AD 625 810

FINAL REPORT

PLASMA-JET COATING OF TUNGSTEN ON STEEL

Contract Nr. N-123-(60530)-24981A

Richard L. Landingham, Robert A. Damon, Daniel J. Murphy

College of Mines

ENGINEERING RESEARCH LABORATORIES

COLLEGE OF ENGINEERING
UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

PLASMA-JET COATING OF TUNGSTEN ON STEEL

FINAL REPORT

The Fusion Bonding of Plasma-Jet Coatings to Metals

Contract Nr. N-123-(60530)-24981A

February 6, 1961 to April 30, 1962

by

Richard L. Landingham, Robert A. Damon, Daniel J. Murphy

College of Mines

ENGINEERING RESEARCH LABORATORIES
COLLEGE OF ENGINEERING
THE UNIVERSITY OF ARIZONA
TUCSON 25, ARIZONA

ABSTRACT

Three methods for bonding plasma-jet sprayed tungsten to steel were developed and evaluated in an approach to the problem of providing heat-resistant materials for the design and fabrication of components for high temperature applications.

Three types of coating were sprayed by plasma-jet on 1020 steel substrates: (1) an all tungsten coating, (2) a coating graded from 1020 steel at the interface to tungsten at the outer surface, and (3) a coating graded from iron at the interface to tungsten at the outer surface. By the latter two coating methods, a less severe thermal expansion gradient was developed between the substrate and the coating. Pre-heating the substrates increased the fusion bond at the interface. Post-heat treatments eliminated residual stresses within the coating and promoted grain growth and diffusion across the fusion zone. The tungsten-iron graded coating on the 1020 steel substrate displayed excellent resistance to shock and withstood high temperature corrosion conditions 2 1/2 times longer than uncoated substrates.

The investigation emphasized the potential of the plasma-jet gun in providing a means for depositing a protective coating on a metallic substrate.

TABLE OF CONTENTS

Page

1. INTRODUCTION

To contain and control high-temperature reactions and processes, materials having exceedingly high melting points are needed. Such materials and unique employment of them in engineering design must be developed to solve the high temperature problems encountered in current space technology. It is only since 1940 with the war-influenced interest in power plants and faster aircraft, that designers have been confronted dramatically with the 'materials barrier'.

Up until recently, engineers designed systems around the materials at hand. As better materials came along, new systems were drawn or older ones modified to take advantage of improved material properties. The fast pace of the current race to build planes, rockets, and missiles has accentuated the need for superior materials to replace the already outdated "superalloys" of cobalt and nickel for high temperature applications. Materials that retain desirable properties at 2000°F and higher are presently needed. Since the useful service temperature for any material is approximately 0.6 of its melting point, researchers are interested in materials that have melting points of over 3000°F.

Researchers at the Battelle Memorial Institute have tabulated 122 compounds that melt at temperatures above 3272°F (1800°C). For such service, metals are preferred because of their ductility. Though the list contains eighteen metals or metalloids, only four metals out

of the eighteen are useful for other than very specialized applications. Of these, columbium and molybdenum will compete in applications between 1800°F and 3000°F; tantalum and tungsten for applications above 3000°F. While highly promising, the use of high density refractory metals introduces weight disadvantages and gives rise to considerable fabrication difficulties when designers call for even slightly complex shapes. It is no wonder, then, that considerable effort is being invested in attempts to combine the good workability, lower density, and high strength properties of steels, with the high melting characteristics of refractories by the application of improved coating techniques.

A relatively new approach of considerable promise is the plasma-jet spraying of refractories on steels. The type of coatings in this category, reported up to the present time, are those which are bonded mechanically to the base metal and do not withstand high temperature corrosion and/or thermal shock. This deficiency has pointed up the need for the development of more promising methods for coating steel. An approach to this problem has formed the basis for the investigation reported upon in the following sections.

2. EXPERIMENTAL BACKGROUND

There have been many coating processes developed to meet the ever-increasing demands placed on materials by our rapidly-advancing technology (Bertossa, 1958; Browning, 1959). One of the most recent of these developments has shown great promise in the coating of base materials with refractories, refractory metals, and cermets (Oechale, 1957; Levinsten, 1962). The process employs equipment of unique design which utilizes both high pressure and high temperature (Linde Company, 1959; Mash, Weare, and Walker, 1961) to spray oxidation-resistant and temperature-resistant coatings on base materials (Dickinson, 1958; Linde Company, 1959).

Effective conditions are obtained when an inert gas at a pressure of approximately 50 to 150 pounds per square inch is ionized by passing it through an electric arc (Thermal Dynamics Corporation, 1961). The resultant flame of the stream produced has become known as a "plasma-jet". By introducing high temperature coating materials in finely divided powder form into the head of such a plasma-jet, it is possible to transform the powdered materials into a plastic, molten, or even a vaporized state by the time they leave the jet. Like particles of most materials are capable of fusing together under these extreme conditions to form a well-bonded coating (Eisenlohr, 1961; Hayes and Johns, 1961). Unfortunately, this fusion between particles of the same type does not extend in many cases to the material on which

they are sprayed.

A literature search reveals very little material released to date concerning plasma-jet sprayed refractories on substrates. This dearth of information may be attributed to several factors: (1) it is a relatively new field of study, (2) the initial cost of equipment is high with no guarantee for results from the investment of time and money, and (3) most of the investigations that have been conducted are classified or are awaiting patent right protection before the release of any pertinent information obtained. Recent reports in the literature and actual micro-examination of bonds between various coatings and base materials reported by two leading manufacturers of plasma-jet type of equipment indicate the bonding to be of a mechanical and interlocking nature, with little or no fusion bonding involved. Fusion bonds, however, have been reported by others (Dickinson, 1958; Linde Company, 1959). Such bonds are stated to have been developed when hot particles of the coating material strike the surface of the substrate. The fusion zone produced by this process is usually very thin and lacks shear strength. Both this type or bond and the mechanical type bond have many applications in corrosion-resistance problems (Shepard, 1960) under normal conditions, but they have little or no value as protective coatings for subjection to thermal shock conditions and high temperature environments (Batchelor, 1958).

From the foregoing consideration of the progress to date in the development of high-temperature-resistant coatings for base metals of construction, it is quite evident that there continues to be a need

for improvement in the fundamental mechanism of bonding the coating to the substrate. The problem seems to arise out of differences in the expansion characteristics of the coating and base material. Expansion of the coating and base material during heating develops an excessive shearing stress at the interface due to differences in the coefficients of thermal expansion of the two materials. It is very difficult, if ot impossible, to match or mix coating powders to produce expansion characteristics in them sufficiently similar to those of the base material on which they are sprayed to suppress the occurrence of spalling.

The stress produced, though it can be minimized by the proper selection of coating powders, is generally large enough under thermal shock conditions to cause the weakly-bonded coatings, described above, to shear off. It would appear that the key to a solution of this problem might be in the elimination or reduction of the harmful shearing stresses at the interface between the applied coating and the base metal to which it is applied. To this end, several approaches have been devised and evaluated experimentally. The results obtained form the basis for this report.

3. OBJECTIVES OF INVESTIGATION

The objectives of this investigation were as follows:

To study the mechanism by which a heat-resistant tungsten coating, deposited by a plasma-jet spray gun, may be caused to adhere to the surface of a base metal of 1020 steel, and

To develop techniques for the application of the plasma-jet spray directed toward producing an improved fusion-bonded coating which would withstand the stress of thermal shock and mechanical shear.

4. EXPERIMENTAL PROCEDURES

The principal unit of experimental apparatus used in this investigation was the Giannini Plasmatron P-160 System. Other equipment of an auxiliary nature was specially designed and constructed or adapted to provide the environment and controls essential for the optimum application of the Plasmatron. A schematic diagram of the experimental apparatus as it was installed for operation is shown in Figure 1. As previously indicated, its purpose was to deposit a heat-resistant tungsten or tungsten-base coating on 1020 steel. Variables such as plasma-jet operating pressure and temperature, particle size of coating material, and composition of the deposited coating were investigated to determine characteristics for inducing a suitable fusion bond. The temperature of the substrate (1020 steel) was elevated to establish different steel phases prior to the coating procedure. The effects of phase transformations, atomic activation, and crystal structure on the fusion at the interface of the coating and the substrate were studied. The coating procedure was conducted inside the inert atmospheric chamber to reduce oxidation at the surface of the substrate and within the deposited coating. Controlled cooling rates of the coated specimens were used to reduce residual stresses developed at the interface during thermal contraction. Post-heat treatments were employed to further bonding through diffusion and to eliminate residual stresses.

Figure 1

Identification List of Experiment Equipment

1. Plasma-Jet Head Assembly
2. Plasmatron Control Panel
3. 20 Kilowatt Transformer-Rectifiers
4. Argon Gas Bottles (300 Cubic Feet)
5. Water Softener Unit
6. Water Pump
7. Nitrogen Gas Bottle (250 Cubic Feet)
8. Variable Transformer (Controls nitrogen gas pre-heating furnace)
9. Variable Transformer (Controls post-heat treatment furnace)
10. Nitrogen Pre-Heating Furnace
11. Inert Atmospheric Chamber
12. Check Valve (4 1/2 inches - inside diameter)
13. Four Electrical Inlet Plugs
14. Mechanical Vacuum Pump
15. Inert Atmosphere Chamber Door
16. Six Thermocouple Inlet Plugs
17. Rubber Glove Port
18. Pyrex Glass Window
19. Copper Tubing (3/16 inches)
20. Rapid-Action Gas Valves
21. Powder Hoppers
22. Post-Heat Treatment Furnace
23. Jig (Used to position specimens to be coated)
24. Level Platform for Jig
25. Specimen Holder
26. Plasma-Jet Flame

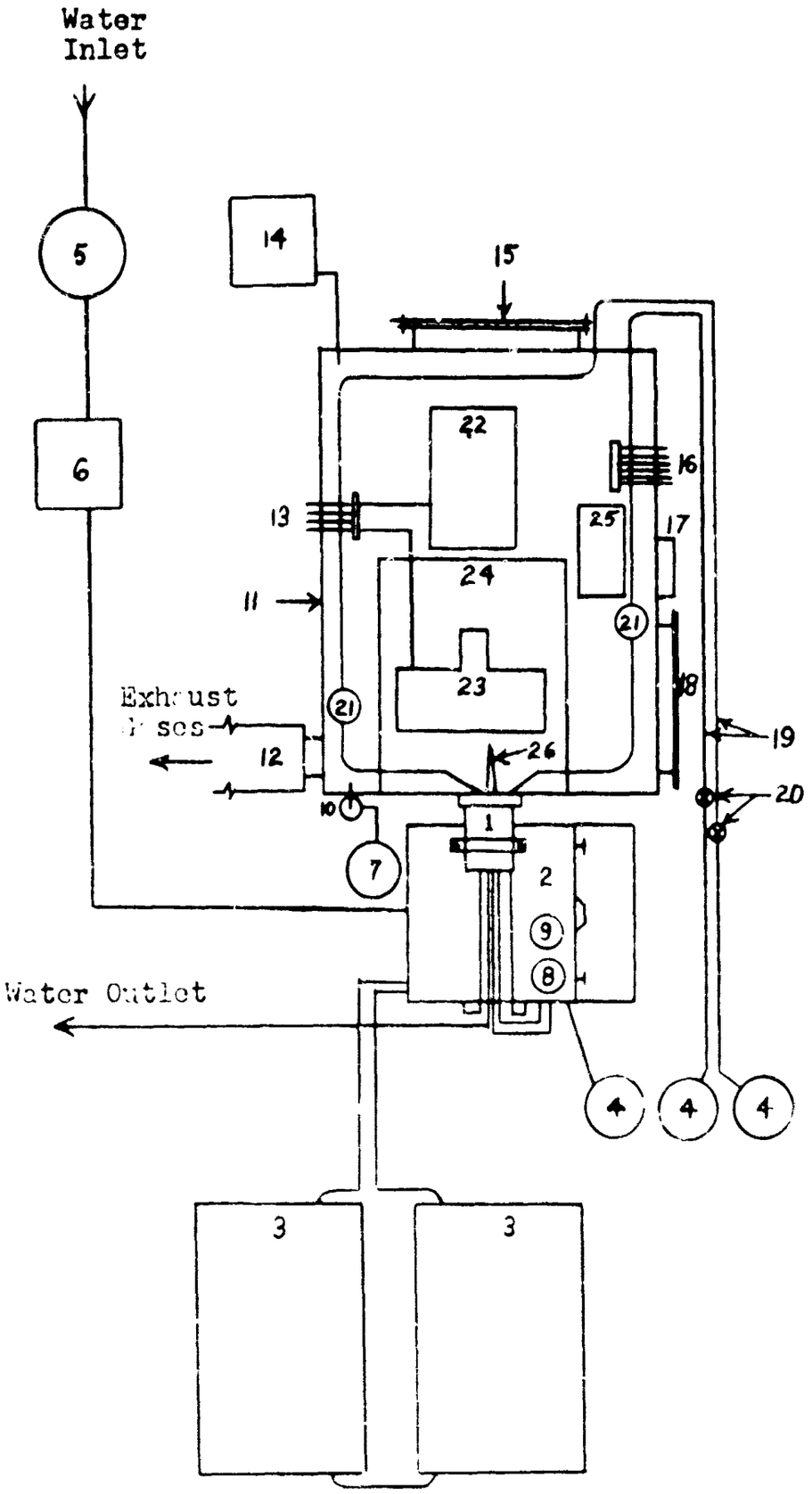


Figure 1. Schematic Diagram of Experimental Equipment

A more detailed description of the equipment as it was employed in the investigation is given in the following sections:

4.1 Technical Details of Apparatus

4.11 Plasmatron Apparatus

Two 20 kilowatt transformer-rectifiers (3) (Figure 1) were connected in parallel to supply an H-50 Plasmatron head assembly (1) (also shown photographically in Figure 2) with a maximum power input of 40 kilowatts. These transformer-rectifiers supplied a constant voltage of 25 volts to the electrodes in the Plasmatron head assembly during operation. The current to the electrodes in the Plasmatron head was regulated by a variable transformer mounted in the center of the console panel (2) (also shown photographically in Figure 3). Argon gas was supplied to the Plasmatron head-assembly from a 300 cubic foot bottle (4). The working pressure was regulated by a two-stage argon regulator. The gas flow was regulated by a flow meter mounted on the lower right hand side of the console panel. The flow meter on the lower left hand side of the panel regulated the water flow used to cool the Plasmatron head when it was in operation. The plasma-jet flame (26) was stabilized in front of the Plasmatron head.

The front electrode of the Plasmatron head had two powder-injection orifices through which coating powders were injected under pressure into the plasma-jet. Each injection orifice was connected by copper tubing (19) to standard Plasmatron powder-hoppers (21). One

tee-joint was inserted in each feed line at a distance of one inch from the point of connection ot the Plasmatron head. A copper tube was connected to these two tee-joints and passed over the Plasmatron head (see Figure 4). This arrangement balanced the pressure at the two injection orifices so that the plasma-jet was not deflected when the two powder hoppers were being operated at different pressures. It was possible to replace this dual-powder feeding-system by a single-powder feeding-system whenever a requirement arose to feed both injection orifices from one powder hopper. The powder flow from the hoppers was reduced by limiting the exit orifice of each hopper to the same size diameter as the venturi in each hopper.

4,12 Inert-Atmosphere Chamber

An inert-atmosphere chamber (11)(as shown also in Figures 5a, 5b, and 5c) was designed and constructed to contain the essential devices for applying the coatings. The chamber was constructed of 14 gage sheet steel and was equipped with water-cooled cooling jackets. A flange with a metallic O-ring provided a tight closure of the Plasmatron head to the chamber. The chamber was fitted with a large pyrex viewing window (18), glove port (17), self-regulating exhaust port (12), and rear access door (15). The chamber was also equipped with an internal lighting system, four electrical inlets (13), and six thermocouple inlets (16). A small electric annealing furnace (22) was mounted in the chamber at the end opposite to the Plasmatron head.

4.13 Resistance-Heating System

A direct current, battery-operated resistance-heating system was installed in the chamber to pre-heat the 1020 steel substrates. Two six volt, 130 ampere-hour batteries in parallel, allowed tensile shaped specimens (minimum cross section: 1/8" x 1") to be brought to temperatures in the vicinity of 2000°F.

4.14 Purging of the Inert-Atmosphere Chamber

The quantity of nitrogen purging gas (7) used was minimized by pre-heating it to approximately 300°F before feeding it into the inert-atmosphere chamber. A tubular, pebble heater was designed and built for this purpose (10). The heater was constructed from an eight-inch length of steel pipe (1" inside diameter). It was wrapped with 30 feet of 0.7 ohm/ft. electrical heating wire and was thermally and electrically insulated with a one-inch layer of magnesia mud. The steel pipe was filled with small copper filings to eliminate any oxygen present in the nitrogen being pre-heated. A mechanical vacuum pump (14) was connected to the chamber to reduce the purging time and consumption of nitrogen.

4.15 Substrate-Positioning Jig Assembly

A jig was designed and constructed to move specimens at a uniform rate in front of the plasma-jet while being coated (23). Figure 7 shows the jig holding a 7" x 2" x 1/4" steel specimen. This jig and a stainless steel shield were mounted on rollers and placed on a level runway (24) inside the chamber. With this setup, a specimen

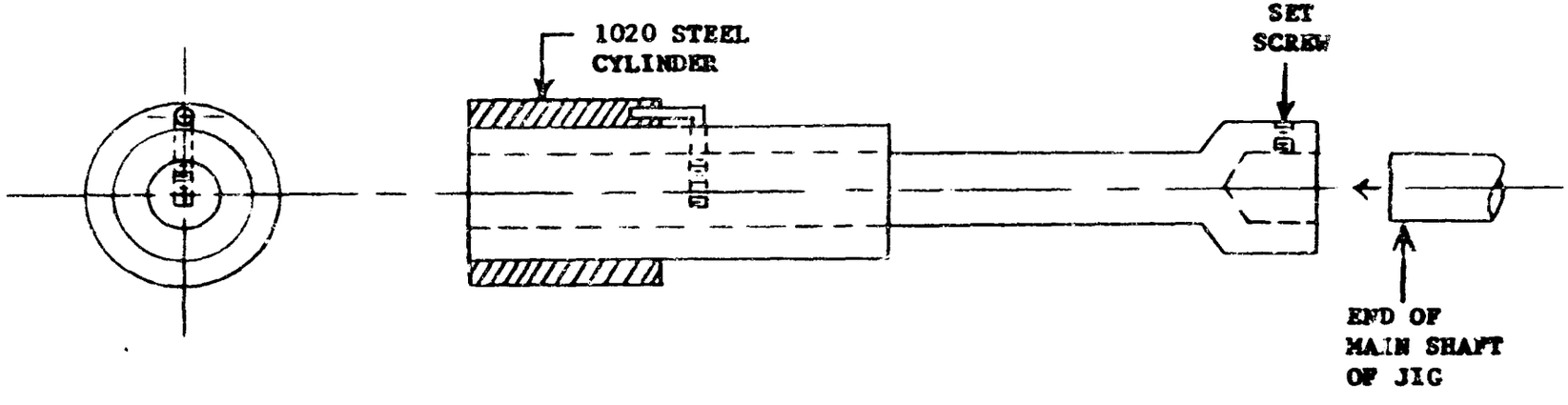


Figure 8. Schematic Diagram of Extended Portion of Jig Used to Rotate 1020 Steel Cylinders During the Coating Procedure

mounted on the jig behind the shield could be positioned at any desired distance from the Plasmatron head. The shield had an adjustable hole in it which was lined up between the orifice of the Plasmatron head and the center of the specimen. In this way, only the center portion of the plasma-jet spray could coat the specimen, which was moved in a zig-zag fashion by the jig in front of the adjustable hole in the shield.

The jig was modified slightly to handle the cylindrical specimens coated for the mechanical shear tests (see Figure 7). For this purpose the assembly used to hold the plate specimens was first removed. The main driving shaft of the jig was extended an additional 4 1/2" beyond the jig assembly through a hole in the side of the protective housing. An alumina cylinder was set over the end of the extended portion of the main shaft to protect the shaft from overheating during the coating operation. A 1020 steel cylinder to be coated was slid over the protected shaft and engaged by a hook connected to the shaft as shown in the schematic diagram in Figure 8. The jig rotated the cylinder while passing it back and forth through the plasma-jet.

4.2 Application of Coatings

Using the apparatus described above, three types of coatings were applied as follows:

(1) Tungsten on 1020 steel substrates.

(2) Graded coating of tungsten - 1020 steel mixtures on 1020 steel substrates.

(3) Graded coating of tungsten-iron mixtures on 1020 steel substrates.

Many improvements in the coating techniques were developed in progressing from the first to the third type of coating listed above. The general technique was established while investigating most of the variables related to the application of tungsten on 1020 steel. The results from this procedure suggested a graded coating technique as a possible solution to the difficulties encountered in the first type of coating. Several modifications in procedure and equipment were necessary before the tungsten-1020 steel graded coating technique was successful. The undesirable properties of this second type of coating were eliminated by the development of the tungsten-iron graded coating.

The ultimate development of the coating procedure that produced a thermal shock-resistant coating was the direct result of investigations conducted on all three of the coating techniques listed above. A detailed description of the development of this latter coating technique is given in the following three sub-sections which take up the three types of coatings in the order in which they were investigated.

4.21 Tungsten Coated on 1020 Steel Substrate

The first attempt to develop a protective coating of tungsten on steel with the aid of the plasma-jet, used the most direct approach. It consisted of spraying tungsten directly on steel and investigating

the effects of the variables described below. Cold-rolled 1020 steel plate (2" x 7" x 1/8") was chosen as the substrate to be coated with tungsten because of its low carbon and alloy content. All specimens to be coated were first pre-heated to induce metal to metal bonding through increasing the internal energy of the atoms of the metals involved.

4.211 Pre-Heating Substrates

Pre-heating the substrate with the battery-operated resistance-heating system proved inconvenient due to the number of specimens to be tested and the difficulties encountered in making good electrical connections with the specimens inside the chamber.

Tests were conducted to determine the usefulness of the plasma-jet itself as a possible source for pre-heating the specimens. Three chromel-alumel thermocouples were spot welded to the back side of a typical steel specimen (7" x 2" x 1/8"). Two of these thermocouples were located at the extreme opposite edges of the area to be coated. The third thermocouple was placed in the center of this area (1 1/2" x 1 1/2"). This specimen was placed in the jig and positioned 6 1/2" from the front electrode of the Plasmatron head. Millivolt readings were taken with the center thermocouple at different time intervals after the plasma-jet arc had been struck. The temperature of the specimen leveled off after 250 seconds as shown in Figure 9. Readings taken with the other two thermocouples at this temperature plateau agreed within 40°C even while the specimen was being moved by

the jig in a zig-zag fashion in front of the plasma-jet. The center thermocouple, therefore, was able to detect the temperature of the coating area (1 1/2" x 1 1/2") to within $\pm$ 20°C. The pre-heating temperatures of all plate specimens used in the investigation were obtained from a thermocouple spot-welded to the side opposite to the side prepared for coating and in the center as described above.

4.212 Coating Procedure in the Normal Atmosphere

By the above pre-heating procedure, only the first two lower temperature phase-regions (alpha and alpha plus gamma) of steel were investigated. The first nine specimens were coated with tungsten in air so that results could be compared with future coatings in an inert atmosphere. All plasma-jet control-settings were the same for these first nine specimens (see Table Ia).

The single powder-feeding-system was employed for these coatings. The venturi of the hopper was adjusted to 2T-0 (two turns out from the flush position). This setting produced a steady flow of tungsten into the plasma-jet stream without overloading it. It resulted in a coating build-up of approximately 0.01[illegible] inches of tungsten per minute on the substrate at the settings used for the first nine specimens.

The surface of each specimen that was to be coated with tungsten in the normal atmosphere was manually ground with abrasive papers to a surface smoothness corresponding to 500 grit size just before it was pre-heated with the plasma-jet. Each specimen was

placed in the jig, pre-heated by the plasma-jet, and coated with two layers of tungsten by allowing the jig to move the specimens in front of the plasma-jet twice while tungsten powder (+325 mesh) was being injected into the plasma-jet stream under a pressure of 10 psig (pounds per square inch gage). The power input to the plasma-jet was slowly decreased to 100 amperes after each coating procedure before turning the plasma-jet off completely. This procedure tended to prolong the life of the electrodes and reduced the residual stresses developed at the interface of coated specimens during cooling. Table Ib shows the pre-heating temperatures and stand-off distances (distance from Plasmatron head to coating surface) used for each specimen.

4.213 Coating Procedure in an Inert-Atmosphere

The procedure used to coat 1020 steel substrates (2" x 7" x 1/8") with tungsten in an inert atmosphere was as follows:

The initial purging of the chamber to obtain an inert atmosphere was carried out by partially evacuating the air with a mechanical vacuum pump and then introducing nitrogen gas, pre-heated to approximately 300°F. The chamber was first evacuated by the vacuum-pump until the rubber chamber-glove was stiffly erected inside the chamber. The vacuum-pump valve was then shut and pre-heated nitrogen was introduced until the glove was stiffly erected outside the chamber. After repeating this procedure twenty times in the course of one hour, the nitrogen flow was left on while the locks on

the 4 1/2" check valve were released. The plasma-jet arc was struck and the plasma-jet was left on for two minutes. The heat from the plasma-jet expanded the chamber gases, resulting in additional purging. The gas remaining in the chamber after this initial firing was slightly yellow in color, indicating the formation of nitrogen oxides. A second purging by ignition of the plasma-jet for three minutes eliminated all signs of nitrogen oxides present in the chamber.

Before the initial purging, nine steel-specimens were polished and placed inside the chamber in a rack. Number 500-grit abrasive paper and +325-mesh tungsten powder (dried at 150°C for 15 hours) were also placed in the chamber before the initial purging operation.

All specimens were polished a second time with No. 500 grit abrasive paper while they were in the inert atmosphere, just prior to the pre-heating and coating procedures. Table Ib lists the individual pre-heating temperatures for each specimen. The same coating procedure was used as that described in the previous section. The plasma-jet control settings were increased when the last two specimens were coated so that a comparison of power input versus relative coating density could be made by microexamination.

4.22 Graded Coating of Tungsten - 1020 Steel Mixtures on 1020 Steel Substrate

It was the objective during this phase of the investigation to deposit a coating on 1020 steel such that a graduated region ranging

from 1020 steel at the inner interface to 100 per cent tungsten at the outer surface would be obtained. It was felt that such a coating would provide a more gradual thermal expansion gradient between the steel plate and the tungsten layer and would also promote fusion at the interface.

4.221 Dual Powder-Feeding-System

A dual powder-feeding-system was installed to facilitate the deposition of the graded coating. Each of the two feed inlets in the Plasmatron front electrode were fed from separate Plasmatron powder-hoppers. Separate argon pusher-gas pressure systems were connected to each of these hoppers.

Several modifications and adjustments were tried on the dual feeding-system before any attempts were made to deposit a graded coating on a prepared specimen. The venturi on each powder hopper was adjusted until the lowest feeding rate was established for the two different powders. Both hoppers were moved as close to the Plasmatron head as possible (1 1/2 feet) to reduce the flow resistance in the copper tubing that connects the hoppers to the head. The dual powder-feeding-system finally adopted was that described under 4.11, Plasmatron Apparatus.

