FHR 3422
31 March 1967

Final Report

Research on Electric Heating of Metals for
Thermal Treatment

Contract No. NAS 8-20064
Control No. DCN 1-5-30-12523 (1F)

Thomas A. Gorecki

Manufacturing Research
Fairchild Hiller
/ Republic Aviation Division
Farmingdale, New York

Prepared for
George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Huntsville, Alabama 35812

FOREWORD

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont'd)

LIST OF ILLUSTRATIONS (Cont'd)

LIST OF TABLES

ABSTRACT

A solution heat treating practice employing electrolytic heating was developed during this contract for the 2219 Al alloy and the Ti-6Al-4V alloy. Electrolytic heating was achieved by submerging the material to be heated in an aqueous electrolyte and applying a controlled potential between an anode plate and the material.

A heating system was designed and fabricated to investigate the electrolytic heating process as a possible production tool for solution heat treating. The system included a power supply, control circuits, a heat treating vessel, and auxiliary control equipment. Numerous factors which effect the electrolytic heating process were investigated, including 1) electrolyte composition 2) electrolyte concentration 3) electrolyte temperatures 4) specimen material 5) specimen size 6) specimen temperature 7) power requirements.

These investigations led to the development of solution treating practice which employed an 8% solution of K ($C_2H_3O_2$) operating at 130°F as the electrolyte for heating both the Ti-6Al-4V alloy and the 2219 Al Alloy. Mechanical test results on material electrolytically solution treated and conventionally aged were comparable to results obtained through conventional heat treatments.

The process offers fast heating rates, 150° to 300°F/sec., fast quenching rates, 600°F/sec., and short cycle times. Inadequacies of the process include poor temperature uniformity over the specimen and limited specimen size due to high power requirements.

SECTION I

INTRODUCTION

Contract number NAS 8-20064, "Research on Electric Heating of Metals for Thermal Treatment" was awarded to study electrolytic heating of metals for use as a production tool for solution heat treating.

The study program consisted of four phases with the following objectives:

Phase I required the design of an electrical heating system with controls capable of heating various metals to their solutioning temperature in an aqueous electrolyte. In addition to the electrical system a heat treating vessel with an electrolyte temperature control system had to be designed capable of accepting a test component up to 30" long x 12" wide x 12" high.

Phase II of the program required that all system components designed in Phase I be fabricated.

Phase III required the evaluation of process parameters. These parameters included but were not limited to the following: 1) selection of an electrolyte, 2) temperature and heating rate as a function of power, 3) uniformity of temperature control, 4) quench rate, 5) effect of electrolyte temperature, and 6) effect of geometry on heating.

Phase IV required that the feasibility of thermally treating metals by electrolytic heating be determined. To complete this phase of the contract a solution treating practice for 2219 Aluminum alloy was to be developed which would result in a T-6 final condition after conventional aging. In addition a solution treating practice for Ti-6Al-4V was to be developed.

SECTION II

BACKGROUND

Electrolytic heating of metals was reported as early as 1844. However, in 1949 Yasnogorodski, a Russian, claimed origination. His work, which began in 1932, has resulted in the use of the process for production heat treatment (Reference 1). The most complete description of Yasnogorodski's work is contained in his 1949 publication (Reference 2), which was translated into German in 1952 and subsequently translated into English. The translation is available from OTS-FTD-TT-61-70. "Electrolytic Hardening and Heating of Metal Alloys in Electrolytes", 189 pages.

More recent Russian technical periodicals (References 3 and 4) treat electrolytic heating as a production practice, stating that variants such as electrolytic jet heating are widely used. The use of automatic machines to electrolytically heat valve tappets at 600 per hour for swaging and hardening is described as economically advantageous. The heating conditions are given as:

1) The workpiece is the cathode, the metal container is the anode

2) The electrolyte is 5 to 10% $Na_2 CO_3$ or $K_2 CO_3$

3) The voltage is 200 to 300 volts

4) A 2000°C hydrogen jacket forms when the current density reaches 3 to 40 amperes per square centimeter

5) Process stability requires that the current density of the workpiece cathode exceed that of the anode tank

The advantages cited are simplicity, speed, and absence of air. A disadvantage is the nonuniform surface heating that occurs with parts of complex shapes. For heavier sections, surface heating is begun at high voltages; and, during soaking to permit heat transfer into the interior, a lower voltage is used.

Several Japanese industrial research organizations began investigations which followed the initial Russian work. However, Japanese reports do not indicate that production practice has been realized. In 1959 the Japanese author, Kogyo Gijutsu, prepared a rather complete text which is research orientated and extends the original Yasnogorodski text with more extensive experimentation and more detailed description of procedures and results. Small industrial workpieces such as screw drivers and razor blades were used to establish process parameters in a wide range of operating conditions.

Gijutsu cites the following advantages for the electrolytic heating process:

1) By masking with insulation, parts can be selectively heated

2) Little oxide scale occurs

3) Because the rate of heating is high, surface hardening is obtainable

4) Depending on the electrolytic solution, carburization, sulfurization, and nitriding are possible

5) Quenching can follow heating without transfer

6) The rapid quenching of the electrolyte produces extreme hardness

7) Step heat treatments, in which several successive temperature ranges are required, are possible by merely changing the voltage

According to Gijutsu, factors that affect the heating process include:

1) Type of electrolyte

2) Concentration and temperature

3) Voltage

4) Wave form of the current

5) Time of current flow

6) Surface finish of the workpiece

7) Heat capacity and shape of the workpiece

The following process parameter data and results are summarized from the Japanese text.

1) Curves of current density versus voltage for various concentrations of H_2SO_4, Na_2CO_3, Na_2SO_4, $(NH_4)_2$, SO_4

2) The general shape of the current density – voltage curve is discussed, but the difference between the voltage rise curve and the voltage decrease curve is not explained phenomenologically
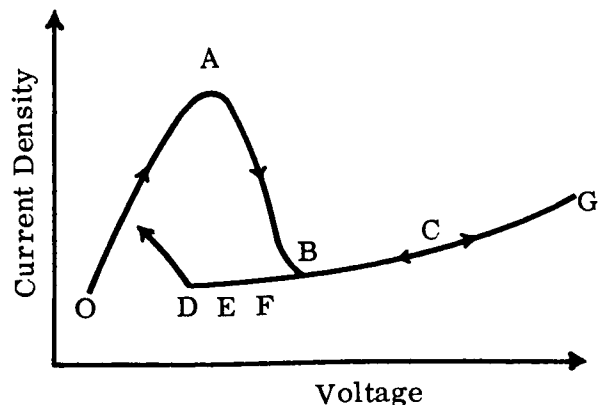
3) The current density-voltage curve can be divided into segments where OA represents normal electrolysis, A represents unstable intermittent arcing. AB represents an increase in arcing, B represents the point where arcing first becomes continuous and workpiece temperature rises abruptly, G is the melting point, and D is the minimum voltage at which heating continues.

4) The workpiece is heated only in the BGCFED range, but point A, where arcing begins, determines the electrical power required. Preheating the workpiece before immersion markedly reduces the height of A

5) Increase in electrolyte concentration reduced the voltage required if increased concentration causes increased conductivity

6) The current density-voltage curves of copper, iron and aluminum workpieces were essentially alike

7) Melting voltages for various materials do not correspond to the melting temperatures for these materials. It is believed to be due to the metal constituent which may compose the gas envelope about the workpiece (also believed to contain hydrogen and water vapor)

8) Curves of voltage versus electrolyte concentration are given for 21 electrolytes, for each of the following voltages:

    a) Initial stable voltage, B*
    b) Steel melting voltage, C
    c) Minimum heating voltage, D
    d) Curie temperature voltage, E

9) Increase in solution temperature decreases the voltages (except for voltage B or over 130°F), but the effect is not marked

10) The workpiece thickness increase only affects the initiating voltage B, which increases markedly. When the equilibrium voltage, F, from which quench will be made, is lower than B, it is useful to apply only voltage F, which is insufficient to initiate the gas envelope, which creates heating, and then to apply a spike of voltage greater than B. The spike must be of very short duration to avoid overheating and melting of the workpiece.

* the letter refers to the curve on the preceding page

11) Several maskants for selective heating were evaluated, and colloidal aluminum silicon resin covered with nitrocellulose lacquer was found best

12) The quenching that takes place as the electrolyte is removed is very rapid and heat treats (steel) to higher strength but lower toughness than obtained in normal (oil) quenching

13) In attempting to control quench temperature by measuring the heating time at a particular voltage, relatively low heating voltages (close to the equilibrium voltage) give close temperature control, but such long-time exposure can corrode the workpiece. Heating at a rapid rate makes the voltage cutoff time critical and gives poor accuracy. This method is preferred if a workpiece temperature sensing method could be devised

Despite the extensive analytical test work conducted by the author with various electrolytes, workpiece materials, and methods, it is important to note that he concludes that

1) The process is still in the research stage

2) Production utilization is hindered due to difficulty of temperature control and tendency to overheat the workpiece surface (and workpiece projections), because the heating rate tends to exceed conduction to the interior

SECTION III

DESIGN OF EQUIPMENT
FOR ELECTROLYTIC HEATING

The design phase of this contract included a literature survey of the work of the two previous investigators described in section II and a review of the research conducted by the Republic Aviation Corporation in 1957-58 and 1963.

Basicly electrolytic heating of metals consists of placing two pieces of metal in a liquid which will conduct a current and applying a potential between them. The specimen to be heated is called the cathode and the other piece of metal is the anode. The conducting liquid is an electrolyte.

With the cited information for reference and the contract requirements for a guide, a design for the electrical system needed for electrotytic heating, including the power supply, control circuits, electrolyte conditioning circuit and cpacitor start-up circuit, was formulated. A schematic diagram of these circuits is shown in figures III-1 and III-2. Appendix A contains a list of materials describing the switches, relays, timers, meters, capacitor bank and power supply.

The power supply for the designed system was a 3-phase 440 volt motor-generator set which effectively isolated the DC system from the power line variations and supplied essentially a non-pulsating signal. Start-up of this unit was at the generator with safety lockout switches at the control panel and the generator. Operating voltages and current adjustment was provided at the control panel next to the voltmeter and ammeter.

A capacitor bank was designed in the system to provide a rapid voltage spike for large specimens during the initial part of the heating cycle. Energizing the 27,000 μf capacitor bank was separately controlled by a 0-500 V power supply. A multiple tap switch was used to provide various levels of capacitance.

The designed system provided for process startup to be initiated at the control point only, and both voltage sensing and timing were provided to complete the heat treating cycle. Four timers were provided, to delay before application of the high voltage pulse, to time the first heating, to time the second heat or quench and to time the final quench before removing the work from the electro-lyte. The system also provided manual control for exploratory work.

The operation of the designed system shown in figure III-2 would be as follows:

1) Start station 1 controls the main power source (0 to 300 volts) for the process with a safety lockout key switch at the control panel.

2)   Start station 2 controls the auxiliary power source (500-volt) for the process. It is interlocked with R1 because it is not required without the main power source.

3)   Field rheostats are adjusted for the required voltage: F1, initial, F2, second stage, and F3, final stage. Press appropriate button switch for voltage reading.

4)   Start station 3 is interlocked with a safety lockout at the work station to control the start of the process. A normally closed relay contact, R7, resets the circuit at completion of the cycle.

5)   Relay R3 locks itself in and energizes R4, controlling the DC out-put relay.

6)   On closure of R4, a voltage appears across R, which closes to energize timers T1 and T2, which act to control the time of application of the tickler (high-voltage starting impulse) and second heat step.

7)   Timer 1 times out, and the tickler is applied by operation of relay R5.

8)   Relay R5 also repeats the tickler, should the selector switch be thrown to the repeat position.

9)   In the single-shot position, the tickler can be manually controlled during the first period (before operation of timer 2).

10)   Timer T2 then operates to control R6.

11)   Relay R6 locks itself in and switches the field control to the field rheostat F2. Relay R6 also energizes timer T3.

12)   Timer T3 times out and energizes Relay R7 and timer T4.

13)   Relay R7 operates to bring field control F3 into action, controlling the final quench level.

14)   Timer T4 times out, energizing relay R8 which locks in and simultaneously resets the starting relay, R3, for the next process cycle.

15)   Manual operation is secured by operating the manual automatic switches in the order, 1-2-3-4-6-8-9-10.

To complete the electrolytic heat treating system, an electrolyte tank was designed with a continuous circulation system and temperature control system. The heat treating area of the tank was 31" x 15" x 12" and contained a 8" x 8" plexiglas window for viewing the specimens during heating. A reservoir area was also provided in the tank for continuous circulation and a means of maintaining a constant liquid level. Figure III-3 is a sketch of the heat treating tank and complimentary systems.
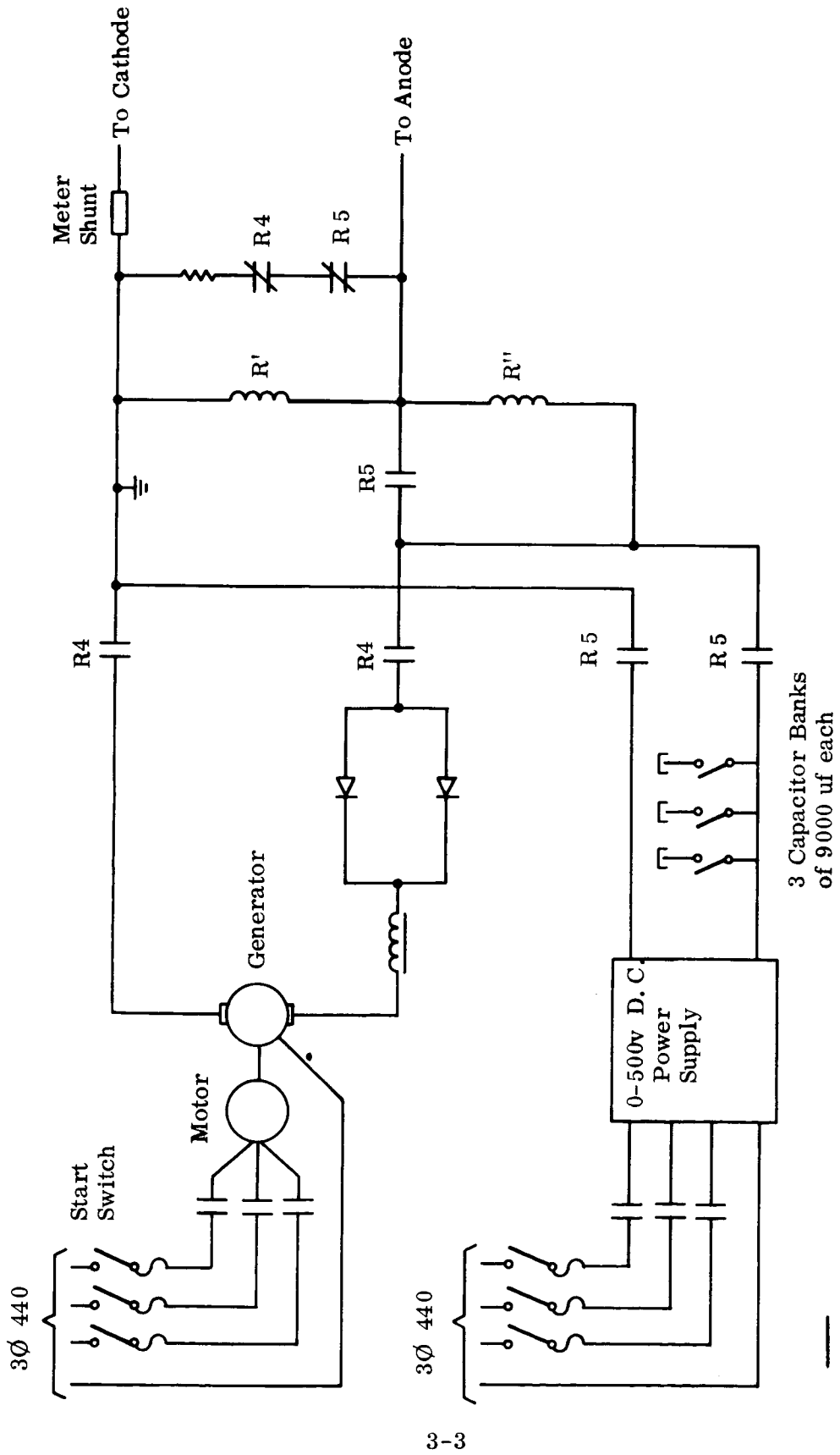
ELECTROLYTIC POWER CIRCUIT

Figure III - 1

CONTROL CIRCUIT
FOR PROPOSED HEATING
SYSTEM
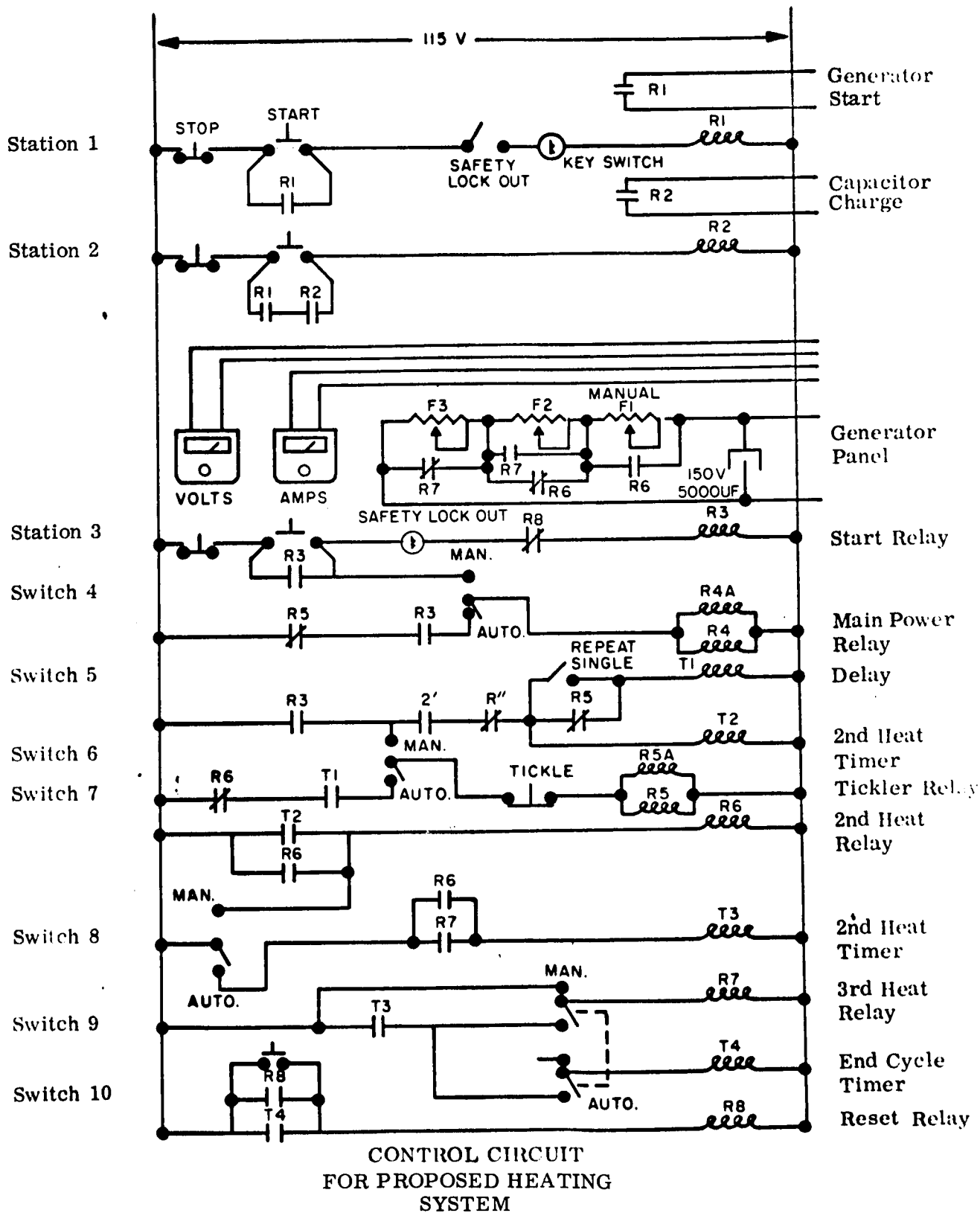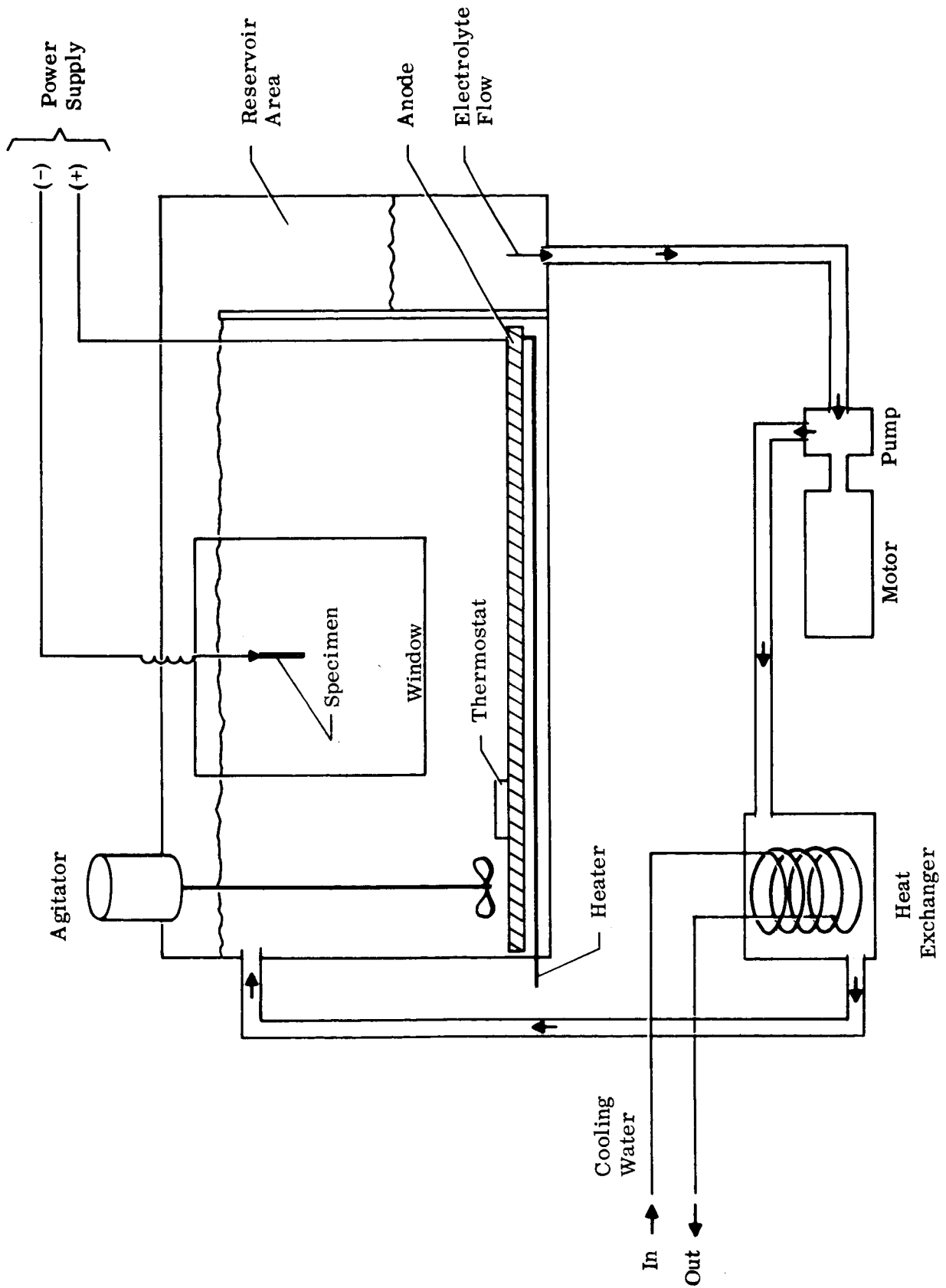
Figure III - 2

ELECTROLYTIC HEAT TREATING SYSTEM

Figure III – 3

SECTION IV

PHASE II - FABRICATION

During Phase II of the contract the equipment designed in Phase I was fabricated and installed in the Manufacturing Research Laboratory of the Republic Aviation Division. This work included the following:

1. The purchase of a 30KW, Westinghouse motor generator, 100 ampere 300 volt, D. C. power supply with starter, field control, main breaker and meters.

