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APPLICATION OF MOLYBDENUM SURFACES TO HEAVY METAL

S. Katz

(This program was carried out by M. Feller, S. Katz and S. Steingiser)

November 11, 1944

Abstract

Three methods of applying molybdenum coats to heavy metal are described. Such coats definitely increase the corrosion resistance. Further work is required to evaluate the usefulness of the methods.

699-1

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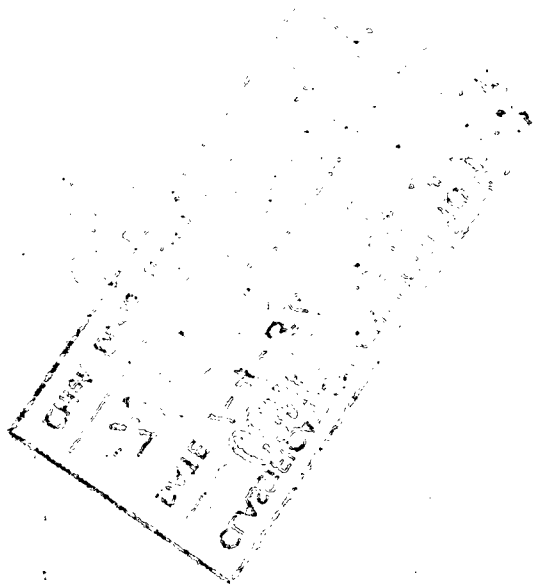

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Application of Molybdenum Surfaces to Heavy Metal

S. Katz

(This program was carried out by M. Feller, S. Katz and S. Steingiser)

In conjunction with our program on the formation of corrosion resistant heavy metal, a study was made of applying thin molybdenum surfaces to heavy metal slugs. The general plan was to apply a coat first and then to diffuse it in thermally. The attempts made may be classified under these headings:

1. Vacuum diffusion.
2. Powder metallurgy.
3. Chemical deposition.

1/ The vacuum diffusion experiments were conducted in a cylindrical metal bomb fitted with a central, tantalum-lined chamber and two end chambers connected to the center one by small orifices. Initially, the bomb was constructed with a Wilson seal, to permit evacuation and sealing before starting the run. Later runs were made with continuous evacuation. In the earlier runs, the side chamber was packed with calcium turnings, and in the central chamber the heavy metal slug was placed, surrounded with molybdenum powder. Runs were made at 800°, 900°, and 1075°. In all cases extreme corrosion of the surface of the slug occurred, and no evidence of the diffusion of molybdenum into the heavy metal could be detected. 1/

This work is being continued in Mr. Foote's group.

1/ Another phase of this investigation dealt with attempts to form a surface layer by means of powder metallurgy methods. The heavy metal was buried in 325 mesh molybdenum and was pressed at between 50 and 100 tons per square inch. It was found that pressures as low as 15 tons per square inch formed acceptable compacts consisting of molybdenum in close contact with the heavy metal. The compact was then sintered under vacuum at 1000-1100°C. 2

The first experiments run in this manner were pieces compacted at high pressure. The sintering was done at 1050°C. When removed from the furnace, the molybdenum had sintered hard and cracked off from the slug readily. The latter had a clean steel gray surface. Microscopic examination failed to confirm conclusively the existence of a surface alloy layer. The cracked surface of the molybdenum also indicated a coefficient of expansion which is greater than that of U. This undoubtedly tends to separate the two surfaces, thus making it more difficult for an alloy to form. 2

A second group of pieces were made by a water-die technique using pressures of 10 and 50 tons per square inch. These pieces were sintered at 1070°C in vacuum and upon removal showed partial or local fusion at various points. Definite indications of alloy formation were observed, three types of alloys being present. One was a uranium-molybdenum layer in the molybdenum; another was a uranium-molybdenum layer in the uranium; the third was a uniform molybdenum-uranium alloy distributed throughout the heavy metal. Fingers of heavy metal protruding into the molybdenum showed that some undesirable fusion or flow had occurred. 1/3

Chemical Methods of Coating Heavy Metal with Molybdenum. 699-2

Work on the electrochemical deposition of molybdenum on heavy metal has been carried

out elsewhere and has not been investigated by our group.

