogen is supplied to the surface, the concentration of adsorbed atomic hydrogen is increased; therefore the rate of the second reaction is increased. In particular, we calculate from the results of Reference 9 that for molecular hydrogen under the conditions of our experiments (900°C, 1 torr H_2 , 0.4%C in steel) that the rate of carbon removal would be $5 \times 10^{-12} \text{ g. cm}^{-2} \text{ sec}^{-1}$. This rate would be too small to observe, in agreement with our observations that molecular hydrogen at low pressures did not decarburize the steel. In our experiments with atomic hydrogen the rate of carbon removal decreased with time. The shortest time for which we have data is 30 min. At that time the rate of carbon removal was $2 \times 10^{-7} \text{ g cm}^{-2} \text{ sec}^{-1}$, i.e., about five orders of magnitude faster. If the 3/2 power dependence of rate on hydrogen pressure is valid, we estimate that a pressure of 5 atm of molecular hydrogen would be required to produce the decarburization rate observed with atomic hydrogen. Since the rate at times smaller than 30 minutes was presumably larger, the effective H_2 pressure was also presumably larger than the calculated value.

Thermodynamically, the pressure of molecular hydrogen that would be in equilibrium with 0.1 torr of hydrogen atoms at 1200 K can be calculated from equilibrium data¹⁵ to be 10^5 atm. Therefore the hydrogen atom pressure was equivalent to much higher pressures of molecular hydrogen than the 5 atm required to account for the observed decarburization rate.

It is interesting to compare these results with the reactions of hydrogen with graphite. The reaction rate of atomic hydrogen with graphite reaches a maximum value at about 500°C, then drops off rapidly

as the temperature of the solid is increased.¹⁶ This is in contrast to the present study in which the rate of decarburization of steel increases with temperature. The difference between the kinetic behavior of the atomic hydrogen-graphite system and that of the 4340 steel apparently reflects the fact that at 900°C, the carbon in the steel exists in solid solution in the iron phase. Carbon atoms at the surface of such a phase evidently are considerably more reactive than carbon atoms bound in a graphite crystal lattice. Support for this contention is provided by recent studies on the reactivity of carbon adlayers on the surface of nickel methanation catalysts.¹⁸ In these experiments it was demonstrated that graphitic carbon is substantially less reactive with hydrogen than carbon bound to the metal with carbidic bonds.

In summary, atomic hydrogen decarburizes steel. The rate of the process is determined by the rate of diffusion of carbon in austenite. The overall process results in the formation of methane. The probable site of the reactions that form methane is the surface of the steel. The observed changes in the microstructure and in the properties of the steel result from the combined action of decarburization and heat treatment.

Nitrogen Atoms

The bond energy of the nitrogen molecule (227 kcal mole⁻¹) is more than twice that of the hydrogen molecule. Hence the extent of the dissociation of nitrogen molecules by the microwave discharge is rather small, ~ 0.5%. Strips of 4340 steel were exposed to the partially dissociated nitrogen in the same apparatus used for the hydrogen atoms study but without the U-tube. Vacuum fusion analysis showed that the nitrogen content of the specimen increased when the specimen was exposed to the dissociated nitrogen for two hours at 900°C. After this nitriding

*The nitrogen atom concentrations during the experiments was not measured.

treatment, the hardness of the specimen was 730 VPHN (R_c 62) at the surface and the hardness decreased to 670 VPHN (R_c 59) at a depth of about 100 μ m. No change in hardness was noted below the 100- μ m depth.

Under similar conditions of exposure but in the absence of the microwave discharge, the specimen showed no increase in nitrogen content or in surface hardness. The microstructure of all the specimens exposed either to nitrogen molecules or atoms was that of martensite. The results of heating 4340 steel samples in nitrogen under various conditions are summarized in Table 4.

