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NICKEL ELECTROBONDED QUARTZ BLANKS

Joseph M. Stanley

August 1971

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By

Joseph M. Stanley
Electronic Components Laboratory

AUGUST 1971

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Abstract

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INTRODUCTION

Radio frequencies in communication equipment are maintained within tolerances by crystal controlled oscillators. Crystals used for these applications are suitably oriented and mounted in evacuated or gas filled and hermetically sealed crystal holders. To provide the mechanical strength and electrical conductivity needed, conventional resonators are usually bonded with conductive cement.

When this material is handled properly the bonds are adequate for most applications. However, when crystal units bonded in this manner are subjected to high acceleration forces they undergo large frequency changes. In addition cement bonded crystals do not have the uniformity or reliability needed for satisfactory performance in such environments. Because of this, cements were not considered as suitable materials for bonding 1000 g crystal units needed for Sensor application.

Preliminary information[1, 2] obtained from crystal units bonded with nickel deposited from sulfamate solutions showed that such crystals were more uniform, and underwent smaller frequency changes in high shock environments than cement bonded units. This information also showed that relatively high and repeatable bond strengths could be obtained from this electroplating process. This subsequently led to a decision to use this bonding material on high shock crystal units being developed for a Sensors project. Additional information had to be acquired, however, on bond strengths under various conditions to confirm the basic suitability of nickel films of this type for such applications.

The nickel sulfamate solutions used in this investigation were developed by the Barrett Chemical Products Company. Exceptionally low internal tensile stress nickel is electrodeposited from these solutions without the use of additional agents. The plating solution used in this process consists of a concentrated solution of pure nickel sulfamate buffered with boric acid. It has low sensitivity to impurities and permits the use of high current densities at lower operating temperatures.

Nickel Sulfamate Plating Solutions

Nickel films deposited from nickel sulfamate solutions are reported by the manufacturer to have the following average physical properties:

Hardness	150 - 300 VHN
Elongation in 2"	20 - 30%
Tensile strength	90,000 psi max.
Internal stress	500 psi tensile
Color of deposit	White
Appearance of deposit	Semi-Matte to lustrous

Type SN nickel sulfamate solution supplied by Barrett Chemical Products has the following composition:

Nickel sulfamate	60 oz/gal
Nickel metal content	10.2 oz/gal
Boric acid	4.0 oz/gal
Anti-pit agent	0.05 oz/gal

Type SNR solution is a concentrate which is supplied primarily for replenishment of nickel in Type SN solutions. The concentrate contains only nickel sulfamate and requires dilution and purification and additions of the chemicals used in the SN solutions before it can be used as a plating bath.

To obtain optimum results with nickel sulfamate solutions it is essential that pH be maintained within 3.5 to 5 and density within 29-31° Baume. Control of pH is accomplished by additions of sulfamate nickel acid (SNAC) compound when the hydrogen ion concentration is too low and nickel carbonate when it is too high. If the nickel concentration in the sulfamate solution decreases to the point where the specific gravity drops below the specified limits, additions of the basic SN nickel sulfamate or the concentrated SNR are made to bring the Ni concentration back again. The concentration of boric acid in the sulfamate solution should also be maintained. An analysis of the solution for boric acid should be made periodically by the mannitol method. SN solutions supplied by the manufacturer contain 4 oz. of boric acid per gal. At 110°F the boric acid concentration should not be less than 4.50 oz/gal and at 140°F it should not be less than 5.50 oz/gal. To reduce the number of periodic additions the manufacturer recommends that the boric acid concentration be maintained close to saturation by keeping a bag of granular boric acid suspended in the plating solution at all times.

Maximum current densities for plating in nickel sulfamate solutions can be increased by increasing the rate of agitation.[3] Recommended maximum is 300 amperes/sq ft at 140°F and 150 amperes/sq ft at 100°F. Agitation can be accomplished by continual movement of the cathode or solution.

Internal stress in nickel electroplated films may cause loss of corrosion protective properties as a result of cracking and enlargement of pores.[4,5,6] Stresses may also cause flaking of the deposit and consequent loss of fatigue strength and they may also induce premature fatigue failure of the underlying substrate.[7]

Internal stresses in electroplated nickel films vary with current density, increasing at an even rate as current increases.[4] Increased plating temperatures[8] in nickel sulfamate solutions on the other hand produce lower stress values in films deposited from such solutions.

Foreign cations and anions present in nickel sulfamate solutions have been shown[9,10] to be major factors in the creation of internal stresses in electroplated nickel films. Among the ions which cannot be tolerated even in very small amounts are trivalent or hexivalent chromium, tin, lead, phosphate, nitrate and certain forms of sulfur.

Experimental Procedure

In this investigation the bond between the quartz blank and stainless steel mounting clip is a nickel film deposited from a basic SN nickel sulfamate solution onto a copper spot on the crystal blank and the mounting clip in contact with the spot. The spots are located opposite each other on the edge of the blank on both surfaces. Bonding films can be as thin as 0.00025" without affecting their usefulness for high g applications. The clips are of the subminiature type made of #302 stainless steel, 0.066" x 0.030", and are designed for mounting blanks at either 120 or 180°.

Blanks used in this investigation were of the AT type, polished, 0.550" in diameter, and 0.011" thick. Spots with successive layers of chromium, chromium and copper and copper, 0.05 cm^2 in area, were deposited on the blank in a high vacuum vacion system. The thickness of each of the three layers of the spot was determined with a 5 MHz monitor crystal. In terms of frequency the thicknesses were as follows.

Chromium	800 Hz
Chromium & Copper	400 Hz
Copper	8800 Hz

The spotted blanks used for the bonding and pull test experiments are shown in Figure 1. To immerse them in the plating solution, stainless steel mounting clips were first welded to lengths of stainless steel ribbon. The clips were then pressed over the spots on the blank. A blank with the ribbon and clip attached in this manner is shown in Figure 2. The blanks are then immersed in the nickel sulfamate solution using the plating fixture shown in Figure 3 and electrobonded to the mounting clip. Initially the electrobonding experiments were made at room temperature at various current densities and later at elevated temperatures (40-50°C).

After being electrobonded the bonds were subjected to a pull test using the jig shown in Figure 4. Basically it consists of a small vise where the bonded spot on the resonator is held in line with an overhead pulley. The stainless steel ribbon attached to the mounting clip is welded into a loop for easy engagement to a hook fastened to one end of a piece of dial cord. The other end of the cord is fastened to a metal ring. The pull test is made by having the hook on a spring scale engage the ring and pulling in a horizontal plane over the pulley.

The pull strength referred to throughout the text is the pull strength of one set of mounting spots.

The procedure followed in bonding quartz blanks with nickel included cleaning of the blanks, mounting clips and attached ribbons, welding the ribbons to the clips, adjusting the clip spring to accomodate the 11 mil thick quartz blank, application of a nickel flash film to the clip to provide necessary adhesion for the subsequent thicker nickel film, inserting and adjusting the blank in the clip, mounting the clip, ribbon and blank in the plating jig and adjusting current density and immersion depth of the blank and mounting clip. In general the immersion depth was restricted

to just cover the spot and mounting clip. Blank washing was accomplished with detergent, followed by a rinse in distilled water and another in methyl alcohol. The ribbon, although welded to the clip was not immersed in the nickel sulfamate solution. A six volt DC battery provided the energy needed for the plating experiments. Plating currents were set and maintained with a variable resistor. Pure nickel sheet was used for the anode material. It is important to note that the above steps are taken with an absolute minimum of storage time between steps.

Examination of Nickel Electrobonds

Some of the electrobonded units were examined microscopically after being sectioned and polished. Microphotographs (86X) were then taken of the section. A photograph of an early unit is shown in Figure 5. It can be seen from this photograph that the electroplated nickel does not adhere too well to the stainless steel mounting clip. The adherence between the copper spot and electroplated nickel, however, is quite good. To overcome the deficiency in adhesion of the nickel electrobond to the stainless steel clip, the clips were given a flash (10 second) nickel plating in a solution of nickelous chloride and hydrochloric acid prior to being electrobonded. The voltage used for the flash nickel electroplating was on the order of 6 volts DC and pure nickel sheet was used for the anode material. Flash plating of the mounting clips was carried out at room temperature in a solution of the following composition:

Nickelous Chloride ($NiCl_2 \cdot 6H_2O$)	32 oz
Hydrochloric Acid (HCl-conc)	500 cc
Water to make	1 gal

Quartz blanks mounted in flash plated clips were electrobonded with nickel at a current density of 72 ma/sq. in. and then were mounted in plastic, sectioned, polished and microphotographed again. The distinct improvement in the adhesion between the stainless steel mounting clip and the electrobonded nickel can be seen in Figure 6. There is still a faint line of demarcation, however, between the stainless steel clip and the nickel electroplating.

Comparison of the pull strengths of nickel electrobonds with and without flash plated clips is made in Table I.

Table I. Pull Strength of Flashed and Unflashed Nickel Electrobonds

Resonator Clips	Current Density (ma/sq. in.)	Time (mins)	Pull Strength (oz)
With flash plating	72	45	20
Without flash plating	72	45	15

It is apparent from Table I that the pull strength is appreciably increased, 33%, by flash plating the mounting clips with nickel prior to electrobonding with nickel.

