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ANALYSIS OF THE THERMOCOMPRESSION BONDING OF GOLD WIRE TO NICKEL

by
Clifford Wayne Hunter

A Thesis

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

Lehigh University

1964

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

23 Sept. 1964
(date)

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ABSTRACT

There is a definite need for information regarding the solid state bonding of many metals because of the increasing importance of solid state joining processes in industry. In an effort to obtain information on two important metals, the thermocompression bonding of 0.001" gold wire to 0.010" nickel sheet was examined from room temperature to 570°C and at bonding forces from 5 grams to 600 grams. More specifically, the electrical resistance and mechanical pull strength of the bonds were determined as a function of bonding temperature and bonding force, and an attempt was made to analyze and explain the phenomena encountered. A reliable procedure for producing, testing, and metallurgically examining the bonds was developed, which may be employed for future studies.

The formation of the gold to nickel bond was affected more greatly by bonding temperature than by bonding force, although at a specific temperature the bond quality may be optimized by selecting the proper bonding force. Below 200°C bonding did not occur, while between 200°C and 320°C the bonding was poor, yielding pull strength values from one to two grams. The bonding was satisfactory above 320°C, and above 400°C the bonding was ideal, with pull strengths approaching the gold wire strength of 3.5 to 4.0 grams. Throughout this temperature range the electrical resistance was very low, one to three milliohms, and consisted primarily of spreading resistance in the nickel sheet. The reason for the bond strength variation in the above temperature range was the variation of the adherence strength per unit area. The

achievement of satisfactory adherence strength requires sufficient diffusivity to permit threshold atom movements necessary in eliminating stiuctural irregularities in the interface region. The important role of this microscopic diffusion enables one to bond at a low temperature and then heat treat at a higher temperature to produce bond strengths normally obtained only by bonding at the higher temperature.

At bonding temperatures above 440°C, at which oxide formed on the nickel sheet, the gold was found to adhere very readily to the nickel oxide, a phenomenon which was not expected. The suggested mechanism of adherence was the interlocking in the nickel oxide of fine gold paths, which formed by the diffusion of the gold on the surfaces of voids and fractures in the nickel oxide. Other adherence mechanisms considered involved solid solution of gold in nickel oxide, reduction of nickel oxide, and surface roughness of the oxide. A more complete understanding of the gold to nickel oxide adherence should certainly enlighten other fields of metal to nonmetal adherence.

INTRODUCTION

In the last 18 years solid state welding processes have become important production tools and have thus induced much interest in the study of metal to metal adhesion. Cold welding, which was developed in Britain in 1946, is the formation of a joint by room temperature deformation of soft metals such as copper and aluminum.[1,2] Ultrasonic welding was discovered in 1950 and has been found effective in joining softer metals as well as difficult combinations like aluminum to stainless steel.[3,4] Thermocompression bonding was invented in 1957 as a technique using heat and pressure to connect electrical leads to semiconductors.[5,6] More recently roll bonding methods have been developed to fabricate clad metal products.[7,8] Since all of these methods depend upon solid state metallic adhesion, it is natural to expect that much interest in metallic adhesion has been stimulated. In addition, solid state metallic adhesion is not just important to the above joining processes, but is also important in the study of friction[2,9,10], wear,[2,9,10] electrical contacts,[11] and powder metallurgy.[2]

There has been much investigation of the mechanism of solid state metallic adhesion, which over a period of years has yielded concepts of the requisites for metallic adhesion. Although there has been no universally accepted listing of the important concepts of metallic adhesion, it appears that there is enough agreement to make such a listing enlightening. Therefore, a brief statement of the requisites

for solid state metallic adhesion has been prepared and is included in Appendix I.

Although there has been much investigation of the adhesion mechanisms, few metal systems have been extensively studied because the investigation emphasis has been upon basic mechanisms. On the other hand, the investigators of joining processes have developed the processes and selected the materials for a particular purpose, thus again avoiding more extensive study. This has been the case for thermocompression bonding which was developed for electrical connection to semiconductor devices. Small gold wire was found to be satisfactory and thus thermocompression bonding of gold has been a vital process in the semiconductor industry for seven years. More recently there has been some study of other materials. The feasibility of thermocompression bonding of gold, platinum, aluminum, copper, tantalum, titanium, silicon, and nichrome has been examined by McKinnon and Hoeckelman.[12] There has been much interest throughout the semiconductor industry in replacing gold wire bonds with aluminum, because of reliability problems;[13,14,15] and Wasson has examined different alloys of aluminum.[16] However, these investigations were limited because they were intended for application to semiconductor production; usually only a particular temperature range was examined and compatibility with the semiconductor material placed stringent restrictions on the investigations. It seems then that less production-oriented investigations of thermocompression bonding should yield additional information that would be of value to the semiconductor industry as

well as of interest to the field of solid state adhesion.

The purpose of this investigation was to obtain information on the thermocompression bonding of gold to nickel over a wide range of temperature and pressure. In particular the intent was to obtain the electrical resistance and pull strength of the bonds as a function of temperature and pressure of bonding. Also an objective was an increased understanding of solid state adhesion, especially at elevated temperatures. To carry out the above objectives, it was necessary to establish a reliable procedure for evaluating electrically, mechanically, and metallurgically thermocompression wire bonds; and it was intended that this evaluation procedure be applicable to future wire bond studies.

This investigation consisted of thermocompression bonding 0.001" gold wire to 0.010" nickel sheet, and then obtaining the electrical resistance and mechanical pull strength of the bonds. Because of the size of the bonds, the direct applicability of the data is certainly size limited. However, most of the information, especially the important effects of temperature and the discussions of adherence mechanisms, is general enough to be applicable to any size and technique of solid state welding.

The reasons for selecting the investigation of gold to nickel thermocompression bonding stem from the availability, simplicity, and applicability of this system. Thermocompression bonding was chosen because of experience with the process, availability of the equipment, and applicability of the process to semiconductor production. The gold to nickel system was chosen because of the availability and usefulness of each material and the relative simplicity of gold-nickel

alloys. Some pertinent properties of gold, nickel, and the gold-nickel system are presented in Appendices II, III, and IV. The phase diagram and alloy properties of gold-nickel indicate that no difficulties of brittle or weak phases should be experienced during bonding or service.

APPARATUS AND EXPERIMENTAL PROCEDURE

The intent of the experimentation was to determine the bond electrical resistance and pull strength as a function of bonding force and temperature, while maintaining all other factors constant. To accomplish this it was necessary to obtain reliable equipment and establish a fixed procedure for

(1) producing the sample bonds,

(2) testing to determine the electrical resistance of the bonds, and

(3) testing to determine the pull strength of the bonds.

The description of the apparatus and test procedure for each of these operations is described later.

Samples were bonded at 12 temperatures between 200°C and 570°C; at each of these temperatures samples were produced throughout the permissible bonding force range with intervals of 10 to 20 grams between each sample. Each sample consisted of 10 to 15 gold wires bonded to a small nickel sheet all at a particular temperature and bond force. All samples were bonded, stored and tested in air. The reasons for the 200°C to 570°C temperature range are that 200°C was found to be the lower limit of bonding and 570°C was the upper temperature which could be maintained without failure of the heat sink.

BONDING APPARATUS AND OPERATION

The important features of the thermocompression bonder are shown in Figure 1, with a close-up view of the bonding needle in Figure 2.

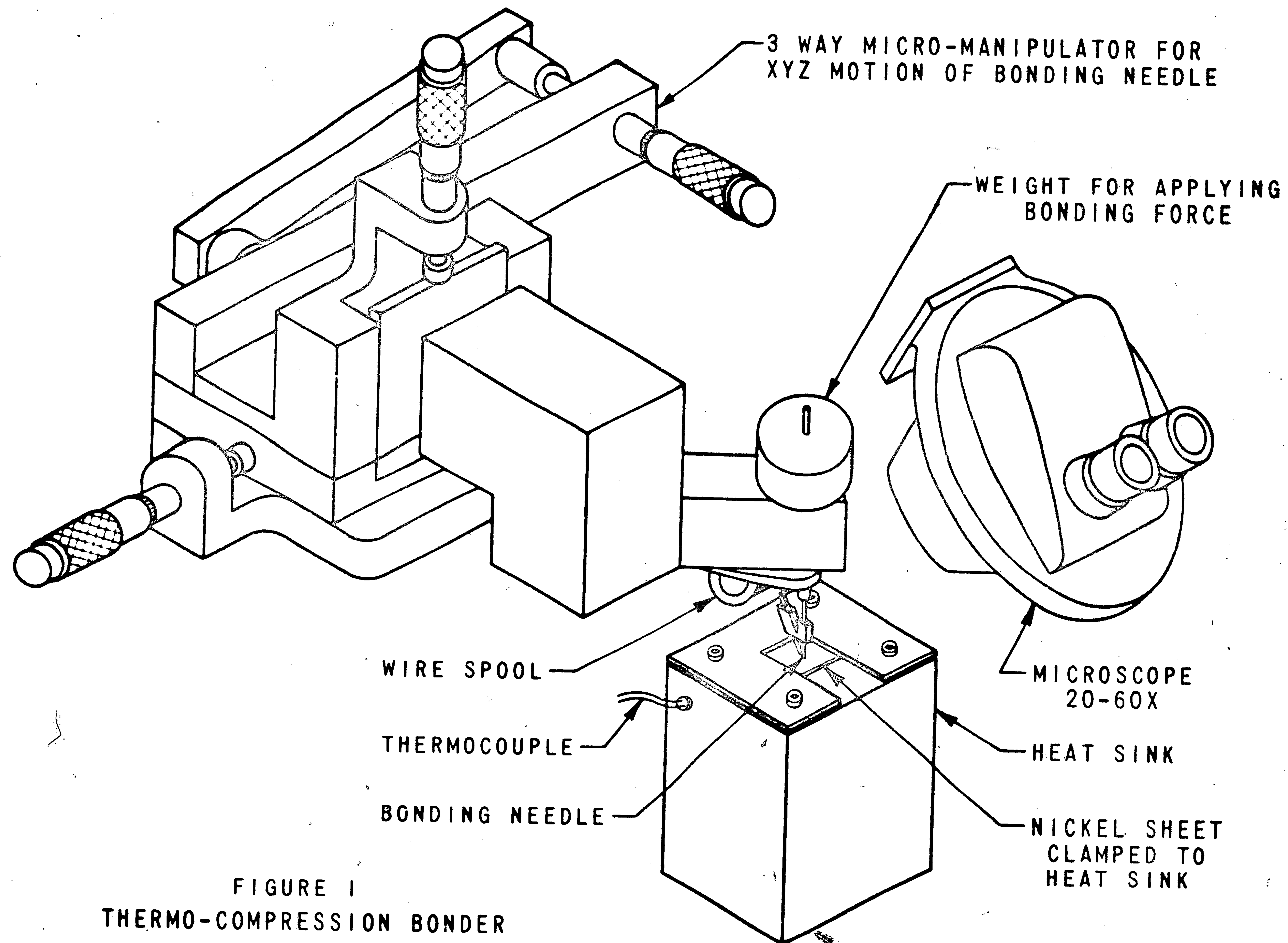


FIGURE I
THERMO-COMPRESSION BONDER

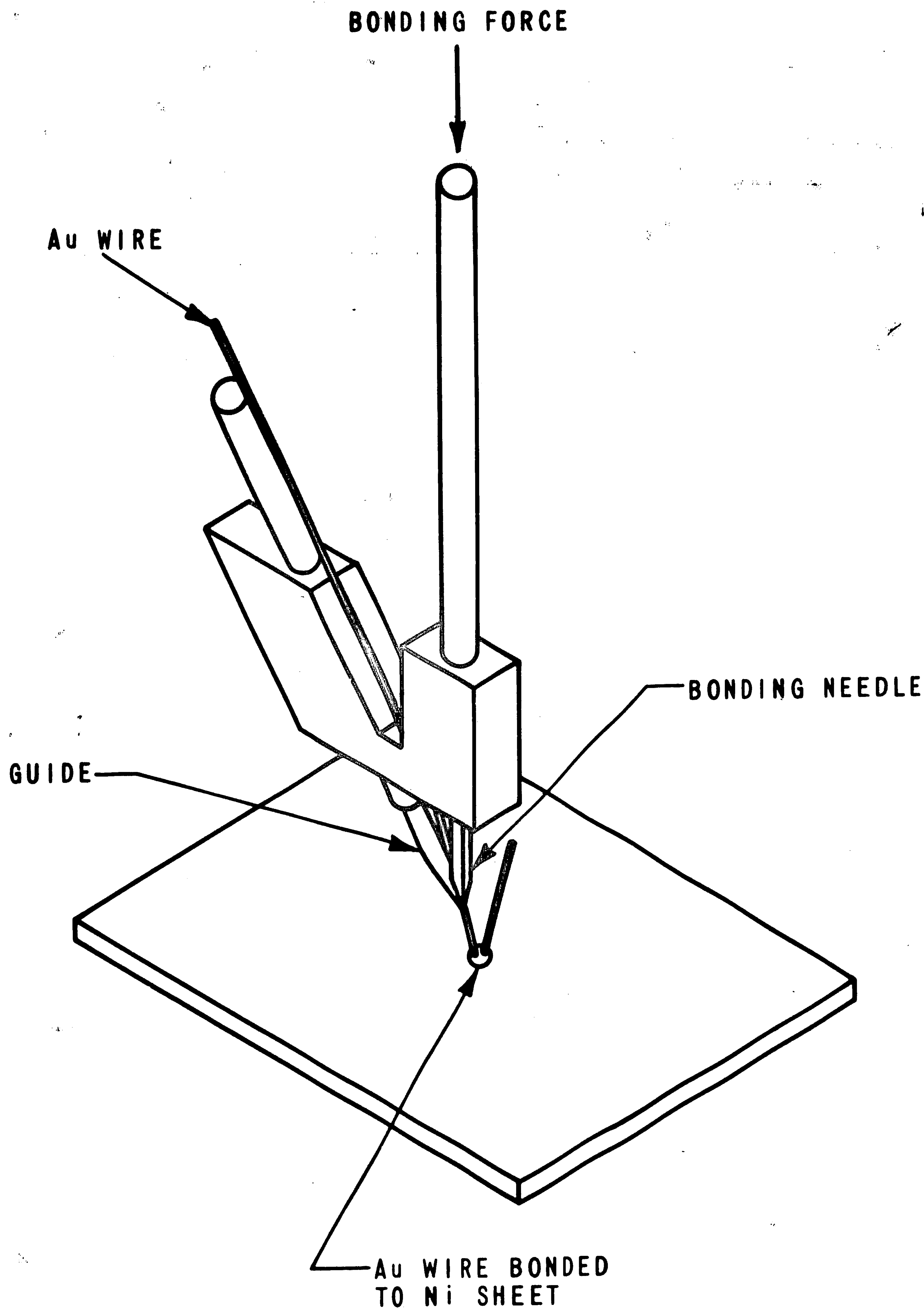


FIGURE 2

DETAILS OF BONDING NEEDLE

The four basic elements are the heat sink, the bonding needle, the manipulator for positioning the bonding needle, and microscope to observe the work. The nickel sheets were clamped to the stainless steel heat sink which contained a 525 watt cartridge heating element. The power to the heating element was controlled by a variable transformer, and a chromel-alumel thermocouple calibrated at 100°C and 500°C was used to measure the bond temperature. An accurate determination of the actual bond temperature was not attempted; the thermocouple was placed on the heat sink surface so that it was at approximately the same temperature as the nickel sheet. The bond should have been nearly the same temperature as the nickel sheet, since the bonding needle was an insulator and the gold wire was so fine. It is estimated that the bond temperature was ±15°C from the measured temperature.

The micromanipulator provided accurate, three-dimensional movement of the bonding needle which was vital when bonding fine wire. The bonding needle design and condition were very important to proper bonding. Its primary functions were to position the gold wire and then press the wire against the nickel sheet. As shown in Figure 2, it was designed so that the wire would pass freely between the bonding needle and guide, and would still be held under the bonding needle for future bonds. The end of the bonding needle was approximately 0.003" square and contained a groove so that the bond would have a ridge, thus reducing the chance of totally shearing the wire. The detailed dimensions of the bonding needle are shown in Appendix V. During the experiment the bonding needles were replaced whenever they became dirty

or showed signs of wear. These bonding needles were designed and made by Vallorbs Jewel Co. of Lancaster, Pa., and have been used successfully in semiconductor manufacture. The bonding needle was fastened to the manipulator through an override mechanism so that only the force of the weights was applied to the bonding needle. Because of the sizes involved, the clearances throughout the bonder were maintained at a minimum.

During operation of the bonder, the gold wire was fed from the spool down to the bonding needle and was held in place against the bonding needle by the guide, as shown in Figure 2. As the bonding needle was lowered, the gold wire was pressed against the nickel sheet producing satisfactory conditions for bonding as described in Appendix I. The bonding needle was then raised above the nickel surface until the bond wire length was sufficient for testing, and the gold wire was then cut with a small pair of surgical scissors. It was very important that the gold wire moved freely through the needle and that extreme care was exercised throughout the bonding and the testing.

ELECTRICAL RESISTANCE MEASUREMENT

First a regular ohm meter was used; this measured the resistance of the gold wire, the bond, and the nickel sheet in series. However, it was found that the resistance of the gold wire was so great that it masked the bond resistance. To measure just the bond resistance, it was necessary to employ a method that measured the voltage drop across the bond only. This was achieved by using a constant current

and voltage probe method shown in Figures 3 and 4. Bonds were produced leaving a length of gold wire on each end of the bond, so that the tweezers of the test fixture could be attached to each wire end. The fixture in Figure 3 was assembled with two micromanipulators so that the tweezers could be attached independently to the wire ends, and the constant current and voltage probe applied as in Figure 4. Figure 5 is a schematic of this measurement technique; as shown only the voltage drop across the bond was measured.

The instrument used in the resistance test was a Keithley Model 502 Milliohm Meter. It has 13 scale ranges from 0.001Ω to 1000Ω full scale, and could be read to two percent of the scale range. The meter was compared with standard resistances and its precision was commensurable to the ability to read the scale.

BOND PULL STRENGTH

The bond pull strength was determined using the test fixture in Figures 6 and 7. This fixture was originally developed for testing wire bond strength on transistors,[17] but was modified by replacing the transistor holding jig with a clip to hold the nickel sheets. During operation the tweezers fastened to the force gage were attached to the gold wire, and then the right hand manipulator was advanced to the right, gradually applying force. The force to produce failure of the bond was then registered on the gage. The lifting probe in Figure 6 was used to open the normally closed tweezers so that the tweezers could be attached to the gold wire. As shown in Figure 7, the direction of the force was 25° above the nickel sheet, and in a