Partially Dissociated Carbon Monoxide and Methane

Preliminary experiments were conducted with partially dissociated carbonaceous gases. A 10% CO in He mixture was passed through the microwave discharge and was then allowed to impinge on the steel specimen, which was maintained at 900°C. A large amount of carbon soot was deposited throughout the reactor. After a two-hour exposure, the specimen did not show any increase in hardness other than that caused by the heat treatment alone. Carbon analysis of the specimen also indicated no significant carburization.

A 3% CH₄ in He mixture was also passed through the microwave discharge and allowed to react with the specimen at 900°C. The amount of soot formed during this process was much smaller than that formed with the 10% CO in the mixture, and the soot was confined to the discharge region. After a two-hour exposure, the specimen showed significant carburization. The hardness at the surface of the specimen was extremely high 940 VPHN (R_c 68), and the hardness in the interior of a sectioned sample (~700 VPHN, R_c 60) was also higher than the hardness in the specimens heated in helium. No bulk analysis was performed. Metallographic observation revealed the presence of fine martensite.

A similar exposure of the samples to an undissociated CH₄ in He mixture did not result in an increase in hardness. The carburization

Table 4

EFFECT OF NITROGEN GAS AND NITROGEN ATOMS ON 4340 STEEL STRIPS^a

Reactant	Temperature (°C)	Time (Min)	Hardness ^b (VPHN)	Nitrogen Content ^c (wt %)
N ₂	900	120	593	0.008
N + N ₂	900	10	670	--
N + N ₂	900	120	670	0.1

^aMicrostructure consisted of fine martensite in all specimens.^b200-g load.^cChemical analyses performed by Oregon Metallurgical Corporation,
530 W 34th Avenue, Albany, Oregon.

of steel by dissociated methane using radio frequency discharge has been reported earlier.¹⁹

Effect of Hydrogen Atoms on Coated Steels

Preliminary experiments were also conducted to examine the effect of hydrogen atoms on steel surfaces coated with additives, such as chromium and titanium dioxide. These coatings were deposited onto clean steel by radio frequency sputtering. A layer of chromium (about 1.5- μm -thick) or a layer of TiO_2 (less than 0.5- μm -thick) was coated on strips of 4340 steel. SEM examination revealed that the coatings were very adherent to the steel.

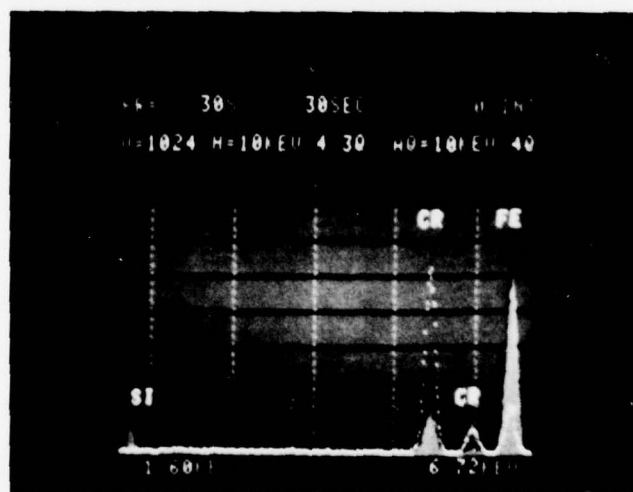
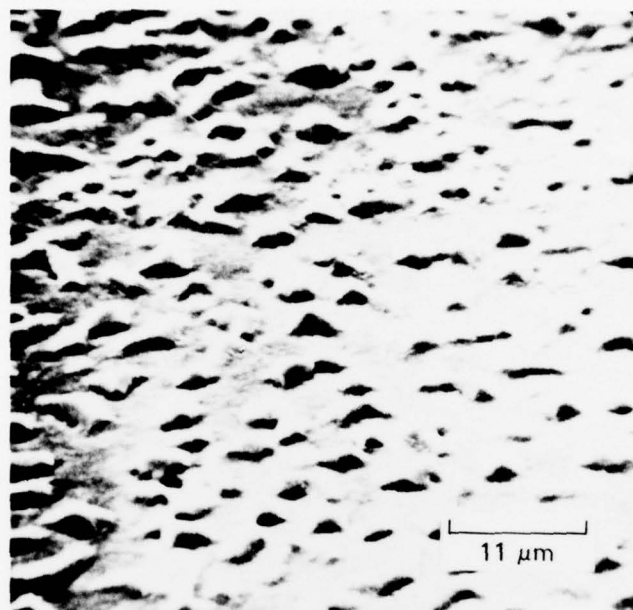
The coated strips were heated to 900°C and exposed to hydrogen atoms for two hours. The hardness of the chromium-plated specimen after exposure was 730 VPHN (R_c 62) and that of the TiO_2 -coated sample was 590 VPHN (R_c 55). The hardnesses of the unreacted, coated specimens were 460 VPHN (R_c 46), that is, the same as the uncoated samples.