4.222 Graded Coating Procedure

The surface on one side of each of thirteen 1020 steel specimens (7" x 2" x 1/8") was ground down .02 inches with a surface grinder to eliminate any skin effects that might interfere with the coating

technique. Chromel-alumel thermocouples were spot-welded on the side of the specimen opposite the surface which had been prepared on the surface grinder. The surface-ground face was manually ground with number 500 grit abrasive paper just prior to coating. Two specimens (No. 19 and No. 20) were pickled, after manual sanding, in a solution of 50 per cent HCl plus 50 per cent alcohol. Table IIa lists the control settings used for each of the thirteen specimens coated during that period.

The same purging procedure was followed when coating specimens in an inert atmosphere as was outlined in the previous section. A five-minute preliminary firing of the plasma-jet was again made before attempting to coat any specimens.

The 4 1/2" check valve was shut after each coating procedure when the operator was ready to turn the plasma-jet off. This resulted in an increase in pressure inside the chamber. By gradually decreasing power to the plasma-jet, the pressure inside the chamber was reduced. A slight positive pressure was maintained inside the chamber during the shut-down period by a balance between the two above changes in pressure. This procedure was used to eliminate any chance for oxygen to be drawn into the chamber through the check valve during the shut-down period when pressure conditions inside the chamber were unsteady.

Seven of the thirteen specimens (No. 19, No. 25-27, No. 30, and 31), prepared for this phase of the investigation, were coated in an inert atmosphere. All seven specimens were positioned at a stand-off distance of seven inches and pre-heated to temperatures below the first

transformation temperature of steel (723°C).

The actual coating technique used during this coating period for each specimen was the same in each case. 1020 steel was sprayed onto a specimen for the first two passes. This was followed by spraying both tungsten and 1020 steel for the next two passes, and finally, during the last two passes, only tungsten was deposited. Variables such as power input to the plasma-jet, flow and pressure of the pusher-gas to the powder hoppers, and particle-size of the coating powders were adjusted during these coating procedures to eliminate clogging of the injection orifices in the Plasmatron head.

4.223 Heat Treatment Studies

Microexaminations were made on specimens as indicated in Table IIa. From these microexaminations Specimen No. 30 was chosen for use in studies of the effect of heat treatments on this type of multiple coating. The section of Specimen No. 30 used for the initial microexamination was cut in half. One half was heat treated at 650°C for one hour and the other half at 950°C for one hour. Both halves, were furnace-cooled after treatment at a rate of 15°C/min. They were then mounted, polished, etched (3 per cent nital), and microexamined. Hardness readings were taken before and after each heat treatment on a Leitz microhardness tester (Vickers Hardness - 100 g load).

4.23 Graded Coating of Tungsten-Iron Mixtures on 1020 Steel Substrate

An attempt was made to deposit a graduated coating on 1020 steel plate, ranging from pure iron at the inner interface to 100

per cent tungsten at the outer surface. The reasons for trying to deposit this type of coating on 1020 steel plate were as follows:

1. In the annealed condition, an iron coating could be expected to be more ductile at both room temperature and at elevated temperatures than a corresponding 1020 steel coating.
2. In a graded coating containing iron there would be no possibility of the formation of carbides within the zone adjacent to the pure tungsten zone.
3. The coefficient of thermal expansion of iron (6.5 micro-in./in./^{o}F) lies between the coefficients of thermal expansion for 1020 steel (8.0 micro-in./in./^{o}F) and tungsten (2.55 micro-in./in./^{o}F).
4. Only slight changes in crystalline structure and transformation temperatures could be expected to occur upon the replacement of steel by iron in the graded coating. It would be unlikely, therefore, that the degree of fusion bonding previously developed through the use of steel powder, would be decreased.

4.211 Graded Coating Procedure

Four 1020 steel plates (7" x 2" x 1/8") were first coated in the normal atmosphere with this second type of graded coating (see Table IIIa). The same coating procedure was followed as that used in depositing the first type of multiple coating. A modification of the

powder hopper reduced the powder flow so that the plasma-jet would not be overloaded. This was accomplished by reducing the exit orifice of each hopper to the same diameter as the venturi in each hopper.

4.232 Heat Treatment Studies

One of the more promising specimens (No. 34) from these first attempts was microexamined. The specimen was then heat treated at 950°C for one hour and furnace cooled (7 1/2°C/min.). The specimen was remounted, polished, etched, and microexamined. Microhardness readings were taken before and after the heat treatment.

Three specimens (No. 40, No. 41, and No. 43) were coated in an inert atmosphere. Immediately after coating, each specimen was placed in a tubular furnace, previously located inside the chamber. Specimens No. 40 and No. 43 were held at 950°C for one hour before furnace cooling. Specimen No. 41 was furnace cooled when it reached 950°C in the tubular furnace. Microexaminations and microhardness surveys were made on Specimens No. 41 and No. 43. The three specimens were then heat treated in a vacuum furnace for one hour at 950°C and then furnace-cooled. Microexaminations and microhardness surveys were made on all three specimens.

The general procedure for depositing the tungsten-iron graded coating was established by the above investigations. Slight modifications in this procedure were necessary in the preparation of specimens used in the following evaluation tests. The preparation

of these specimens will be described along with their respective evaluation test in the following section.

4.3 Coating Evaluation Tests

The nature of the bonds established by the coating processes were investigated by optical microscopy and x-ray diffraction techniques where applicable. Microhardness surveys were used in support of the above investigation techniques. A radioactive tracer technique was developed to study diffusion rates at the interface. A mechanical test method proposed (Metallizing Engineering Company, 1957) for testing the shear strength of the bonds was evaluated. The results obtained from such mechanical shear tests were correlated with the variables employed during the coating procedure. The plasma-jet was used to test the most promising bonds under conditions of thermal shock and normal atmosphere. A more detailed description of the coating evaluation techniques used during this investigation are given in the following sub-sections.

4.31 Development of Radioactive Tracer Technique

4.311 Preliminary Investigations

A radioactive tracer technique as a means for checking coating diffusion was tried because of its accuracy, ease of application, and the ready availability of tracer preparation facilities at The University of Arizona. Several refractory materials that have melting points above 2800°C (tungsten, tungsten carbide, tantalum, tantalum carbide, and zirconia) and a selected variety of structural steels

(1017, 1040, 4140, and 8640) were first investigated to establish whether a tracer technique was possible for each case. At least one isotope for each refractory proved favorable for studying diffusion by the tracer technique. The quantity and half life of the characteristic radiations from the isotope (s) present in the steels investigated was low enough so that they would not tend to mask the radiations from the refractory materials themselves.

A trial run was made to confirm the above observations before any attempt was made to investigate a controlled diffusion study by the technique described below.

A disk (1/2" diamter - 1/8" thick) of 1017 steel was coated on one side with a thin layer of tungsten (1/100" thick) by the Plasmatron equipment in the normal atmosphere. This specimen was irradiated in the university nuclear reactor and then placed in a lead container for 24 hours to allow the background radiation caused by the isotopes in the steel to decay. After this period, a radiation spectral analysis was made on the specimen to detect isotopes still present. Only a small trace of one isotope in the steel, Mn-56, was detected, while all four of the tungsten intensity peaks for isotope W-187 persisted with comparatively large radiation counts per minute. The coated surface would have been surface-ground and checked for tungsten content (counts per minute) to establish the depth of penetration of the tungsten in the steel if this had been a controlled diffusion study.

4.312 Controlled Diffusion Study

A controlled diffusion investigation was conducted to establish the usefulness of this tracer technique for diffusion studies of tungsten into steel and to establish a standard procedure to follow in investigating diffusion produced by the Plasmatron equipment. Tungsten powder (-325 mesh) and 1017 steel disks (3/4" dia.) were used for the controlled diffusion study. Tungsten had the longest half life and largest neutron absorption cross section of the refractories investigated and 1017 steel gave rise to the least radiation background counts of the structural materials investigated. The controlled diffusion study was conducted in a vacuum tubular furnace since the Plasmatron and supporting equipment were not completely operational at that time. Six disks of 1017 steel were ground on a surface grinder to the same thickness (.1754 in.). One side of each specimen was in firm contact with tungsten powder during a five hour heat treatment at 910 $\pm$ 10°C. This particular temperature was selected since the first complete phase change occurs at this temperature in both the iron-tungsten (alpha to gamma) and the iron-carbon (alpha + Fe_3C to gamma) constitutional diagrams.

Starting with the first specimen (surface-ground a second time to its original .1754 inch thickness) each specimen was then surface ground 1/10,000 of an inch more than the preceding specimen.

The six specimens plus one control disk (a 1017 steel disk surface-ground and heat treated without any contact with the tungsten powder) were then irradiated for three hours at 2.8 x 10" neutrons/cm^2/sec in the university nuclear reactor. The specimens were "cooled" for

three days to allow the isotopes in the steel to decay to a background count that would not interfere with the analysis of the radiation emitted from the tungsten.

Further use of this technique was anticipated when a fusion bond between plasma-jet sprayed tungsten and a steel substrate had been developed.

4.313 Conversion Curve of Counts per Minute to Weight of Tungsten

Counts per minute versus weight of tungsten curves were established for ease of conversion in calculating the concentration of tungsten in steel from counts per minute. Once the tungsten concentration had been established at different penetration depths in the steel specimens, the diffusion coefficient of tungsten could be determined from Fick's Second Law for that particular specimen. The standard conversion curve for tungsten was made by the following procedure:

Increasing amounts of tungsten were weighed out and placed in the standard irradiating vials used to contain samples being irradiated in the university nuclear reactor. In order to keep the seven powdered-tungsten samples from dispersing throughout their respective vials, which would cause a different geometry for each sample during the counting operation, the vials were filled with commercially sterilized cotton to keep the tungsten in a fixed position while being irradiated, transferred, and counted.

These seven vials, plus one vial containing only cotton, were irradiated for 2 hours at 2.8 x 10" neutrons/cm^2/sec and allowed to

"cool" for 48 hours before counting in a well-type scintillation counter. The amount of background radiation emitted by the cotton and vials was obtained from the vial containing only cotton. These additional counts per minute were subtracted from the values obtained from the seven vials containing tungsten. The corrected values (counts/min.) of the two largest characteristic tungsten intensity peaks (0.686 and 0.480 Mev) can be seen in Table IV in the Appendix. The corresponding weights of tungsten are also given. From these values, the counts per minute versus weight of tungsten curves were established as indicated in Figure 10.

4.32 Microexamination and Microhardness Surveys

Microexamination of each type of coating was used as the initial evaluation test. By studying the microstructure of heat treated samples of the steel coated with tungsten, it was possible to determine an appropriate pre-heating temperature that would limit phase transformations to the surface (approximately 1/100" thick) of the substrate. Since the temperature of the substrate rose during the coating process, it became possible for the entire substrate to undergo a phase transformation if the pre-heating temperature exceeded approximately 650°C. Transformations of this extent had to be guarded against since they introduced stresses sufficient to cause spalling during cooling.

The tungsten coatings were evaluated on a relative basis by recording such factors as the extent of their laminar structure, penetration into the substrate, oxidation layers, and porosity.

These relative values were correlated with the console settings, stand-off distance, and pre-heating temperature. This correlation minimized much of the guesswork in the selection of proper settings when the tungsten-1020 steel graded coating was being developed. Microexaminations of these latter coatings were conducted mainly to determine how uniformly gradual the mixed coating could be when produced with the dual powder-feeding-system.

Microhardness readings were taken on one specimen (No. 30) of this second type of coating (tungsten-1020 steel graded coating) that displayed the most promise according to microexaminations. This hardness survey was repeated after the specimen had been heat treated at 950°C for one hour and furnace cooled at the rate of 15°C/min. From these studies, the effects of the heat treatment on the microstructure and hardness of the specimen were obtained.

Since the first two coating techniques served mainly as guides to the development of the third coating (tungsten-iron graded coating), a more detailed description of the two evaluation tests discussed above will be made in the following sub-section on this third type of coating.

4.321 Tungsten-Iron Graded Coating on 1020 Steel Substrate

Microexamination of this type of coating was conducted mainly to study the amount of fusion it produced and the extent to which uniform dispersion could be developed in it. The preparation of specimens used for these studies was as follows:

Tungsten-iron graded coatings were deposited on ten 1020 steel specimens (7" x 2" x 1/8"). The same coating procedure was followed

as that described in Section 4.23. The ten specimens were furnace cooled (rate of cooling - 7 1/2°C/min.) from 950°C immediately after coating. On four of these ten specimens (Nos. 49, 50, 54, and 56), the pure tungsten layer was omitted so that x-ray diffraction studies, described in the next section, could conveniently be made on the tungsten-iron mixture. The remaining six specimens were used for microexaminations and microhardness surveys. The plasma-jet coating data for these ten specimens are summarized in Table IIIb.

Specimens to be microexamined were mounted in black bakelite, polished, etched with 3 per cent nital for 10 seconds, and examined and photographed with a Reichert Metallograph (magnification range - 75x to 2500x).

Detailed microhardness surveys were conducted to provide further correlation with the microexaminations and x-ray diffraction studies (as described in the next section) which were conducted on the tungsten-iron graded coatings. Preparation of specimens for microhardness surveys was the same as that used to prepare specimens for microexaminations. The microhardness surveys were made on Specimens No. 34, 40, 41, 43, 51, 52, 53, 55, 56, 57, and 65. The hardness readings taken across each of these sectioned specimens were spaced as indicated in Figures 11-20. It was not possible to take hardness readings in a straight line on the coating due to the oxide layers and inclusions present. Readings were taken within a narrow band across the sections while maintaining the desired spacings between the readings (see Figure 44). Hardness readings in the tungsten-iron

region were taken in the centers of those iron-rich areas and tungsten-rich areas large enough to support the diamond indentor.

One microhardness survey was made on Specimen No. 34 after it had been coated and air cooled (A.C.). This survey was repeated after this specimen had been heat treated for one hour at 950°C and furnace cooled (F.C.). One microhardness survey was made on Specimen No. 40 after the above heat treatment.

Microhardness surveys were conducted on Specimens No. 41, 51, 52, 53, 55, 56, and 57 after they had been coated and furnace cooled (F.C.) from 950°C. These specimens plus Specimen No. 43 were then heat treated (H.T.) at 950°C for one to three hours, as indicated in Figures 13-20, before repeating the microhardness survey.

4.33 X-Ray Diffraction

X-ray diffraction techniques were applied to the tungsten-iron graded coating to investigate (1) the effects of heat treatments on the tungsten-iron regions and (2) the types of tungsten concentration gradients developed in the tungsten-iron regions by two alternate coating procedures. To accomplish these investigations, it was first necessary to set up certain x-ray diffraction standards.

4.331 Standard for X-Ray Diffraction Studies

Three twenty-gram powder compacts of tungsten (-325 mesh) and iron (-325 mesh) were made up and melted in an induction vacuum furnace The weight percentages of tungsten in these three compacts were 20, 62, and 69 per cent respectively. They were selected to coincide with significant compositions in the tungsten-iron alloy system. These

compacts and one sample of commercially supplied ferrotungsten (80 per cent - W, 0.60 per cent - C, Balance - Fe) were used as x-ray standards.

A Norelco x-ray unit (North American Philips Company) with a copper tube (Cu-Kα_1, wavelength 1.54050 A^{o}) was used in conjunction with a scintillation-counter and strip-chart recorder for all the x-ray diffraction studies. The x-ray unit was operated at 35 kilovolts and 15 milliamperes. A scan from $2\theta = 15^{o}$ to 115^{o} was used in analyzing the four specimens prepared as x-ray standards. The relative peak intensities of the four constituents identified are given in Table V.

The relative intensities of the iron peaks were not used for quantitative analyses. Secondary fluorescence is encountered according to Klug and Alexander (1954) when

$$\Delta Z = Z_1 - Z_2 = 2 \text{ or } 3$$

where Z_1 = atomic number of target material

and Z_2 = atomic number of element in specimen under investigation

$\Delta Z = 3$ when using a copper x-ray tube and iron as the specimen. Tungsten peaks are not troubled by this effect since secondary fluorescence is scarcely detectable for values of ΔZ larger than 5 (Klug and Alexander, 1954).

In order to determine the concentration of tungsten present within tungsten-iron regions, a tungsten concentration versus relative percentage intensity curve was needed. Eleven compacts were prepared for this purpose. Tungsten and iron powder (-325 mesh) were accurately

weighed out, thoroughly mixed, and compressed (40,000 psi) to give a mechanical mixture of tungsten and iron. The weight percentages of tungsten in these tungsten-iron compacts were 0, 10, 20, 30, 40, 50, 62, 69, 80, 90, and 100 per cent respectively. X-ray diffraction patterns were made of each of the eleven compacts. The relative percentage intensity as indicated by the highest tungsten peak ($2\theta = 40.42$, $d = 2.23$) for each compact was plotted against its weight percentage of tungsten, in Figure 21. The concentration of tungsten present in a tungsten-iron mixture can be found directly from this figure if the height of its tungsten peak ($d = 2.23$) is known.

4.332 Heat Treatment Effects on the Tungsten-Iron Region

With further reference to the four specimens (Nos. 49, 50, 54, and 58) mentioned in Section 4.321 which were designated for x-ray diffraction studies, one specimen (No. 54) was dealt with as follows:

1. The outer layer, the tungsten-iron mixture, was surface ground to provide a smooth surface for x-ray diffraction studies.
2. After the coating procedures, an x-ray diffraction pattern was obtained on the smooth tungsten-iron surface.
3. The specimen was heat treated for three hours at 950°C in an inert atmosphere (Argon) and the x-ray procedure followed in step No. 2 was repeated.

4. The specimen was heat treated for another six hours at 950°C and the x-ray procedure followed in step No. 2 was repeated.

Specimen No. 54 was then heated in an induction furnace under a vacuum to 1500 ± 25°C. This treatment was the same as that given the three compacts used as standards in Table V. Specimen No. 54 was cooled when the coating began to melt. The same x-ray diffraction scan was made on this coating as was used on the standards described above.

4.333 Tungsten Concentration Gradient

Two general types of coating techniques were selected for evaluation of the tungsten concentration in the tungsten-iron region. The first type (as used to coat Specimen No. 49) was the result of gradually increasing the pressure of the pusher gas connected to the tungsten powder hopper while maintaining a constant pressure of 15 psi on the iron hopper during the coating procedure. Once the pressure to the tungsten hopper reached 15 psi, the pressure on the iron hopper was slowly reduced to zero. The pressure to the tungsten hopper was immediately cut off at this point so that the tungsten-iron region would not be completely covered by a pure tungsten layer. This control made the tungsten-iron region accessible for x-ray diffraction studies.

The second method of depositing a tungsten-iron coating was used on Specimens No. 50 and No. 58. Two layers of iron were deposited on these two specimens at a hopper pressure of 20 psi. This was followed by the immediate injection of tungsten powder into the plasma-jet at a hopper pressure of 10 psi. This resulted in four tungsten-iron

layers of varying composition over two iron layers on both specimens. The coating procedure was then terminated to provide accessibility to the tungsten-iron layer for x-ray studies.

The three above specimens (No. 49, No. 50, and No. 58) were pre-heated at nearly the same temperature (see Table VI), furnace cooled from 950°C after coating, and heat treated for one hour at 950°C (furnace cooling rate - 7 1/2°C/min.). A smooth surface was obtained on the coated side of these specimens by surface grinding. X-ray diffraction scans were made on these smooth surfaces. Each specimen was surface ground and x-rayed seven more times. The concentration gradient of tungsten in the tungsten-iron layers was easily viewed by plotting the distance from the interface against the relative height of the highest tungsten peak (d = 2.23) detected at that distance (see Figure 22). The weight percentage of tungsten is also shown in Figure 22 as determined from the curve of Figure 21.

4.34 Thermal Shock Test

The plasma-jet itself provided the thermal shock needed to test the bond strength of the coatings. The primary reason for this test was to check for spalling. The effect of coating thickness on "time of burn through" was of secondary importance. The "time of burn through" is defined as the time required for the plasma-jet to burn a hole completely through a specimen positioned perpendicularly in front of the plasma-jet stream.

Tests were conducted primarily in the normal atmosphere. The test specimens were positioned perpendicular to the plasma-jet stream.

The stand-off distance and the console settings for these tests were determined by first burning through thin sheets of tungsten and 1020 steel plates. The selection of stand-off distance and console settings was made on the basis of "time of burn through" data collected during Firings 69-86 (see Table VIa). A stand-off distance of two inches with a power input setting of 700 amps allowed sufficient "time for burn through" such that errors introduced by manual timing were insignificant.

Seven specimens coated with a graded tungsten-iron coating were prepared for thermal shock studies. The coating procedure which produced the best coatings previously examined was employed in the preparation of these specimens (see Table VIb). The seven specimens were heat treated after coating for one hour at 950°C and furnace cooled (7 1/2°C/min.).

The same method for depositing the three different coating layers was followed as that described for Specimens No. 50 and No. 58 in Section 4.333. The coating time for the tungsten-iron layers was varied from 19 to 89 seconds. The coating times for the iron and tungsten layers were the same for each specimen (see Table VIb).

Thermal shock tests were made on six of these specimens. The same settings and conditions were used as those given for Firing Nos. 77-82 in Table VIa.

Specimen No. 65 was prepared under the same conditions as the six specimens used in the thermal shock tests. It was used for microexamination and a microhardness survey.

4.35 Mechanical Shear Test

A sensitive method was needed to test the fusion bond strength between the substrate and its coating. It was felt that such a method might indicate the effectiveness of heat treatments and the advantages of different coating techniques. Since coatings frequently fail under shear stresses, it appeared that a mechanical shear test would provide the most beneficial data. A literature search led to the mechanical shear test described below (Metallizing Engineering Company, 1957).

Figure 23 shows the components needed for this mechanical shear test. The cylinders were machined from 1020 steel bar stock (see Figure 23a). The jig used to move the flat specimens in a uniform zig-zag fashion was modified to handle these cylinders. The jig rotated the cylinders while passing them back and forth through the plasma-jet.

The same coating procedure was followed as that described in Section 4.33. The cylinders were plasma-jet pre-heated below the first transformation temperature of steel (723°C), coated with pure iron, and then furnace cooled from 950°C in an inert atmosphere (Specimens No. 103 and 113 were air cooled). The coated cylinders were machined as indicated in Figure 23b. The machined specimens were finally forced through the die shown in Figure 23c. An Instron tensile tester was used to record the compressive load required to shear the coating from the cylinder (see Figure 23d). The history of each specimen was correlated with its shear load.

The maximum shear strength of thirty specimens was obtained from the mechanical shear test procedure described above. Figure 24 indicates the method used in obtaining the maximum shear strength values from the two general types of curves recorded on the Instron strip recorder during the mechanical shear tests. The curve for Specimen No. 97 indicates ductile behavior. The iron coating spalled off gradually. This resulted in numerous peaks as shown in Figure 24. The curve for Specimen No. 103 represents brittle fracture. The iron coating was sheared off abruptly.

The first six specimens (Nos. 87-92) of the thirty-four specimens coated with iron were not coated in an inert atmosphere. The last four specimens (Nos. 117-120) were coated and then sectioned for microexamination.

5. RESULTS AND DISCUSSION

5.1 In General

Of the three coating methods developed during this investigation, the graded coating of tungsten-iron on 1020 steel proved to be the most effective. The previous development of the other two coatings, however, was beneficial in establishing the method used to produce the tungsten-iron graded coating. Detailed results obtained during the evaluation of the three coatings are discussed in the following subsections. The initial evaluation of each type of coating was accomplished by microexamination. The results from the other evaluation tests used to study the three types of coatings are considered in the order that the evaluation tests were applied. Discussion of the radioactive tracer technique has been placed at the end of the report in view of the fact that it was not applied to the three types of coatings developed during this investigation.

5.2 Plasma-Jet Sprayed Coatings

5.21 Tungsten Coating on 1020 Steel Substrate

The plasma-jet control settings used to deposit tungsten on 1020 steel substrates are summarized in Table Ia. The results obtained from microexamination of this first type of coating are summarized in Table Ib. Column 9 in this latter table indicates whether or not the

coating spalled during cooling. Specimens pre-heated below 531°C did not spall while those specimens pre-heated at 602°C or above did spall during cooling.

The evaluation of the coatings by microexamination was based on the four items that head Columns 5-8 in Table Ib. Figure 25 provides a visual illustration of the terms "laminar layers" and "coating porosity" referred to in Table Ib. Figure 26 illustrates the meaning of the terms "tungsten penetration" and "extent of oxidized coating." The amount of tungsten that penetrated through the oxide layer at the interface and into the 1020 steel surface indicates the relative amount of tungsten penetration reported in Table Ib. The fine grains at the regions of tungsten penetration are to be noted. Their presence resulted from surface recrystallization of the cold-rolled steel brought on by the hot tungsten which penetrated the surface (see Figure 27).

Microexamination of the specimens which had been coated in a inert atmosphere revealed less porosity, less oxidation, and finer laminar layers than those which had been coated in the normal atmosphere (see Figure 2?). In the former, a significantly larger amount of tungsten had penetrated through a very thin oxide layer at the interface. Within these regions, recrystallization had occurred, and what appeared to be a thin alloyed layer (metallic red luster), formed between the steel and the tungsten coating (see Figure 29).

Figure 30 illustrates the relative increase in the density of the sprayed tungsten (on Specimen No. 18) when the power input to the

plasma-jet was increased some 52 per cent above that for the previous specimens.

The bond between the sprayed tungsten and 1020 steel substrate was, in general, weak and brittle. Sudden heating or a sharp blow with a hammer caused this type of coating to spall. The first attempt to overcome these difficulties was tried through the development of the tungsten-1020 steel graded coating.

5.22 Graded Coating of Tungsten-1020 Steel on 1020 Steel Substrates

Table IIa gives the plasma-jet control settings, pre-heat temperatures, hopper pressures, and particle sizes of the powder used during each firing. This table also indicates which of the coated specimens were microexamined and which coatings spalled during cooling.

Microexaminations were conducted on the tungsten-1020 steel graded coatings for three main reasons: (1) to ascertain whether a good graded coating was being deposited by the dual powder-feeding-system, (2) to compare the amount of oxidation that occurred at the interface of specimens cleaned chemically with those specimens cleaned mechanically just prior to coating, and (3) to determine the type of bond that was developed at the interface. The results obtained from these microexaminations are as follows:

Figure 31 illustrates the best graded coating developed during this phase of the investigation. Even this coating, however, lacked the desired uniform gradient varying from 1020 steel at the interface to 100 per cent tungsten at the outer surface. Frequent difficulties

encountered with the powder-feeding system during some of the firings caused complete segregation of the two metals being coated as illustrated in Figure 32. Such studies enabled the dual powder-feeding-system to be modified until it was capable of depositing graded coatings which surpassed in uniformity the one shown in Figure 31.

The surface of the specimen cleaned chemically after mechanical polishing and coated in an inert atmosphere displayed larger amounts of oxidation at the interface (see Figure 33) than specimens cleaned mechanically and coated in the normal atmosphere (see Figures 34 and 35) or in an inert atmosphere (see Figures 36 and 37). Evidently, the inert atmosphere contained enough oxygen so that a chemically cleaned surface could still be readily oxidized. One specimen was coated in the normal atmosphere immediately after being cleaned chemically, but was highly oxidized, probably due to a surface reaction between residue from the chemical cleaning reagents and the oxygen. The coating spalled as a result of this excessive oxidation.

Figure 36 shows the best adhered coating produced during this phase of the investigation. This specimen lacked good graded coating, however, due to powder-feeding difficulties. Examination at higher optical power showed excellent fusion at the interface between the sprayed 1020 steel and the substrate (see Figure 37). Unfortunately, the 1020 steel powder used in coating this specimen was slightly oxidized before the coating procedure got under way. This condition permitted the formation of most of the oxide layers observed within

the coating and interfered with desirable grain growth between steel layers and across the interface.

