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INTERACTION OF METHANE, ETHANE, ETHYLENE, AND ACETYLENE WITH AN IRON (001) SURFACE AND THEIR INFLUENCE ON ADHESION STUDIED WITH LEED AND AUGER

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16. Abstract

Adhesion studies were conducted with iron (001) surfaces in the presence of various adsorbed hydrocarbons: methane, ethane, ethylene, and acetylene. Data indicate that an increase in the number of carbon atoms from 1 to 2 results in a decrease in adhesive forces between metal surfaces. Further, the greater the degree of bond unsaturation, the lower the adhesive force for equivalent surface coverages. All the hydrocarbons adsorbed to clean iron at 20° C, indicating additional activation energy is not required for chemisorption of hydrocarbons to iron. Oxygen and sulfur were found to displace ethylene and acetylene films from an iron surface.

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SUMMARY

Adhesion studies were conducted with iron (001) crystal surfaces in the presence of various hydrocarbon films. The hydrocarbons examined to determine their influence on adhesion were methane, ethane, ethylene, and acetylene. The influence of oxygen and sulfur on adsorbed hydrocarbon films was also examined. Adhesion experiments were conducted with a 3.0-millimeter-diameter iron flat contacting a larger 8.0-millimeter-diameter iron flat with applied loads of from 20 to 350 dynes. Measurements were made at 20° C in a vacuum of 10^{-11} to 10^{-10} torr.

The results of the investigation indicated that methane was not as effective in reducing the adhesion of iron to itself as was ethane. The degree of bond saturation also influenced adhesion. The adhesive forces were greater with ethane than with ethylene; and, in turn, greater with ethylene than with acetylene. With acetylene, adhesive forces were less with a full monolayer of coverage than with a quarter monolayer present. When oxygen and hydrogen sulfide were admitted to ethylene- and acetylene-covered surfaces, displacement of the hydrocarbon by oxygen and sulfur occurred.

INTRODUCTION

Ferrous alloys are the most widely used materials in mechanical components for lubrication systems. Hydrocarbons are the principal lubricants for such surfaces (ref. 1). Alloy constituents in iron can markedly influence its interaction with the lubricant. It is, therefore, desirable to study the nature of lubricant-surface interaction using elemental iron initially. Once the behavior of lubricants in contact with iron is

understood, alloying elements can be added to iron to determine their part in the lubrication of ferrous surfaces.

While hydrocarbons normally contact oxidized ferrous surfaces, nascent metal surfaces are generated during lubrication operation (ref. 2). It is, therefore, of interest to know the nature of the interaction of hydrocarbons with a clean iron surface. This can be accomplished by generating clean iron surfaces in a vacuum and then selectively adsorbing the hydrocarbon to the surface.

Normally, liquid hydrocarbons will contain dissolved oxygen and additives. A principal class of additives in hydrocarbons is sulfur-containing compounds (ref. 3). These additives react with ferrous surfaces under severe mechanical conditions to provide protective sulfide surface films. The exact nature of oxygen and sulfur action on hydrocarbon-covered iron surfaces is not fully understood (ref. 4).

Low-energy electron diffraction (LEED) and Auger emission spectrometer analysis of iron surfaces can assist in the determination of these surface phenomena. LEED provides the capability of determining surface structural changes that take place with surface films present. Auger spectrometer analysis identifies the elements present on the surface.

This investigation was conducted to study (1) hydrocarbon adsorption to a clean iron surface, (2) the influence of hydrocarbon films on the adhesion of iron to itself, and (3) the stability of these films in the presence of oxygen and sulfur. The hydrocarbon gases adsorbed were methane, ethane, ethylene, and acetylene. The latter two gases were used to determine the influence of bond saturation. Simple low-molecular-weight hydrocarbons were used to facilitate adsorption studies and to simplify interpretation. Adhesion studies were conducted with a 3.0-millimeter-diameter iron flat contacting a larger 8.0-millimeter-diameter surface at applied loads of from 20 to 350 dynes. Both iron surfaces were single crystals with the (001) face parallel to the surface.

MATERIALS

The specimens were of triple-zone-refined iron with the following impurities in ppm: carbon, 8; oxygen, 7; nitrogen, 7; calcium, 2; nickel, 1; sulfur, 10; and all others in concentrations of less than 1 ppm. The methane, ethane, and ethylene gases were all reagent-grade, having a minimum purity of 99.99 percent. Acetylene had a minimum purity of 99.5 percent. The oxygen gas used was reagent-grade, 99.995 percent minimum purity.

APPARATUS

The apparatus used in these studies is shown schematically in figure 1. The single-crystal surface mounted in the center of the chamber could be rotated 360°. This rotatability allowed for the making of adhesion measurements on the crystal surface shown in figure 1, then rotating the crystal and obtaining both an Auger analysis and a LEED pattern from the crystal surface in the adhesion contact area. The crystal could also be moved in the lateral and vertical directions.

The crystal specimen was supported in the chamber by means of two metal rods (insulated) which were used to resistance heat the crystal. A 100-ampere alternating-current power supply was used for resistance heating.

The 3.0-millimeter-diameter, flat-ended, iron single-crystal fiber specimen, which contacted the single-crystal metal surface, was mounted in a stainless-steel holder which was, in turn, mounted to a 1.5-millimeter-diameter stainless-steel beam. The beam was mounted in a bearing-containing yoke. At the end of the beam beyond the pivot point, and opposite the smaller cylindrical specimen, was a small permanent magnet. Outside the chamber wall were two electromagnets. The permanent magnet and electromagnets were positioned in such a manner as to have like poles facing each other. A variation in the current applied to the magnets could be used to move the beam.

The current applied to the electromagnets was calibrated in terms of the force applied in the adhesion experiments. Load applied to the surfaces in contact was measured, as was the force required to separate the crystal surfaces.

The basic LEED and Auger systems were obtained commercially. The LEED electron optics and the vacuum system were of the standard type used by those engaged in LEED studies. The Auger spectrometer gun was located at a position 90° from the LEED gun (see fig. 1). The electron optics of the LEED was of the Varian three-grid type with a fourth grid added for Auger analysis. The LEED beam diameter was 0.6 millimeter. The vacuum system consisted of vacsorb pumps, an iron pump, and a sublimation pump. The system pressure was measured with a nude ion gage, and all experiments were conducted with the vacuum system in the range of pressures from 10^{-11} to 10^{-10} torr. No cryopumping was used.

EXPERIMENTAL PROCEDURE

The iron crystals used in this study were cut from a rod into specimens: one having a diameter of 8.0 millimeters and a thickness of 3.0 millimeters, and a length of 6.0 millimeters. The steps used to prepare the iron surfaces for adsorption studies are

outlined in reference 1. The crystal orientations were checked after electropolishing, and the specimens were placed in a vacuum tube furnace. They were heated to 600° C and held under vacuum for 24 hours, at which time hydrogen gas was admitted. The system was then reevacuated. This procedure was repeated for a 2-week period. The purpose of heating was to attempt to drive carbon and sulfur from the bulk to the surface. Hydrogen was admitted to remove the carbon and sulfur from the surface by reaction. After this treatment, the crystals were held in vacuum at 800° C for a prolonged period to remove hydrogen from the iron.

When this process was complete, the crystals were removed from the vacuum tube furnace, repolished, and electropolished. They were then placed into the apparatus for adhesion, LEED, and Auger studies.