3/ Other work consisted of two sets of studies, one involving deposition from molten salts of molybdenum and the other the deposition of molybdenum from the carbonyl on the metal surface; the latter seems to be very promising at this stage and is described in considerable detail at the end of this page.

The fused salts used were molybdenum trioxide and molybdenum chloride ($MoCl_2$).

The oxide fuses at 800°C. Several runs were made in air and in vacuum at 900-1050°C with the heavy metal immersed in the molten oxide. In all cases a hard, dark coating which was 75% UO_2 formed. The corrosion resistance of this coat, while better than ordinary heavy metal, was still not good.

Attempts to work with $MoCl_2$ failed, due mainly to the extremely hygroscopic nature of the material.

Of the methods studied up to the present, the molybdenum carbonyl procedure seems most promising. It appears quite feasible, at this stage, to plate out molybdenum from the carbonyl on a hot heavy metal surface which has been prepared properly. There seems to be some carbide formation on the surface, as evidenced by its reactivity, but the overall carbon has been reduced to 25% of its original value. 4/ The reduction of the overall carbon content of the slug suggests a new approach to the problem of its removal from heavy metal. This is discussed later.

4/ So far, it has been found necessary first to deposit and diffuse in a layer of nickel to undercoat the molybdenum. The nickel is also deposited from its carbonyl but at a lower temperature and is diffused in thermally. At 700°C the nickel acts as a carrier, allowing greater diffusion of the molybdenum into the slug. Further studies would be desirable to determine the minimum concentration of nickel necessary to carry on this diffusion of molybdenum. The total nickel added at present is of the order of 300-600 ppm and should have an insignificant effect on pile operation; and even this concentration could possibly be lowered further to reduce this effect. The possible alternative use of chromium instead of nickel is indicated, since it, too, is available as the carbonyl, and it, as well as nickel, forms an eutectic with molybdenum. Further study of the Ni-Mo-U and Cr-Mo-U systems would merit consideration.

The apparatus is shown in the accompanying photograph. A manifold arrangement permits the passage of any one or a combination of gases into the system. From the manifold, the gases may be passed through or bypassed around a glass reservoir containing the molybdenum carbonyl and from there to the reaction chamber. The system is adjusted to feed the carbonyl into the system at its vapor pressure at 25°C. The carbonyl and carrier gases pass into the reaction chamber by means of a water-cooled spiral copper tube, with tiny orifices drilled into it. The chamber itself consists of a double-walled glass bell jar, water cooled between the two walls, sealed to a brass base. A central platform supports the slug, and a thermocouple reads temperatures. The bell is evacuated through a trap, an oil diffusion pump and a hypervac. The slug inside the reaction chamber is heated by means of a 6 KVA induction heater.

Five runs have been made up to the present (Table I). Initially, the slug was subjected to mechanical or electrolytic polishing to prepare the surface. It was then placed in the reaction chamber, evacuated and outgassed with heating. In some runs the system was flushed with CO at this stage after which the carbonyl and the carrier gas were admitted. A post-plating heat treatment at 800°C for a half hour in uranium terminated the operation in all cases except the last one.

699-3

The first four runs must be regarded as exploratory. From the observation on the results of the last run, it is believed that the procedure will ultimately lead to a method of protecting the slug against water corrosion. At the end of this run the surface of the slug was covered with encrustations at the points of exit of carbonyl from the supply nozzles. These encrustations were apparently nickel, predominantly. The rest of the slug surface was smooth and the deposit appeared quite coherent.