SEM analysis of the TiO_2 -coated specimen showed that the exposure to hydrogen atoms did not cause any significant change, either in appearance or in composition as revealed by X-ray fluorescence analysis.

However, the exposure of the chromium plated specimen at 900°C to hydrogen atoms produced pyramid type islands of the iron substrate, penetrating through the chromium plating (see Figure 8). On the basis of our limited data, we decided that further analysis of this specimen and speculation on the cause of the phenomenon was unwarranted.

Application of the Present Results to Gun Barrel Conditions

During firing, the interior surfaces of gun barrels are exposed to high temperatures (~ 3000 K) and high pressures ($\sim 40,000$ psi) for milliseconds.¹ In an average gun tube, the temperature at the bore surface may rise at the rate of 10^6 K sec^{-1} and the pressure rise may be of the order of 10^5 psi sec^{-1} . Hence, most of the processes occurring at the



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FIGURE 8 EFFECT OF HYDROGEN ATOM EXPOSURE (or heating) ON CHROMIUM-PLATED STEEL AT 900°C.

Top figure is the morphology observed in SEM. Bottom figure is X-ray emission from the surface. The broken line represents the emission from the substrate and the solid line represents the emission from top of the islands.

bore surface do not occur under equilibrium conditions. Under such non-equilibrium conditions, the concentration of free radicals is expected to be high; therefore, we studied the effects of some of the free radicals on steel under laboratory steady state conditions.

We have shown that the atomic free radicals are more reactive on gun barrel steel than their molecular counterparts. The surfaces of the steel specimens are affected considerably by these free radicals, even at the low pressure ($\sim 10^{-6}$ atm) used in our study. To quantitatively apply our low pressure results to the actual high pressure conditions in a gun barrel requires extrapolating the data over several orders of magnitude; thus, one can speculate only qualitatively about the effects of free radicals on steel under conditions of gun firing.

Kamdar et al.²⁰ have shown that white layers, which consist of high carbon austenite and hard ϵ -carbide similar to those found in gun barrels, can be produced in the laboratory by pulse heating and quenching steel specimens in a high pressure methane (1000 psi) atmosphere. They concluded that carbon is charged into steel in the high pressure methane atmosphere and that the rapid quenching retains the high temperature austenite phase.

Carbon charging of a steel surface can be greatly enhanced in dissociated methane. Grube and Gay¹⁹ have shown that steel can be case-carburized rapidly in a glow discharge plasma at a methane pressure of 10 to 20 torr and at a substrate temperature of 1050°C. They have found that the carbon absorption rate greatly exceeds the diffusion rate of carbon into steel. The present study confirms the very high activity of dissociated methane even at the low pressure of 0.05 torr. Moreover, the steel substrate need not be situated inside the plasma but can be positioned at some distance downstream. The increased carbon content results in a lower martensite formation temperature²¹ so that an increased amount of austenite is retained by quenching.