The vacuum system was evacuated to 10^{-11} torr, and the crystals were ion bombarded for 12 hours after the system pressure was raised to 8.0×10^{-5} torr with argon gas. The ion gun voltage was 250 volts. The crystals were then heated to 250° C for 10 minutes to remove trapped argon, and a clean iron surface for adsorption studies was obtained, as indicated by LEED and Auger analysis.

RESULTS AND DISCUSSION

Clean Iron Surface

Adhesion studies have been conducted with clean iron (001) and (011) surfaces; the results of such studies were reported in references 1 and 2. With applied loads of 20 dynes, for a 3.0-millimeter-diameter iron flat contacting a larger flat of the same orientation, the adhesive forces exceeded 400 dynes (the limit of the measuring capabilities of the apparatus of fig. 1).

Figure 2(a) is a LEED photograph of a clean iron (001) surface before adhesive contact. After adhesive contact, the diffraction spots not shown become elongated because of lattice strain produced as a result of adhesive contact. The lattice strain results principally from tensile fracture of the adhesive junction. An Auger analysis was made of the iron surface before and after adhesive contact. The trace taken after adhesive contact is presented in figure 3. The peaks detected are for iron. The absence of any peaks in the trace for other elemental materials reflects the cleanliness of the iron surfaces. The trace was basically the same before and after adhesive contact.

Methane-Covered Surface

Methane gas was admitted to the vacuum system containing the clean iron surface. After an exposure of 10 Langmuirs (1 Langmuir = 10^{-6} torr-sec), a 2×2 type of structure developed on the clean iron surfaces as indicated by the LEED photograph of figure 2(b) (see ref. 5 for description of 2×2 structure). The diffraction spots caused by iron are in the same approximate orientation as the spots of figure 2(a). They are at the four corners of the pattern in figure 2(b). Intermediate diffraction spots appear at half spaces between the iron diffraction spots. Because of the reciprocal nature of diffraction, methane has twice the lattice spacing in figure 2(b) of the iron in both the [10] and [11] directions.

Each site occupied by the methane appears to give an elongated double diffraction spot rather than a single sharp spot. The elongation occurs in the same crystallographic direction. With the chemisorption of oxygen in an earlier study, sharp diffraction spots were obtained (refs. 6 and 7). Oxygen dissociates and chemisorbs atomically. Methane chemisorbs as a molecule, and the diffuse nature of the diffraction spots may reflect the effects of hydrogen (ref. 8).

Auger analysis of the iron surface revealed a carbon peak, indicating the presence of methane. The authors of reference 3 found that to achieve adsorption of methane, the iron surface had to be heated (170° C). In this investigation the iron was at 20° C when chemisorption occurred, indicating that the addition of energy to activate the adsorption process is not necessary for a clean surface. Chemisorption of methane to clean iron will occur at 20° C.

Adhesive contact was made to the 2×2 methane structure, and the results obtained are presented in table I. The adhesive force exceeded 400 dynes with an applied load of only 20 dynes, indicating that very strong adhesion of iron can occur even in the presence of a methane film. The surface was exposed to methane in the range of 10 to 100 Langmuirs with no difference in adhesion results. Exposures to 1000 Langmuirs resulted in no basic change in the LEED pattern of figure 2(b). Further, no notable change in the Auger peak for carbon was observed. It appears that at 20° C, a quarter of a monolayer of methane is all that an iron (001) surface will accept.

With a quarter monolayer of coverage (2×2 methane structure of fig. 2(b)), considerable iron-iron bonding can occur and result in the high adhesive force indicated in table I. In reference 1, and Fe(001) C(2×2)-O structure resulted in adhesive forces of 120 dynes. Thus, a quarter of a monolayer of oxygen is more effective in inhibiting the adhesion of iron than is a quarter of a monolayer of methane. The admission of oxygen to the methane-covered surface resulted in the complete displacement of the methane by oxygen. This preferential adsorption of oxygen will be discussed in more detail in reference to results obtained with ethylene and acetylene.

TABLE I. - EFFECT OF VARIOUS HYDROCARBONS

ON ADHESION OF IRON (001) SURFACES

Gas adsorbed to iron (001)	Exposure to develop a 2 × 2 structure, Langmuirs	Adhesion force,[a] dynes (or 10^{-5} N)
Methane (CH_4)	10 to 100	>400
Ethane (C_2H_6)	1000	280
Ethylene (C_2H_4)	500 to 1000	170
Acetylene (C_2H_2)	1	80

[a]Applied load, 20 dynes; contact time, 10 sec; ambient pressure, 10^{-10} torr at 20° C.

Ethane-Covered Surface

Ethane was next admitted to a clean iron (001) surface. In order to develop a surface coverage equivalent to that obtained with methane, an exposure of 1000 Langmuirs was required. In reference 8 a temperature of 70° C was necessary to achieve the required activation energy for iron to chemisorb ethane. Ethane adsorption did occur at 20° C in the present study. These results indicate that the additional energy is not necessary to accomplish chemisorption. Further, in reference 8, ethane was found to chemisorb more readily than methane. The results of this investigation indicate that methane chemisorbs more readily.

Adhesion experiments were conducted with surfaces containing a chemisorbed layer of ethane on iron. With an applied load of 20 dynes, an adhesive force of 280 dynes was recorded in table I. These high adhesive forces indicate that, as with methane, considerable iron contact occurs across the interface. The adhesive force was less than that observed with methane, indicating that the larger ethane molecule affords greater protection of the iron surface.

Adhesion force measurements were also made as a function of applied load. The results obtained in these experiments are presented in figure 4. The data of figure 4 indicate that the adhesive force is relatively independent of applied loads to 250 dynes. Above 250 dynes, the adhesive force increased markedly. In these experiments, ethane is at the interface. Deformation may not be sufficient at loads below 250 dynes to result in any significant increase in metal-to-metal contact. At 300 and 350 dynes, suf-

ficient deformation may occur to cause an increase in the metal-to-metal contact, thereby increasing the adhesive force.

The admission of oxygen to the ethane-covered surface resulted in complete removal of the ethane from the iron surface. These results indicate that hydrocarbons can be displaced from metal surfaces by more active gases. This will be discussed in greater detail in reference to results obtained with ethylene and acetylene.

Hydrogen has been found to displace ethane from a nickel surface (ref. 9). Hydrogen, in the present study, did not displace ethane from iron. If the ethane film were heated to 500° C for 15 minutes, ethane desorbed. No carbon peak was detected by Auger analysis of the resulting surface. This result indicates that the ethane, on heating, does not dissociate to hydrogen and carbon completely. If it did, a carbon residue should have been left on the iron surface. The fact that it was not indicates that desorption of a hydrocarbon took place. There may be a stepwise dissociation with the loss of some, but certainly not all, the hydrogen from the molecule.

Ethylene-Covered Surface

Ethylene was next chemisorbed to iron. The LEED pattern obtained from the iron (001) surface after exposure to 500 Langmuirs of ethylene is presented in figure 5(a). The basic pattern is not markedly different from that obtained with methane in figure 2(b). Increasing the exposure to 1000 Langmuirs resulted in no change in the LEED pattern.

An Auger analysis of the surface of figure 5(a) is presented in figure 6. The presence of a carbon peak at 270 electron volts is indicative of the ethylene on the iron surface.

Adhesion measurements were made between the ethylene-covered iron surfaces under the same conditions with which methane and ethane were examined. The results obtained are presented in table I. The adhesion force of iron to itself in the presence of ethylene was less than with ethane or methane.

