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CHARACTERIZATION OF BORE SURFACE LAYERS IN GUN BARRELS

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Specimens containing white layers were taken from the bore surface of the unplated and chrome plated fired gun tubes. These were examined metallographically and the presence of various "white layers" was established. The chemical and structural nature of these layers was determined by Auger/ESCA and x-ray diffraction techniques. The outermost white layer contained up to seven percent carbon and was identified as cementite - Fe_3C. The subsequent white layers had approximately one percent carbon and were identified as high carbon

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20. ABSTRACT (CONT'D)

austenite. The significance of these results is discussed in terms of solution and diffusion of carbon from burnt propellant gases into iron during firing. The carbonaceous gases from the burnt propellant are responsible for the formation of white layers and are the cause of erosion and cracking in the bore surface. During heating and cooling of fired gun barrels, stresses are generated by the differences in the coefficient of expansion and volume changes associated with cementite, austenite, and matrix metal phases. Cracks are produced in the white layer and are propagated in the substrate steel matrix. The high carbon-containing phases are lower melting than steel. These molten phases are eroded away by the sweeping hot propellant gases, thereby eroding the bore surface of the gun barrel. These and other results are discussed in terms of their effects on erosion and wear in the gun barrel bore surfaces.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

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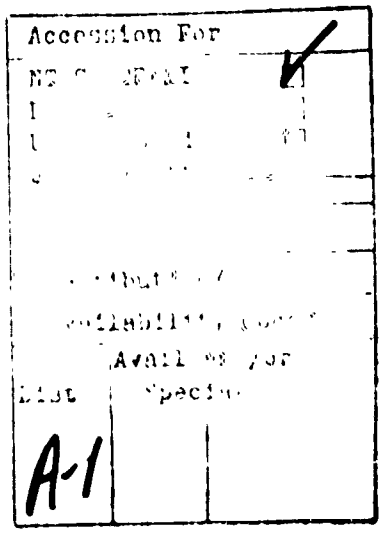

INTRODUCTION

It is known that so-called nonetching "white layers" containing cracks are formed on the bore surface during the first firing of a gun (ref 1). During second and subsequent firing some of these layers erode away and new layers are reformed. These surface alterations and damage that occur in fired guns are the primary cause of erosion in the zone near the origin of rifling in the gun barrel and cause reduction in the useful life of the gun (ref 2). The chemical nature and the structural (phases) identity of these layers is not known so far, because the layers are thin (a few microns thick) and cracked and therefore are difficult to analyze by conventional analytical methods. However, the chemical and structural characterization of these layers is crucial to providing insights into the mechanisms for the formation of white layers as well as for the nucleation and the propagation of cracks in the layers. Such mechanistic understanding should provide means for reducing surface damage and increase the useful life of the gun barrel.

Recent developments of new surface sensitive analytical techniques such as Auger and ESCA spectroscopy provide a unique opportunity to investigate the chemical and the structural nature of these layers. Therefore, an investigation was undertaken to characterize the white layers formed on fired gun barrel specimens using optical and electron microscopy, Auger and ESCA spectroscopy, and x-ray diffraction techniques. The results of these analyses

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[1] R. B. Griffin, J. Pepe, and C. Morris, "Metallographical Examination of Bore Surface Damages in Five-Inch Guns," Metallography, 8, 1975, pp. 453-471.
[2] I. Ahmad, "The Problem of Gun Barrel Erosion - An Overview," Proceedings of the Tri-Service Gun Tube Wear and Erosion Symposium, (I. Ahmad and J. P. Picard, Eds.), ARRADCOM, Dover, NJ, 29-31 March 1977, pp. I1-I49.

are used to suggest mechanisms for the formation of white layers and for the formation of cracks in the white layers and in the matrix. The chemical effects of interaction between hot propellant gases and bore surface in causing surface melting and erosion are also discussed.

IDENTIFICATION OF LAYERS

Many specimens from fired gun barrels with and without chrome plating were examined metallographically for the presence of various white layers. Several specimens with sufficiently thick white layers and least number of cracks were cleaned by ultrasonic methods, chemical methods, and by stripping replicas from the surface to remove firing debris and other material. The cleaned specimens with various white layers, including the black layer in the cracks, are shown in Figure 1.

Black Layer

These layers were characterized chemically and structurally by using metallography and electron microscopy, Auger/ESCA spectroscopy, and x-ray diffraction techniques. The results are given in the following sections. A Tracor energy dispersive system (EDS) attached to a JOEL JSM-U3 scanning electron microscope (SEM) was used, and elemental analysis for elements heavier than sodium was made on the black layer. To accomplish this, the 200 Å diameter electron beam was positioned over areas such as A, D, and E in Figure 1, which had previously been determined by optical microscopy for the presence of the black layer. The x-ray emission spectra, Figure 2, indicate that the principal chemical constituents in the black layer are sulfur and zinc with smaller quantities of copper, iron, and chromium.

To determine whether these elements exist as a compound or in elemental form, x-ray diffraction patterns were obtained from bore surfaces of several gun barrel samples. The diffraction patterns indicate that the black layer consists principally of α-ZnS. ZnO is also present in much smaller quantities. Some areas examined by EDS, e.g., D in Figure 1, exhibit large sulfur concentrations but not zinc. Therefore, the diffraction pattern was examined for evidence of free sulfur. Sulfur was not detected. The presence of free sulfur however, should not be discounted, since this element readily forms an amorphous structure which would not give rise to diffraction lines.

The observation that the bore surface contains large amounts of sulfur (as ZnS, and possible free sulfur) may be significant because of the embrittling effect of sulfur on steel. Sulfur mapping was used to determine penetration of sulfur by diffusion into the steel matrix. The sulfur map, Figure 3, obtained by imaging the sample in the SEM using the sulfur K_α emission line, indicates that although sulfur is contained in all the cracks, no detectable concentration occurs within the steel itself. In spite of this observation, the possibility exists that sulfur may embrittle grain boundaries since the amount of sulfur required to embrittle steel, 0.1 percent, is below the limits of detectability in this method. It is evident that the roll of sulfur on cracking can be best determined by examining the specimens fractured in an ultra high vacuum chamber by Auger spectroscopy, secondary ion mass spectroscopy (SIMS), or other techniques.