5.221 Effects of Heat Treatments

Table IIb indicates the effects of two different heat treatments on the microhardness of a tungsten-1020 steel graded coating on a 1020 steel substrate. Both the steel substrate and the coated steel were stress relieved. The average hardness values of the coated tungsten were not effected by these heat treatments.

There was no significant change in the microstructure of the specimen heat treated at 650°C for one hour. However, in the specimen heat treated at 950°C for one hour, (Figure 38), recrystallization and grain growth are evident, as would be expected at this higher temperature.

In an attempt to eliminate carbides at the interface and within the tungsten-1020 steel region of the graded coating, the 1020 steel powder used in the coating procedure was replaced with pure iron powder. This change resulted in the development of the tungsten-iron graded coating.

5.23 Graded Coating of Tungsten-Iron on 1020 Steel Substrates

Tables IIIa and IIIb give the plasma-jet coating data used during the deposition of tungsten-iron graded coatings on 1020 steel substrates that were prepared for microexamination, microhardness surveys, and x-ray diffraction studies. The maximum thickness of each coating is also given in these tables. The results of each of the four

types of evaluation tests conducted on the tungsten-iron graded coatings is discussed in the following sub-sections.

5.231 Microexamination Studies

Figure 39 illustrates the typical surface recrystallization that resulted when specimens were pre-heated at temperatures below the first transformation temperature of steel (723°C), prior to being coated. Figure 40 shows the type of microstructure which resulted from a heat treatment after coating. It was noted that specimens allowed to air cool after coating spalled if they were not heat treated within 24 hours. As a result of the post heat treatment, however, grain growth occurred in the iron coating, in the 1020 steel substrate, and across their common interface. Even graded coatings which were as thick as the substrate itself did not spall after the coating procedure if they were immediately post-heated and furnace cooled. Additional results of the beneficial effects of heat treatments on this type of graded coating were obtained by microhardness surveys and x-ray diffraction studies discussed in the next two sub-sections.

Figure 41 shows the improved graded coating made possible by the modified dual powder-feeding-system with the plasma-jet settings used in Table IIIA. Figure 42 indicates the improved fusion and grain growth across the interface of specimens post-heat-treated and furnace cooled. These specimens, coated in an inert atmosphere, had relatively fewer oxide layers compared with specimens coated in the normal atmosphere (see Figure 40). This comparison again indicates the value

of coating in an inert atmosphere.

Figure 43 illustrates the typical graded coating obtained with the coating procedure used for specimens listed in Table IIIb.

5.232 Microhardness Surveys

The results of microhardness surveys taken across eleven tungsten-iron graded coatings on 1020 steel specimens, whose plasma-jet coating data are listed in Tables IIIa and IIIb, are given in Figures 11-20. Figure 44 indicates the procedure used in obtaining these microhardness values. The curves connecting the various types of points shown in Figures 11-20 indicate the general hardness trends in the 1020 steel substrate region and in the graded coating region. The broken line curves represent hardness trends after the coating procedure and the solid line curves represent hardness trends after a heat treatment. Hardness values taken after a heat treatment were more uniform within any one region and, in general, were lower than those taken before the heat treatment. This condition indicated that the iron, steel, and tungsten had experienced stress relief during the heat treatment.

It is to be noted that after the heat treatment the hardness values of the iron tended to increase and those of the tungsten tended to decrease in the tungsten-iron region. This behavior may be attributed to a conversion of tungsten oxide to tungsten during the heat treatment. Since the free energy of formation for iron oxide is approximately twice that for tungsten oxide (Kubaschewski and Evans,

1958), oxygen taken up by the tungsten particles during the coating procedure would tend to migrate to the iron during the heat treatments. Such a process would account for the decreased hardness of tungsten and the increased hardness of iron in the tungsten-iron region and for the retained hardness of the tungsten in the pure tungsten layer after heat treatment (see Figures 11-20).

Although x-ray diffraction studies indicate the formation of a solid solution of iron and tungsten in the tungsten-iron region during heat treatment at 950°C (discussed in the next section), the oxygen migration mentioned above, which increased the hardness of the iron component, masked any normally expected increase in tungsten hardness by solid solution hardening.

5.233 X-Ray Diffraction Studies

X-ray diffraction studies were conducted on the tungsten-iron region of the four specimens specially prepared for this type of examination. The results of the two objectives investigated by x-ray diffraction techniques are discussed in the following sub-sections, 5.2331 and 5.2332.

5.2331 Detection of Components Present in the Tungsten-Iron Region

From the four tungsten-iron alloy specimens prepared for x-ray diffraction standards, the relative peak intensities of the four constituents present are listed in Table Va. It is apparent from these results that as the weight percentage of tungsten increased the amount of the intermetallic compound $Fe_{36}W_6$ decreased and that of Fe_7W_6

increased. The "d spacings" obtained for these two compounds agree with the A.S.T.M. Diffraction Data Cards. The results obtained from these standards were compared with x-ray diffraction patterns taken on the tungsten-iron regions of the plasma-jet sprayed coatings specially prepared for x-ray diffraction studies. In the latter, no peaks corresponding to intermetallic compounds were evident indicating that the coatings were a mechanical mixture of tungsten and iron only.

The effects of heat treatments on the x-ray diffraction pattern of the tungsten iron region are listed in Table Vb. The "d-spacing" increased with increasing time at the listed temperature for each x-ray intensity peak recorded. There was a decrease in the relative heights of the tungsten intensity peaks with increasing time at the listed temperature. The intensities of the iron peaks remained constant or increased. The shift of "d-spacing" and decrease in tungsten intensity strongly suggest the formation of a solid solution during the heat treatments (Klug and Alexander, 1954).

Only a trace of Fe_7W_6 was disclosed by x-ray diffraction studies on the tungsten-iron region after it had been partially melted at 1500 $\pm$ 25°C. There are two major disadvantages in obtaining an intermetallic compound or large amounts of solid solution by melting. They are (1) distortion, and (2) loss of strength of the substrate, both of which would result from any heating at such an elevated temperature. Lack of any alloying or compound formation between the tungsten and iron is attributed to the short residence time of these metal particles in the plasma-jet stream.

5.2332 Tungsten Concentration in the Tungsten-Iron Region

Figure 22 illustrates the tungsten concentration gradients obtained for the two different coating procedures described in Section 4.333. The ordinate on the right side of this figure corresponds with the abscissae in Figure 21. The ordinate on the left side corresponds with the ordinate in Figure 21.

The maximum peaks shown in Figure 22 for the curves of Specimens No. 50 and No. 58 were the results of the initial surge of powder from the tungsten powder-hopper when it was first turned on. A steady flow of powder was not established for several seconds according to these concentration curves. By increasing the power input to the plasma-jet by 18 per cent, the tungsten concentration in the tungsten-iron region was nearly doubled, increasing as it did from 32 to 70 per cent tungsten, as indicated by these two curves.

The concentration gradient of tungsten in the tungsten-iron region was greatly improved by using the coating technique described in Section 4.333 for Specimen No. 49 as indicated in Figure 22. Unfortunately, the conditions present during this coating procedure, which involved low pushing pressure on low-melting metals, favors clogging at the injection orifices in the Plasmatron head and is, of course, detrimental to the coating procedure.

5.234 Thermal Shock Tests

The plasma-jet coating data for the tungsten-iron graded coatings on 1020 steel specimens which were prepared specially for

evaluation by thermal shock tests are listed in Table VIb. Figure 44 shows the typical type of coating deposited for these thermal shock tests. The tungsten layer is approximately twice as thick as the iron or tungsten-iron regions. This thickness correlates closely with the coating-time used in the application of these coatings to the 1020 steel substrates (see Table VIb).

The "burn through times" obtained from the thermal shock tests are entered in Column 13 of Table VIb. None of the tungsten-iron graded coatings spalled during the thermal shock tests. The "time of burn through" was increased by approximately two and one half times that obtained for steel specimens which were not coated. The improved resistance to spalling demonstrated in these severe thermal shock tests indicated no need for the development of further heat treatments directed toward forming additional bonds between iron and tungsten particles. This indication was confirmed by exploratory heat treatments (5.2331).

5.3 Mechanical Shear Test

The mechanical shear test was applied to 1020 steel cylindrical specimens whose exterior surfaces had been coated with iron rather than with a graded coating of a tungsten-iron mixture, as explained in Section 4.35.

The plasma-jet coating data for the thirty-four specimens prepared for mechanical shear tests are shown in Table VIIa. The heat treatment of each specimen after the coating procedure and just

prior to shear testing is given in Table VIIb. The maximum shear strengths of the thirty specimens tested are given in both of these tables. Figure 24 illustrates the method used in obtaining the maximum shear strength values from the two general types of curves recorded on the Instron strip chart recorder during the mechanical shear tests. Specimens that displayed brittle fracture have a symbol after their Firing No. in Tables VIIa and VIIb. The maximum shear strengths in pounds per square inch, shown in the last columns of Tables VIIa and VIIb, were calculated from the total coated area (1.57 square inches) and the maximum compressive loads (pounds) applied during the shearing operation. The shear test data collected in these two tables have been plotted in Figures 45-49.

Figure 45 shows an increase in coating thickness with increase in the power input for three separate coating times. The 37 seconds (coating time) curve approached an upper limit in coating thickness. By estimating the highest point on the 37 seconds curve to be at 75 per cent of its maximum, it was possible to establish a relative percentage figure, which might be called a "coating efficiency." Such a "coating efficiency" is defined as the actual coating thickness divided by the maximum theoretical coating thickness possible for given plasma-jet settings and a particular coating time.

In order to extend the estimation which provided a 75 per cent efficiency valve for the 37 second curve to the curves for 74 seconds and 111 seconds coating time, it seemed logical at this point to assume that doubling the coating time would double the coating thickness,

as indicated in Columns 1 and 3 of the following tabulation. The measured coating thicknesses (Column 2) then provide corresponding relative efficiencies (Column 4).

Curve	Coating Thickness	Coating Thickness at 100 °/o Eff.	Relative °/o Eff.
Col. 1	Col. 2	Col. 3	Col. 4
37 seconds	.010	.0132	75 (estimated)
74 seconds	.015	.0264	56.9
111 seconds	.0195	.0396	49.2

Note: Increase in coated area during the coating procedure was small enough to be neglected.

The above calculations suggest that even though coating time is doubled or tripled for given conditions, "coating efficiency" does not increase correspondingly.

Figure 46 shows more dramatically the effect that power input has on the coating thickness. According to the slope of the curves, the most significant increase in coating efficiency occurred between the 650 ampere curve and the 850 ampere curve. Figure 46 also emphasizes the fact that the coating thickness is not a linear function of the coating time.

Figure 47 shows the increase in the ultimate shear strengths obtained as higher power input settings to the plasma-jet were used to coat iron on the 1020 steel test cylinders. This effect was observed for specimens coated in both types of coating environments used. The ultimate shear strengths of specimens coated in an inert

atmosphere were superior to those coated in the normal atmosphere. This condition was obviously due to the increased oxidation that occurred during the coating procedure in the latter case. A distinction between specimens coated for 37 seconds and for 74 seconds was made in Figure 47. The shear strengths of the thicker coatings (74 seconds) were lower for specimens coated in the normal atmosphere than they were for corresponding specimens coated in an inert atmosphere. However, the general trend of the shear strength versus power input curves was not materially affected by the above differences in coating thicknesses.

It is evident from Figure 48 that the heat treatments performed on the shear test specimens after the coating procedure also affected the ultimate shear strength. Higher ultimate shear strengths were obtained from specimens furnace cooled from 950°C than from those specimens air cooled or heat treated at 650°C after the coating procedure. Significant increases in ultimate shear strength and ductility were obtained when specimens were heat treated at 950°C after the coating procedure. The rapid decrease in shear strength, shown by specimens that were heat treated at 950°C for more than five hours, was attributed to excessive grain growth. Detailed curves that indicate the effects that two heat treatments, one just below the lower critical temperature of steel (723°C) and the other just above the upper critical temperature of steel (910°C), have on the ultimate shear strength of iron coated specimens are given in Figure 49.

As mentioned previously, this shear test, which was conducted on iron-coated specimens rather than tungsten-iron coated specimens, was investigated to establish its general value as a useful tool for testing plasma-jet coatings. It was not the intent of this investigator to use this test as a means of finding the best possible heat treatment or coating technique for tungsten-iron graded coatings on 1020 steel substrates. Rather, the shear test was developed as an indication of resistance to spalling under thermal shock to provide a means of revealing the degree of improvement which would be imparted to a given coating by a particular heat treatment.

5.4 Radioactive Tracer Technique

The preliminary investigations that were conducted on several refractory materials whose melting points are above 2800°C, (tungsten, tungsten carbide, tantalum, tantalum carbide, and zirconia) and a selected variety of steels (1017, 1040, 4140, and 8640) indicated the usefulness of the radioactive tracer technique to study the diffusion rates of refractory coatings into steels. The controlled diffusion investigation of tungsten into 1017 steel described in Section 4.31 confirmed these results and enabled establishment of a standard procedure which might be followed in investigating diffusion produced by the Plasmatron equipment. Figure 10 shows the conversion curves which have been developed for counts per minute versus weight of tungsten. Such curves will enable the determination of the tungsten concentration in the given specimens if the number of counts per minute and the cross sectional areas of the specimens being investigated are known.

Controlled diffusion studies of plasma-jet sprayed tungsten into steel were not conducted during this investigation because the investigation concerned itself with graded mixtures rather than pure elements, in view of the greater promise indicated by the mixed type. Further, the presence of oxide layers and inclusions, unless eliminated by improved coating tehcniques and equipment, would act as obstructions and would have great effect on the reproducibility of diffusion rates.

6. CONCLUSIONS

The observations made and the results obtained during this investigation have enabled the following conclusions to be drawn:

1. Extensive fusion will take place between plasma-jet sprayed 1020 steel or iron and a 1020 steel substrate if there are no oxide layers present at the interface.
2. It is possible to form an intermediate alloy between tungsten and steel with the plasma-jet. However, even very thin oxide layers on the surface of these metals will prevent the formation of this intermediate alloy.
3. Coating tungsten directly on steel will not produce a thick enough intermediate alloy zone, between the steel and the tungsten coating, to provide an expansion gradient that will withstand severe thermal shock conditions.
4. The hotter and more plastic that the tungsten particles are just before striking the substrate, the greater is the density of the coating.
5. The density of the tungsten coating is improved by depositing the tungsten on the steel in an inert atmosphere.
6. Fusion bonding is increased at the interface of a plasma-jet sprayed coating of tungsten, iron, or steel substrate if the substrate is pre-heated below the first transformation

temperature of steel.

7. Heat treatments at 950°C will increase the fusion bond at the interface of the graded coatings on 1020 steel substrates.
8. There is no apparent advantage to heat treating graded coatings of tungsten-iron on 1020 steel substrates at 950°C for more than one hour.
9. The graded coatings discussed in this investigation will not spall after the coating procedure if they are immediately heat treated and furnace cooled.
10. The coating efficiency is mainly dependent on the power input to the plasma-jet. The coating efficiency is increased with increased power input.
11. The coating efficiency decreases with increasing coating time.
12. The mechanical shear test is a satisfactory method of testing the shear strength of plasma-jet sprayed coatings.
13. The ultimate shear strengths of specimens coated in an inert atmosphere are superior to those of specimens coated in a normal atmosphere.
14. Higher ultimate shear strengths can be obtained as higher power input settings to the plasma-jet are used when coating iron on 1020 steel cylinders.
15. Difference in the coating thicknesses of the shear test specimens will not affect the general trends

being investigated by this mechanical shear testing method.

16. The tungsten-iron gradiated coating on 1020 steel substrate can withstand extreme thermal shock conditions without spalling.

RECOMMENDATIONS

It is believed that the equipment used in this investigation could be improved. The atmospheric chamber requires excessive inert gas to establish an inert atmosphere. A vacuum chamber large enough to contain the same equipment used inside the present chamber would be more desirable. This vacuum chamber should have at least two glove parts or a pair of mechanical hands. A larger access door and an interlock chamber would increase working efficiency.

The present feeding system causes clogging of the injection orifices and does not allow sufficient residence time of coating powders in the plasma-jet. Both of these difficulties could be eliminated with a commercially available modulator assembly. A mechanical powder-feed system should be adapted to eliminate fluctuation in the feeding rate caused by the hydrostatic head variations in the present pressure-hopper feed system. The present feed system could not be controlled sufficiently to permit desired dispersion of tungsten in the tungsten-iron region to be obtained.

Increased fusion bonding without distortion of the steel might be possible if the entire substrate were to be pre-heated to 950°C and immediately coated. This procedure might be accomplished at the end of any heat treatment normally given a steel if slow cooling could be tolerated. A plasma-jet and supporting equipment adapted to an inert atmospheric furnace would provide the means for

this procedure.

The versatility of the plasma-jet gun could be greatly increased if at least an 80 kilowatt power supply were available. This increase would allow the use of inert gases other than argon in the gun to establish the plasma-jet. The maximum coating efficiency could then also be obtained for most coating materials.

REFERENCES

Batcheler, L. E., "Sprayed Aluminum Reduces Compressor Clearance," American Machinist, Vol. 102, October 20, 1958, pp. 140-141.

Bertossa, R. C., "New Metals and Processes," Metal Treating, Vol. 9, November-December, 1958, pp. 2-4.

Browning, J. A., "Plasma-Substitute for the Oxy-Guel Flame," Welding Journal, Vol. 38, September, 1959, pp. 870-875.

Dickinson, T. A., "Flame Spraying Ceramic Coatings," Production, Vol. 41, March, 1958, p. 84.

Eisenlohr, A., "Properties of Plasma-Sprayed Materials," Quarterly Progress Report 1 and 2, Sponsored by W.A.D.C. Air Force Contract No. 33 (616) - 6376, (1961).

Hayes, G. A., and Johns, D. L., "An Investigation of the Feasibility of Forming Alloy Coatings With a Plasma Jet," Naval Ordnance Test Station (N.O.T.S. TP 2615, NAVWEPS Report 7617), February 2, 1961, p. 38.

Klug, H. P., and Alexander, L. E., "X-Ray Diffraction Procedure," John Wiley and Sons, Inc., (1954).

Levensten, M. A., "Properties of the Refractory Metals Sprayed Under Controlled Environment," Journal of Metals, Vol. 14 No. 2 February, 1962, p. 137.

Linde Company, "30,000 Degrees With the Plasma Jet," Journal of Metals, Vol. 11, January, 1959, pp. 40-42.

Linde Company, "Plasma Arc Torch Ushers in New Fabricating, Coating Methods," Iron Age, Vol. 182, December 4, 1959, pp. 136-137.

Linde Company, "Plasma Arc Process Coats and Forms Refractory Material," Space Aeronautics, Vol. 32, July, 1959, pp. 105-109.

Mash, D. R., Weare, N. E., and Walder, D. L., "Process Variables in Plasma Jet Spraying," Journal of Metals, Vol. 13, No. 7, July, 1961, pp. 473-478.

Metallizing Engineering Company, "Method for Measuring Bond Strength of Sprayed Metal Coatings," New York (1957).

Oechsle, S. T., "Metal Spraying-Development and Application," Metal Finishing, Vol. 55, December, 1957, pp. 66, 71-76.

Shepard, S. W., "Refractory Metal: W, Ta, Cb, and Re," High Temperature Materials, John Wiley and Sons, New York 16 (1959) pp. 306-318.

Thermal Dynamics Corporation, "Plasma Temperature as a Function of Gas Energy," graph, Hanover, N. H. (1961).

Table Ia

PLASMA-JET SETTINGS USED WHEN COATING TUNGSTEN ON 1020 STEEL SUBSTRATES

Firing No.	Console Settings				Hopper Pusher Gas (Argon) Pressure psig
	Arc Gas (A)		Power Input (25 volts)		
	Flow Meter	Psi	Variac Setting	Amps	
Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6
1-16	3.5	100	4.5	750	10
17	7.0	100	5.5	885	10
18	5.0	100	7.5	1150	10

APPENDICES

APPENDIX A

TABLES

Table IIa

SUMMARY TABLE OF PLASMA-JET COATING DATA FOR TUNGSTEN-1020 STEEL GRADED COATINGS ON 1020 STEEL SUBSTRATES

+ Firing No.	Pre-Heat Temp. °C	Console Settings γ		Hopper Flushing Gas (A) Pressure		Particle Size△ (mesh)	Coating++ that Spalled	Specimens Micro-Examined
		Power Setting	Input @ Amps.	For Steel	For W	1020 Steel		
Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col. 8	Col. 9
(19)	487	4.5	750	2 psi	2 psi	+325		x
20	487	4.5	750	2	2	+325	x^1	x
21	348	3.5	550	10	2	+325	x^2	x
22	348	3.5	±550	15	10	+325		x
23	348	3.5	±550	15	10	+200	x^1	x
24	466	4.5	750	15	10	+200	x^1	x
(25)	450	4.0	600	15	10	+200	(Feed clogged)	
(26)	466	4.0	600	15	10	+200	x^1	x
(27)	466	4.0	600	15	10	+200	(Feed clogged)	
28	466	6.0	850	15	10	+200	x^1	x
29	466	6.0	850	25	20	+200	x^1	x
(30)	701	6.0	850	25	20	+200		x
(31)	701	6.0	850	25	20	+200	(Feed clogged)	

Note: Venturi Settings: 1T-0 for 1020 steel powder; 2 T-I for tungsten powder
Stand-off Distance = 7 inches

\+ The Firing Nos. that are in parenthesis indicate coatings procedure was performed in an inert atmosphere.

± Power was increased to 750 amps when spraying W only

@ 25 volts

++x^1 indicates spalling occurred when sectioning the specimen for microexamination

x^2 indicates spalling occurred during cooling after coating

γ Argon Flow Meter - 3.5 (100 psi)

△ Tungsten Particle Size - +325

Table Ib

SUMMARY TABLE OF PLASMA-JET COATINGS OF TUNGSTEN ON 1020 STEEL SUBSTRATES

*Fired No.	Stand-off Distance Inches	Pre-heat Temp. °C.	Spec. that Recrys.	Evaluation of Coatings: Laminar Layers L M S	Tungsten Penetration L M S	Extent of Oxidized Coating L M S	Coating Porosity L M S	Coatings that Spalled	Specimens Micro-Examined
Col. 1	Col. 2	Col. 3	Col. 4	Col. 5	Col. 6	Col. 7	Col. 8	Col. 9	Col. 10
7	7	530		x	x	x	x		x
8	7	443	-	- - -	- - -	- - -	- - -		
(10)	7	485		x	x	x	x		x
(11)	7	508		x	x	x	x		x
(12)	7	490	-	- - -	- - -	- - -	- - -		
9	6	602	-	- - -	- - -	- - -	- - -	x	
(13)	6	701	-	- - -	- - -	- - -	- - -	x	
(14)	6	659	x	x	x	x	x	x	x
(15)	6	654	x	x	x	x	x	x	x
1	5	602	-	- - -	- - -	- - -	- - -	x	
2	5	626	-	- - -	- - -	- - -	- - -	x	
3	5	602	-	- - -	- - -	- - -	- - -	x	
4	5	618	-	- - -	- - -	- - -	- - -	x	
5	5	628	x	x	x	x	x		x
(16)	5	770	x	x	x	x	x	x	x
(17)	5	---	-	- - -	- - -	- - -	- - -	x	
(18)	5	---	-	x	Completely	x	x	x	x
6	4	788	-	- - -	- - -	- - -	- - -	x	

*The firing Nos. that are in parenthesis indicate coating procedure was performed in an inert atmosphere.

L - Large
M - Moderate
S - Small

Table IIIa

SUMMARY TABLE OF PLASMA-JET COATING DATA FOR TUNGSTEN - IRON GRADED COATINGS ON TO 1020 STEEL SUBSTRATES

*Firing No.	Preheat Temp. °C	Console Settings				Hopper Pushing Gas(A) Pressure		Standoff Distance (in)	Maximum coating thickness (in)
		Arc Gas (A)		Power Input					
		Flow Meter	Psi	Setting	Amps.	For Steel	For W		
33	443	3.5	100	5.7	850	15	15	6 1/2	1/32
34	490	3.5	100	5.7	850	15	15	6 1/2	1/32
35	679	3.5	100	5.7	850	15	15	6	1/32
39	606	3.5	100	5.7	850	15	15	5 1/2	1/32
(40)	606	3.5	100	5.7	850	15	15	6	1/8
(41)	630	3.5	100	5.7	850	15	15	7	1/8
(43)	583	3.5	100	5.7	850	15	15	8	1/8

*The Firing Nos. that are in parenthesis indicate coating procedure was performed in an inert atmosphere.

Table IIb

MICROHARDNESS SURVEY OF A TUNGSTEN-1020 STEEL
GRADED COATING ON 1020 STEEL SUBSTRATE

Condition of Specimen No. 30	Vickers Diamond Pyramid Hardness - 100 g load		
	1020-Steel Plate	Coated 1020 Steel	Coated Tungsten
Col. 1	Col. 2	Col. 3	Col. 4
As coated	146	205	464
Heat Treated at 650°C - 1 hour	110	149	464
Heat Treated at 950°C - 1 hour	108	146	464

Table IV

COUNTS PER MINUTE VS. WEIGHT OF TUNGSTEN

Specimen No.	Weight Tungsten (gm)	Counts per Minute Spectrum Peaks of Tungsten	
		.686	.480
1	.0002	133,215	44,558
2	.0006	184,399	130,972
3	.0012	258,436	186,043
4	.0015	315,794	234,223
5	.0028	493,633	367,240
6	.0035	579,400	434,709
7	.0056	873,086	650,081

Table IIIb

SUMMARY TABLE OF PLASMA-JET COATING DATA FOR TUNGSTEN - IRON GRADED COATINGS ON TO 1020 STEEL SUBSTRATES

Firing No.[@]	Preheat Temp. °C	Console Settings				Hopper Pushing Gas(A) Pressure		Standoff Distance (in)	Maximum coating thickness (in)
		Arc Gas (A)		Power Input					
		Flow Meter	Psi	Setting	Amps.	For Iron	For W		
49	590	3.5	100	5.5	850	15	15	6	.058
50	621	3.5	100	5.5	850	20	10	6	.060
51	584	3.5	100	5.5	850	20	10	6	.065
52	602	3.5	100	5.5	850	20	10	6	.086
53	572	3.5	100	5.5	850	20	10	6	.083
54	626	3.5	100	5.5	850	20	5	6	.050
55	602	3.5	100	5.5	850	20	5	6	.105
56	602	3.5	100	5.5*	850	20	5	6	.130
57	620	3.5	100	5.5*	850	20	5	6	.120
58	608	3.5	100	7.5	1000	20	10	6	.065

* Power was increased to 1000 amp. while spraying Fe-W mixture and W.

@ All specimens were coated while in an inert atmosphere.