The bond between the electroplated nickel and the copper layer on the spot and the electroplated nickel and stainless mounting clip was examined by electron microbeam probe techniques to determine the physicochemical nature of the metal plating and the metal-quartz interface. Figure 7 is a photograph of an electron micro probe scanning image of a nickel electro-bonded cross section similar to those shown in Figures 5 and 6. This image was obtained by scanning the electron beam in a line across the sample. The image generated was then used to modulate the y-deflection of the CRT beam. Element distribution along a line in the sample was then mapped, wherein Y-deflection on the resultant line profile is proportional to element concentration. The electron microprobe examination of the bonded areas showed that Cu and Cr are distributed on the quartz side of the stainless steel clip-quartz join; further, the probe indicates the presence of two distinct nickel plating layers between the clip-quartz interface, one coinciding with the Cu-Cr plating layers in the spot and on the clip side of the interface. Doubling of the nickel plate is due to simultaneous deposition on both clip and the metallized quartz surfaces. There is no evidence from the probe studies to indicate any chemical reaction or diffusion of metal associated with the bonds in question. The magnification in Figure 7 is 18 μ/cm.

Since one of the primary objectives of the investigation was to bond quartz 20 MHz resonators without inducing strains in the quartz, examination was made of the cross section of a nickel bonded quartz test blank in a stainless steel mounting clip. In this case the blank was not pressed against the back of the clip. As described previously the mounted resonator was imbedded in plastic; ground, polished and then microphotographed (80X) through crossed polaroid lenses. As can be seen in Figure 8, there is no indication of strains in the quartz in the area constrained by the clip. The electrobond in this case was made by plating at a current density of 288 ma/sq. in. for 15 mins in a commercial nickel sulfamate type SN solution. Prior to mounting the resonators, the clips were flashed for 10 seconds in a nickelous chloride hydrochloric acid solution using 6 volts DC. However, with another blank mounted similarly but pressed against the back of the clip and electrobonded with nickel, appreciable strain was induced in the quartz. This is shown in Figure 9. The strain extends from the edge of the quartz pressed against the mounting clip to the point where the mounting clip begins to constrain the quartz. The pressure in question here is that resulting from the usual manipulation involved in inserting blanks in the clips. The above results demonstrate that care should be exercised during this operation to make sure the edge of the crystal blank does not touch the back of the clip.

Previous studies[11] have shown that the causes of internal stresses in electroplated nickel films are many; the main ones, however, are as follows:

1. Changes in parameters of the lattice
2. Changes in the distance between deposit electrolytes
3. Grain coarsening of the deposit
4. Formation of chemical compounds with impurities present in the electrolyte.

The difference in the grain size of nickel films plated in nickel sulfamate solutions at 2 current densities, 72 and 144 ma/sq. in., can be seen in Figures 10 and 11. The larger grain size in the film deposited at 144 ma, Figure 11, does not affect pull strength if the plating thickness is the same as that deposited at 72 ma.

The magnification in Figures 10 and 11 is 156X.

Other studies[6] of the thickness of nickel films deposited from nickel sulfamate solutions showed that the internal tensile stress is quite high initially with films on the order of 0.2-0.5 mils and that an equilibrium value is reached thereafter. The high initial internal stresses are considered to be due to the substrate material; that is, the initial deposit attempts to duplicate the structure of the substrates.

Bond Strengths of Nickel Films

A series of electrobonding experiments were made under the following conditions:

Solution	Type SN nickel sulfamate solution
Quartz Blanks	0.550"D & 0.011" thick
Spot Composition	Chromium, chromium + copper, and copper
Spot Area	0.05 cm^2
Mount	Stainless steel clips and stainless ribbon
Plating Temp	48° C
Plating Current	1, 2, 3 and 4 ma/pair of spots
Plating Voltage	6 VDC
Anode	Pure nickel sheet

Prior to inserting the quartz blanks in the mounting clips and electrobonding, the clips were flash plated with nickel as described previously, with a minimum time lapse allowed between the two operations.

The pull strengths of nickel electrobonded quartz resonators obtained from the series of experiments made at constant current are summarized in the graph of Figure 12. The pull strength increases linearly with plating time as the latter is increased, at constant current, from 15 to 75 minutes. At 1 ma (36 ma/sq in) the pull strength increases from 6.5 oz after 15 minutes of plating period to 30 oz for a 75 minute period. At 3 ma (108 ma/sq in) the pull strength increases from 13 oz for a 15 minute period to 44 oz for a 75 minute period. Test blanks bonded at 4 ma (144 ma/sq in) had average pull strengths of 15 oz after being plated for 15 minutes at this current and

after being plated for 75 minutes the pull strength increased to 50 oz. It is not known at this time how far the pull strength would continue to increase as the current is increased incrementally for the same time periods. Also as the plating increases in thickness internal stresses in the film itself should drop off markedly. The highest stresses should occur in thin nickel films electroplated at a fairly rapid rate. None of the nickel electrobonded films studied however, appeared to induce strains in the bonded area of the quartz blank. This is considered to be due in part to the fact that nickel electrobonding was performed in almost all cases at elevated temperatures (40-50°C).

Bond failure in the pull strength tests resulted in most cases from failure of the chromium-quartz bond. In the case of extremely thin bonded nickel films, 72 ma/sq in/10 mins, the bonded film generally pulled off in the area of the clip. With thicker films the bonded film and spot generally pulled off in part or completely. A typical example of this type of failure is shown in Figure 13. The spring clip and resonator which was formerly mounted in it were electrobonded with nickel at a current of 72 ma/sq in for 20 mins. As can be seen, part of the spot and the nickel electrobond lifted in the area where the spring clip had been bonded to the spot.

Another group of spotted blanks were electrobonded with nickel at current densities ranging from 72 to 324 ma/sq in. The plating time at each current level was restricted to 15 minutes. Pull tests were then made on all the bonded units. Average results of these tests are summarized in the graph of Figure 14. The pull strength at each current level increased linearly from 6 oz at 36 ma/sq in to 30 oz at 324 ma/sq in. Failures in all cases stemmed from the pulling away of the chromium bottom layer of the spot from the quartz blank. The exact mechanism responsible for this kind of failure is not known at this time.

Quartz blanks were also nickel electrobonded at these current densities with the plating time varied so that the product of current density and plating time was a constant; 2.2 ampere mins in one case and 3.1 in the other. Average pull strengths obtained under these conditions are summarized in Tables II and III. In Table II where the product is 2.2 amp mins, pull strengths vary from 13.0 to 15.0 oz and in Table III from 17 to 21.0 oz. It would appear that the pull strengths listed in each table should have constant values; minor changes in resonator processing, electrobonding and pull testing are believed responsible for the variations encountered.

Pull strengths of nickel electrobonded quartz resonators are compared to the thickness of such films in the graph of Figure 15. Here again pull strength increases linearly from 9 oz at a plating thickness of 0.25 mils to 53 oz at 2.25 mils.

Figure 16 compares pull strength with current density at 4 different time periods. Pull strength in this case also increases linearly as current increases. For a 15 minute plating time the pull strength increases from 6 oz at 36 ma/sq in to 15 oz at 144 ma/sq in. When plated for 30 mins the pull strength increases from 9 oz at 36 ma to 25.5 oz at 144 ma. Similarly when plated for 45 mins pull strength increases linearly from 11 oz at 36 ma/sq in to 38 oz at 144 ma/sq in. After being plated for 75 minutes pull strength increases from 17 oz at 36 ma/sq in to 54 oz at 144 ma/sq in.

Since electrobonded crystal units for Sensor application are vacuum baked prior to being coldweld sealed it was considered advisable to determine the effect of such treatment on the pull strength of electrobonded blanks. To obtain this information a group of six 0.011" polished and spotted blanks were mounted in stainless steel clips and electrobonded in a nickel sulfamate solution. The blanks were then baked for two hours at a temperature and pressure of 250°C and 10^{-8} Torr, respectively. A control group of six units was processed at the same time without any vacuum bakeout. The twelve units were then subjected to a pull test using the jig shown in Figure 4. Table IV compares the average pull strength of the vacuum baked and unbaked electrobonded blanks.

Table IV. Pull Strength of Vacuum Baked and Unbaked Electrobonded Blanks

	Current Density (ma/sq. in.)	Time (mins.)	Pull Strength (oz.)
Vacuum Baked (2 hrs. at 250°C)	72	45	21
Unbaked	72	45	20

The pull strengths shown in Table IV demonstrate that vacuum baking has little effect on this property.

CONCLUSIONS

Investigation of the bonding capabilities of nickel films deposited from nickel sulfamate solutions have shown that such films produce strong, reliable and apparently strain free bonds between copper spots on quartz resonators and stainless steel mounting clips.

Nickel sulfamate solutions provided by the manufacturer for nickel electrobonding can be used for extended periods of time provided the pH, density and boric acid concentrations are checked periodically and reasonable care is taken to keep the solution as pure as possible.

The bond strength between stainless steel quartz resonator mounting clips and evaporated copper spots on quartz blanks is increased by flash plating mounting clips with nickel prior to mounting and electroplating in nickel sulfamate solutions.

Electrobonding with nickel at elevated temperatures permits use of higher current densities and induces less internal stresses in the metal film.

Examination of nickel electroplated bonds by electron microprobe techniques has indicated a bond composed mainly of adhesive forces.

Grain size in nickel electroplated films is a function of current density and does not appear to materially affect bond strength. The thickness of the bonded film is the controlling factor in determining the numerical value of this property.

The bond strength between nickel electroplated films deposited on quartz resonator mounting clips and copper spots on the blanks increases linearly with current density, plating time and plating thickness. Maintaining the product of current density and plating time at a constant number gives a constant pull strength and thickness.

Quartz blanks and mounting clips electrobonded in nickel sulfamate solutions at current densities ranging from 72 to 144 ma/sq in. for 15 minutes have sufficient bond strengths (9, 13 & 15 oz) for 1000 g shock applications.

The procedure to be followed for bonding crystals of this type is outlined in the Appendix.

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APPENDIX

ELECTROPLATING SPECIFICATIONS

The following procedure should be followed when bonding quartz blanks to stainless steel mounting clips with films deposited from nickel sulfamate solutions.