2. The purchase of electrical hardware, including three 9000 uf capacitor trays, relays, timers, switches, and meters, to control the heat treating process.

3. The purchase of circulation and temperature control equipment which included a monel centrifugal pump, Teflon tubing, stainless steel electric heaters, and thermostats.

4. The fabrication of the electrolytic heat treating tank, a stainless steel anode plate, and a specimen support fixture.

5. The fabrication of a stainless steel heat exchanger, and stainless steel tank fittings.

6. The assembly of the control panel and capacitor bank for the heat treating process.

7. The installation and assembly of all the components into a complete unit. This included installation of the following: the electrical supply to operate all the auxiliary equipment, the ventilation system, the water supply and drains, the D. C. power supply, the capacitor bank, the tank and circulation system and the control panel.

Figure IV-1 is a photograph of the overall facility assembled during Phase II of the contract. Figure IV-2 is a close-up of the power supply system which was used to heat the specimens. The D. C. generator provided the necessary energy to maintain heating of the specimen. The capacitor bank provided a momentary surge of power to generate a gas envelope around the workpiece and initiate heating. Previous work indicated that about 7 to 10 times more power was required to initiate heating than to maintain heating of the specimen.

The large unit hanging on the wall in the left hand corner is the starter for the 30KW D. C. power supply which is located directly below the starter. The large black cabinet located next to the power supply contains the conventional DC
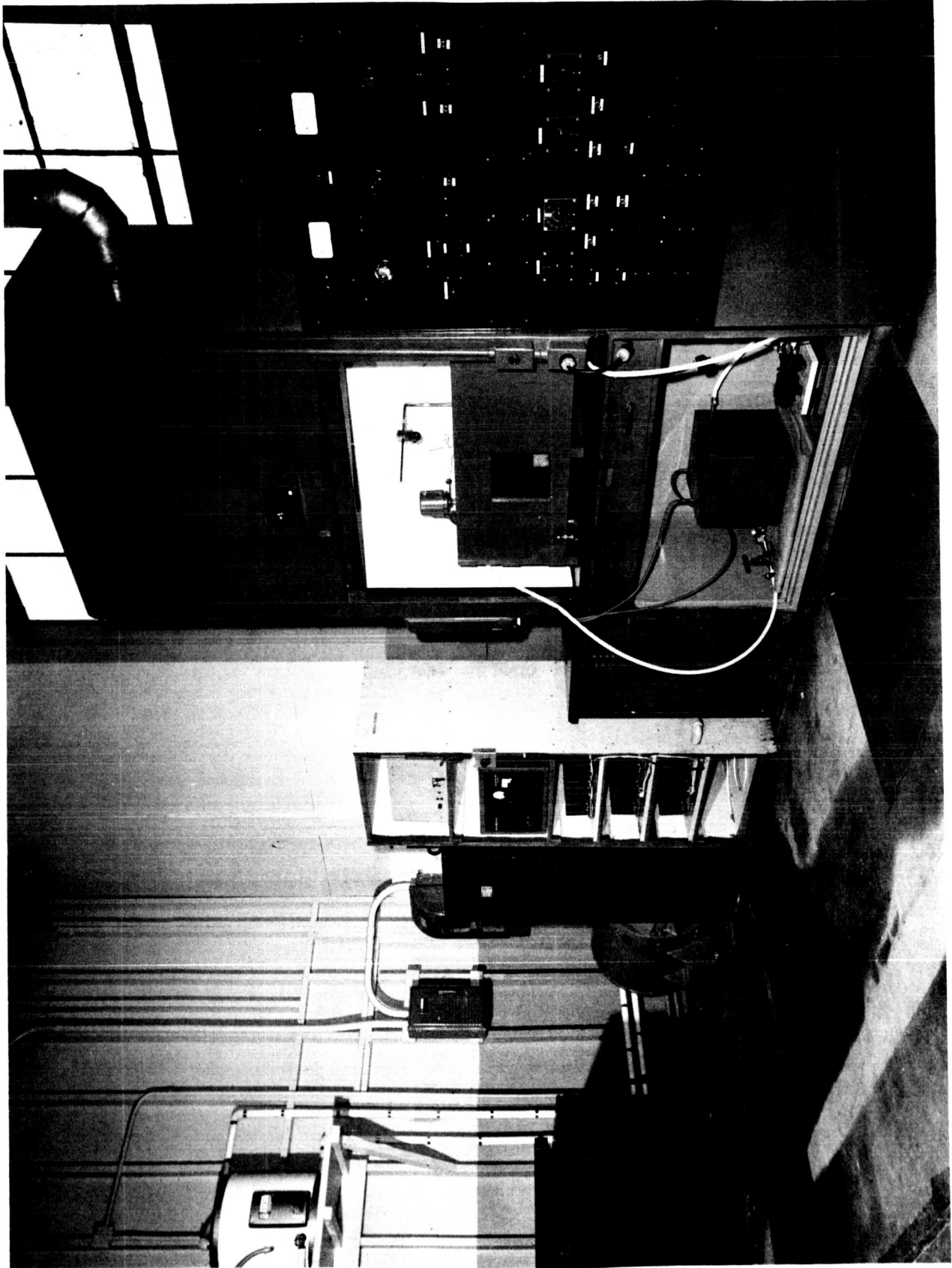
FIGURE IV-1 Overall View of the Electrolytic Heat Treating Facility Assembled During Phase II of Contract No. NAS 8-20064

Photo No. 4592

SELECTOR SWITCH

POWER SUPPLY

STARTER

CAPACITOR BANK
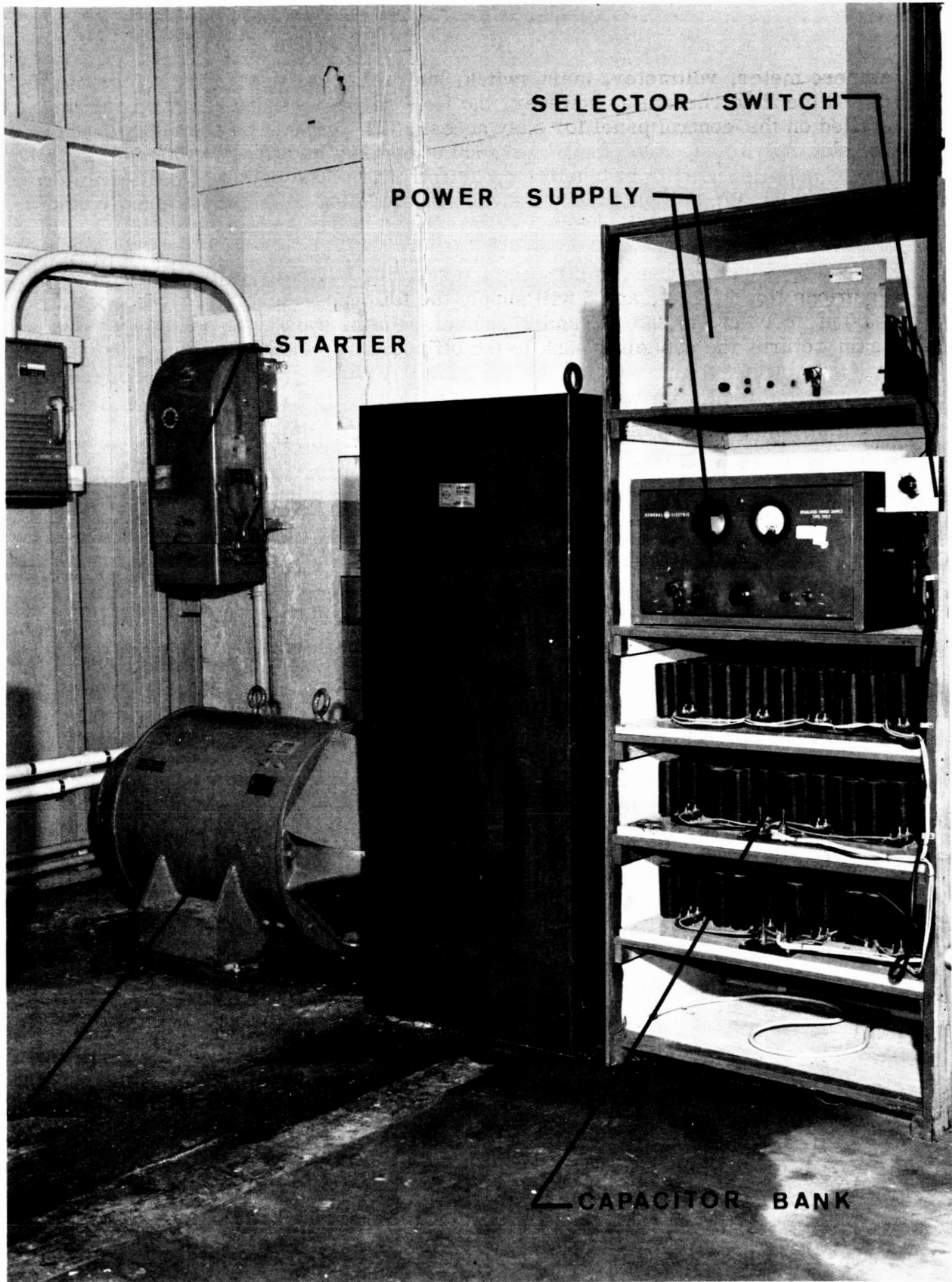
FIGURE IV-2   Close-up View of the Power Supply System Which Will Be Used To Heat the Specimens. The D.C. Generator is a 30KW, 100 Ampere, 300 Volt Power Supply   Photo No. 4590

4-3

ampere meter, voltmeter, main switch, and field resistor. This unit also contained the field rheostats, however, the field rheostats were removed and installed on the control panel for easy access. The cabinet on the right contains the electrolytic capacitor bank of 27,000 uf nominal and the two (500 volt D.C.) power supplies used to charge the capacitor bank. The output of the capacitor bank is controlled by the selector switch located next to the power supply on the second shelf.

The capacitor bank is off when the selector switch is in the No. 1 position. Positions No. 2, 3, 4, and 5 will supply the following capacitance respectively: 4500 uf, 9000 uf, 18,000 uf, and 27,000 uf. Position 6 on the selector switch again returns the capacitor bank to the off position. Each position on the selector switch contains an arc suppressor resistor. A bleeder resistor is permanently connected across each bank to discharge residual energy on completion of an operating cycle.

This safety precaution will prevent the capacitor bank from retaining its charge when the operation is closed down. With the two power supplies, the capacitor bank is capable of being automatically recharged and discharged approximately 6 times a minute.

Figure IV-3 is a photograph of the heat treating area of the entire system. The black panel on the far right of the photograph is the control panel for the system. Figure IV-4 is a close-up of the control panel.

The meter on the upper left is a 0-250-500 D.C. ampere meter. When the switch to the left of the meter is depressed, the meter scale range is from 0-250 D.C. amperes.

The meter on the right is a 0-250-500 D.C. voltmeter. The switch to the right of the meter converts the scale range to 0-250 volts D.C. The switch located between the two meters is a safety switch which must be turned on before the D.C. power supply can be started. Even though the power supply is running, the circuit to the specimen is not complete until the key switch on the panel has been turned to the "on" position.

The three knobs located below the meters are the field rheostats which are preset to control the D.C. generator output voltage to the levels required by the heat treating process. Below the field rheostats are a series of switches which activate the power supplied for the capacitor bank, the ventilation hood, the electrolyte heaters and the circulation pump.

On the lower panel are 4 timers which control the time interval of the various preset voltages. The timers are activated by relays which can be controlled manually or automatically by the row of switches located below the timers. The tickle switch, located below the 4th timer, can be used to discharge the capacitor bank manually when the second switch below timer No. 2 is in the single position. The capacitor bank discharges automatically when this switch is in the repeat position.

FIGURE IV-3 This Photograph Shows the Heat Treat Area of the System Which
Includes the Control Panel, Heat Treat Tank, Ventilation Hood, and Sink
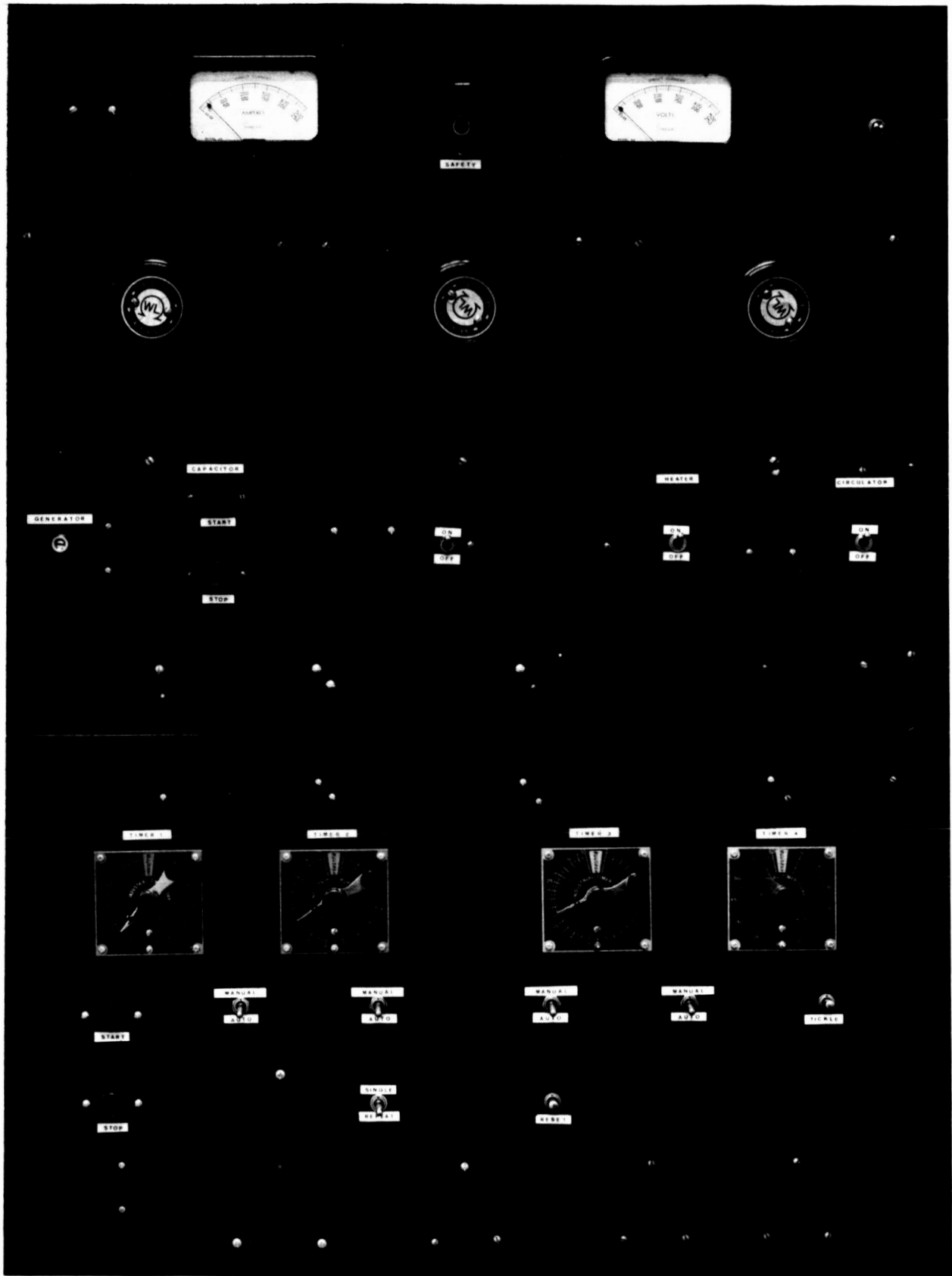
Photo No. 4588

FIGURE IV-4 Close-up View of the Control Panel
Fabricated to Control Heat Treating Operation
Photo No. 4591

The field rheostats, switches, and timers are controlled by relays so that the preset voltages will be activated on a controlled time cycle to provide the necessary heat for the process.

The button on the left of the bottom row will close down the entire operation at any point in the cycle. The switch on the right in the bottom row will reset all the relays and timers in preparation for the next operating cycle.

The small unit on the extreme left of Figure IV-3 is a chemical sink. It will be used to wash samples and supply the cooling water for the heat exchanger.

The center unit in Figure III-3 is a chemical fume hood, which contains the electrolyte tank, the circulation pump and the heat exchanger. Figure IV-5 shows a close-up of the heat treating system. The upper portion of the chemical hood contains the electrolyte tank. The tank was fabricated from 1/2" thick marine plywood with internal dimensions as follows:

Heat Treating Volume - 31-1/2" x 14-1/2" x 13"

Reservoir Volume - 7" x 14-1/2" x 13"

The inlet, outlet, and drain fittings on the tank have been fabricated from 1/2" diameter stainless steel tubing. The internal area of the tank was painted with seven coats of the Turco 522 maskant to seal all joints and to provide a watertight tank.

All exposed screws were carefully coated to prevent chemical attack from the electrolyte. The exterior of the tank was painted with one coat of the maskant to protect the surface from accidental spillage.

The anode for the tank was fabricated from 5/16" thick annealed AISI Type 321 stainless steel. This plate is 30" x 12" in size and has six 1/2" diameter holes for drainage purposes. Four wooden cleats were fastened to the bottom of the anode to provide an area for the heaters and for any sludge build-up. The wooden cleats were also coated with the Turco maskant as described above.

A 1/4" diameter stainless steel rod was welded to the rear left hand corner of the plate to serve as the electrical contact.

Two 2500 watt, 240V Chromalox heaters were installed in the botton of the tank. The two U-shaped heaters are 28" long with the electrical connections on the lower left hand side of the tank (see sketch). The anode plate fits on top of the heaters and is equipped with two preset contact thermostats 125°F and 135°F in a sealed stainless steel container. The thermostats will control the heating cycle of the heaters.

Heater Description
Chromalox No. T1-11245F
2.5KW - 240V - 1/2" dia.
Incoloy sheath heaters
with bulkhead fittings and
standard 8-32 threaded
terminal pins
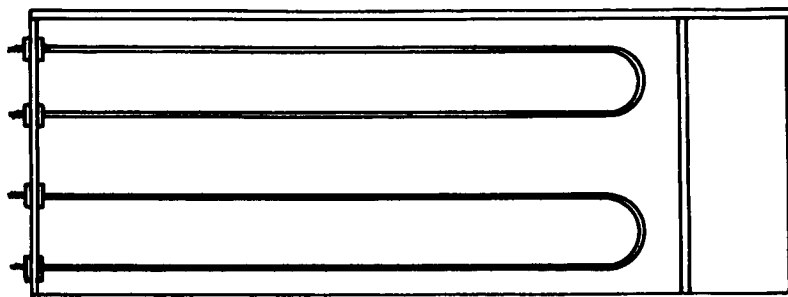
The tank is also equipped with a 8" x 8" plexiglas window, as shown in the photograph, which will be used for viewing the electrolytic heating operation during Phase III. In addition, an agitator is mounted on the side of the tank and can be moved anywhere around the edge of the heat treating area. The speed of the agitator is controlled by a variac to provide various degrees of agitation.

The specimen support stand is mounted on the rear of the tank. The stainless steel rod support can swivel and contains a pulley which can be positioned anywhere over the width of the tank. With the swivel rod and movable pulley, the specimen can be located anywhere over the anode plate.