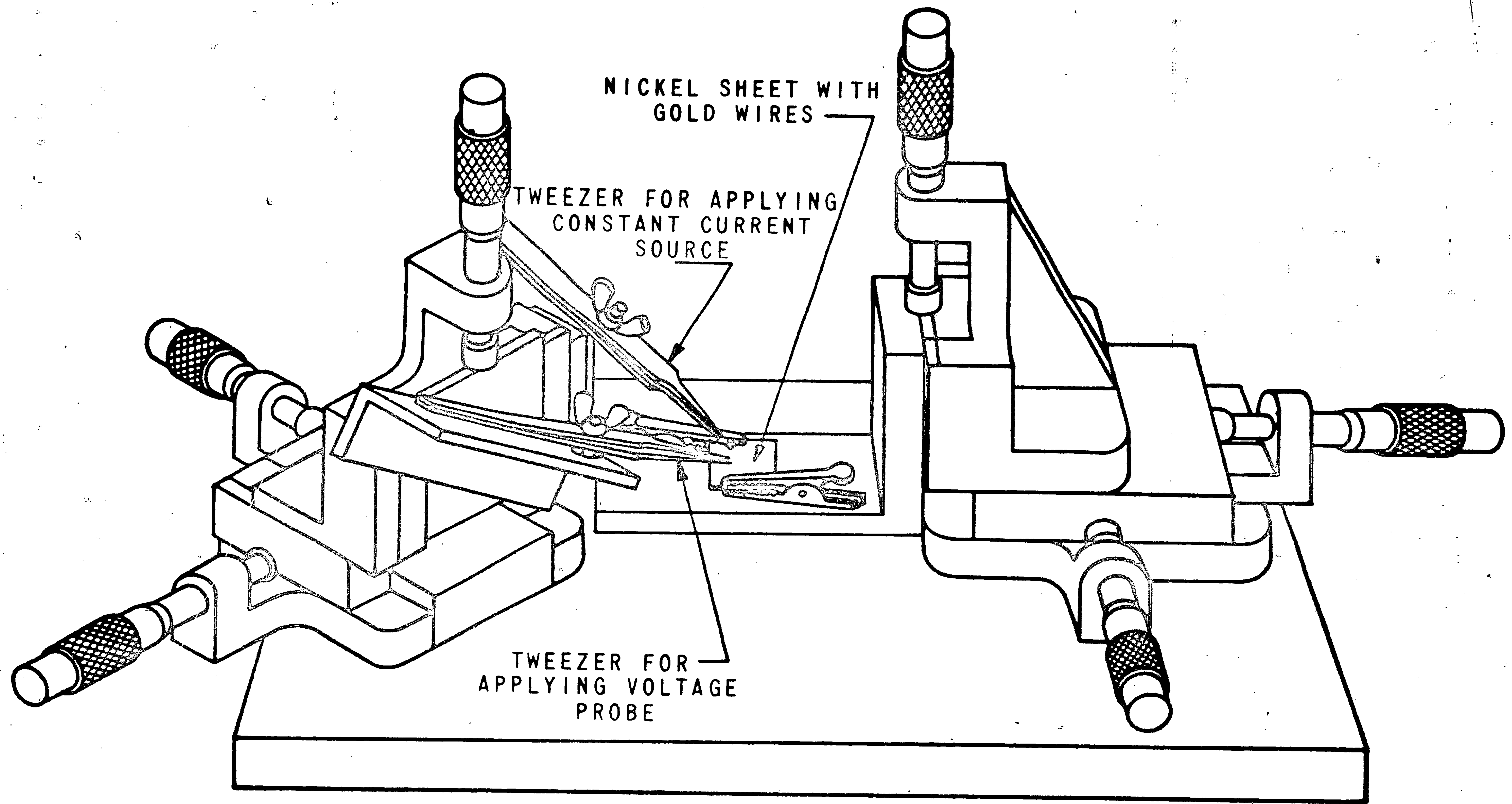


FIGURE 3
ELECTRICAL RESISTANCE TEST FIXTURE

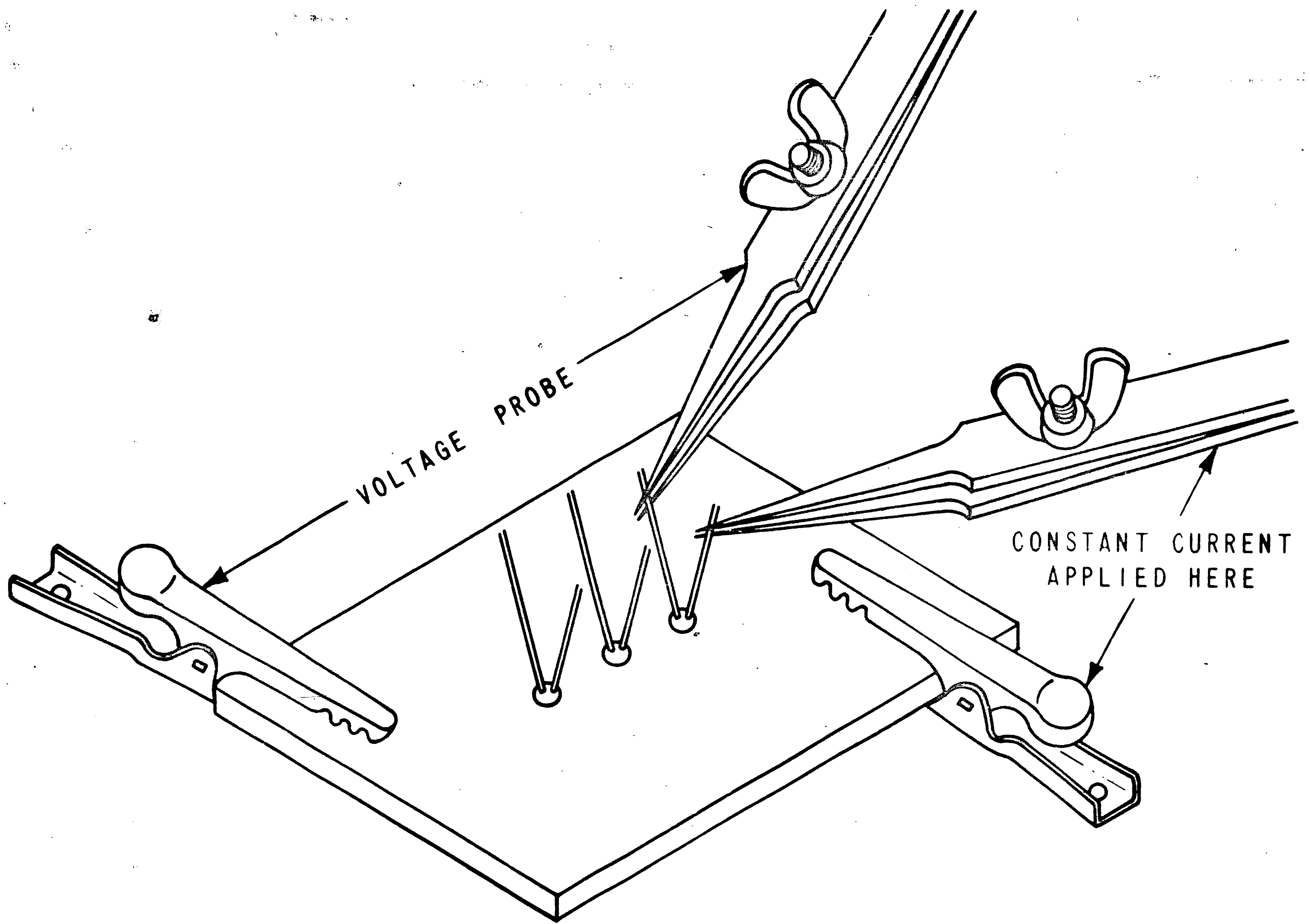


FIGURE 4

MEASUREMENT OF BOND RESISTANCE

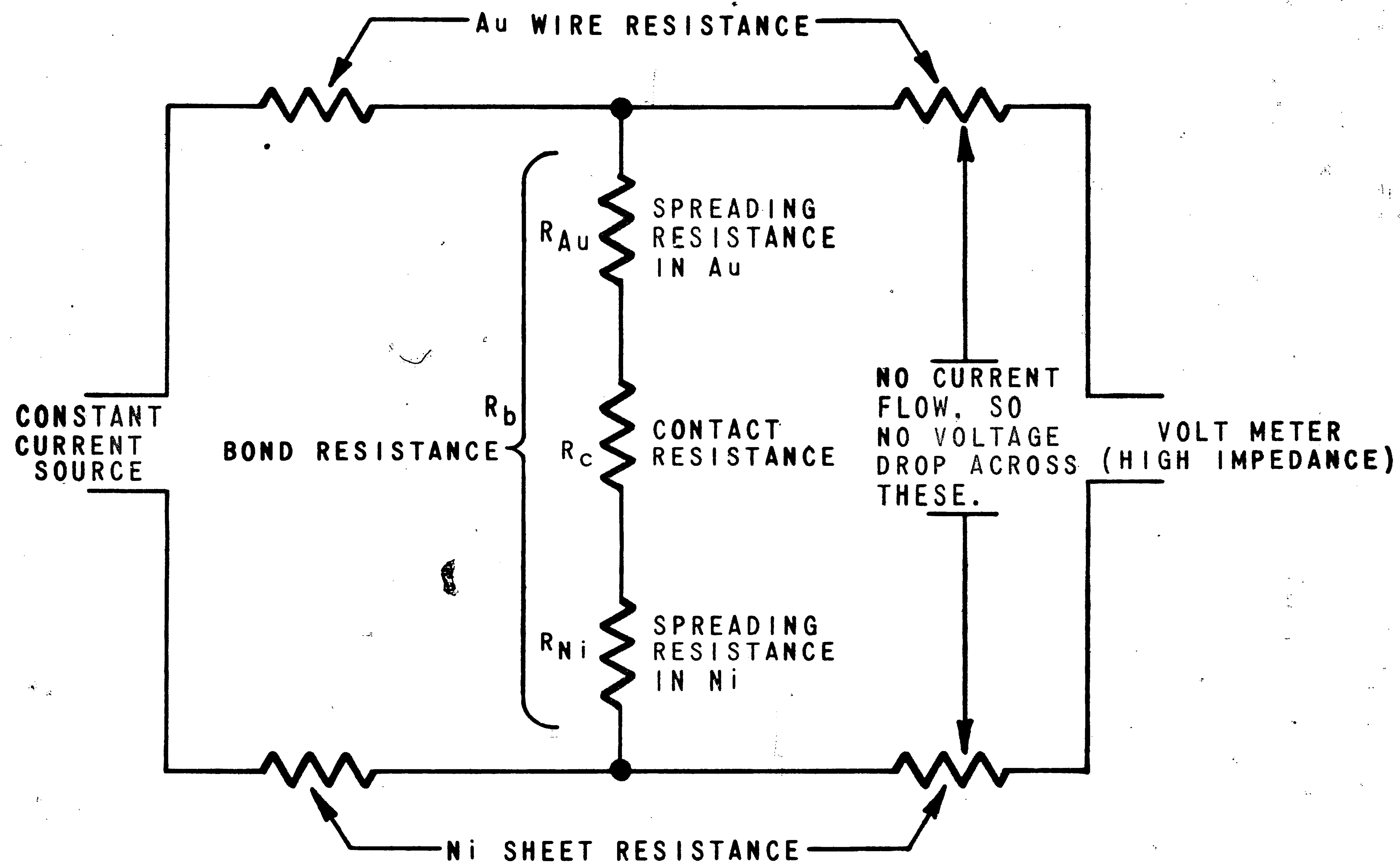


FIGURE 5
SCHEMATIC OF ELECTRICAL RESISTANCE TEST

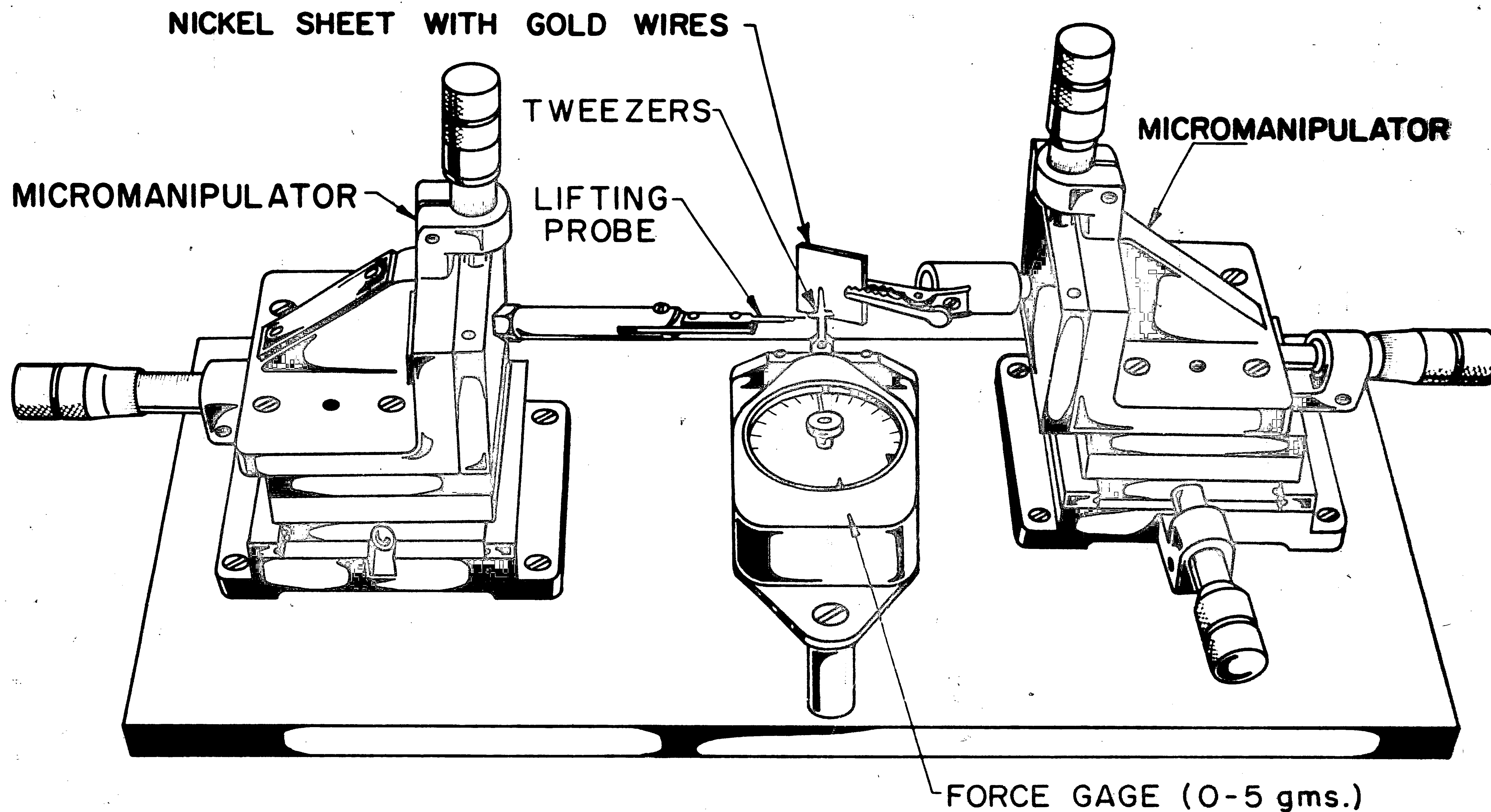


FIGURE 6

BOND PULL STRENGTH TEST FIXTURE

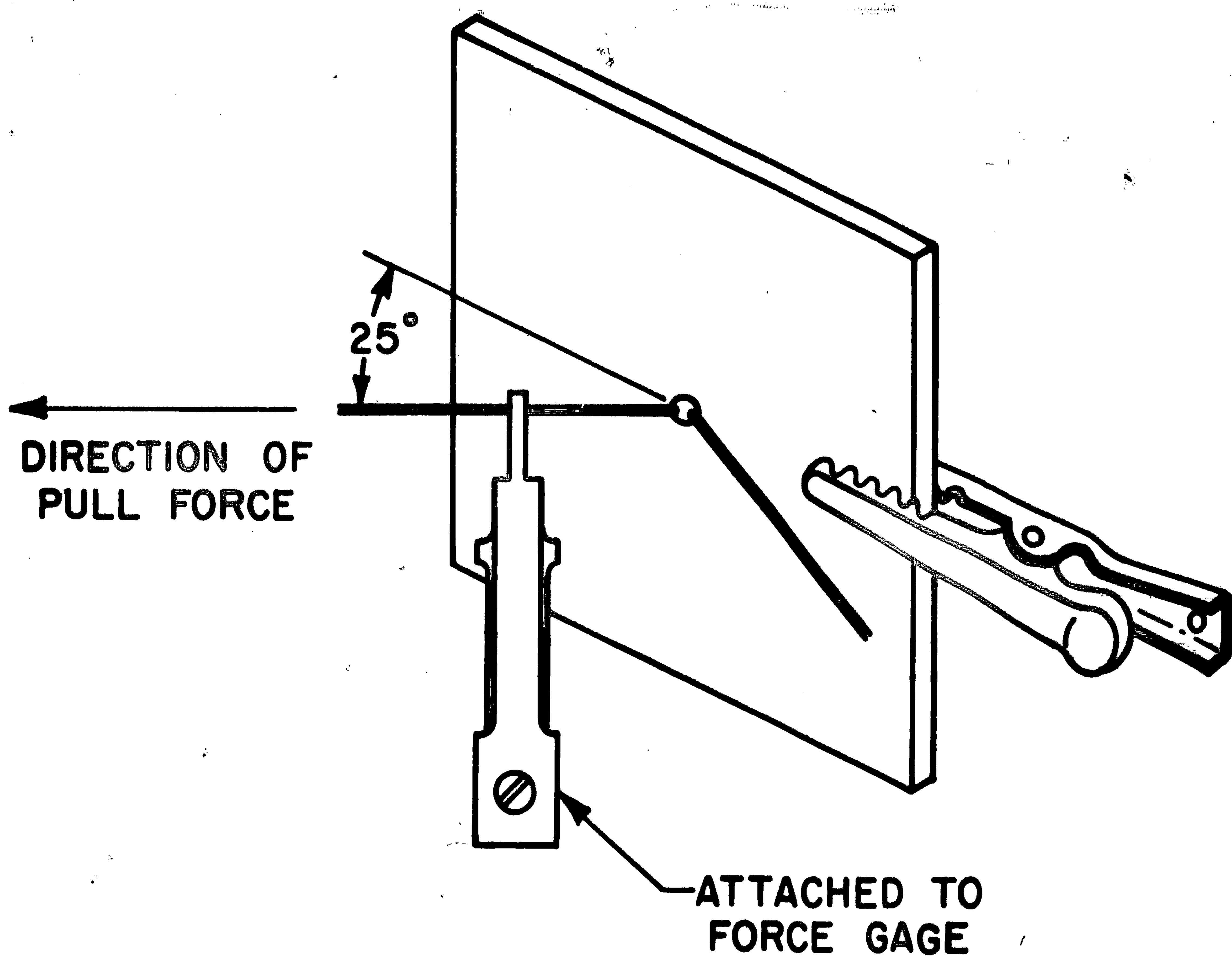


FIGURE 7

PULL STRENGTH TEST

TABLE I

ANGLE FROM NICKEL SHEET	PULL STRENGTH
5°	1.44 GRAMS
25°	1.63 GRAMS
45°	1.38 GRAMS
90°	1.43 GRAMS

25° PULL ANGLE WAS SELECTED
AS SHOWN IN FIGURE 9 ABOVE.

plane which both contained the gold wires and was perpendicular to the nickel sheet. The force gage registered from zero to five grams in one-tenth gram intervals.

The 25° angle was selected after an initial test to determine the effect of the angle of pull. Forty gold to nickel bonds were produced at 320°C at 80 grams bond force and the pull strengths were determined at four different angles. The results given in Table I indicate that the bonds were strongest at 25°, although the angle certainly did not have a great effect. The 25° pull angle was selected as a result of this test and because it corresponded closely to the angle of maximum force experienced by transistor leads during service.

This pull strength test was a significant test from two standpoints. Strengths obtained from a test like this have been shown to correlate with performance under shock and centrifuge service tests.[16] Secondly the type or nature of the bond failure indicated certain characteristics of the bond. The different failure types and their indications were:

(1) peel indicated that failure occurred at the gold to nickel interface and that the metal to metal adhesion was weak,

(2) next to the bond indicated that the wire was excessively deformed in the area of the bond, and

(3) wire indicated that the gold to nickel adhesion was good with little deformation so that the bond was stronger than the gold wire.

During the experimentation, the type of bond failure was always recorded.

MATERIALS

The 0.001" diameter gold wire used in this experiment was supplied by Secon Metal Co. as 99.99% pure gold. Spectographic analysis showed that silver and copper were present in amounts less than 0.01 percent. The wire was received in the stress relieved condition with room temperature properties of 6.0 to 7.0 grams tensile strength and four to six percent elongation. However, since the annealing temperature of gold is 300°C, the wire bonded much above 300°C would have been annealed or dead soft with properties of 3.5 to 4.0 grams tensile strength and eight to twelve percent elongation. The cleaning of the gold wire was performed by the supplier and was proprietary, but it involved:

(1) solvents to remove drawing lubricants,

(2) removal of particles, and

(3) deionized water wash.

The 0.010" thick nickel sheet was supplied under the trade name "Nickel 270" by Accurate Metal Co. The "Nickel 270" was 99.95 percent pure. The nickel sheet was received in the bright annealed condition, with a grain size of ASTM No. 7, hardness Rockwell B 40, and surface finish less than seven micro-inches. Since the supplier performed no special cleaning, five different cleaning procedures were examined in an effort to select a standard cleaning procedure that would be most suitable for bonding. The five cleaning methods are listed in Table II. Gold wire was bonded at 320°C at 80 grams bonding force to samples of the five cleaning methods and the pull

TABLE II

CLEANING PROCEDURES

DESIGNATION	CLEANING METHOD
A.	AS RECEIVED.
B.	DEGREASE IN TRICHLOROETHYLENE AND ACETONE FOR 3 MINUTES EACH; ULTRASONIC BATH OF NON-IONIC DETERGENT AND WATER FOR 2 MINUTES; DEIONIZED WATER CASCADE FOR 5 MINUTES.
C.	SAME AS B, PLUS 15 MINUTES AT 900°C IN H_2 SATURATED WITH WATER AT ROOM TEMPERATURE.
D.	SAME AS C, PLUS 20 SECONDS IN INTERNATION NICKEL Co. BRIGHT DIP TO REMOVE TARNISH.
E.	SAME AS C, PLUS 50 SECONDS IN 50-50 HCl-H_2O TO FORM A COHERENT THIN OXIDE; DEIONIZED WATER CASCADE FOR 5 MINUTES.

strength was determined. The pull strength results for a sample size of 12 bonds are presented in Table III. It was observed that cleaning procedure "C" required a higher temperature to form a tan tarnish than did the others, while "D" apparently formed an oxide more readily than did the others. Sample "D" formed a tan tarnish at 300°C while greater than 400°C was required for "C", and "A", "B", and "E" were in between in that order. It was also observed that the grain size of "C", "D", and "E" was ASTM No. 4 to No. 5 due to grain growth in the 900°C heat treatment. Cleaning procedure "C" was selected as the standard for this experiment and is the suggested procedure for preparing nickel for bonding to gold by any solid state welding technique. It is possible for some applications that the grain growth is not desirable; however, this is a small point since ASTM No. 4 to No. 5 certainly is not excessively large.

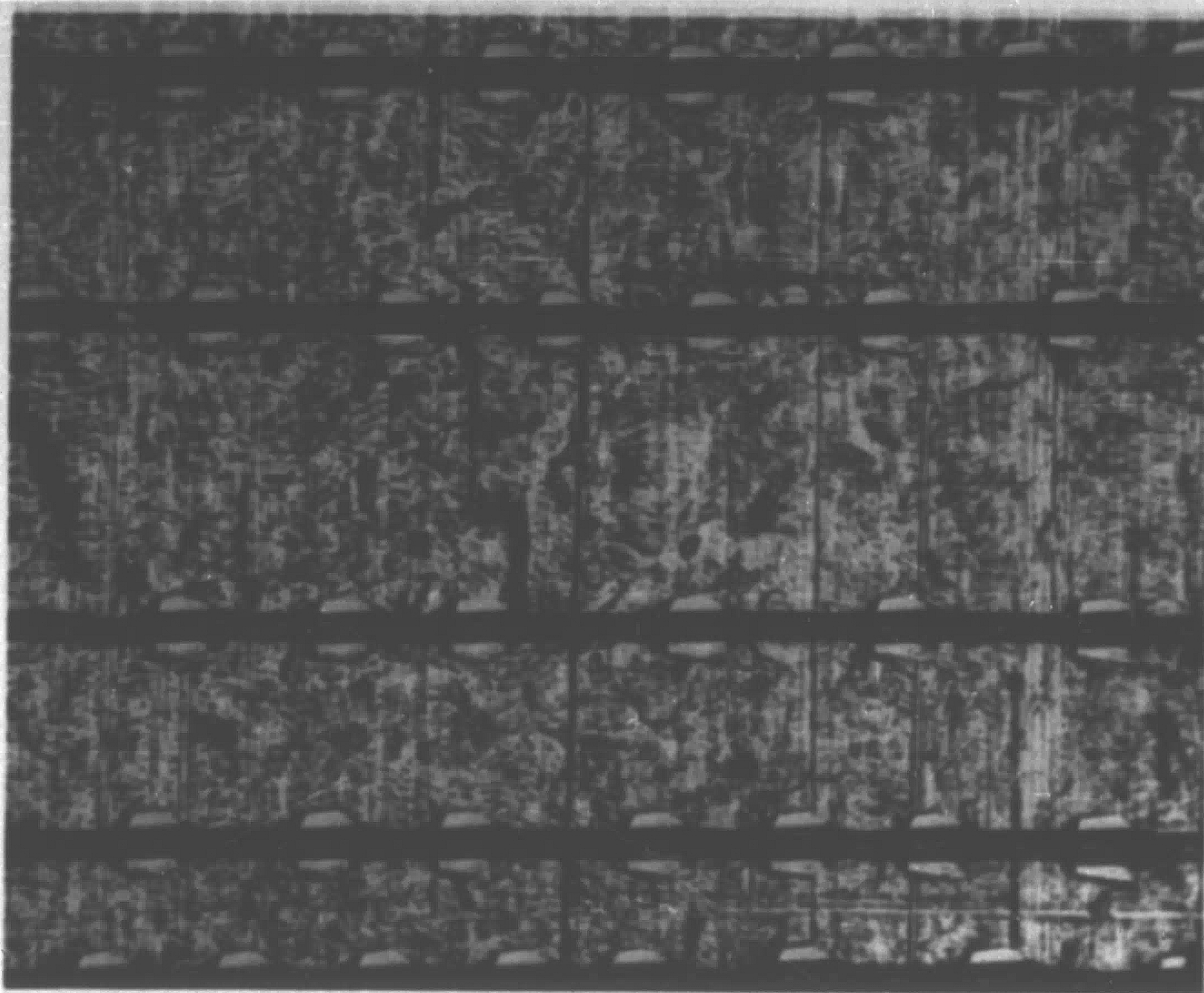
METALLURGICAL EXAMINATION

Because of the small sizes involved, to obtain a cross section through a bond it was necessary to produce a large number of bonds on a single nickel sheet and then randomly section through the area. This was accomplished by making parallel rows of bonds as shown in Figure 8. The sheet with bonds was then mounted in epoxy, and sectioned and polished perpendicular to the rows of bonds. Thus with 15 rows of bonds on a nickel sheet, a section was obtained which passed through five or six bonds. A typical section through a bond appears in Figure 9. A hard epoxy resin was used for mounting

TABLE III

EVALUATION OF CLEANING PROCEDURES

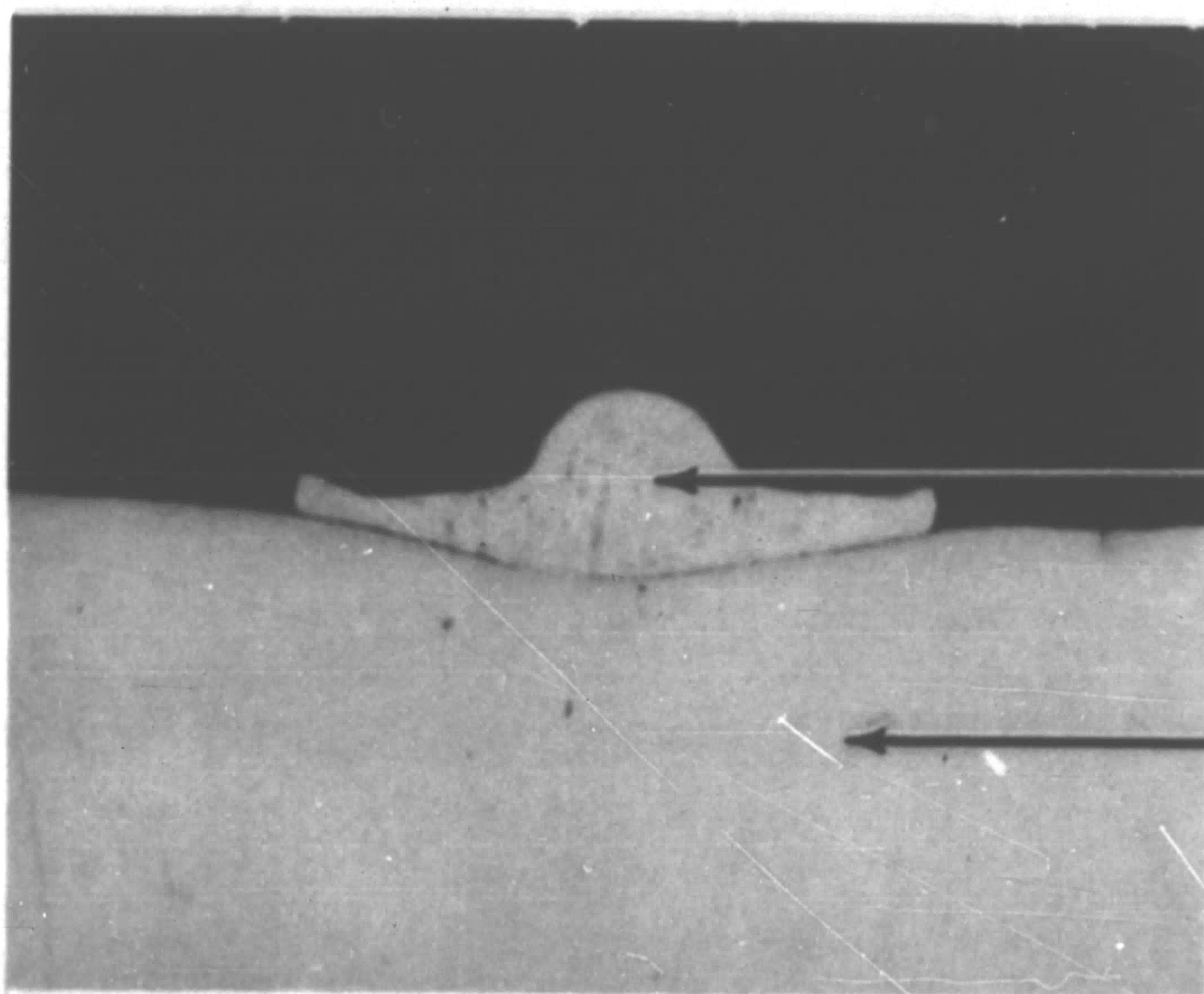
SAMPLE	PULL STRENGTH RANGE	AVG.
A	1.3 - 2.1	1.63
B	1.7 - 1.9	1.78
C	2.1 - 2.35	2.23
D	1.4 - 2.0	1.73
E	1.2 - 1.95	1.61



100X

FIGURE 8

APPEARANCE OF BONDS ON THE NICKEL SHEET. ROWS OF BONDS WERE PRODUCED AND THEN THE SAMPLE WAS CROSS-SECTIONED PERPENDICULAR TO THE ROWS, YIELDING A METALLURGICAL SECTION SUCH AS BELOW.