First White Layer

The white layer nearest the bore surface (first white layer) was examined by EDS and Auger/ESCA spectroscopy to determine its chemical composition. The

EDS spectra were obtained from a tapered cross-section of the specimen that exhibited well-developed white layers. For comparison purposes, spectra were obtained from each of the white layers and the matrix, at positions marked 1, 2, and 3, in Figure 4. An analysis of these data indicates that the spectra for each of the regions are similar, but that the first white layer contains significantly less iron than in the second white layer or the matrix as shown in Figure 5. This observation suggests that the first white layer contains a significant concentration of an element (or elements) that is not detected by the EDS technique, i.e., an element lighter than sodium. Accordingly, another technique (Auger/ESCA), which is sensitive to light elements was used in order to fully characterize the white layer.

An Auger spectrum of the first white layer was obtained by examining the bore surface of the specimen shown in Figure 4. The black layer on this sample was chemically removed to fully expose the first white layer. These data, Figure 6, indicate that the first white layer contains a significantly higher concentration of carbon than is present in the matrix, Figure 7. Adjustments were made for differences in the sensitivity of the technique for detecting different elements and it was concluded that the iron-to-carbon ratio in the first layer is approximately 3:1, i.e., the first white layer contains approximately 7 wt. percent carbon. Moreover, the presence of the satellite structure (Figure 6) associated with the carbon peak, indicated that the carbon in the first white layer exists in the form of a compound, i.e., carbide.

The crystallographic structure of the first white layer was examined by x-ray diffraction. The part of the spectrum showing the major peaks is shown in Figure 8. The data are interpreted as follows:

1. The spectrum represents the superposition of diffraction lines from three different materials, Fe_3C, Austenite, and α-Fe.

2. The carbon content (~ / wt. percent) of the first white layer determined by means of Auger analysis is consistent with the carbon content of Fe_3C. Austenite or α-Fe are not stable phases in this part of the high carbon, Fe-C phase diagram.

3. It follows, therefore, that the first white layer is Fe_3C and that the other diffraction lines must be derived from material lying immediately below the first layer within the penetration depth of the x-ray beam.

Second White Layer

The EDS spectrum for the second white layer shown in Figure 5 indicates that it has approximately the same chemical composition as the matrix. However, the reduction in intensity of the iron peak relative to that of the matrix suggests by analogy with the results on the first white layer that some carbon has diffused into this region also.

The crystallographic structure of this layer was determined by x-ray diffraction. The specimen from which the first white layer was removed by taper sectioning, thereby exposing sufficiently large areas, was used to obtain diffraction data. The major diffraction peaks observed are shown in Figure 9. For comparison, a diffractogram of the steel matrix covering the same 2θ region is shown in Figure 10. The interpretation of these data are as follows:

1. A comparison of diffraction patterns in Figures 9 and 10 from the second white layer and the matrix shows that the second white layer is an austenite.

2. Austenite, the high temperature phase, is not stable at room temperature. It is known to be stabilized by other elements such as carbon. The presence of austenite is consistent with the evidence presented above and indicates that carbon has diffused into the bore surface. Evidently, the presence of the carbon promotes the formation of carbides (first white layer) at the near surface where the carbon content is high (~ 7 w/o percent); and at greater depths, where the carbon content is too low (~ 1 w/o) to form carbides, it forms stabilized austenite (second white layer).

3. The precise quantity of austenite in the second white layer could not be established. The relative x-ray peak heights of α-Fe and austenite in Figure 9 could not be used to make such a determination since the intensity of the α-Fe peak almost certainly contains a contribution from the matrix material lying immediately below the second white layer within the penetration depth of the x-ray beam. A quantitative determination was attempted using transmission electron microscopy (TEM), but this approach was not successful. The extensive cracking associated with the bore surface made it impossible to obtain a thin section of the material suitable for examination in the TEM. However, metallographic examination of specimens in Figure 6, indicates that the second white layer is a single phase suggesting that this white layer is composed almost entirely of austenite.

CONCLUSIONS AND DISCUSSION

The results reported here lead to characterization of various layers as follows:

1. Black layer: This layer, which covers most of the bore surface and penetrates into cracks that form at the surface, consists principally of the elements sulfur and zinc in the form of α-ZnS and perhaps free sulfur. The elements, sulfur and zinc, which are the major constituents of the black layers, are probably derived from the propellant. Apparently, these elements react at the high temperatures experienced during firing to form the compound ZnS which is then retained as a residue on the bore surface.

2. First white layer: This layer contains only those elements that are present in the original gun steel, except that it has large amounts of carbon (~ 7 w/o). As a consequence, its structure has been converted from that of α-Fe to Fe_3C.

3. Second white layer: This layer also contains only those elements that are present in gun steel except that its carbon content is high (~ 1 w/o). It differs from the gun steel matrix in that it is primarily austenite.

The presence of carbon and carbon-containing phases on the bore surface layers is the most significant finding in our study. This suggests the following mechanisms for the formation of white layers and cracks and for erosion in the origin of rifling zone of the gun barrel. Carbon-containing reducing gases such as methane, carbon monoxide, etc., from the burnt propellant gases interact with steel at the bore surface at high temperatures. As a consequence, large amounts of carbon of up to 7 w/o or more are dissolved via local melting or by diffusion into the bore surface metal. The carbon-

containing phases, cementite and high carbon austenite, are formed at high temperatures and are retained as non-equilibrium high temperature phases at ambient temperatures due to extremely fast heating and cooling rates associated with the fired gun (ref 3). Kamdar et al (ref 3) and Fisher et al (ref 4) have produced white layers in methane, carbon monoxide, and carbon dioxide gases in a laboratory setup which simulates gun barrel firing conditions. These investigations provide further support for the above mechanisms. The rate effects noted above, i.e., sharp temperature gradients, are also manifested by the formation of thin layers with very sharp boundaries associated with the white layers (Figures 1 and 3) and explain why in spite of large concentrations of carbon, its diffusion or presence is limited to the white layers only.