The electrolyte is continuously cycled from the reservoir area, through Teflon tubing to a monel centrifugal pump (see Figure IV-5). The electrolyte is forced into the top of the heat exchanger on the right hand side and exits on the lower left hand side. The flow of solution back to the tank is controlled by the hand valve on the exit side of the heat exchanger. The heat exchanger contains a 20 ft. cooling coil with water as the cooling media. The entire 40 gallon electrolyte system is recycled about every 10 minutes.

After the systems were checked out and several heating trials were made, some changes and additions were made to the system. These changes included

1. A Honeywell Visicorder which was adapted to the system to monitor the voltage change, amperage change, and temperature change during a heating cycle. The visicorder proved to be a valuable tool by providing a permanent record of each heating trial.

2. During the capacitor discharge experiments the output of capacitor bank was tested with and without the generator. When the capacitor bank was operated in conjunction with the generator the power spike across the specimen was very low. A review of the circuits indicated that most of the surge from the capacitor bank was being fed back through the generator circuit. To correct the situation, two IN 3168 diodes in parallel were placed in series with the generator output, thereby preventing the flow of current from the capacitor bank through the generator circuit. This change provided full power from the capacitor bank across the specimen in addition to that supplied by the generator.
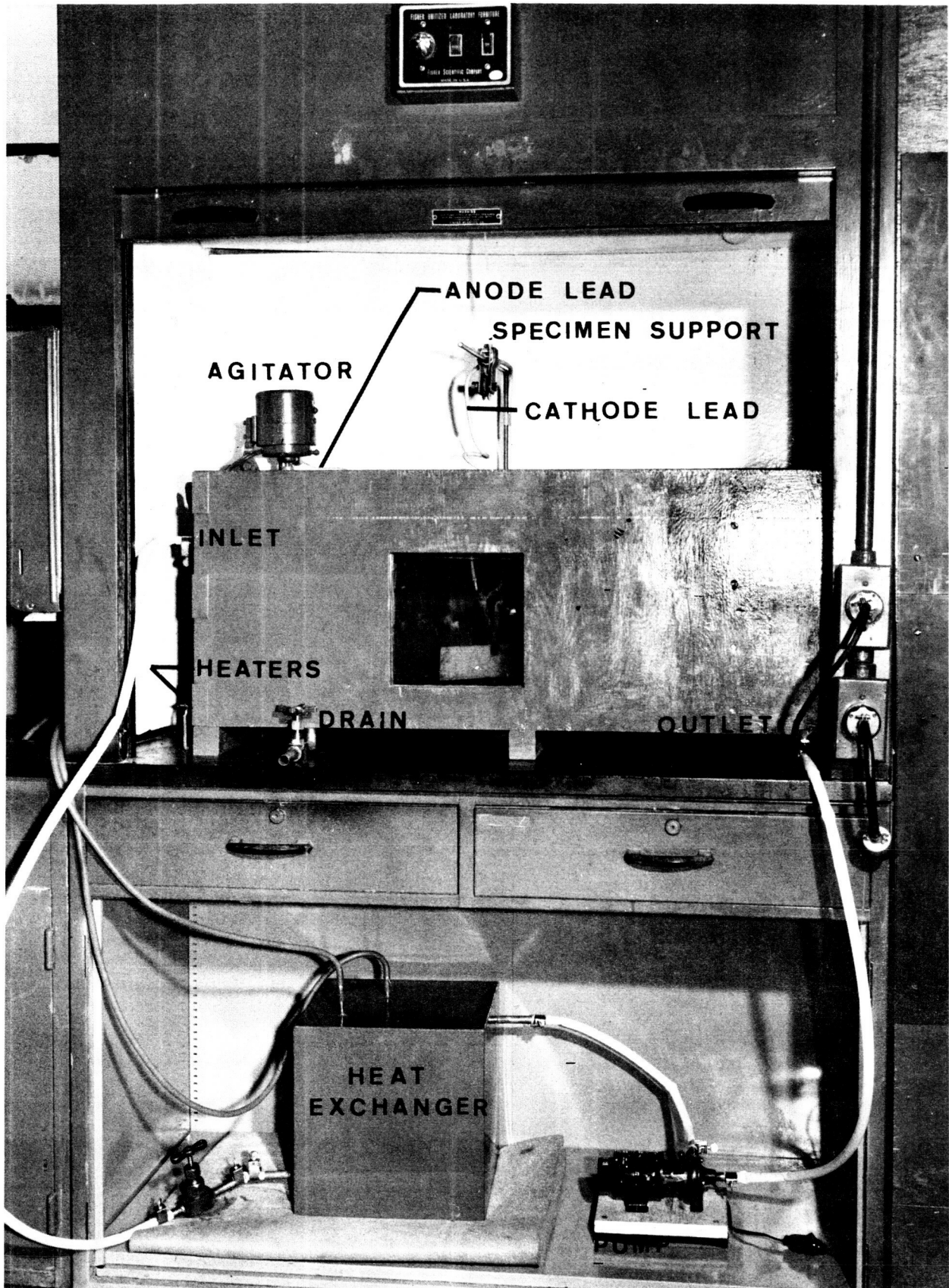
FIGURE IV-5   Close-up View of the Heat Treating Tank and Circulation System.
Note the sample visible through the plexiglas window.   Photo No. 4589
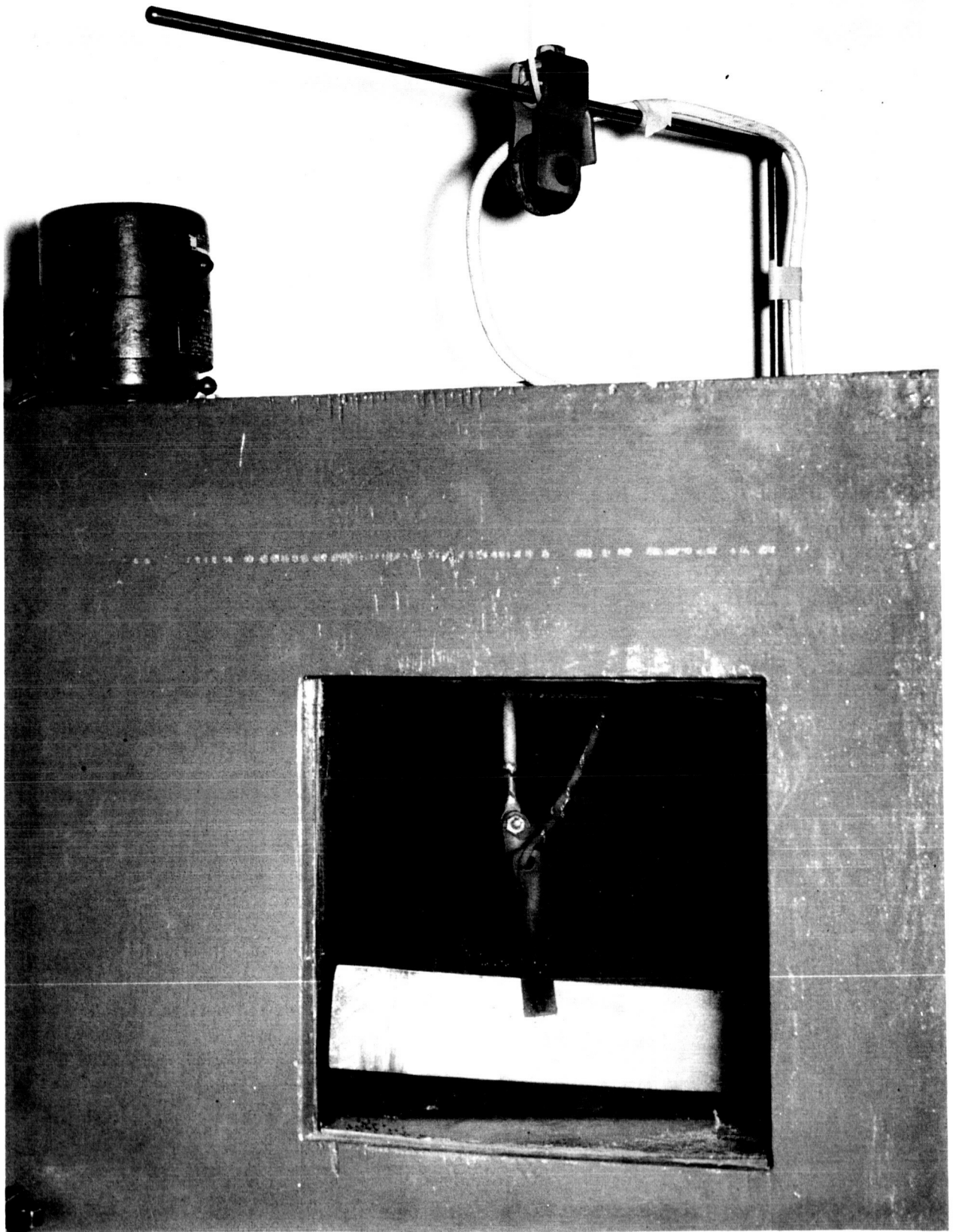
FIGURE IV-6 Close-up View of a Suspended Sample through the Tank Window.
Photograph also shows specimen support fixture.   Photo No. 4587

CONTROL CIRCUIT
FOR FABRICATED SYSTEM
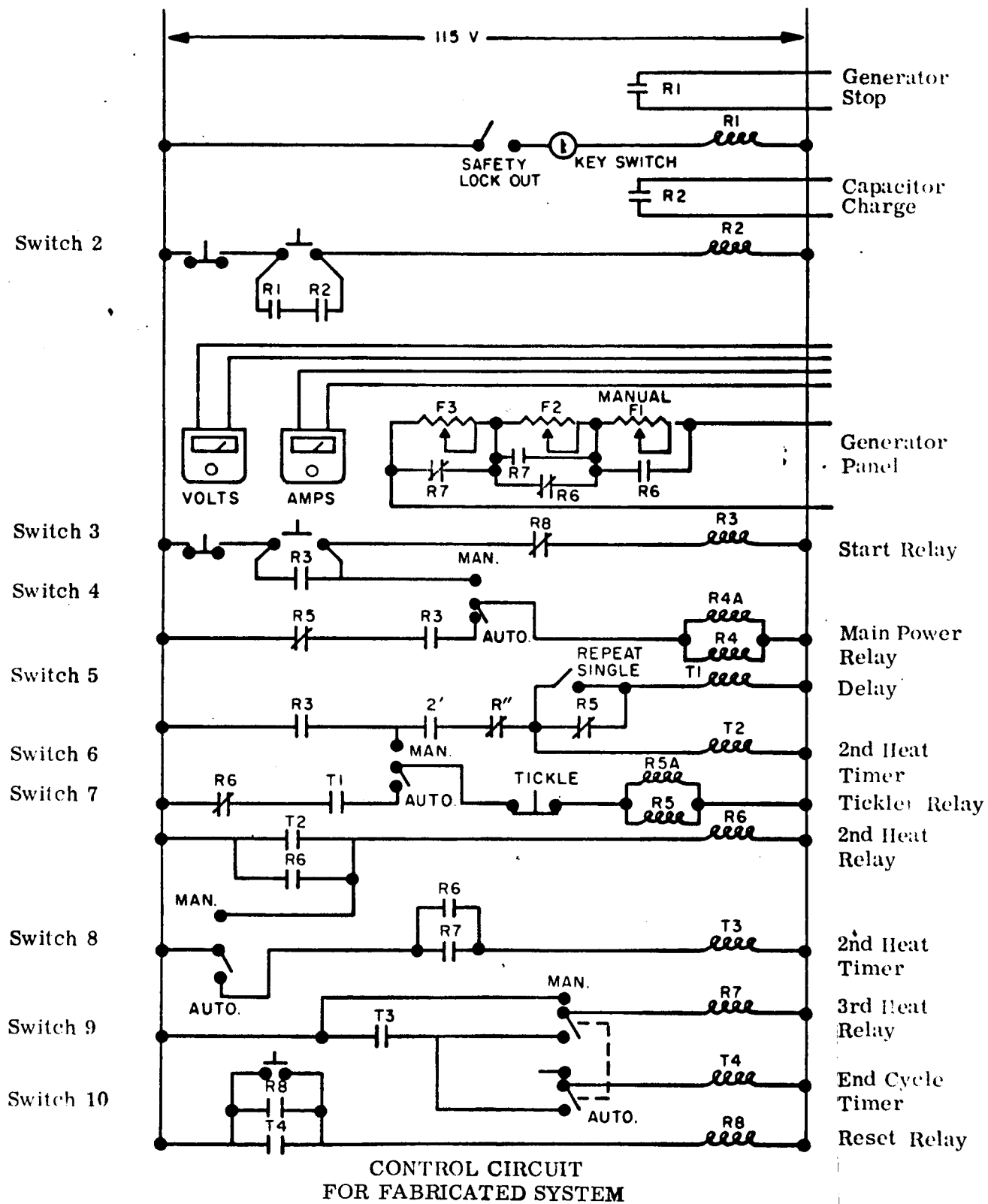
FIGURE IV-7

SECTION V

PHASE III – PROCESS EVALUATION

Phase III of this contract was directed toward the evaluation and understanding of electrolytic heating as a method of thermally treating metallic components. To evaluate this process required on understanding of the many variables which effect the process. Some basis for evaluation was needed to place the variables in proper perspective and after considerable examination the variables were grouped into three general categories:

A. With respect to the electrolyte
B. With respect to temperature
C. With respect to process mechanism

All the variables were then evaluated on the basis of how they affected or were related to the power requirements of the process.

When a potential is applied between two metallic components immersed in an electrolyte, the relationship between the applied voltage and the current density tends to follow a general form, see sketch:

D. C. Voltage - Volts
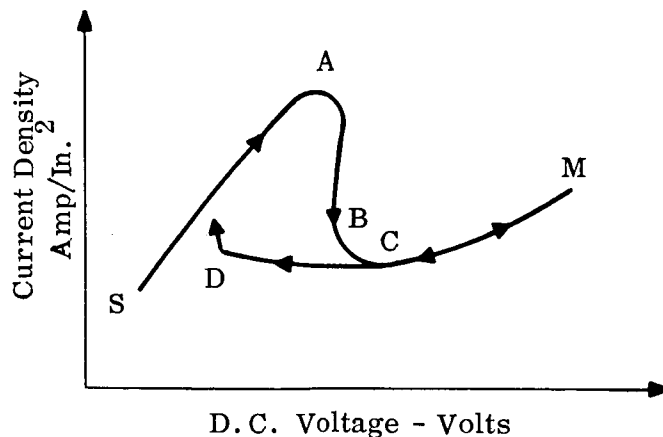
When the parameters of the process are varied, the shape of the curve changes; however, the basic shape remains the same. Examination of the process with respect to this curve, see sketch, indicates that as the voltage is increased there is a corresponding increase in current density until point A on the curve is reached. During this period of the process there is a bubbling action at the specimen or cathode which becomes more vigorous as the voltage is increased.

This bubbling action which is the liberation of gas, hydrogen from cathode and oxygen from the anode is known as electroysis.

When the voltage has increased to point A on the curve, a very small intermittent arc can be seen along the edges of the specimen. As the voltage is further increased, arcing increases and the current density decreases until the arcing becomes continuous over the entire specimen at point B on the curve. If the voltage is increased again, arcing becomes more vigorous until point C is reached, at which time the temperature of the specimen increases very rapidly. An additional increase in voltage is accompanied by a slight increase in current density and a considerable increase in specimen temperature. A sufficient increase in voltage will cause the specimen to melt.

Once the voltage has been increased to point C on the curve and the specimen has started to heat, the voltage can be decreased along the line of CD and arcing will be maintained. The temperature of the specimen will decrease as the voltage is reduced toward point D and arcing will continue with less intensity. At point D the arcing condition can no longer be supported; the arcing condition ceases with an increase in current density and a vigorous boiling action again occurs.

Regardless of the conditions imposed upon the system the process will follow the basic curve described; however, the voltage and current density at which each phase of the process actually occurs is dependent upon the process conditions. The remainder of this section will be devoted to how the various individual conditions affect the process cycle.

A. PROCESS EVALUATION WITH RESPECT TO THE ELECTROLYTE

Since the overall program was aimed at the development of a heat treating process for the 2219 aluminum alloy and the titanium -6 Al-4V alloy, it was decided to conduct the electrolyte evaluation portion of the program using these two grades of material.

1. Selection of Electrolytes

In general, any solution which conducts an electric current is an electrolyte. The type of electrolyte used in a particular process is dictated by several variables. In the case of electrolytic heating, the electrolyte should have the following characteristics:

1) Inert to the electrolytic cell and to the product to be heated

2) Highly conductive electrically

3) Capable of achieving sufficient heating at low voltages and small currents

4) Of low toxicity and non-fuming

5) Inexpensive

In addition to the general variables, each electrolyte must be evaluated in particular for heating characteristics in conjunction with the type of material being heated, the concentration, and the available power requirements.

There are several types of electrolytes; the most common being aqueous electrolytes. These solutions are the most convenient to prepare and use. Non-aqueous solutions and fused salts have been considered for electrolytes by various researchers, but to date these electrolytes have not gained sizeable or widespread use and therefore were not considered during this contract.

On the basis of the general characteristics outlined previously in this section, the following compounds were selected as possible electrolytes for evaluation with the two grades of materials.

a.	Sodium Carbonate	-	Na_2CO_3
b.	Sodium Sulfate	-	Na_2SO_4
c.	Sodium Hydroxide	-	NaOH
d.	Potassium Hydroxide	-	KOH
e.	Sodium Acetate	-	$NaC_2H_3O_2$
f.	Potassium Acetate	-	$KC_2H_3O_2$
g.	Ammonium Sulfate	-	$(NH_4)_2SO_4$
h.	Calcium Chloride	-	$CACl_2$

2. Testing Procedure

The procedure used to evaluate the electrolytes was to conduct a series of heating trails with each electrolyte at various concentrations with each of the two grades of material. About 150 specimens of each material were prepared. The Ti-6AL-4V specimens were prepared from annealed sheet and cut 1/2" x 2" x .056". A line was scribed on each side of the specimen 1" from the bottom to denote 1 square inch of surface area. The 2219Al specimens were cut the same size as the titanium specimens from a piece of .080" thick annealed stock.

To reduce the quantity of chemicals required, it was decided to conduct the concentration heating trials in a 2000 ml beaker using all of the other facilities fabricated during Phase II. A stainless steel anode was made for the bottom of the beaker. The large heating tank was drained, cleaned and half filled with water to provide a cooling media for the heat treating beaker which was placed in front of the tank window. With this setup, the specimen holder for the large tank would be used, the solution could be cooled, and the heating action could be observed. A Honeywell Visicorder was added to the system to monitor the voltage and amperage change during each heating cycle. The solutions were prepared by calculating the amount of compound needed to make a desired concentration on a weight % basis.

The calculated quantities were weighed out on a chemical balance and added to 1500 ml of distilled water. After thorough mixing the solution was cooled to 60°F and checked with a hydrometer calibrated in Degrees Baumé. The Baumé reading was converted directly into weight % from tables in a chemical handbook. The concentrations were adjusted and rechecked if necessary.

To conduct a heating trial, a specimen was placed in the sample holder and lowered into the solution to the scribed line, exposing one square inch of surface area. A thermometer was also placed in the solution to measure the temperature of the solution during heating. The D. C. generator was started and the voltage increased in steps by adjusting the rheostats until continuous arcing was established. The voltage and corresponding amperage were recorded on the visicorder. The voltage was then increased until the specimen became red hot (in the case of Ti-6Al-4V). In some cases the voltage was increased until melting started and then the voltage was quickly reduced to an intermediate point. The procedure was then reversed by decreasing the voltage in steps until the minimum voltage was obtained with the rheostat. The voltage, amperage, and observations were recorded. The complete process was repeated at least 3 times for each concentration of solution using a new sample each time. In some cases an additional specimen was heated and quenched from red heat by cutting the power at the control panel.

3. Electrolyte Test Results and Evaluation for 2219 Al Alloy

The results of the heating trials of the eight electrolytes tested were evaluated using the following observations as criteria:

1) Minimal precipitation in the electrolyte

2) Lack of chemical attack prior to heating

3) Minimum surface attack during heating

4) Reaction of solution at start of the heating cycle and during the heating cycle

5) Maximum control during heating cycle

The results of the 2219 Aluminum alloy heating trials with respect to the electrolyte were as follows:

a. Sodium Carbonate - Na_2CO_3

A series of 2219 Aluminum specimens 2" x 1/2" were heated in solutions of Na_2CO_3. The concentration was varied from 1% to 10%. Figure V-1 is a graphical representation of the voltage versus current density data obtained from this series of heating runs. Evaluation of the heating runs indicated the following:

(1) Considerable precipitation occurred during the heating runs producing an extremely cloudy solution.