With hydrocarbons other than methane, the question arises as to whether C-H or C-C bonds are broken to achieve attachment to the metal surface. Hayward and Trapnell (ref. 10) indicate that for ethane it is the C-C bonds. The mechanism of attachment for ethylene would be at two points

$$\begin{array}{l} CH_2{=}CH_2 \\ Fe{-}{-}Fe \end{array} \longrightarrow \begin{array}{l} CH_2{-}{-}CH_2 \\ \;\;|\qquad\;\; | \\ Fe{-}{-}Fe \end{array}$$

Both carbon atoms bond directly to the iron. Ethylene will undergo self-hydrogenation to ethane at temperatures below 60° C (refs. 11 and 12). Above 60° C, methane (CH_4) begins to form; and at temperatures in excess of 200° C, methane is the only product liberated, with elemental carbon remaining on the surface (ref. 11). The ethylene-covered surface was heated to 500° C to dissociate the adsorbed ethylene. An Auger spectrometer scan of the surface was made after the specimen cooled to room temperature, and the trace is presented in figure 7. Examination of figure 7 indicates considerable carbon remained on the iron surface. The 500° C is considerably above the 200° C found necessary in reference 11 to dissociate ethylene to methane and elemental carbon. The results of figure 7 confirm the observation that elemental carbon will remain on the surface.

Adhesion experiments were made to the iron surface containing the elemental carbon. Adhesive forces measured were slightly greater than that observed for the surfaces with ethylene present. This may have occurred as a result of two factors: (1) hydrogen was no longer present on the surface, thereby allowing a closer approach and bonding of iron not bonded to carbon; and (2) the total percentage of the surface covered by a contaminant film may have been reduced. Some of the carbon is lost from the surface in the liberation of methane as a decomposition product.

Acetylene-Covered Surface

Acetylene was chemisorbed to a clean iron (001) surface. With acetylene, an exposure of only 1.0 Langmuir was necessary to obtain a 2×2 surface structure. The 2×2 structure obtained with the adsorption of acetylene is shown in the LEED photograph of figure 5(b). The diffraction spots obtained with acetylene were much sharper than those obtained with methane, ethane, and ethylene.

Adhesive contact was made to the iron surface containing acetylene, and the adhesive force measured in dynes (1 dyne = 10^{-5} N) is presented in table I. In table I, the lowest adhesive force was measured with acetylene chemisorbed to the iron surface. With acetylene adsorption, each adsorbed molecule of acetylene occupies four iron sites (ref. 10). Thus, with the adsorption of acetylene a greater number of iron surface atoms can be bonded to carbon than with ethane or ethylene. This reduces the total amount of iron-iron contact across the interface with equivalent surface coverage. As expected, the adhesive force was also reduced (table I).

Acetylene was adsorbed on iron with varying total acetylene exposures. LEED structure, Auger relative intensities, and adhesive forces for three acetylene exposures are presented in table II. With both 1 and 10 Langmuirs of acetylene, the LEED structure remained basically a 2×2 structure. The Auger peak intensities relative to one of

TABLE II. - ADSORPTION OF ACETYLENE ON IRON (001)

SURFACE AND ITS INFLUENCE ON ADHESION

Acetylene exposure, Langmuirs	LEED pattern observed	Auger relative intensities, I_C/I_O	Adhesion force,[a] dynes (or 10^{-5} N)
1	2 × 2	0.75	80
10	2 × 2	.76	80
100	1 × 1	.98	40

[a]Applied load, 20 dynes; contact time, 10 sec; ambient pressure, 10^{-10} torr at 20° C.

the iron peaks were relatively unchanged. Adhesion forces measured at both exposures were the same.

When the iron surface was exposed to 100 Langmuirs of acetylene, a new (1 × 1) LEED structure developed and the relative intensity of the carbon peak to the iron peak increased.

The difficulty with the preceding proposed mechanism for the bonding of acetylene to iron is that it does not agree with the LEED pattern of figure 5 which is shown in the suggested arrangement for the acetylene on the iron (001) surface in figure 8. An examination of figure 8 indicates that the acetylene is chemisorbed with the carbons alined in the [11] direction and bonded to two iron atoms lying in that direction. From the LEED pattern and the proposed adsorption model, it would appear that the carbon of the acetylene can bond to only two iron atoms. These differences can be reconciled if the bond forces are sufficiently strong and long-ranged to result in bonding of the carbon atoms to iron atoms in both ⟨11⟩ directions. This would give rise to the bonding of each acetylene molecule to four iron atoms, commensurate with the earlier proposed mechanism.

Adhesive forces measured with the new structure, representing more acetylene adsorbed to the surface, were less. In table II the adhesive force at 100 Langmuirs exposure was 40 dynes or one-half the value obtained at 1 and 10 Langmuirs exposure. Further exposure to 1000 Langmuirs resulted in basically no change from the results obtained at 100 Langmuirs exposure.

Adhesive force for iron to itself after exposure to 1000 Langmuirs of acetlyene was measured as a function of applied load, and the results obtained are presented in figure 9. At applied loads to 150 dynes, the adhesive force was essentially unchanged for the reasons cited earlier in reference to the data obtained in figure 4 with ethane. With application of loads greater than 150 dynes, adhesive force increased with applied load.

These results are believed to reflect the increase in metal-to-metal contact with increasing loads.

If the data of figure 9 are compared to those of figure 4 with ethane present on the surface, it can be seen that, at all loads investigated, acetylene afforded lower adhesive energy of the surfaces than did ethane. The data of table I together with those of figures 4 and 9 indicate that the degree of bond unsaturation in a hydrocarbon influences adhesion. The greater the number of carbon-to-carbon bonds, the lower the adhesive force for equivalent surface coverage.

Acetylene will undergo some degree of self-hydrogenation to form ethylene on metal surfaces (ref. 13). The data of this study indicate that, though this may occur to some degree, considerable differences in adhesive behavior exist for iron in the presence of acetylene and ethylene.

In practical lubrication systems, oxygen is frequently available for interaction with hydrocarbon-covered iron alloy surfaces. It is of interest to know what type of interaction will occur. Experiments were therefore conducted to determine the effect of oxygen on an iron (001) surface covered with ethylene or acetylene.

Oxygen was bled into the vacuum system with an ethylene film present on the iron surface, and Auger spectra were taken at various oxygen exposures. Figure 10 presents the Auger traces obtained. At an oxygen exposure of 1 Langmuir (fig. 10(a)), oxygen chemisorbs to the surface, as indicated by the presence of oxygen in the trace. With further exposure to 10 Langmuirs (fig. 10(b)), the oxygen peak grows. When the oxygen exposure was taken to 100 Langmuirs, the carbon peak disappeared completely (fig. 10(c)), indicating that the ethylene was completely displaced from the iron surface by oxygen. The hydrocarbon must have been completely displaced rather than simply buried by adsorbing oxygen because, if the hydrocarbon were still present, a carbon peak should be detected. The iron substrate in figure 10(c) is readily detected; anything above it should also be detected.

The effect of oxygen exposure on the Auger carbon peak was measured for both ethylene- and acetylene-covered surfaces, and the results obtained are presented in figure 11. In figure 11, the relative intensity of the carbon peak to the oxygen peak is plotted as a function of oxygen exposure in Langmuirs. As was indicated by the data of figure 10(c), the ethylene film is completely displaced from the iron surface by the oxygen at 100 Langmuirs.

In figure 10, oxygen exposures to 1000 Langmuirs did not result in complete displacement of the acetylene film. At oxygen exposures to 100 Langmuirs, very little displacement of acetylene occurred. The data of figure 10 indicate that acetylene is more resistant to displacement from an iron surface by oxygen than is ethylene.