Forty hours of corrosion testing in W-water at 90° showed no corrosion, but at the end of 88 hours corrosion pits began to appear. The general surface condition was good; most of the corrosion occurred at the encrustation points. The accompanying photographs show the general surface condition of the slug at several points in the test. Microscopic examination of the polished and etched surface shows a very definite alloy structure with well-defined precipitation lines, possibly a three-phase system. The edge has a very definite crystal structure differing from that of heavy metal. This is shown in the accompanying photomicrographs.

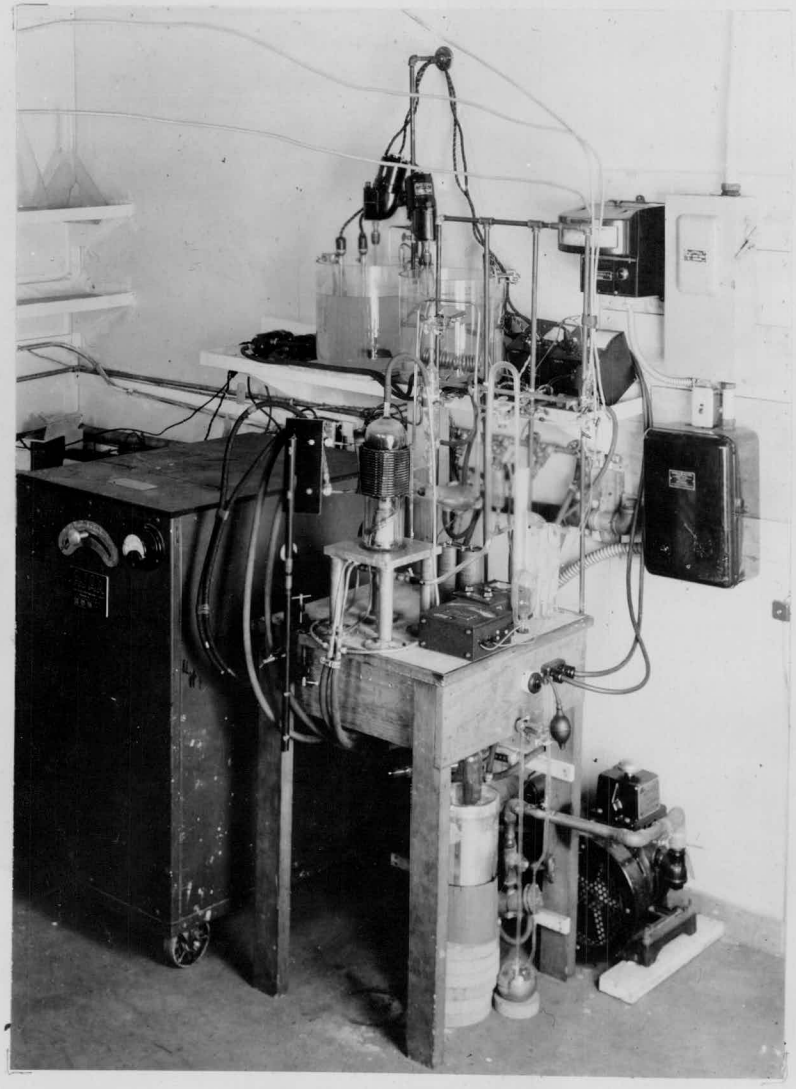
At the present time, the apparatus is being modified by the installation of a rotating turn table in the bell-jar assembly. This will rotate the slug at about 2 r.p.m., thus depositing a more uniform metal coat on the slug and eliminating the encrustations. It should also speed up deposition of the metal from the carbonyl. Later on, a faster speed of rotation and a more efficient injection nozzle arrangement might be used to hasten the process.

In its present state, the system tends to deposit finely divided nickel on areas other than the hot slug. This is probably due to the pumping speed of the system which does not remove the CO rapidly enough, and thus allows the pure nickel to diffuse all through the system. If the rate of input of nickel carbonyl be reduced by dilution with a carrier gas, the amount of nickel deposited indiscriminately through the system is materially reduced. The entire subject of pumping speeds should be investigated.