Voltage versus Current Density Curves for Heating 2219 Al in Various Concentrations of Na_2CO_3

Solution Concentration 1%

Solution Concentration 2%

Solution Concentration 10%

CURRENT DENSITY AMPS/SQ. INCH

D.C. VOLTAGE VOLTS

FIGURE V-1

5-5
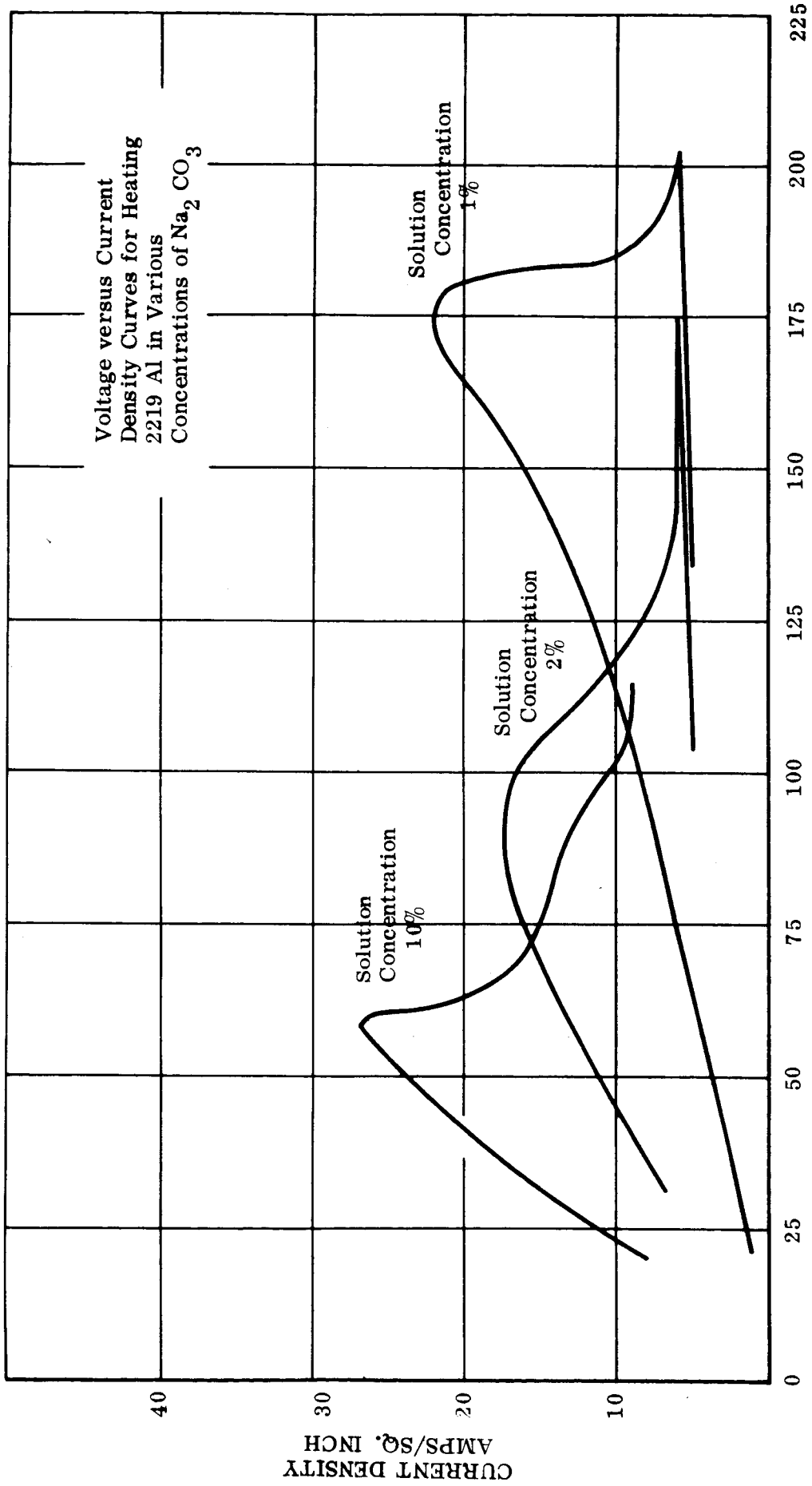
(2) Surface attack was noted prior to applying the power in the 10% solution of Na_2CO_3.

(3) Considerable metal removal was noted during the heating cycle on those specimens heated in the 6% and 10% solutions.

(4) The characteristic voltage to start arcing (point A) decreased with increasing concentration, while the amperage increased with increasing concentration.

(5) The voltage necessary to maintain a steady arc (point B) decreased as the concentration increased; however, the amperage remained approximately constant.

(6) The voltage at which the temperature of the specimen increases suddenly (point C) is slightly higher than the "B" voltage and decreased as the concentration increased. The amperage at point "C", like point "B", remains approximately constant. A change in the color of the arc at the sample was also noted at the "C" point.

Based on the results described above under 1, 2, and 3, it was felt that the Na_2CO_3 would not be a satisfactory electrolyte for heating 2219 aluminum alloy.

b. Sodium Sulfate-Na_2SO_4

The second electrolyte evaluated for heating the 2219 Aluminum alloy was NA_2SO_4. Specimen size remained constant and solution concentration varied from 1.2% to 7%. Figure V-2 is a graphical representation of voltage versus current density at the various concentrations tested. An evaluation of the heating runs with the Na_2SO_4 indicated the following:

(1) A brown precipitate formed after the first heating run at each concentration tested.

(2) Metal loss was noted after heating in all concentrations tested. The specimen after heating was thinner in the area which was exposed to the electrolyte.

(3) The voltage and current density trends for the heating cycle were similar to those described for the Na_2CO_3 solutions.

More difficulty was encountered in controlling the heating cycle with the Na_2SO_4 solutions than with the Na_2CO_3 solution. The specimens were melting before a uniform arc appeared to be established.

Voltage versus Current Density
Curves for Heating 2219 Al
in Various Concentrations
of Na_2SO_4

1%

4%

7%

Solution
Concentration

CURRENT DENSITY
AMPS. /SQ. INCH

50   40   30   20   10

0   25   50   75   100   125   150   175   200

D.C. VOLTAGE - VOLTS
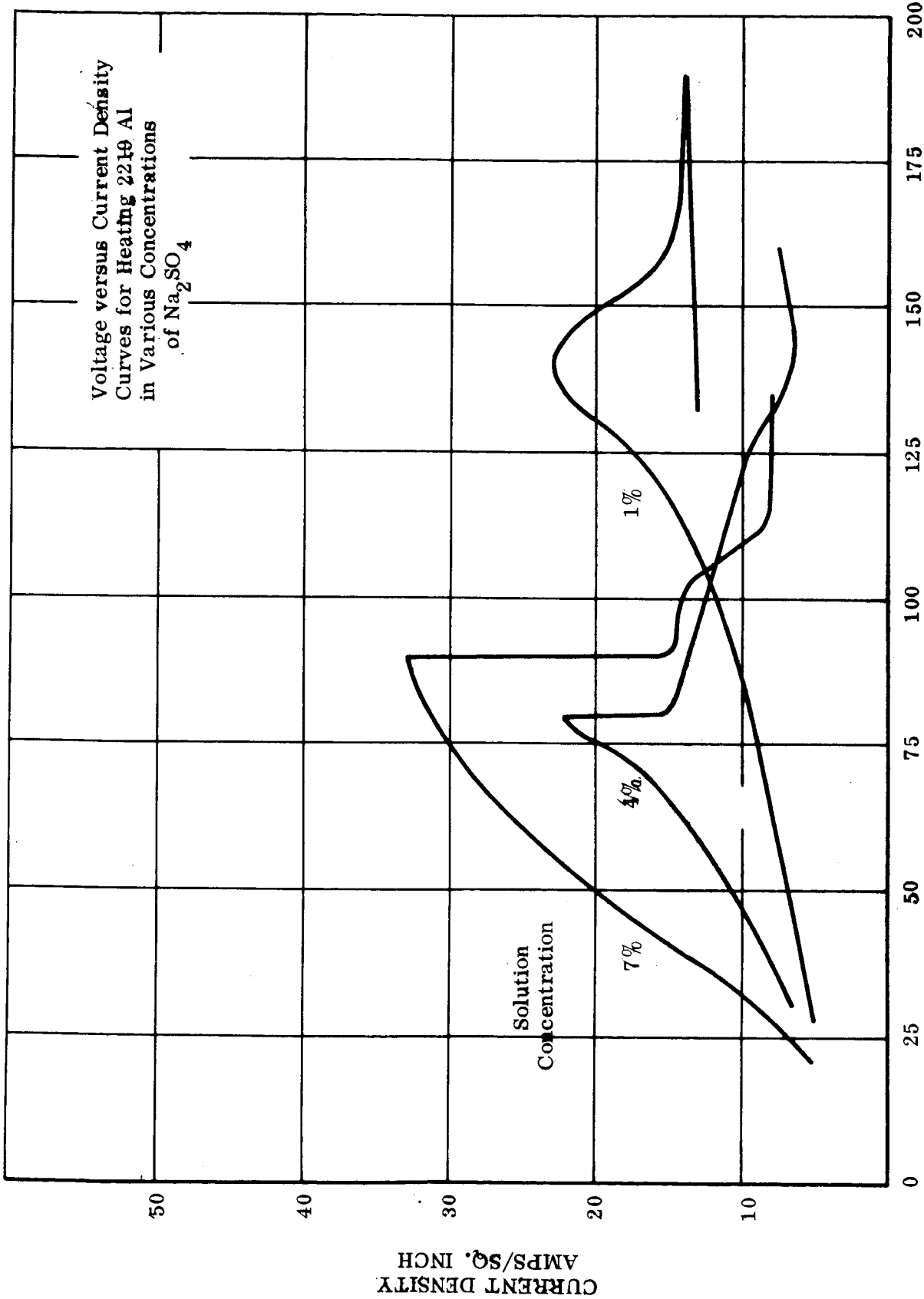
FIGURE V-2

Based on the observations described in 1 and 2, and the unstable control during heating, it is felt that the Na_2SO_4 solutions would not be satisfactory as an electrolyte for heating 2219 aluminum alloy.

c. Sodium and Potassium Hydroxide-NaOH and KOH

The next two electrolytes which were evaluated consisted of 1%, 4%, and 10% solutions of NaOH and 1%, 4%, and 9% solutions of KOH. It was known that the 2219 aluminum alloy would react with the hydroxide solutions; however, both hydroxides had shown favorable results as electrolytes with Ti-6Al-4V in the earlier work conducted by Republic. In view of the short heating times involved, it was advisable to test the solutions with the aluminum alloy.

Figures V-3 and V-4 show the voltage-current density relationship for the NaOH and KOH solutions respectively. It should be noted that the voltages and corresponding current density for a given concentration were almost the same for both hydroxide solutions. Evaluation of the two hydroxide solutions indicated the following:

(1) Both hydroxides exhibited a surface reaction with the specimen at all concentrations prior to heating.

(2) Some precipitation was noted in both solutions at all concentrations; however, the amount of precipitate was small compared to that observed with the Na_2CO_3 and Na_2SO_4 solutions.

(3) Some metal loss was noted on the specimens; however the surface of the specimens was smoother than those heated in the first two electrolytes. A comparison of the two electrolytes, NaOH and KOH, showed the specimens heated in the KOH to contain a smoother surface.

(4) The same general trends in voltage response were noted on both hydroxide solutions as were noted with the Na_2CO_3 and Na_2SO_4 solutions.

(5) One additional condition was noted with the help of the Visicorder which was not previously observed. The voltage at which melting occurred was less than the voltage necessary to start heating. An example of this condition is shown with the 4% NaOH solution (see sketch on following page). In order to maintain a continuous arc over the entire sample a minimum voltage of 106V was required. To achieve heating of the specimen the voltage must be increased to 136V and then quickly reduced below 77V. A stable heating condition exists between 60V and 77V; however, if the voltage is increased beyond 77V once heating has been achieved the specimen will melt. If the voltage is reduced below 60V the arc will be extinguished.

5-8

Voltage vs. Current Density Curves to Heat 2219 Al in Various Concentrations of NaOH

FIGURE V-3

CURRENT DENSITY
AMP/SQ. INCH

D.C. VOLTAGE - VOLTS

Solution Concentration

10%

4%

1%

Voltage vs. Current Density Curves to Heat 2219 Al in Various Concentrations of KOH

Solution Concentration

9%

4%

1%
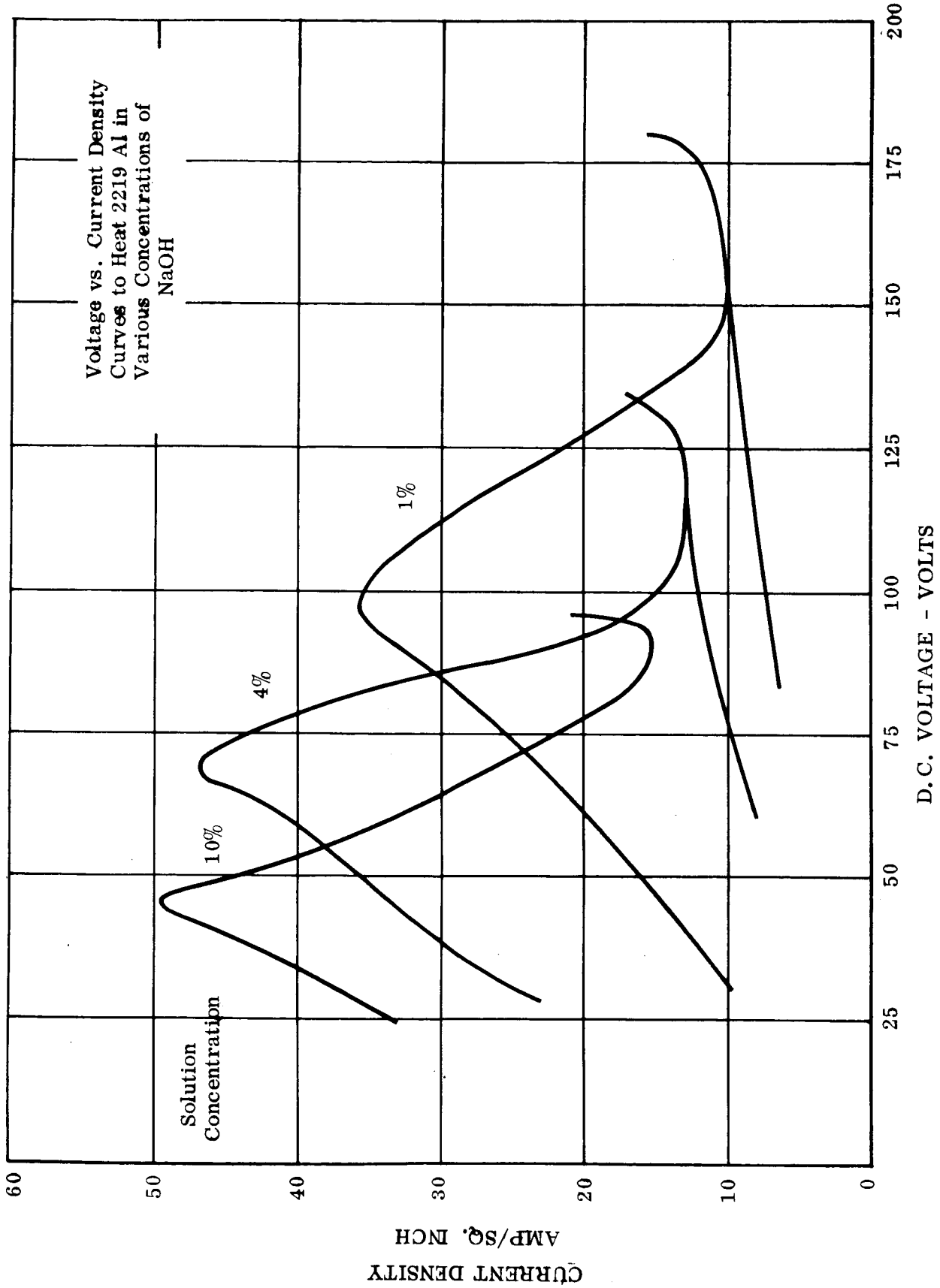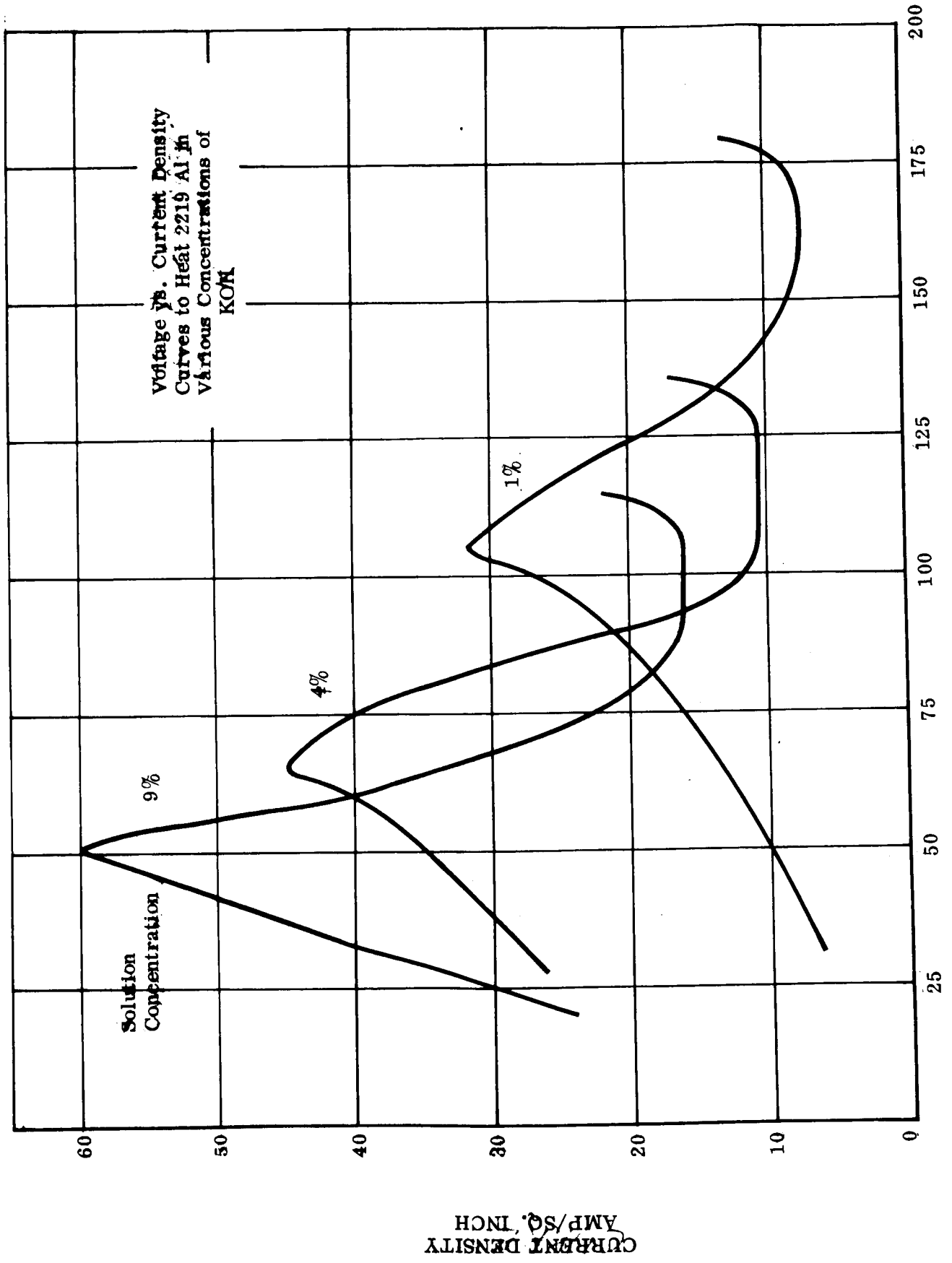
D.C. VOLTAGE - VOLTS

FIGURE V-4

CURRENT DENSITY AMP/SQ. INCH

5-10

Matl: 2219 Al.
Elect: 4% NaOH

A = 68V
B = 106V
C = 136V
M_{2219} = 77V
D = 60V

Current Density Amps/Sq. In.

A

B   C

D $M_{2219\ Al}$

D.C. Voltage
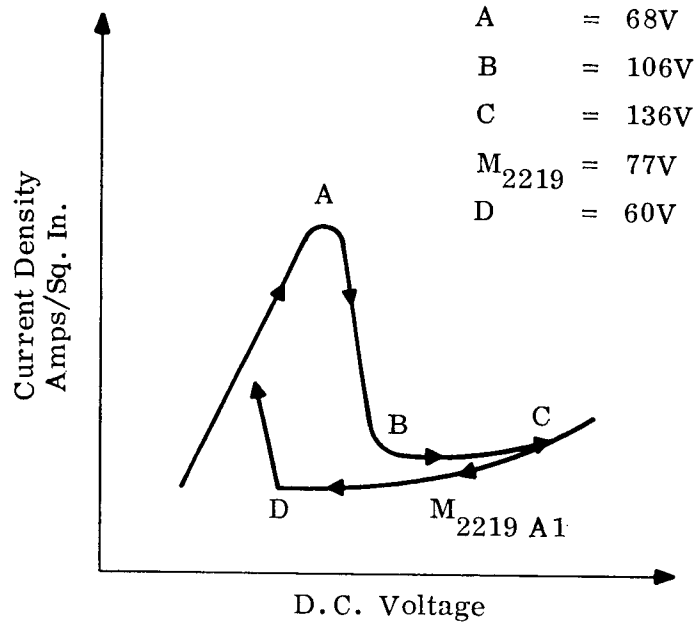
(6)   Based on the observations made during the hydroxide evalua-
tion; heating can be achieved with either electrolyte; however,
in view of the results shown in sub sections 1, 3, and 5, the
hydroxide solutions would not be satisfactory as an electrolyte.
Heating control will be very difficult on the 2219 alloy with
the melting voltage below the voltage necessary to start heating.

d.   Sodium Acetate - $Na(C_2H_3O_2)$

Specimens 2" x 1/2" x .080" of 2219 aluminum were prepared for
heating in 1%, 2%, 4% and 8% solution of $Na(C_2H_3O_2)$. One inch of the speci-
men was exposed to the electrolyte and the anode to cathode distance was main-
tained at 3.75" (from the bottom edge of the sample to anode). Figures V-5
and V-6 are a graphical representation of the average voltage versus current
density at the various concentrations. The graphs represent the data from a
total of 20 heating runs. Evaluation of the heating runs indicated the following:

(1)   A white gelatinous precipitate formed during heating at all
concentrations. This precipitate is believed to be aluminum
hydroxide.

(2)   There was no visible chemical reaction on the specimen prior
to heating at any concentration.

(3)   There was no visible metal loss on the specimen after heating;
      however, if aluminum hydroxide is being formed, the aluminum
      would have to be supplied from the specimen, resulting in some
      loss of material. Any metal loss that did occur was very uni-
      form over the entire surface. There was no evidence of under-
      cutting on the specimen at the air liquid interface.

(4)   The surface finish of the heated specimen was much smoother
      than those heated with KOH solution. A comparison of the two
      sets of specimens showed some very fine pitting on those speci-
      mens heated in the KOH solutions and very little change in the
      surface of those specimens heated in the $Na(C_2H_3O_2)$ solutions.