TABLE Vb

EFFECT OF HEAT TREATMENTS ON X-RAY DIFFRACTION PATTERNS OF SPECIMEN No. 54

	'd Spacings'			Relative Intensity		
Heat Treatment	Furnace Cooled From 950°C	Three Hours at 950°C	Nine Hours at 950°C	Furnace Cooled From 950°C	Three Hours at 950°C	Nine Hours at 950°C
Element						
W	2.2413	2.2435	2.2499	68	64	45
Fe	2.0299	2.0333	2.0386	73	75	77
W	1.5863	1.5863	1.5848	14	12	8
Fe	1.4316	1.4375	1.4395	10	10	10
W	1.2919	1.2934	1.2964	20	17	12
Fe	1.1705	1.1724	1.1741	12	12	12
W	1.0004	1.0024	1.0026	9	8	6

Table Va

RELATIVE PEAK INTENSITIES OF TUNGSTEN - IRON ALLOYS
FOR X-RAY DIFFRACTION STANDARDS

Specimen Composition Weight Per Cent			Constituent Present												
			Fe				W			Fe_2W			Fe_7W_6		
Fe	W	C	d-space	2.02	1.43	1.17	2.23	1.29	1.00	2.36	2.18	2.01	2.37	2.19	2.08
80	20	-		50	6.5	10				6	6	3			
28	62	-		27	4.5	11.5	15	18	3	7	9	5.5	10.5	9	12
21	69	-		15	4	--	15	7	2.5	4.5	6	3.5	15	4.5	11
Bal.*	75	0.60		17.5			152.5	45	20				20	25	23.5

* Ferrotungsten Composition

Table VIb

SUMMARY TABLE OF THERMAL SHOCK TESTS ON TUNGSTEN - IRON GRADED

Firing No.	Preheat Temp. °C	Console Settings Arc Gas (A) Flow Meter	Psi	Power Input Variac Setting	Amp	Pushing Gas (A) Pressure Fe	W	Coating Thickness (in.)	Coating Time (sec.) Fe	Fe-W	W	Burn Through Time (sec.)
Col. 1	Col. 2	Col.3	Col.4	Col. 5	Col. 6	Col.7	Col.8	Col. 9	Col.10	Col.11	Col.12	Col. 13
59	626	3.5	100	5.5	850	20	10	.115	37	37	74	120
60	626	"	"	"	"	"	"	.101	"	19	"	121
61	637	"	"	"	"	"	"	.140	"	89	"	138
62	624	"	"	"	"	"	"	.121	"	47	"	125
63	626	"	"	"	"	"	"	.128	"	47	"	115
64	626	"	"	"	"	"	"	.126	"	47	"	122
65*	624	"	"	"	"	"	"	.120	"	47	"	--

* Used for microexamination and microhardness survey.

Table VIa

SUMMARY TABLE OF STANDARDS FOR THERMAL SHOCK STUDY

Firing No.	Material Under Investigation	Thickness	Console Settings Arc Gas (A) Flow Meter	Psi	Power Input Variac Setting	Amps	Standoff Distance (in.)	Burn Through Time (sec.)
69	1020 Steel Plate	.120"	5.0	100	4.0	675	3	200
70	"	"	"	"	"	"	2 1/2	200
71	"	"	"	"	5.0	850	2 1/2	90
72	"	"	"	"	"	"	2 1/4	75
73	"	"	"	"	"	"	"	65
74	"	"	"	"	"	"	"	55
75	"	"	"	"	"	"	"	45
76	"	"	"	"	3.5	650	"	200
77	"	"	"	"	4.2	700	2	54
78	"	"	"	"	"	"	"	54
79	"	"	"	"	"	"	"	50
80	"	"	"	"	"	"	"	53
81	"	"	"	"	"	"	"	46*
82	"	"	"	"	"	"	"	48.5*
83	W sheet	.006"	"	"	"	"	1 1/2	12
84	"	"	"	"	"	"	2	25
85	"	"	"	"	"	"	"	24
86	"	"	"	"	"	"	"	25

* Specimen had been previously heated above its lower critical point.

Table VIIa

SUMMARY TABLE OF PLASMA-JET COATING DATA FOR SHEAR TEST SPECIMENS

Firing No.	Console Setting				Coating		Maximum Shear Strength	
	Arc Gas		Power Input					
	Flow Meter	psi	Variac Setting	Amps	Time (sec.)	Thickness (in.)	lb.	psi
87	3.5	100	2.9	500	37	.0045	1480	942
88	3.5	100	4.0	650	74	.008	1440	918
89	3.5	100	2.9	500	74	.006	1070	682
90	3.5	100	4.0	650	37	.007	1430	911
91 #	3.5	100	5.5	850	37	.009	1940	1239
92	3.5	100	5.5	850	74	.012	620	395
93	3.5	100	2.9	500	74	.007	2550	1695
94	3.5	100	6.0	850	74	.012	3500	2235
95	3.5	100	2.9	500	37	.005	2300	1525
96	3.5	100	6.0	850	37	.010	2850	1815
97	3.5	100	4.0	650	37	.007	2350	1495
98	3.5	100	4.0	650	74	.0085	3200	2045
99#	3.5	100	6.0	850	74	.013	2200	1400
100#	3.5	100	6.0	850	74	.011	1900	1210
101	3.5	100	6.0	850	74	.012	4025	2560
102#	3.5	100	6.0	850	74	.012	1450	922
103#	3.5	100	6.0	850	74	.011	1080	688
104	3.5	100	6.0	850	74	.012	3800	2420
105#	3.5	100	6.0	850	74	.013	2200	1400
106	3.5	100	2.5	400	74	.005	2020	1285
107	3.5	100	6.0	850	74	.012	2520	1605
108	3.5	100	6.0	850	111	.014	3250	2080
109#	3.5	100	6.0	850	74	.011	1170	745
110	3.5	100	6.0	850	74	.011	1500	955
111	3.5	100	6.0	850	74	.012	3750	2390
112#	3.5	100	6.0	850	74	.010	1775	1130
113#	3.5	100	6.0	850	74	.011	820	521
114	3.5	100	7.9	1000	74	.016	4925	3140
115	3.5	100	2.5	400	37	.0035	1725	1100
116	3.5	100	7.9	1000	37	.010	4675	2980
117	3.5	100	4.0	650	111	.0085	----	----
118	3.5	100	7.9	1000	111	.0195	----	----
119	3.5	100	2.5	400	111	.006	----	----
120	3.5	100	2.9	500	111	.007	----	----

Stand-off Distance - 6 1/2"

Pre-heated to 600$\pm$ 25°C

Specimen that displayed brittle fracture under shearing stresses

Table VIIb

SUMMARY TABLE OF SHEAR TESTS

Firing No.	History of Coated Specimens Before Shear Test				Maximum Shear Strength C	
	Air Cooled	Furnace Cooled From 950°C	Hours Heat Treated at 650°C	Hours Heat Treated at 950°C	lb.	psi
87		*		1	1480	942
88		*		1	1440	918
89		*		1	1070	682
90		*		1	1430	911
91#		*		1	1940	1239
92		*		1	620	395
93		*		1	2550	1625
94		*		1	3500	2235
95		*		1	2300	1525
96		*		1	2850	1815
97		*		1	2350	1495
98		*		1	3200	2045
99#		*			2200	1400
100#		*	1		1900	1210
101		*		1	4025	2560
102#		*	3		1450	922
103#	*				1080	688
104		*		3	3800	2420
105#		*	9		2200	1400
106		*		1	2020	1285
107		*		9	2520	1605
108		*		1	3250	2080
109#		*			1170	745
110		*	1		1500	955
111		*		5	3750	2390
112#		*	5		1775	1130
113#	*				820	521
114		*		1	4925	3140
115		*		1	1725	1100
116		*		1	4675	2980
117		*			----	----
118		*			----	----
119		*			----	----
120		*			----	----

Specimen that displayed brittle fracture under shearing stresses.

@ 0.05 in/min. strain rate

APPENDIX B

FIGURES

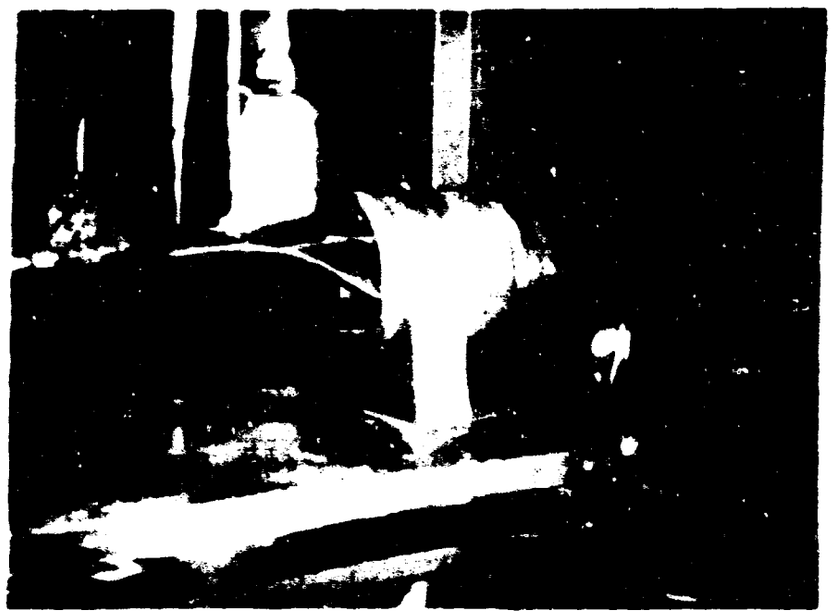


Figure 2. H-50 Plasmatron Head Assembly Supported on Top of the Console and Connected to the Atmosphere Chamber. A stainless steel O-ring makes this connection air tight. Nitrogen gas pre-heater and working pressure gauge are shown in the background.

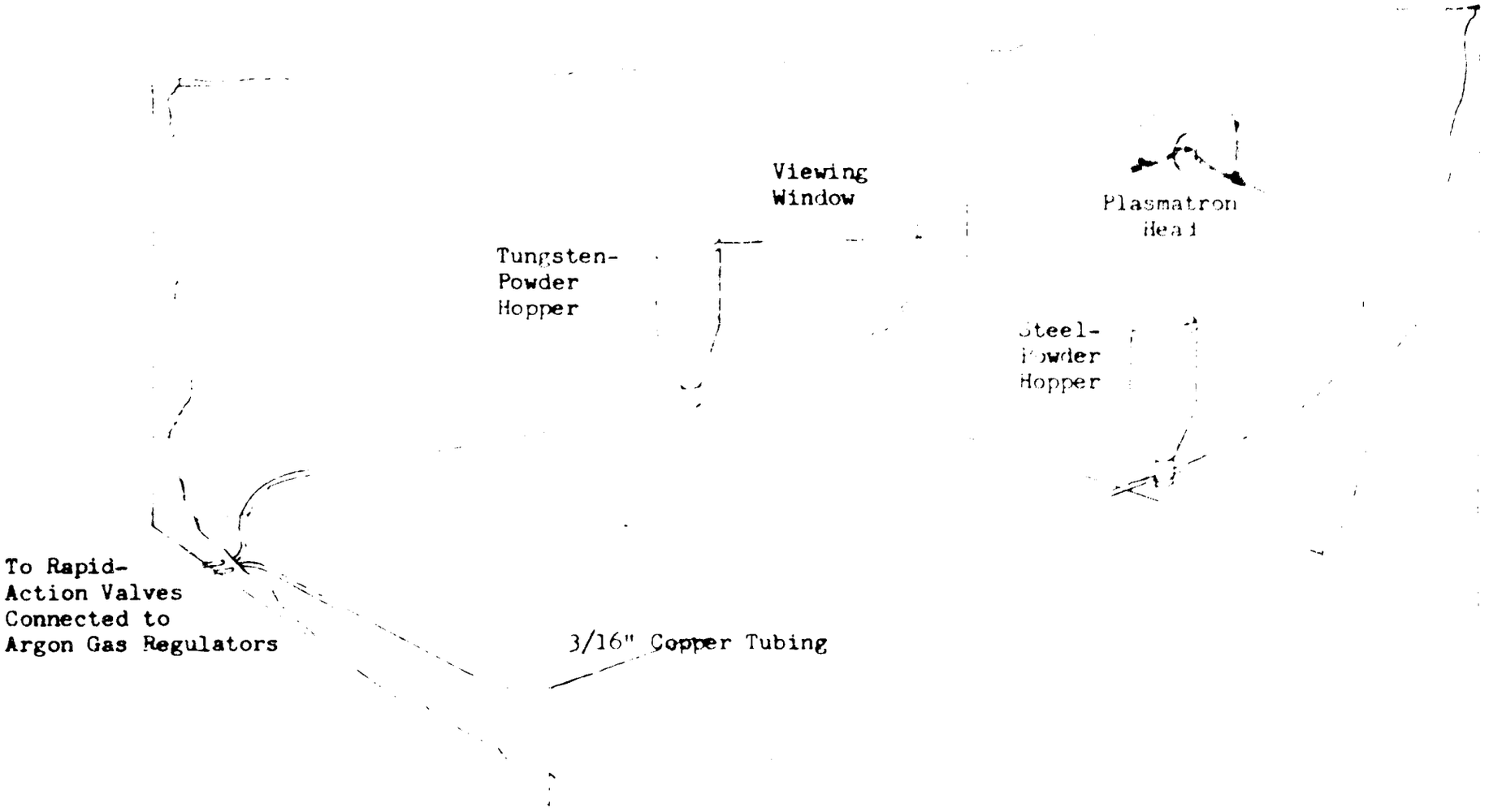


Figure 4. Duel Feeding-System

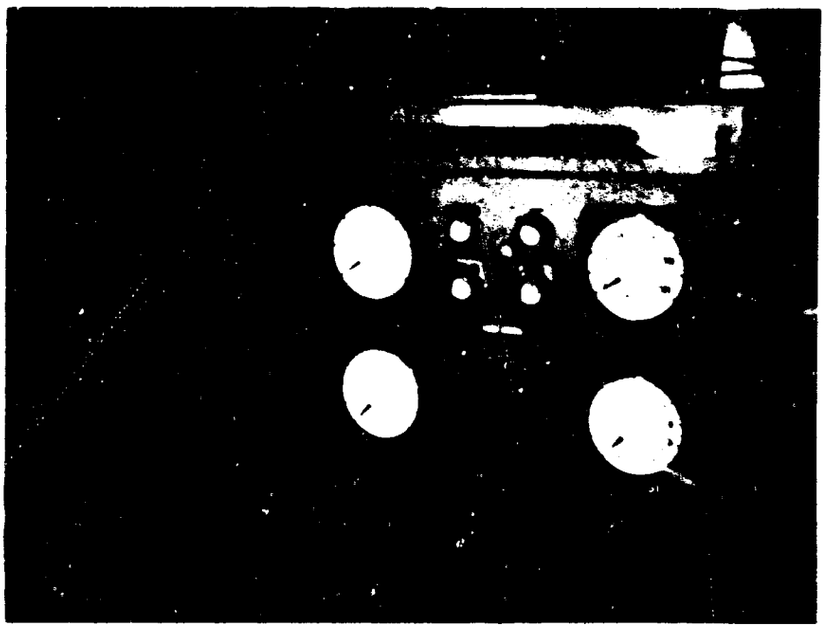


Figure 3. Plasmatron Console Panel. The two variable transformers on top of the console supply the power to the nitrogen gas pre-heater and the tubular furnace mounted inside the chamber.

Figure 5a. Plasmatron Equipment and Inert-Atmosphere Chamber. Battery resistance-heating systems is on top of the chamber. Ultraviolet shield was removed to show powder hopper inside the chamber.

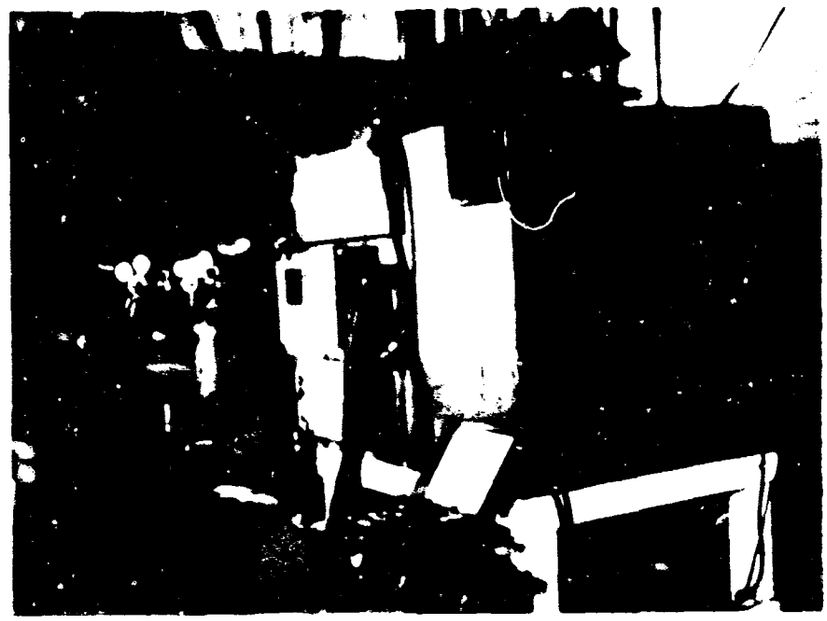
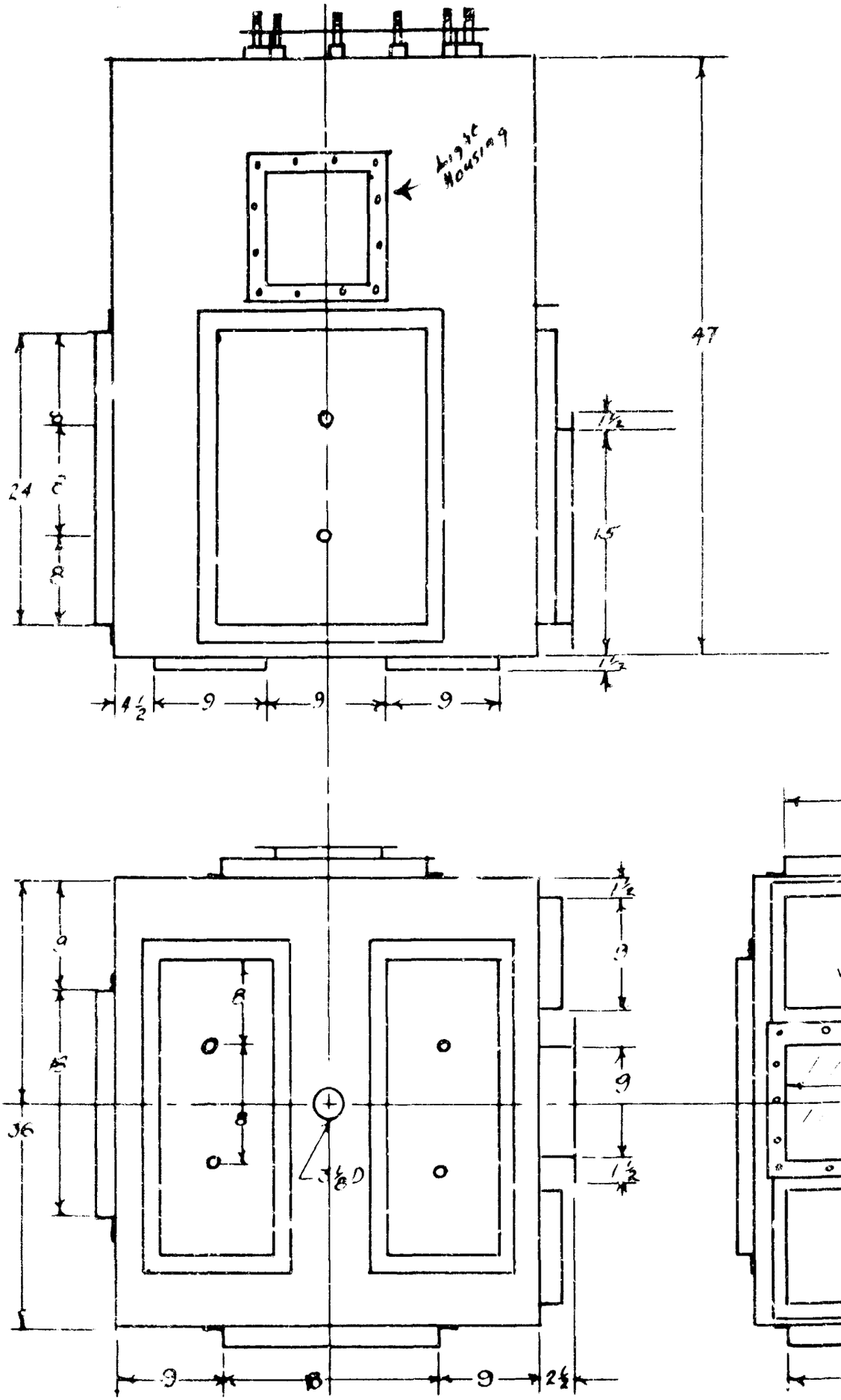
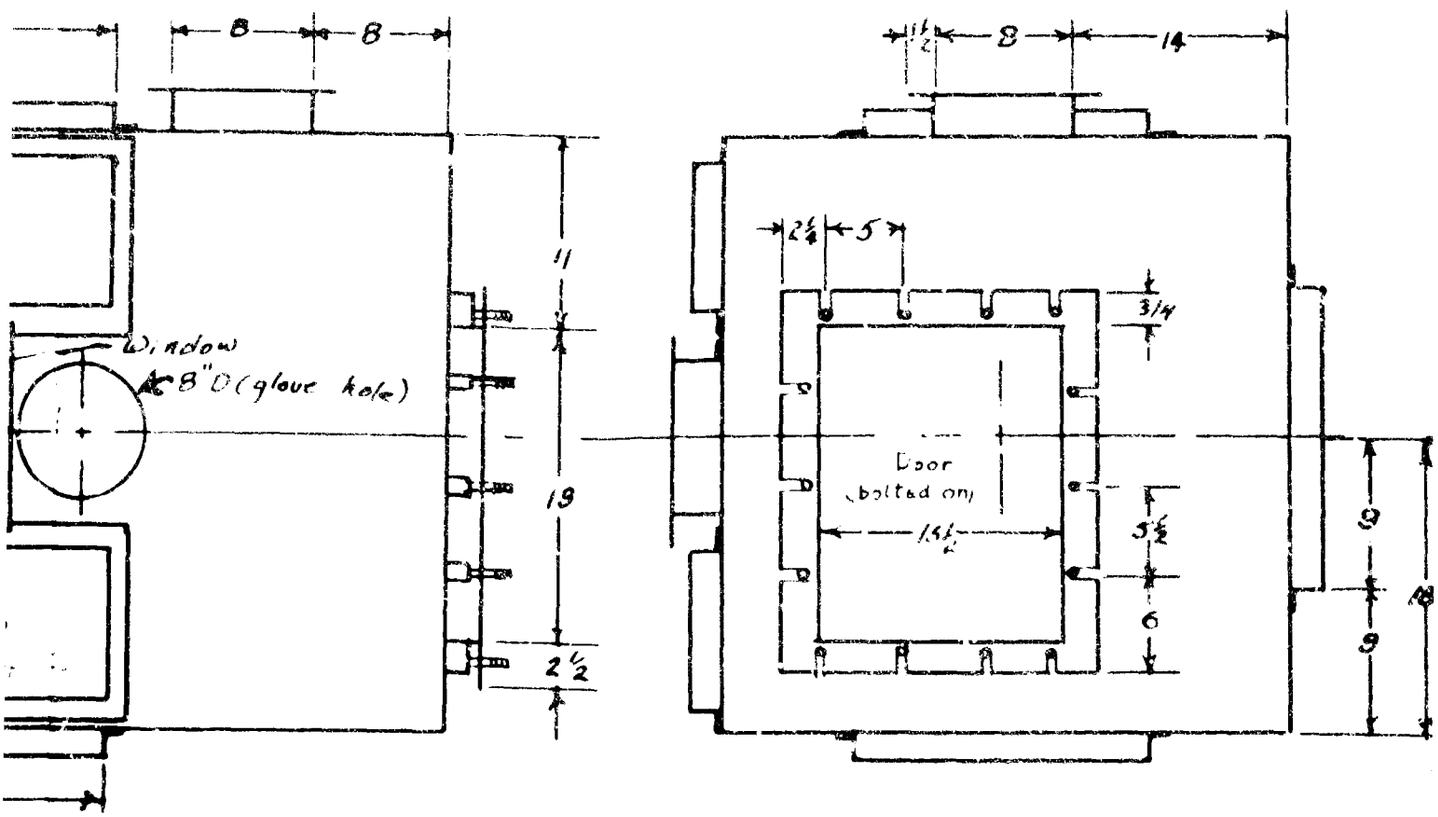


Figure 5b. Rear View of Inert-Atmosphere Chamber. The ultraviolet shield is in place. The internal lighting system is shown on top of chamber. Three argon bottles are located near the console. Two bottles supply the two powder hoppers and the third bottle supplies the plasma-jet.


Light Housing
47
24
8
8
1½
15
1½
4½
9
9
9
24
9
8
15
36
8
3⅛ D
1½
9
9
1½
9
18
9
2½
24
24

Scale 1" = 12"	The University of Arizona	
Date 2-20-61	Name Plasmatron Inert	
Drawn By R.L.L.	Atmospheric Chamber	
Traced By R.L.L	Material Hot Roll Steel - 14 gage	
Checked By R.A.D.	Code 4200	Contract No. 60-Q-32
No. Sheets 1		

Figure 5. Schematic Blueprint of Atmospheric Chamber



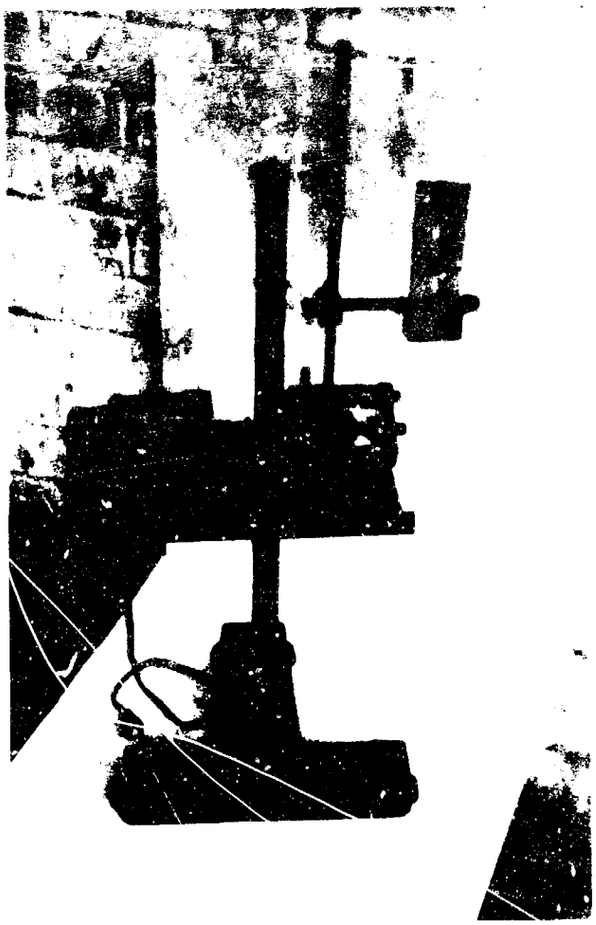


Figure 6. Jig with Assembly for Positioning 7" x 2" x 1/8" Plate in Front of the Plasma-Jet. Protection cabinet for jig has been removed.