Sulfur is another element of interest with respect to its interaction with hydrocarbon-covered surfaces. Sulfur compounds are frequently added to hydrocarbons

to provide protective sulfide surface films. Some experiments were conducted to determine if the sulfur-containing gas hydrogen sulfide could displace a hydrocarbon film, as oxygen did with ethylene. Ethylene-covered iron was exposed to various amounts of hydrogen sulfide. The sulfur-containing gas was found to displace the ethylene just as oxygen did.

The Auger trace of figure 12 was obtained after an ethylene-covered iron (001) surface was exposed to 1000 Langmuirs of hydrogen sulfide. The Auger trace was taken on a less-sensitive scale than earlier traces presented herein because, at the sensitivity used in the other traces, the sulfur peak was so large that it went off the ordinate scale. The sulfur peak indicates that sulfur was obviously present on the iron surface and that it had nearly completely displaced the hydrocarbon.

The chemisorption of hydrogen sulfide on an iron surface occurs dissociatively at 20° C with the liberation of hydrogen (refs. 14 and 15). Thus, in figure 12, when the hydrocarbon is displaced by the hydrogen sulfide, all that remains chemisorbed to the iron surface is sulfur.

CONCLUSIONS

Based upon the data obtained in this investigation with the adsorption of various hydrocarbons on an iron (001) surface and the influence of these gases on adhesion as well as the influence of oxygen and hydrogen sulfide on some of these chemisorbed gases, the following conclusions are drawn:

1. The greater the degree of bond unsaturation, the more strongly the hydrocarbon is chemisorbed to iron. This results in a decrease in the adhesion of iron to itself. With ethane, ethylene, and acetylene under equivalent conditions of surface coverage, the binding energy of the hydrocarbon to iron was greatest; and adhesive forces were least when acetylene was present on the iron surface.

2. With equivalent surface coverage, two-carbon-atom ethane gave lower adhesive force for iron in contact with itself than did methane, which contains a single carbon atom.

3. The adhesive force of iron to itself decreased with an increase in surface coverage of acetylene. With a quarter of a monolayer, the adhesive force was twice the value obtained with a full monolayer of surface coverage.

4. Chemisorption of the hydrocarbons methane, ethane, ethylene, and acetylene to iron occurred at 20° C; and no additional activation energy was necessary to achieve chemisorption, contrary to what has been previously indicated in the literature.

5. The admission of oxygen to iron surfaces covered with ethylene or acetylene resulted in the displacement of the hydrocarbon from the iron surface. With ethylene,

100 Langmuirs of oxygen was sufficient to result in a complete displacement of ethylene from the surface.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 25, 1970,
129-03.

REFERENCES

1. Bisson, Edmond E.; and Anderson, William J.: Advanced Bearing Technology. NASA SP-38, 1964.
2. Bowden, F. P.; and Tabor, D.: The Friction and Lubrication of Solids. Vol. 1. Clarendon Press, Oxford, 1950.
3. Prutton, C. F.; Turnbull, D.; and Dlouhy, G.: Mechanism of Action of Organic Chlorine and Sulphur Compounds in Extreme-Pressure Lubrication. J. Inst. Petroleum, vol. 32, no. 266, Feb. 1946, pp. 90-118.
4. Swanson, L. W.; et al.: Literature Review of Adsorption on Metal Surfaces, Vol. 1. Field Emission Corp. (NASA CR-72402), July 27, 1967.
5. Wood, Elizabeth A.: Vocabulary of Surface Crystallography. J. Appl. Phys., vol. 35, no. 4, Apr. 1964, pp. 1306-1312.
6. Buckley, Donald H.: Effect of Sulfur, Oxygen, and Hydrogen Sulfide Surface Films on the Adhesion of Clean Iron. NASA TN D-5689, 1970.
7. Buckley, D. H.: LEED and Auger Studies of Effect of Oxygen on Adhesion of Clean Iron (001) and (011) Surfaces. NASA TN D-5756, 1970.
8. Wright, P. G.; Ashmore, P. G.; and Kemball, C.: Dissociative Adsorption of Methane and Ethane on Evaporated Metal Films. Trans. Faraday Soc., vol. 54, 1958, pp. 1692-1702.
9. Selwood, P. W.: The Mechanism of Chemisorption: Ethylene and Ethane on Nickel. J. Am. Chem. Soc., vol. 79, no. 13, July 5, 1957, pp. 3346-3351.
10. Hayward, D. O.; and Trapnell, B. M. W.: Chemisorption. Second ed., Butterworths Publ., 1964.
11. McKee, Douglas W.: Catalytic Decomposition of Ethylene on Nickel. Nature, vol. 192, 1961, pp. 654-655.

12. Beeck, Otto: Catalysis - A Challenge to the Physicist. Rev. Mod. Phys., vol. 17, no. 1, Jan. 1945, pp. 61-71.

13. Douglas, John E.; and Rabinovitch, B. S.: Some Catalytic Exchange and Hydrogenation Reactions of Acetylene and Ethylene. J. Am. Chem. Soc., vol. 74, no. 10, May 20, 1952, pp. 2486-2489.

14. Roberts, M. W.; and Ross, J. R. H.: Kinetics of the Dissociation of Hydrogen Sulphide by Iron Films. Trans. Faraday Soc., vol. 62, 1966, pp. 2301-2308.

15. Saleh, J. M.; Kemball, C.; and Roberts, M. W.: Interaction of Hydrogen Sulphide With Nickel, Tungsten and Silver Films. Trans. Faraday Soc., vol. 57, 1961, pp. 1771-1780.