(5)   The voltage versus current density relationship was similar
      to that reported for the previous electrolytes tested. A com-
      parison of the power requirements for the heating cycle be-
      tween the KOH solutions and the $Na(C_2H_3O_2)$ solutions showed
      that more power was required with the $Na(C_2H_3O_2)$ solutions
      throughout the heating cycle at similar concentrations. It
      was noted that the operator had more control in heating the
      specimens in the acetate solutions.

(6)   It should be noted that the melting characteristic discussed
      with respect to the hydroxide solutions were also observed
      with the $Na(C_2H_3O_2)$ 2219 aluminum system. The data indicated
      that a greater voltage was necessary to start heating the
      aluminum specimens (Point C, Figure V-5) than to melt the
      specimens once heating was achieved (Point M, Figure V-5).
      Figure V-5 indicates that arcing over the entire specimen
      starts at Point B on the voltage versus current density curve,
      but heating does not start until the voltage has increased to
      Point C. When the voltage reaches Point C, it must be
      quickly reduced below Point M (melting point) or the specimen
      will melt. The degree of heating is controlled between Point M
      and Point D (arc is extinguished).

      If the voltage should be reduced before reaching Point C on the
      voltage versus current density curve, the voltage does not follow
      the original path through Point A but returns along path B E
      (see Figure V-5). This is probably due to the slight increase
      in heat of the specimen (200°F) which tends to reduce the voltage
      to start arcing.

(7)   As mentioned in subsection 6, the degree of heating is controlled
      between points M and D. As the concentration of the $Na(C_2H_3O_2)$
      solution increased, the voltage range to control heating decreased.
      At 1% $(Na(C_2H_3O_2))$ the range was 74 volts and at 8% $Na(C_2H_3O_2)$
      the range was reduced to 35 volts. This information will be
      discussed in greater detail later in the report.

Voltage vs. Current Density
Curves to Heat 2219 Al in
Two Concentrations
1% Na ($C_2H_3O_2$) ———
2.2% Na ($C_2H_3O_2$) - - - -

CURRENT DENSITY
AMP/SQ. INCH

D.C. VOLTAGE - VOLTS

FIGURE V-5

Voltage vs. Current Density Curves to Heat 1 sq" of 2219 Al in 4% and 8% Na(C₂H₃O₂)

4% — — —
8% ————

FIGURE V-6

CURRENT DENSITY - AMP/SQ. INCH
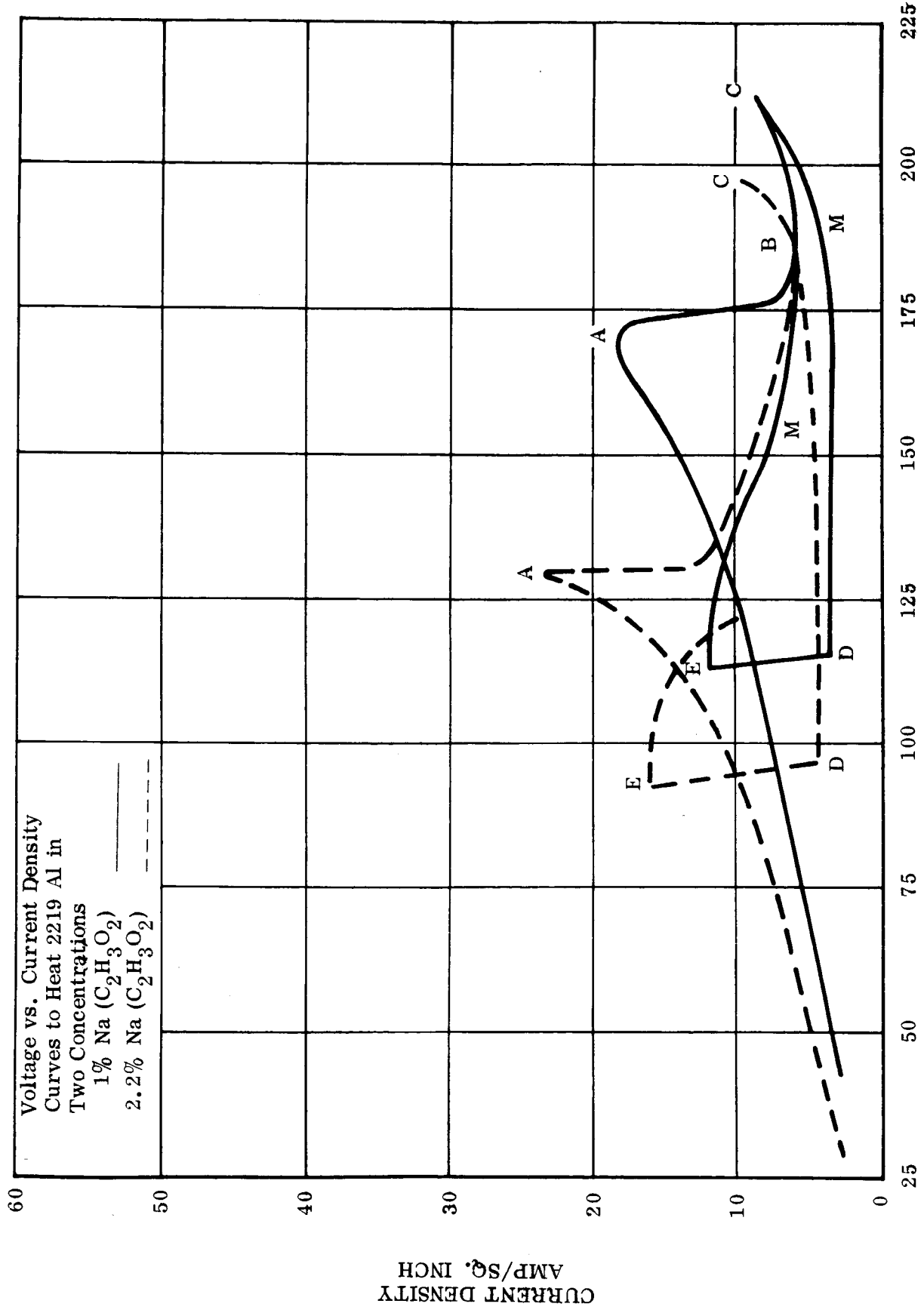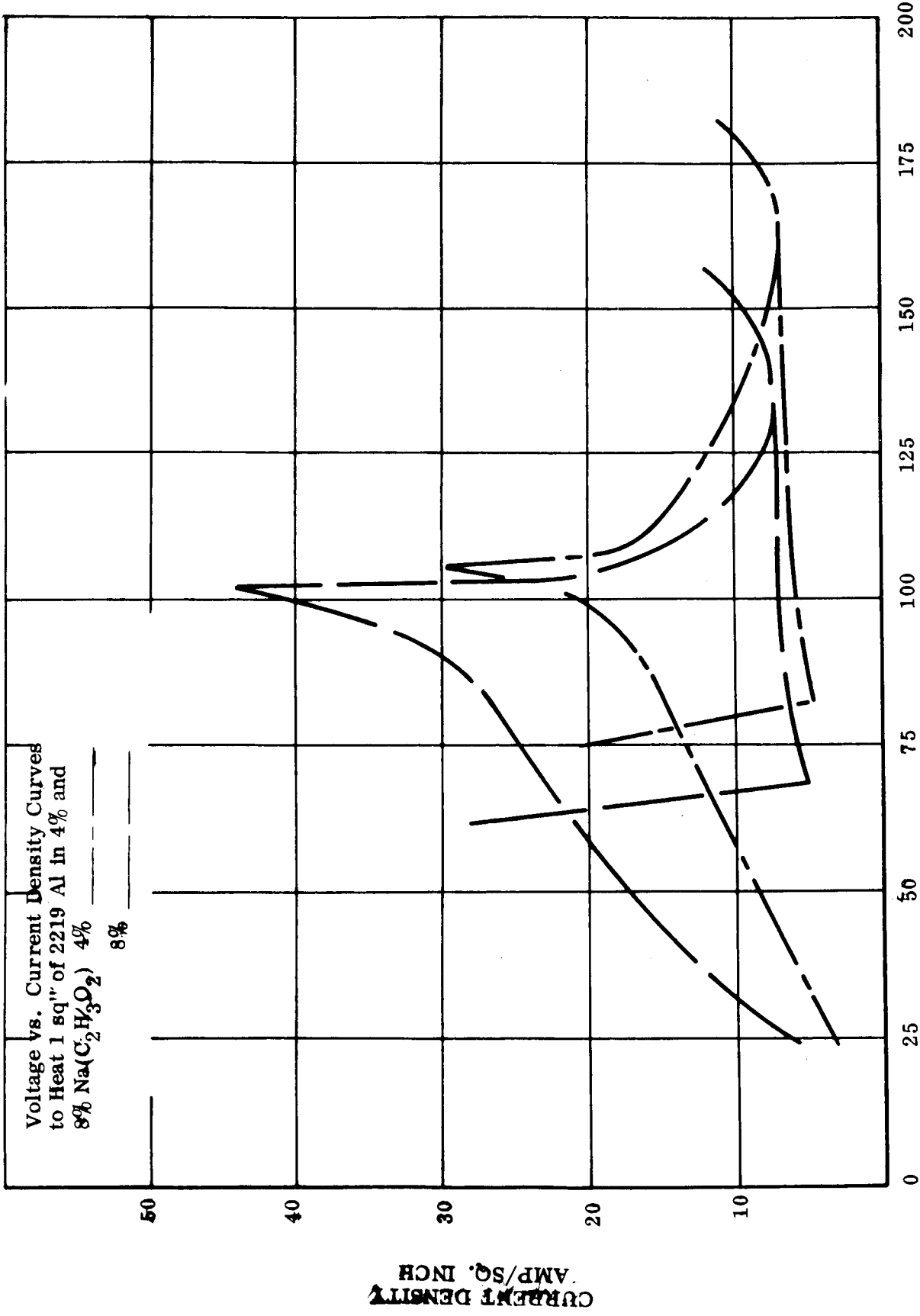
D.C. VOLTAGE - VOLTS

Based on the observations and results discussed in subsections 1 through 7, the sodium acetate solutions would be satisfactory as an electrolyte to heat the 2219 aluminum alloy.

e.   Potassium Acetate-K $(C_2H_3O_2)$

Thirty (30) specimens of 2219 aluminum 2" x 1" x .080" were prepared for heating in various concentrations of $K(C_2H_3O_2)$. The heating procedure was the same as that described for the previous electrolytic solutions; however, concentration was varied from 1% to 15%. Figure V-7 is a graphical representation of the average voltage versus current density at the various concentrations. The results of the heating trials indicated the following:

(1)   All of the observations described in subsections 1 to 7 for the $Na(C_2H_3O_2)$ solutions also apply to the $K(C_2H_3O_2)$ solutions.

(2)   Two differences noted between the $Na(C_2H_3O_2)$ solutions and $K(C_2H_3O_2)$ solutions were:

(a)   At similar concentrations, in most cases slightly less power was required throughout the heating cycle with the $K(C_2H_3O_2)$ solutions.

(b)   At low concentrations, 1% to 4%, the range of heating control, difference between Point M and Point D, was greater with the $Na(C_2H_3O_2)$ solutions; however, the 8% solution of $K(C_2H_3O_2)$ exhibited a greater control range by 10 volts.

(3)   One additional condition noted was that the specimens heated in the $K(C_2H_3O_2)$ solution appeared to have a more uniform temperature than those specimens heated in the $Na(C_2H_3O_2)$ solutions. In the potassium acetate solutions, melting occurred along the sides of the specimens as well as the bottom; however, in the $Na(C_2H_3O_2)$ solutions, melting seemed to be concentrated at the bottom of the specimens nearest the anode.

Based on the heating trials and the observations discussed above, the author feels the $K(C_2H_3O_2)$ solutions, about 8%, would be a better electrolyte than the $Na(C_2H_3O_2)$ for heating the 2219 aluminum alloy.

f.   Ammonium Sulfate-$(NH_4)_2SO_4$

Three specimens of 2219 aluminum were heated in a 4% solution of $(NH_4)_2SO_4$ using the same procedure previously described. A very high voltage, 250V, was required to start heating. A heavy sputtering condition existed throughout the heating runs and could not be eliminated even at melting. This electrolyte would not be satisfactory to heat the 2219 aluminum alloy.

Voltage vs. Current Density Curves to Heat 2219 Al in Various Concentrations of $K(C_2H_3O_2)$

FIGURE V-7

D.C. VOLTAGE - VOLTS

CURRENT DENSITY AMP/SQ. INCH
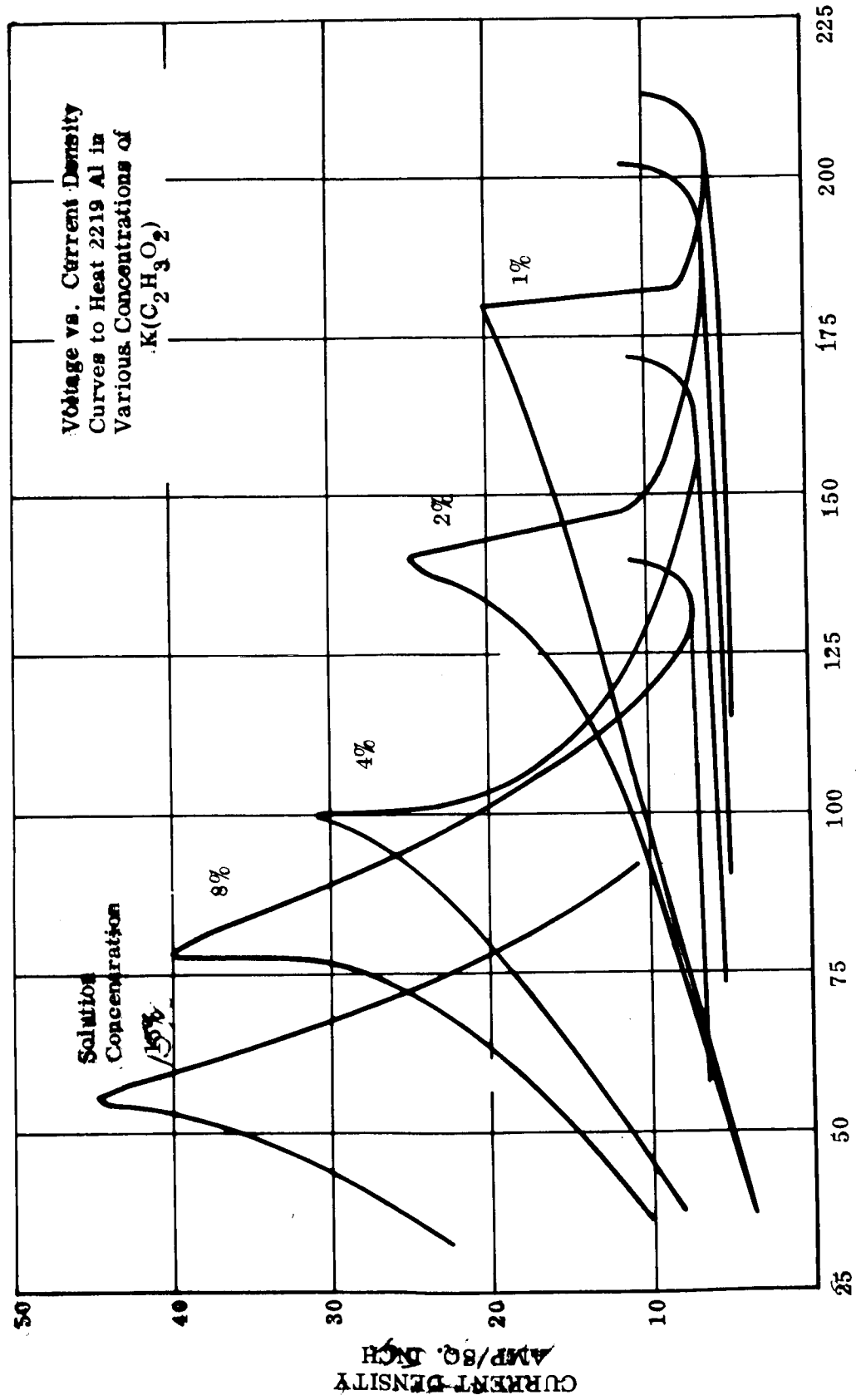
g. Calcium Chloride - $CaCl_2$

Several specimens of 2219 aluminum were heated in a 4% solution of $CaCl_2$. In each case, a heavy coating was deposited on the specimen which prevented a good arcing condition. This coating was probably CAOH which is insoluble and would not be acceptable for heating. On this basis, no additional concentrations were tested and the electrolyte was considered unacceptable.

On the basis of the observations made during the evaluation of the eight electrolytes, the best solution for heating the 2219 aluminum alloy would be the $K(C_2H_3O_2)$ at a concentration of 8% by weight. Additional testing was scheduled for this particular electrolyte.

4. Electrolyte Test Results & Evaluation for the Ti 6Al-4V Alloy

A similar series of evaluation tests were conducted using Ti-6AL-4V as the specimen material. The criteria used to evaluate the tests was the same as that used in section 3. The procedure for the heating trials and solution preparation was the same as that used for the 2219 aluminum alloy. The results of these heating trials were as follows:

a. Sodium Acetate - $Na(C_2H_3O_2)$

Specimens of Ti-6Al-4V were prepared 2" x 1/2" x .056" from annealed sheet. The specimens were heated in solutions of $Na(C_2H_3O_2)$ which varied in concentration from 1% to 8%. The voltage and amperage was monitored with the Visicorder and the following observations and results were noted:

(1) There was no chemical reaction with the specimen prior to heating.

(2) There was no visible precipitation in the electrolyte during the heating run. The solution remained clear and the arcing condition could be clearly observed.

(3) There was no apparent chemical attack of the specimen during heating.

(4) The voltage versus current density relationship at various concentrations followed the same general trends as described for previous electrolytes. As concentration increased, the respective voltages along the voltage versus current density curve decreased.

(5) The melting voltage for the Ti-6Al-4V specimens was at all concentrations higher than the voltage required to start heating, by at least 50 volts.

(6) The range of heating control difference between melting voltage "M" and no arc voltage "D") increased for concentrations between 1% and 4% from 86 volts to 127 volts and then decreased to 89 volts at the 8% level.

(7) At all concentrations on the thin specimens, heating appeared to start at the same voltage required to establish arcing over the entire specimen.

Based on the above observations, the $Na(C_2H_3O_2)$ solutions would be acceptable as an electrolyte for heating Ti-6Al-4V.

b. Potassium Acetate - $K(C_2H_3O_2)$

Fifteen Ti-6Al-4V specimens 2" x 1" x .056" were heated in the following concentrations of $K(C_2H_3O_2)$: 1%, 2%, 4%, 8%, and 15%. The amperage and voltage during each heating run was monitored on the visicorder and voltage versus current density graphs were constructed from the data (see Figure V-8). The results of these heating trials indicated the following:

(1) All of the observations made with respect to the $Na(C_2H_3O_2)$ solution in the preceeding section also apply to the solutions of $K(C_2H_3O_2)$.

(2) The range of heating control for the $K(C_2H_3O_2)$ solutions (voltage difference between the melting point "M" and the no arc point "D") followed the same trend as the $Na(C_2H_3O_2)$ solution; however, the voltage range was larger for the 8% $K(C_2H_3O_2)$ solution, 120 volts.

(3) The heating pattern with the $K(C_2H_3O_2)$ was similar to that noted with 2219 aluminum samples. Heating appeared to occur along the edges as well as at the bottom edge of the specimen. When the specimen melted, the edges of the specimen melted in a tapered pattern instead of just along the bottom nearest the anode.

Based on the results described under subsections 1 through 3, it is felt that the $K(C_2H_3O_2)$ is a better electrolyte than the $Na(C_2H_3O_2)$ for heating the Ti-6Al-4V alloy.

c. Ammonium Sulfate - $(NH_4)_2SO_4$

Several standard specimens of Ti-6Al-4V were heated in a 4% solution of $(NH_4)_2SO_4$. A heavy precipitate was formed immediately during the heating run and heavy sputtering throughout the heating run could not be eliminated. The $(NH_4)_2SO_4$ would not be satisfactory as an electrolyte for heating Ti-6Al-4V.

d. Calcium Chloride - $CaCl_2$

Several specimens of Ti-6Al-4V were heated in a 4% solution of $CaCl_2$. A steady arcing could not be obtained because of the buildup of what is thought to be CaOH. Calcium hydroxide is not soluble in water and quickly builds a resistant film on the specimen which prevents the arcing condition. For this reason, $CaCl_2$ would not be acceptable as an electrolyte.