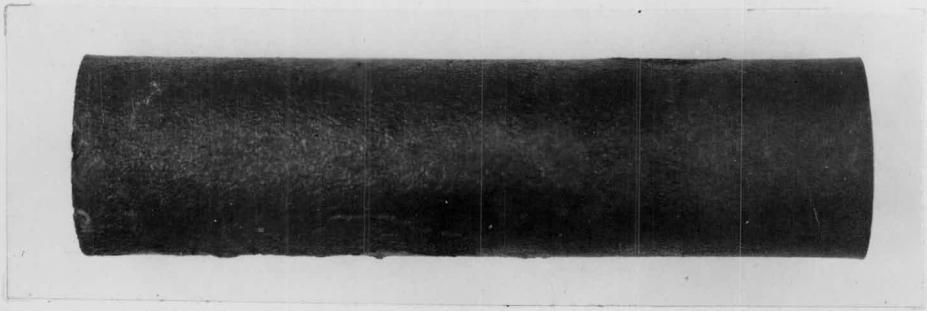
Reference has been made to the reduction of carbon in the slug during treatment. The normal carbon content of a slug is about 1200 ppm. In the course of these experiments, this was reduced to 300-400 ppm. Possibly the molybdenum forms carbide at the expense of the uranium carbide. This too should receive further study.

On the basis of these few experiments, it may be stated that a thin molybdenum coat will increase the corrosion resistance of heavy metal. It is proposed now to attempt to deposit a layer, possibly .05" thick, of a concentration of 5-10% molybdenum. In the absence of surface flaws, adequate protection of the slug should be obtained. These higher concentrations can undoubtedly be obtained by longer or more rapid plating of the molybdenum.

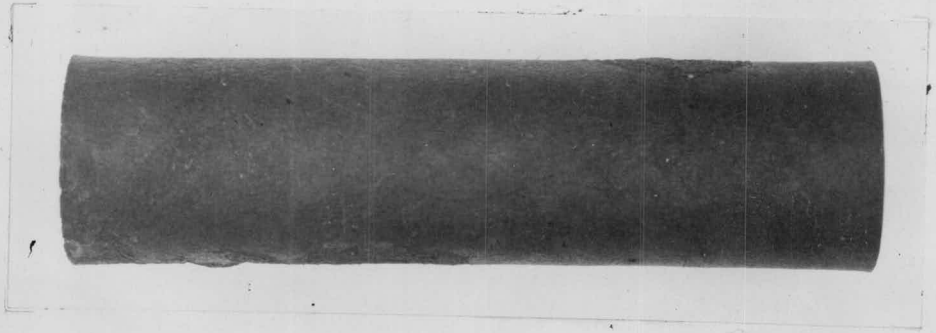
Experiment Number	Surface Preparation	Initial Pressure	Degassing Temperature	Initial Treatment		Carrier	Carbonyl Schedule	
				Temp.	Reducing Agent		Slug Temperature	Plating Operation
1	Electrolytic	3×10^{-6}mm	700°	700°	CO	Argon at 6×10^{-2}mm	700°C	Mo for 2½ hours.
2	Electrolytic	1×10^{-5}mm	700°	700°	None	Argon at 8×10^{-2}mm	700°C	Mo for 6 hours.
3	Mechanical	3×10^{-5}mm	300°	300° 300°	H_2 CO	Argon at 8×10^{-2}mm	400°C 600°C	Ni at .08 mm for ½ hr. Mo for 6 3/4 hours.
4	Electrolytic	5×10^{-5}mm	700°	600° 600°	H_2 CO & CO_2	CO_2 at .1 mm	450° 6-700°	Ni at .08 mm for 3.4 hrs.
5	Mechanical	3×10^{-5}mm	800°	600°	CO	CO for Ni; Argon for Mo	600° 6-700°	Ni for 1 hour. Mo for 7½ hours.