Cementite and austenite phases are undesirable because they will promote surface cracking. The carbide is brittle, its thermal shock resistance is poor, and it is well known to nucleate cracks in steel. Thus, it could nucleate and propagate cracks in the white layers and in the surface of the heat affected steel matrix. The austenite on the other hand, is expected to give rise to stresses because its specific volume is about five percent less than that of α-Fe (ref 4). This volume change and fast cooling rate can generate high tensile stresses which can cause cracking in the second white

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[3] M. H. Kamdar, A. Campbell, and T. Brassard, "A Metallographic Study of White Layers in Gun Steel," ARRADCOM Technical Report No. ARLCB-TR-78012, Benet Weapons Laboratory, Watervliet, NY, August 1978.

[4] R. M. Fisher, A. Szirmae, and M. H. Kamdar, "Metallographic Studies of Erosion and Thermal Cracking of Cannon Tubes," ARRADCOM Technical Report No. ARLCB-TR-83022, Benet Weapons Laboratory, Watervliet, NY, May 1983.

layer and in the substrate base metal heat affected zone. These effects can arise individually or synergistically leading to cracking on the bore surface.

Cementite has a lower melting point than carbon and its formation on the bore surface will cause local melting. The melted layer will be eroded away by the hot sweeping gases. Such melted layers are often found on fired gun barrels (ref 2) and also in specimens heated in methane gas in laboratory experiments which simulate firing conditions in a gun barrel. On the other hand, the cracked white layers will be removed by thermal spalling and mechanical wear caused by the thermal shock and the moving projectile. Thus, melting and thermal-mechanical cracking will cause erosion and wear of the bore surface when a gun is fired.

Chromium plating and tantalum liners are often used to protect the bore surface metal from the reactive hot propellant gases. However, these metals are also known to form brittle carbides in reducing gaseous atmospheres. It is clear that erosion and wear will be reduced by eliminating the presence of carbon by decreasing the presence of reducing gases. This can be achieved by proper combustion and by increasing the amount of oxidizing agents in the propellant mixture. Thus, the presence or absence of hot, reducing gases determines the erosion and wear that occurs on the bore surface of a gun barrel.

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[2]I. Ahmad, "The Problem of Gun Barrel Erosion - An Overview," Proceedings of the Tri-Service Gun Tube Wear and Erosion Symposium, (I. Ahmad and J. P. Picard, Eds.), ARRADCOM, Dover, NJ, 29-31 March 1977, pp. I1-I49.

Extensive and detailed investigations similar to that described in this report to quantify and microstructurally characterize the surface layer are in progress. Also under investigation are the formation of white layers in laboratory simulation studies and the effects of gas species and their pressure and temperature on the formation and characteristics of white layers. These investigations will be reported in a future report.

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1. R. B. Griffin, J. Pepe, and C. Morris, "Metallographic Examination of Bore Surface Damages in Five-Inch Guns," Metallography, 8, 1975, pp. 453-471.
2. I. Ahmad, "The Problem of Gun Barrel Erosion - An Overview," Proceedings of the Tri-Service Gun Tube Wear and Erosion Symposium, (I. Ahmad and J. P. Picard, Eds.), ARRADCOM, Dover, NJ, 29-31 March 1977, pp. I1-I49.
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4. R. M. Fisher, A. Szirmae, and M. H. Kamdar, "Metallographic Studies of Erosion and Thermal Cracking of Cannon Tubes," ARRADCOM Technical Report No. ARLCB-TR-83022, Benet Weapons Laboratory, Watervliet, NY, May 1983.

Figure 1. SEM Micrograph os gun barrel cross-section at the bore surface. The labeled dots indicate regions from which EDS spectra were obtained. A, D, and E are on the black layer, B is on the steel matrix, and C is on the chrome plate. The spectra obtained from these areas are shown in Figure 2 (300X).