Plating solution	- Type - SN nickel sulfamate pH range - 3.5 - 5.0 electrometric Density (degrees Be) - 29 - 31°
Solution composition	- Nickel sulfamate - 60 oz/gal Nickel metal content - 10.2 oz/gal Anti-pit agent (SNAP) - 0.05 oz/gal Boric acid conc. - 4 oz/gal Max Plating temp - 140°F
Mounting Clips	- Metal, stainless steel Cleaning procedure - tri chlor ethylene, detergent, distilled water and methyl alcohol
Nickel flash plating	- Solution Nickelous chloride (N_iCl_2 - $6H_2O$) - 32 oz Hydrochloric Acid (HCL - Conc.) - 500 cc Water to make - 1 gal Time - 10-60 sec. Voltage - 6 VDC
Tank Voltage	- 6 - 9 VDC
Current Density	- at 140°F - 0.32 amp/cm^2 - at 100°F - 0.16 amp/cm^2

Impurities to exclude from plating bath, plating fixtures, evaporated spots and mounting clips - Cr^{+3}, Cr^{+6}. Sn, Pb, PO_4^{-3}, NO_3^{-1}, and S.

Plating jig can be of any design to hold firmly and immerse spotted quartz resonators in plating bath just enough to cover mounting clip and spot. Evaporated spots - 0.05 cm^2 in area on opposite edges of both surfaces. Spots are composed of a chromium layer, chromium and copper layer and a copper layer on top. Thicknesses of the three layers in terms of frequency determined by a 5 MHz monitor crystal are as follows:

Chromium	800 Hz
Chromium & Copper	400 Hz
Copper	8800 Hz
Mimimum Plating Current	1 mA
Minimum Plating Time	15 mins
Minimum Plating Thickness	0.25 mils

Anode - Rolled and depolarized nickel or pure nickel sheet material formed and welded for inclusion in plating bath.

After removal from plating bath the bonded resonators are rinsed in distilled water, washed with detergent, rinsed in distilled water then with methyl alcohol, and made ready for electrode plating.

Infrequently during the bonding operation a black or green deposit will form on the spots and clips. This is usually caused by one of the following:

a. Low boric acid content
b. Insufficient agitation
c. Low temperature
d. Low nickel content
e. Current too high

Pitting in nickel films can be remedied by the following:

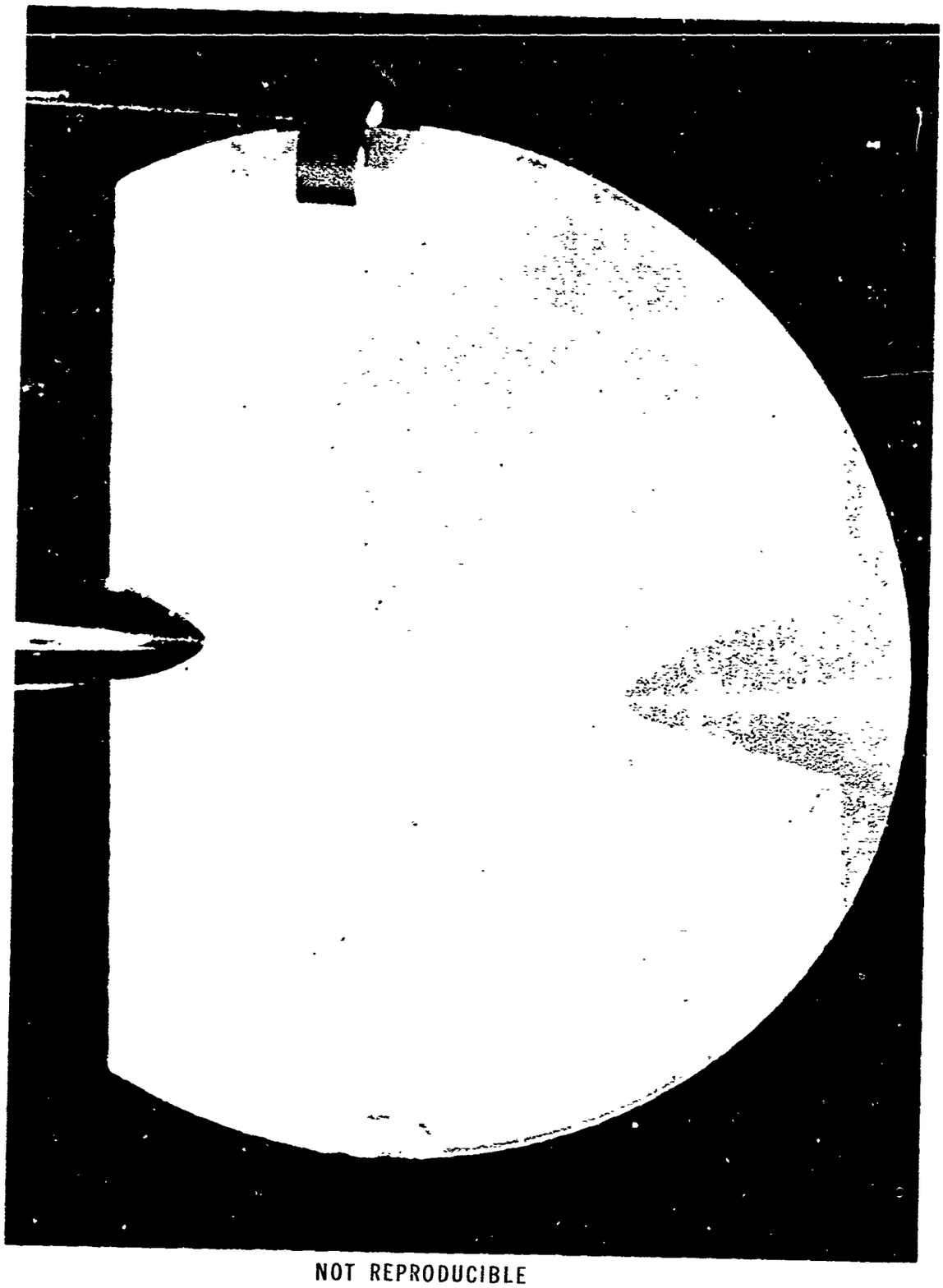
a. Adding boric acid to the plating bath
b. Increasing SNAP content
c. Using a dummy plate to remove iron contamination
d. Reducing pH with SNAC

Roughness in nickel films can be controlled to a certain extent by filtering the plating solution or by lowering the pH.

Electrobonding should be done shortly after the nickel is deposited on the mounting clip.