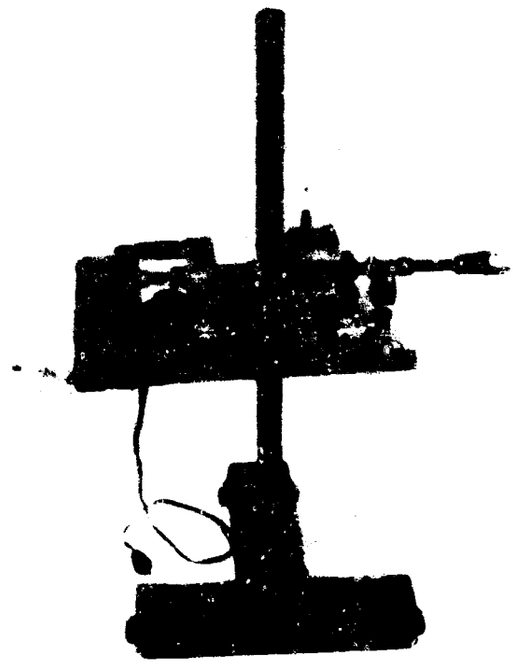


Figure 7. Jig with assembly for positioning 1" dia. x 1" long cylinders used for shear tests. Protective cabinet for jig has been removed.

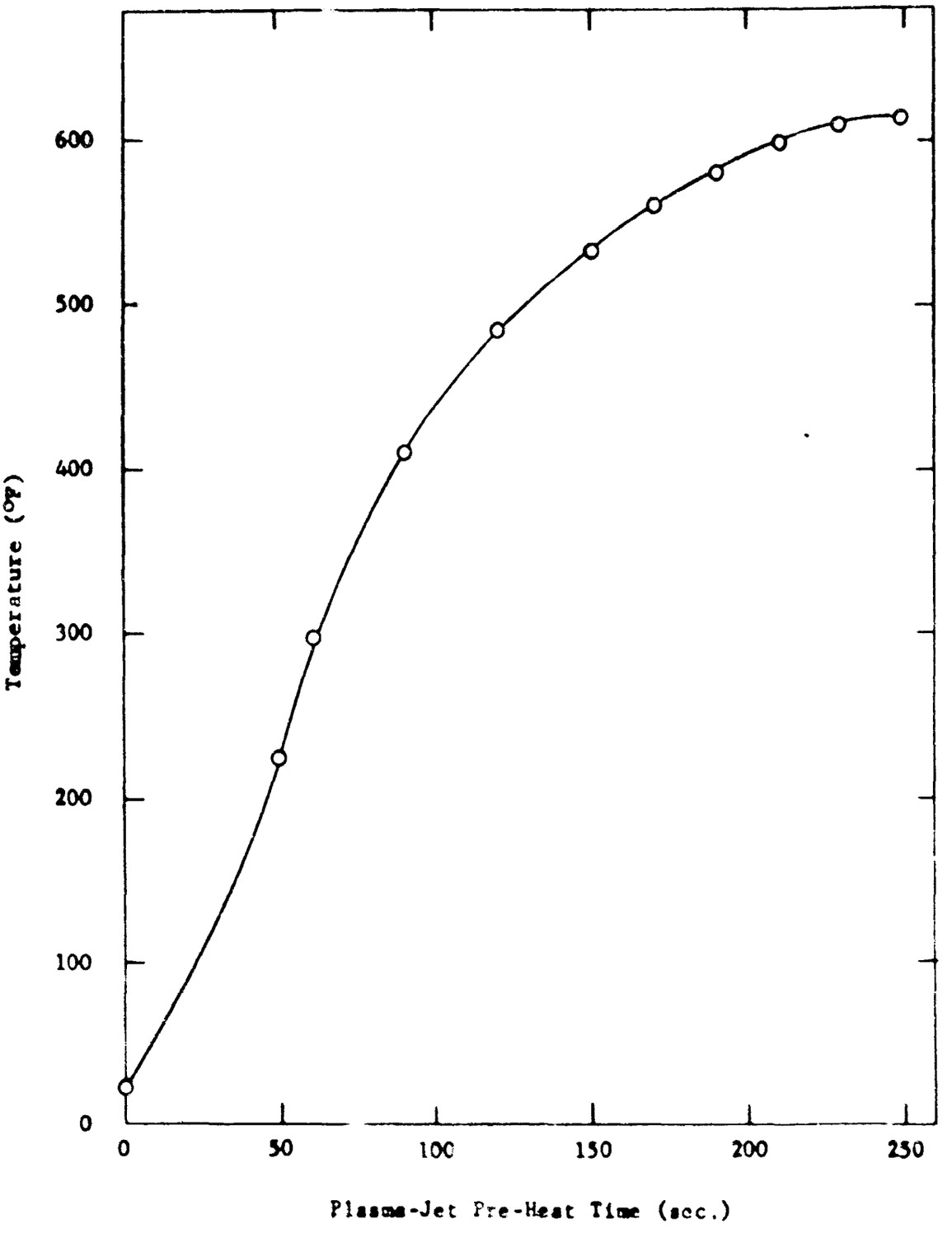


Figure 9. Typical time-temperature curve for 1020 steel plate specimens (7" x 2" x 1/8"), pre-heated with the plasma-jet. Specimen was 6-1"2" from front electrode (Argon flow meter at 3.5 (100 psi) and variable transformer set for 850 amps).

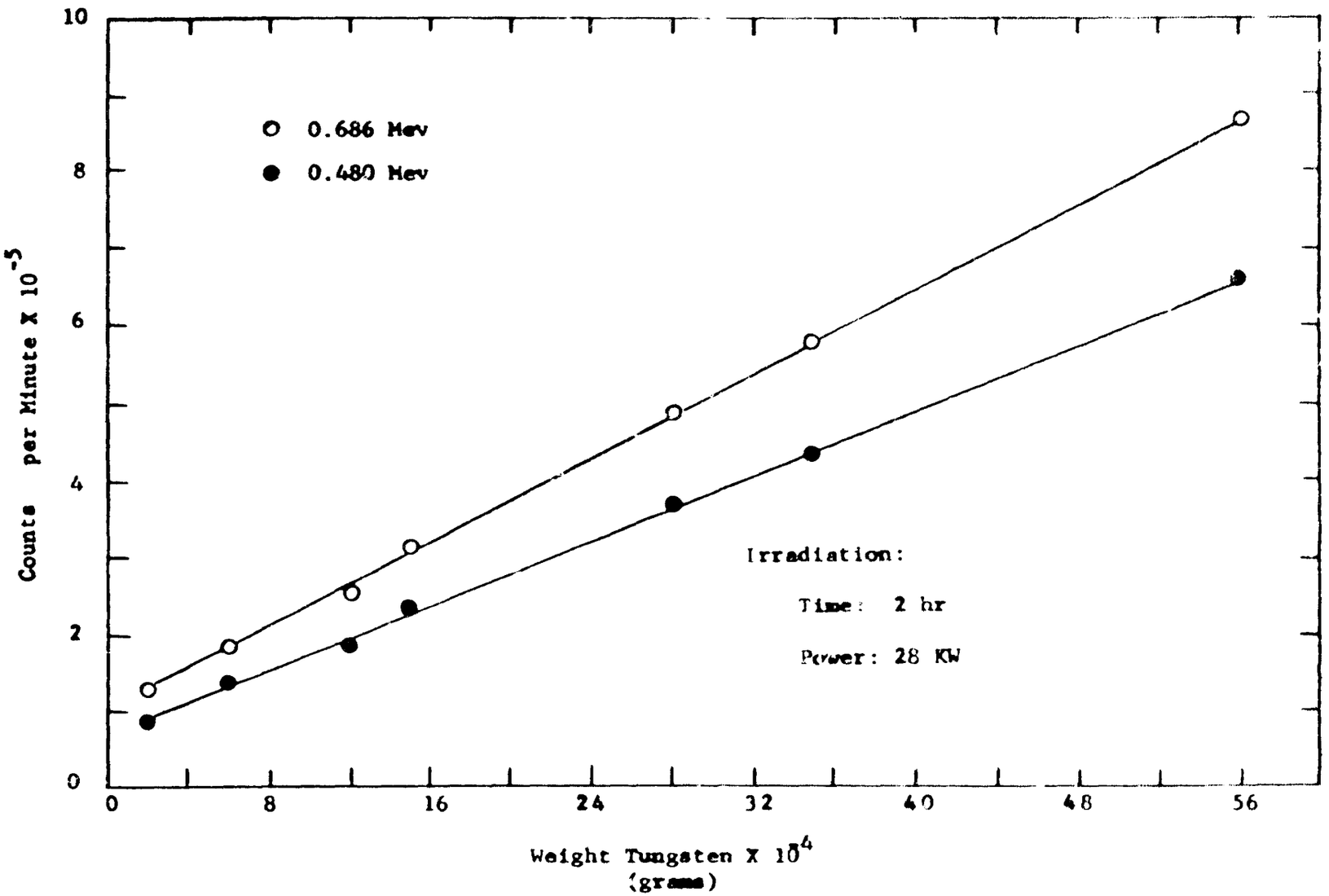


Figure 10. Conversion curves for counts per minute to Tungsten concentration.

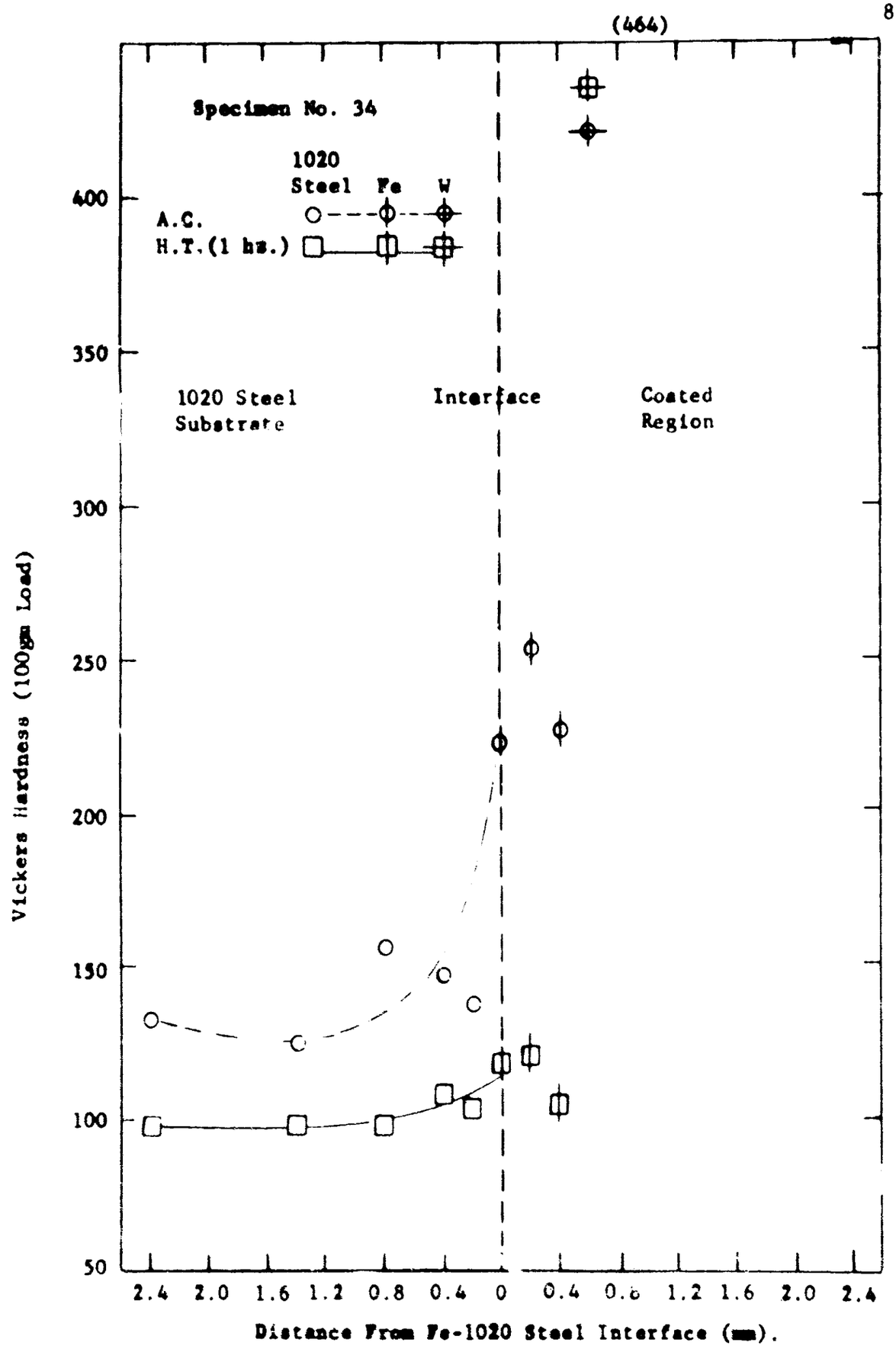


Figure 11. Microhardness survey of a W-Fe graded coating on 1020-Steel plate (7" x 2" x 1/8").

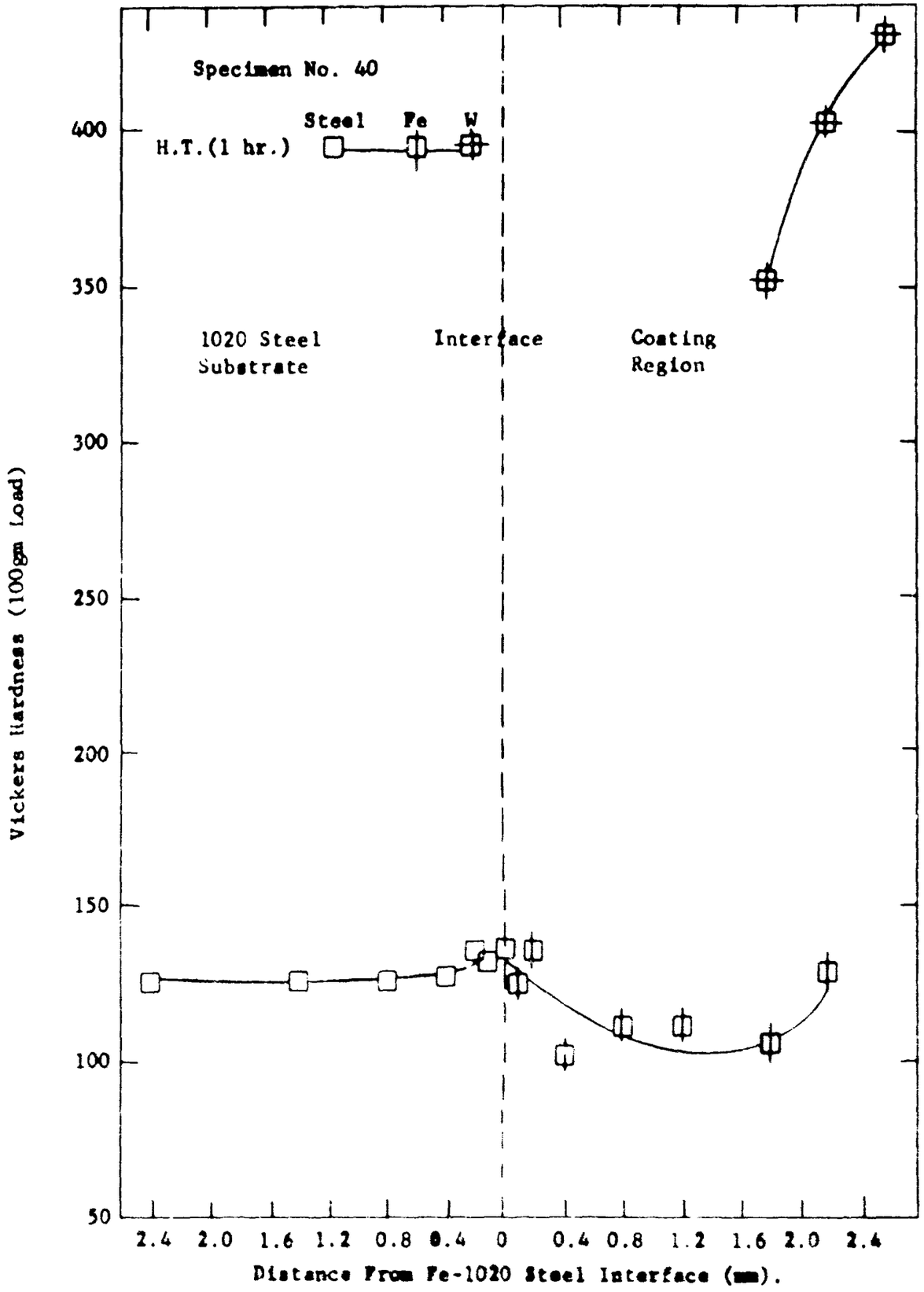


Figure 12. Microhardness survey of a W-Fe graded coating on 1020-steel plate (7" x 2" x 1/8").

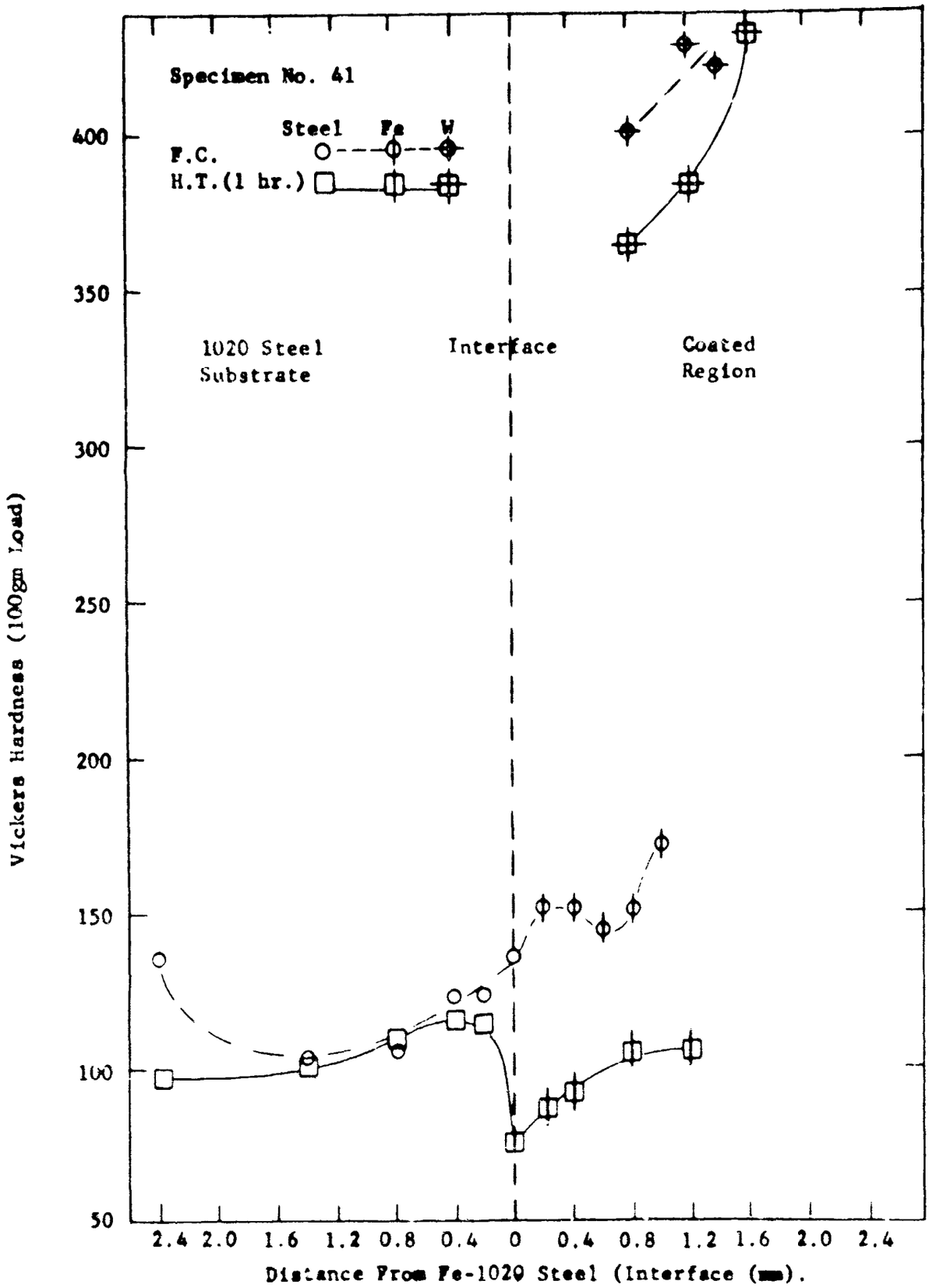


Figure 13. Microhardness survey of a W-Fe graded coating on 1020-steel Plate (7" x 2" x 1/8").

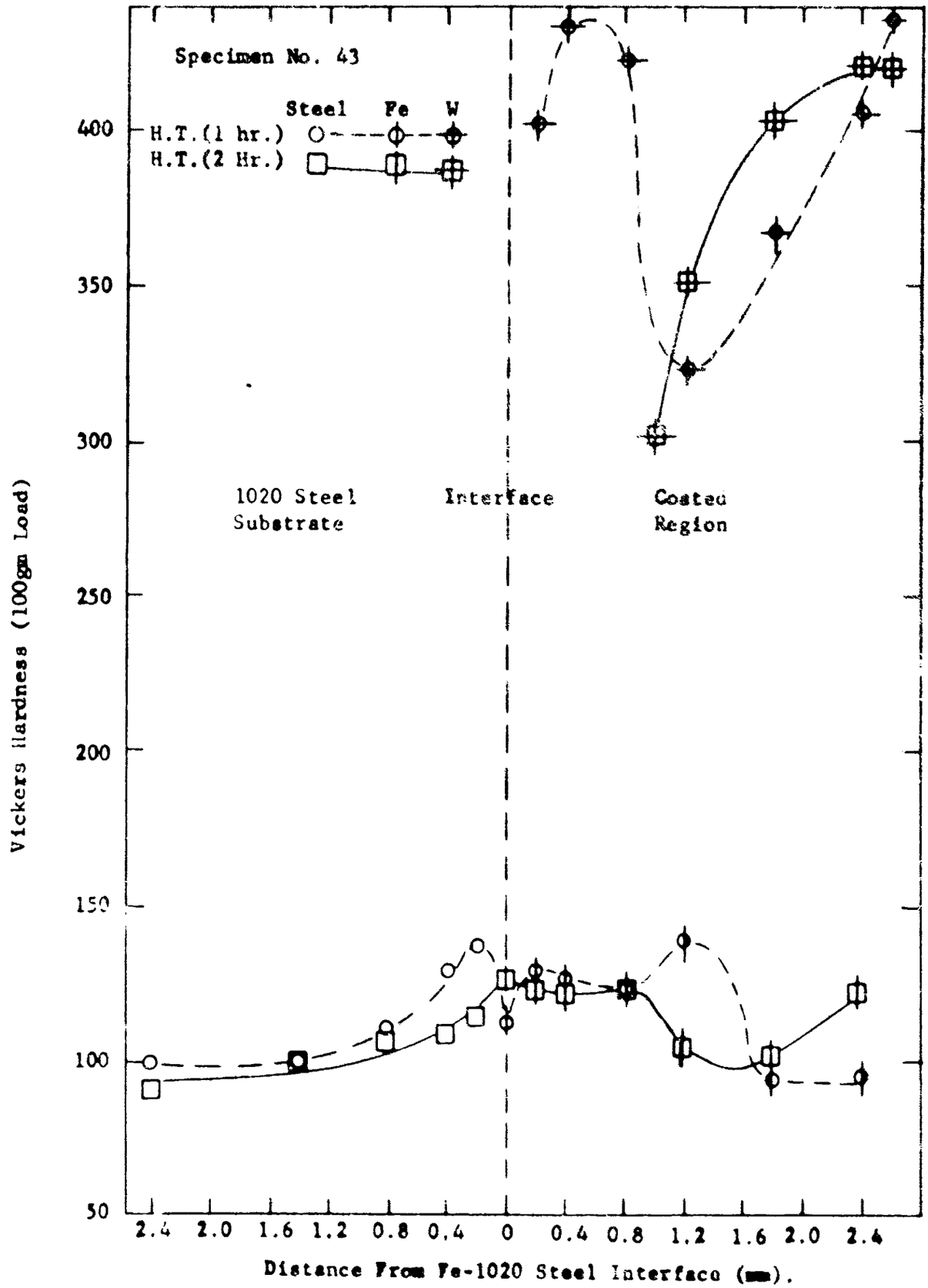


Figure 14. Microhardness survey of a W-Fe graded coating on 1020-steel Plate (7" x 2" x 1/8").

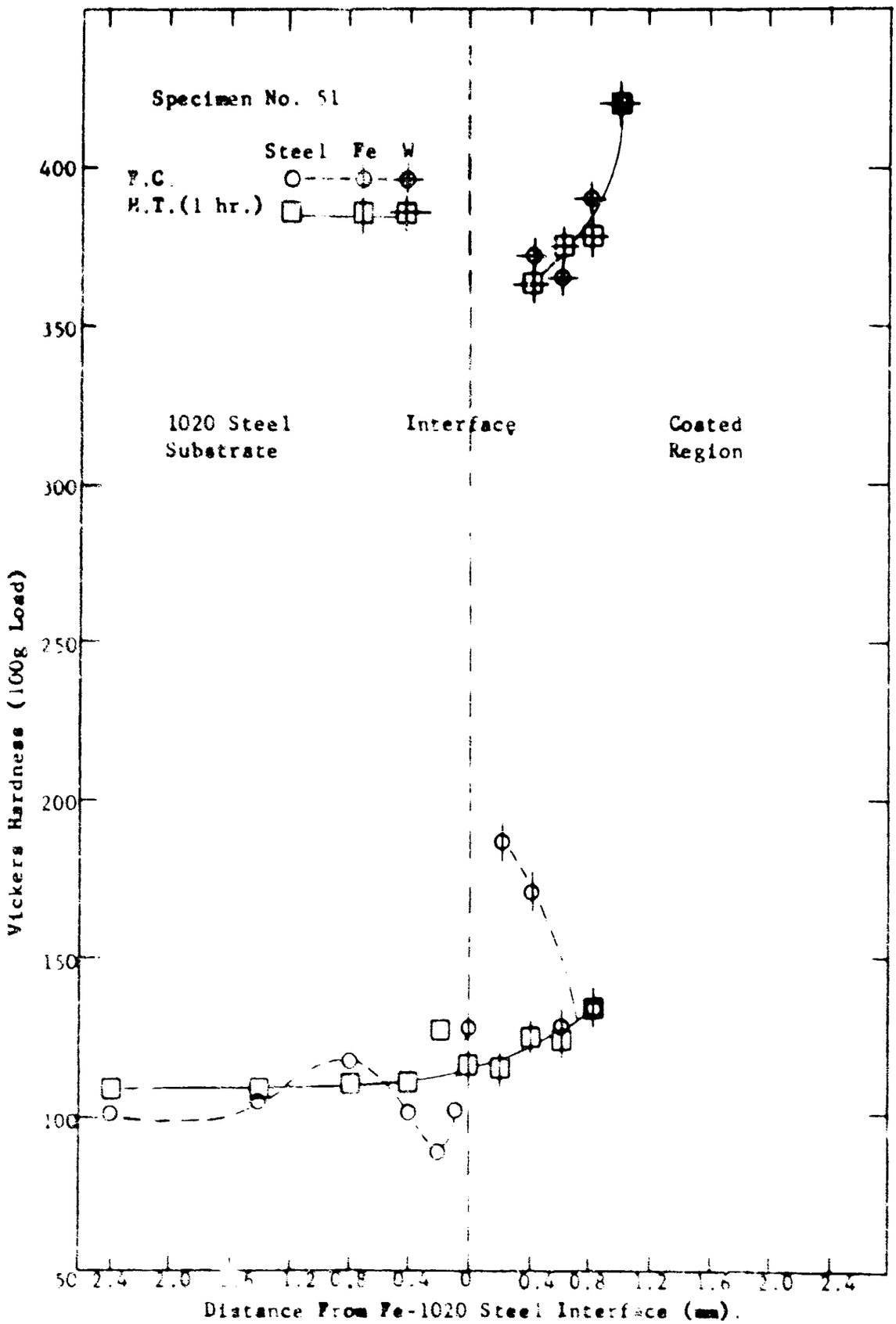


Figure 15. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8").