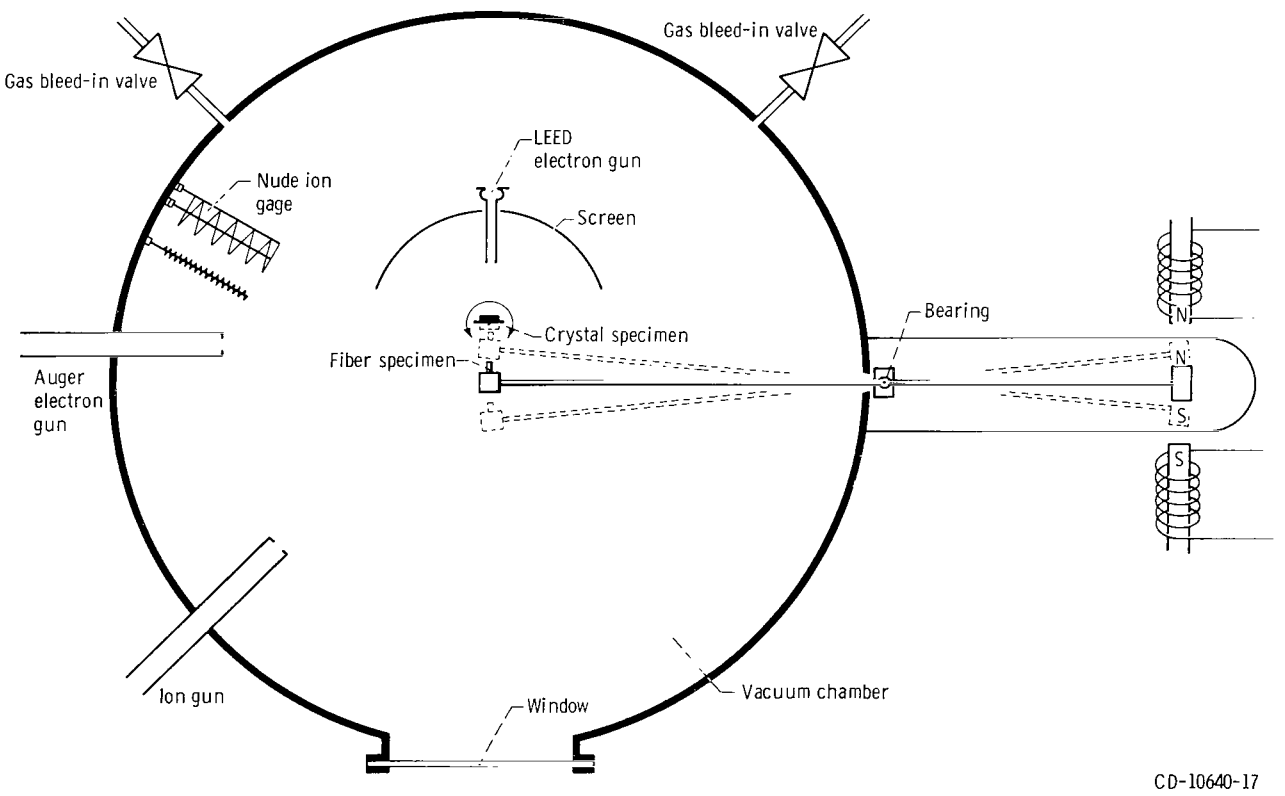
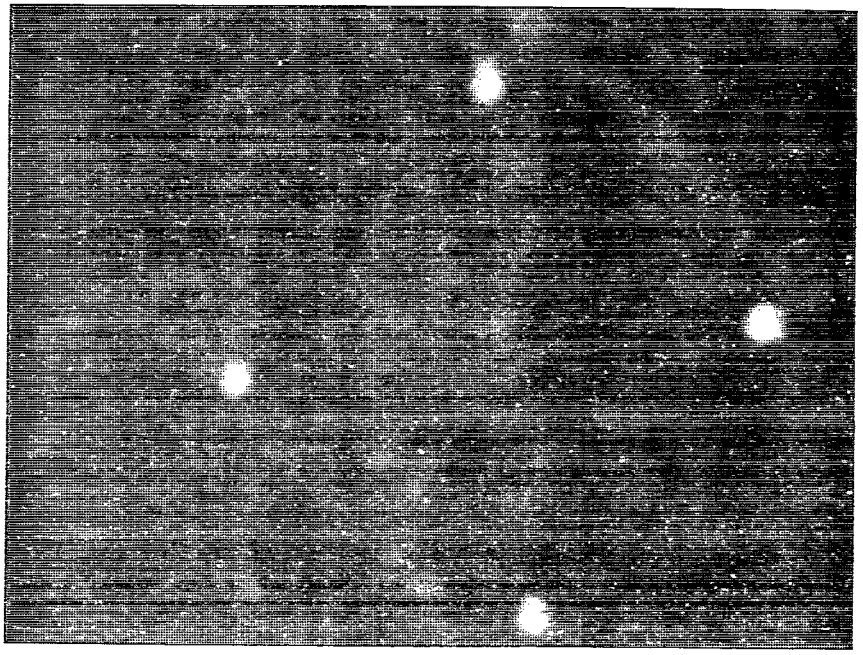
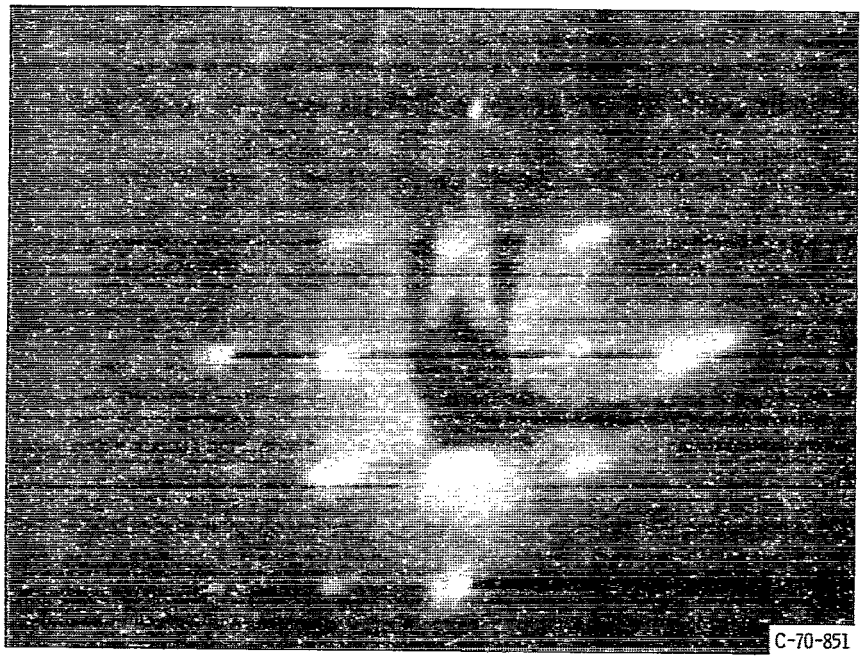


Figure 1. - Low-energy electron-diffraction (LEED) adhesion apparatus.



(a) Clean iron (001) surface.



(b) Methane-covered iron (001) surface.

Figure 2. - LEED patterns for an iron (001) surface in the clean state and with a monolayer of methane present.