875X NO ETCH

FIGURE 9

TYPICAL METALLURGICAL SECTION THROUGH A BOND.

to reduce edge rounding of the gold and permit some vision through the mold to aid in sectioning. With this preparation, one can estimate diffusion, observe nickel oxide, and estimate the bond contact area.

RESULTS AND DISCUSSION

The pull strength and electrical resistance of the gold to nickel bonds as a function of bonding temperature and bonding force are presented in Figure 10. The solid curves are lines of constant pull strength measured in grams, and the dotted curves are lines of constant electrical resistance, which are measured in milliohms (mΩ) or kilo-ohms (KΩ). Figure 10 is a compilation of the 12 isothermal curves obtained in the experiment. As previously described, at each of 12 temperatures between 200°C and 570°C, the electrical resistance, and pull strength were determined as a function of bonding force. This data of the electrical resistance and pull strength at each bonding temperature and bonding force were far too copious to be presented here. Therefore the data were averaged and used to draw curves of the electrical resistance and pull strength at the 12 bonding temperatures, and then from these isothermal curves Figure 10 was constructed.

Based on typical pull strength results, an estimate of the confidence interval of the data was determined. For a sample size of 11 bonds, there was 95 percent confidence that the actual strength was ±0.158 grams of the average pull strength. The 99 percent confidence interval was ±0.224 grams. The data and calculations from which this estimate was obtained are included in Appendix VI.

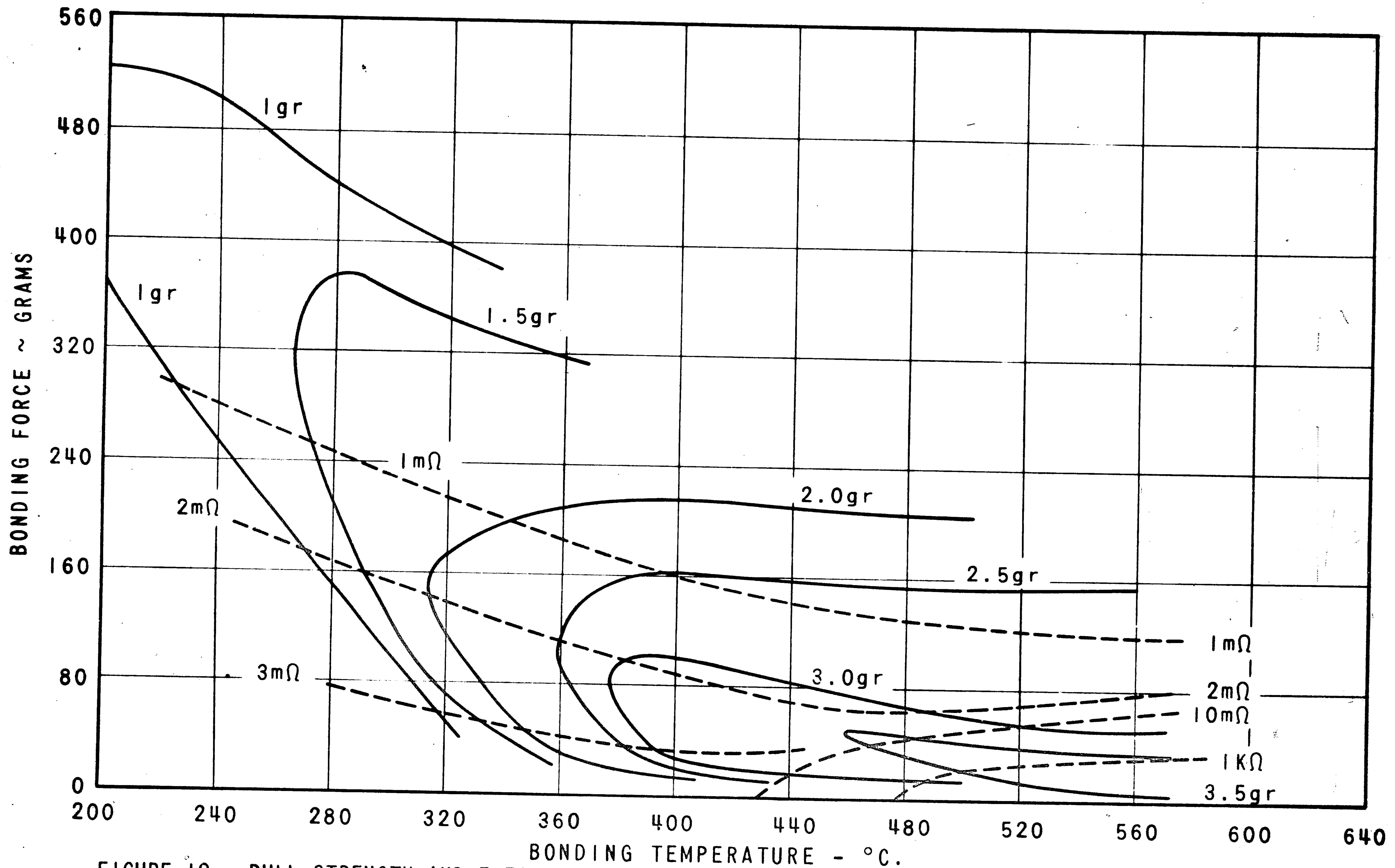


FIGURE 10 - PULL STRENGTH AND ELECTRICAL RESISTANCE AS A FUNCTION OF BONDING TEMPERATURE AND FORCE

The permissible ranges of bonding temperature and bonding force are outlined by Figure 10. The friction in the wire feed of the bonding needle was such that a bond must have had a strength of nearly one gram to survive bonding; therefore at temperatures below 320°C the one gram line defines the limit of bonding. Above 320°C there was no upper bonding force limit, and the pull strength remained constant as the bonding force was increased; e.g., at 400°C the pull strength remained two grams for all bonding forces greater than 200 grams. The lower bonding limit between 320°C and 570°C decreased from 50 grams to 5 grams, and along this lower limit at any particular temperature the pull strength increased very rapidly with bonding force. For example, at 480°C the pull strength increased from less than one gram at 10 grams bonding force to three grams pull strength at 15 grams bonding force. Thus this region of Figure 10 would have been more correctly drawn if the pull strength lines had been continued and compressed together, rather than discontinued as has been done.

ISOTHERMAL VARIATION OF PULL STRENGTH AND ELECTRICAL RESISTANCE

If the more important effects of temperature on bonding are to be considered, it is expedient first to understand the variation of pull strength and electrical resistance with bonding force alone. Figure 11 presents such a variation for a bonding temperature of 400°C. The solid and dotted curves were drawn from an isothermal section of Figure 10, and the points are the experiment data.

Considering first the electrical resistance, it can be

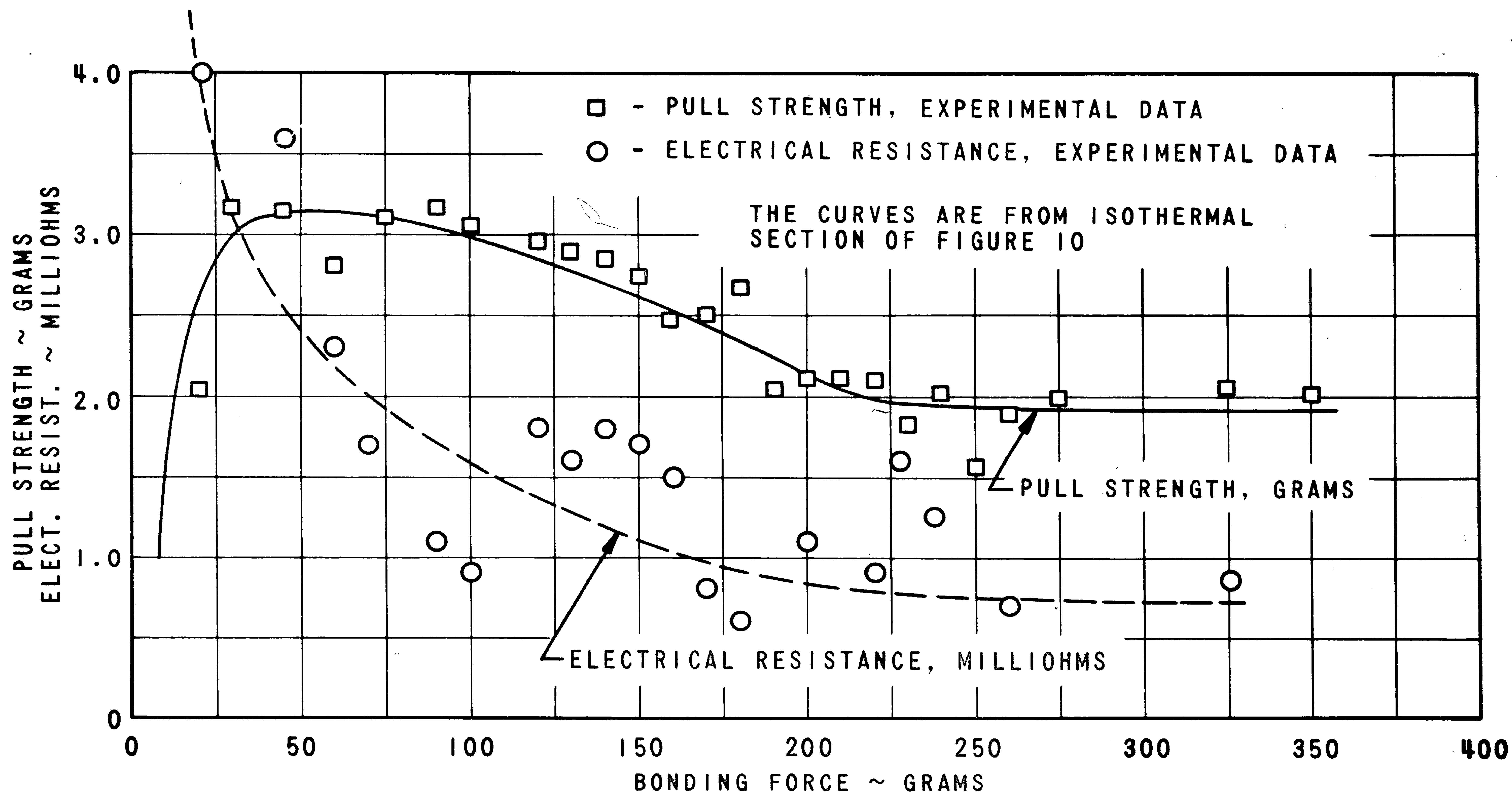


FIGURE 11 - PULL STRENGTH AND ELECTRICAL RESISTANCE AT 400°C.

demonstrated that the electrical resistance variation is consistent with the calculated spreading resistance. Spreading resistance results when current flows through a constriction and is a resistance term in addition to the standard conductor resistance given by the relation $\rho \ell/\text{Area}$, where ρ is the volume resistivity, ℓ the length of the conductor, and Area the conductor area. Spreading resistance has been discussed by Schockley in relation to contact to semiconductors[19] and by Bowden and Tabor in relation to the area of contact between metals.[9] The spreading resistance may be calculated from the relation

$$R_s = \frac{\rho}{4a} \quad \text{where}$$

$$\rho = \text{volume resistivity}$$

$$a = \text{radius of the area of contact.}$$

The calculated spreading resistance may be compared with the observed resistance as follows:

> For the bonding condition of 100 grams at 400°C the apparent interface area is an ellipse 0.0023" x 0.0020". So the equivalent radius is 27.2 microns. The calculated spreading resistance is equal to the sum of the spreading resistance in the gold and nickel.

$$R_s = R_{Ni} + R_{Au} = \frac{\rho_{Ni} + \rho_{Au}}{4a} \quad \text{where}$$

$$a = 27.2 \times 10^{-4} \text{cm}$$

$$\rho_{Ni} = 6.84 \times 10^{-6} \Omega\text{-cm}$$

$$\rho_{Au} = 2.35 \times 10^{-6} \Omega\text{-cm}$$

Therefore,

$$R_s = \frac{(6.84 + 2.35) \times 10^{-6}}{4(27.2 \times 10^{-4})}$$

$$R_s = 0.85 \times 10^{-3} \Omega$$

which accounts for a large portion of the observed value $1.6 \times 10^{-3} \Omega$. As the bonding force increased, the interface area increased, thus decreasing R_s; and as the bonding force decreased, R_s increased. (This relation between bond area and bonding force seems reasonable and later was correlated with photographs and measurements - - - see Figure 24.) Consequently the bond area with its associated spreading resistance accounts for the variation of the electrical resistance with bonding force.

However, in the calculation above, the spreading resistance, R_s, did not account for the entire observed bond resistance R_b, and in general this has been found to be the case. Referring to Figure 5, the bond resistance is composed of the spreading resistance and another resistance term which may be called the contact resistance; i.e.,

$$R_b = R_s + R_c = R_{Ni} + R_{Au} + R_c.$$

Therefore, the increased resistance may be considered as contact resistance; i.e., in the above calculation,

$$R_c = 0.71 \times 10^{-3} \Omega.$$

Considering the origins of this contact resistance, a possibility is that it was due to contact potential;[20] this apparently was not the source, however, because reversing the polarity of the current source caused no measurable voltage change. A more likely possibility is that oxides and contaminants reduced the area of contact so that the effective bond area was less than the apparent area.

Also undoubtedly the many imperfections at the interface region increased the resistivity and decreased the effective area of contact. Finally, diffusion of nickel into the gold, and gold into the nickel, would have caused increased resistance; for example, one weight percent nickel in gold increases the resistivity of the gold from 2.35 to 5.45 micro-ohm-cm, and also gold-nickel alloys show increased resistivity because of precipitation.[21] In order for the alloying to be most effective in increasing resistivity, the crystal structure should be nearly perfect; therefore, the atoms would first have to diffuse through the imperfect regions on either side of the interface, and the diffusivity was not large enough at this temperature to permit this during the short times at the bonding temperature. Therefore, the resistivity effects associated with diffusion were probably not responsible for the contact resistance.

Considering Figure 11 again, the variation of pull strength at a given temperature may be explained by considering how the bond interface area and wire deformation varied with bonding force. Increasing the bonding force increased the bond area which increased the bond strength; but at the same time, the increased bonding force deformed the gold wire which weakened the wire next to the bond and did not permit all the increased bond area to contribute to the strength of the bond. These opposing effects are depicted in Figure 12, where the strength of the bond is first limited by the amount of interface area and secondly by the wire deformation and area contributing to bond strength. Figure 13 is a bond cross section whose apparent interface area (as viewed during bonding such as in Figure

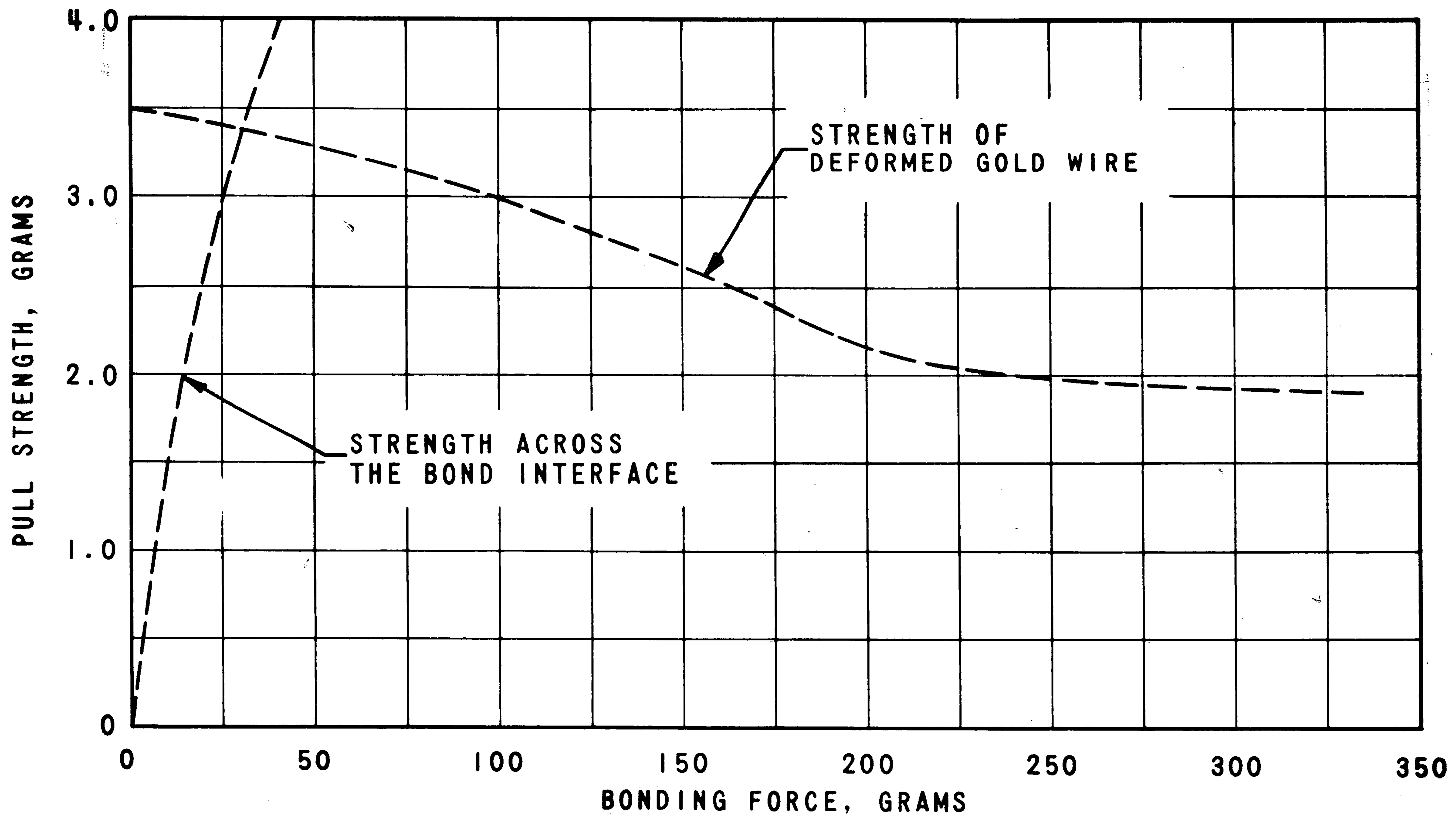


FIGURE 12 - COMPONENTS OF BOND STRENGTH AT 400°C.

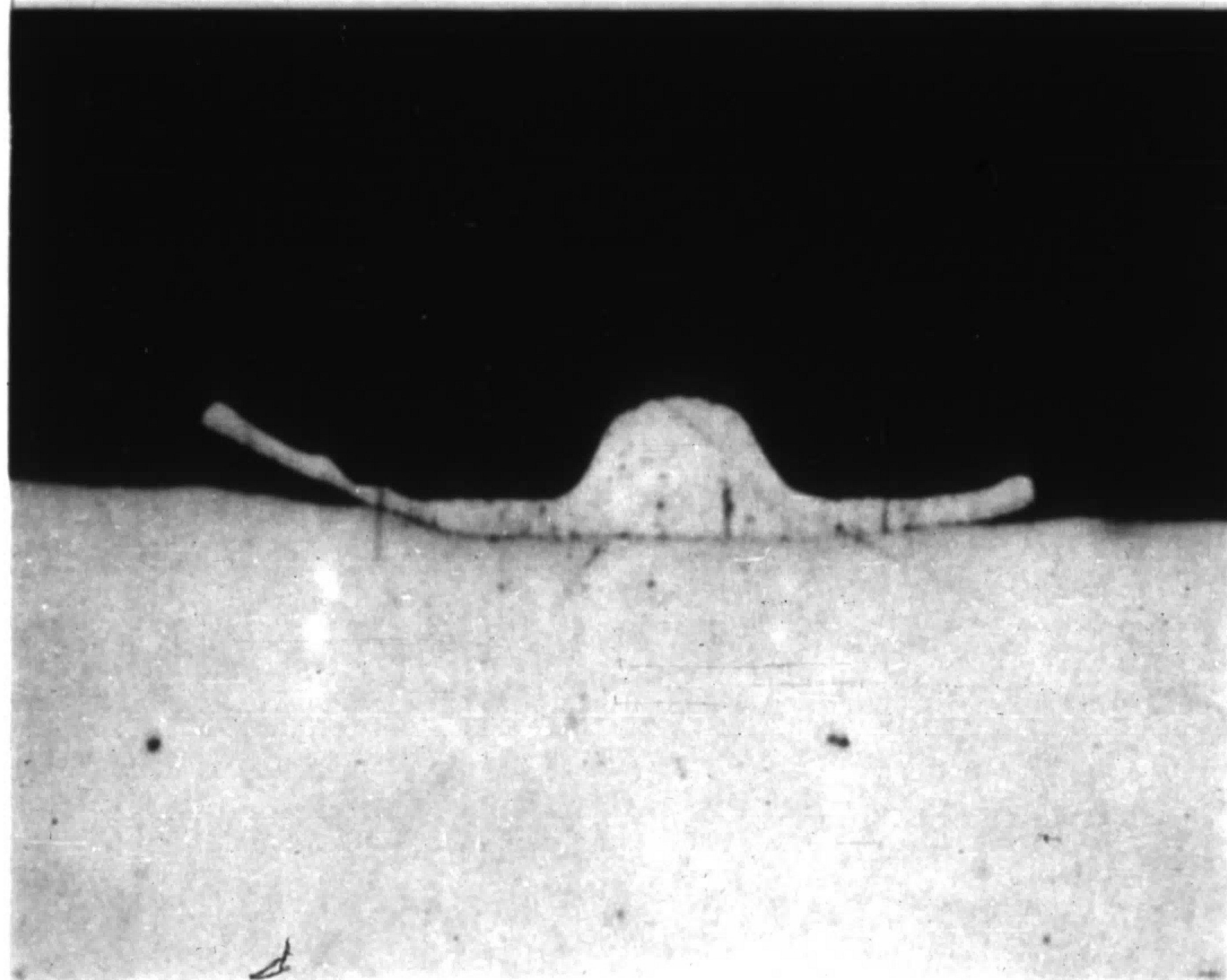


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FIGURE 13

BOND CROSS SECTION IN WHICH THE ACTUAL AREA IS MUCH LESS THAN THE APPARENT AREA.