MOLYBDENUM CARBONYL PLATING APPARATUS



Coating of Slug with Molybdenum and Nickel from the Carbonyls.
Experiment # 6
Corrosion Tested in W-water at 90°C for 44 hours
Nov. 4, 1944



Coating of Slug by Molybdenum and Nickel from the Carbonyl.
Experiment # 6
Tested in W-water at 90°C for 88 hours.
Nov. 6, 1944

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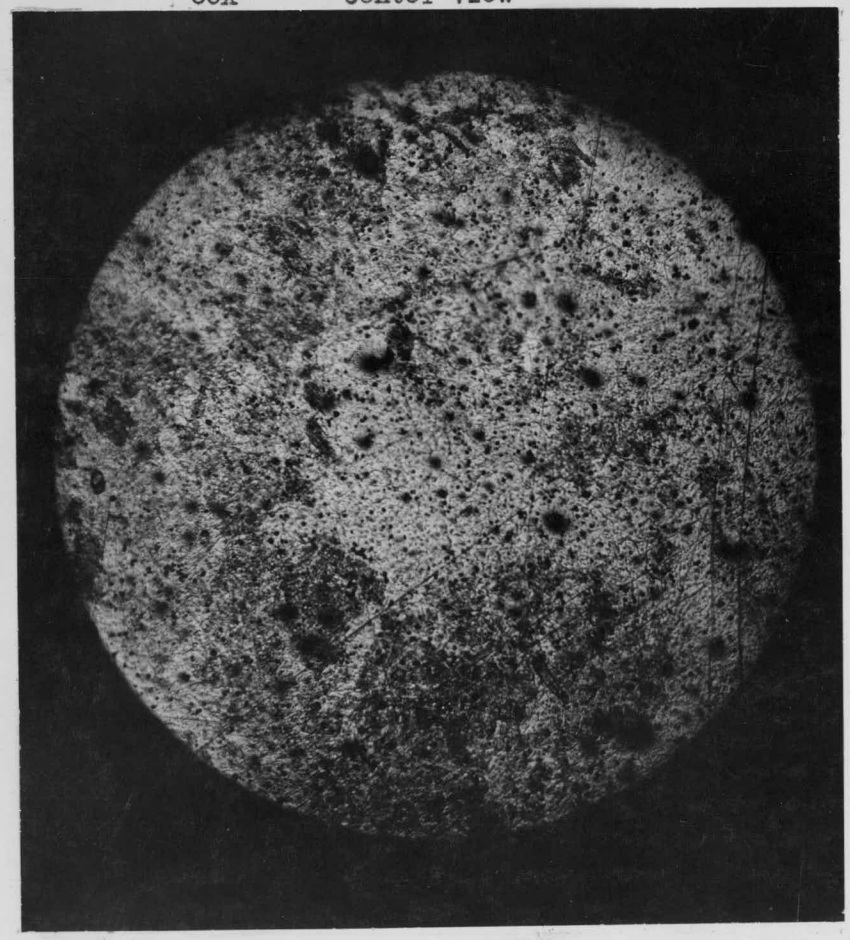
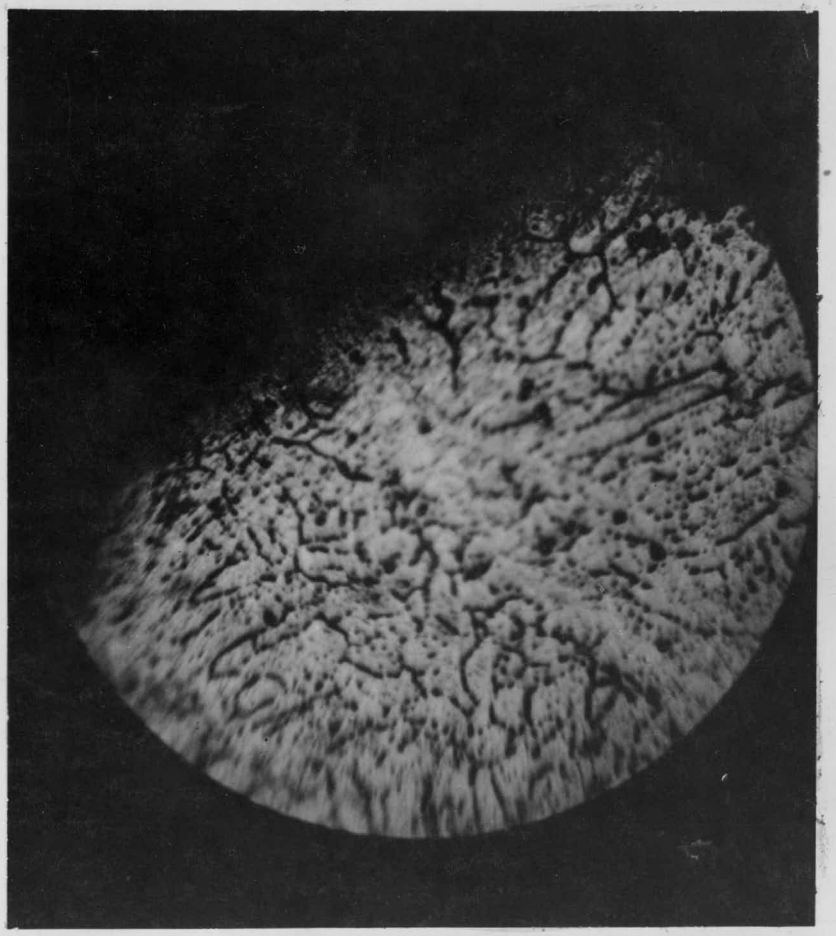
Sample # 6A Top of Slug
50X Center View