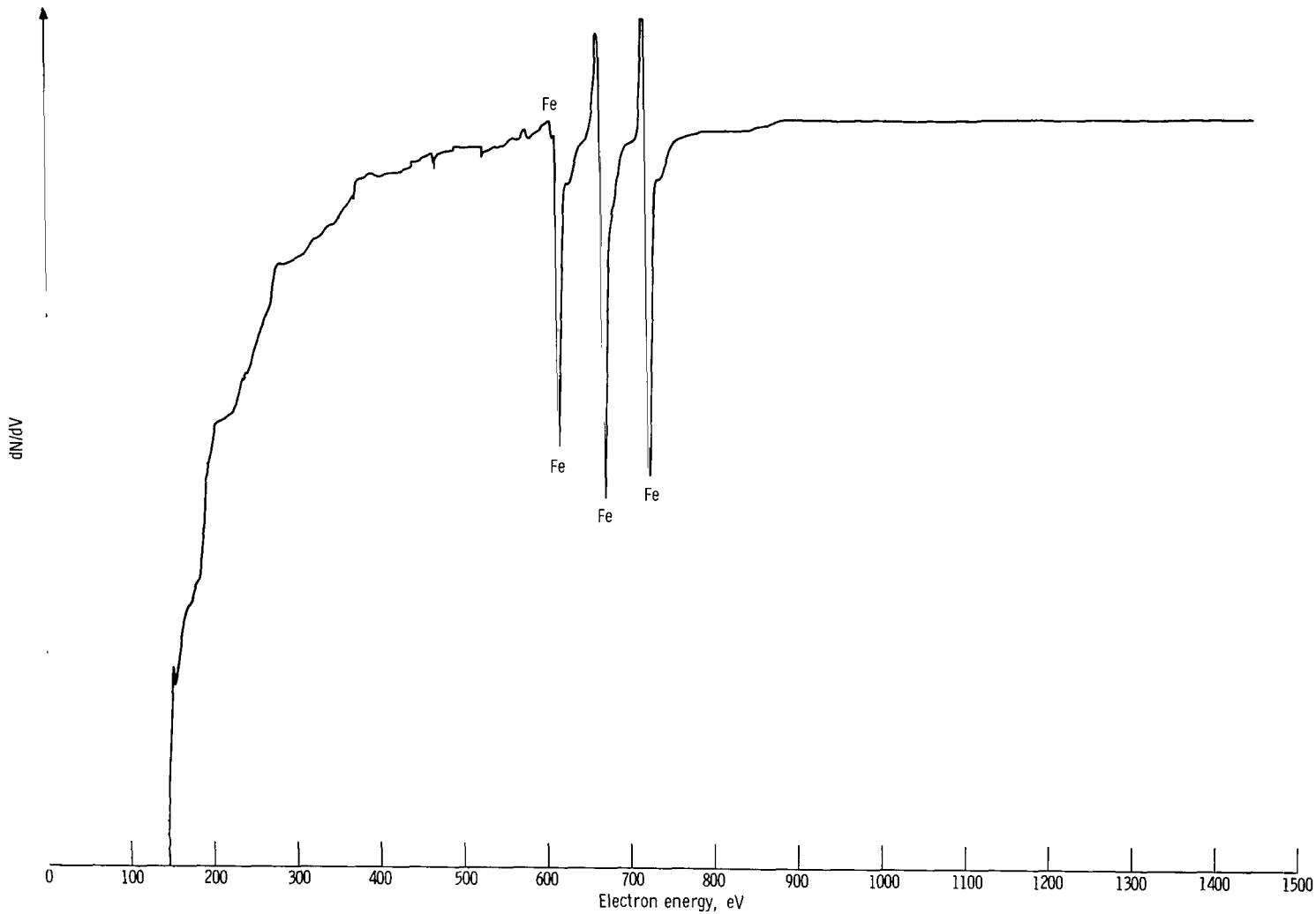


Figure 3. - Auger electron spectrometer analysis of an iron (001) surface after adhesive contact with an iron (001) surface.

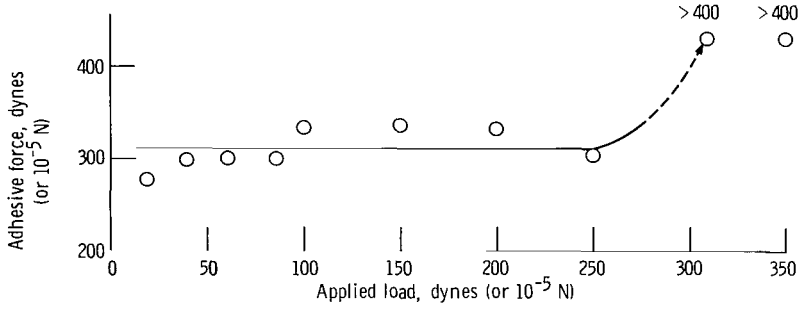
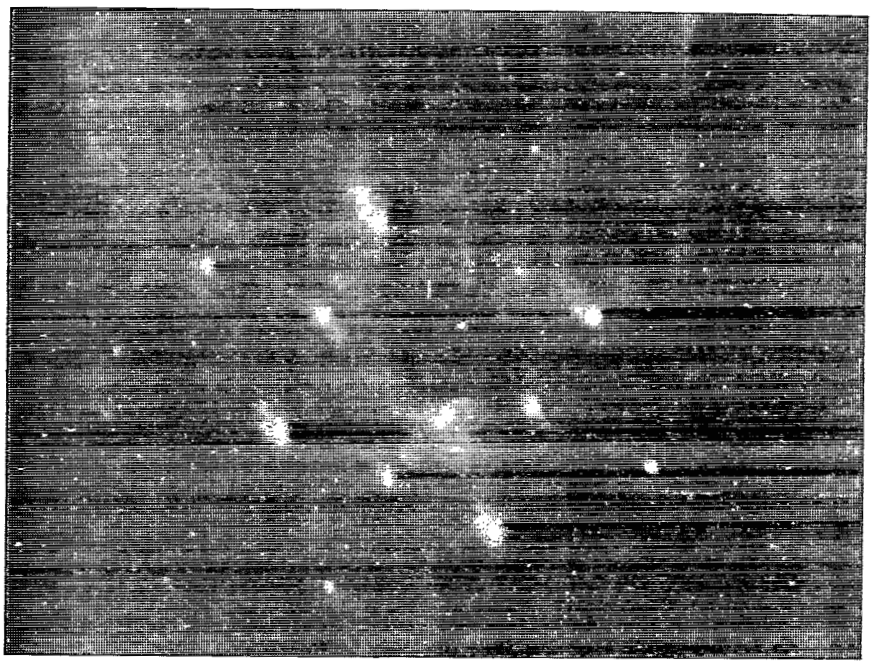
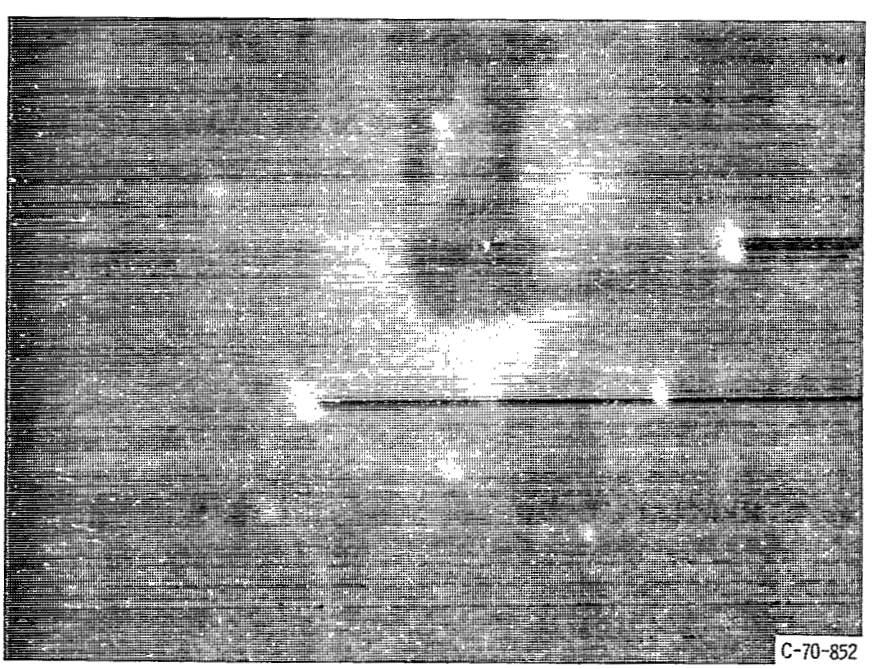


Figure 4. - Adhesion force at various applied loads for an iron (001) surface in contact with an iron (001) surface, where both surfaces are covered with ethane (H_3C-CH_3). Contact time, 10 seconds; temperature, 20° C; ambient pressure, 10^{-10} torr.



(a) Ethylene-covered iron (001) surface.



(b) Acetylene-covered iron (001) surface.

Figure 5. - LEED patterns for an iron (001) surface with ethylene and acetylene present.