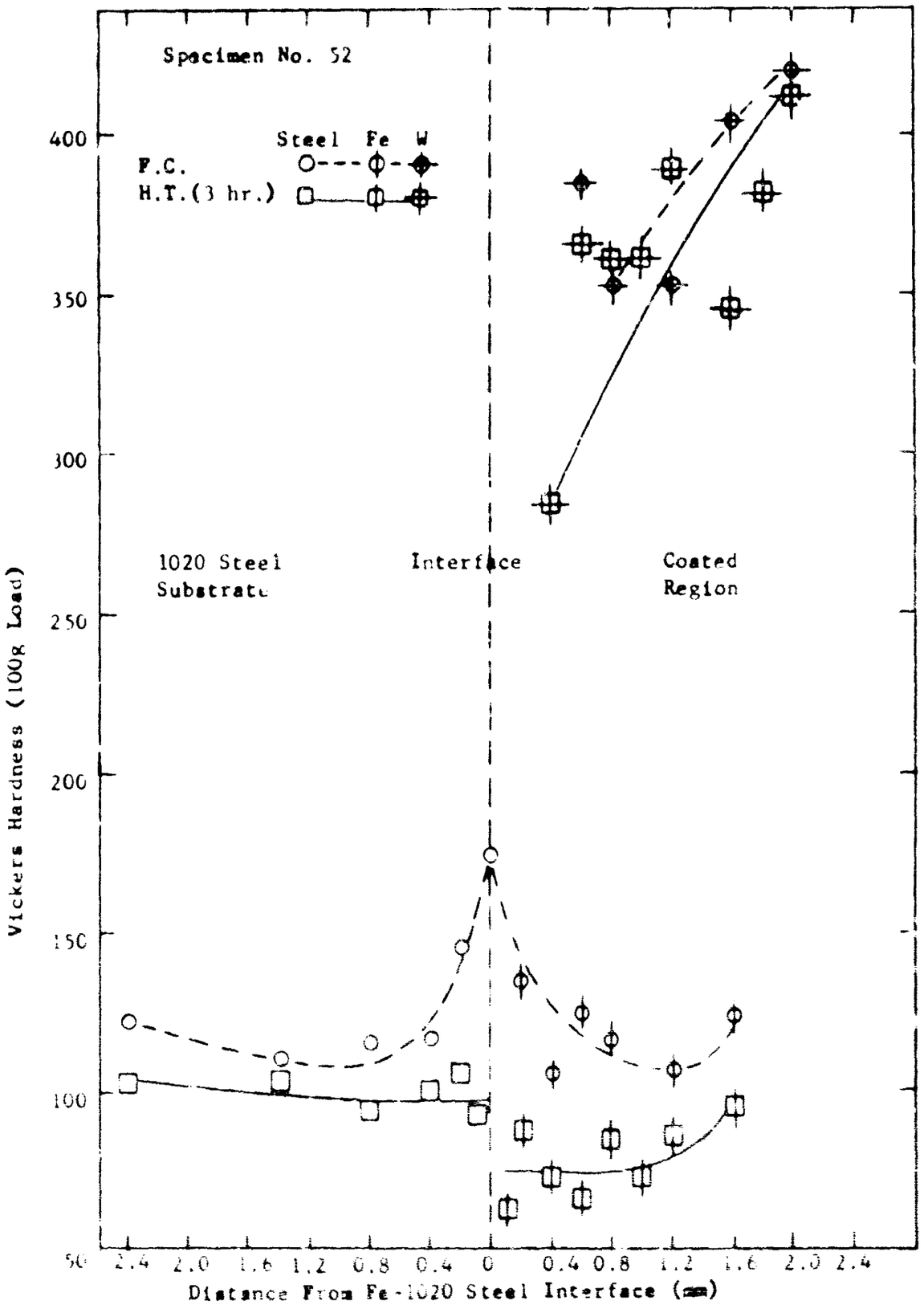


Figure 16. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8")

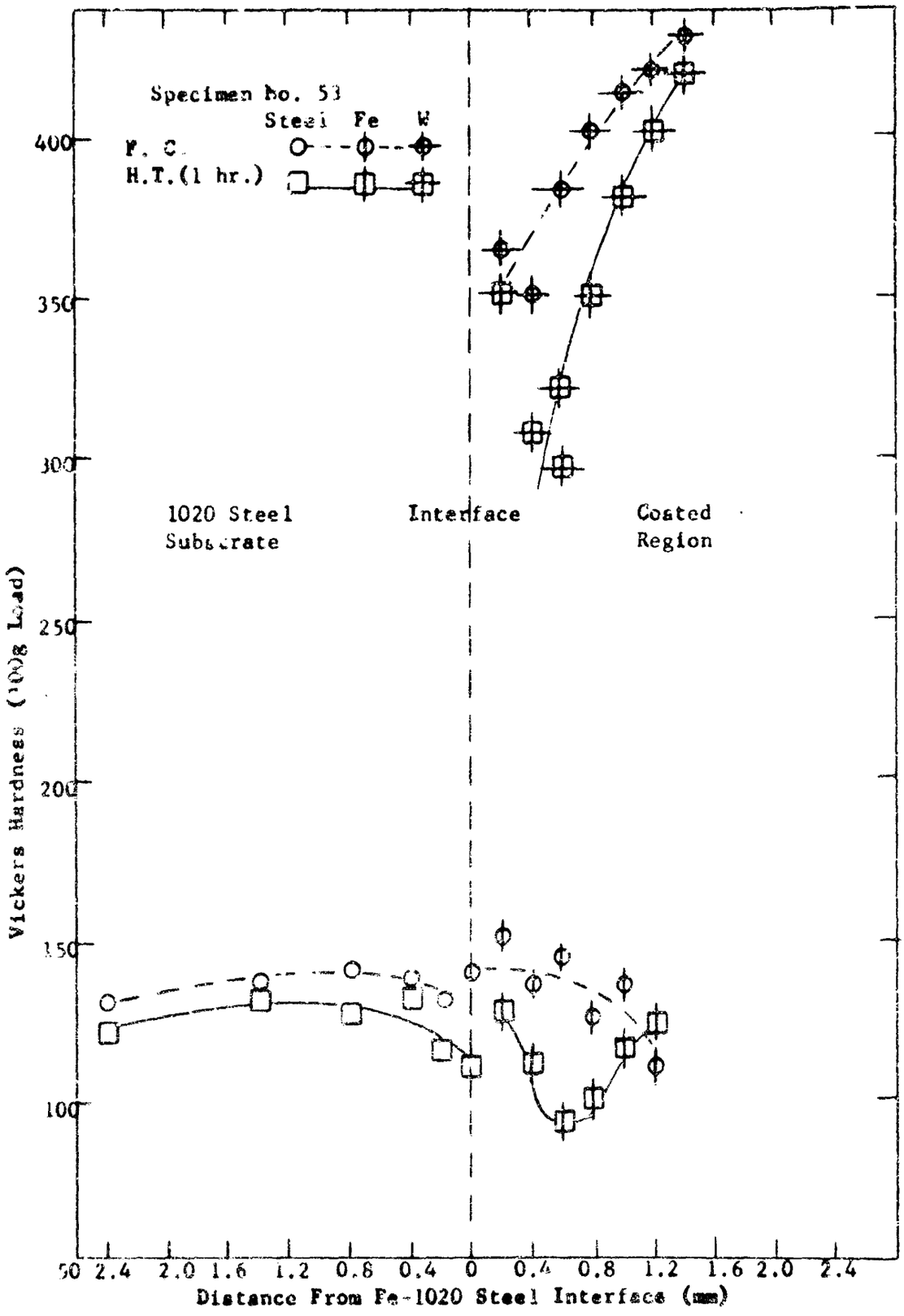


Figure 17. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8").

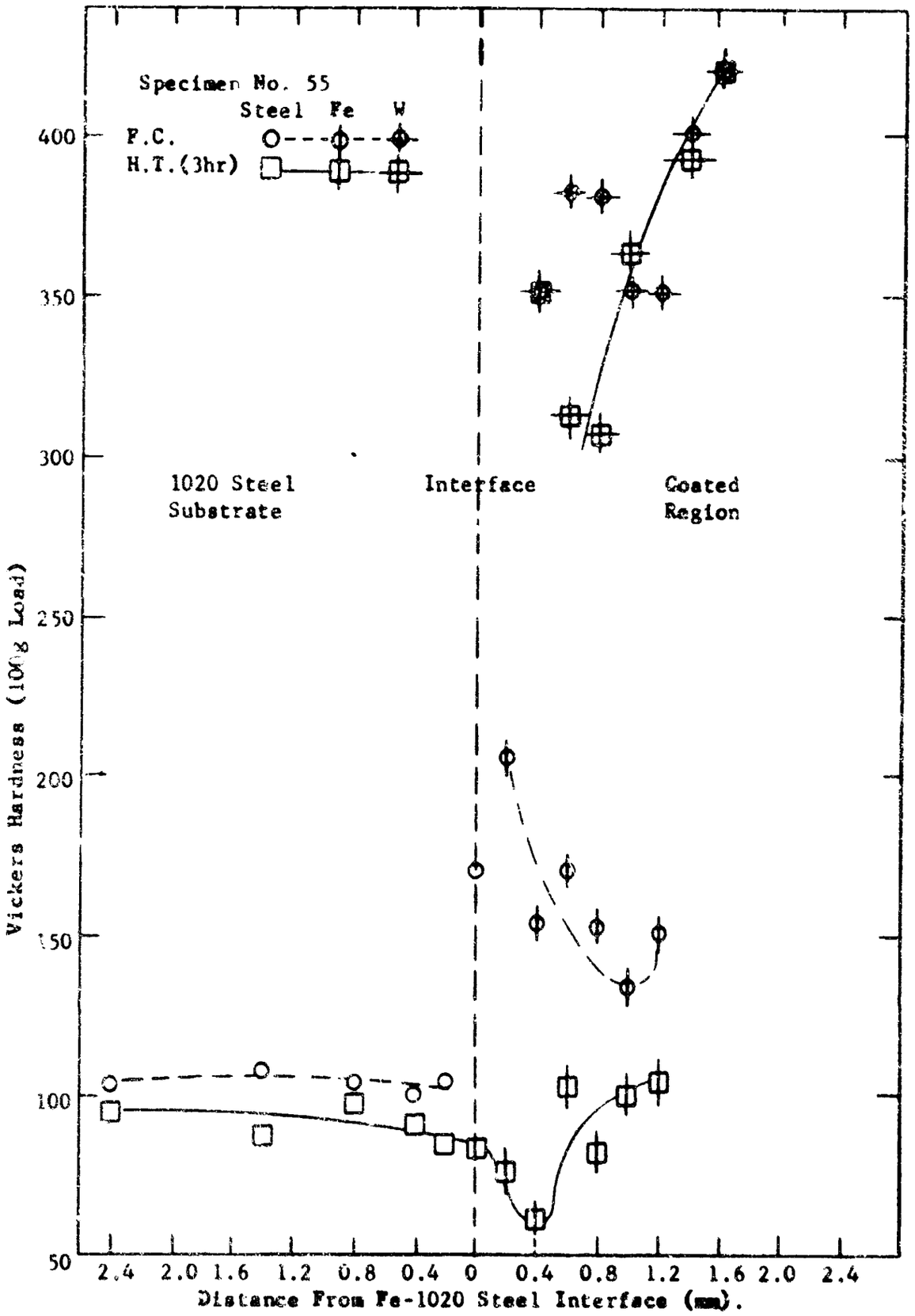


Figure 18. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8").

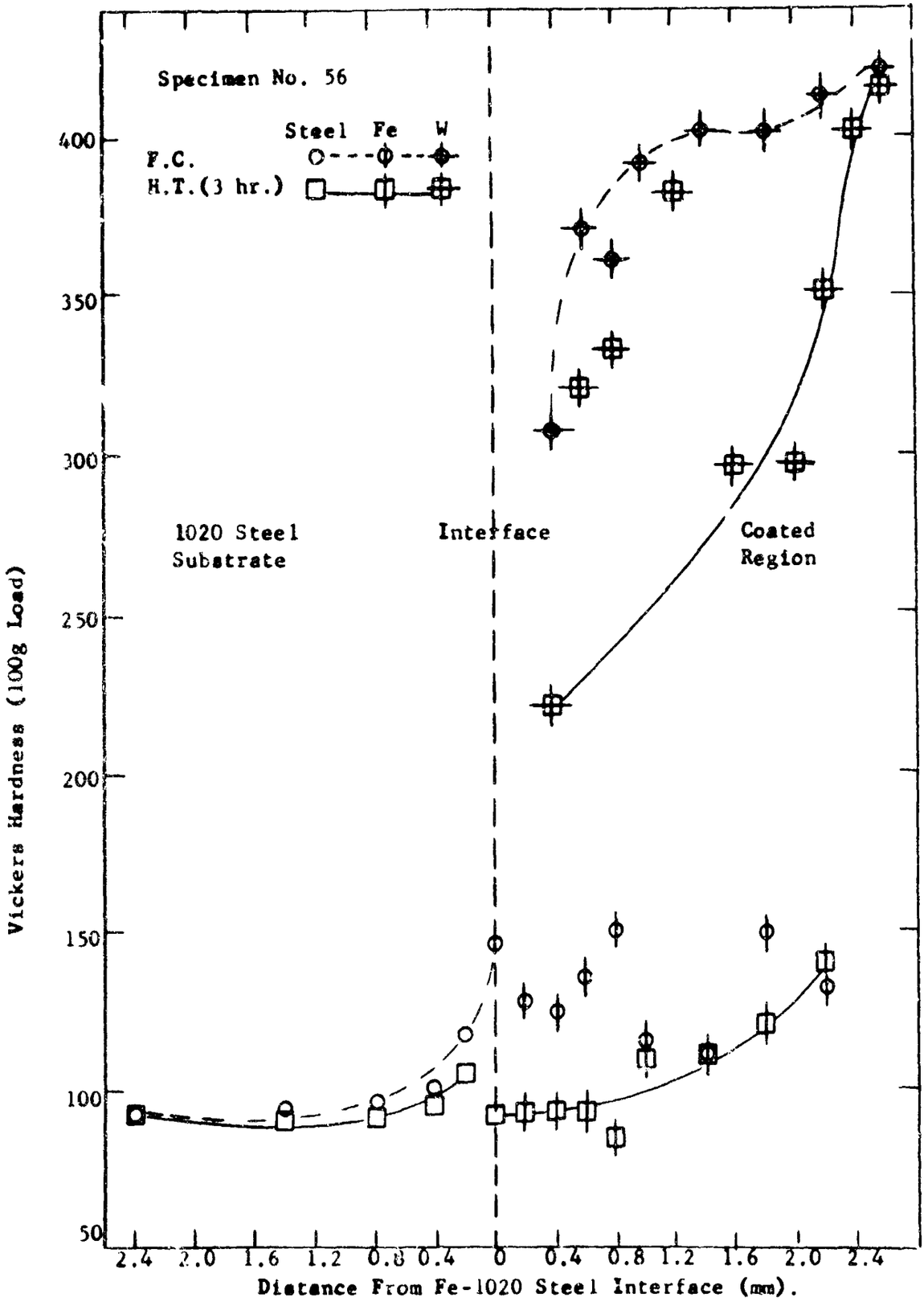


Figure 19. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8").

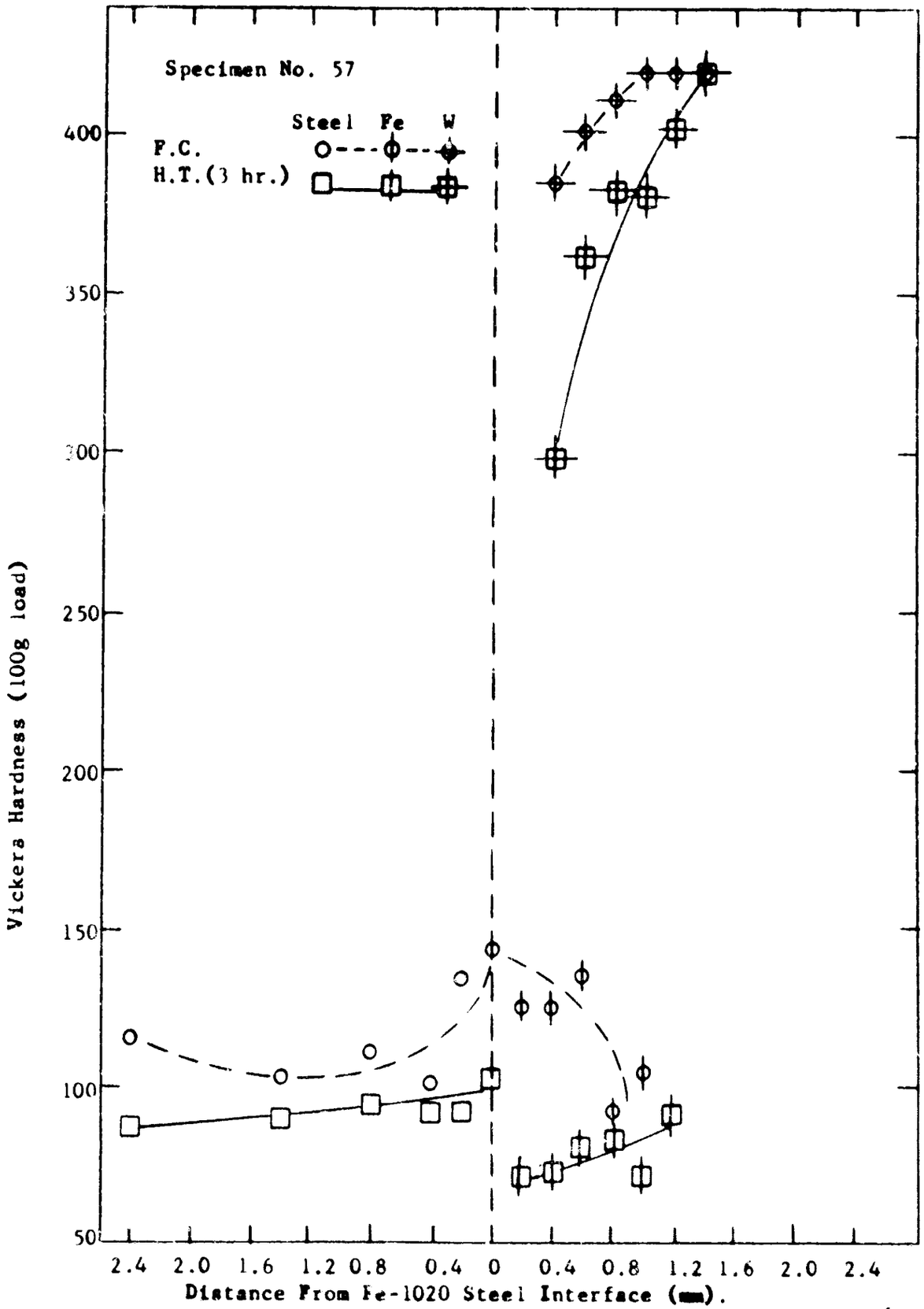


Figure 20. Microhardness Survey of a W-Fe Graded Coating on 1020-Steel Plate (7" x 2" x 1/8").

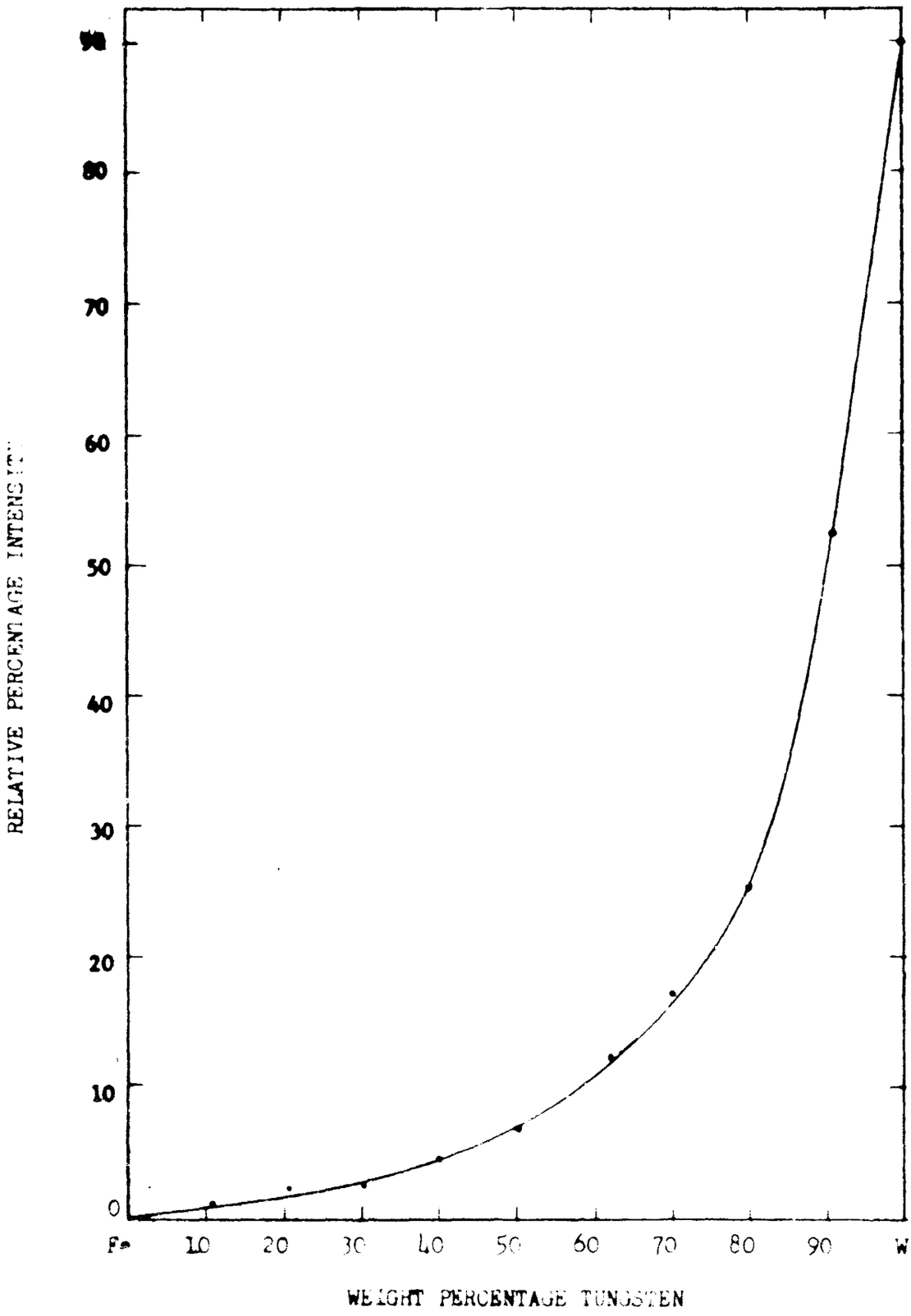


FIGURE 21. RELATIVE X-RAY INTENSITY STANDARDS FOR Fe-W COMPACTS. CURVE BASED ON TUNGSTEN PEAK (d=2.23).

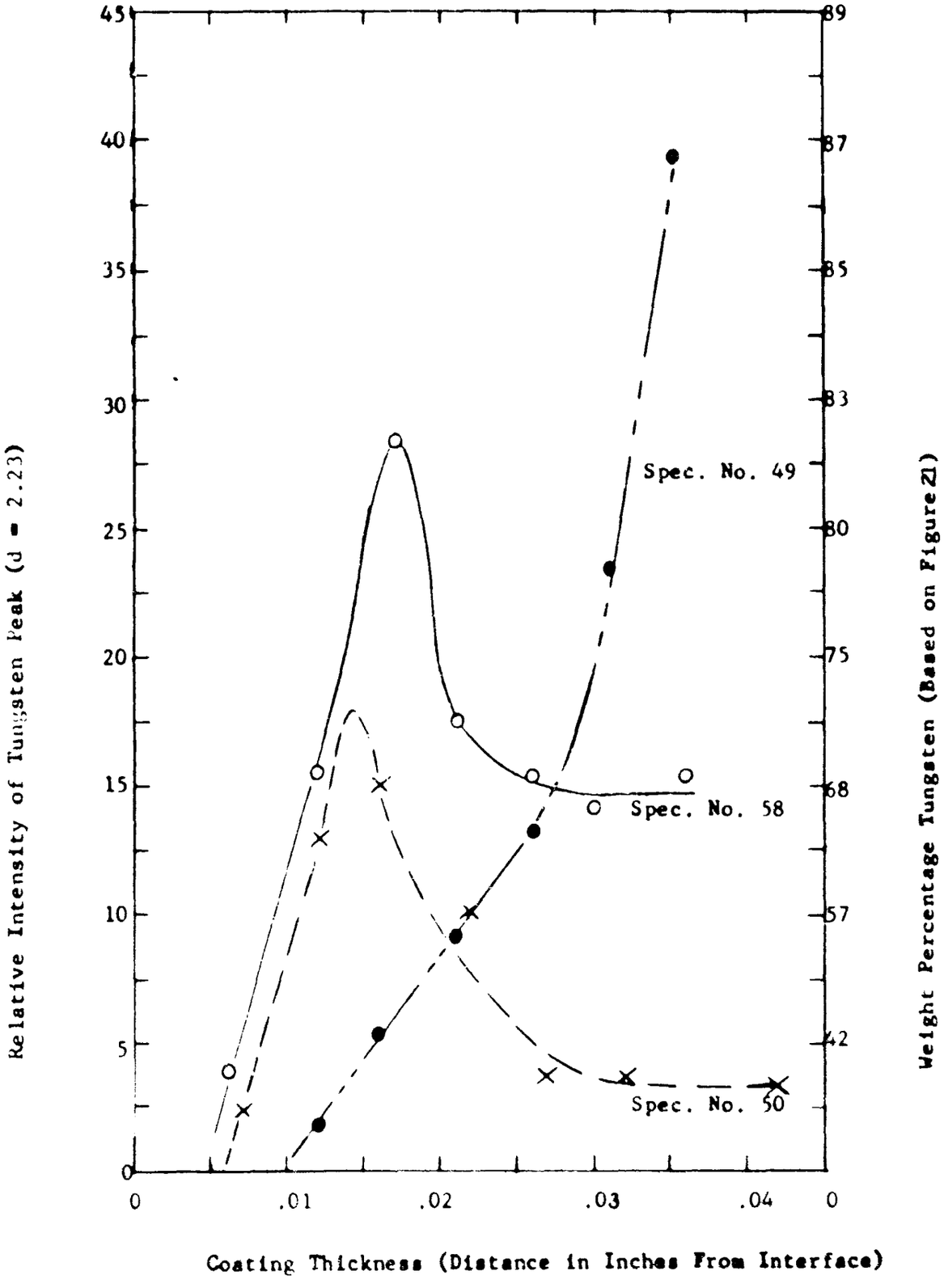
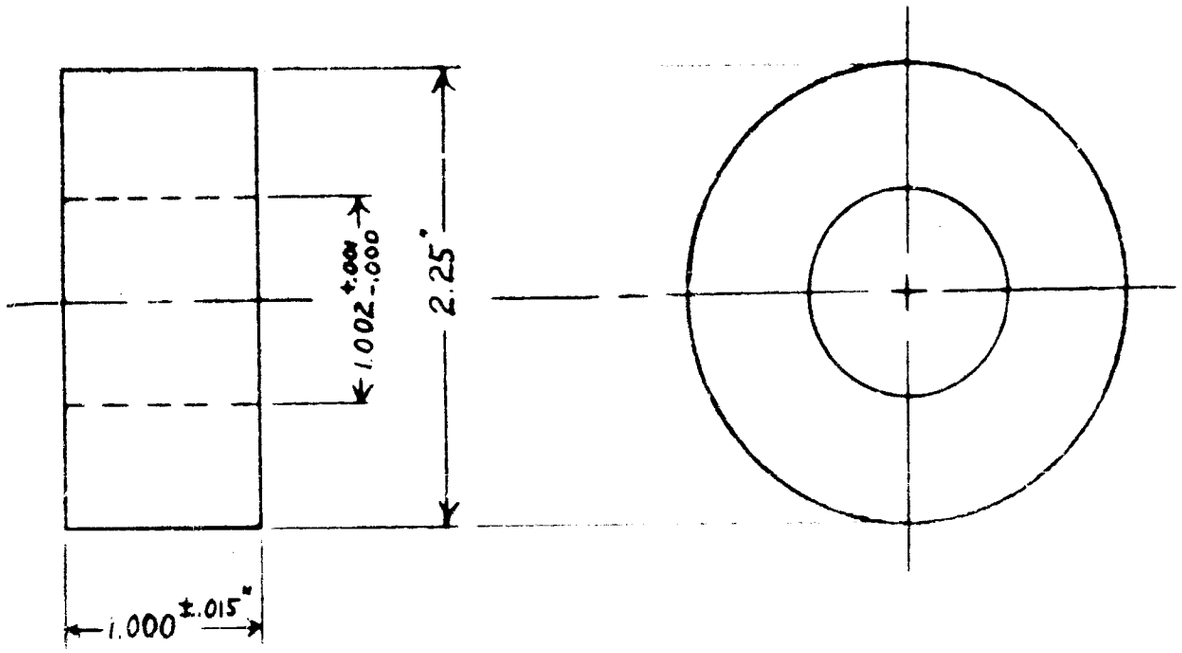
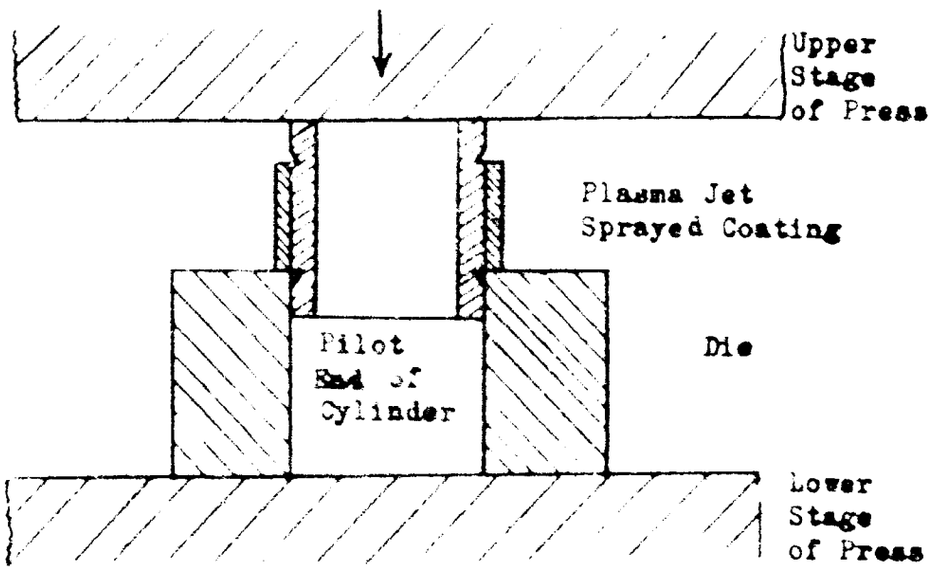


Figure 22. Tungsten Gradient in W-Fe Region of Graded Coating of W-Fe on 1020 Steel.