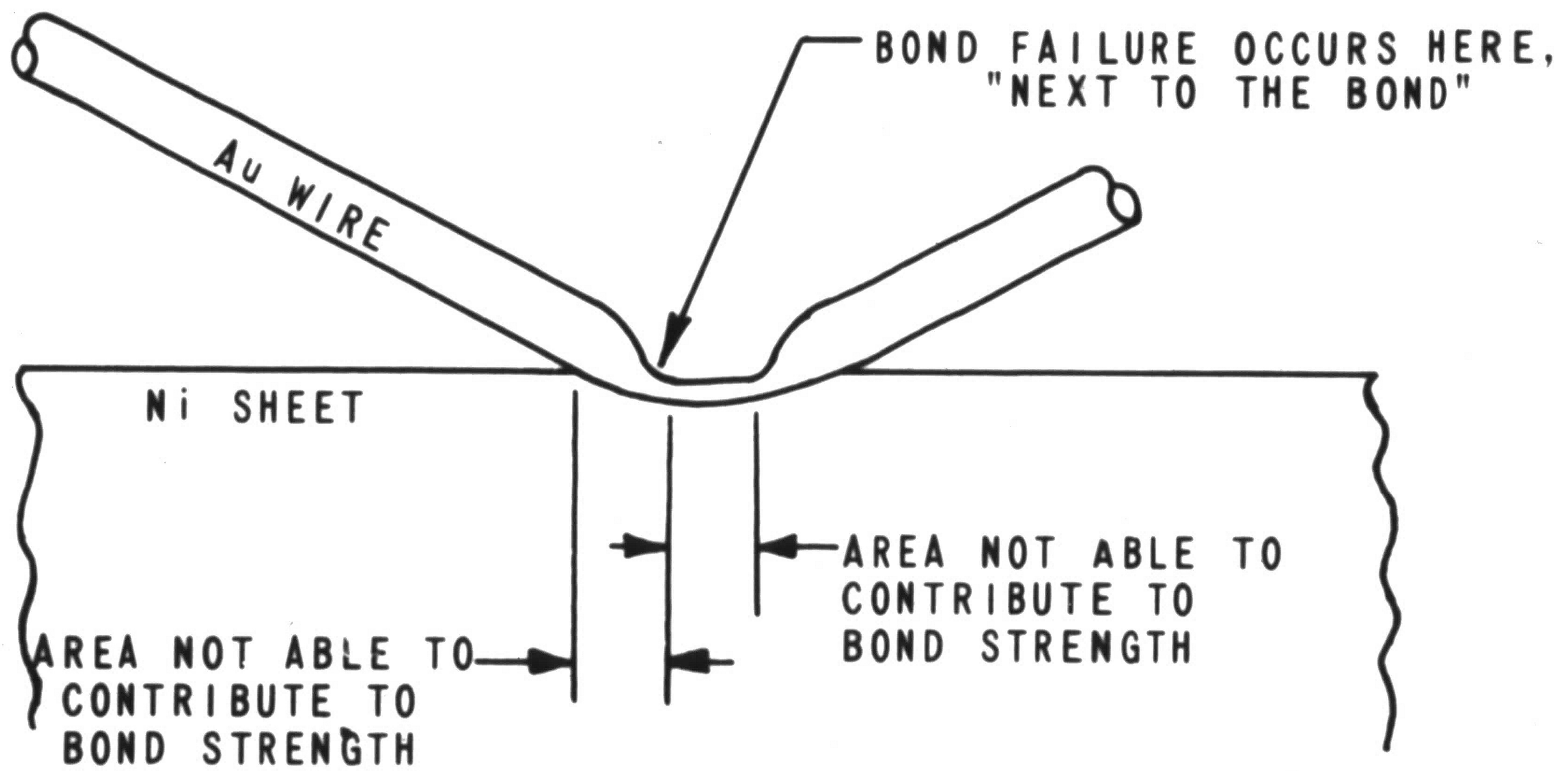

FIGURE 14
LONGITUDINAL VIEW OF BOND

8) was obviously much greater than the actual interface area and thus much area was unable to contribute to the bond strength. Figure 14 is a longitudinal sketch of a bond which has been bonded with a large force. Much of the area is unable to contribute to bond strength, so the strength of the bond is determined by only the contributing area. It appears then that as the bonding force was increased, the gold wire was further flattened and pressed into the nickel sheet, but the contributing area remained constant, thus maintaining the pull strength constant for the high bonding forces.

The point of this discussion has been to demonstrate the importance of the contributing interface area, but also very important was the strength per unit interface area. The strength per unit interface area was dependent upon the nature of the adhesion across the interface and the adhesion was greatly affected by the bonding temperature, as will be considered subsequently.

NOTABLE BONDING PHENOMENA

The first interesting phenomena were several characteristics associated with low temperature bonding. Defining low temperature bonding as bonding performed below 400°C, it may be observed in Figure 10 that both the bonding force and bond pull strength vary greatly. These characteristics may be stated more explicitly as:

(1) between 300° to 400°C the pull strength increased rapidly,

(2) as the temperature was lowered below 320°C the force necessary to produce a bond increased greatly.

Both of these will be considered later in the section entitled "Low Temperature Bonding."

The most unusual and unexpected phenomena were those associated with bonding of gold on the nickel oxide; of particular interest was the mechanism responsible for the strong adherence of the gold to the nickel oxide. Since there was no apparent explanation for the adherence and it is believed that such an adherence has not been reported before, many additional experiments were conducted in an effort to better understand the gold bonding on the nickel oxide, and these will be described in the following section.

BONDING ON THE NICKEL OXIDE

At temperatures above 440°C the formation of a visible oxide was observed on the nickel sheet. Above 480°C and at low bonding forces (below 30 grams) the bonds that formed had a very high electrical resistance. As indicated in Figure 10, for bonds formed under such conditions the electrical resistance was over 1000Ω; this was six orders of magnitude greater than the metal to metal spreading resistance and suggested that there was no metallic contact between the nickel and gold. Metallographic examination indicated that the gold was adhering to the nickel oxide and that the nickel oxide formed a continuous layer between the gold and the nickel. Figures 15 and 16 are photomicrographs of sections through gold bonds on the nickel oxide. At this bonding temperature of 570°C the nickel oxide was one to 1.5 microns thick. Dark field illumination outlines the oxide well in Figure 16, while, as a comparison, no oxide is evident in Figure 17, which was bonded at 400°C.

First it is interesting to examine how higher bonding forces were able to disrupt the nickel oxide to permit metal to metal contact. A large part of the literature dealing with solid state welding has been devoted to the discussion of this problem because the removal of oxides is one of the main requisites for adhesion. The conceptual mechanism which has received the most acclaim has been that which embodied the removal of oxides by tangential forces and shear strains at the interface. Careful observation in this

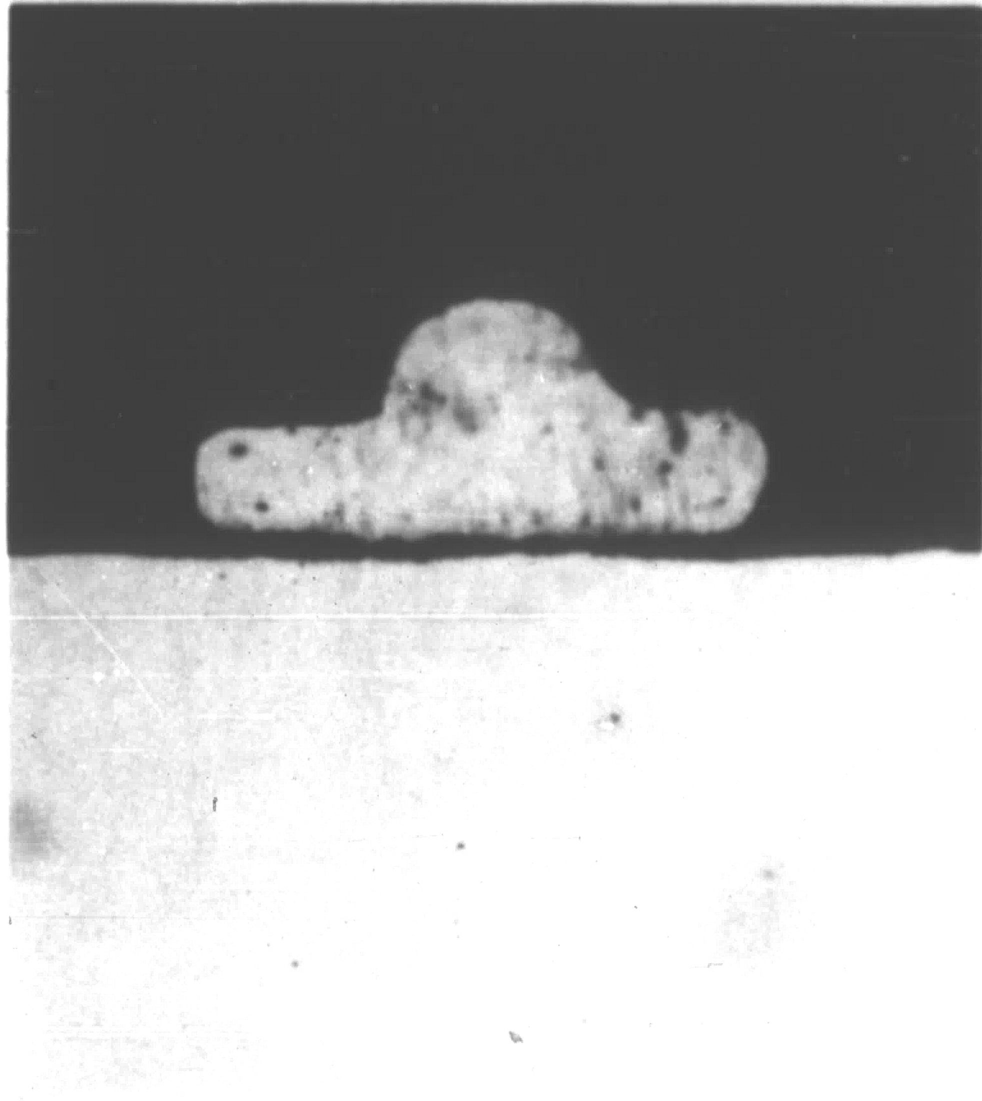

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FIGURE 15

BRIGHT FIELD

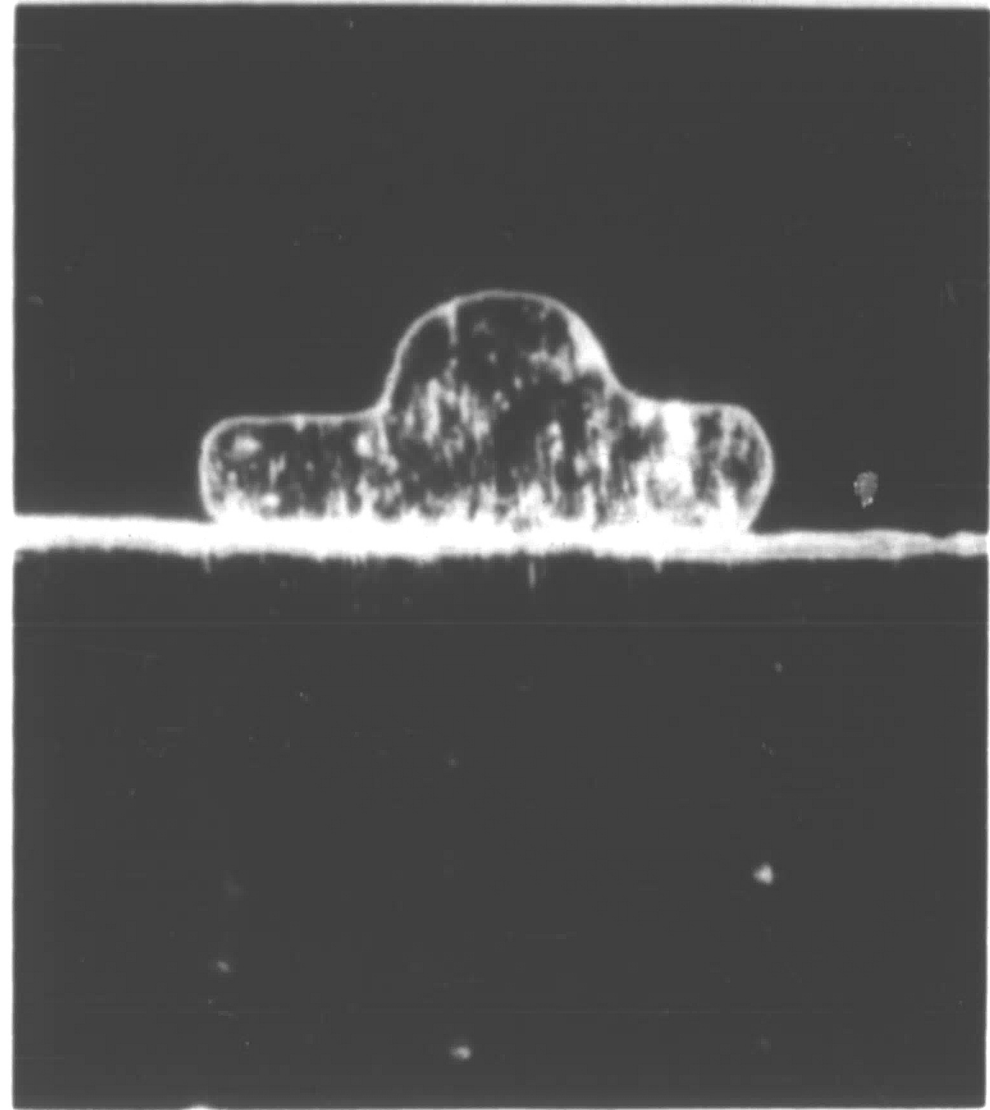

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FIGURE 16

DARK FIELD

GOLD BONDS ON NICKEL OXIDE. SAMPLE BONDED AT 25 GRAMS AT 570°C. THE OXIDE IS 1.0 TO 1.5 MICRONS THICK. THE HIGH ELECTRICAL RESISTANCE AND ALL METALLOGRAPHIC SECTIONS EXAMINED INDICATE THE PRESENCE OF A CONTINUOUS LAYER OF NiO BETWEEN THE GOLD AND NICKEL UNDER THESE BONDING CONDITIONS.

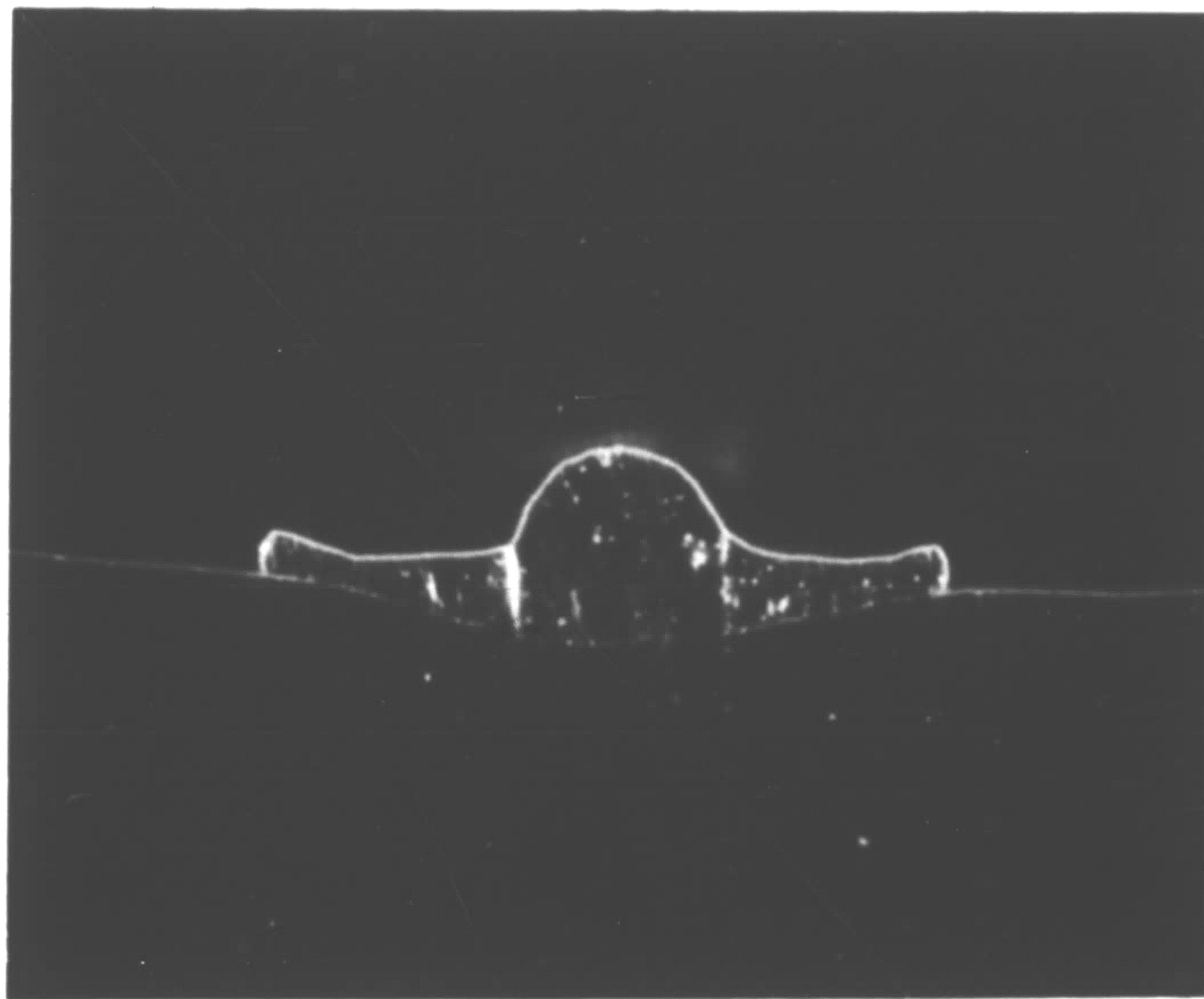

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FIGURE 17

DARK FIELD PHOTO-MICROGRAPH OF BOND CROSS SECTION SHOWING NO OXIDE. BONDED AT 100 GRAMS AT 400°C.

experiment of gold bonds as they broke through the nickel oxide has indicated that another factor in addition to shear strains was vital to effect removal of oxides.

BONDS THAT BREAK THROUGH THE OXIDE

Returning to the high temperature side of Figure 10, it may be observed that at bonding forces greater than 30 grams the electrical resistance decreased from its high value; at still larger bonding forces, bonds were produced with a much lower electrical resistance, approaching that of the spreading resistance. Typical electrical resistance data for bonds made at 570°C is presented in Table IV. A resistance change such as this was produced by first just breaking through the oxide and then achieving metallic contact over much of the bond area.

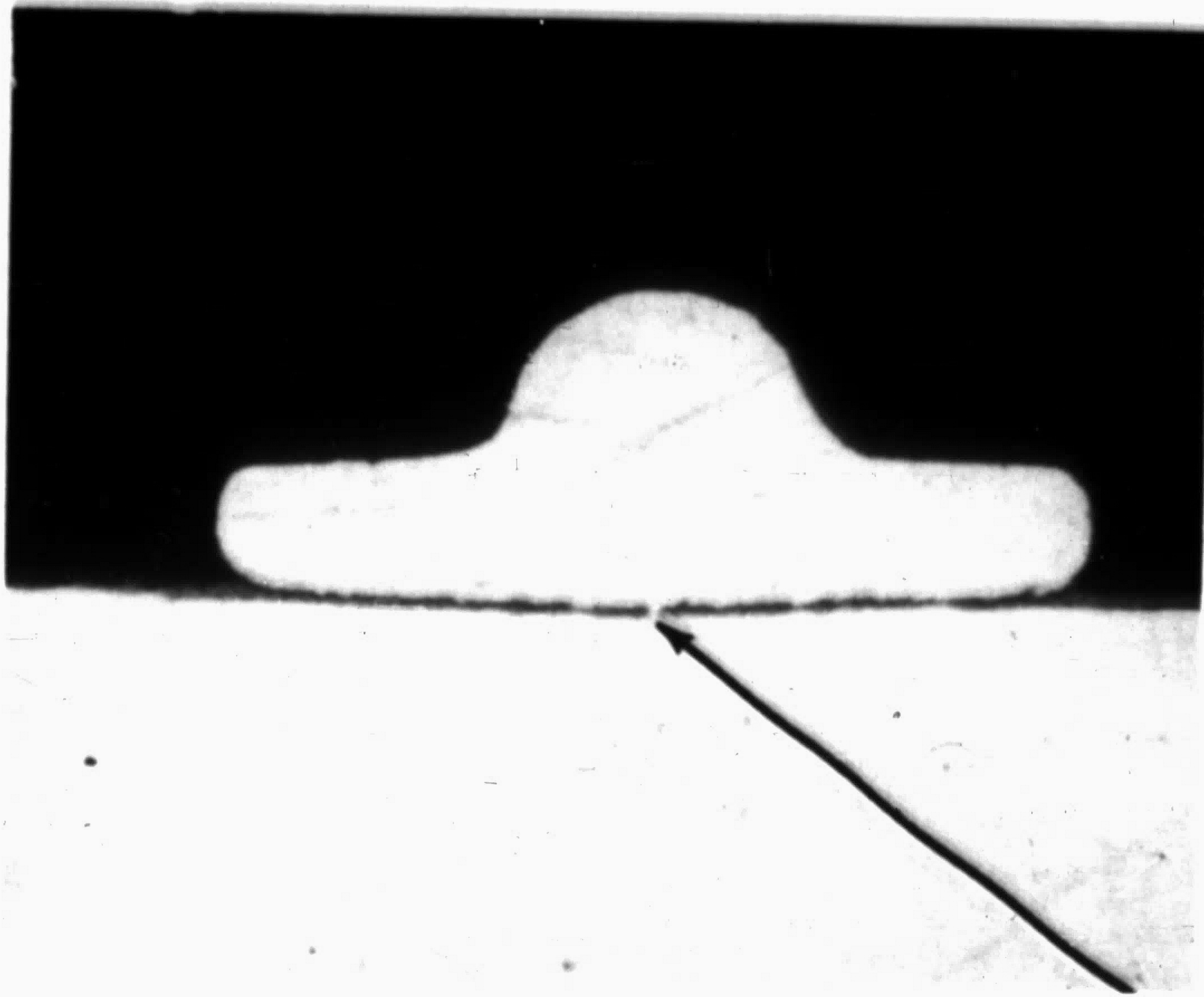
To accomplish this, it appears that the nickel surface must have been indented so that its surface area was increased and this disrupted the continuous oxide layer. The nickel oxide has such low ductility that when the surface area of the nickel was increased very slightly, the nickel oxide was unable to maintain a continuous layer. Fractures, which have a total area equal to the increased nickel surface area, then resulted in the oxide and permitted metallic contact. Photomicrographs of this process in bonds produced at 35 grams at 570°C are shown in Figures 18 and 19. Very slight indentations have increased the nickel surface area sufficiently to achieve very fine metallic contact. The indentation, especially in Figure 19, can best be observed by holding a straight edge along the

TABLE IV

ELECTRICAL RESISTANCE--OHMS

BONDED AT 570°C

30 GRAMS	40 GRAMS	60 GRAMS	80 GRAMS
> 1000 Ω	0.83 Ω	0.031 Ω	0.0052 Ω
"	22	0.035	0.0037
"	3.3	0.023	0.0034
"	1.4	0.76	0.0032
"	25.	0.068	0.0025
0.9	3.2	2.4	0.0045
> 1000	1.25	0.078	0.0018
"	3.3	12.	0.0076
	40.	0.32	0.0019
0.12	10.	0.11	0.0058



1400X

FIGURE 18

OXIDE BREAK UP BY SURFACE AREA INCREASE. BONDED AT 35 GRAMS AT 570°C. ONE METALLIC BREAK THROUGH THE NICKEL OXIDE IS EVIDENT.