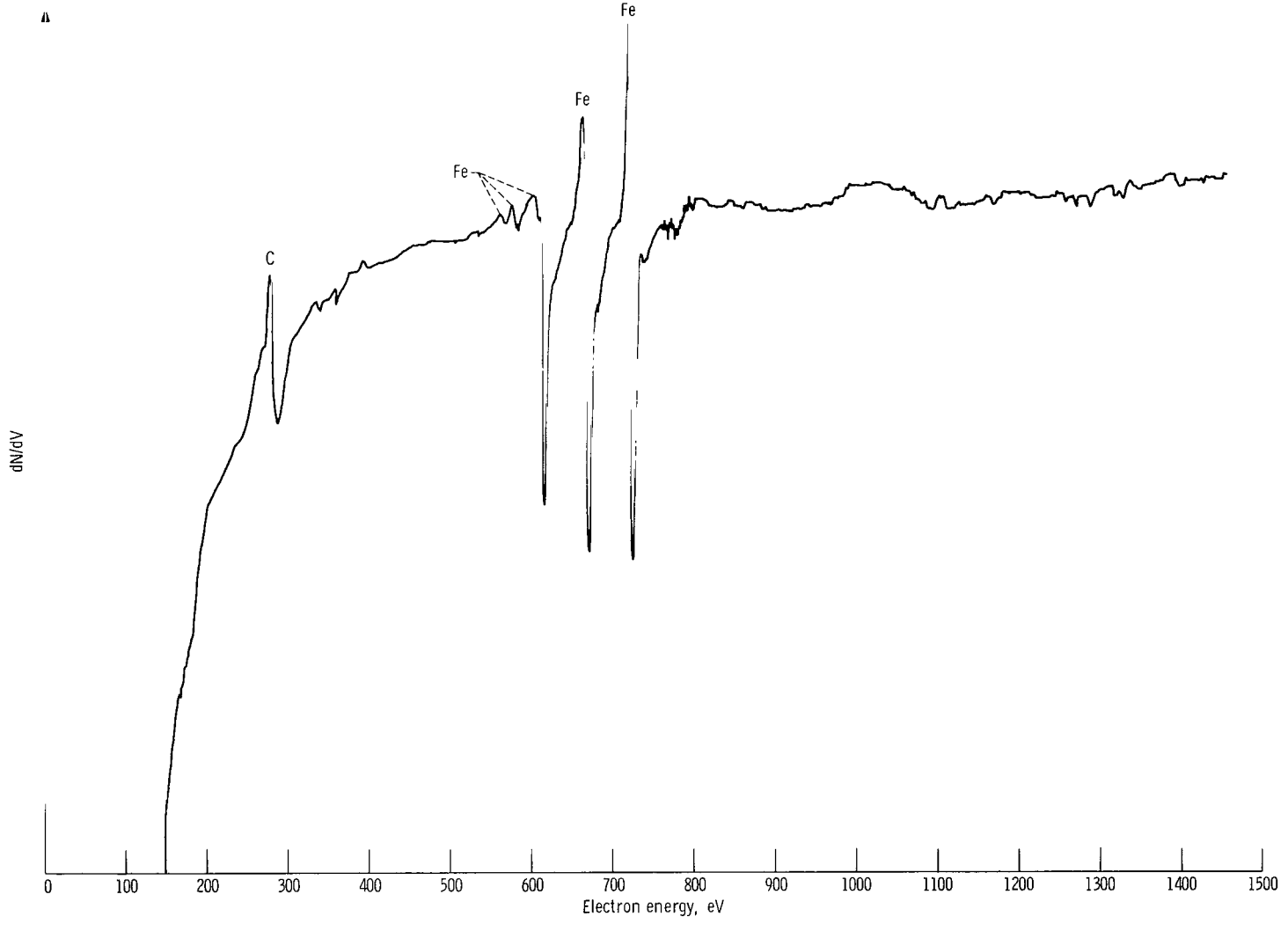


Figure 6. - Auger electron spectrometer analysis of an iron (001) surface with ethylene present.

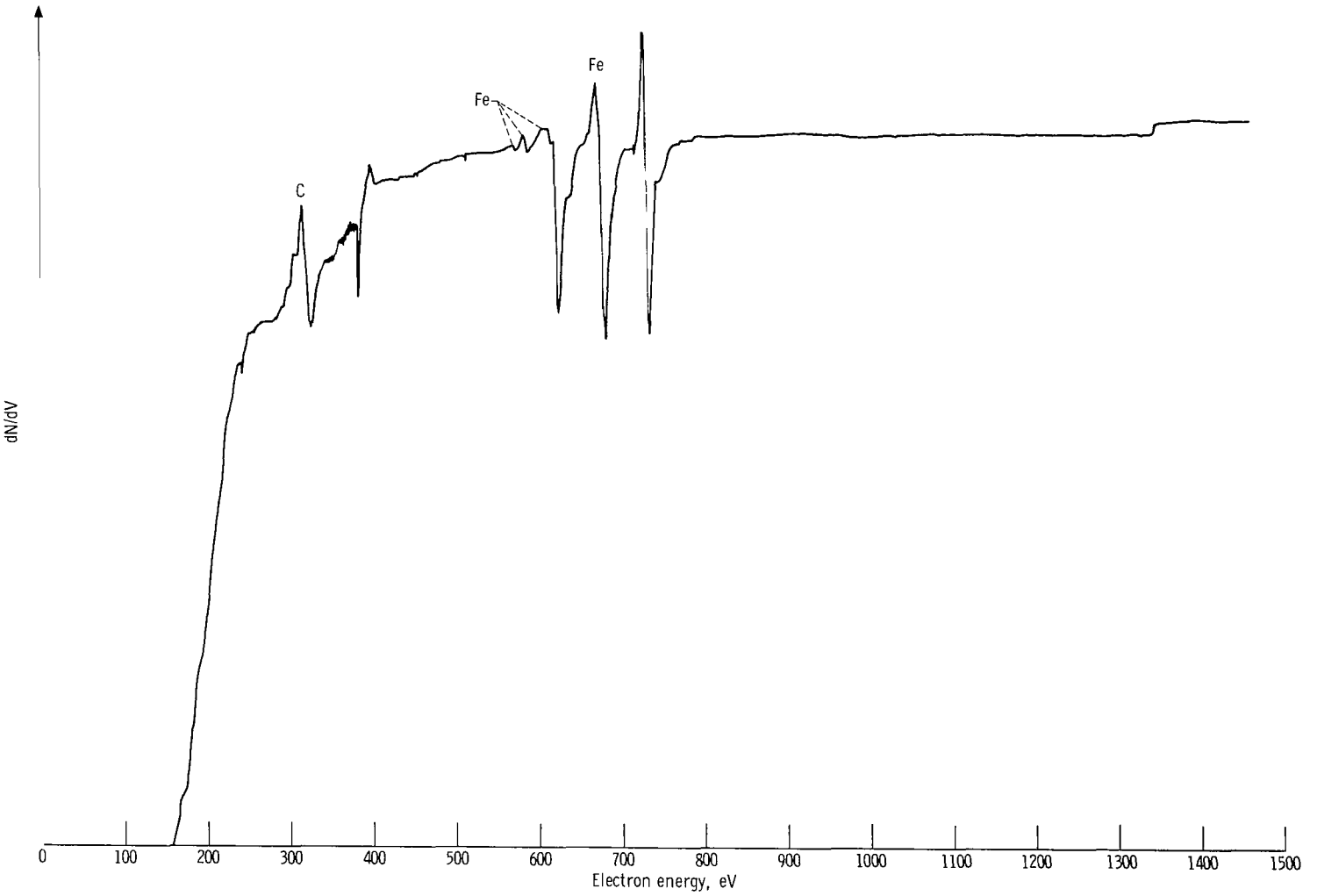


Figure 7. - Auger electron spectrometer analysis of an iron (001) surface with ethylene, after heating to 500° C.