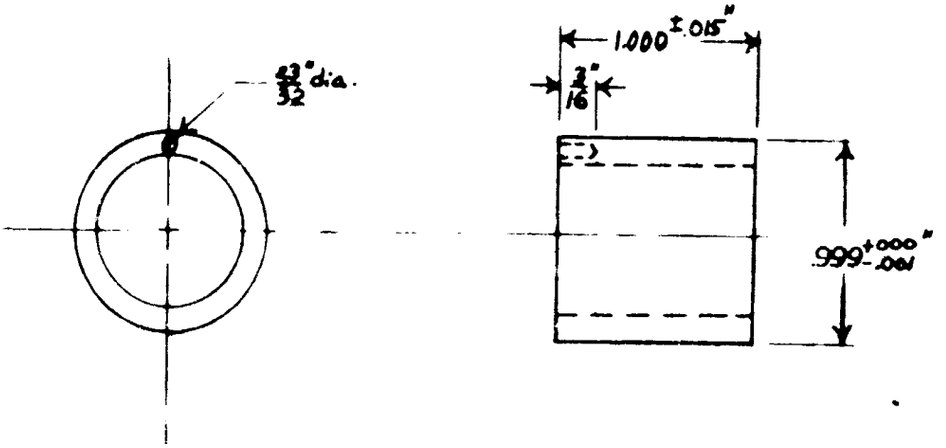


c. Tool Steel Die (R_c55)

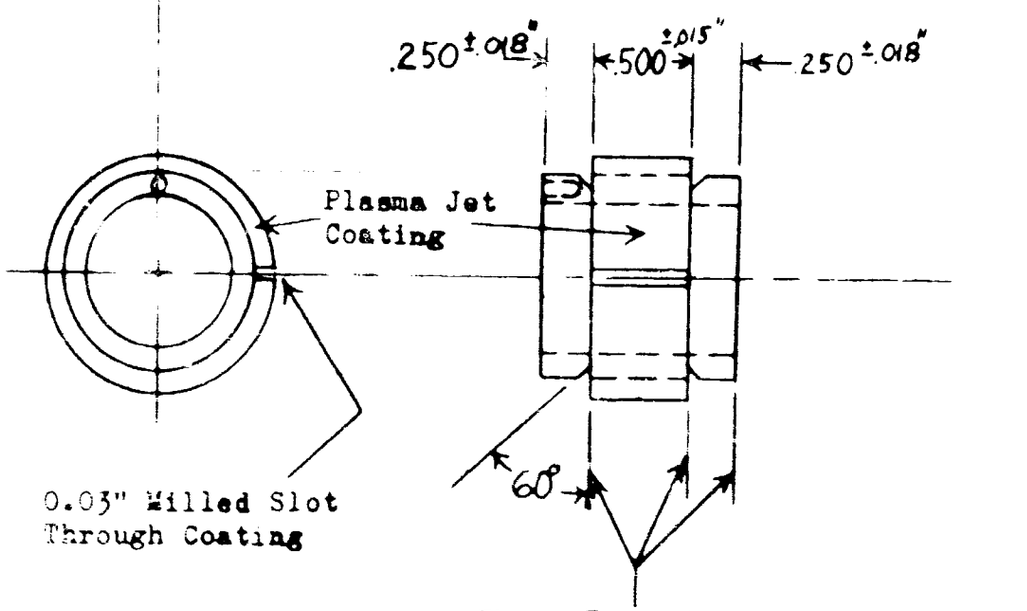


d. Position of Specimen During Test

Figure 23. Mechanical Shear Test for Plasma Jet Coatings.



a. Cylinder Before Coating.



b. Machining Requirements After Coating.

Figure 23. Mechanical Shear Test for Plasma-Jet Coatings.

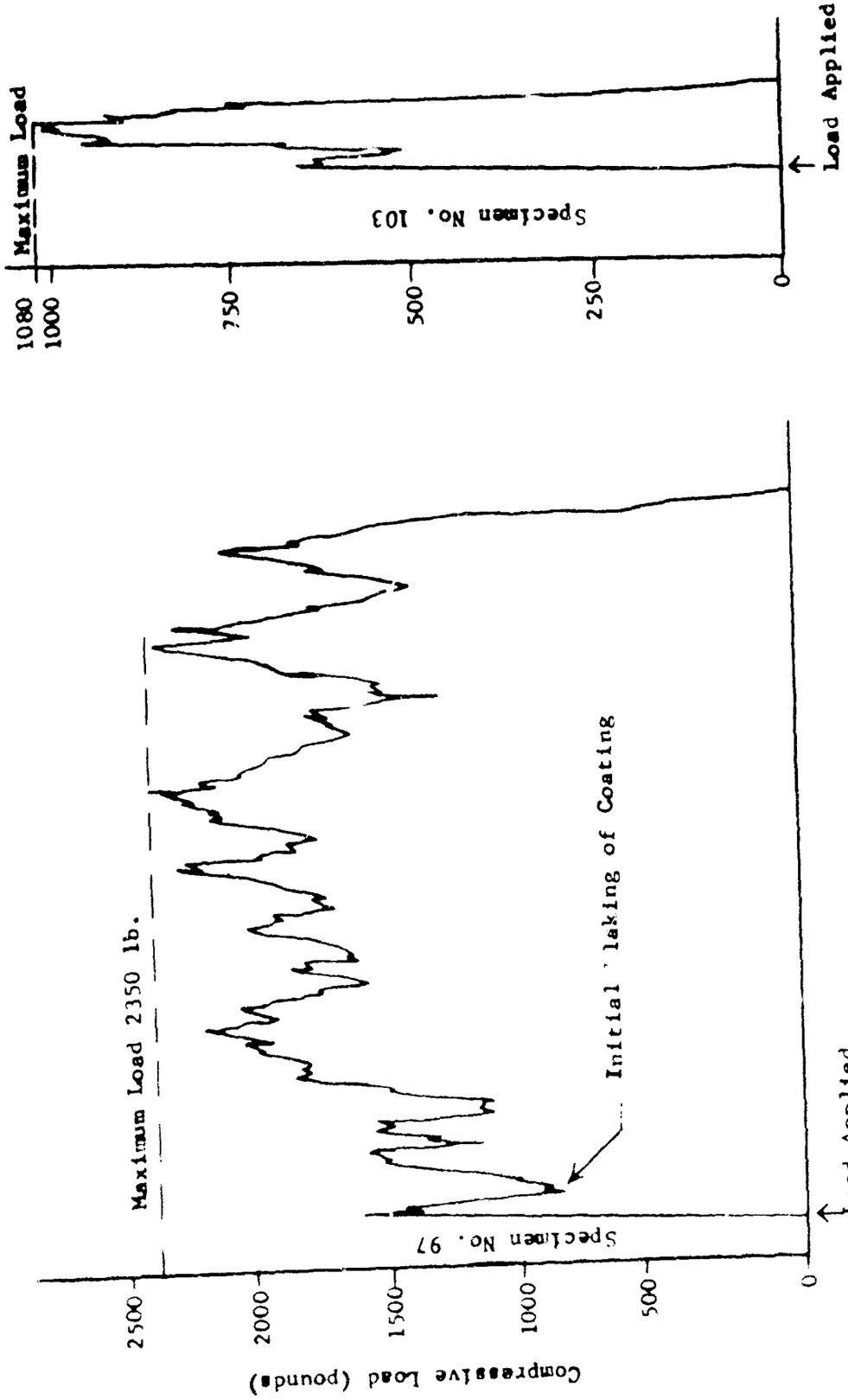


Figure 24. The Two Typical Types of Curves Obtained in the Mechanical Shear Tests.

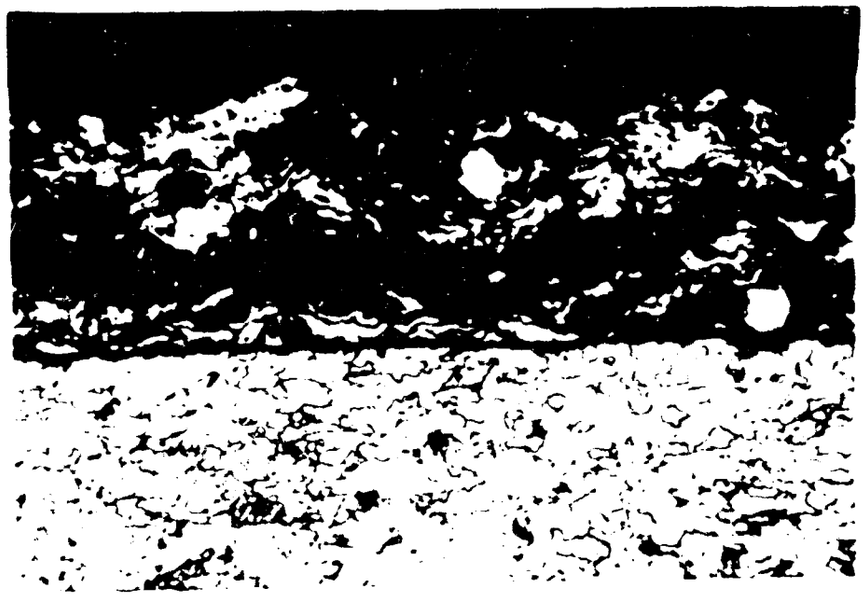


Figure 25. Specimen No. 7 Preheated to 530° C and Then Coated With Tungsten Powder (+325 mesh) in Air; Etched with 3 per cent Nital for 10 sec. (125x).

Figure 26. Specimen No. 7 Preheated to 530°C and Then Coated With Tungsten Powder (+325 mesh) in Air; Etched with 3 per cent Nital for 10 sec. (700x).

Figure 27. Specimen No. 10 Preheated to 485° C and Then Coated with Tungsten Powder (+325 mesh) in an Inert Atmosphere; Etched with 3 per cent Nital for 10 sec. (700x).

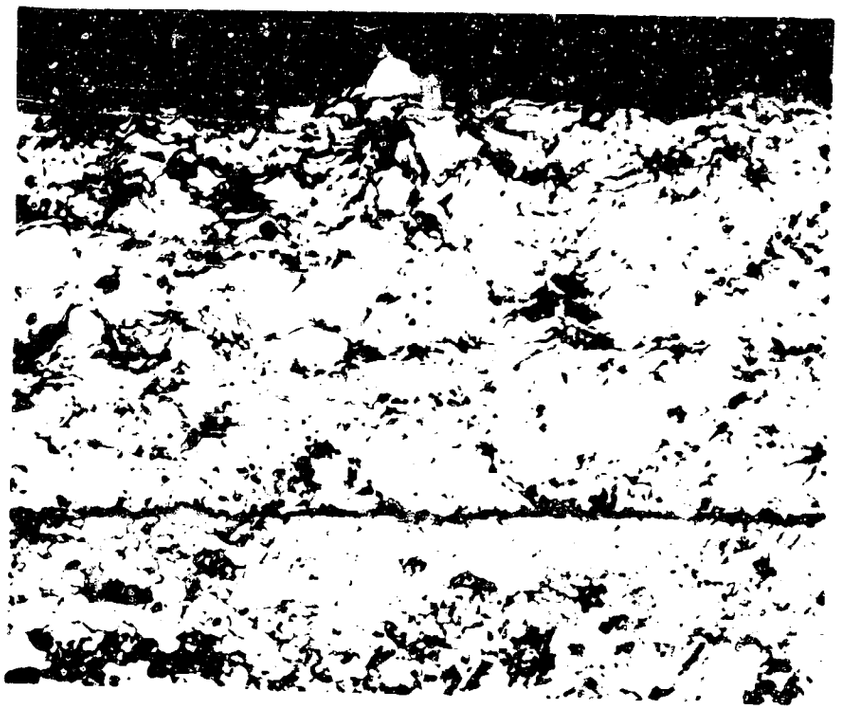


Figure 28. Specimen No. 11 Preheated to 508° C and Then Coated with Tungsten Powder (+325 mesh) in an Inert Atmosphere; Etched with 3 per cent Nital for 10 sec. (125x).

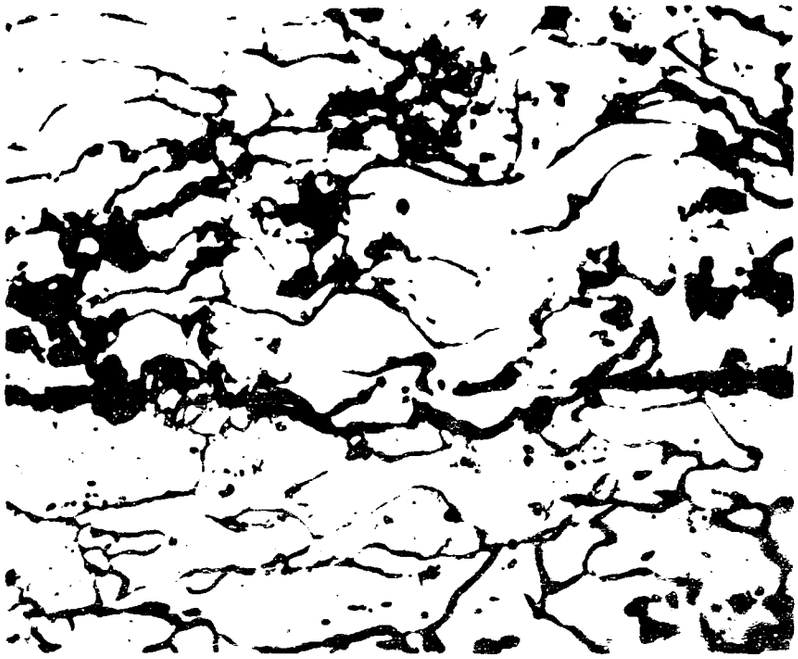


Figure 29. Specimen No. 11 Preheated to 508°C and Then Coated with Tungsten Powder (+325 mesh) in an Inert Atmosphere; Etched with 3 per cent Nital for 10 sec. (700x).

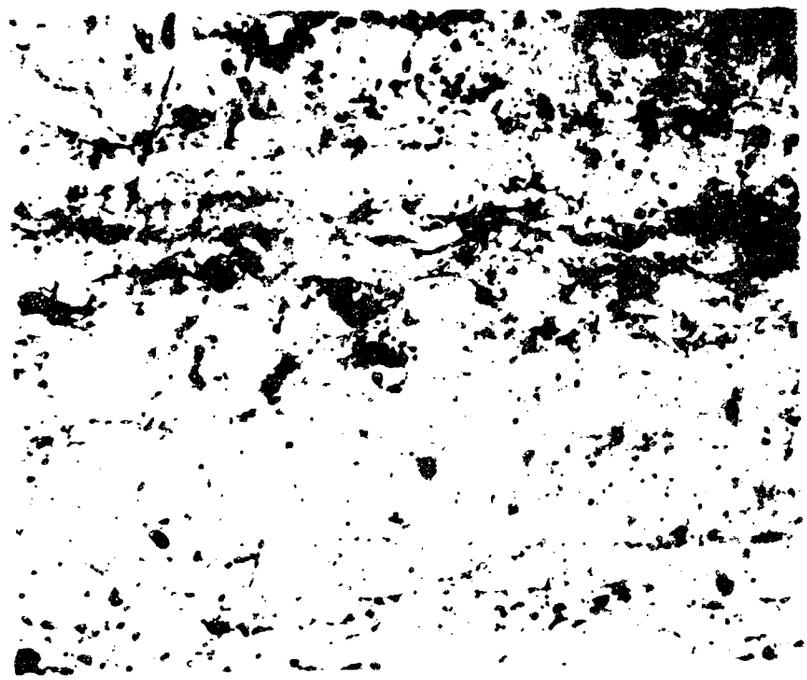


Figure 30. A Cross-Sectional View of the Coating That Spalled From Specimen No. 18 During Cooling (As Polished, 125x).

Figure 31. The Spalled Coating of Specimen No. 21. Graded Coating of 1020 Steel (+325 mesh) and Tungsten (+325 mesh). Etched with 3 per cent Nital for 10 sec. (75x).

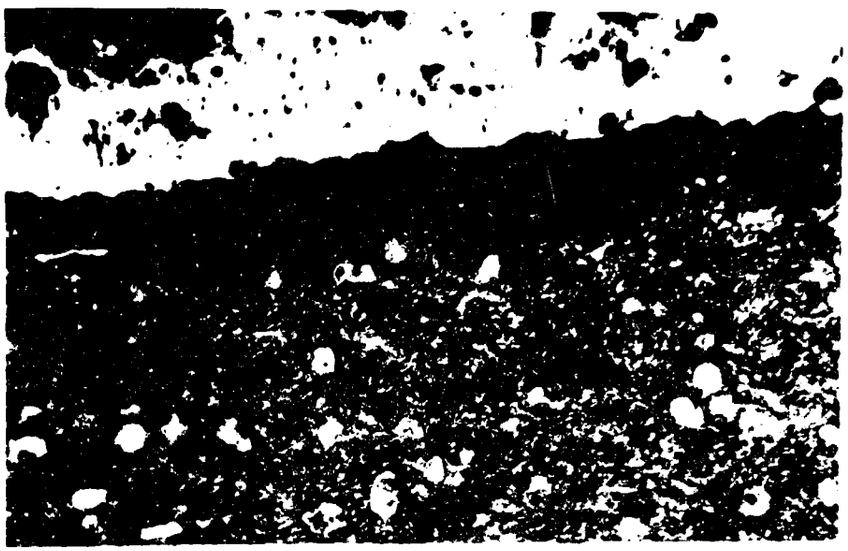


Figure 32. Graded Coating of Tungsten and 1020 Steel, Sprayed on 1020 Steel Plate Pre-Heated to 487°C. in an Inert Atmosphere (Specimen No. 19). Etched with 3 per cent Nital for 10 sec. (75x).

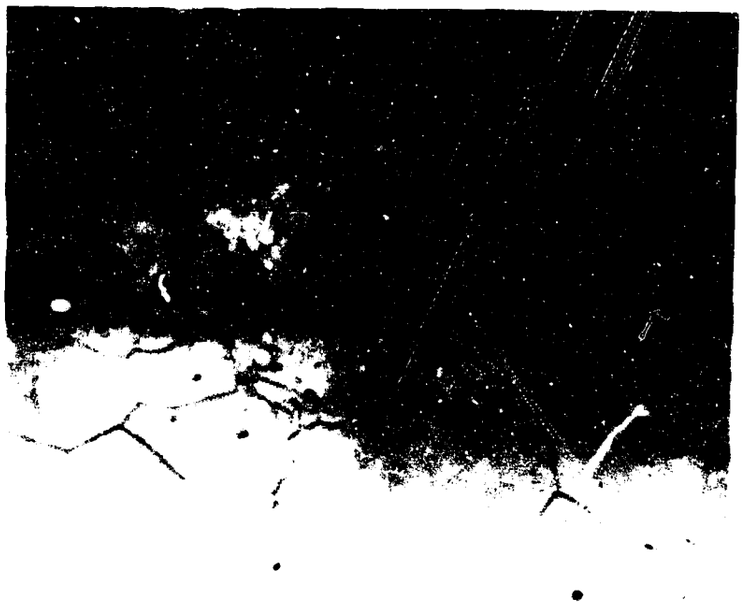


Figure 33. Graded Coating of Tungsten and 1020 Steel, Sprayed on 1020 Steel Plate Pre-Heated to 487°C (Specimen No. 19). Etched with 3 per cent Nital for 10 sec. (1000x).

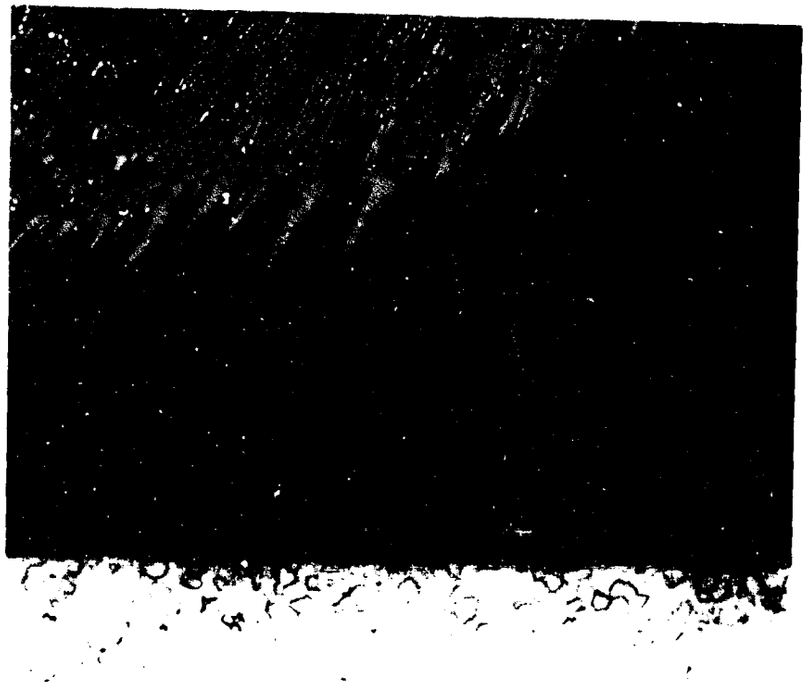


Figure 34. Graded Coating of Tungsten and 1020 Steel, Sprayed on 1020 Steel Plate Pre-Heated to 348°C in Air (Specimen No. 22). Etched with 3 per cent Nital for 10 sec. (75x).

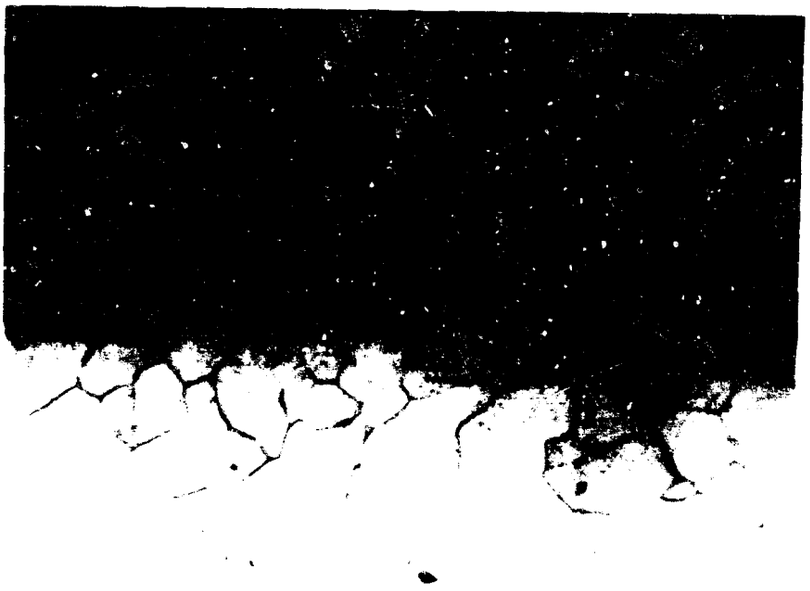


Figure 35. Graded Coating of Tungsten and 1020 Steel, Sprayed on 1020 Steel Plate Pre-Heated to 348°C in Air (Specimen No. 22). Etched with 3 per cent Nital for 10 sec. (400x).