NOT REPRODUCIBLE

Fig. 1. Spotted Quartz Blank



NOT REPRODUCIBLE

Fig. 2. Spotted Quartz Blank with Mounting Clip

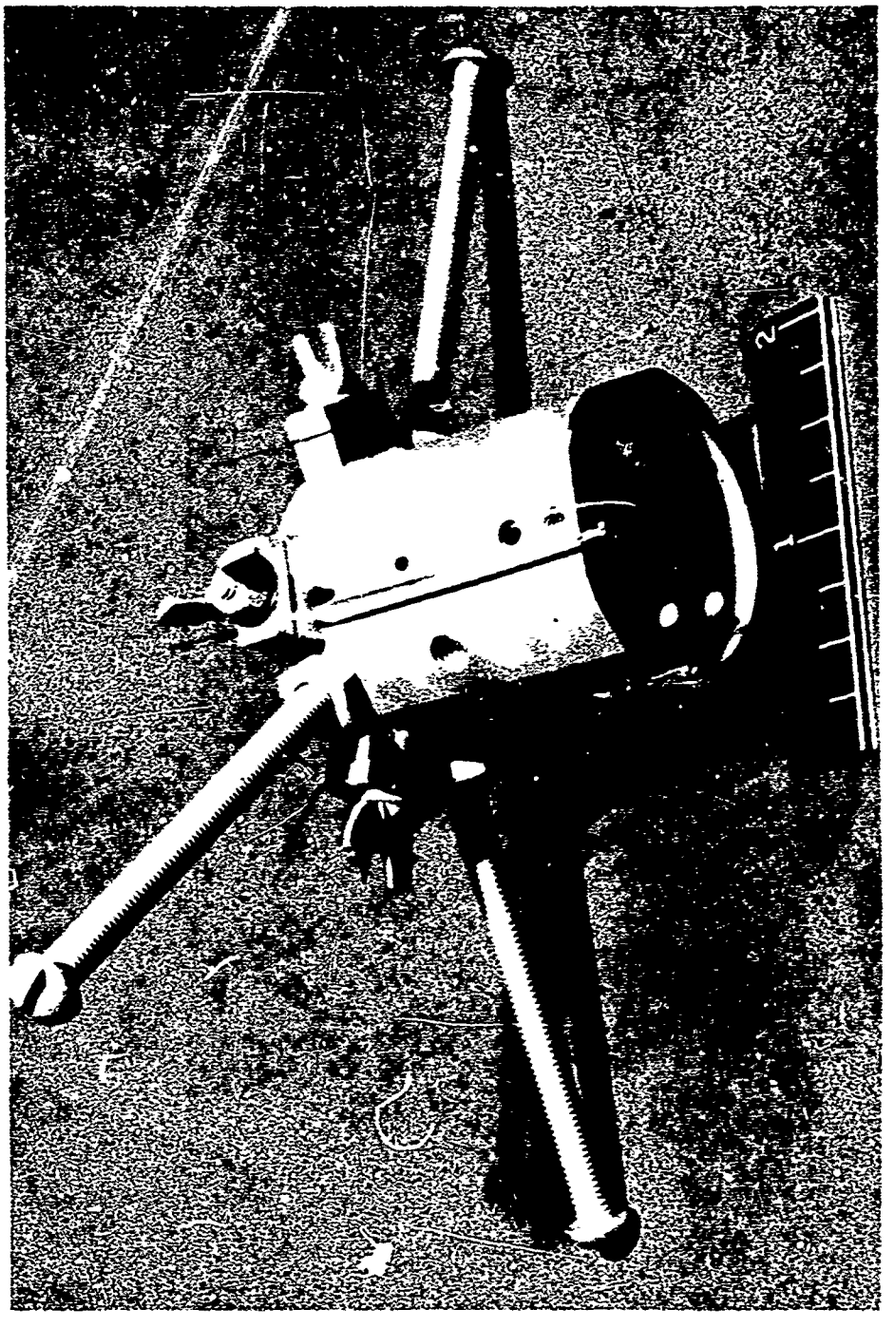


Fig. 3. Electrobonding Jig

NOT REPRODUCIBLE

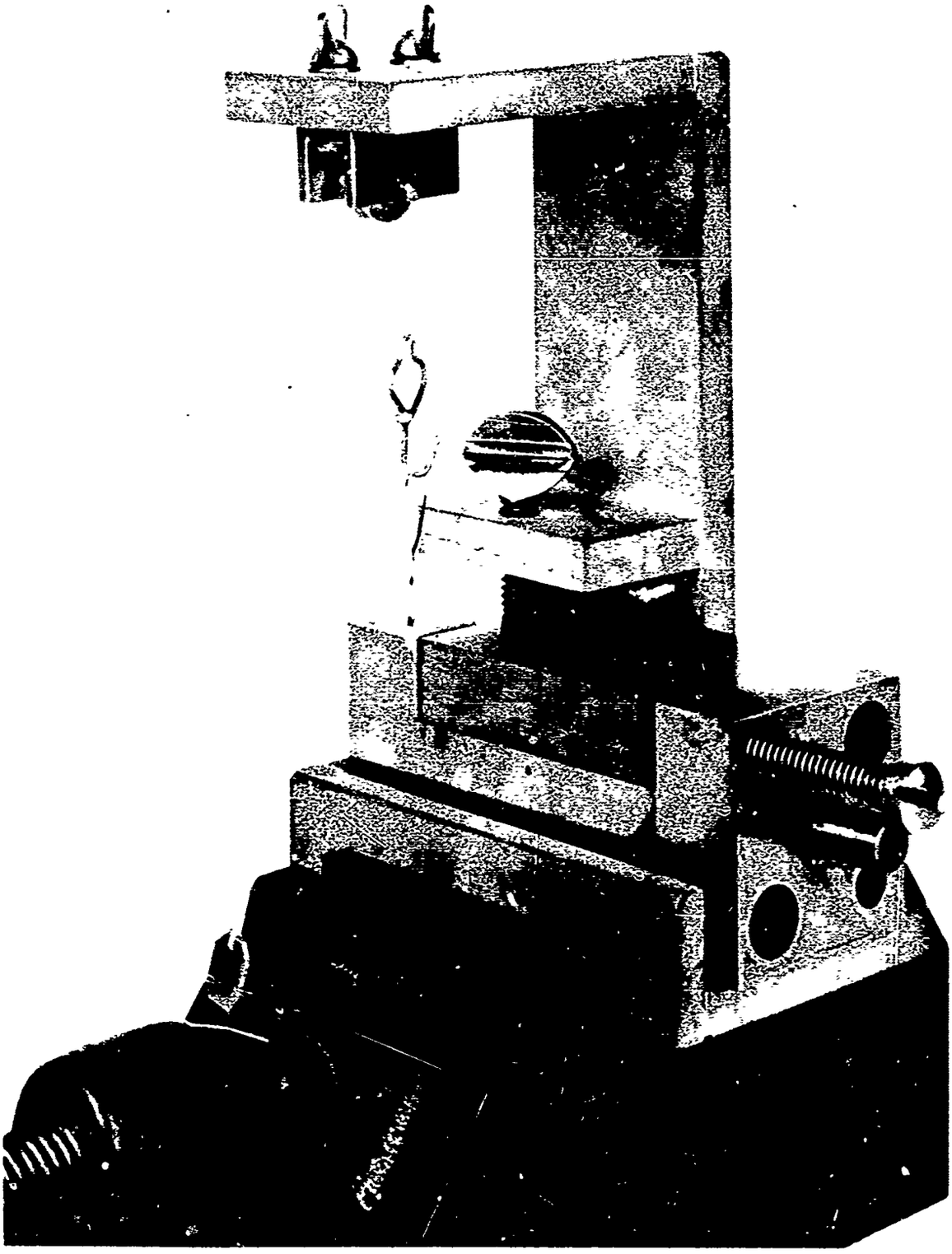


Fig. 4. Pull Test Jig

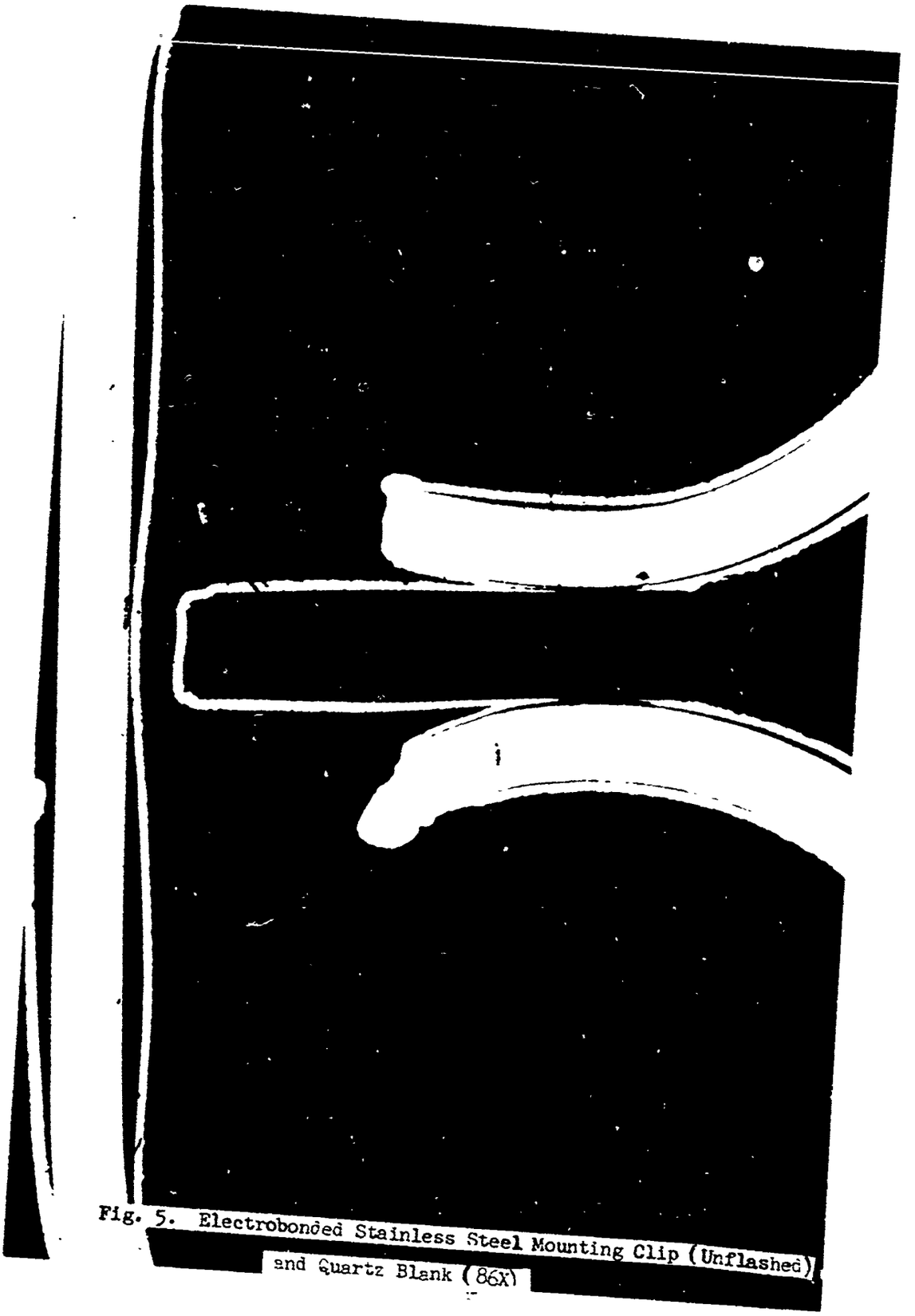


Fig. 5. Electrobonded Stainless Steel Mounting Clip (Unflashed) and Quartz Blank (86X)