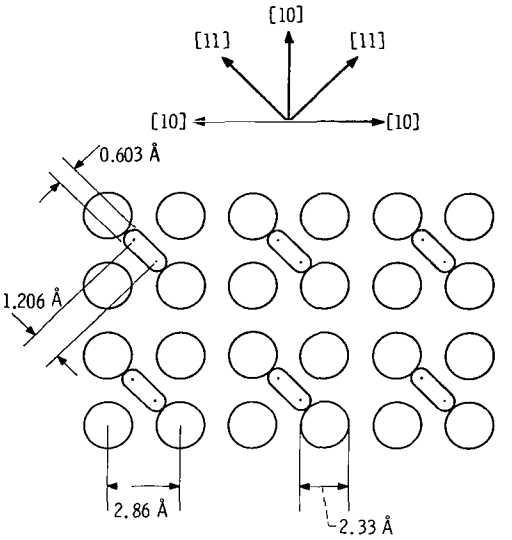


Figure 8. - Suggested model for adsorption of acetylene on an iron (001) surface, producing 2x2 structure.

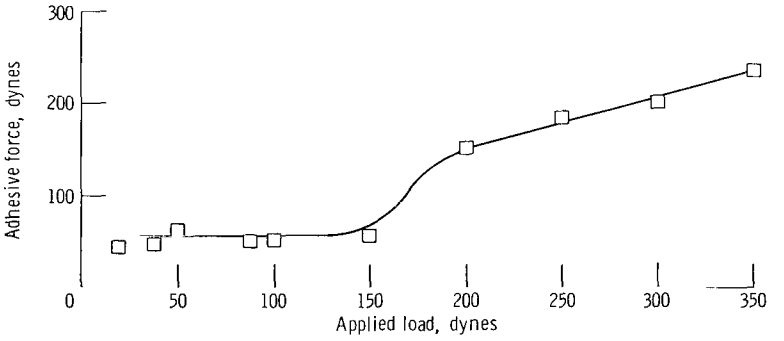
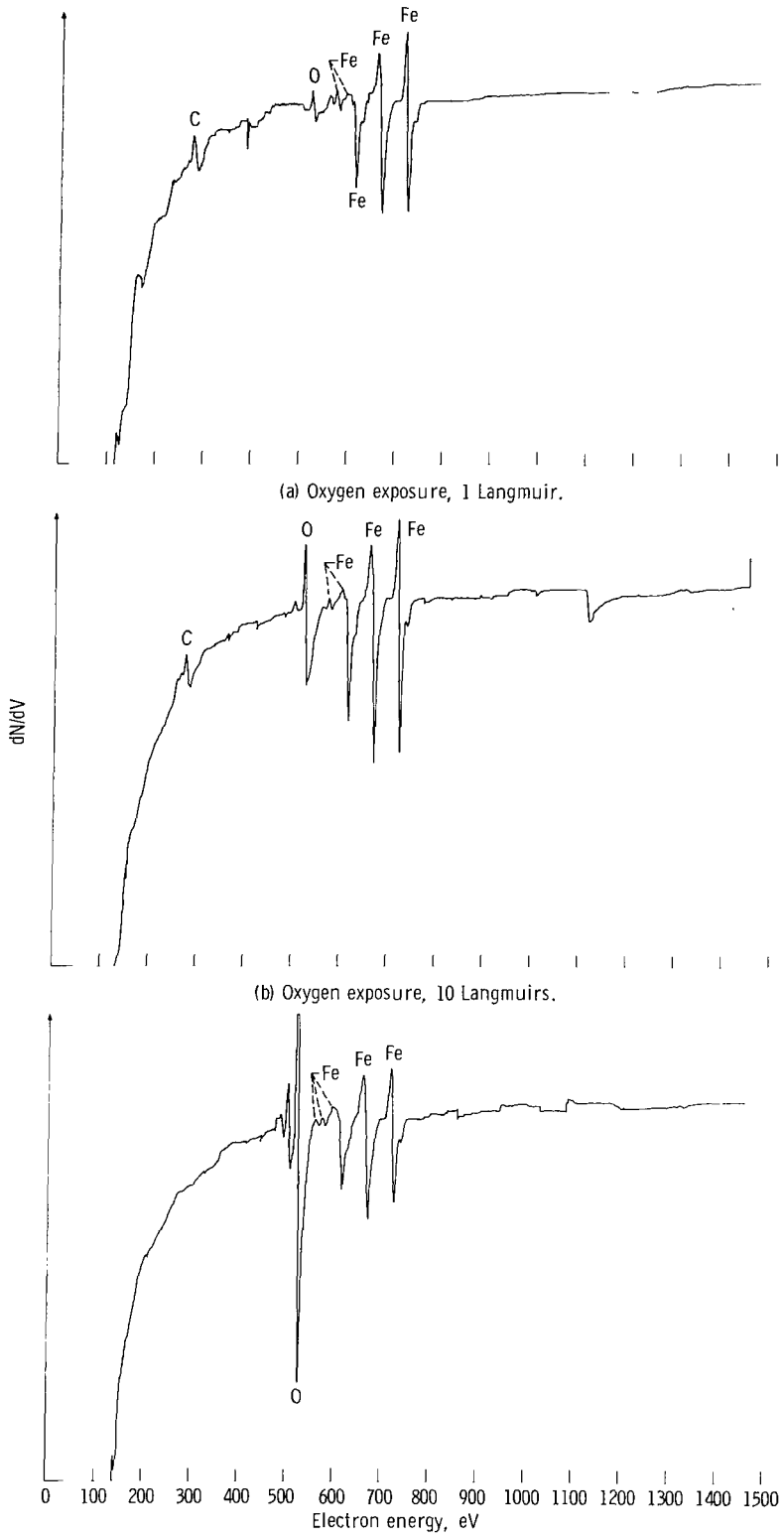


Figure 9. - Adhesion force for an iron (001) surface in contact with an iron (001) surface, where both surfaces are covered with a monolayer of acetylene (HC ≡ CH). Contact time, 10 seconds; temperature, 20° C; ambient pressure, 10^{-10} torr.



(a) Oxygen exposure, 1 Langmuir.

(b) Oxygen exposure, 10 Langmuirs.

(c) Oxygen exposure, 1000 Langmuirs.

Figure 10. - Auger electron spectrometer analysis of an iron (001) surface covered with ethylene and exposed to oxygen.

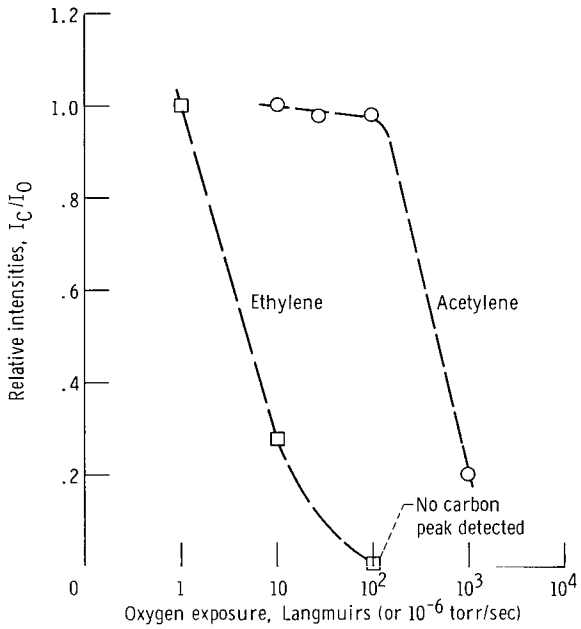


Figure 11. - Displacement of ethylene and acetylene from an iron (001) surface by oxygen. Auger carbon and oxygen peaks monitored at various oxygen exposures.

Figure 12. - Auger electron spectrometer analysis of an iron (001) surface covered with acetylene and exposed to 1000 Langmuirs of hydrogen sulfide (H_2S).

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