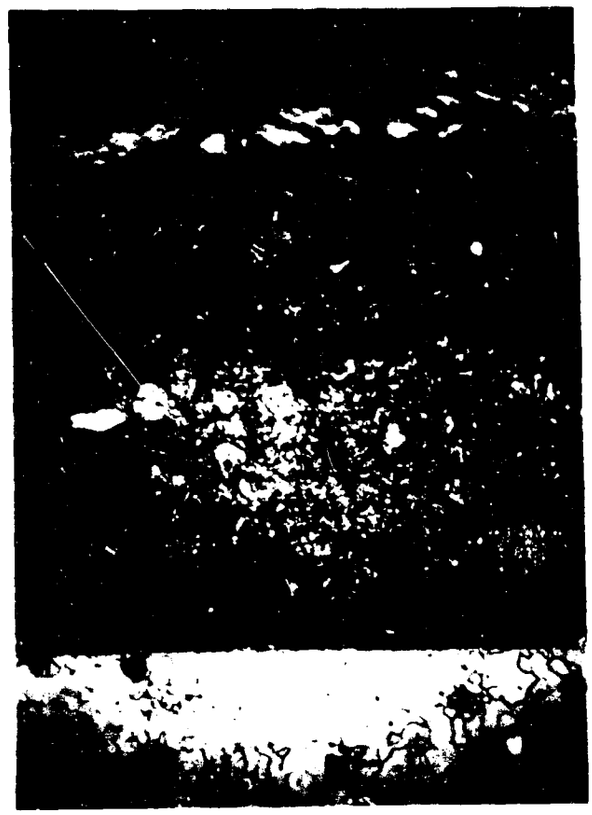


Figure 36. Graded Coating of Tungsten and 1020 Steel, Sprayed on 1020 Steel Plate Pre-Heated to 701°C in an Inert Atmosphere (Specimen No. 30). Etched with 3 per cent Nital for 10 sec. (75x).

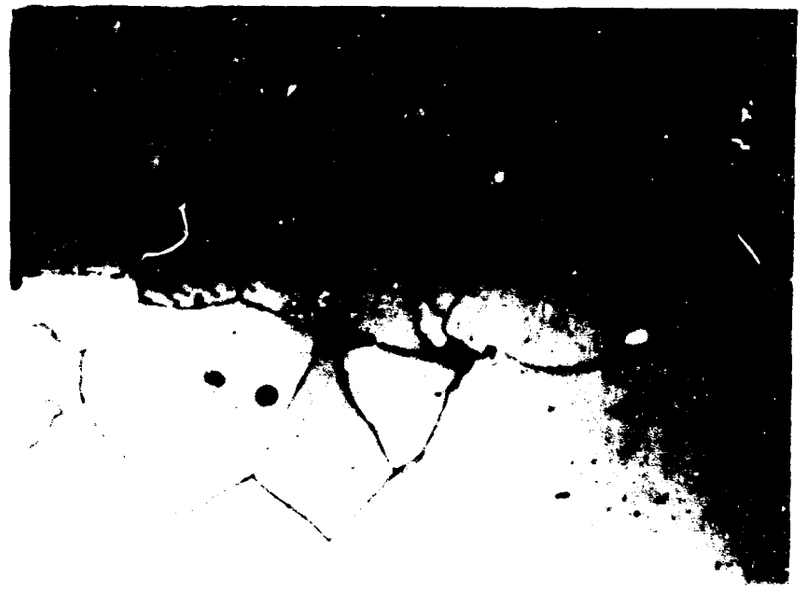


Figure 37. Graded Coating of Tungsten and 1020 Steel Sprayed on 1020 Steel Plate Pre-Heated to 701°C in an Inert Atmosphere (Specimen No. 30). Etched with 3 per cent Nital for 10 sec. (1100x).

Figure 38. Graded Coating of Tungsten and 1020 Steel Sprayed on 1020 Steel Plate Pre-Heated to 701°C in an Inert Atmosphere (Specimen No. 30). Heat treated for 1 hour at 950°C and Furnace Cooled (15°C/min). Etched with 3 per cent Nital for 10 sec. (150x).

Figure 39. Plasma-Jet Coating of Iron on 1020 Steel Substrate in an Inert Atmosphere. The substrate was pre-heated to 490°C (Specimen No. 34). Etched with 3 per cent Nital for 10 sec. (400x).

Figure 40. Plasma-Jet Coating of Iron on 1020 Steel Substrate in an Inert Atmosphere. The substrate was pre-heated to 490°C. (Specimen No. 4). The specimen was air cooled and then heat treated for 1 hour at 950°C. Etched with 3 per cent Nital for 10 sec. (400x).

Figure 41. Tungsten-Iron Graded Coating on 1020 Steel Substrate (Specimen No. 41). The substrate was pre-heated to 630°C, coated in an inert-atmosphere and furnace cooled from 950°C immediately after coating. Etched with 3 per cent Nital for 10 sec. (75x).

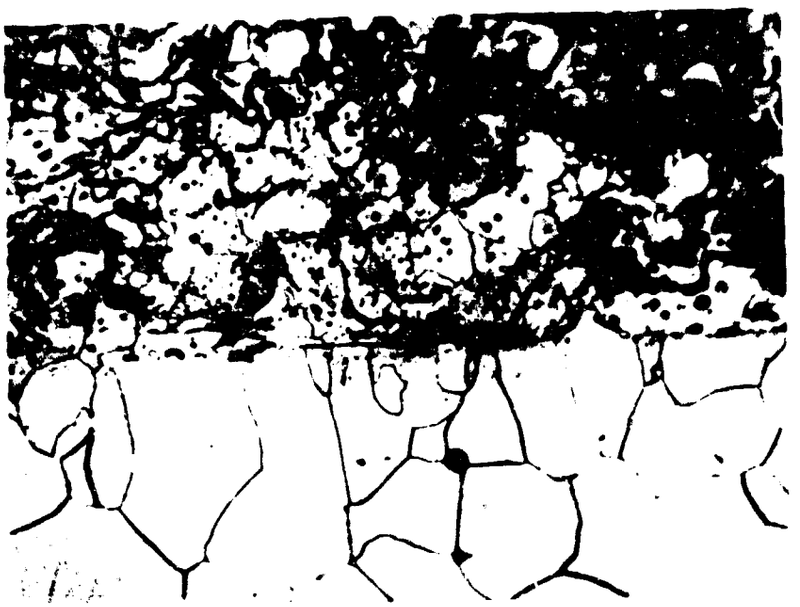


Figure 42. Plasma-Jet Coating of Iron on 1020 Steel Substrate (Specimen No. 41) in an Inert Atmosphere. The substrate was pre-heated to 630°C; furnace cooled (7 1/2°C/min) from 950°C immediately after coating, and heat treated for 1 hour at 950°C and furnace cooled. Etched with 3 per cent Nital for 10 sec. (450x).

Figure 43. W-Fe Graded Coating on 1020 Steel Substrate (Specimen No. 53). Heat treated for 1 hour at 950°C. Etched with 3 per cent Nital for 10 sec. (75x).

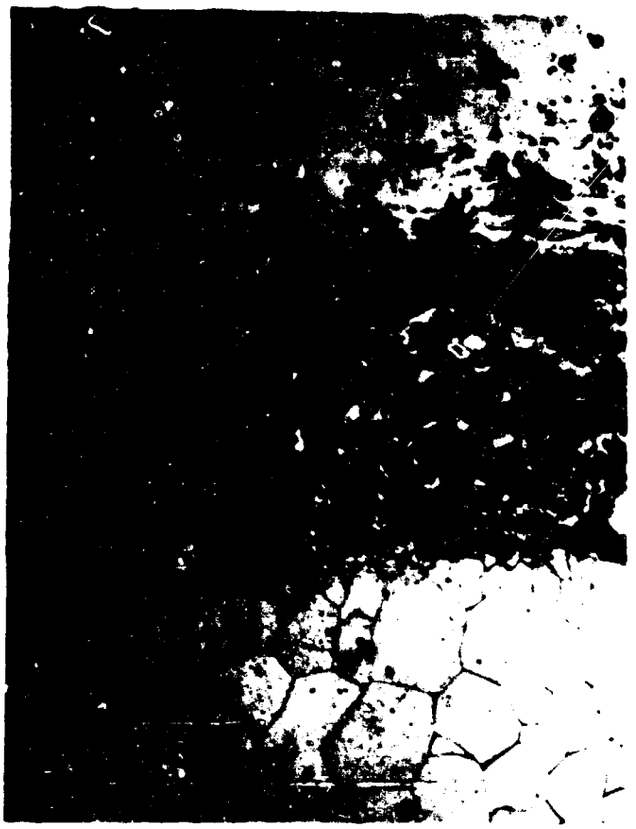


Figure 44. W-Fe Graded Coating on 1020 Steel Substrate (Specimen No. 65). Etched with 3 per cent Nital for 10 sec. (150x).

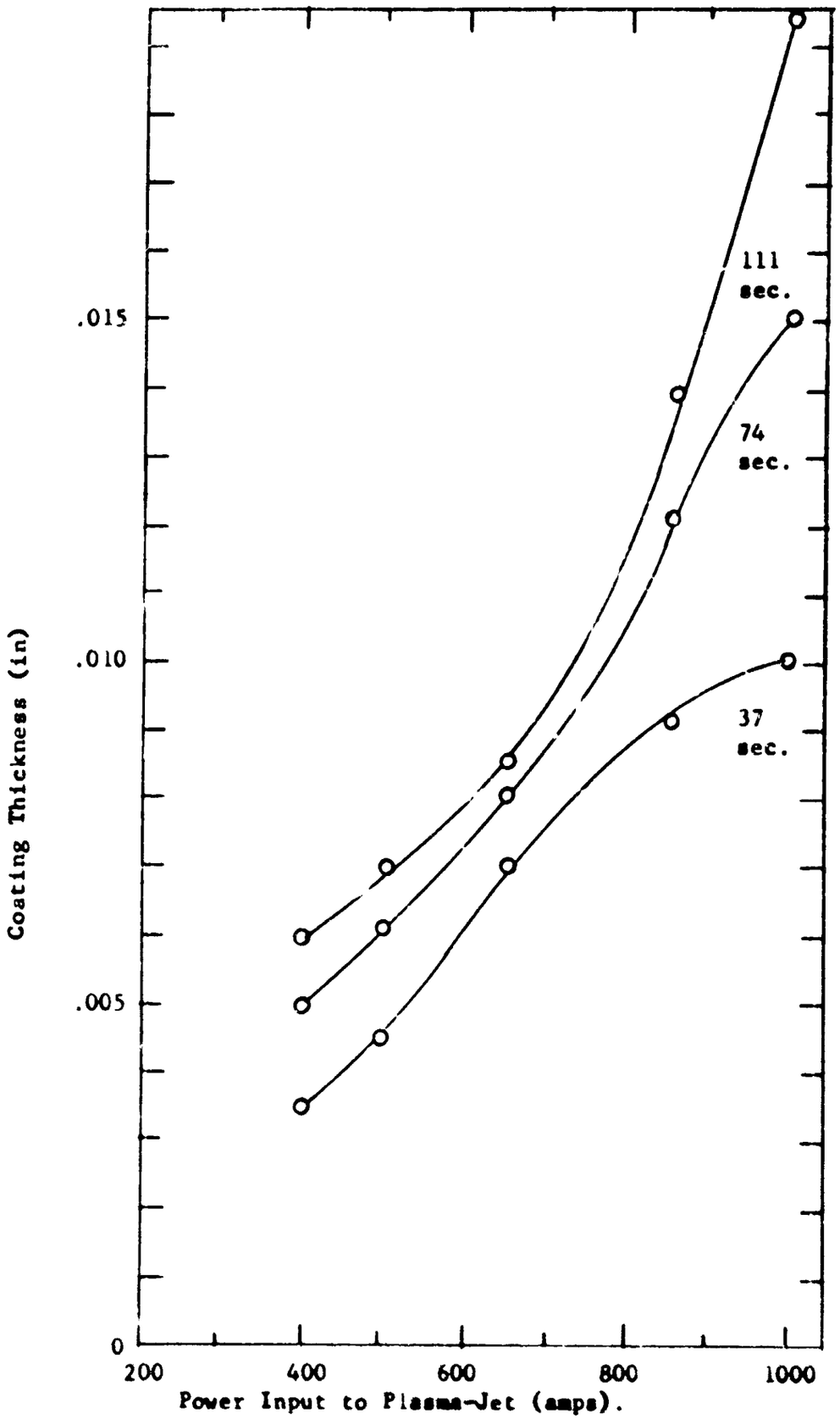


Figure 45. Effect of Power Input to Plasma-Jet on Coating Efficiency for Three Different Coating Times.

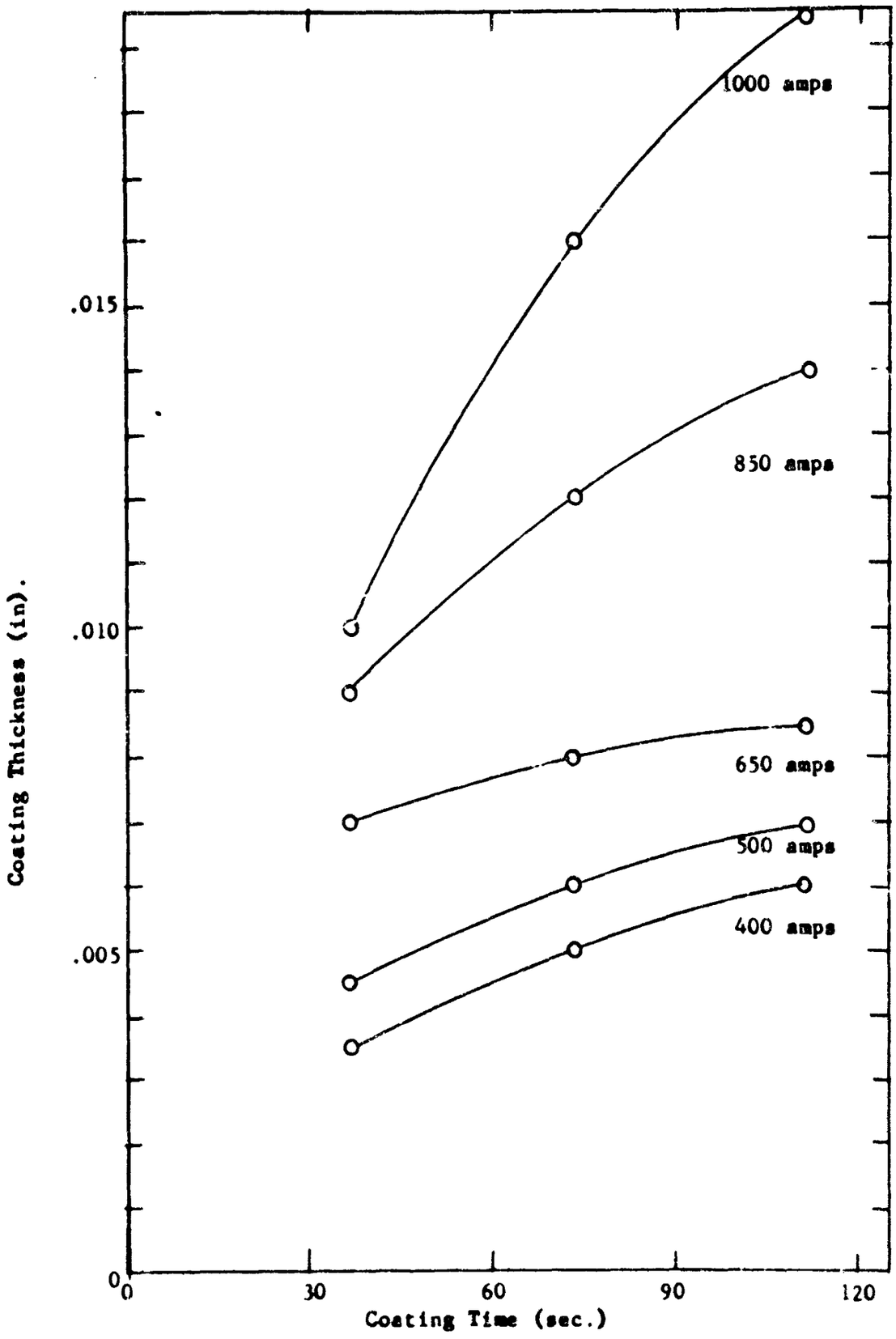


Figure 46. Effect of Power Input to Plasma-Jet and Coating Time on Coating Efficiency.

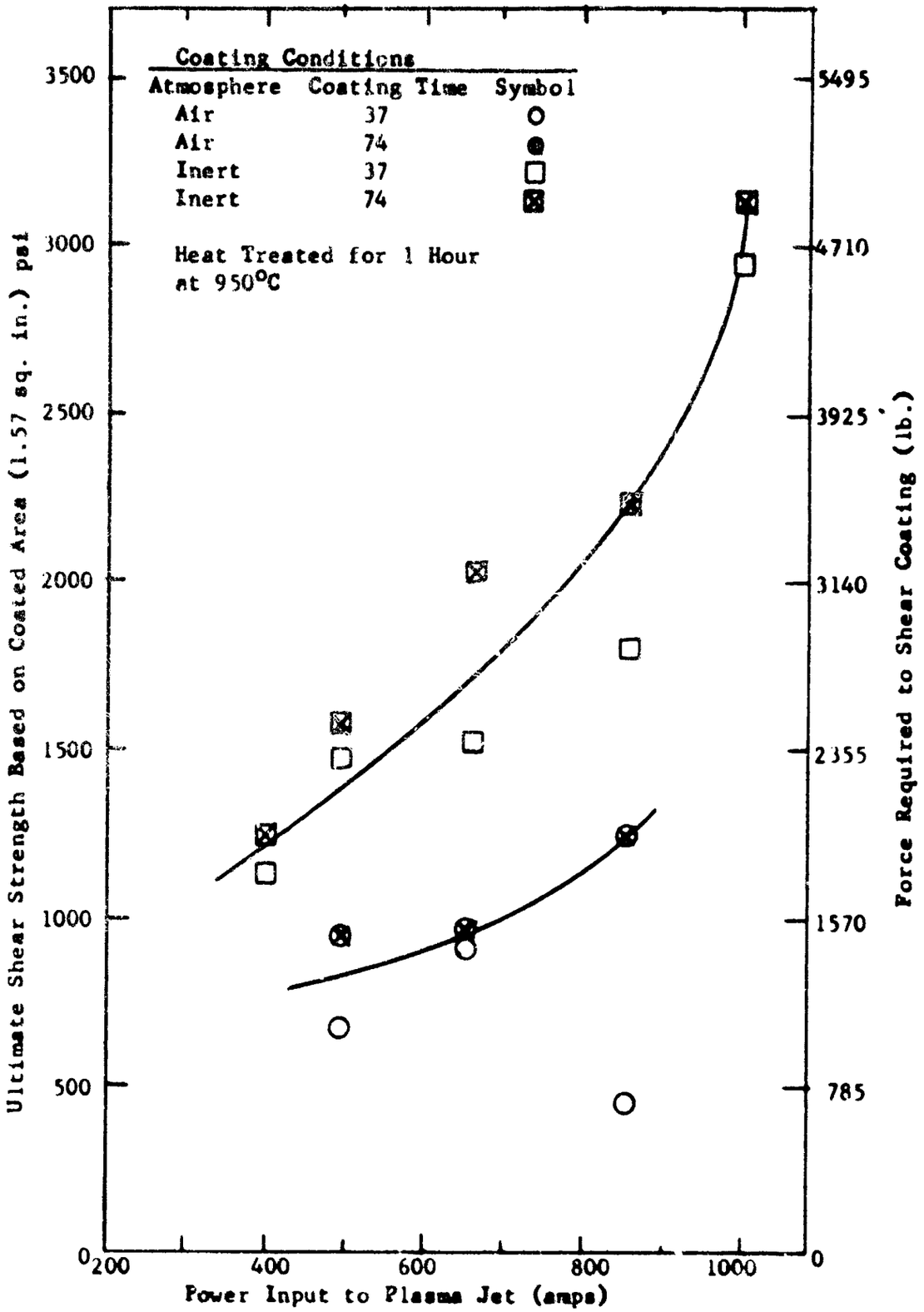


Figure 47. Effect of the Power Input to the Plasma-Jet on the Shear Strength of Iron Coatings on 1020 Steel Cylinders.

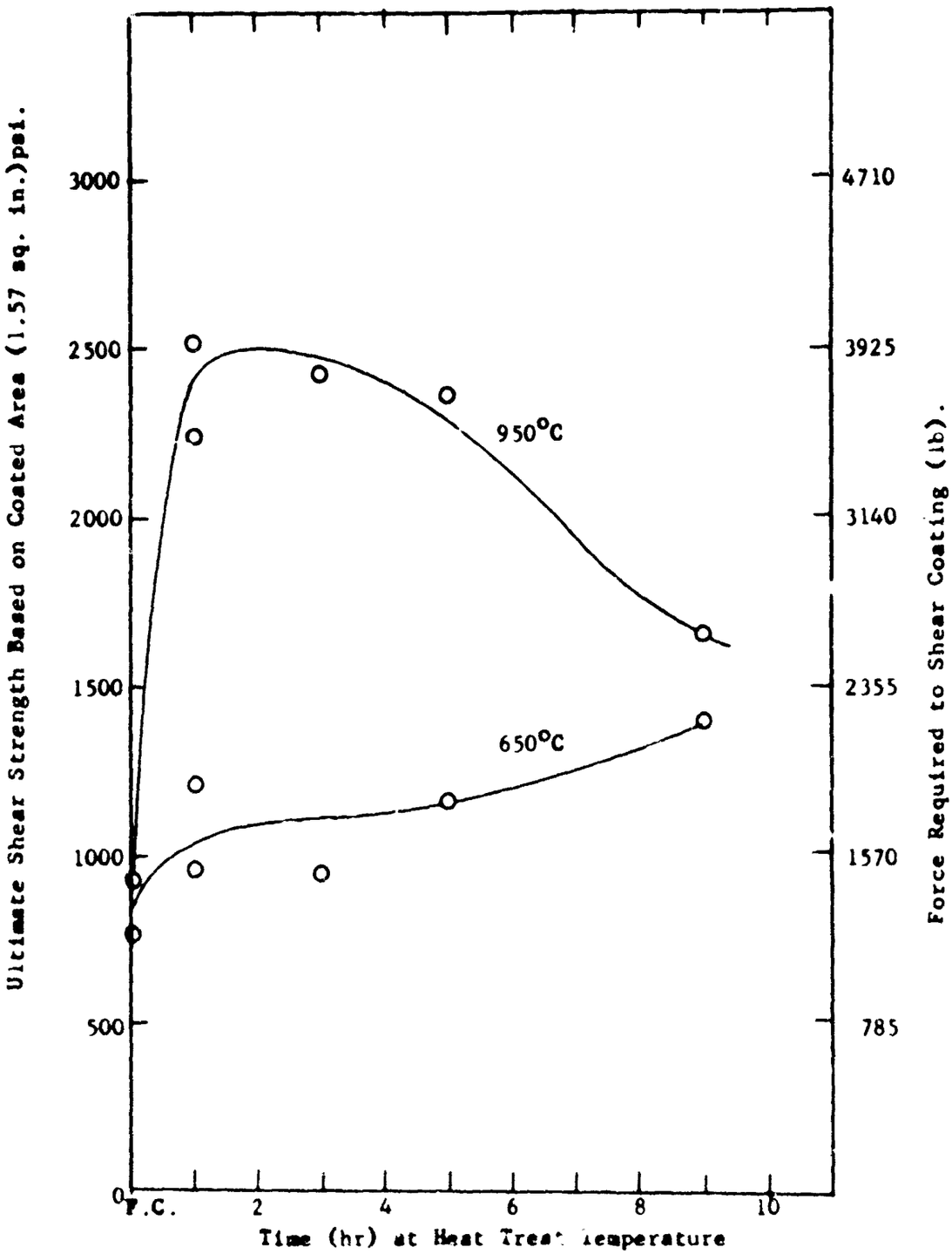


Figure 49. Effect of Heat Treatments on the Shear Strength of Iron Coated on 1020 Steel Cylinders.

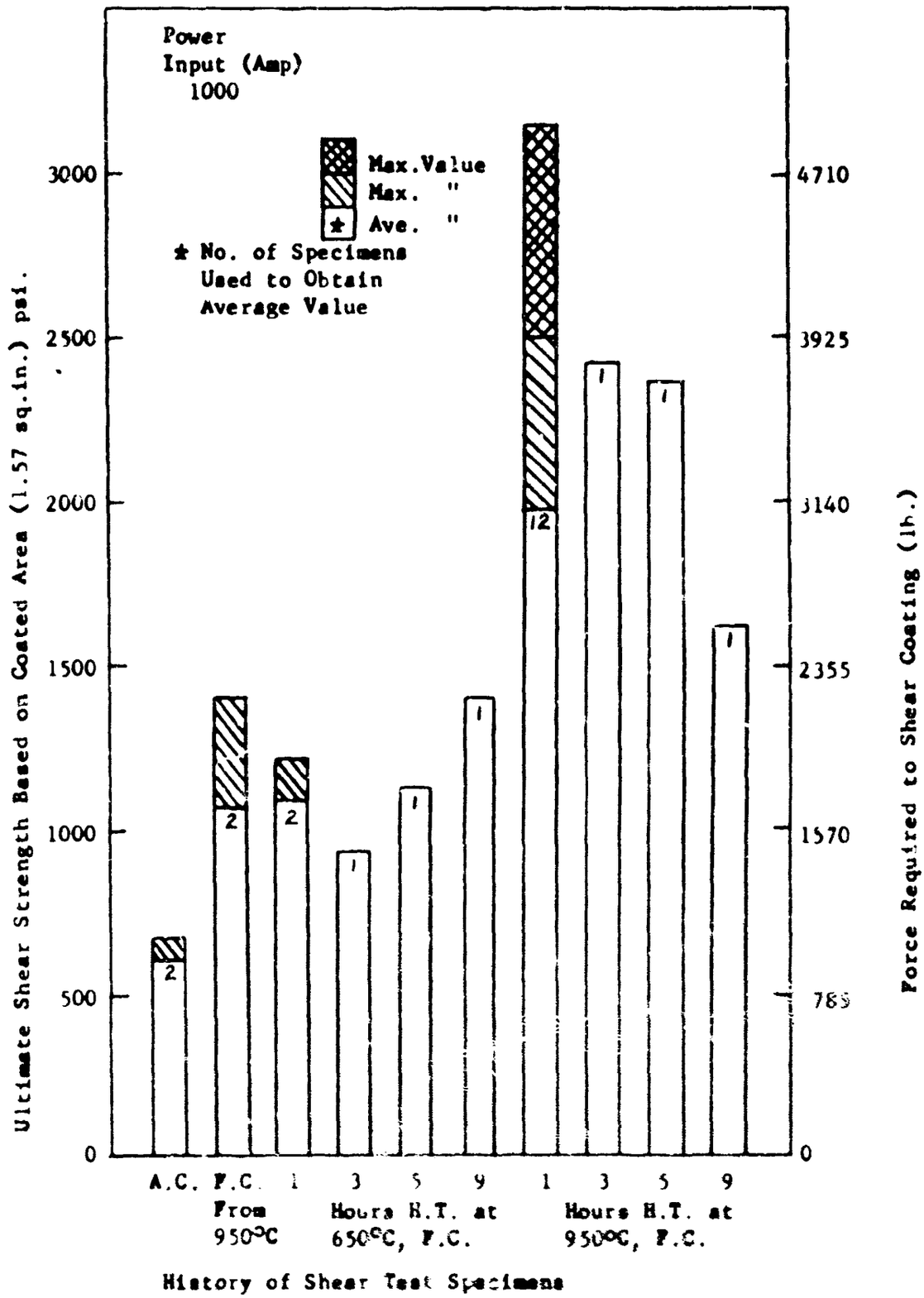


Figure 48. Effect of Specimens History on the Shear Strength of Iron Coated on 1020 Steel Cylinders.