A similar phenomenon for nitriding steel is found when dissociated nitrogen gas is used. Studies²² have shown that in a nitrogen plasma

produced in a r.f.-dc field, alloy steels can be nitrided rapidly at a temperature in the range of 500 to 600°C and a white layer of Fe_4N is formed on the surface of steel. Studying the mechanisms involved in ion nitriding, Hudis^{2,3} found that the dc field responsible for nitrogen ion bombardment of the metal surface is necessary for nitrogen incorporation and nitriding. Preliminary experiments conducted in SRI's laboratory have shown that nitrogen atoms produced in a microwave discharge cavity can effectively nitride 4340 steel at 900°C and that ion bombardment is not necessary for nitrogen incorporation.

The present study has shown the efficiency of hydrogen atoms in decarburizing 4340 steel. At 900°C, decarburization is rapid even at a hydrogen atom pressure of 10^{-4} atm, and the kinetics are governed by the diffusion of carbon from bulk to the surface. The present experimental results, obtained by exposing steel specimens at 0.1 torr hydrogen atom pressure for durations of thousands of seconds, must be extrapolated to be the pressure expected in propellant gases during gun firing, that is, to 1 atm hydrogen atom pressure for millisecond durations. It has been shown that formation of a CH_3 radical is rate-determining step^{9,14} in decarburization of austenite by molecular hydrogen, and that the rate is proportional to $p_{\text{H}_2}^{3/2}$. If the formation of CH_3 radical is still the rate-controlling step in the surface reaction of carbon in steel with gaseous hydrogen atoms, then it can be shown that the surface reaction rate would be proportional to p_{H}^3 . If the reaction rate (diffusion-controlled rate) observed at the experimental 0.1 torr pressure is extrapolated to 1 atm hydrogen atom pressure using this cube power relationship, then even when the steel is exposed for millisecond, the decarburization will be limited by solid state carbon diffusion.

Even though decarburized layers have not been found in gun barrels, other potential effects of hydrogen free radicals cannot be ignored. For example, studies of ion nitriding^{2,3} have shown that a plasma of nitrogen-hydrogen mixture is superior to nitrogen plasma alone in

in nitriding steel. The action of hydrogen atoms or ions in nitriding is not established. Two prevalent hypotheses are (1) the reduction of surface oxides by hydrogen atoms, thus providing a clean surface for nitriding, and (2) the reaction of steel with $N_x H_y$ free radicals in nitriding steel. In propellant combustion gases, the formation of such complex free radicals is likely, and nitriding of a gun barrel bore surface by such radicals must be considered. The "white layers" observed on the bore surface have been shown to contain¹ the iron nitrides Fe_2N_x and Fe_4N .

The above discussion is qualitative because of the inability to produce atomic free radicals in a controlled manner at high pressures. Also, the composition of free radicals in propellant combustion gases is not known with certainty. We have shown that free radicals of the gases tested are substantially more reactive with gun barrel steel than their molecular counterparts, even in the limit of very low pressures.

4. CONCLUSIONS

On the basis of our experimental results, we make the following conclusions:

- At 900°C and at a pressure of 0.1 torr hydrogen atoms, 4340 steel is decarburized rapidly. The decarburization is proportional to the square root of the exposure time, and the kinetics of the decarburization are controlled by the diffusion of carbon from bulk to the surface. At 600°C, there is evidence for surface decarburization, but at 400°C the rate is too small to be observed under our experimental conditions.
- Significant amounts of nitrogen are incorporated into 4340 steel strips at 900°C by exposing the strips to gaseous nitrogen atoms.
- Dissociated methane is effective in charging carbon into steel at 900°C, and caused the formation of a carburized layer near the surface.
- Under our experimental conditions (1 torr pressure and 900°C) the changes produced when the steel specimens were exposed to undissociated hydrogen, nitrogen, and methane were found to be negligible.

The results of our study have demonstrated that several atomic and free-radical species in the gaseous state react rapidly with 4340 steel to produce profound changes in composition of the steel and in its mechanical properties. The observed effects indicate that the effects of transient species in gun barrel erosion should be considered with regard to their role in introducing interstitial elements into gun barrel surface layers during firing. Thus studies of the interactions of transient species and free radicals containing N and C would be particularly relevant.

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