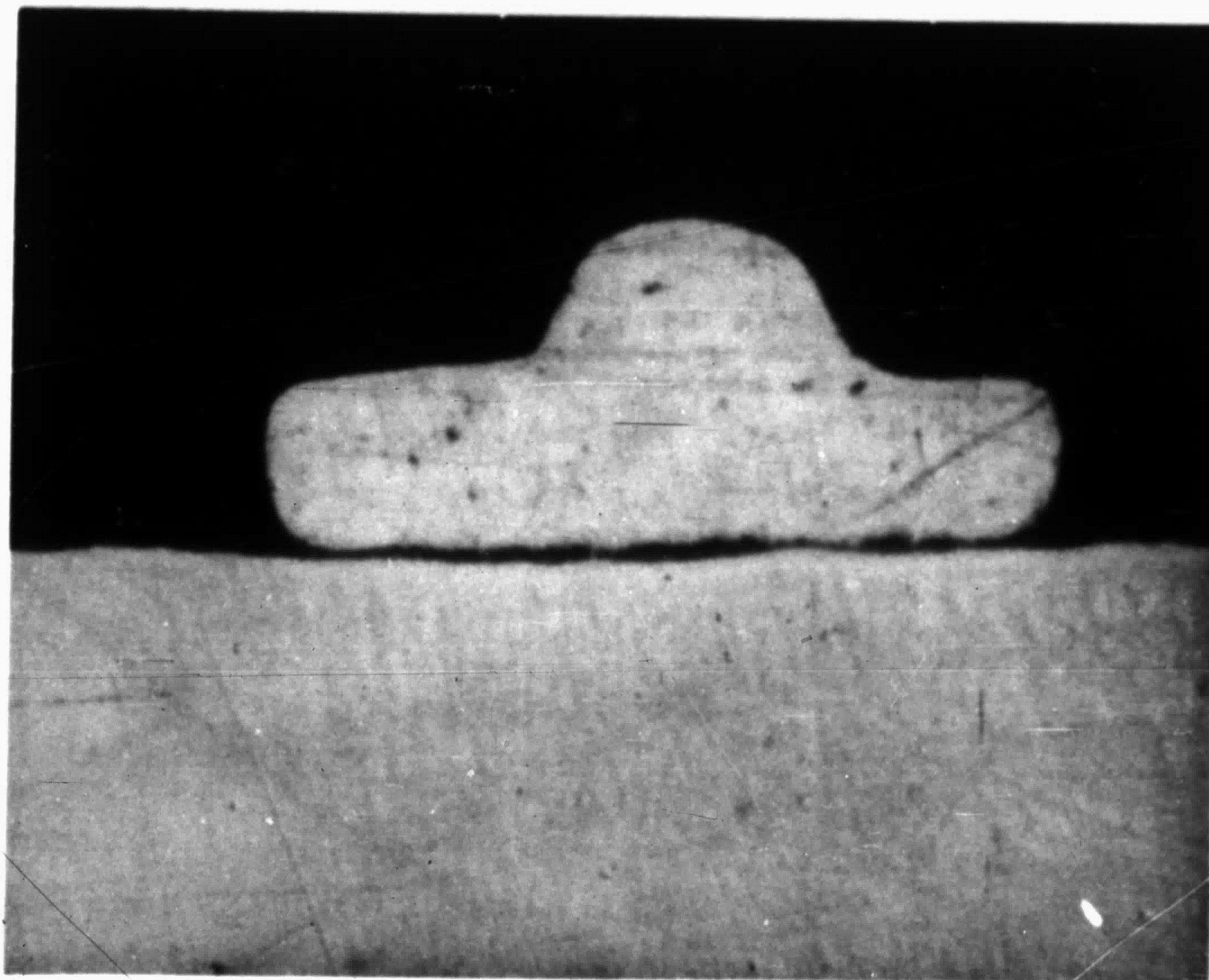


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FIGURE 19

OXIDE BREAK UP BY SURFACE AREA INCREASE. BONDED AT 45 GRAMS AT 570°C. A SLIGHT INDENTATION OF THE NICKEL MAY BE OBSERVED BY HOLDING A STRAIGHT-EDGE ALONG THE NICKEL SHEET.

nickel surface.

At larger bonding forces the nickel oxide became more fractured and irregular as shown in Figures 20 and 21, and apparently at this stage shear strains were able to scrape the oxide from large areas. Larger bonding forces have produced more indentation of the nickel and the resulting fracture of the oxide; and in addition the larger forces have deformed the gold more, producing shearing action which dispersed the fractured oxide to permit more metallic contact.

It is concluded that shearing action alone was unable to effect oxide removal; the bonds in Figures 18 and 19 certainly experienced shearing action, but metallographic inspection and the electrical resistance indicated that metallic contact occurred first only by the indentation process. In fact, only in bonds formed at 80 grams or more was there evidence that shearing action had been effective in removing the oxide as in Figure 21.

OXIDE BONDING MECHANISM

Without a doubt the most unusual and unexpected phenomenon encountered in this investigation was the adherence of the gold to the nickel oxide, and it definitely required an explanation. The gold to nickel adhesion was not expected, and it is a well accepted requisite for solid state welding that oxides and contaminants must first be removed. As described previously, the electrical resistance and metallographic examination definitely dictate that gold to nickel oxide adhesion occurred at low bonding forces and high temperatures (above 480°C and below 30 grams bonding force).

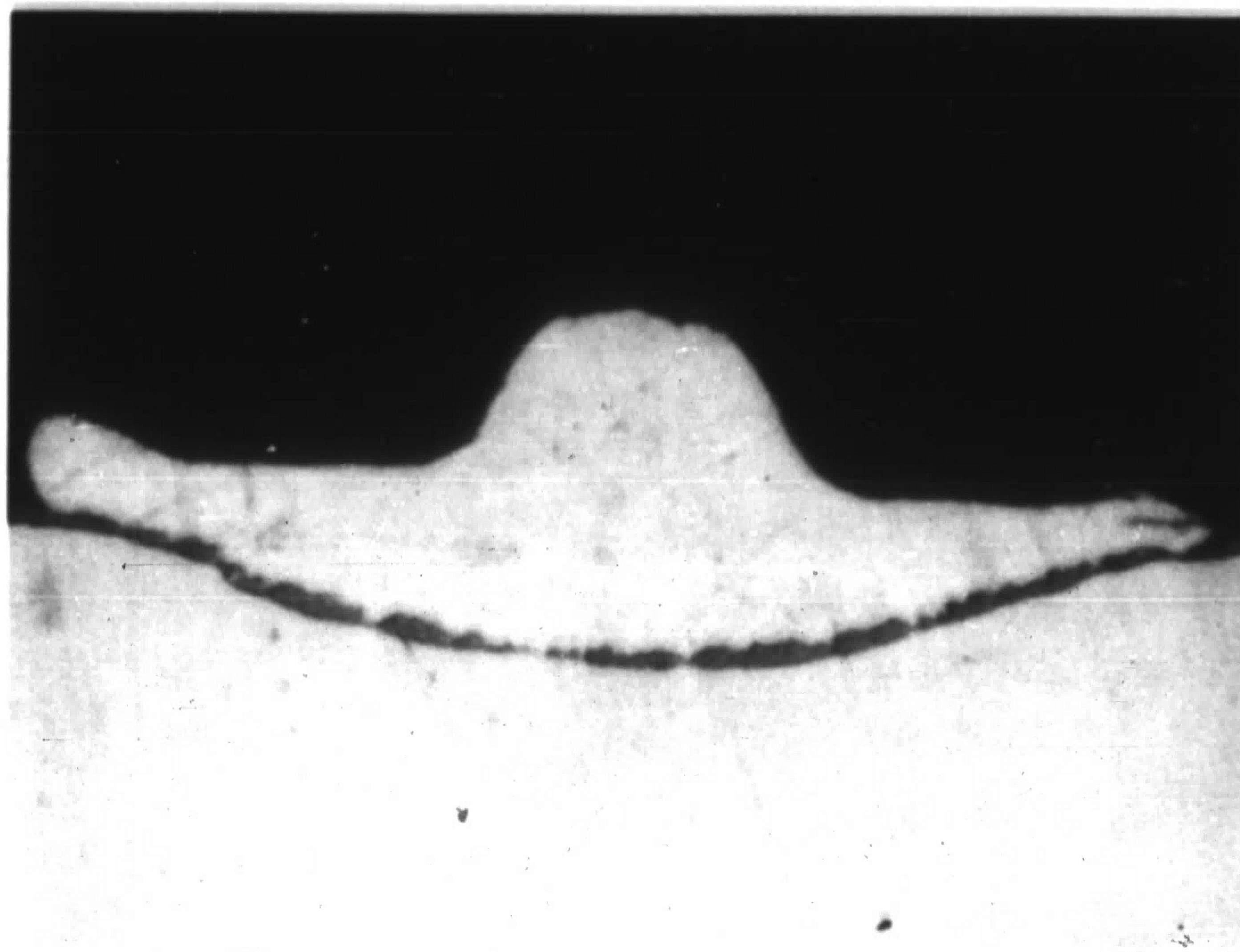

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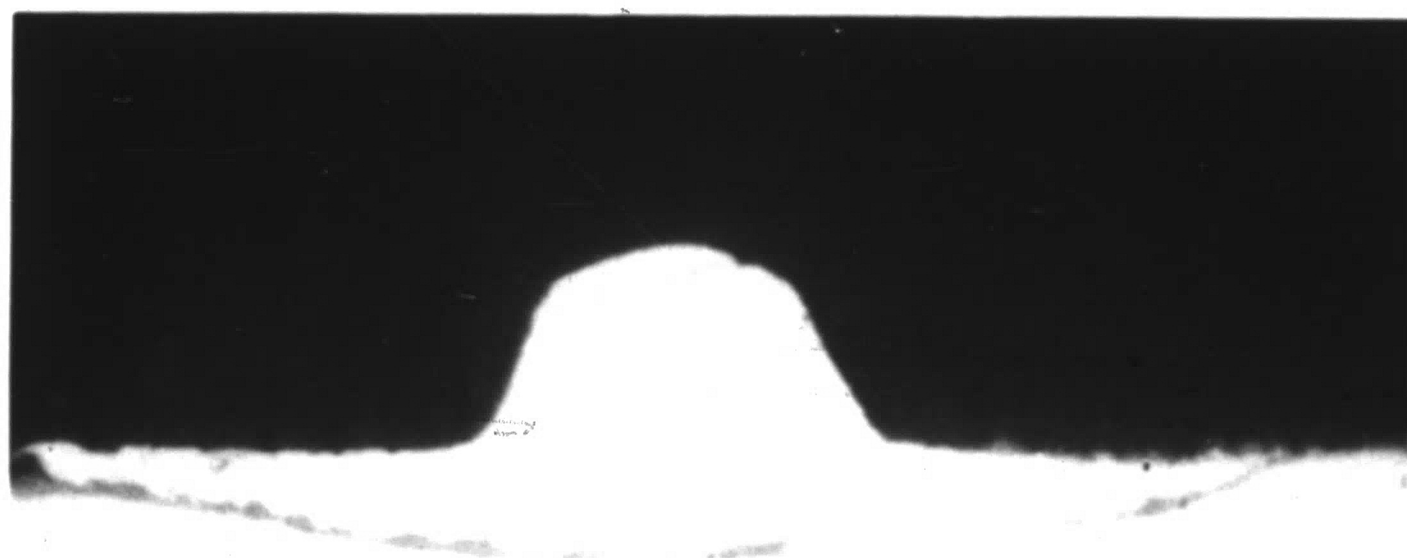
FIGURE 20

OXIDE BREAK UP BY SURFACE AREA INCREASE AND SHEARING ACTION. BONDED AT 100 GRAMS AT 570°C.



1400X

FIGURE 21

LARGE AREA OXIDE REMOVAL BY SHEARING ACTION. BONDED AT 100 GRAMS AT 570°C. ON THE RIGHT SIDE OF THIS SECTION THERE IS MUCH METALLIC CONTACT. APPARENTLY AFTER THE OXIDE WAS FRACTURED THE SHEARING ACTION OF THE FLOWING GOLD WAS ABLE TO SCRAPE THE OXIDE FROM A LARGE AREA TO PERMIT METALLIC CONTACT.

In addition the adhesive force per unit interface area was very high as evidenced by the high bond strength at low bonding forces, i.e., greater than 3.5 grams pull strength at 10 grams bonding force at 570°C for which the bond interfacial area was even less than that in Figures 15 and 16.

INITIAL POSSIBLE EXPLANATIONS: The first possible explanation considered was that the gold was adhering to metallic nickel in the nickel oxide; this was not likely because the bond strength would not be so high and nickel oxide is a metal deficit oxide, so there would not be any metallic nickel.[22] The second explanation considered was that possibly a rough surface on the oxide provided a mechanical bond. The surface roughness and surface profile were measured using a Model 3 Talysurf surface measuring instrument. This instrument which was manufactured by Taylor-Hobson employed a stylus with a radius of 0.0001". The average surface finish was found to be seven microinches and Figure 22 is a typical oxide surface profile. It appears that the vertical amplitude of the surface variations was too small and the horizontal spacing between the variations was too large to provide appreciable mechanical bonding. However, if a smaller diameter stylus had been available it might have revealed surface variations which could have contributed to bond strength. The third consideration was that the gold to nickel oxide bonding was due to some mechanism that was dependent upon temperature, such as a reaction or diffusion. This possibility proved to be a fruitful avenue of investigation as described below.

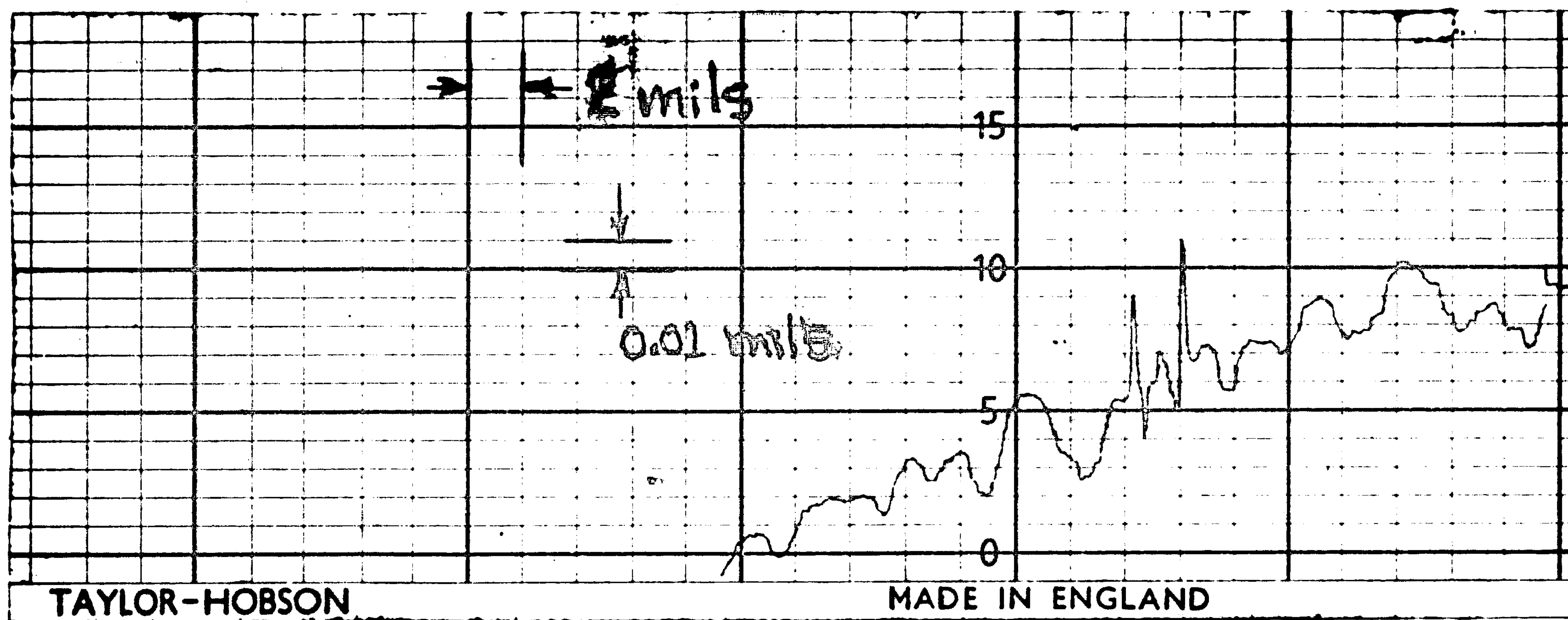


FIGURE 22

TALYSURF MEASUREMENT OF THE NICKEL OXIDE SURFACE. STYLUS RADIUS WAS 0.0001". AVERAGE SURFACE FINISH IS 7 MICRO-INCHES. EXAMINING THE SURFACE FOR POSSIBLE MECHANICAL BONDING, IT IS SEEN THAT THE WIDTH OF THE VARIATIONS IS 2.5 MILLI-INCHES, WHICH IS TOO WIDE TO PROVIDE MECHANICAL LOCKING. IN ADDITION THE HEIGHT OF THE SURFACE VARIATIONS IS ONLY 1/50 OF THE DIAMETER OF THE GOLD WIRE. A SMALLER STYLUS MIGHT REVEAL A LARGER VARIATION ON A SMALLER WAVE LENGTH.

IT IS INTERESTING TO NOTE THAT THE WIDTH OF THE VARIATIONS, (2.5 MILLI-INCHES) IS EQUIVALENT TO THE AVERAGE DIAMETER OF THE NICKEL GRAINS (ASTM NO. 4-5). THIS INDICATES THAT OXIDATION IS AFFECTED BY GRAIN ORIENTATION.

OXIDE BONDING EXPERIMENTS: To determine if the adherence between gold and nickel oxide was dependent upon temperature, the bonding of gold on nickel oxide at lower temperatures was examined. Oxide was formed on nickel sheets by heating them for ten minutes at 570°C on the heat sink used for bonding so that the oxide was similar to that formed during normal bonding at 570°C. (Samples such as this will be referred to as "oxidized nickel sheets" throughout the rest of this paper.) Gold was then bonded to the oxidized nickel sheets at lower temperatures and the electrical resistance of the bonds was measured to indicate whether the bond was just to the oxide, or whether it was also breaking through the oxide. It was found that below 360°C it was impossible to effect bonding without breaking through the oxide. Thus the oxide adherence was quite temperature dependent and was not operative at lower temperatures. This also further discredited the possibility of surface roughness adherence.

It then seemed reasonable to heat treat the low temperature oxide bonds at higher temperatures. Gold was bonded at 40 grams at 380°C on a large number of oxidized nickel sheets and then the electrical resistance of every bond was measured to assure that the bonds had not broken through the nickel oxide. These oxide bonds were then heat treated at 450°C, 500°C, and 570°C for times from five seconds to two hours, after which the bond pull strength was measured. The initial pull strength before heat treatment was just under one gram and the pull strength after the heat treatments is presented in Figure 23. These results of pull strength increase as

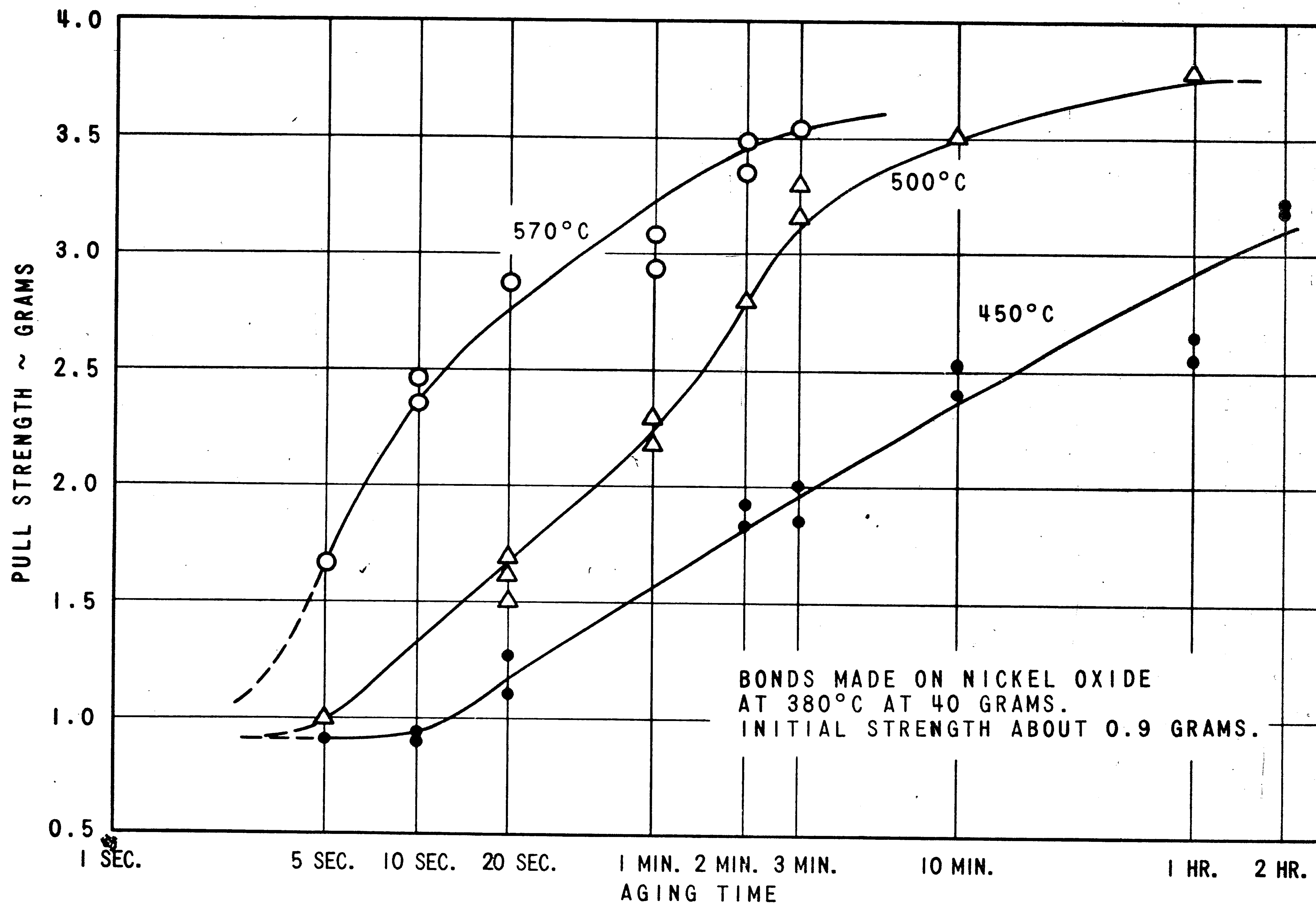


FIGURE 23 - HEAT TREATMENT OF LOW TEMPERATURE OXIDE BONDS

a function of time and temperature of heat treatment suggested that the oxide adherence mechanism was dependent upon diffusion.

Difficulty was encountered with this experiment because of the low strength of the low temperature oxide bonds. Many bonds failed and some were undoubtedly damaged during handling and initial electrical tests; this increased the variation in the pull strength results after heat treatment. It would have been advantageous to have produced the bonds on oxidized nickel sheet at 400°C rather than 380°C so as to attain an initial strength of 1.5 grams rather than 0.9 grams; however, there would then be less possible strength increase to measure after heat treatment. To determine accurately the effect of heat treatment it would be necessary to design an experiment with a large number of samples and considerable redundancy.