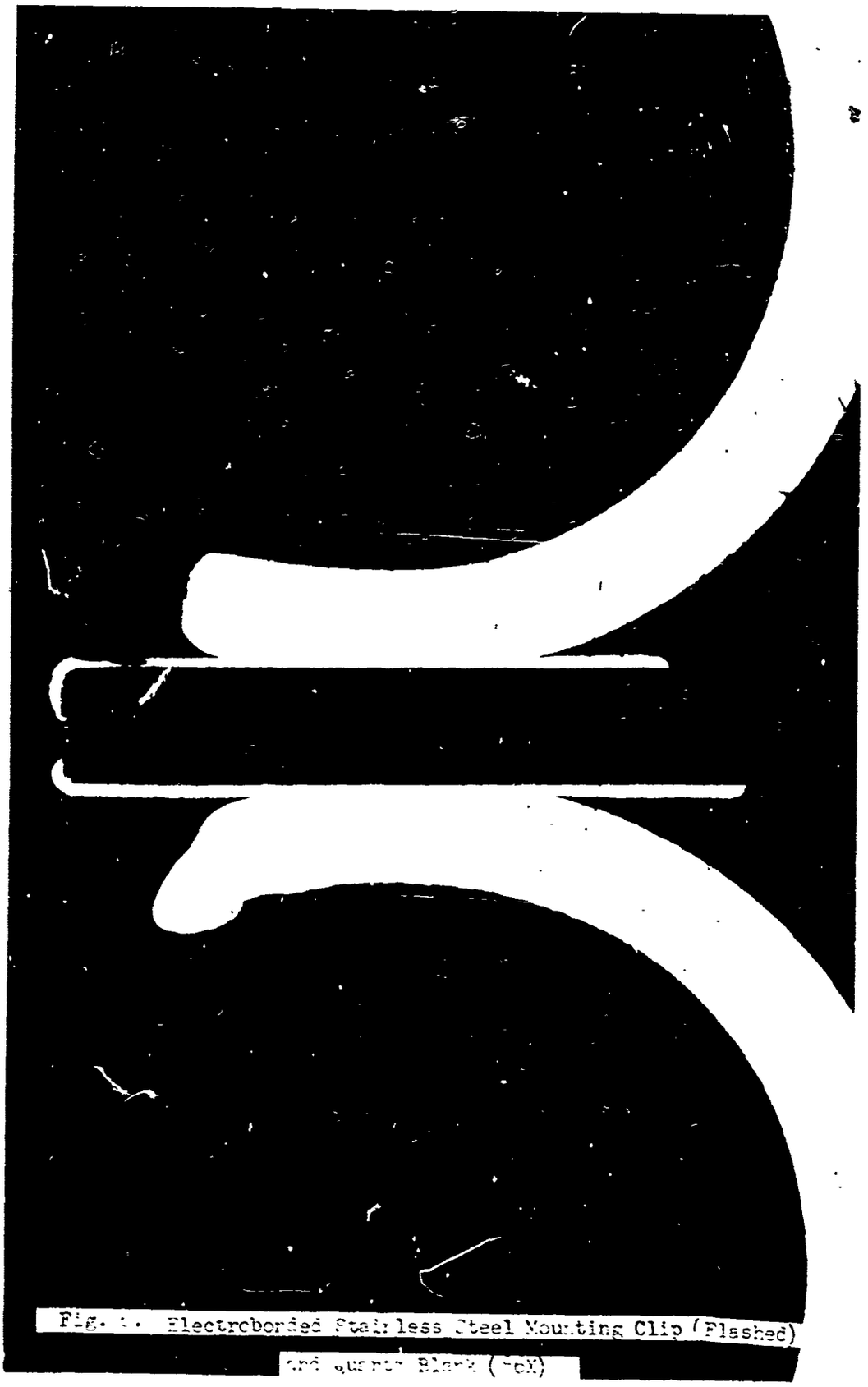


Fig. 1. Electroborided Stainless Steel Mounting Clip (Flashed) and Quartz Blank (TOP)

NOT REPRODUCIBLE

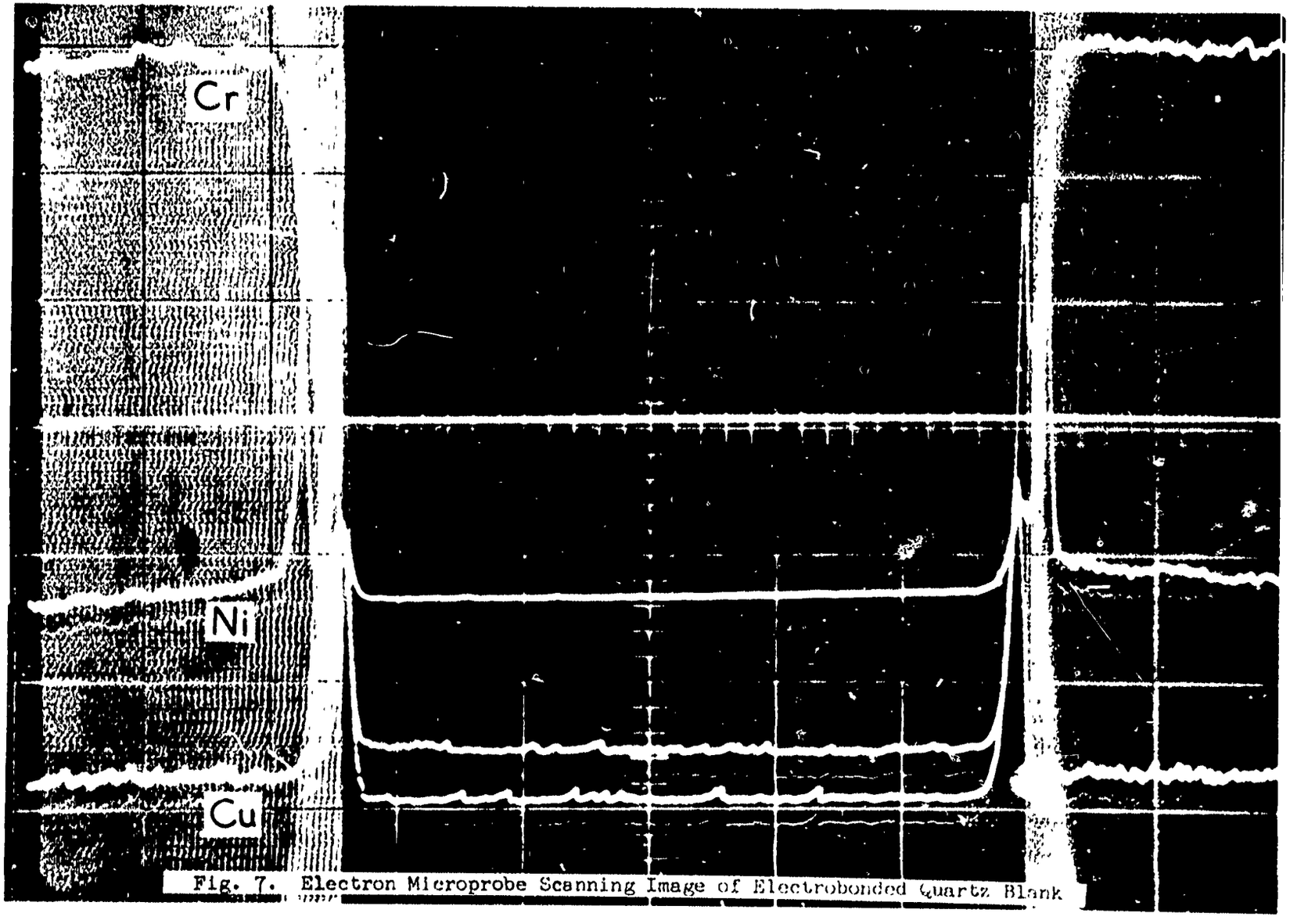
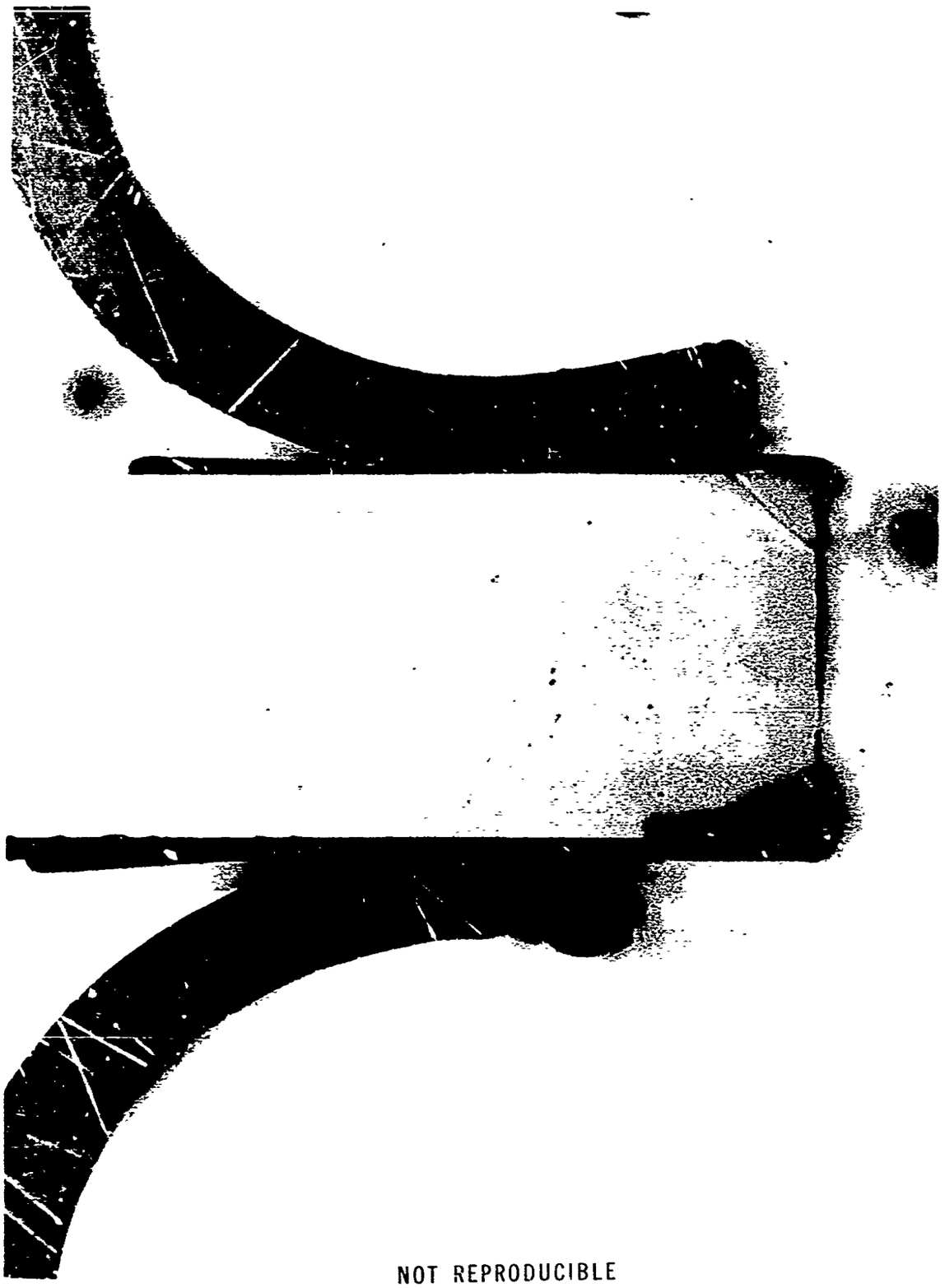