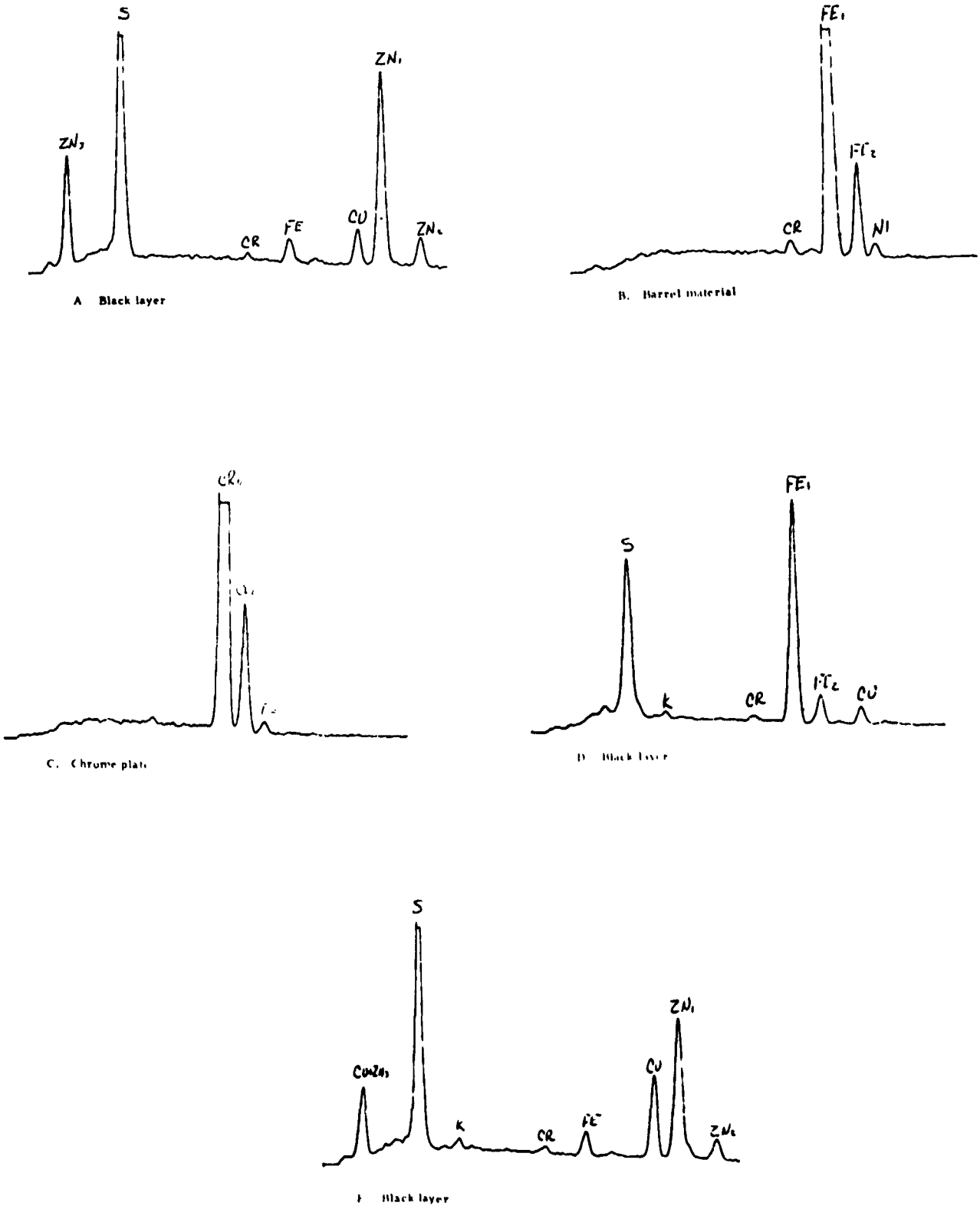
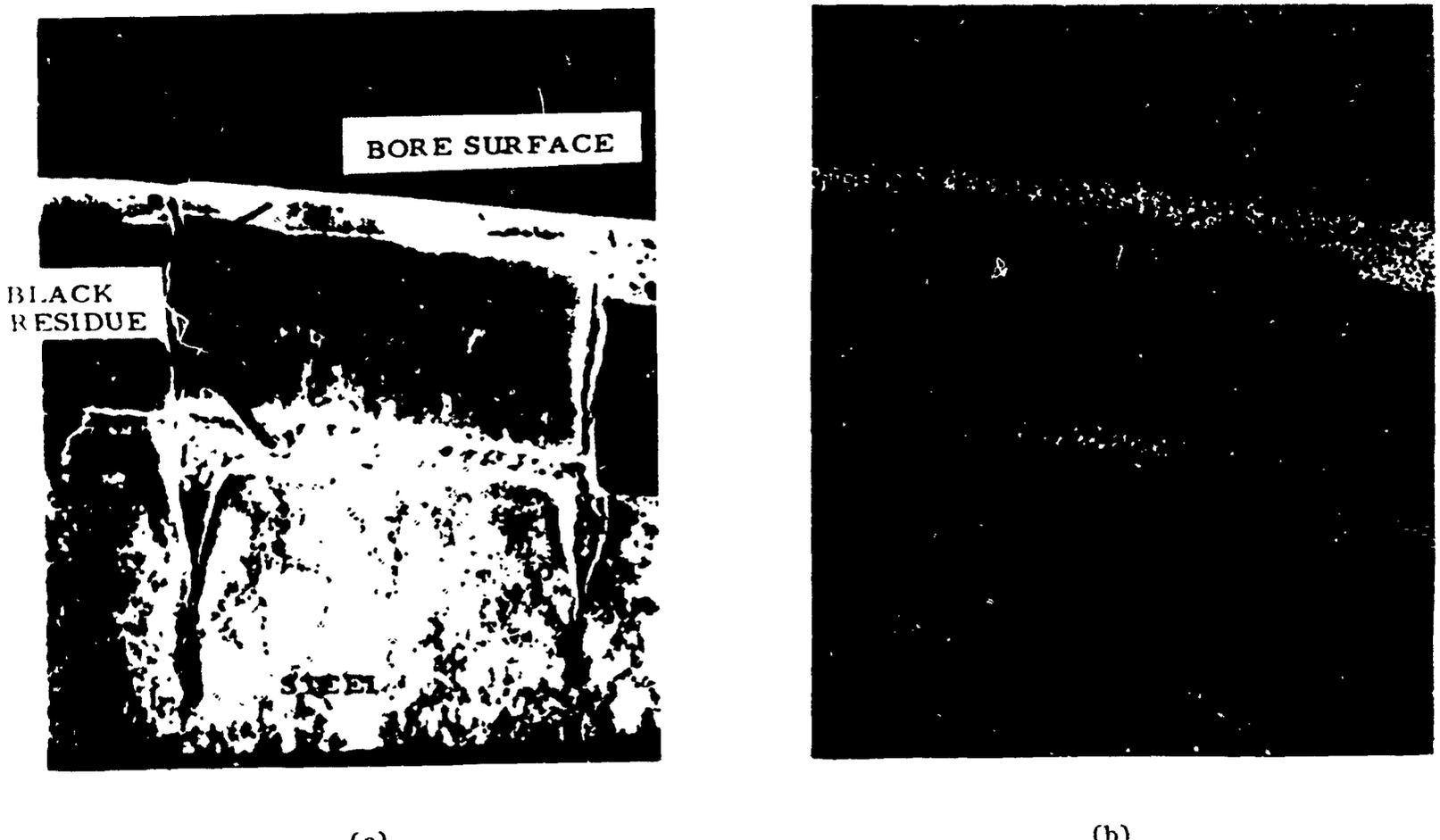


Figure 2. EDS spectra obtained from the areas A, B, C, D, and E shown in Figure 1.



(a) (b)

Figure 3. SEM micrographs of gun barrel cross-section showing (a) the structure near the bore surface, and (b) distribution of sulfur in the sample. Note that the crack openings contain high concentrations of sulfur (450X).