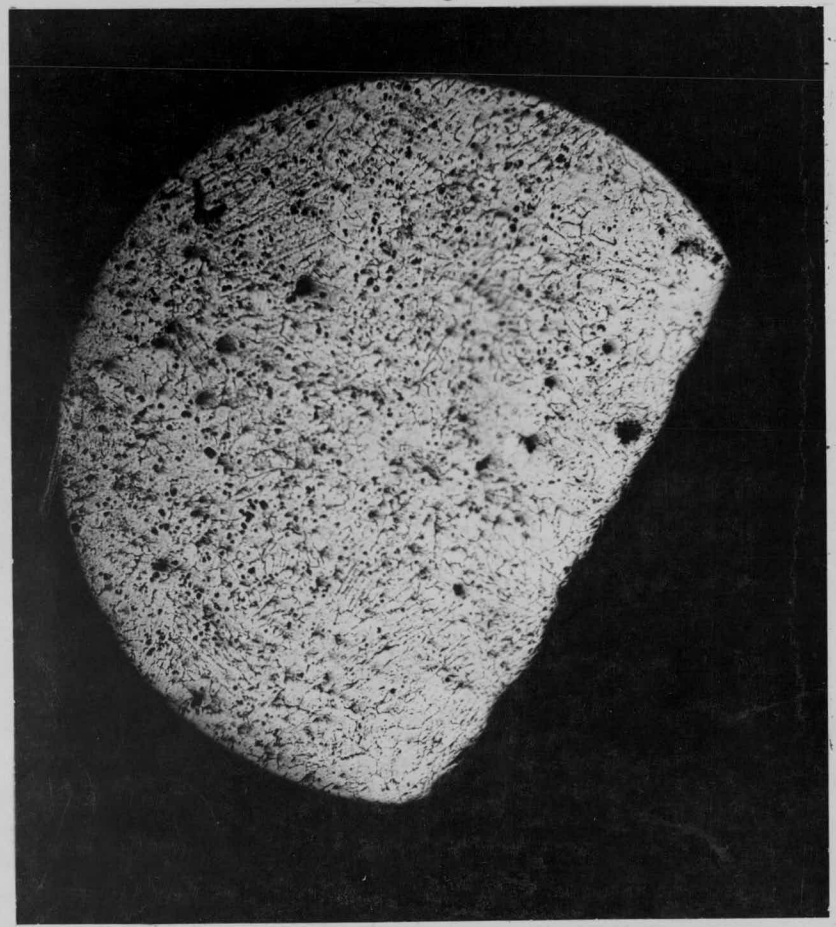
PHOTOGRAPH OF MOLYBDENUM CARBONYL PLATED SLUG
RUN #6

Sample # 6A Top of Slug
300 X Edge View



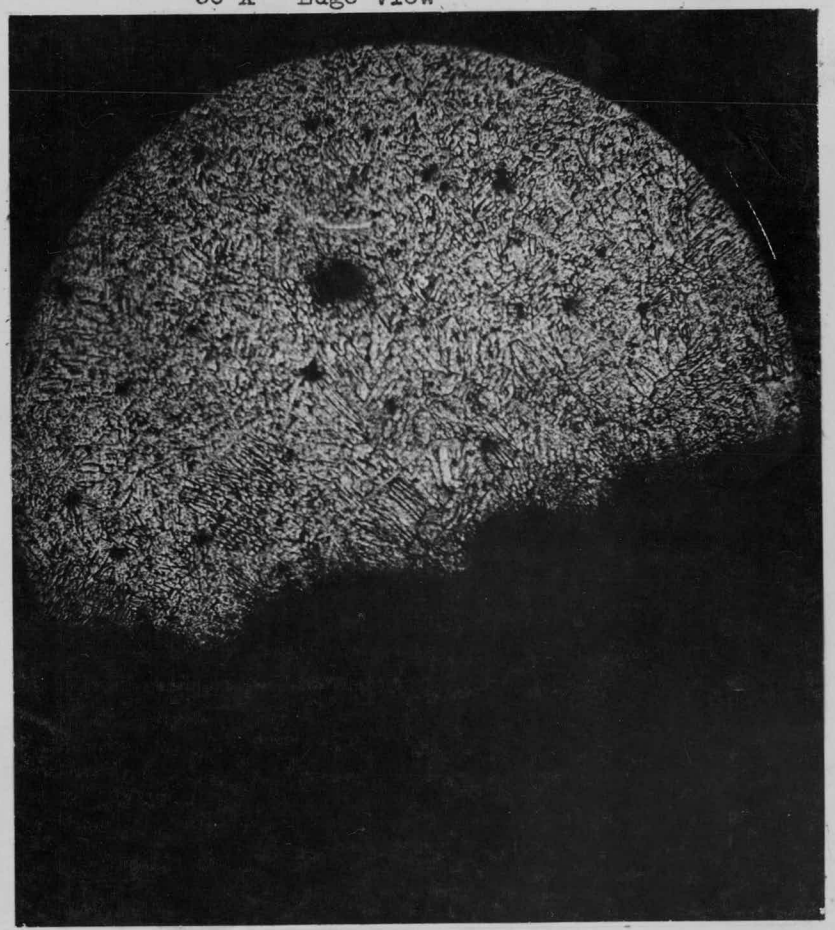
PHOTOMICROGRAPH OF MOLYBDENUM CARBONYL PLATED SLUG
RUN #6

Sample # 6A Top of Slug
50 X Another Edge View



PHOTOGRAPH OF MOLYBDENUM CARBONYL PLATED SLUG.
RUN #6

Sample # 6A Top of Slug
50 X Edge View



PHOTOGRAPH OF MOLYBDENUM CARBONYL PLATED SLUG.
RUN #6

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ISSUED TO: H. J. Wensel

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