It was noticed after the longer time heat treatments that the electrical resistance had decreased from its initial high level. This was more carefully examined with samples bonded at 40 grams at 380°C on oxidized nickel sheet and then heat treated at 570°C. The electrical resistance results measured after successive heat treatments at 570°C for two samples are presented in Table V. Comparing Figure 23 with Table V, it is apparent that the electrical resistance decrease occurred after the oxide bond had attained full strength. In other words, for bonds produced at 40 grams at 380°C on oxidized nickel sheet and then heat treated at 570°C, only a time of three minutes was required to achieve the maximum possible bond strength (which in essence was the gold wire strength), while

TABLE V

ELECTRICAL RESISTANCE OF HEAT TREATED OXIDE BONDS

(Ni SHEETS OXIDIZED 10 MIN. @ 570°C; BONDED 40 GRAMS @ 380°C)

	AS BONDED	TIME OF HEAT TREATMENT AT 570°C						
		5 SEC	25 SEC	80 SEC	4.5 MIN	15 MIN	45 MIN	1.75 HR.
SAMPLE NO. 1	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω	150	36
	"	"	"	"	"	"	>1000Ω	12.5
	"	"	"	"	"	"	19	8.5
	"	"	"	"	"	"	78	38
	1	46	"	"	"	"	>1000Ω	9.1
	>1000Ω	>1000Ω	"	"	"	"	74	10
	"	"	"	"	"	"	60	52
	"	"	"	"	"	"	>1000Ω	>1000Ω
	"	"	"	"	"	140	"	14
	"	"	"	"	"	135	33	14
	"	"	"	"	"	>1000Ω	130	2.2
SAMPLE NO. 2	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω	NO TEST	3.4
	"	"	"	"	"	7.2		2.7
	"	"	"	"	"	>1000Ω		19
	"	"	"	"	"	"		7.4
	"	"	"	"	"	2.25		0.92
	8.4	11.0	110	14	31	67		7.5
	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω	>1000Ω		>1000Ω
	"	"	"	"	"	"		"
	"	"	"	"	"	"		4.2
	"	"	"	"	"	"		3.2

a time of 45 minutes was required to effect conductivity. (Also it was qualitatively observed that the electrical resistance decrease was affected by the apparent oxide thickness, while the strength increase was independent.) Therefore it was not necessary that the attainment of adherence strength and electrical conduction occur at the same time, but it was likely that the same mechanism was responsible for effecting both the bond strength and the increased conductivity.

SUGGESTED OXIDE BONDING MECHAMISM: The suggested mechanism of adherence between the gold and nickel oxide was the diffusion of fine paths of gold into the nickel oxide. The bond strength resulted from the mechanical interlocking of the very fine paths of gold in the oxide and growth of these paths for only a short distance into the nickel oxide was required to effect bond strength. The electrical resistance decreased after a very fine but continuous path of gold had formed from the gold to the nickel.

Considering in more detail the nature of the diffusion, it appears that the diffusion of the gold in the nickel oxide was not substitutional diffusion, because this could not have accounted for the relatively large values of conductivity which the oxide bonds exhibited after heat treatment. In order for substitutional diffusion to occur the gold atoms would have had to ionize and then substitute for the nickel ions on the nickel oxide lattice, and such a solid solution of gold and nickel oxide would still have been an insulator. The possibility of gold diffusing interstitially in the nickel oxide was very unlikely also, because of the size of the

available interstitial voids. For interstitial diffusion the gold atom would have had to fit into the tetrahedral interstitial voids in the nickel oxide and the calculations in Appendix VII indicate that the tetrahedral voids in nickel oxide can only accommodate an atom with a radius of 0.410Å while the radius of the gold atom is 1.433Å. Therefore since substitutional and interstitial diffusion were unlikely, the gold must have diffused along the surface of the voids, fractures, and blisters in the nickel oxide. Probably there was little true atomic adherence between the gold and the nickel oxide except for van der Waals forces. Rather, the adherence of the gold bond to the oxide was due to the physical interlocking of the gold paths with the nickel oxide.

The first continuous and conducting paths of gold through the oxide were about one micron in length since this was the thickness of the nickel oxide at 570°C, as shown previously in Figures 15 and 16. The resistance of such a bond with a fine conducting path between the gold and nickel was dependent upon the resistance along the path rather than upon the spreading resistance. For example, consider a gold path one micron in length by 55Å in diameter, the path resistance is given by

$$R_p = \frac{\ell \rho_{Au}}{\text{Area}}$$

$$R_p = \frac{(2.35\times10^{-6}\,\Omega\text{-cm})(1\times10^{-4}\,\text{cm})}{\frac{1}{4}\,\pi\,(55\times10^{-8})^2}$$

$$R_p = 988\Omega.$$

While the spreading resistance is

$$R_s = \frac{\rho_{Au} + \rho_{Ni}}{4a}$$

$$R_s = \frac{9.19 \times 10^{-6} \Omega\text{-cm}}{4(27.5 \times 10^{-8} \text{cm})}$$

$$R_s = 8.36\Omega.$$

For a path diameter of 6500Å, or 0.65 micron, the path resistance and spreading resistance were nearly equal at 0.0706Ω. It therefore seems reasonable in this experiment that the electrical resistance was a sensitive indicator of the gold path through nickel oxide. When, during the heat treatment of the oxide bonds, the resistance dropped below 1000Ω, a continuous gold path had just formed, and then any observed resistance below this was indicative of the total area of the gold path or paths; i.e., a resistance of 0.14Ω indicated that the effective diameter of the gold paths was nearly two-thirds of a micron. It is interesting to note in this experiment that when the resistance did drop below 1000Ω, it was always to a value below 300Ω; this suggests that the minimum size of gold path that was capable of formation was over 100Å in diameter.

DIFFUSION RATE OF THE GOLD THROUGH THE NICKEL OXIDE: An estimate of the diffusion coefficient has been made from the effect of the heat treatment upon the pull strength and electrical resistance of the low temperature bonds on the oxidized nickel sheet. But this estimate is indefinite because not enough parameters are known about the diffusion to supply meaningful dimensions to the diffusion

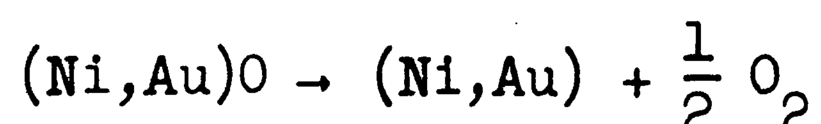
coefficients. Unfortunately the diffusion distances were too small for analysis by even the electron microprobe. Metallographic inspection of high temperature diffusion couples (800°C) indicated that a one micron layer of nickel oxide did present a barrier to the diffusion of the gold into the nickel. From a comparison of gold to nickel couples with and without the nickel oxide layer in between, it appeared at 800°C that the diffusivity of the gold through the nickel oxide was about one-half of that of gold through nickel. Certainly much more investigation of the gold diffusion in nickel oxide is necessary before this process may be satisfactorily understood.

ADDITIONAL POSSIBLE BONDING MECHANISMS: A bonding mechanism based upon gold oxide entering into solid solution with the nickel oxide would account for the remarkable adherence between the gold and nickel oxide. However, as implied before this mechanism was not likely because it cannot account for the conductivity. Also, ionization of the gold seems unlikely because of the properties of Au_2O_3 as outlined in Appendix II. Furthermore, the gold cations are quite large to substitute for nickel cations; the ionic radii are:[20]

$$Ni^{+2} = 0.69\text{Å}$$
$$Au^{+3} = 0.85\text{Å}$$
$$Au^{+1} = 1.37\text{Å}.$$

This last factor is meaningful because the nickel cations completely fill their sites in the nickel oxide lattice.

All the observed oxide bonding phenomena could be explained by an adherence mechanism which embodied the reduction of the nickel oxide. In such a process the gold might have entered into substitutional solution in the nickel oxide which would have then forced the reaction below to the right.



$$(Ni,Au)O \rightarrow (Ni,Au) + \frac{1}{2} O_2$$

Possibly this reaction could be observed metallographically if large gold to nickel oxide couples were heat treated for very long times. Either of these mechanisms which involve solid solution of gold and nickel oxides is less credible when it is considered in conjunction with the description of Kubaschewski and Hopkins concerning the oxidation of gold-nickel alloys.[22] Kubaschewski and Hopkins refer to the oxidation of noble, non-noble alloys as attack of only the non-noble metal, and describe the oxide that forms on gold-nickel alloys at 900°C as "a porous conglomerate of NiO and Au" (Ref. 22, page 124).

The theories of adhesion from other fields concerned with metal to non-metal adhesion were examined in a search for possible explanations of the gold to nickel oxide adhesion. In particular the fields of ceramic to metal and glass to metal adhesion were considered. Briefly stated, the theories for ceramic to metal adhesion either require a chemical reaction between the ceramic and metal, or require adherence between the glass contained in the ceramic and the metal.[23] In glass to metal adhesion the standard theories require the metal to be oxidized.[24] The metal oxide must

then partially dissolve in the glass for adherence, and it has been accepted that the adherence of the noble metals is not good because of the lack of oxides.[25] However, recent work by Pask and Fulrath[25] has shown that there can be some adherence between glass and platinum and gold, and it was suggested that it was due to the absorbed oxygen in the metal surface dissolving in the glass. It is possible then that the adherence between the gold and nickel oxide might have been aided by attraction between the absorbed oxygen in the gold and the nickel oxide (as well as van der Waals forces); however, it still appears that mechanical locking of many fine paths of gold in the oxide was the prime mechanism contributing to bond strength.

The experimental method employed in this study was not suited for extensive examination of gold diffusion in, or reaction with, the nickel oxide. A larger diffusion couple should have been employed -- especially a thicker layer of nickel oxide -- so that electron microprobe and diffraction techniques could have been used. Also very long heat treatments with subsequent metallographic examination would have proved fruitful.

PREFERENTIAL OXIDATION

During the bonding at high temperatures, it was noticed that some grain orientations did not oxidize and therefore permitted metallic bonding at low bonding forces. This preferential oxidation was also apparent from the Talysurf profile of the oxide surface in Figure 22. The preferential oxidation was noticeable after the onset of oxidation at 440°C and below 570°C; above 570°C, all grains had

formed an appreciable oxide. It was also observed that the cleaning procedure greatly affected the oxidation. Therefore, if high temperature metallic bonding were required, preferred orientation of the nickel and proper cleaning would be advantageous.

LOW TEMPERATURE BONDING

As described previously there was a great variation in pull strength and bonding force in the temperature range between 200°C and 400°C. In Figure 10 this variation may be separated into two separate characteristics, namely, the high bonding force below 320°C and the bond strength increase between 300°C and 400°C. In attempting to understand these characteristics, an effort was made to first list and analyze the possible factors which might explain the phenomena and then to perform selective experiments to determine which factors were important.

POSSIBLE EXPLAINING FACTORS

The factors which seemed likely to be important were as follows:

(1) diffusion,

(2) annealing,

(3) break through and removal of nickel oxide,

(4) deformation of the gold,

(5) mechanical wedging of the gold in the nickel.

Microscopic diffusion certainly should be important because, to approach atomic spacing across the bond interface, atom movements are necessary. Annealing or lack of annealing out residual stresses which tend to separate the bond has been thoroughly accepted as important to solid state welding.[2,10,11,26] Removal of any nickel oxide is certainly important since gold does not bond to nickel

oxide at these temperatures. Based upon the previously described observations, one can be assured that the shearing action of the flowing gold will achieve oxide dispersal if the nickel surface has been indented. Therefore, the bonding force required to indent the nickel may be an important factor. Similarly, it is necessary that the gold deform sufficiently to provide adequate bond interface area. Finally, possible mechanical wedging must be considered, because at the high bonding forces the nickel was so greatly indented that the gold wire was pressed into the indentation.

HIGH BONDING FORCE BELOW 320°C

The force to indent the nickel, and thus initiate the removal of any nickel oxide, was examined first. This factor was not expected to be important because at these temperatures the thickness of the oxide was exceedingly slight and the electrical resistance data indicated that there was no difficulty achieving metallic contact.

FORCE TO INDENT THE NICKEL: The ability to indent the nickel during bonding was dependent upon the hardness of the nickel and therefore it was expected that the indentation properties of the nickel would not vary greatly with temperature. However, the following cursory test was performed. Using a Wilson 136° diamond indentor, the force necessary to produce a 0.0015" x 0.0015" square indentation in the nickel sheet was determined at four temperatures between room temperature and 600°C. The results are presented in Table VI and indicate that the force necessary to break through any nickel oxide film

TABLE VI

HARDNESS OF NICKEL SHEET

TEST TEMPERATURE	FORCE TO PRODUCE A 0.0015" X 0.0015" IDENTATION USING A WILSON 136° DIAMOND INDENTOR
25°C	55 GRAMS
200°C	51 GRAMS
460°C	43 GRAMS
600°C	41 GRAMS

certainly cannot explain the great bonding force increase below 320°C. This may be, however, an explanation for the slight bonding force increase in the temperature range down to 320°C.

FORCE TO DEFORM THE GOLD: The deformation of the gold wire as a function of bonding force is presented in Figure 24 for bonding temperatures of 240°C, 360°C, and 440°C. The bond widths were measured from the apparent width of actual bonds such as those photographed in Figure 25; the length of the bonds was constant at about 0.002", since it was determined by the bonding needle design. By comparing the bond widths at different temperatures it may be ascertained that the force to deform the gold accounted partially for the increased bonding force below 320°C, but not entirely. For example, at 360°C in Figure 10, the strongest bond occurred at a bonding force of 100 grams, which from Figure 24 was a bond width of 0.0025"; at 240°C a bonding force of 190 grams was required to produce this deformation, but in Figure 10, 190 grams was well below the lower limit of bonding. Therefore, more bonding force was required to produce a bond at 240°C than that just sufficient to produce adequate bond width. This conclusion is also verified by the electrical resistance curves in Figure 10. The electrical resistance was an excellent indication of the bond interface area and its variation with temperature definitely dictates that the force to deform the gold did not account for all the increased bonding force.

ADHESION STRENGTH PER UNIT AREA: Since there existed adequate bond

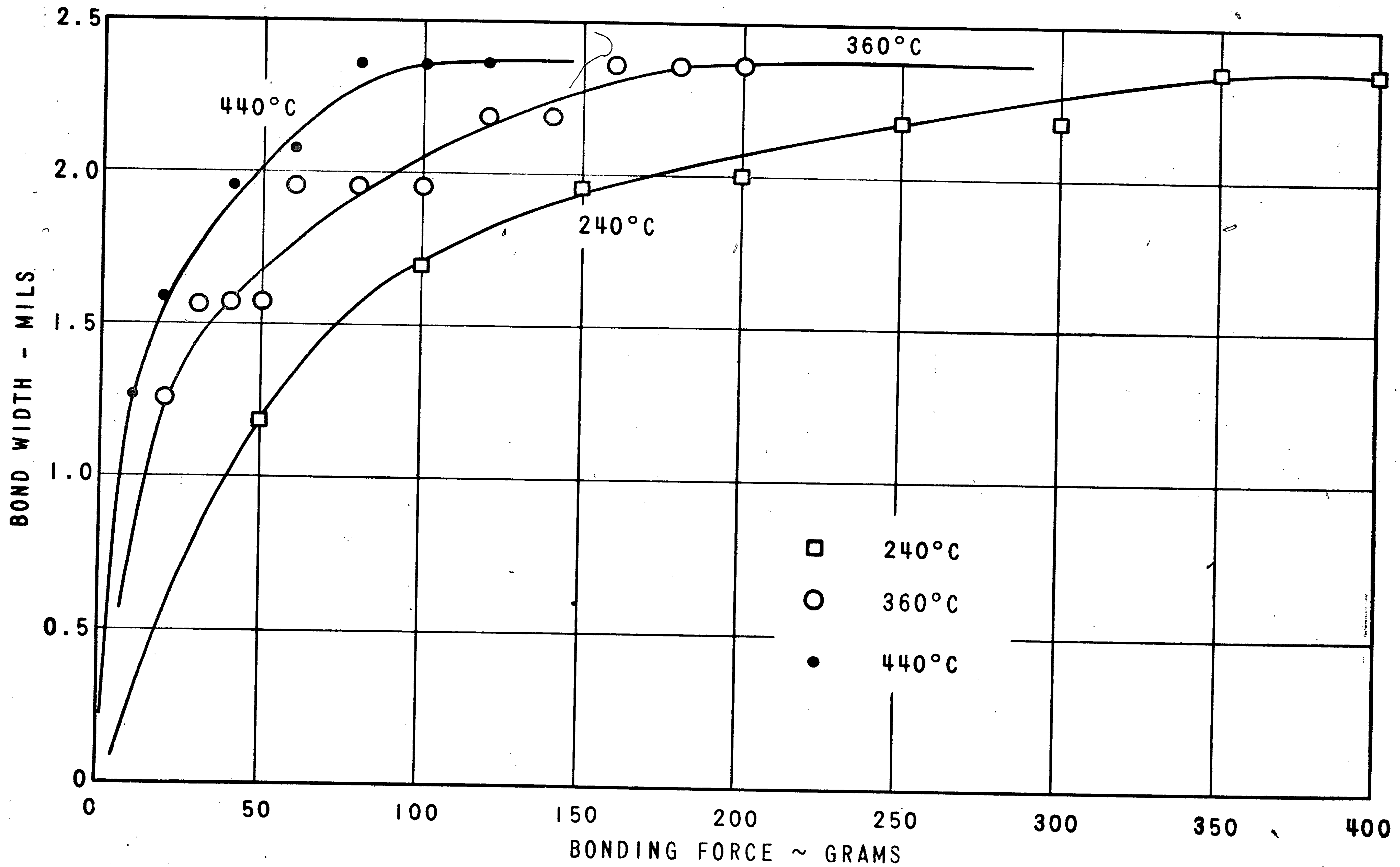
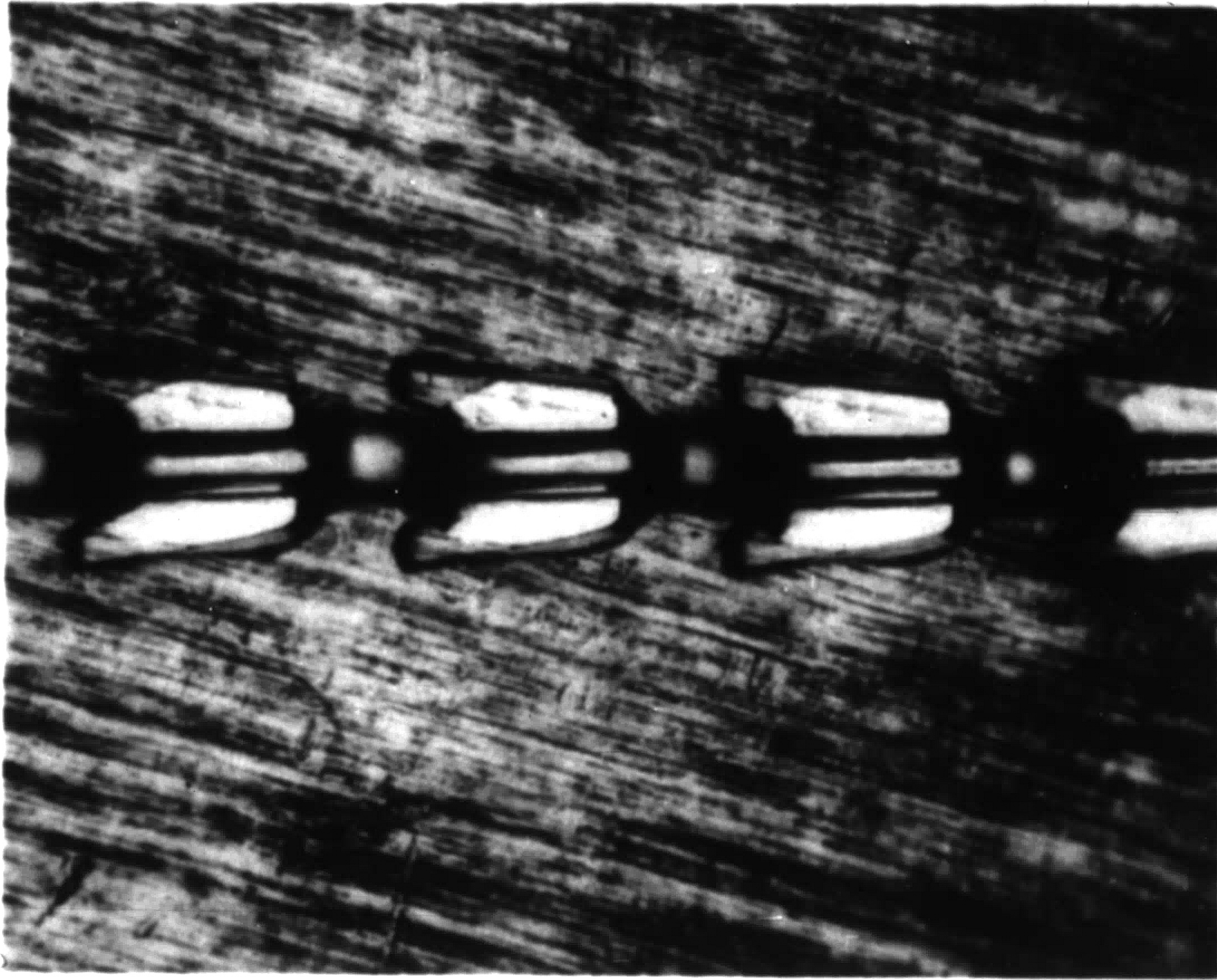


FIGURE 24 - FORCE TO DEFORM GOLD (BOND FORCE VS. BOND WIDTH)



200X

FIGURE 25

MECHANICAL WEDGING OF THE BOND INTO THE NICKEL SHEET. BONDED AT 350 GRAMS AT 240°C.

area and metallic contact, the poor bonding in the region below 320°C must have been due to a low value of the adhesion strength per unit bond interface area. The low adhesion strength per unit area was due to the following two factors:

(1) atomic bonds across the interface were weak because of insufficient atom movements,

(2) residual stresses tended to force apart the bond.

These two points will be considered in greater detail in the section "Bond strength increase between 300°C and 400°C". Because of the low adhesion per unit area in the range below 320°C, greater bonding force was required to produce larger bond area.

MECHANICAL LOCKING: As greater bonding forces were applied the possible effect of mechanical locking became more prominent. At large bonding forces the gold was pressed into the nickel sheet as shown in Figure 25 and this mechanical wedging probably contributed a small amount to bond strength. The force to produce mechanical locking depended upon the hardness of the nickel, which does not vary greatly between 200°C and 320°C; therefore it was determined from observation of bonds such as in Figure 25, that the onset of mechanical locking was about 250 grams throughout this temperature range. Consequently mechanical locking became significant below 240°C, since below this temperature the permissible bonding range was entirely above 250 grams force. Apparently then as the bonding temperature was decreased below 320°C, the adhesion strength continuously decreased, necessitating greater bonding force to produce

greater bond area. And then below 240°C the bond area reached a maximum (as indicated in Figure 24 and dictated by bonding needle size) so that the bond strength became increasingly dependent upon mechanical locking. Finally below 200°C bonding virtually ceased; here the total bond strength provided by adhesion and mechanical locking was less than that necessary for bond survival. Certainly then, the bond strength due to mechanical locking alone was less than one gram.

The upper bonding force limit existed in the temperature range below 320°C because the gold wire was severely flattened and nearly sheared as it was pressed into the nickel sheet. In accordance then with Figure 14, the area able to contribute to strength was small.

BOND STRENGTH INCREASE BETWEEN 300°C AND 400°C

The bond strength variation in this range was largely dependent upon the adhesion strength per unit area because the other possible factors affecting bond strength could not have been important. The bonding forces were below that at which mechanical locking became a factor. Adequate metallic contact area and break through any nickel oxide layer were easily achieved throughout the temperature range as indicated by the bond electrical resistance. Therefore the adhesion strength per unit area was primarily responsible for the bond strength variation between 300°C and 400°C.

As mentioned, the adhesion strength per unit area was dependent upon atomic bonds across the interface and residual stresses. The strength of the atomic bonds across the interface is a function of

atom position; therefore, atom mobility is necessary to achieve desirable positions which minimize gross lattice irregularities. Residual stresses tend to force apart the bond, so that reduction of residual stresses by annealing is important. Therefore, heat treatment of low temperature bonds at a higher temperature should improve the bond strength by both diffusion and annealing.

AGING EXPERIMENT: Bonds were formed at 200 grams at 280°C so that the initial pull strength of the bonds was 1.0 to 1.5 grams. These bonds were then heat treated five seconds to one and one-half hours at 360°C, 400°C, and 450°C. The pull strength after heat treatment is presented in Figure 26.

The heat treatment certainly improved the bond strength; however the question which then arises is which effect was the most important, annealing or diffusion. Annealing certainly is a logical choice since the strength increase occurred in the annealing temperature range of the gold and annealing has been demonstrated to be important to adhesion.[2,10,26] However, a more critical examination indicates that annealing could not have been too important in this aging experiment. In this experiment at the low bonding temperature (280°C), when the bonding force was released much of the elastic stress was released in separating the bond. Therefore, during subsequent heat treatment there would not have been as much residual stress to be annealed. Consequently, in this aging experiment diffusion had a major role in increasing the bond strength.