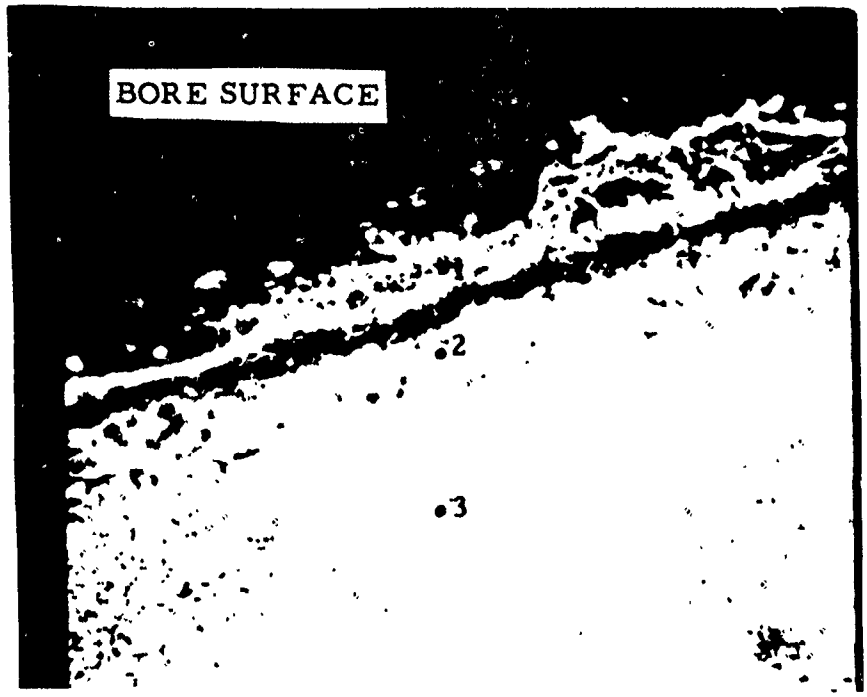


Figure 4. SEM micrograph of tapered section near the bore surface. The labeled dots indicate regions from which the EDS spectra (shown in Figure 5) were obtained. The various regions are (1) first white layer, (2) second white layer, and (3) gun barrel steel (1800X).

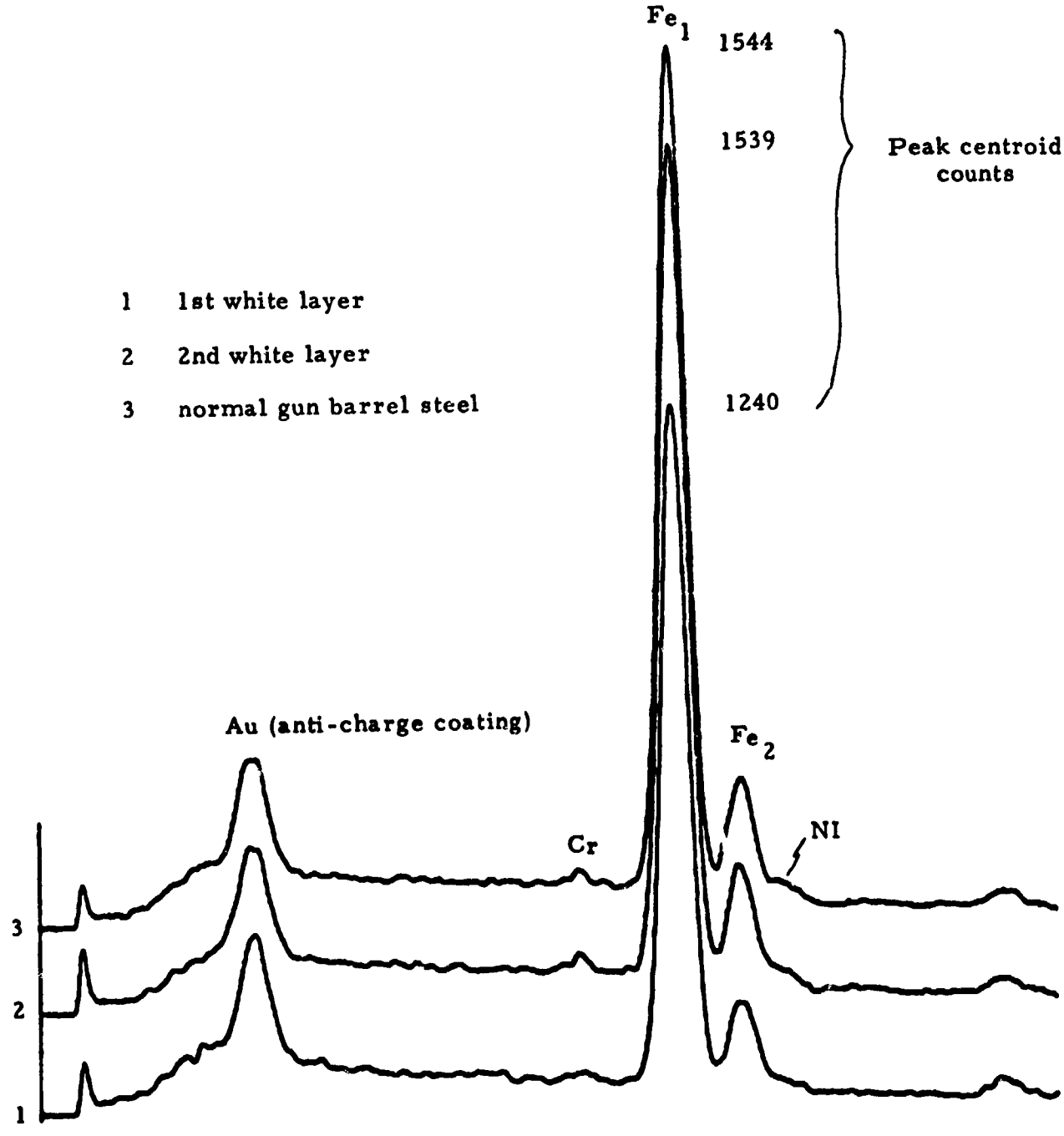


Figure 5. EDS spectra of (1) first white layer, (2) second white layer, and (3) matrix. The concentration of iron (as indicated by the peak centroid counts) is lower in first and second white layers than it is in the matrix.