Voltage vs. Current Density
Curves to Heat Ti-6Al-4V
in Various Concentrations of
$K(C_2H_3O_2)$

Solution
Concentration

15%

8%

4%

2%

1%

CURRENT DENSITY
AMP./SQ. INCH
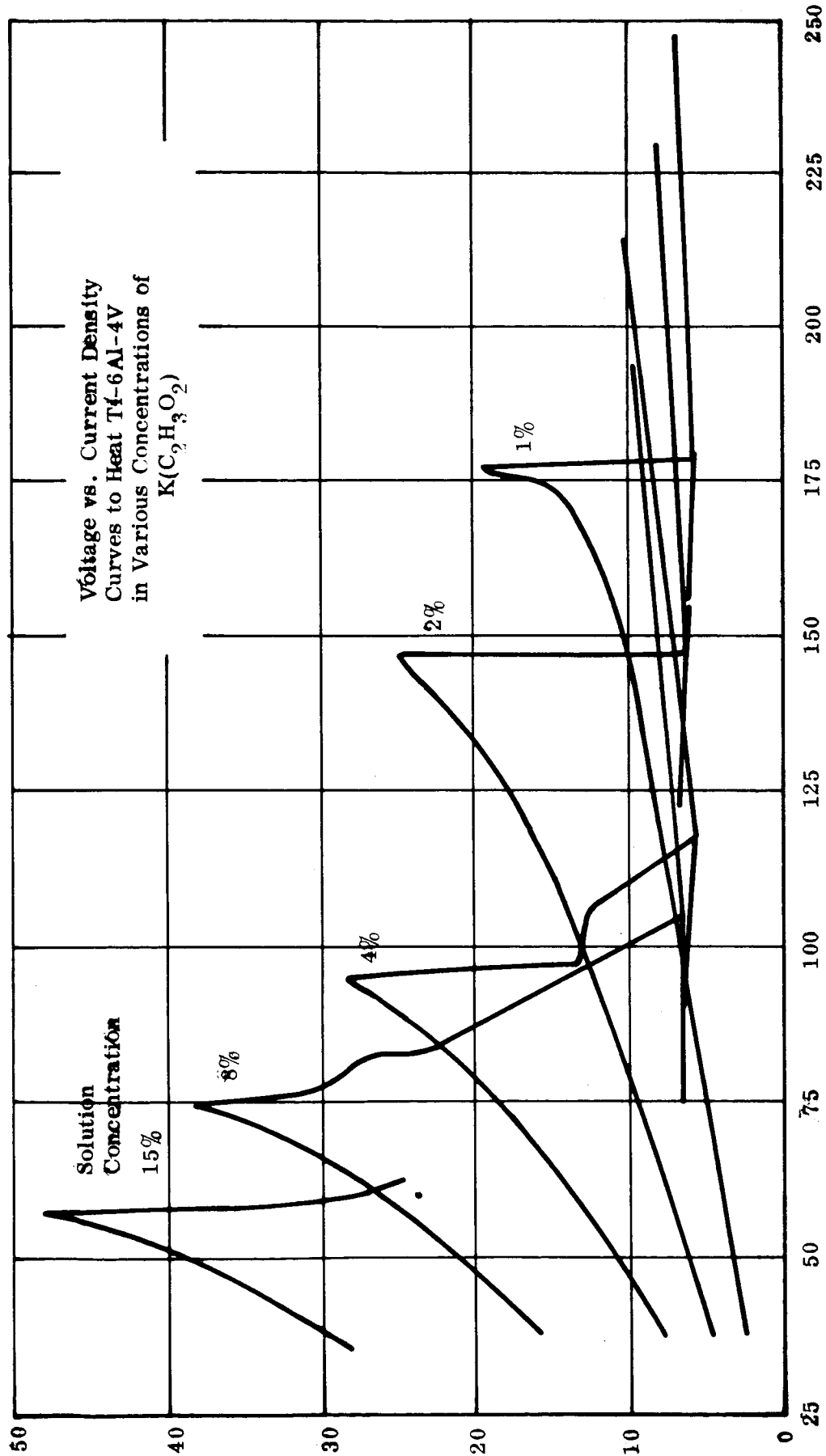
D.C. VOLTAGE - VOLTS

FIGURE V-8

5-19

e.   Sodium Hydroxide and Potassium Hydroxide - NaOH - KOH

        Several sets of specimens were heated in various concentrations of the hydroxide solutions.   The first series of heating trials were conducted before the Visicorder was installed and the data was collected by visually reading the volt and amp meter at each setting.   Later the same tests were conducted again on a fewer number of concentrates with the Visicorder to verify the data.   The two sets of data were almost indentical.   Results of these heating trials showed the following:

(1)   A very light, blue precipitate gradually built up in the solution after 7 or 8 specimens were heated.   This was true for both the NaOH and KOH solutions.

(2)   Little to no reaction occurred on the specimens prior to heating in either solution.

(3)   All the samples heated in both electrolytes contained some surface scale or residue.

(4)   Those samples heated in the lower concentration solutions (1% to 4%) had a much more uniform surface finish with less scale.   The samples heated in KOH appeared more uniform with respect to surface finish than those heated in NaOH.

(5)   Those samples heated in the higher concentrations of both electrolytes exhibited surface attack at the liquid air interface.

(6)   Heavy sputtering was noted in the higher concentrations of both solutions (6% to 15%) even after the arc had become continuous.   The sputtering condition would continue until the sample was red hot, then the solution would settle down to a gentle rolling action at the sample.

(7)   Almost no sputtering occurred when the electrolyte temperature was low, $70°F$ to $100°F$; however, the starting voltage and current density was higher as compared to a solution at $120°F$ to $150°F$ of the same concentration.

(8)   The voltage necessary to start arcing A decreased as the concentration of the solution increases.   The corresponding current density to start arcing increases as the concentration increases.

(9)   The voltage necessary to maintain an arc, B, decreases as concentration increased.

(10)   Based on the observations made during the heating trials, both the hydroxide solutions could be used as electrolytes; however, the $K(C_2H_3O_2)$ appears to be a better electrolyte for heating the Ti-6Al-4V alloy.

5. Electrolyte Concentration and Heating Control

To evaluate the electrolyte tests further all the data generated from the heating trials was collected, averaged, and tabulated with respect to the electrolyte and concentrations. Table I contains the average voltage and corresponding current densities values for heating the 2219 aluminum alloy in the various electrolytes. Table II contains similar information for the heating cycle with the Ti-6Al-4V alloy. Figures V-9 and 10 are typical Visicorder traces used to collect the data for the two tables. Several points were mentioned previously with respect to concentration and heating control; these will be discussed further in the following paragraphs.

a. Electrolyte Concentration

Examination of Tables I and II and the previous graphs indicates in all cases that as the concentration of the electrolyte increases the voltages required throughout the heating cycle decrease. The corresponding amperage increases in all cases during the initial part of cycle or up to the point where arcing starts on the specimens, column A_r. After arcing has started in the cycle the amperage decreases; however, it behaves erratically and does not follow any definite trend.

The tables also show that the amperage and voltage required to start arcing in a particular electrolyte at a given concentration is approximately the same regardless of the material being heated. The following figures illustrate this relationship:

TABLE V-3

$K(C_2H_3O_2)$ Concentration	1%		2%		4%		8%		15%	
Values to start arcing (Point A)	V	A	V	A	V	A	V	A	V	A
2219 Al	179	20	140	25	99	30.5	78	40	55	45
Ti-6Al-4V	177	19.2	147	24.7	94	28.2	74	38	57	48

Once arcing has been obtained the amperage and voltage requirements at a given electrolyte concentration are dependent upon the material being heated.

b. Heating Control

Examination of the general curve of the voltage versus current density relationship, shows that the heating of the specimen is controlled between point "M" the melting point of the specimen, and point "D" the point at which an arc can no longer be sustained (190°F). This range of voltages will be referred to as the voltage control range. Table I indicates that the voltage control range decreases as the concentration increases with respect to the 2219 aluminum alloy, see excerpt from Table V-1.

TABLE V-1

Average Voltage and Current Density Values
for Heating 2219 Aluminum in Various Electrolytes

Solution	Conc. by Wt. %	Matl.	A_V	A_I	B_V	B_I	C_V	C_I	D_V	D_I	M_V	M_I
Na_2CO_3	1	2219 Al	177	22	202	6	202	6	134	5	–	–
	2		90	17.4	167	6	174	6	104	4.5	–	–
	6		69	24	136	10.5	148	13	–	–	–	–
	10		58	27	115	9	125	–	–	–	–	–
Na_2SO_4	1.2	2219 Al	141	19	170	10	191	10	133	9	–	–
	4		79	22	140	6.7	160	7.5	102	8	–	–
	7		89	33	126	8	133	8	76	10	–	–
NaOH	1	2219 Al	96	36	148	10	178	15.5	82	6.8	111	7.8
	4		68	47	106	13.3	136	17.2	60	8	77	8.6
	10		46	50	86	16	97	21	–	–	–	–
KOH	1	2219 Al	106	31.5	154	7.7	180	13.7	–	–	–	–
	4		60	45	105	10.7	137	17	–	–	–	–
	9		51	60	85	17	115	22	–	–	–	–
$Na(C_2H_3O_2)$	1	2219 Al	173	18.8	208	6	212	9	116	3.5	190	4.5
	2.2		129	22.9	185	5.9	190	9.7	97	4.2	155	5.8
	4		106	30	164	6.9	182	11	82	4.6	139	6.8
	8		102	44	136	7.6	157	12.5	70	5.2	105	7
$K(C_2H_3O_2)$	1	2219 Al	179	20	200	6	215	15.7	115	4.8	181	5.2
	2		140	25	182	6.3	202	11.2	90	4.8	153	5.8
	4		99	30.5	157	6.7	172	11	73	5.3	120	6
	8		78	40	130	7.1	140	11	63	6.3	108	7
	15		55	45	106	6.5	122	9.5	60	6.5	92	7
$(NH_4)_2SO_4$	4	2219 Al	99	35	155	7.8	250	8.8	–	–	–	–
$CaCl_2$	4	2219 Al	At 150 volts, 20 amps heavy coating on specimen									

A_V	=	Average voltage to start arcing at specimen
A_I	=	Corresponding average current density to start arcing
B_V	=	Average voltage to maintain arcing over entire specimen
B_I	=	Corresponding average current density to maintain arcing
C_V	=	Average voltage to start heating of the specimen
C_I	=	Corresponding average current density to start heating
D_V	=	Average minimum voltage to maintain arcing
D_I	=	Corresponding average current density to maintain arcing
M_V	=	Average voltage at which melting occurs
M_I	=	Corresponding average current density at which melting occurs

TABLE V-2

Average Voltage and Current Density Values for Heating Ti-6Al-4V in Various Electrolytes

Solution	Concentration by Wt., %	A_V	A_I	B_V	B_I	C_V	C_I	D_V	D_I	M_V	M_I
$Na(C_2H_3O_2)$	1	175	19	182	6	182	6	164	6.5	250	6
	2.2	122	23	142	7	142	7	107	5.5	217	7.5
	4	122	34	127	7.5	127	7.5	93	6.3	220	10
	8	103	46	116	10	116	10	79	7.5	167	13
$K(C_2H_3O_2)$	1	177	19.2	178	5.7	178	5.7	155	6.5	248	6.9
	2	147	24.7	147	6.1	147	6.1	123	6.7	230	8.1
	4	94	28.2	118	5.6	118	5.6	89	6	215	10.3
	8	74	38	104	6.6	104	6.6	75	6.7	195	9.5
	15	57	48	90	8.3	90	8.3	69	6.7	177	9.3
$(NH_4)_2SO_4$	4	98	38	170	8.5	200	10	–	–	200	10
$CaCl_2$	4	169	30	–	–	175	15	–	–	175	15
NaOH	1	89	35	136	13	160	14	97	9	–	–
	2	92	50	137	13	143	13	77	10	–	–
	3	77	57	115	14	135	–	73	10	–	–
	4	55	54	110	14	137	–	73	11	145	11
	5	64	58	91	18	123	–	69	14	–	–
	6	59	62	89	17	128	–	75	11	–	–
	7	57	61	94	20	128	17	70	13	–	–
	9	43	63	73	18	123	–	65	14	–	–
	15	38	75	57	20	79	26	64	23	–	–
KOH	1	110	32	120	18	150	10	107	9	–	–
	2	85	35	124	12	134	13	91	10	–	–
	3	74	49	101	15	129	14	80	13	–	–
	4	67	47	99	14	120	15	70	14	–	–
	5	65	52	92	15	128	15	74	13	–	–
	6	51	50	99	13	120	14	72	11	–	–
	7	49	54	105	12	119	13	72	11	–	–
	9	47	60	93	15	98	15	65	14	–	–
	11	41	66	80	19	97	19	65	13	–	–
	14	36	66	65	17	90	19	67	12	–	–

A_V = Average voltage to start arcing at specimen

A_I = Corresponding average current density to start arcing

B_V = Average voltage to maintain arcing over entire specimen

B_I = Corresponding average current density to maintain arcing

C_V = Average voltage to start heating of the specimen

C_I = Corresponding average current density to start heating

D_V = Average minimum voltage to maintain arcing

D_I = Corresponding average current density to maintain arcing

M_V = Average voltage at which melting occurs

M_I = Corresponding average current density at which melting occurs

Figure V-9. Visicorder trace of amperage and voltage on heating run 102. Electrolyte was 4% NaOH and the material was one square inch of 2219 Aluminum. The various points for the voltage vs current density curve are labeled.
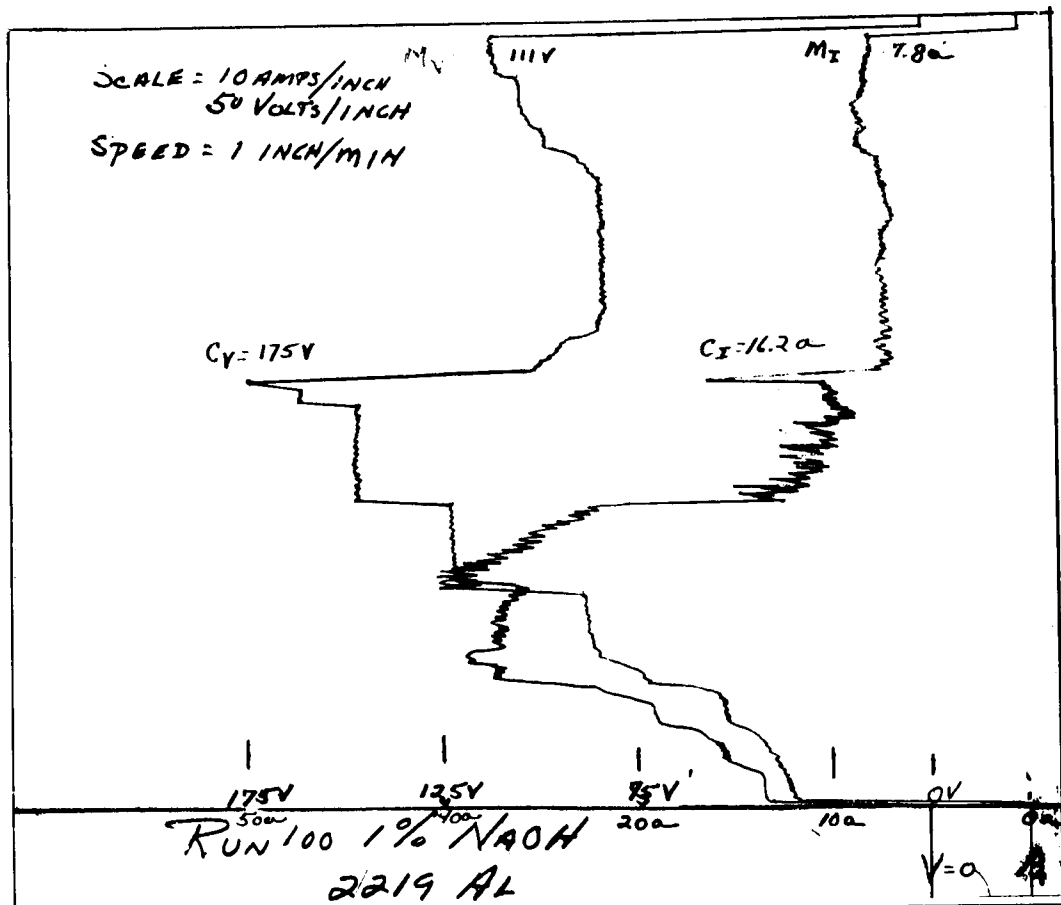
Figure V-10. Visicorder trace of amperage and voltage to determine the heating point and melting point in particular. Electrolyte 1% NaOH, material, one square inch of Aluminum.

TABLE V-4

Electrolyte	Concentration %	M_V	D_V	Voltage Control Range
Na(C$_2$H$_3$O$_2$)	1	190	116	74
Matl - 2219 Al	2	155	97	58
	4	139	82	57
	8	105	70	35
K(C$_2$H$_3$O$_2$)	1	181	115	66
Matl - 2219 Al	2	153	90	63
	4	120	70	50
	8	108	63	45
	15	92	60	32

This same relationship does not hold with reference to the Ti-6Al-4V alloy in the same electrolytes, see excerpt from Table V-2.

TABLE V-5

Electrolyte	Concentration %	M_V	D_V	Voltage Control Range
Na(C$_2$H$_3$O$_2$)	1	250	164	86
Matl - Ti-6 Al-4V	2	217	107	110
	4	220	93	127
	8	167	79	88
K(C$_2$H$_3$O$_2$)	1	248	155	93
Matl-Ti-6Al-4V	2	230	123	107
	4	215	89	126
	8	195	75	120
	15	177	69	108

The voltage control range for the Ti-6 Al-4V alloy reaches a maximum at a concentration of 4% and then decreases as the concentration continues to increase. One additional condition was noted on the 2219Al alloy which was not observed with the Ti-6Al-4V alloy. The voltage at which melting occurs is less than the voltage necessary to start heating. An example of this condition is shown with the 4%

NaOH solution (see sketch). In order to maintain a continuous arc over the entire sample a minimum voltage of 106V is required. To achieve heating of the specimen the voltage must be increased to 136V and then quickly reduced below 77V. A stable heating condition exists between 60V and 77V; however, if the voltage is increased beyond 77V once heating has been achieved the specimen will melt. If the voltage is reduced below 60V the arc will be extinguished.

Matl: 2219 A1.
Elect: 4% NaOH

$A = 68V$

$B = 106V$

$C = 136V$

$M_{2219} = 77V$

$D = 60V$
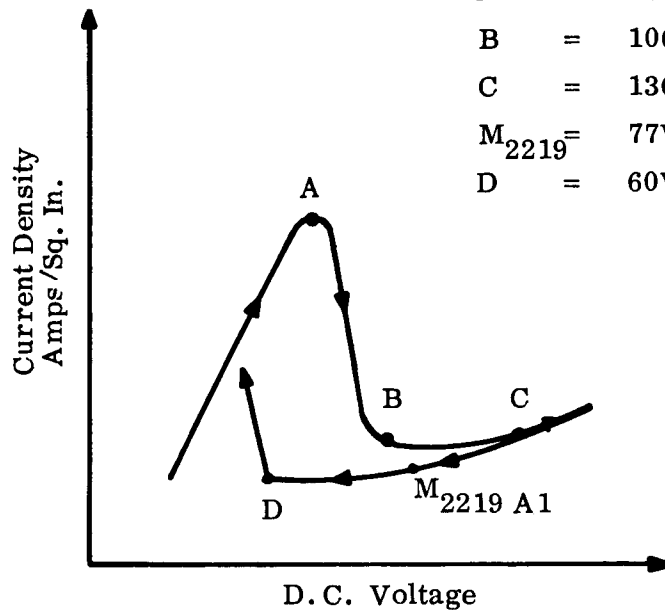
D.C. Voltage

With the Ti-6Al-4V specimens (see sketch) melting always occurred above the voltage necessary to start heating (point C). This condition was noted on all the electrolytes regardless of the concentration of the electrolyte.

Matl: Ti-6Al-4V
Elect: 4% NaOH

$A = 55V$

$B = 110V$

$C = 137V$

$M = 145V$

$D = 73V$

D.C. Voltage
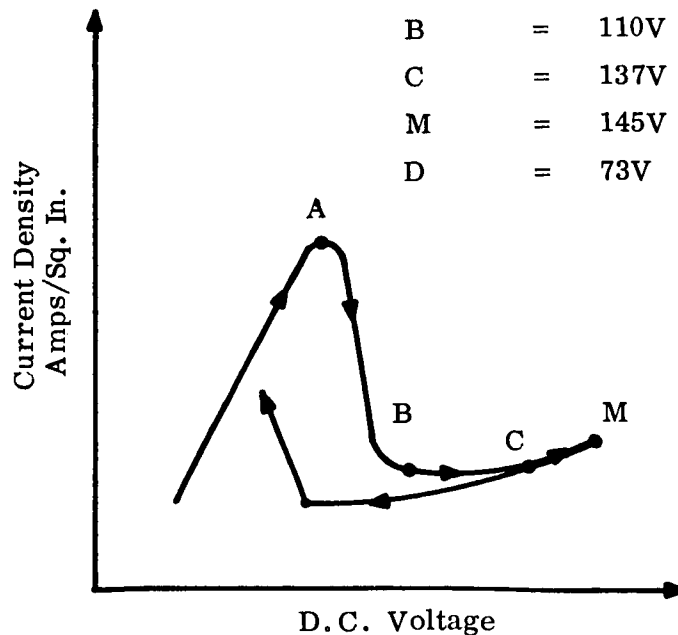
This condition made heating the aluminum specimen difficult but not impossible. This condition is apparently directly related to the heating mechanism of the process which will be discussed later.

In addition to the specimen material, and electrolyte concentration, the electrolyte temperature was found to be an important variable of the process. To investigate this variable two series of tests were conducted. The first test conducted consisted of heating $1/2"$ x $1"$ x $.056$ specimens of Ti-6Al-4V in an 8% solution of $K(C_2H_3O_2)$ at various temperatures and determining the effect on the voltage versus current density curve. Figure V-11 shows the average result of a series of heating trials. This series of graphs shows two facts; 1) as the temperature of the electrolyte increases the curve is shifted to the left reducing the voltage and corresponding amperage at any point on the curve, 2) the voltage control range increases with an increase in electrolyte temperature. The shift in the curves with respect to temperature can be explained by the fact that as the temperature of an aqueous solution increases the conductivity of the solution increases.

The second series of tests consisted of heating specimen of Ti-6Al-4V $1 1/2"$ long x $1"$ wide x $5/32"$ thick. Each specimen was drilled and a chromel-alumel thermocouple embedded to a given depth. The specimens were immersed to a depth of $7/8"$ to provide 2 square inches of surface area for heating. The specimens were heated in an 8% solution of $K(C_2H_3O_2)$ at various temperatures and the voltage, amperage, and specimen temperature was monitored. From this data three plots of voltage versus specimen temperature were prepared. Figure V-12 shows the graphical results of these tests.

The results of these tests indicate that as the solution temperature decreases the degree of temperature control on the specimen also decreases. At a solution temperature of 90°F, a change of only 7 volts was necessary to increase the temperature from 1325°F to 1550°F. At a solution temperature of 130°F, a 14 Volt change was necessary to achieve this same change in temperature and the voltage required increased to 23 volts at a solution temperature of 190°F. Based on the degree of control, the electrolyte temperature should be maintained as high as possible; however, the cooling rate during the quenching cycle will also affect the solution temperature to be used.