Although diffusion has been shown capable of increasing adhesion

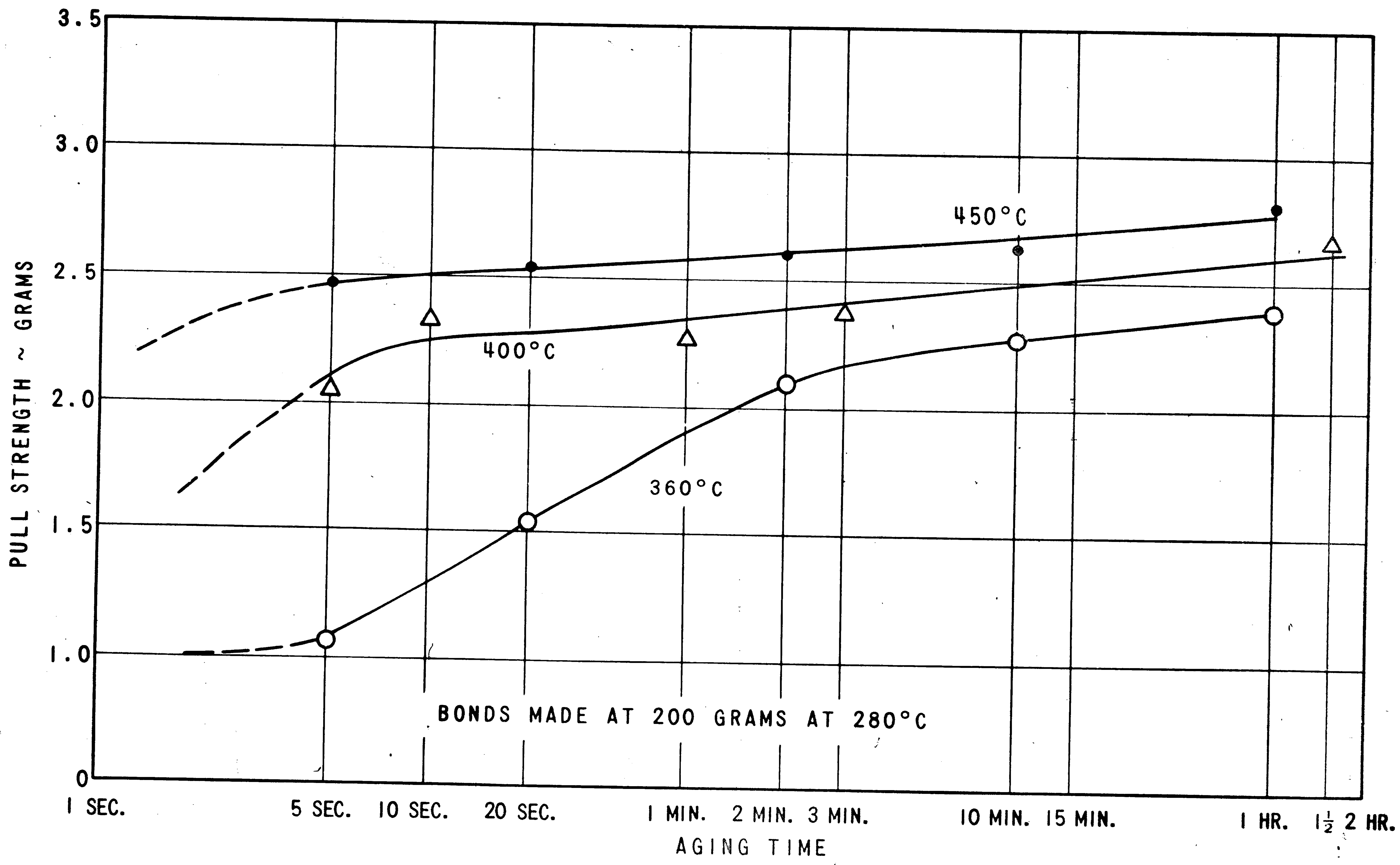


FIGURE 26 - HEAT TREATMENT OF LOW TEMPERATURE BONDS

strength, it still cannot be known whether the adhesion strength during normal bonding (not aged bonds) was primarily dependent upon annealing or diffusion. This is a situation similar to that of the above mentioned investigators, who have too hurriedly given credit to annealing without considering diffusion.

EFFECT OF DIFFUSION ALONE

If bonds were made well above the annealing temperature of the gold and then heat treated, the effect of diffusion alone could be isolated. Bonds were produced at 50 grams at 380°C and then aged for ten minutes at 480°C. The as-bonded strength was 2.49 grams and the strength after heat treatment for two samples of 10 bonds each was 3.85 grams and 3.69 grams. And nearly all the failures occurred in the gold wire, rather than the bond. Certainly diffusion was very important in producing sufficient atom movements so that the many imperfections in the region of the bond interface could be eliminated.

The amount of diffusion required was small. Certainly a classical concept of diffusion as a measurable material transfer through a measurable distance in a finite time was not required. But still, atom movements were vital in effecting a more perfect and continuous lattice structure across the interface.

The previous discussion regarding the separation of annealing and diffusion effects was largely semantic since annealing is so dependent upon diffusion. Nevertheless, annealing is an important phenomenon because it implies that the diffusivity is large enough

to permit a certain threshold atom movement which produces an almost discontinuous property change. Certainly then adherence is also dependent upon threshold atom movements. To achieve satisfactory bonding the atom movements must be equal to the threshold atom movements involved in the annealing of gold, and for the most ideal bonding, the atom movements should be an order of magnitude greater than the threshold movements permitting annealing.

Thus far this discussion has implied that the annealing and diffusion properties of the nickel were not so important as those of the gold. Unfortunately this question cannot be answered without a careful study of the annealing properties of the particular nickel used in this investigation. It was possible in the last experiment that the ten minute heat treatment at 480°C may have permitted some annealing of the nickel which may have contributed to the observed strength increase. However, it is supposed that little or no annealing occurred. As mentioned in Appendix III, the nickel annealing temperature is greatly affected by purity, so that impurities picked up during rolling of the nickel to sheet may have raised the annealing temperature. Furthermore, the temperature to produce annealing in a short time in a material that was not severely cold worked is markedly higher than the listed annealing temperature.[27] Therefore, it has been assumed that the properties of the gold were dominant in affecting the strength increase. Since the gold and nickel lattices are compatible and permit substantial solid solution, it may be sufficient that only the gold half of the bond achieve threshold atom movements. The question of the importance

of annealing the nickel could be examined by using nickel of different purity levels in heat treatment experiments similar to the one above.

The effect of diffusion offers several interesting bonding possibilities. If highest strength (> 3.5 grams), but low resistance (2 to 3 milliohms) bonds are desired, they may only be obtained repeatedly by bonding at a lower temperature (50 grams at 400°C) and then aging a few minutes at 480°C to 500°C. Another possibility is that bonds may be formed at a low temperature and then locally heated rapidly to a higher temperature to effect strength, and thus avoid subjecting the whole component to a high temperature.

SUMMARY AND CONCLUSIONS

Both bonding temperature and bonding force had very important effects upon gold to nickel thermocompression bonding; however the effects of bonding force were less interesting than those of temperature, and from a viewpoint of producing bonds, the bonding force was dependent upon the temperature. Differences in bonding temperature affected the bonding mechanisms and bond quality in an unexpected and partially unexplained manner, while the effects of bonding force were more easily analyzed. At a given bonding temperature the bonding force primarily affected the amount of gold wire deformation, and in this way determined the amount of bond interface area. And at a particular temperature the bond area determined both the electrical resistance and pull strength of the bond. However, there was a difference between the apparent bond area and the area which effectively contributed to the bond resistance and strength. The bond resistance consisted of the spreading resistance through the effective bond area, which was less than the apparent area because there was not intimate contact over the entire area. Thus the electrical resistance was about two times greater than that calculated from the spreading resistance of the entire apparent area. Similarly, the bond strength was determined by the area able to contribute to strength, rather than the apparent area. Here, as the wire was deformed a great amount, the bond area increased; but also the wire was weakened next to the bond so that the entire bond area was ineffective in contributing to strength. Therefore, the

most desirable bonding force was just below the force at which the wire was so deformed that it failed in the weakened section next to the bond. The electrical resistance of the bonds was so low that it is not an important item to consider in selecting bonding parameters, except at temperatures above 440°C where nickel oxide forms at an appreciable rate.

The bonding temperature range investigated was divided into two regions by the nature of the bonding. At lower temperatures, from 200°C to 440°C, solid state metallic bonding occurred, while at higher temperatures, above 440°C, the gold adhered to the nickel oxide -- a phenomenon which was unexpected and certainly required an explanation.

In the lower temperature region, bonding was satisfactory above 320°C, yielding strengths from 2.0 to 3.0 grams; above 400°C the bonding was ideal with strengths approaching the wire strength of 3.5 to 4.0 grams. However, below 320°C a large bonding force increase was required and the strengths were low; below 200°C the bonding virtually ceased. The key to these bonding variations was the bond adherence strength per unit area, and the adherence strength was dependent upon diffusion and annealing. Diffusion is important because it permits atoms to assume desirable positions which minimize irregularities in the interface region. Annealing of residual stresses is also important because these stresses tend to force apart the bond. Since both of these are very dependent upon temperature, the variations of adherence strength and bond strength may be described as resulting from the temperature variation of annealing

and diffusion. Attempts were made to separate the annealing effects from those of diffusion by heat treatment of low temperature bonds, and from these experiments it was concluded that diffusion by itself is capable of effecting bond strength. The importance of annealing has been well accepted;[2,10,26] however, it appears that the temperature sufficient to produce annealing is important to bond strength because it indicates that the diffusivity is great enough to permit threshold atom movements which minimize the structural irregularities at the interface region. In other words, the quality of the adherence is dependent upon the diffusivity becoming large enough to permit certain threshold atom movements. The bonding was satisfactory above 320°C because the diffusivity permitted atom movements similar in magnitude to those required for annealing. For the most ideal bonding the necessary threshold atom movements require a diffusivity about ten times greater than that for annealing.

The ability of diffusion to effect greater adherence opens an avenue of many interesting possibilities. These are based on the concept that low temperature bonds may be heat treated to a higher temperature thus producing strengths normally only obtained by bonding at that temperature. One possibility previously described would entail bonding at 400°C and heat treating at 500°C to produce highest strength, low resistance bonds which cannot be obtained otherwise. This concept of diffusion effecting greater adherence would prove useful to any joining method.

As the bonding investigation proceeded to higher temperatures it was expected that the formation of nickel oxide would most certainly

prohibit bonding, unless the oxide was removed to permit metallic contact. Therefore, it was very surprising to discover exceptional adherence between the gold and nickel oxide -- and indeed it was exceptional because the adherence strength per unit area was greater than the highest metallic adherence observed at any temperature. It is believed that such a phenomenon has not been reported before and that it especially required an explanation because it involved adherence between an oxide and a noble metal.

Many additional experiments provided information about the gold to nickel oxide adherence, which eventually led to a plausible explanation. It was found that the adherence between gold and nickel oxide was dependent upon temperature and time in a manner that indicated diffusion was the controlling factor. In addition, extended aging effected conductivity through the nickel oxide. From this it was concluded that the gold to nickel oxide adherence was due to the diffusion of many fine paths of gold into the voids and fractures of the nickel oxide. The adherence was not a chemical (ionic) bond to the oxide nor a metallic bond, but was rather mechanical interlocking of the fine gold paths in the oxide. Conductivity through the oxide was achieved when a continuous gold path had formed through the oxide and the minimum size gold path was larger than 100Å in diameter. The gold paths formed in the nickel oxide by surface diffusion along the surfaces of the voids and fractures or blisters of the oxide.

Adherence mechanisms which seemed likely, but could not account for all the observations, were adherence due to the surface roughness

of the oxide and adherence due to gold entering into substitutional solid solution in the oxide. A mechanism involving reduction of the nickel oxide could explain all the observations; however, demonstration that such a reduction is possible would be required before this mechanism could be accepted.

In addition to investigation of the oxide adherence, the manner by which removal of the oxide was effected by higher bonding forces was examined. It was found that the shearing action of the gold flowing over the oxide surface was unable to effect oxide removal by itself. Rather, it was necessary first to very slightly indent the nickel surface to increase the surface area and thus rupture the oxide because it lacked sufficient ductility to expand with the nickel surface.

The consideration of any possible degradation which gold nickel thermocompression bonds may experience is certainly important, as it is to any joining method. Extended service at above 500°C would result in considerable diffusion, which would permit precipitation and ordered phases; however this would not be serious at all. The bond resistance might increase to ten milliohms, which is still a negligible value. There is no indication that any of the precipitated or ordered phases are brittle or weak, and in fact the bond strength should increase. At worst, extensive diffusion will decrease the nobility of the gold so that its corrosion characteristics will be similar to those of nickel.

SUGGESTIONS FOR FUTURE WORK

The two general areas of interest are consideration of gold-nickel bonding as a production process and further investigation of the adhesion mechanisms. Important to the first would be the particular materials and processes to be employed in production. If highest conductivity were desired from bonds at temperatures above 400°C, the oxidation characteristics of the nickel would be very important. Proper cleaning and preferred orientation of the nickel should permit metallic bonding to well above 500°C; otherwise, atmosphere control would be necessary. Also important would be the thickness of the nickel employed; it is expected that a thin layer of nickel on a hard substrate would require less bonding force than thicker material. Finally, serious consideration should be given to the heat treatment of low temperature bonds, perhaps locally so as to effect adherence strength at desired locations.

With respect to metallic adherence, continued examination of the effects of microscopic diffusion and annealing would prove interesting. A possible correlation between the onset temperature of satisfactory adhesion and the diffusivity at that temperature for many metals would be very interesting. Unfortunately, most studies of adhesion have been performed at room temperature, so there is little information other than the adhesion quality at room temperature. In this experiment it was concluded that a diffusivity sufficient to permit the threshold atom movements involved in annealing was necessary for satisfactory bonding, and that ten times greater

diffusivity was required for ideal bonding. This implied that the magnitude of the structure irregularities varied from a magnitude similar to those in cold worked material to ten times greater. Continued examination of this might reveal a good estimate of the size of the threshold atom movements necessary for adhesion. Also of interest would be a careful consideration of the increased diffusivity accompanying lattice irregularities and dislocations.[28] Finally, studies of the effect of grain orientation would be most enlightening. Measuring the adherence of large single crystals in prescribed orientations in vacuo would yield information of extreme interest to many fields.

It seems reasonable that a very critical determination of the effect of aging upon the electrical resistance might determine the reasons why the calculated spreading resistance did not account entirely for the observed bond resistance. A suggested experiment would entail bonding samples at 100 grams at 400°C, and then aging at 400°C to 450°C for very long times while continually monitoring the resistance. It is expected that atom movements will first reduce the effect of imperfections and reduced area of contact, and thus decrease the resistance; later the effects of diffusion in increasing the resistance by alloying and precipitation should become important. Aging times of 10 to 100 hours would be necessary before the effects of diffusion should become apparent.

In future examination of the oxide adherence, large couples of nickel oxide to gold -- especially thicker oxide -- would be advisable. Such a couple could be subjected to long term heat treatment

at 600°C and then examined metallographically or with the electron microprobe to determine if paths of gold had formed through the oxide as suspected. Also on such a sample, diffraction techniques could be employed to determine if there had been a structural change in the nickel oxide such as reduction or solid solution. Since surface diffusion of the gold paths in the nickel oxide was the suspected adherence mechanism, it would be well to consider the nature of the surface diffusion of a metal over an ionic crystal. Also vapor phase transport may be important as recently has been suggested.[29] Examination of the adherence between other couples of noble metal to oxides would determine if this phenomenon is unique; likely couples would be gold, platinum, and palladium to oxides of nickel, iron and cobalt. Also the adherence of non-noble metals to oxides would be of interest; if the aging of such bonds effected conductivity, as was the case for gold to nickel oxide, it would be a very strong indication that metallic paths had formed in the oxide. Finally, a better understanding of metal to oxide adherence is certain to contribute information regarding the reaction and adherence between metals and nonmetals, such as metal to glass and metal to ceramic.

APPENDIX I

REQUISITES FOR SOLID STATE METALLIC ADHESION

It is first necessary to differentiate between a fusion weld, a solid state metallic bond, and a mechanical bond. A fusion weld and a solid state metallic bond are joints which exhibit metallic properties continuously from one metal across the interface and into the other metal; while, at best, a mechanical joint involves intimate contact, but no continuity of the metallic properties across the interface. A fusion weld is produced by melting at the interface; a solid state metallic bond is formed by removing interfering material (contaminants and oxides), and rotating and straining the lattice structure sufficiently to achieve metallic continuity[2,11] across the interface. The interface of a solid state metallic bond should, at worst, be an area with high imperfection density approximating a grain boundary.[2] Over the last two decades a set of requisite conditions to form a solid state metallic bond has evolved. These are: (1) the removal[2,26,30] of oxides and contaminants so that atomic spacing may be approached across the interface; (2) the conformity[2,11,30] of the surfaces to provide atomic spacing over a wide area of the interface and conformity of the crystal structures to facilitate atomic bonding; (3) the production of shear strains[2,11,26,30,31] at the interface which are vital in order to obtain (1) and (2) above; (4) normal forces,[2] of course, are essential to obtain close approach and produce deformation, which also aids in achieving the above requisites; (5) the reduction of

APPENDIX I - 2

elastic recovery stresses[2,11,26] to prevent breaking bonds after they have been formed; although the complete elimination of recovery stresses can only be achieved by annealing during bonding, their effect can be minimized by deforming well into the plastic region to form large area bonds; (6) properly elevated temperatures[2, 11] greatly enhance items (2) and (5) and usually permit lower tangential and normal stresses.

APPENDIX II

PROPERTIES OF 99.99 PER CENT GOLD

(All ref. 32, unless noted)

(1) Resistivity: $\rho = 2.35 \times 10^{-6}$ Ω-cm at 20°C

(2) Crystal structure: FCC, $a_o = 4.070\text{Å}$ at 20°C

(3) Annealing temperature: 300°C

(4) Mechanical properties

	BULK PROPERTIES		0.001" WIRE (REF. 33)		
	60% COLD WORK	ANNEALED	FULL HARD	STRESS RELIEVED	ANNEALED
TENSILE	32 ksi	19 ksi	12 GRAMS	8 GRAMS	4 GRAMS
YIELD	30 ksi	NIL			
ELONG.	4%	45%	1-3%	3-8%	8-12%
HARDNESS	58 BHN	25 BHN			

(5) Diffusion: (Ref. 34)

$$D_{Au/Au} = 0.091\, e^{-\frac{41,700}{RT}}\ \text{cm}^2/\text{sec}$$

D at 500°C = 1.382×10^{-13} cm^2/sec

(6) Oxidation: Presence of oxide at the bonding temperature was very unlikely; Au_2O_3 boils at 250°C (Ref. 35) and $\Delta F°$ at 400°C is +25,100 cal/mole (Ref. 36).

Ionic radii are: (Ref. 20)

$Au^{+3} = 0.85\text{Å}$

$Au^{+1} = 1.37\text{Å}$

APPENDIX III

PROPERTIES OF 99.95 PER CENT NICKEL

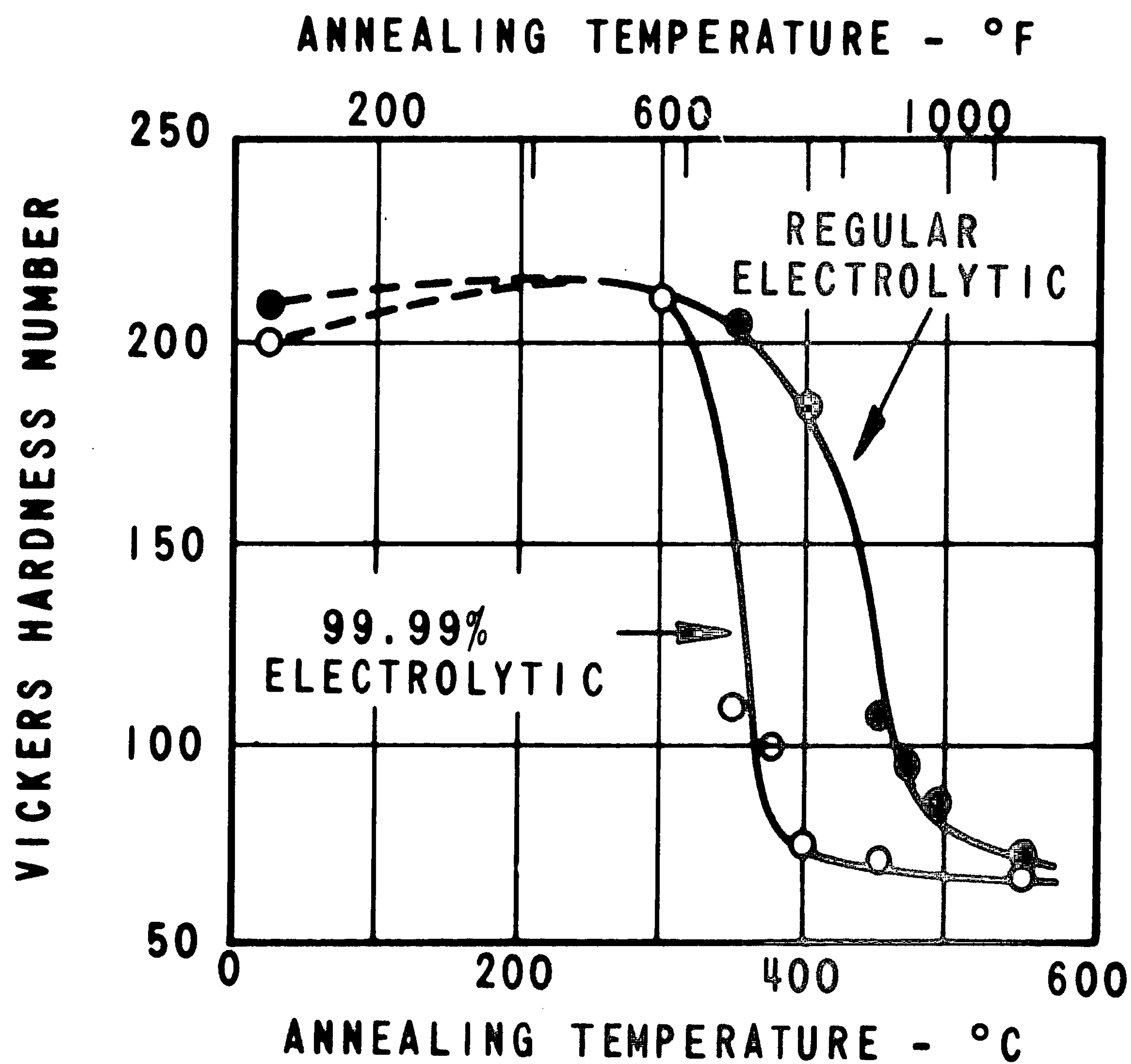
(All ref. 37 unless noted)

(1) Common name: Nickel 270

(2) Resistivity: $\rho = 6.84 \times 10^{-6}$ Ω-cm at 20°C

(3) Crystal structure: FCC, $a_o = 3.5167 \AA$ at 20°C

(4) Annealing temperature: This is very dependent upon purity; the 1961 Metals Handbook gives the following figure:



The Nickel 270 used in this experiment is similar to the "Regular electrolytic," but on rolling it probably picked up impurities, thus potentially raising its annealing temperature.