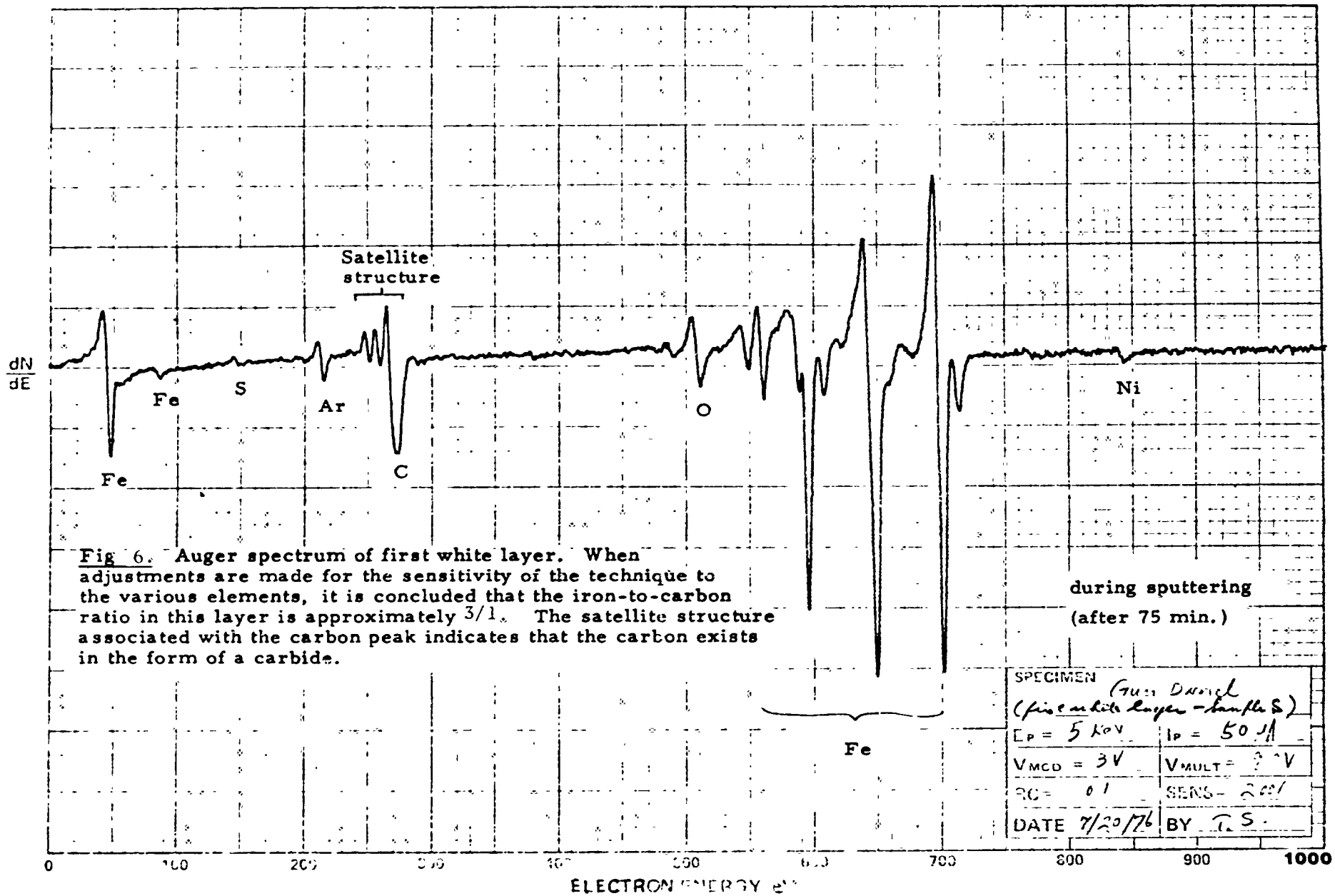


Fig 6. Auger spectrum of first white layer. When adjustments are made for the sensitivity of the technique to the various elements, it is concluded that the iron-to-carbon ratio in this layer is approximately 3/1. The satellite structure associated with the carbon peak indicates that the carbon exists in the form of a carbide.

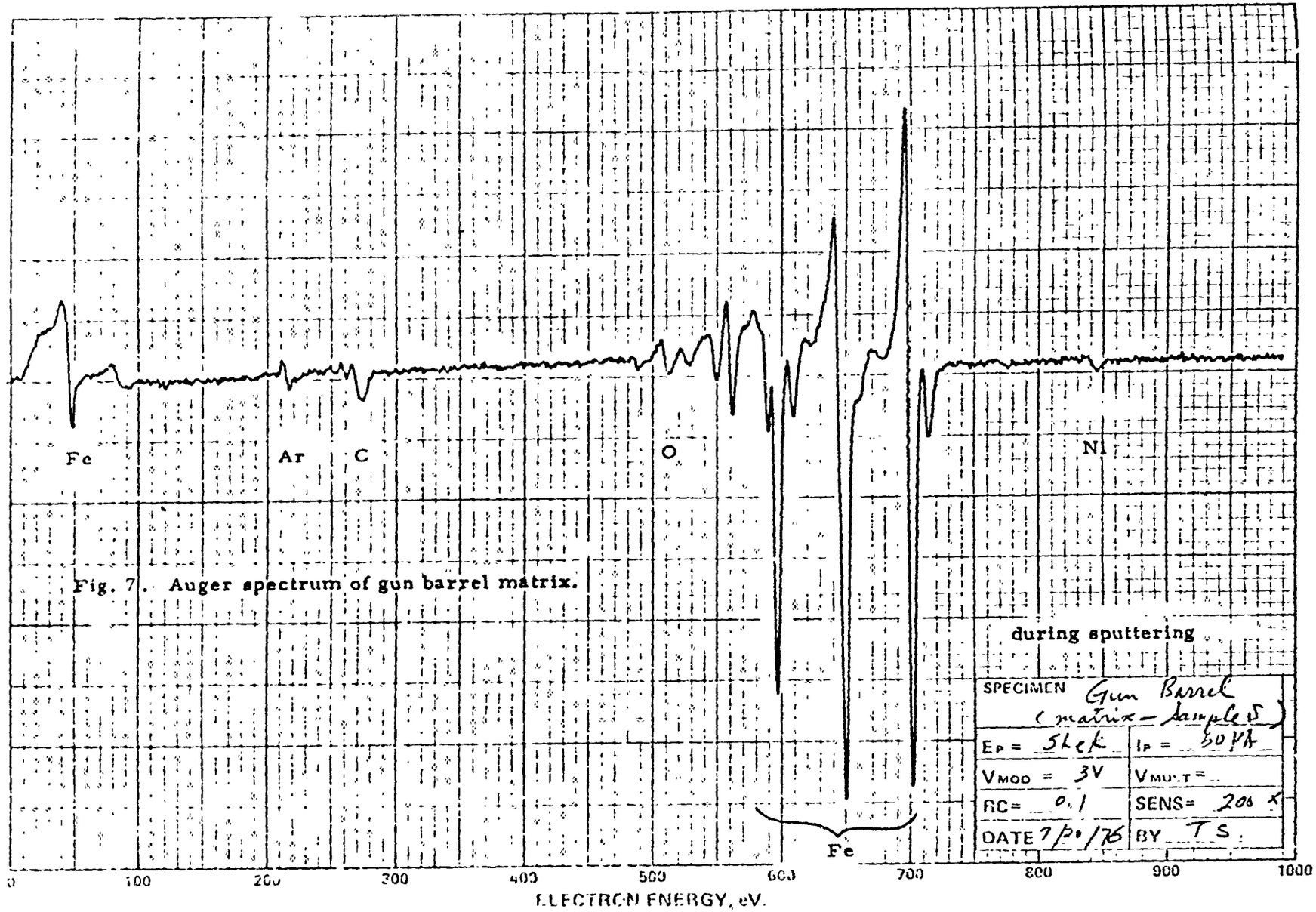


Fig. 7. Auger spectrum of gun barrel matrix.