6.   General Evaluation with Respect to the Electrolyte

An evaluation of all of the electrolytes tested with the Ti-6Al-4V alloy and the 2219 Al alloy indicates that $K(C_2H_3O_2)$ would be the best electrolyte to use for the heating process. Potassium acetate meets all the general characteristics outlined previously for an electrolyte, (page 5-2   and all the special requirements outlined on page 5-4.   Based on the information generated the 8% solution would provide low voltage and amperage to start the heating cycle, low voltage to start the arcing condition, and a wide voltage control range.

Voltage vs. Current Density
Curves to Heat Ti-8Al-4V
in 8% K$(C_2H_3O_2)$ at Various
Electrolyte Temperatures

Specimen Size 1/2" x 1"

90°F

130°F

180°F

CURRENT DENSITY – AMP/SQ. INCH

D.C. VOLTAGE – VOLTS

FIGURE V-11

5-28

Voltage vs. Specimen Temperature
at Various Electrolyte Temperatures
Specimen - 5/32" thick Ti-6Al-4V
Solution - 8% K(C₂H₃O₂)
Electrolyte Temperatures - 90°F-130°F - 190°F

90°F

130°F

190°F
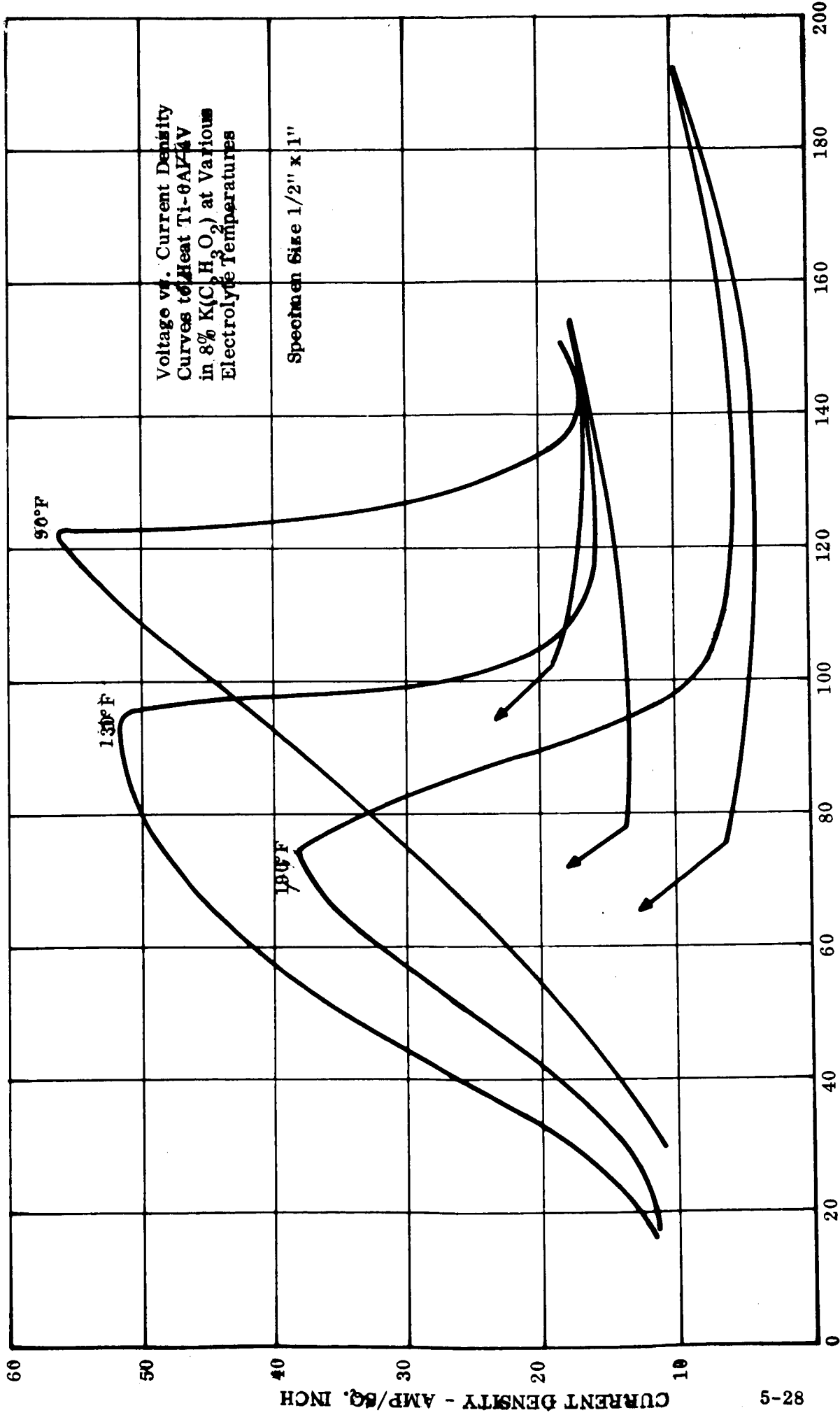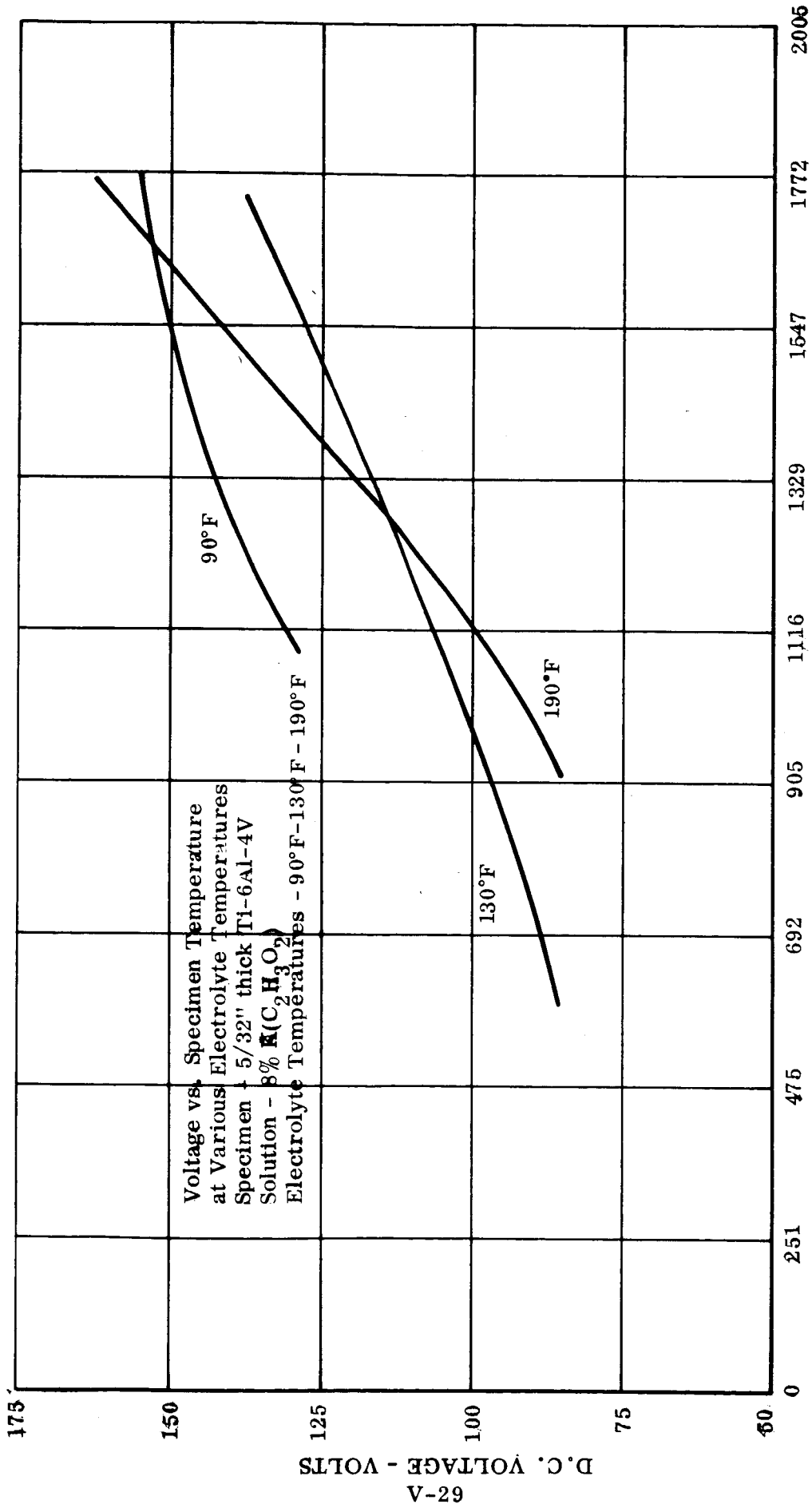
TEMPERATURE °F

FIGURE V-12

D.C. VOLTAGE - VOLTS

V-29

B.   PROCESS EVALUATION WITH RESPECT TO TEMPERATURE

After an electrolyte ($K(C_2H_3O_2)$) had been established for the process, it was necessary to determine a method of monitoring the temperature the specimen was achieving. Once this was determined additional tests were conducted to investigate the following:

1)   The relationship of concentration, voltage, and specimen temperature.

2)   The heating rates that could be achieved.

3)   How the temperature changed with respect to voltage.

4)   The variation in temperature over the specimen.

5)   The effect of anode to cathode distance on the voltage versus current density curve and the temperature of the specimen.

6)   The quench rates that could be achieved from solutioning temperatures.

1.   Temperature Monitoring System

The method used to detect temperature changes during the heating cycle was to embed a chromel-alumel thermocouple in the specimen. The response from the thermocouple was fed into a Minneapolis Honeywell Visicorder which was calibrated to record in millivolts. Traces of the applied voltage and respective current were also made at the same time.

Two specimen configurations were prepared from both alloys to be heated in various concentrations of $K(C_2H_3O_2)$). The first configuration was 2" long x 1/2" wide x .056" for the Ti-6A1-4V and .080" thick for the 2219 aluminum alloy. The specimens were scribed so that one square inch of surface area would be immersed during heating. The 2" x 1/2" specimens were made to test the external thermocouple set-up. The second configuration was designed for an internal thermocouple which would not be in contact with the electrolyte. This specimen was 1-3/8" long x 7/8" wide x 5/32" thick. The specimen was scribed at .71" from the bottom exposing 2 square inches of surface area during heating. A thermocouple hole was drilled from the top of the specimen to locate the thermocouple 1/4" from the bottom of the specimen.

Initial heat trials were conducted on 2" x 1/2" x .056" Ti-6A1-4V specimens. A small hole was drilled in the flat surface of the specimen and a thermocouple peened in the hole. The specimen was heated in a 4% solution of $K(C_2H_3O_2)$). A temperature of about 1550°F was achieved on the specimen before the thermocouple wire melted. The very thin wire acted as though it were a part of the cathode, overheated, and melted. Additional attempts using a maskant on the thermocouple to prevent arcing were unsuccessful. Once the specimen became red hot, the maskant burned away and the couple wire became red hot and finally melted.

A thin specimen of 2219 aluminum was drilled parallel to the thickness dimension (.080") and a small thermocouple encased in a metal protection tube was inserted in the hole. The protection tube was coated with a rubber maskant to protect it from the electrolyte. During the heating run, the coating apparently broke down because the protection tube became red hot and melted about 1/2" from the specimen.

Based on the above results, testing with the external thermocouple was suspended and heating trials with the internal couple were started. The chromel-alumel thermocouple was inserted in the 5/32" thick specimen and the joint covered with the rubber maskant to prevent the electrolyte from splashing in the hole. The millivoltage response was monitored on the Visicorder along with the applied potential and corresponding amperage. Temperatures up to 2000°F were recorded with no difficulty.

A series of samples were heated, monitoring the temperature response with respect to various concentrations of the $K(C_2H_3O_2)$) solutions. Table V-6 shows the various points on the voltage versus current density curve for both alloys. The voltage and amperage necessary to achieve the indicated temperatures are shown. It should be noted that the requirements at each point are different than those discussed earlier. This is due to the increase in area of the specimen and will be discussed in detail later.

2. Temperature Variations During the Heating Cycle

With the establishment of a method for monitoring the specimen temperature, additional heating trials were conducted. To investigate the temperature change with respect to voltage changes, specimens of each alloy were heated in a 1500 ml solution of 8% $K(C_2H_3O_2)$). A chromel-alumel thermocouple was embedded in the center of the specimen to isolate it from the electrolyte. The 5/32" thick specimens were immersed in the electrolyte to expose exactly 2 square inches of surface area. Voltage, amperage and temperature readings were recorded on the Visicorder during each heating trial.

Examination of the data generated during heating indicated that the temperature of the specimen only reached about 190°F as the potential was increased during the initial stage of the cycle. At some critical potential indicated as Point C on Figure V-13 (this is the same potential shown as Point C on the voltage versus current density curves earlier in the report) the temperature of the specimen increased very rapidly. This increase in temperature results with little change in voltage for the Ti-6Al-4V specimens and occurs with a decrease in voltage for the 2219 aluminum specimens. It is necessary to reduce the voltage when heating a 2219 aluminum specimen to prevent melting of the specimen (see Figure V-13).

Once the rapid temperature increase has occurred (about 150°F/second) the voltage can be adjusted to attain a desired temperature. Figure V-13 which is the average of many runs, shows that the temperature of the Ti-6Al-4V specimens in a 190°F solution will vary with voltage according to Curve I. It was also observed that when the solution was maintained at a lower temperature (about 160°F) the temperature-voltage relationship would vary according to Curve II. This change was discussed earlier in Section V. The graph also illustrates the change in temperature with respect to voltage for the 2219 Al specimens in a 190°F solution.

Figures V-14 and V-15 are actual traces of heating runs showing the temperature change with respect to voltage. Other traces indicated that the heating rate for the 5/32" thick titanium alloy reached about 175°F/second. This rate can be controlled by presetting the initial voltage at the start of the cycle and/or adjust-

TABLE V-6

Average Voltage and Amperage Values to Heat Ti-6 Al-4V and 2219 Al
in Various Concentrations of $K(C_2H_3O_2)$

		Specimen Thickness 5/32"						Immersed Area 2 sq. inches		Peak		Couple Reading at T_V T_I mv	
Solution	Material	A_V	A_I	B_V	B_I	C_V	C_I	D_V	D_I	T_V	T_I		Temp.
1% $K(C_2H_3O_2)$	Ti-6Al-4V	180	23.5	183	10.8	194	10.6	154	6.2	257	8.9	38.1	1685°F
2%	"	146	31.1	160	8.8	169	11.7	100	5.3	225	11.1	40.1	1776°F
4%	"	99	37.2	130	8.5	138	12.5	82	6.5	186	11.4	39.5	1749°F
8%	"	78	50.6	106	9.5	132	16	77	8.3	162	12.5	39.6	1754°F
15%	"	65	68.2	88	8	111	17.5	71	10	143	15	40.8	1808°F
1%	2219 Al. Alloy	175	23.7	222	7.8	232	12.5	119	5.7	183	6	22.1	993°F
2%	"	138	31.6	202	9.3	224	15.7	92	6	140	7.3	21.8	981°F
4%	"	99	40.7	155	10.8	185	18.5	75	6.3	115	8	21.7	977°F
8%	"	81	52.2	126	11.5	155	20.2	64	8	105	10.2	22.9	1027°F

A_V = Average voltage to start arcing at specimen

A_I = Corresponding average amperage to start arcing

B_V = Average voltage to maintain arcing over entire specimen

B_I = Corresponding average amperage to maintain arcing

C_V = Average voltage to start heating of the specimen

C_I = Corresponding average amperage to start heating

D_V = Average minimum voltage to maintain arcing

D_I = Corresponding average amperage to maintain arcing

T_V = Average voltage to obtain temperature indicated

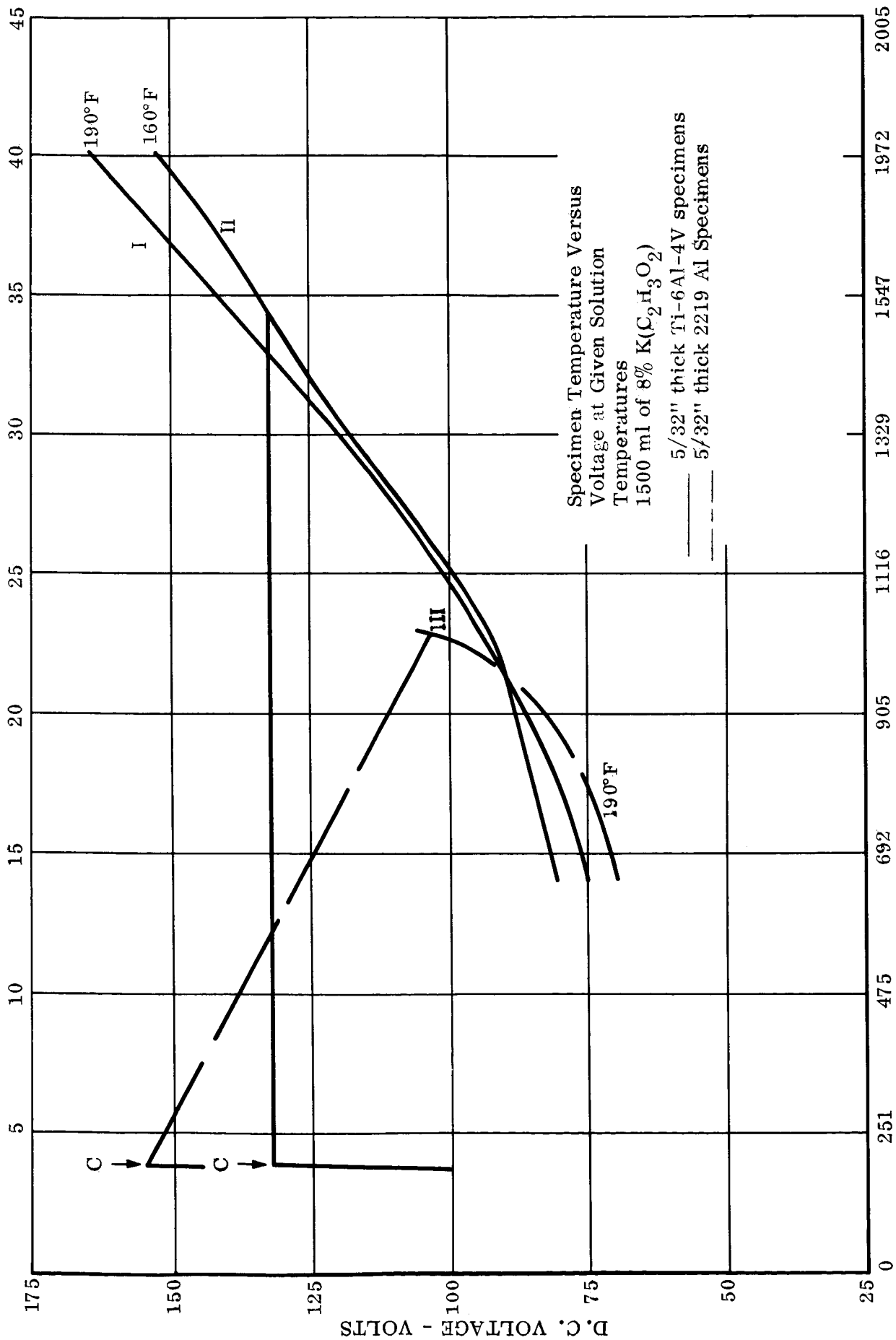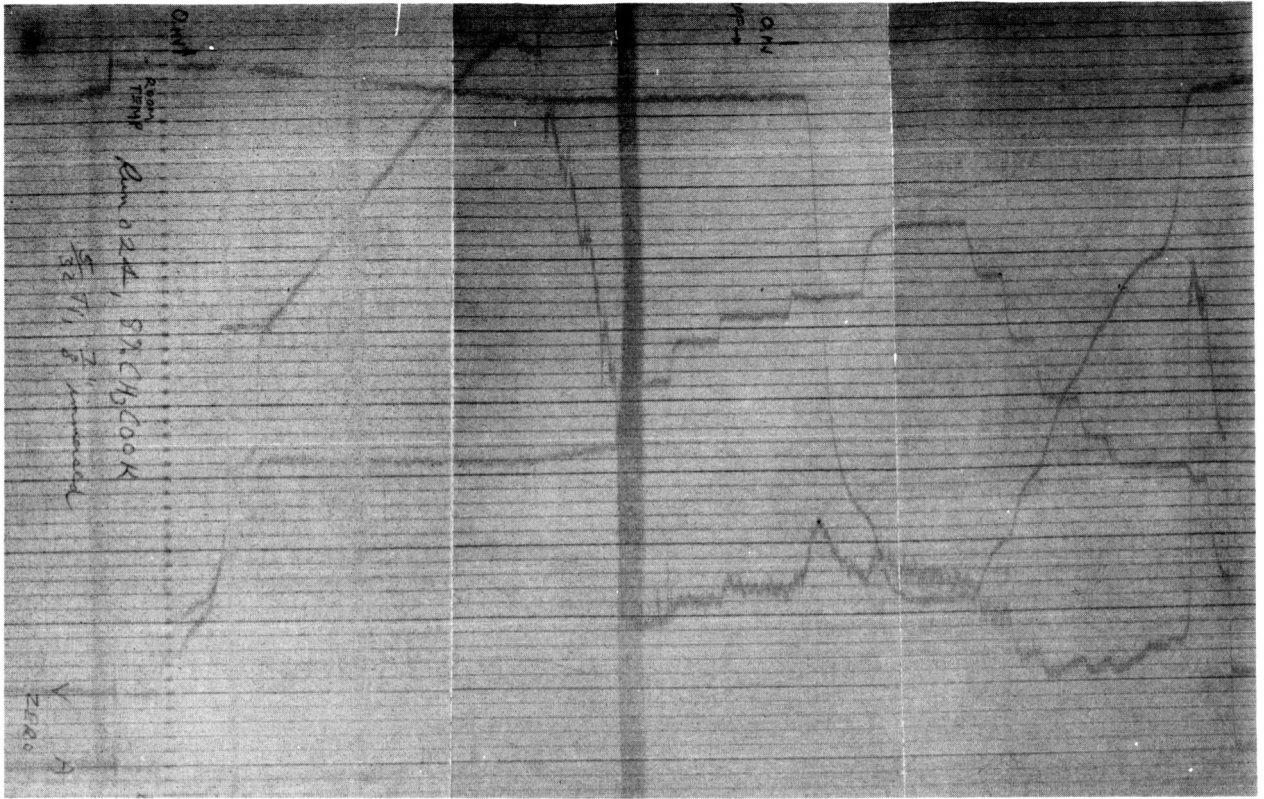T_I = Corresponding amperage to obtain temperature indicated