Fig. 7. Electron Microprobe Scanning Image of Electrobonded Quartz Blank

NOT REPRODUCIBLE



NOT REPRODUCIBLE

Fig. 8. Strain Free Electrobonded Quartz Blank

NOT REPRODUCIBLE

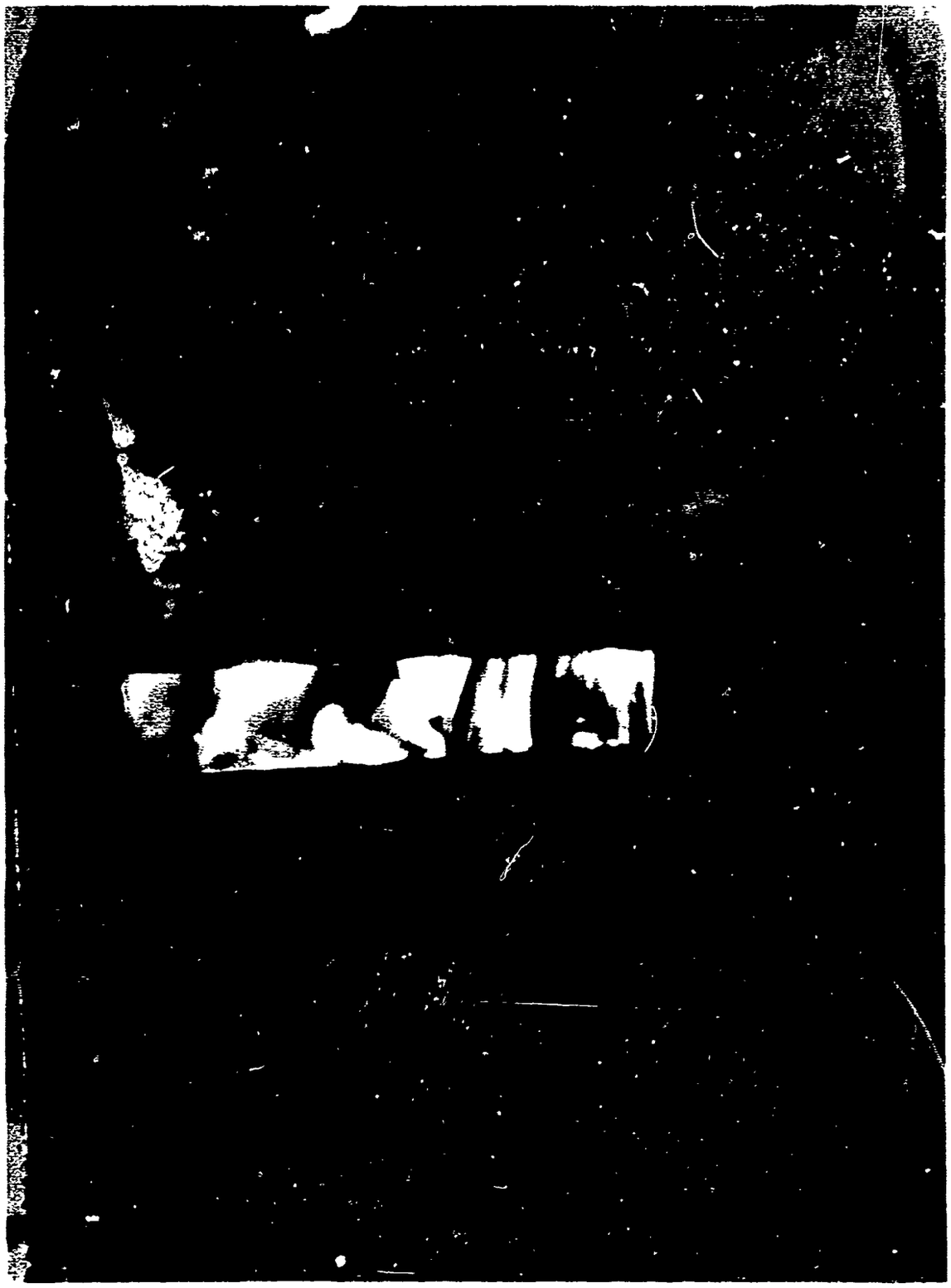


Fig. 9. Strained Electrobonded Quartz Blank

NOT REPRODUCIBLE

Fig. 10. Grain Size (156X) of Nickel Film Plated at 72 ma/sq in

NOT REPRODUCIBLE

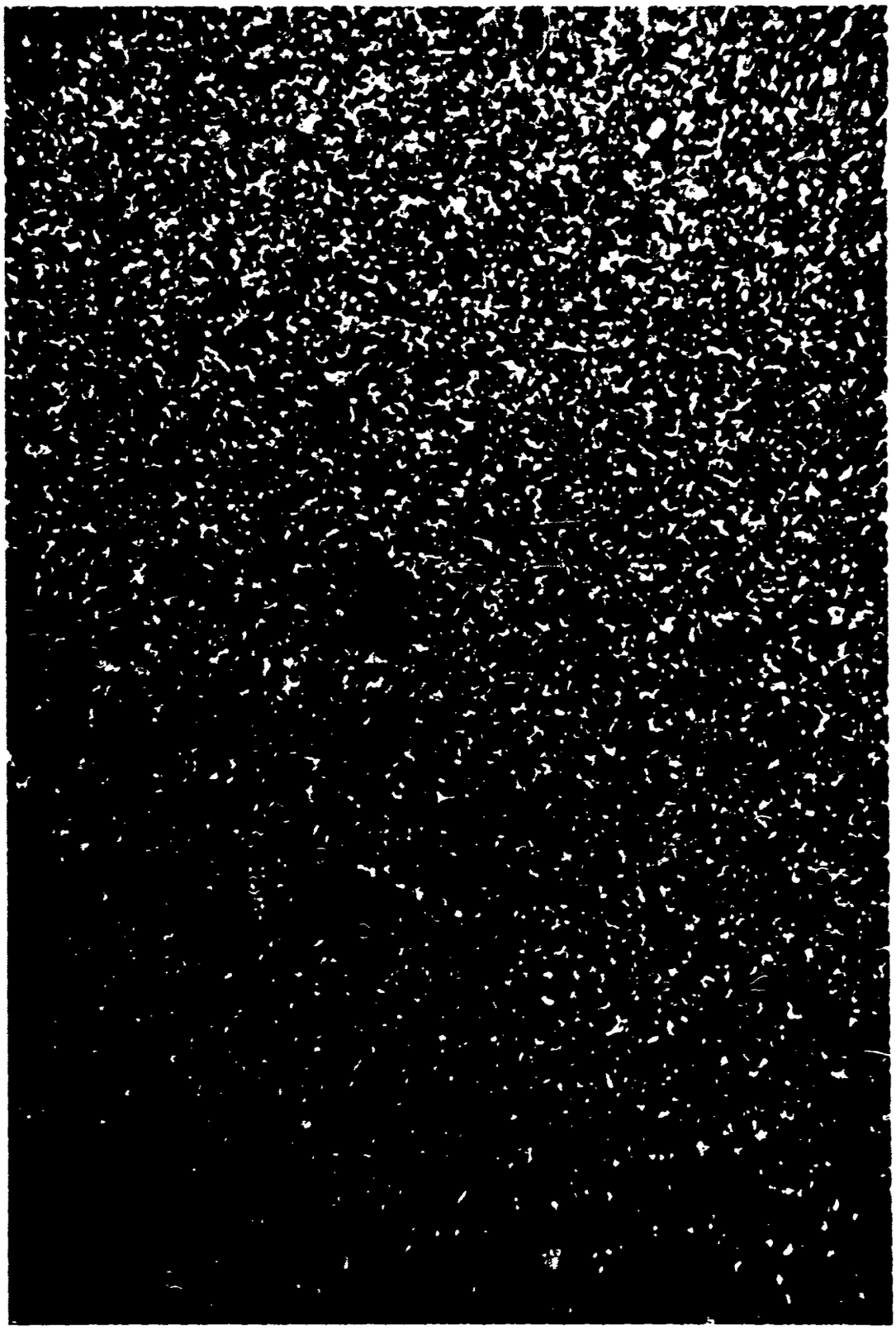