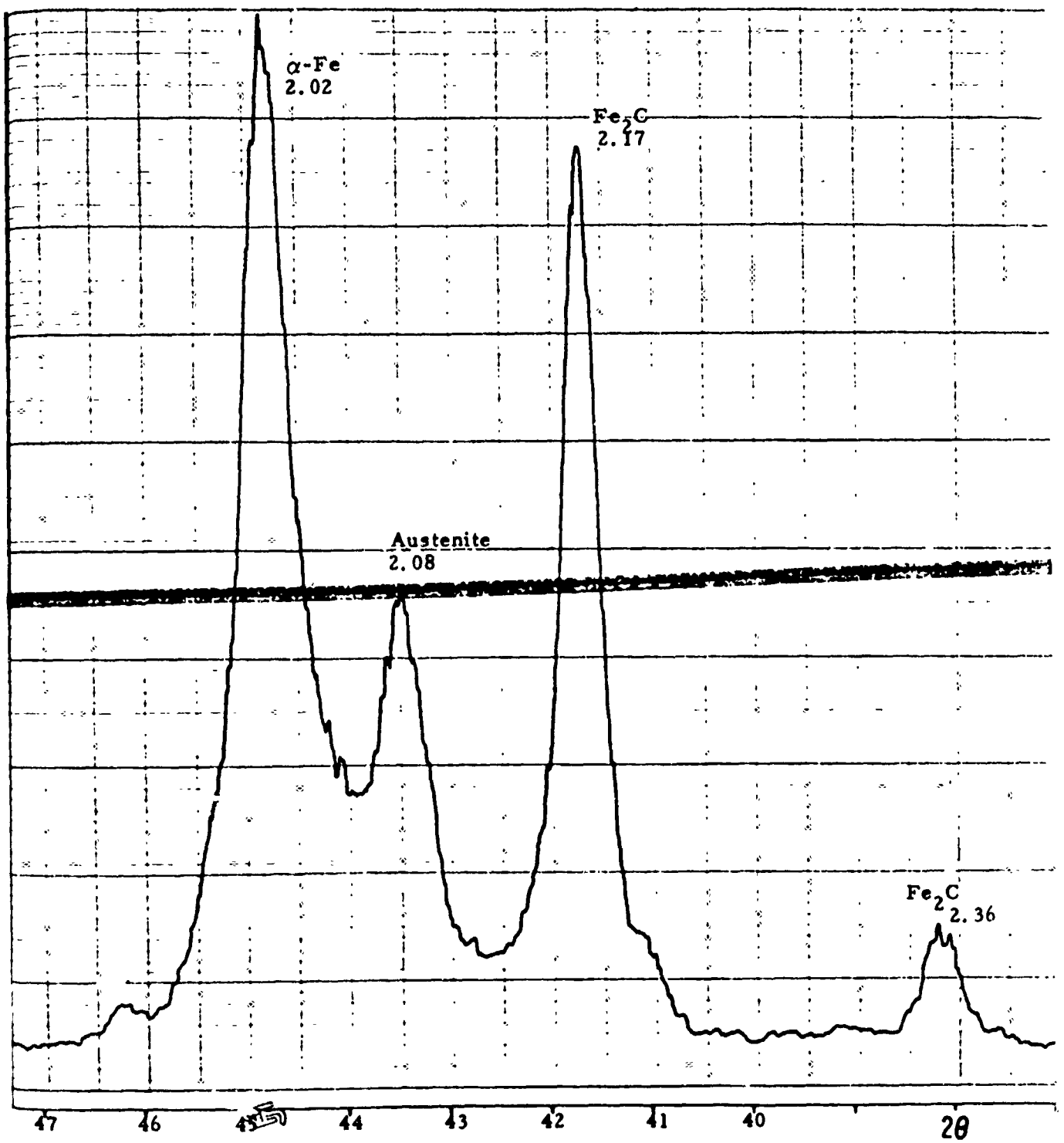


Figure 8. X-ray diffraction pattern of first white layer.