APPENDIX III - 2

International Nickel Co. describes the annealing of pure nickel as follows: at 600°C cold worked nickel begins to recrystallize and soften; at 700°C it requires only 5 to 25 minutes and at 800°C grain growth occurs. (Ref. 38)

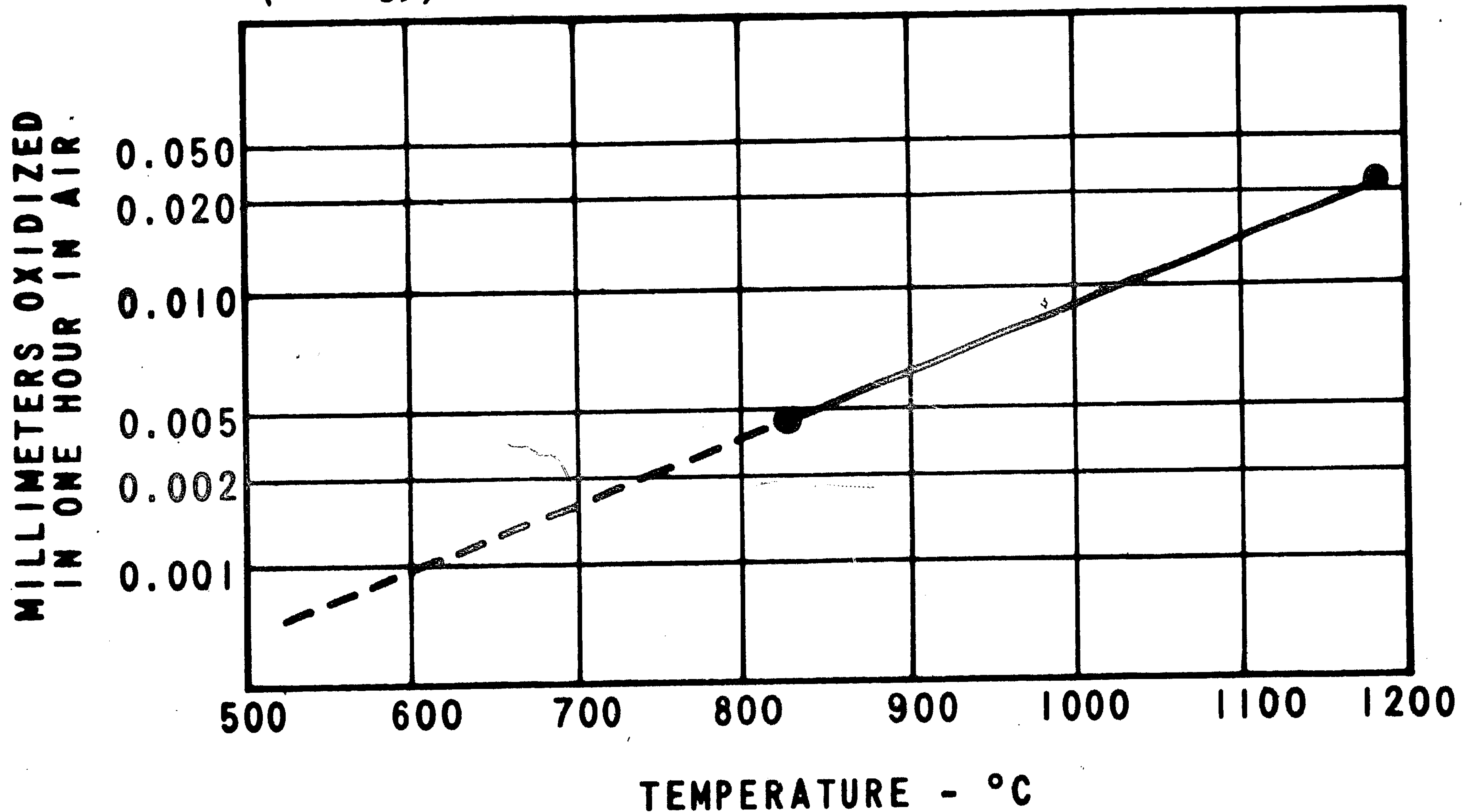
(5) Mechanical properties

	Annealed	Full Hard
Tensile	46 ksi	
Yield	8.5 ksi	
Elongation	30%	
Hardness	40 R_B	95 R_B
	(80 BHN)	(209 BHN)

(6) Diffusion: (Ref. 34) $D_{Ni/Ni} = 1.30 \; e^{-\frac{66,800}{RT}} \; cm^2/sec$

D at 500°C = $1.457 \times 10^{-19} \; cm^2/sec$

(7) Oxidation: International Nickel Co. describes the oxidation of pure nickel in air as shown by the solid line in the figure below. (Ref. 39)



APPENDIX III - 3

Extrapolating this to 600°C indicates that the oxide will be one micron thick and this is close to the observed thickness.

Free energy of formation of NiO at 400°C is,

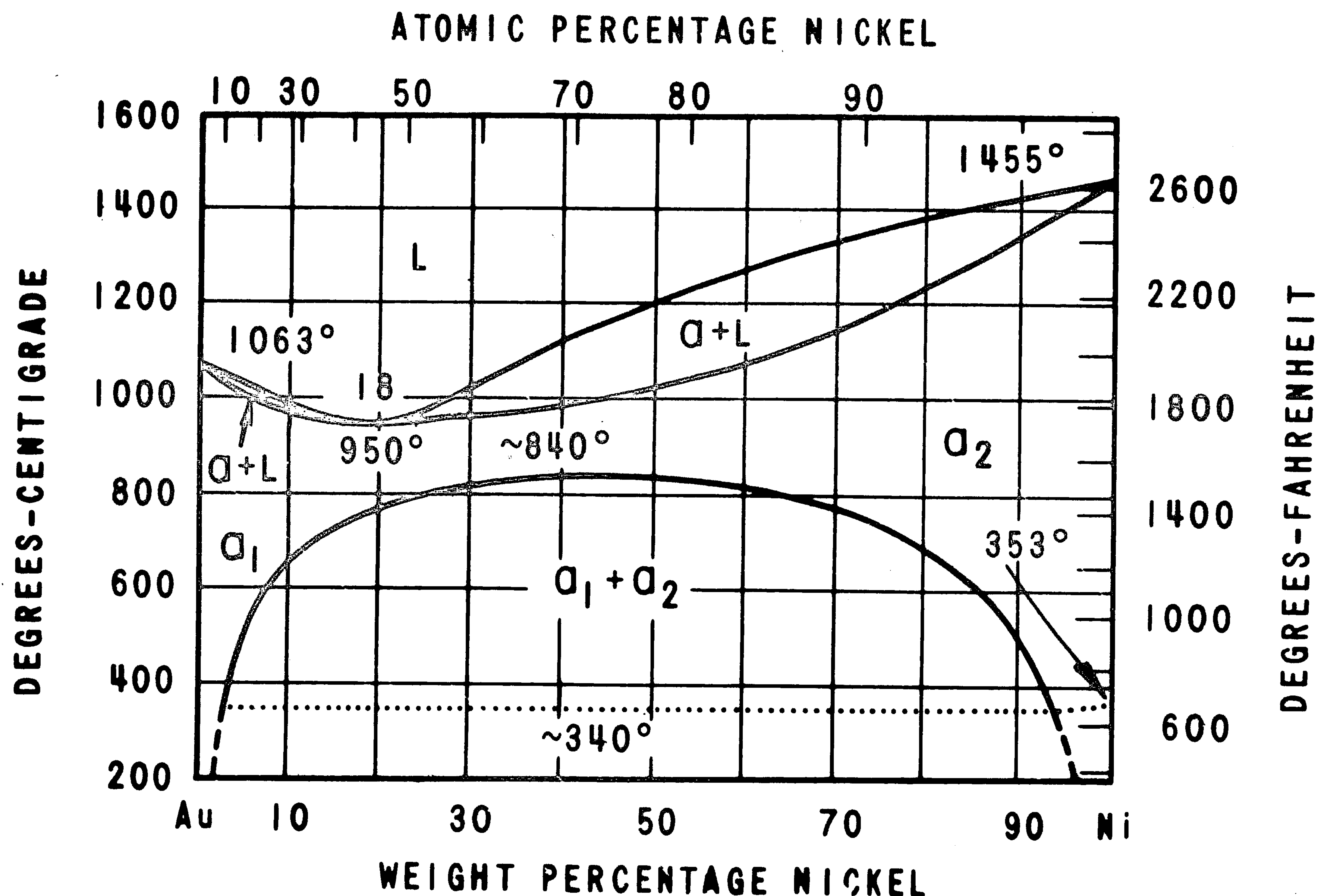
ΔF°_{T} = -48,300 cal/mole. (Ref. 36)

Ionic radii are: Ni^{+2} = 0.69Å
(Ref. 20)
O^{-2} = 1.40Å

APPENDIX IV

PROPERTIES OF THE GOLD-NICKEL SYSTEM

(1) **Phase diagram:** There is a difference of about 12% in the atomic sizes, therefore there should be considerable solid solubility as indicated in the phase diagram below. (Ref. 40)



(2) **Nature of the alloys:** (Ref. 41)

Alloys quenched from above 840°C are homogenous and maintain noble characteristics up to 50 weight % nickel. Annealing the quenched alloy produces a very fine, two phase structure which is not resistant to nitric acid attack.

Some of the alloys permit precipitation reactions which increase the resistivity (Ref. 21) and may produce hardening.

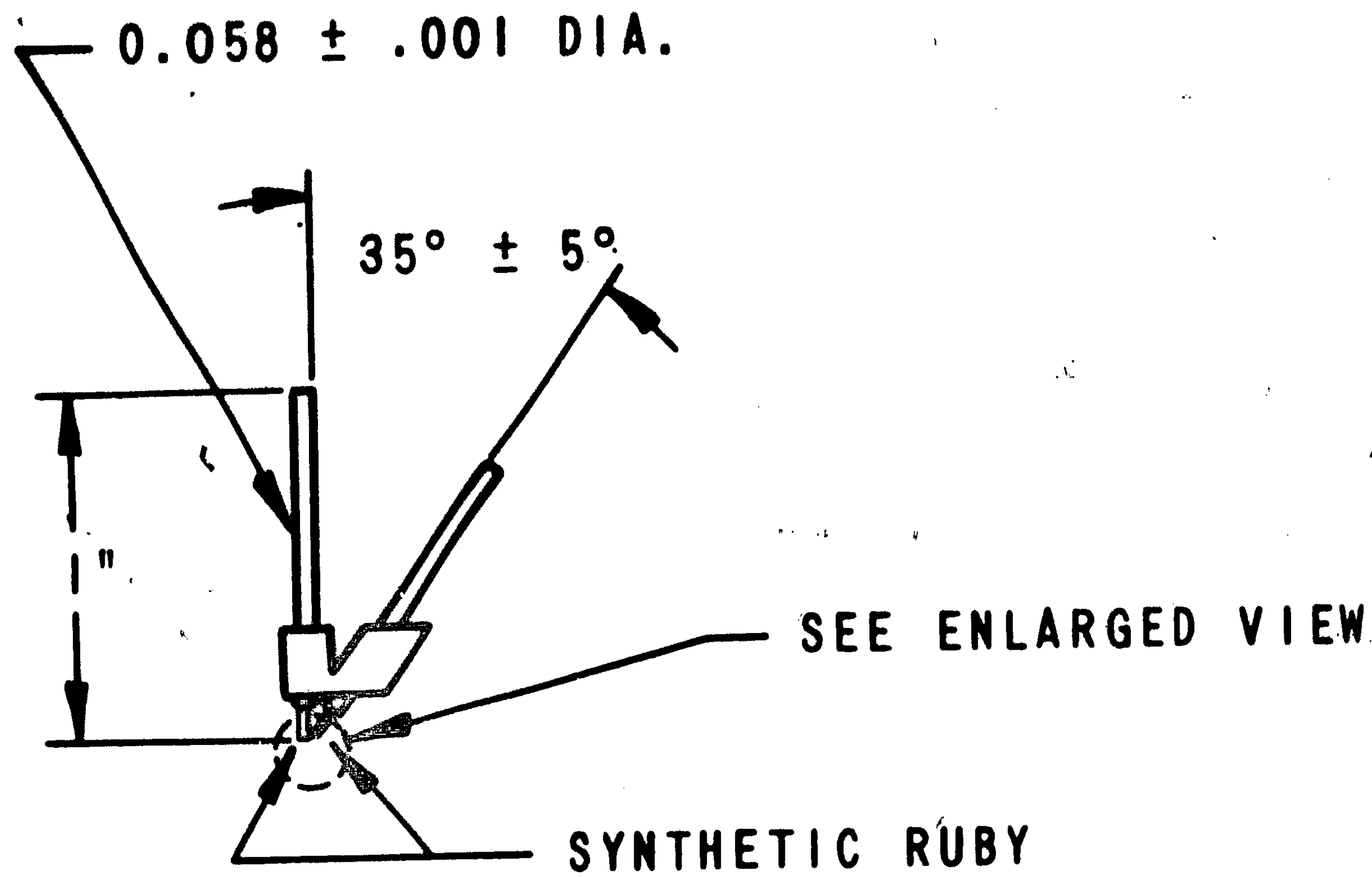
APPENDIX IV - 2

(3) Diffusion: $D_{Ni/Au} = 0.034\ e^{-\frac{42,000}{RT}}\ cm^2/sec$
(Ref. 42)

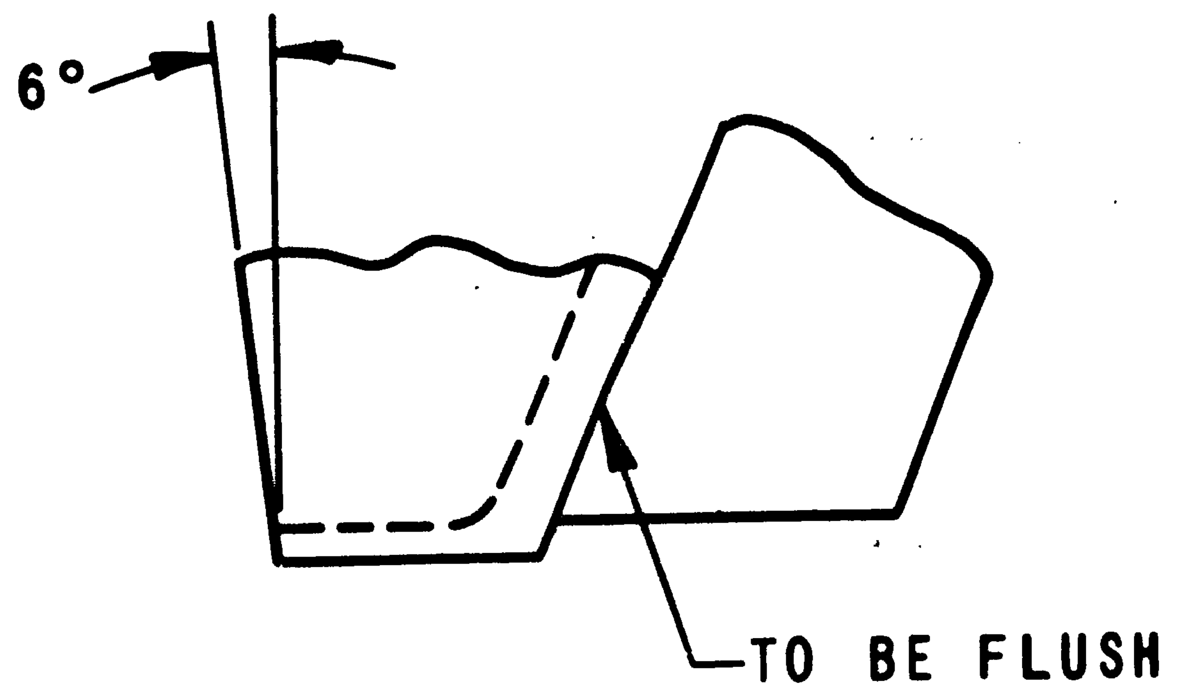
D at $500°C = 9.64 \times 10^{-13}\ cm^2/sec$

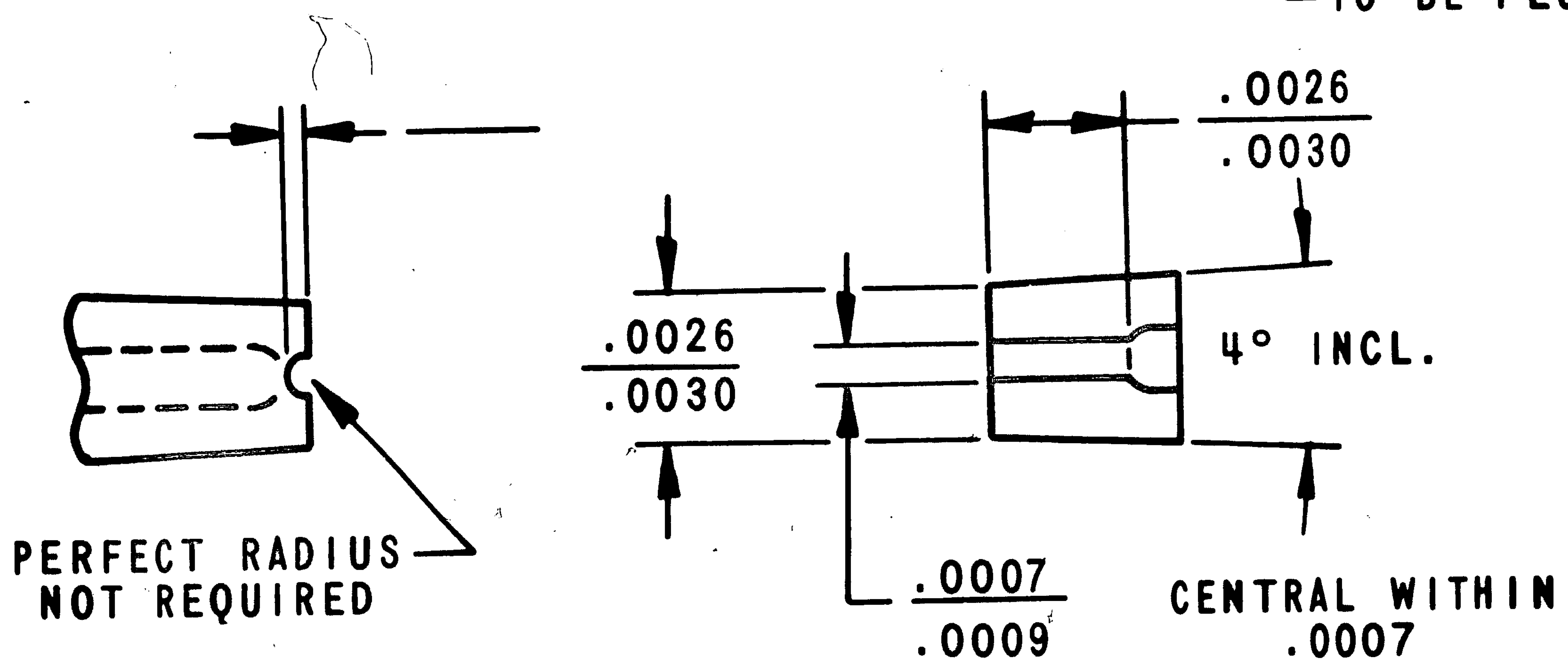
APPENDIX V

BONDING NEEDLE



MAT'L: STAINLESS STEEL AND SYNTHETIC RUBY.





ENLARGED VIEW

20:1

APPENDIX VI

ESTIMATE OF CONFIDENCE INTERVAL

(Ref. 43)

The confidence that the mean of a particular sample is within a certain interval of the true population mean may be calculated from the standard deviation of the sample and a standard "t" table by the relation

$$\bar{\bar{X}} - E = t \frac{\sigma}{\sqrt{n}}$$

where,

$\bar{\bar{X}}$ = sample mean

E = expected or true mean

t = value of "t" from table for a given probability and degrees of freedom

σ = standard deviation of individuals in the sample

n = number of individuals in the sample.

The confidence interval for a given probability is therefore $\pm (\bar{\bar{X}}-E)$.
The pull strength data below was obtained at 100 grams at 400°C, and was used to calculate the confidence interval as shown.

APPENDIX VI - 2

Pull Strength, grams

2.8

3.0

2.8

2.8

2.8

3.8

3.8

3.7

2.4

3.7

2.7

The quantities necessary for the calculation of σ are:

$\Sigma(x^2) = 105.59$

$(\Sigma x)^2 = 1135.69$

$n = 11$

$(\Sigma x)^2/n = 103.244$

$\sigma = [\Sigma(x^2) - (\Sigma x)^2/n]/(n-1)$

$\sigma = (105.59 - 103.244)/10$

$\sigma = 0.2346$

From the "t" table for ten degrees of freedom,

$t = 2.23$ at $P = 95\%$

$t = 3.17$ at $P = 99\%$

At $P = 95\%$, $\bar{X} - E = (2.23)(0.2346/3.317)$

$\bar{X} - E = 0.1577$, or

the Confidence Interval $= \pm\ 0.158$ grams.

At $P = 99\%$, $\bar{X} - E = (3.17)(0.2346/3.317)$

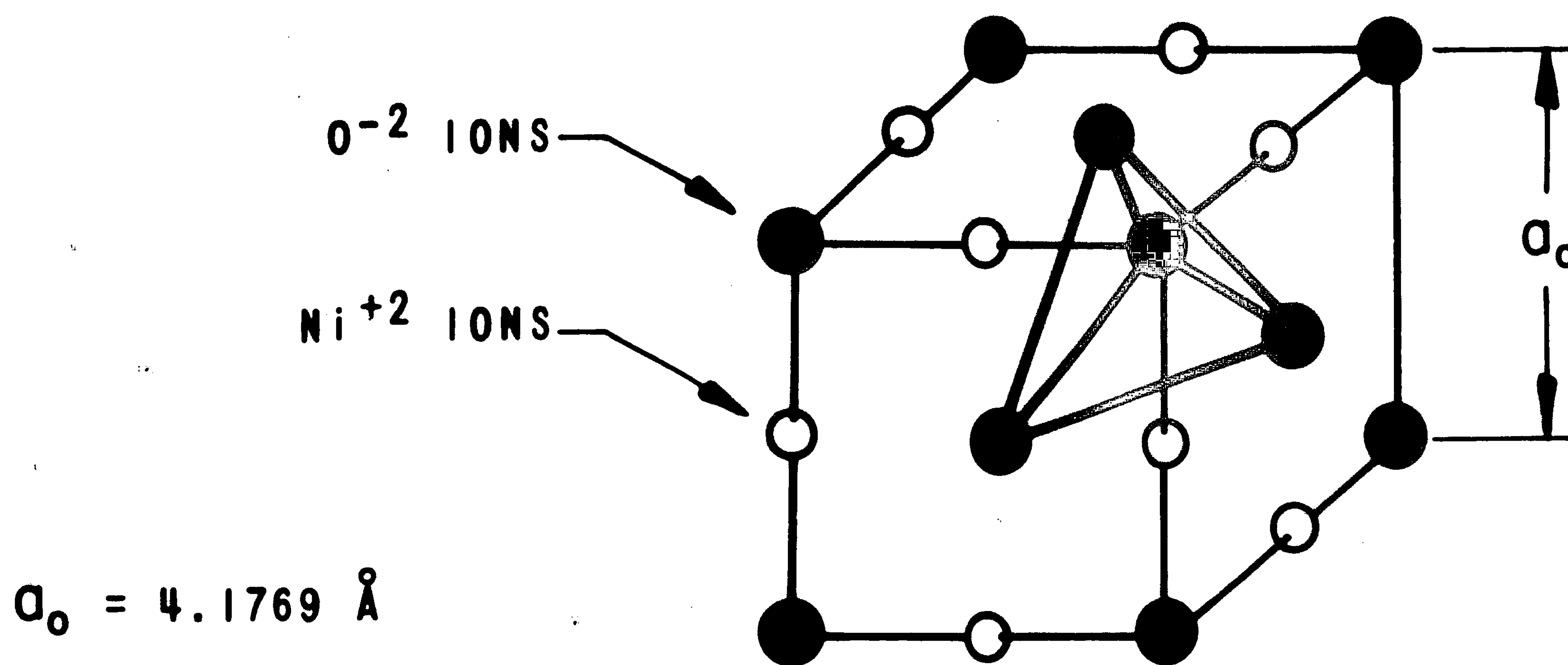
$\bar{X} - E = 0.2242$, or

the Confidence Interval $= \pm\ 0.224$ grams.

APPENDIX VII

GOLD ATOM IN THE NICKEL OXIDE LATTICE

(Ref. 20)



NICKEL OXIDE STRUCTURE.

The nickel oxide cell may be considered as a FCC lattice with the oxygen ions on the FCC lattice sites and the four nickel ions per cell occupying the four octahedral voids in the FCC cell. The only remaining interstitial voids of any consequence are the tetrahedral voids, which may be pictured as a perfect tetrahedron with edges equal to $a_o/\sqrt{2}$ and with each of the four corners occupied by an oxygen ion. The radius of the largest sphere that can fit in this tetrahedral void is

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$$R_{tet} = 0.410\text{Å}$$

and the radius of the gold atom is

$$R_{Au} = 1.443\text{Å}.$$

Therefore, it is very improbable that the gold atom will be in an interstitial void.

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