Fig. 11. Grain Size (156X) of Nickel Film Plated at 144 ma/sq in

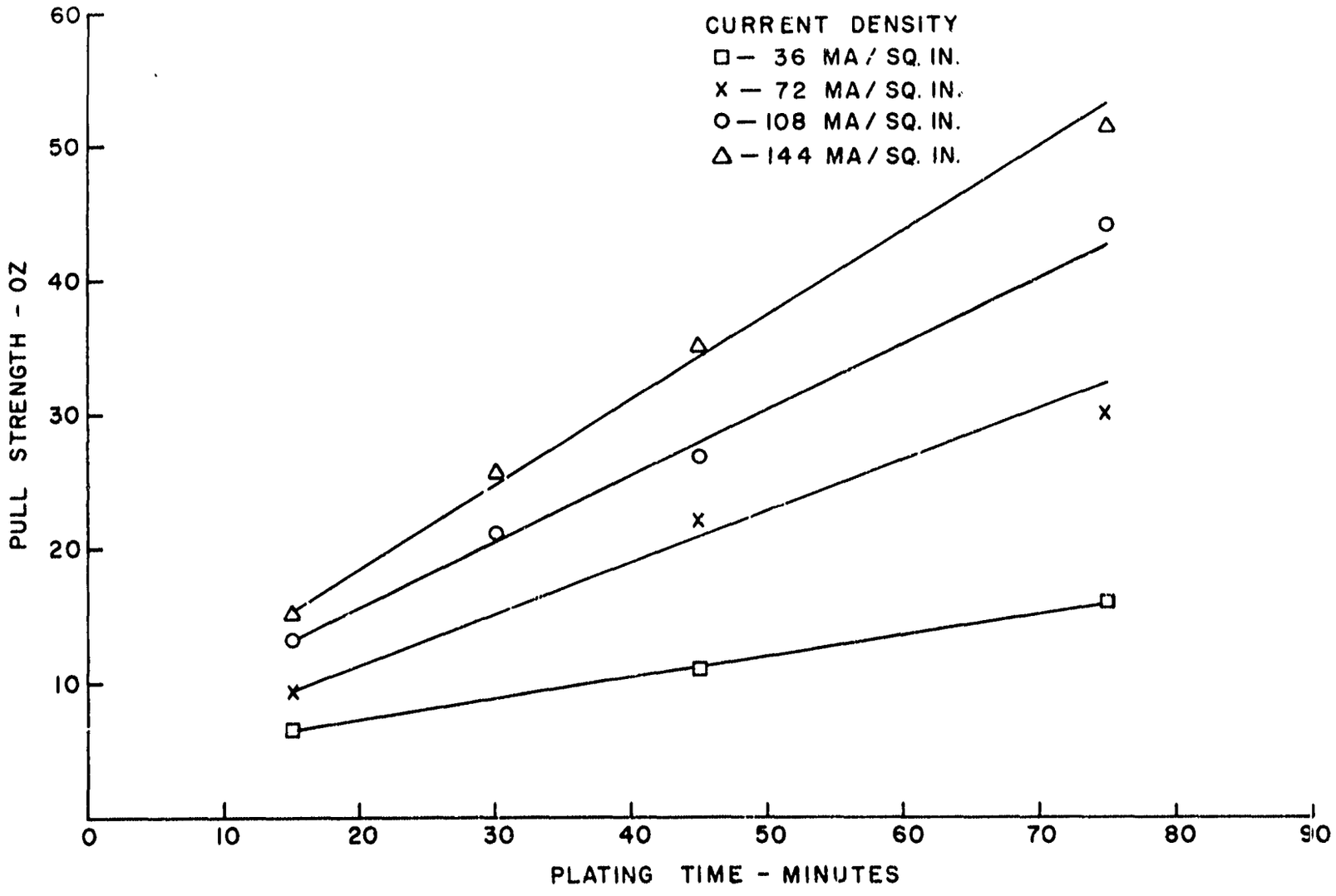
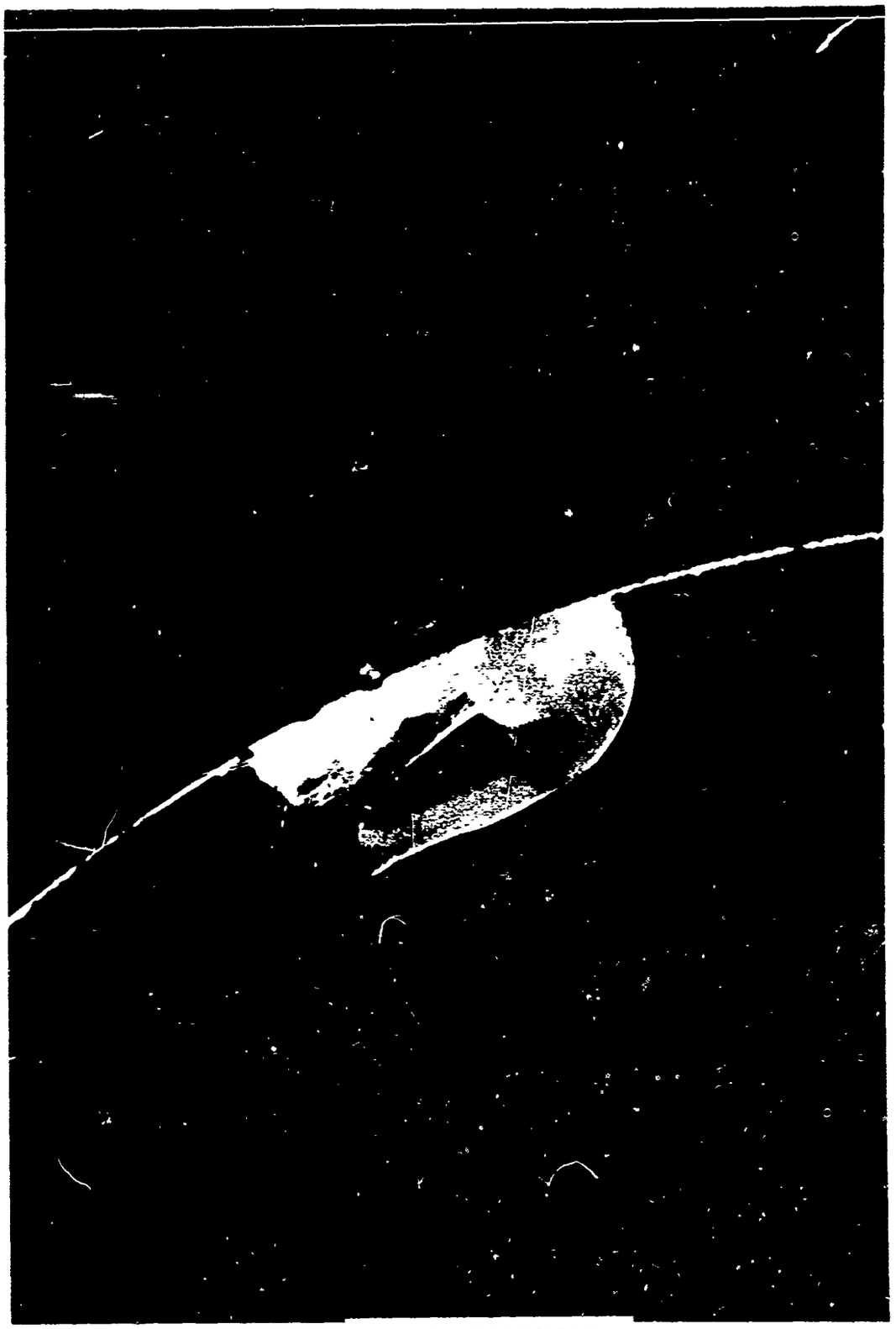


Fig. 12. Pull Strength vs. Plating Time



NOT REPRODUCIBLE

Fig. 13. Typical Electrobond Pull Strength Failure

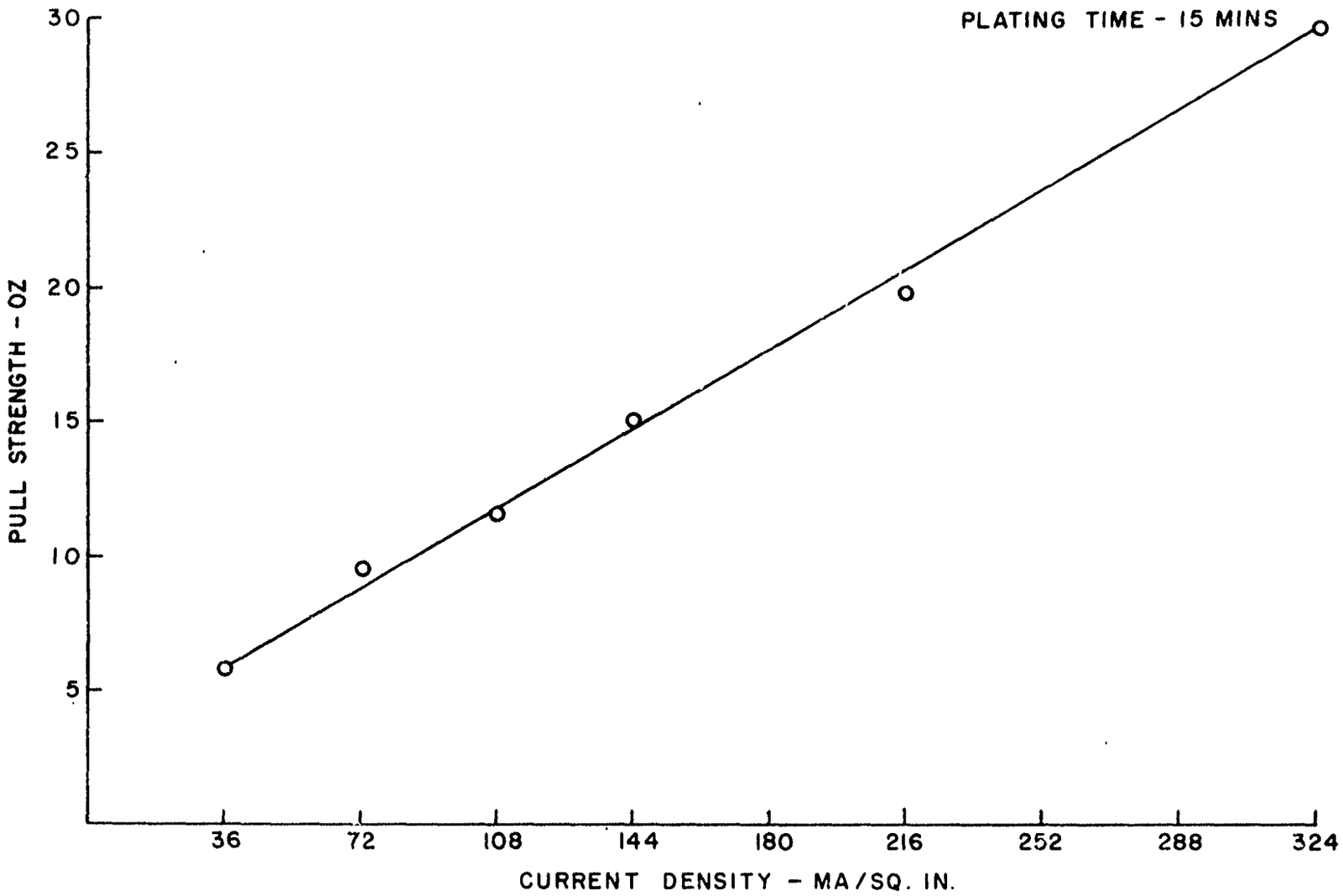


Fig. 14. Pull Strength vs. Current Density (15 Minute Plating Period)