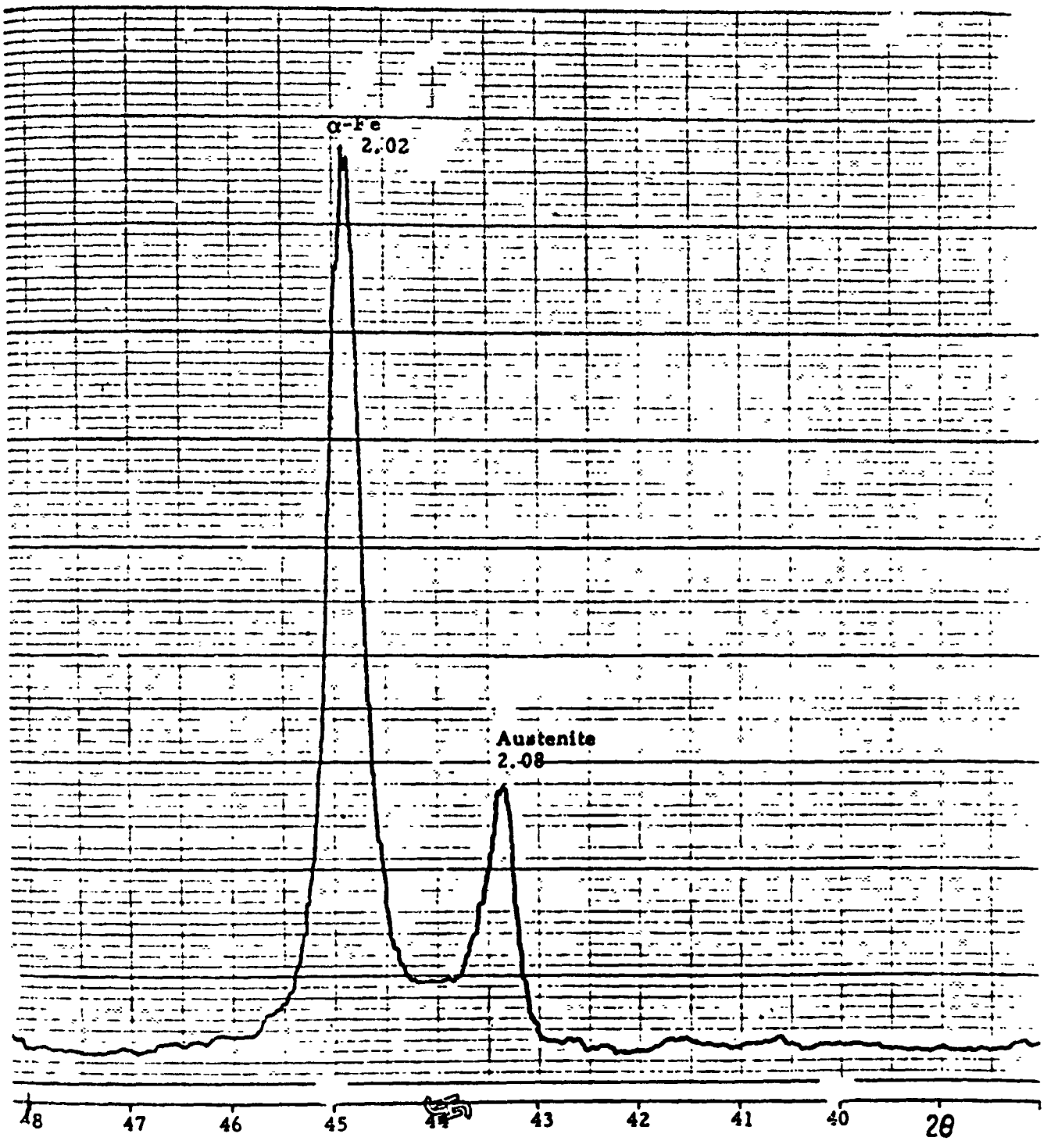


Figure 9. X-ray diffraction pattern of second white layer.

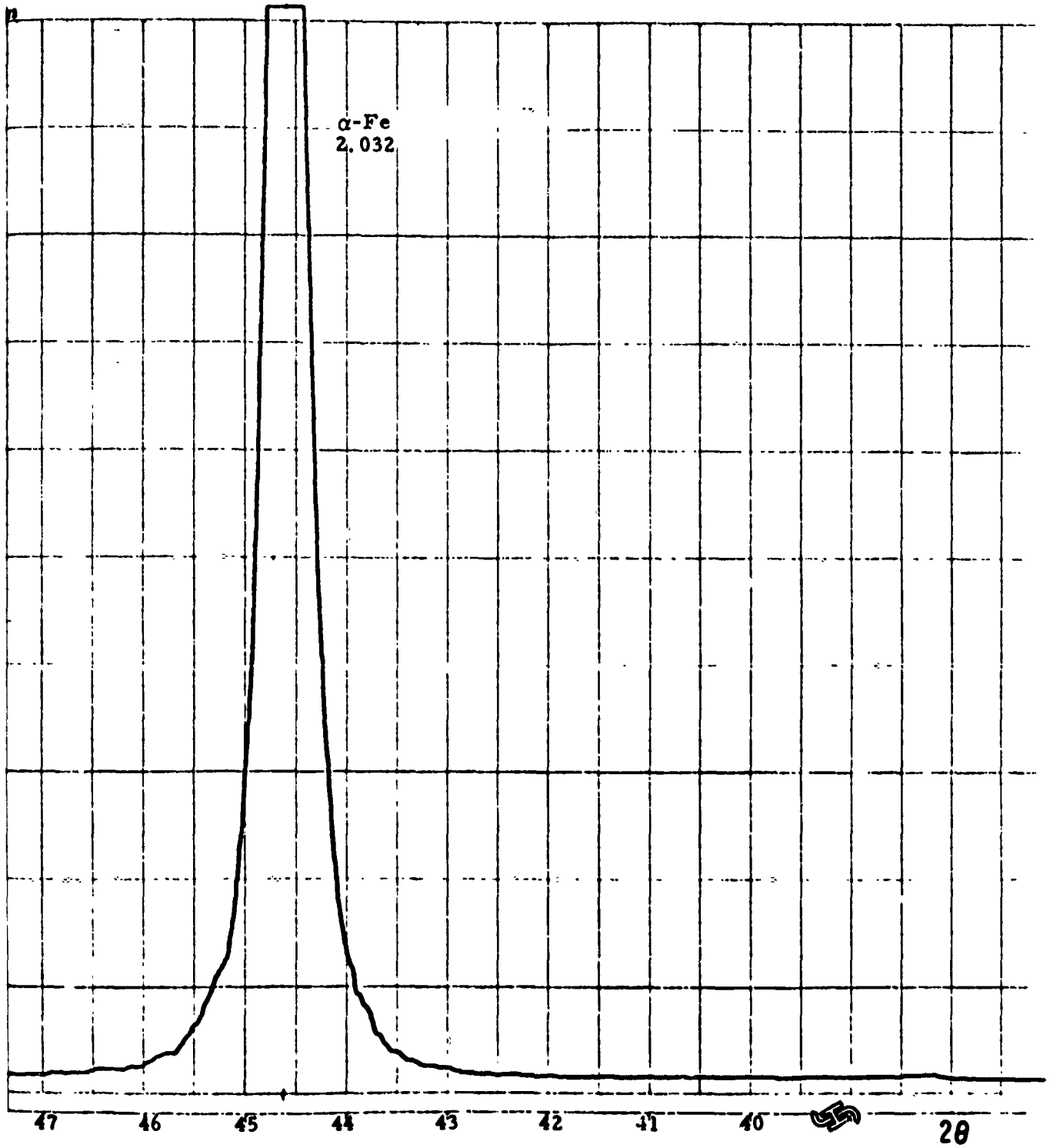


Figure 10. X-ray diffraction pattern of gun barrel steel.

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