Table II. Pull Strength vs. Ampere Mins (2.2)

TABLE II

CURRENT DENSITY	PLATING TIME	PULL STRENGTH
MA/SQ. IN.	MINS.	OZ.
72	30	15.0
108	20	13.5
144	15	15.0
180	12	13.0
216	10	13.5
288	7.5	14.5
360	6	13.5

Table III. Pull Strength vs. Ampere Mins (3.1)

TABLE III

CURRENT DENSITY	PLATING TIME	PULL STRENGTH
MA/SQ. IN.	MINS.	OZ.
72	45.0	21.0
108	30.0	21.0
144	22.5	20.0
180	18.0	17.0
216	15.0	19.5

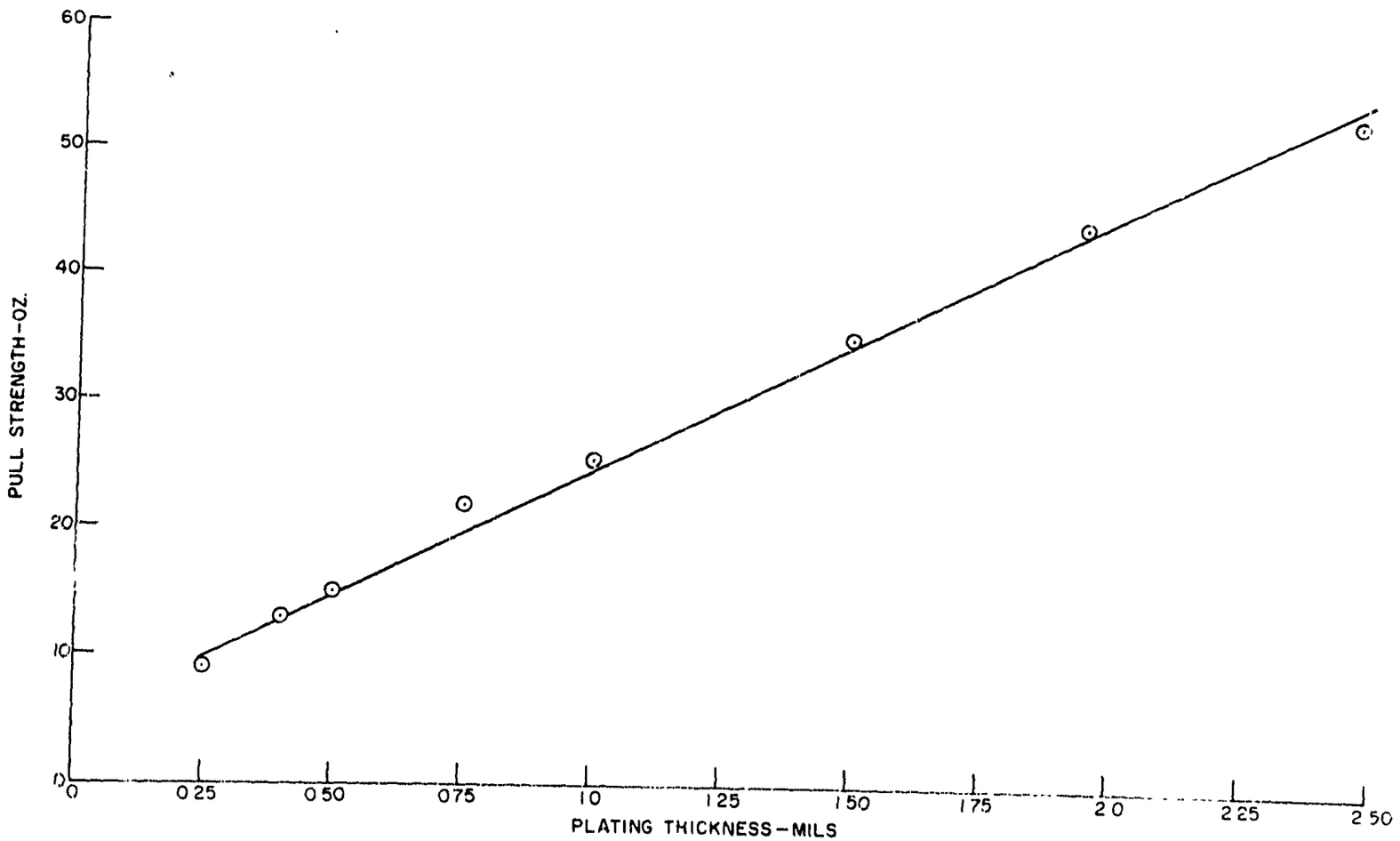


Fig. 15. Pull Strength vs. Plating Thickness

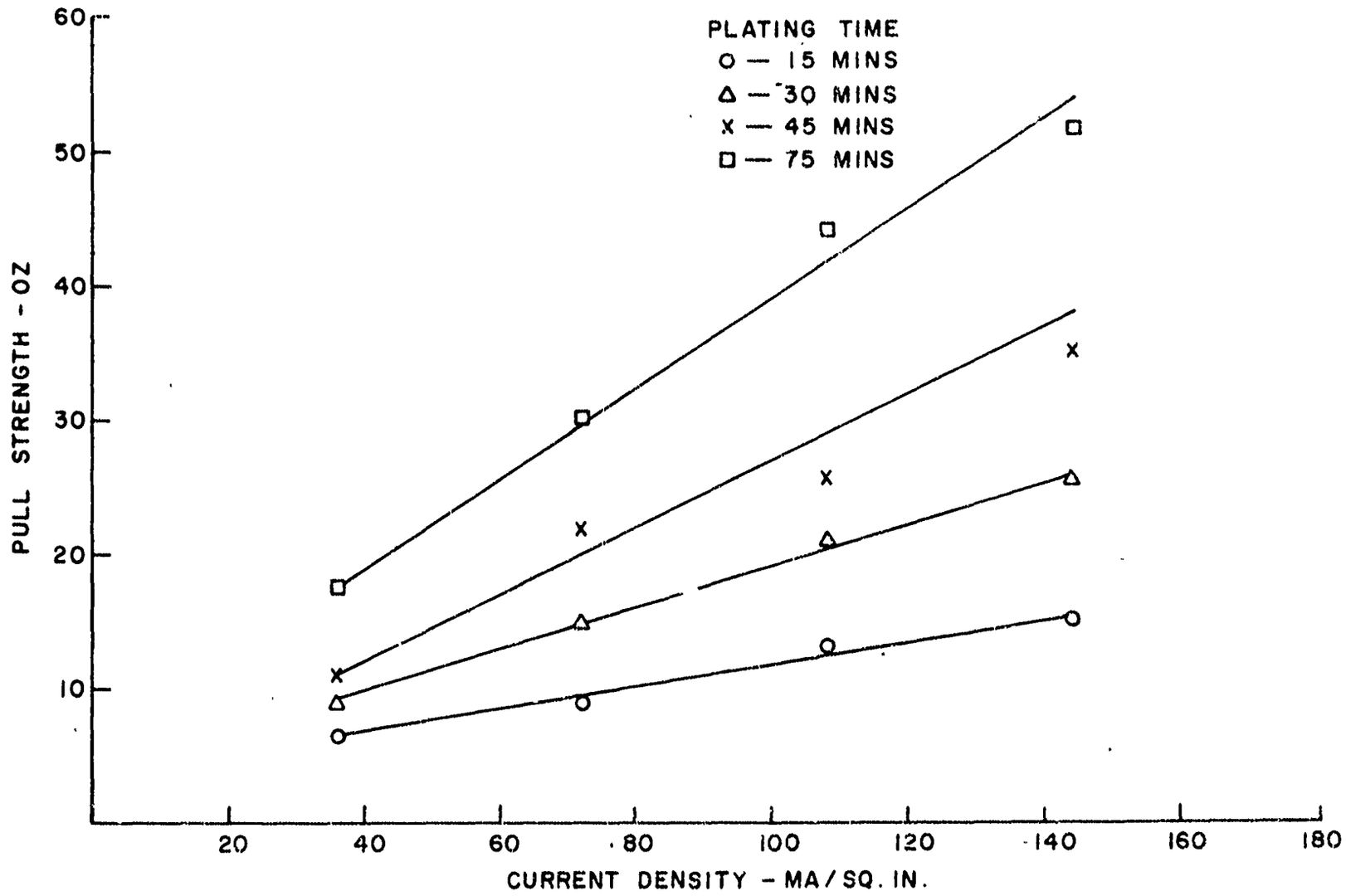


Fig. 16. Pull Strength vs. Current Density (15, 30, 45 and 75 Minute Plating Periods)