5-32

FIGURE V-13

5-33

Voltage and Amperage Increase

Temperature Increase

Figure V-14. Temperature-Voltage trace of heating Run No. 024.
Ti-6Al-4V - 5/32" thick in 8% solution of $K(C_2H_3O_2)$

Voltage and Amperage Increase
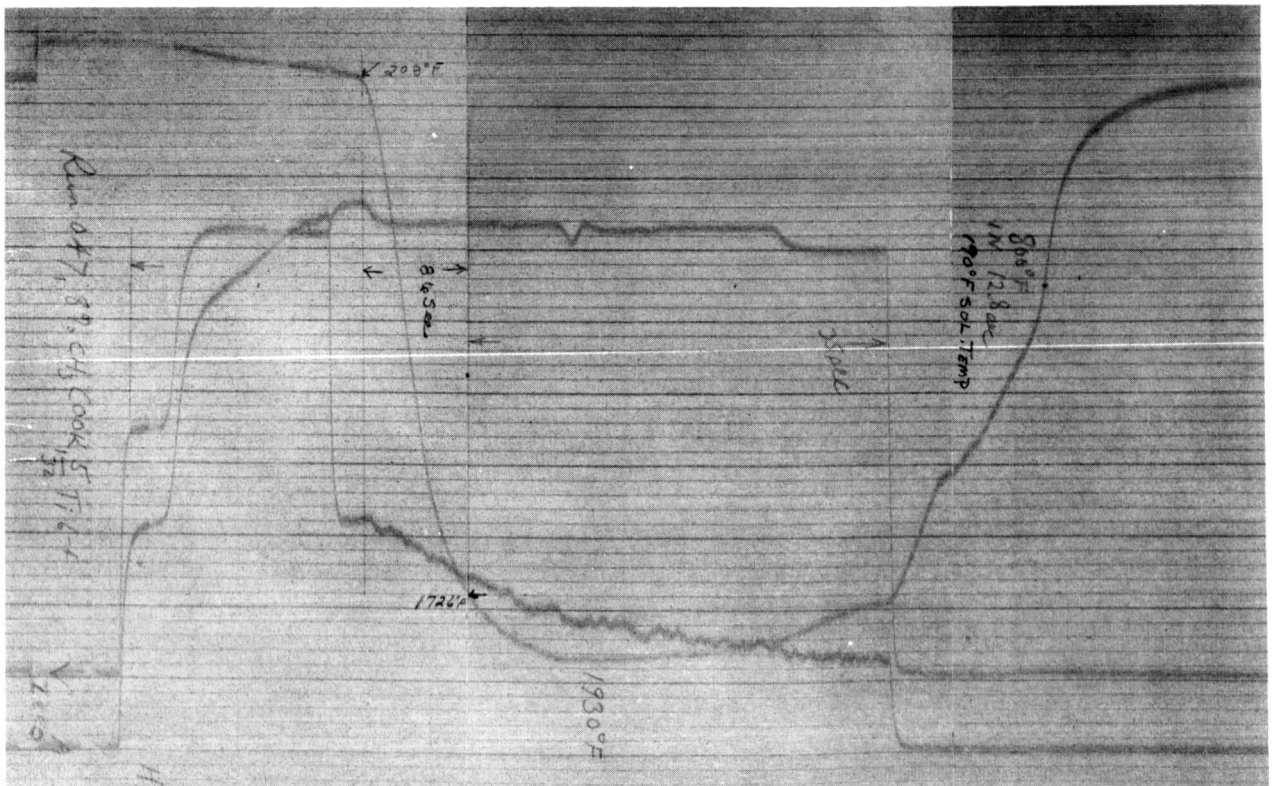
Temperature Increase

Figure V-15. Temperature-Voltage trace of heating Run No. 047
Ti-6Al-4V in 8% $K(C_2H_3O_2)$ - 5/32" thick.

ing the voltage once heating has begun. If the voltage is reduced, as with the 2219 Al specimens, the rate can be slowed down. If the voltage is increased appreciably the heating rate could be easily doubled to about 350°F/second; however, the operator tends to lose control of the temperature rise and the specimen would probably melt.

Initial heating runs with the 5/32" thick 2219 Al specimens were unsuccessful because the operator could not reduce the voltage manually fast enough to prevent melting. To achieve heating with out melting, the voltage on the No. 1 rheostat was preset about 10 volts above the "C" value obtained from the voltage-current density curve. The corresponding timer was set for about 3 seconds and the No. 2 rheostat was set between the "M" and "D" voltages from the curve. When the power was turned on the voltage rose rapidly, the specimen started to arc and heating began. Before the temperature had reached the melting point, the first timer had timed out, the control was switched to the 2nd rheostat, and the voltage fell to a safe heating level. The voltage was then adjusted to produce the required temperature.

3.   Effect of Time at Temperature on the Material

Of considerable interest was the length of time the material had to be held at temperature to obtain sufficient solutioning prior to quenching. For the Ti-6Al-4V alloy, conventional solutioning is achieved by heating the material between 1725°F and 1750°F for 15 to 60 minutes depending on section thickness. Solution treatment for the 2219 Al alloy is conventionally attained by heating the material between 995°F and 1005°F for 15 to 60 minutes depending on section thickness.

With the rapid heating rate provided by the electrolytic heating process, it was felt that the solutioning time could be reduced. The solutioning process would not reach completion with the reduced heating time, however, minimum properties might still be achieved. Specimens of each alloy were solution treated conventionally in a furnance followed by a water quench. Additional specimens were heat treated in an 8% solution of $K(C_2H_3O_2)$ as follows:

Ti-6Al-4V   –   1730°F for 45 seconds-Quenched
                   1730°F for 81 seconds-Quenched

2219 Al   –   1000°F for 30 seconds-Quenched
                   1000°F for 45 seconds-Quenched
                   1000°F for 60 seconds-Quenched

Samples from each of the specimens were mounted and polished for microstructure examination. Figures V-16-17-18 are photomicrographs of the Ti-6Al-4V samples and Figures V 19 through 22 shows the structures of the 2219 Al samples.

These photomicrographs indicate that 45 seconds at temperature for both alloys would probably be sufficient to achieve final properties after convention aging. Tensile tests would have to be conducted for various lengths of time to determine the solutioning time required.

5-35
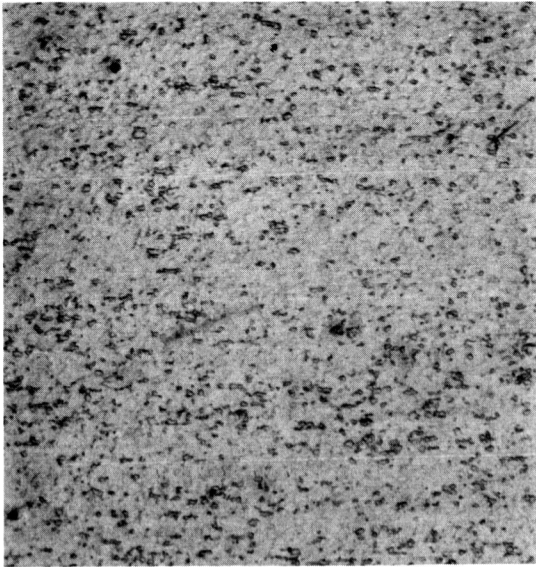
Figure V-16. Photomicrograph showing the general structure of specimen of Ti-6Al-4V solution treated conventionally in a furnace at 1730°F for 30 minutes with water quench.

MAG:100X   Etch-Krolls
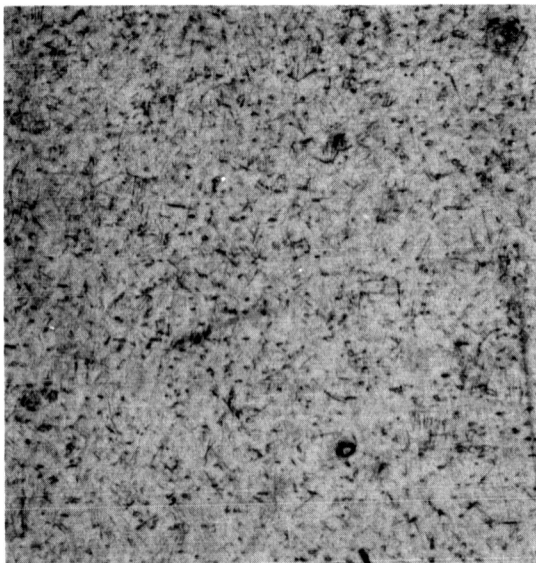
Figure V-17. Photomicrograph showing the gneral structure of a Ti-6Al-4V specimen electrolytically solution treated at 1730°F for 48 seconds followed by a solution quench.

MAG:100X   Etch-Krolls
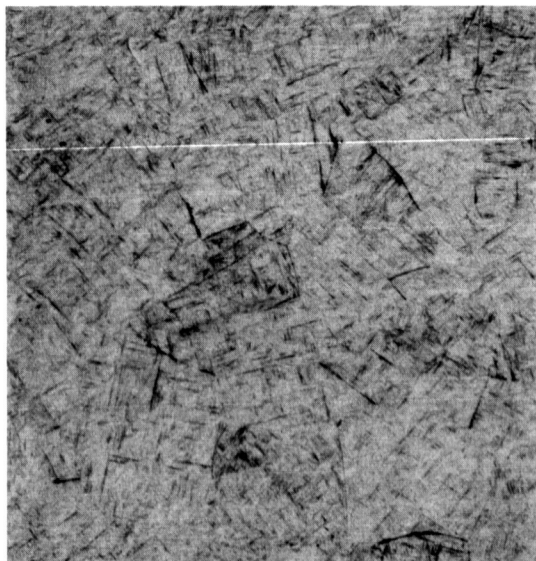
Figure V-18. Photomicrograph showing general structure Ti-6Al-4V specimen electrolytically solution treated for 81 seconds and quenched. Specimen was heated above the beta tronics before quenching.

MAG:100X   Etch-Krolls

MAG:100X   Figure V-19   Etch:Kellers

General structure of a 2219 Al specimen, conventionally solution treated at 1000°F for 45 minutes and water quenched.

MAG: Figure V-20   Etch: Kellers

General structure of a 2219 Al specimen electrolytically solution treated at 100°F for 30 seconds and quenched.

MAG: 100X   Figure V-21   Etch: Kellers

General structure of a 2219 Al specimen electrolytically solution treated at 1000°F for 45 seconds and quenched.

MAG: 100X   Figure V-22   Etch: Kellers

General structure of a 2219 Al specimen electrolytically solution treated at 1000°F for 60 seconds and quenched.

4. Temperature Uniformity

During the examinations of numerous microstructures in the previous subsection, it was noted that grain size near the bottom of specimen was larger than that near the top of the specimen. On some of the 2219 Al specimens, incipient melting was noted in the grain boundaries at the bottom of the specimen even though the indicated temperature was below the melting point. This indicated that a temperature gradient existed along the specimen and that the bottom edge of the specimen was above the solutioning treatment temperature. To determine the extent of the thermal gradient, a series of heating tests were conducted using thermocouples at various locations within the specimen. Ti-6Al-4V specimens 5/32" thick were heated in an 8% solution of $K_2(C_2H_3O_2)$ with three thermocouples located as follows:

#1 - 1/32" from the bottom of the specimen

#2 - 1/4" from the bottom of the specimen

#3 - 3/4" from the bottom of the specimen

The specimens were immersed to a depth of 7/8" in the large tank system to expose two square inches of surface area to the electrolyte. The electrolyte solution was maintained at 130°F throughout the heating runs. The Visicorder was used to monitor the amperage, voltage, and temperature during each heating run.

During the initial portion of the heating run, the temperature was monitored with the #1 thermocouple located 1/32" from the bottom of the specimen. Once the temperature had peaked and stabilized, the temperature of the other two thermocouples was read by switching from #1 to #2 to #3 and back through the cycle. Figure V-23 is a photograph of a trace from one of the heating runs showing the difference in temperature at the three couple locations. Through a series of similar heating runs a plot of voltage versus temperature was constructed showing the temperature gradient of the specimen as monitored by the three thermocouples, see Figure V-24.

These heating runs indicate that a very large temperature gradient does exist over the specimen. When the temperature at 1/32" from the bottom of the specimen was recorded to be 1750°F, the temperature 1/4" from the bottom of the specimen was 1592°F and only 1127°F at a distance of 3/4" from the bottom of the specimen. Part of the temperature gradient is attributed to the portion of the specimen not immersed in the solution which provides a larger heat sink, however, the rest of the gradient is attributed to the heating mechanism of the process which will be discussed later in the report. Several other heating trials were conducted in which the specimen was completely submerged below the electrolyte and held in a horizontal position. The temperature was not monitored at this time; however, the color of the specimen was uniform over the entire surface.

5. Effect of Anode to Cathode Distance

A series of tests were conducted to determine the effect of anode to cathode distance with respect to power requirements and temperature. Specimens

Paper Feed ⟶
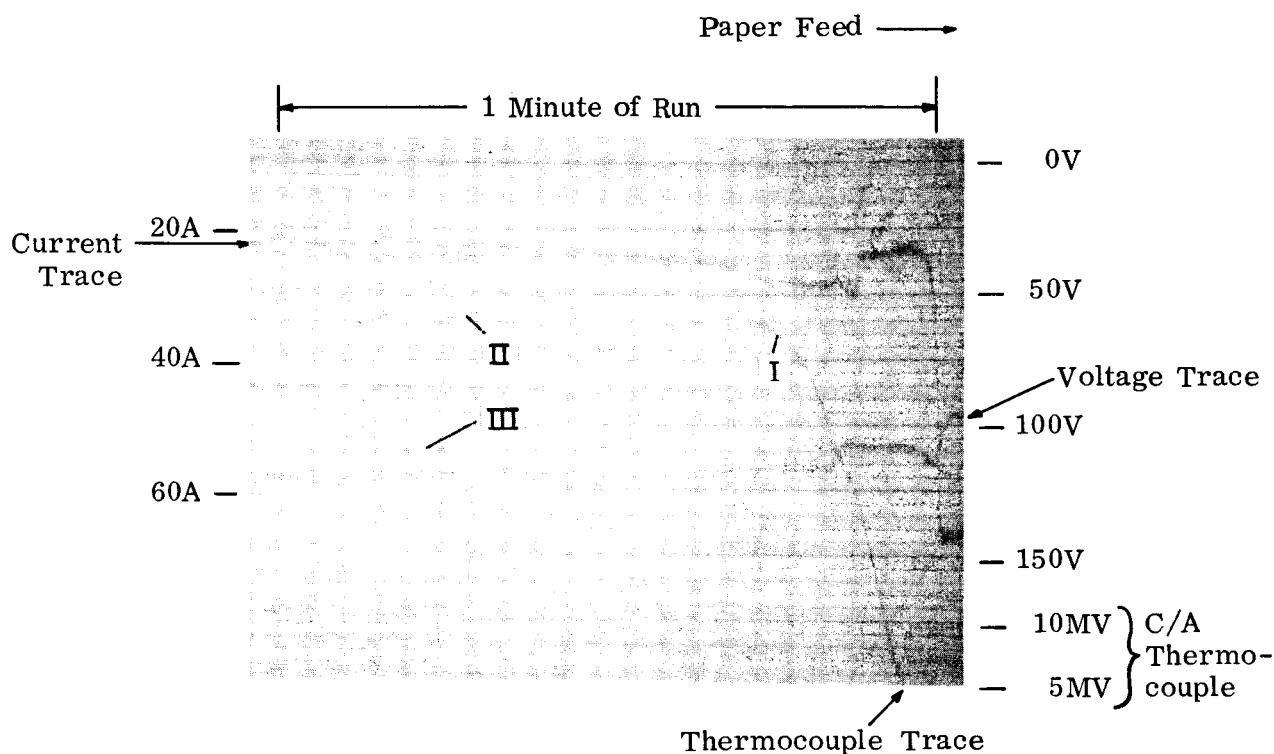
FIGURE V-23

This photograph is on actual trace from the Visicorder monitoring the applied voltage, amperage, and the response of the three thermocouples located at various position in a 5/32" Ti-6Al-4V specimen. See Figure V-24 for location of thermocouples. A considerable temperature gradient is shown.

CHROMEL-ALUMEL THERMOCOUPLE READINGS
IN MILLIVOLTS

Thermocouple Locations
Immersed Depth 7/8"
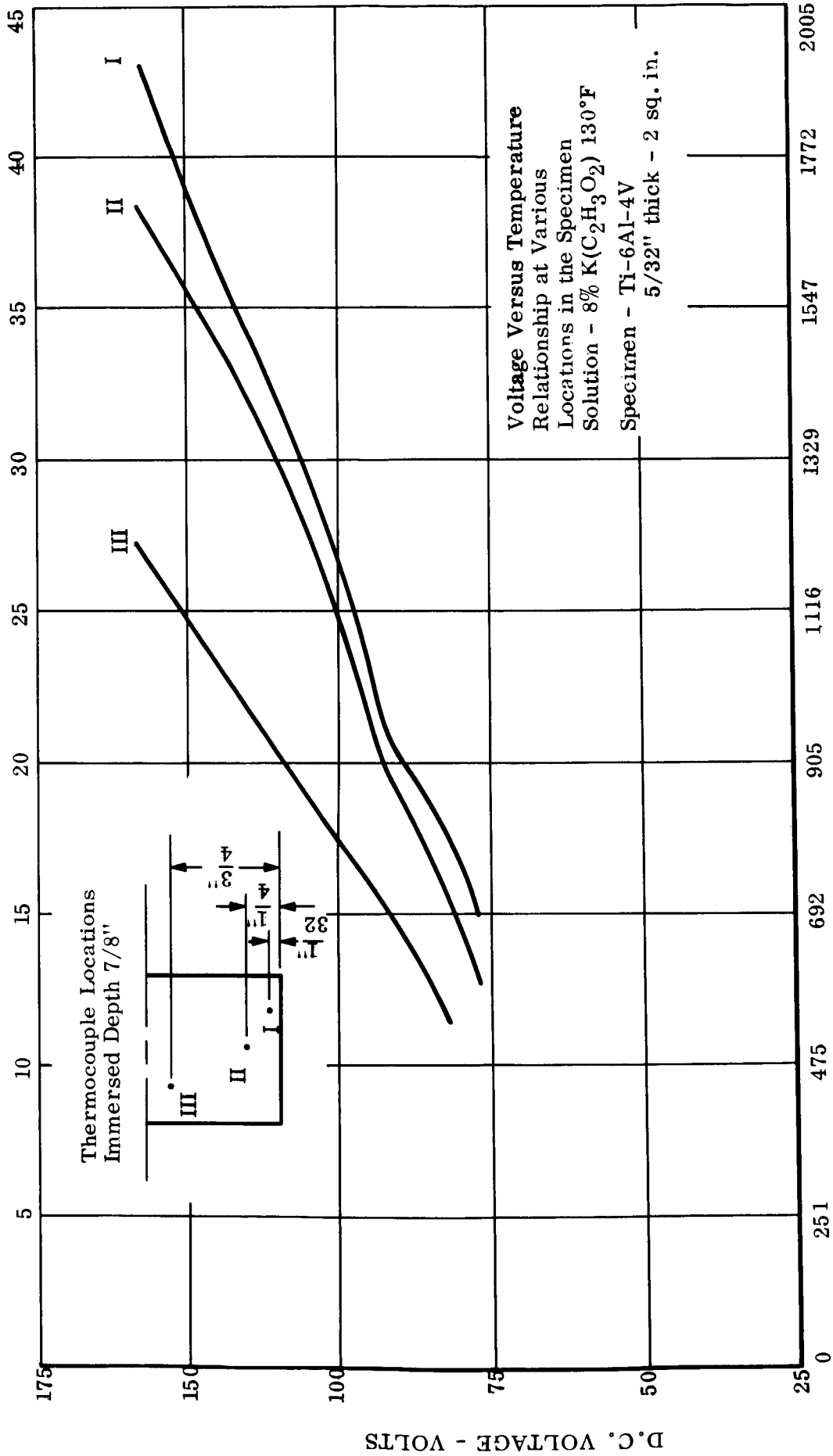
Voltage Versus Temperature
Relationship at Various
Locations in the Specimen
Solution - 8% K($C_2H_3O_2$) 130°F

Specimen - Ti-6Al-4V
5/32" thick - 2 sq. in.

TEMPERATURE °F

FIGURE V-24

D.C. VOLTAGE - VOLTS

5-40

of Ti-6Al-4V and 2219 Aluminum were heated in a 1500 ml beaker containing an 8% solution of $K(C_2H_3O_2)$. The immersed surface area of the specimen was held constant with each heating run while the distance between the anode plate and the bottom of the specimen (cathode) was varied from 3-3/4" to 7/16". The change in distance was achieved by reducing the quantity of solution in the beaker. There was no significant difference in temperature, voltage, or current with respect to the change in distance.

During the heating runs it was noted that the voltage at which arcing first occurred decreased as the anode to cathode distance decreased. This decrease was attributed to the rapid increase in the solution temperature which occurred as the distance and amount of solution decreased. To verify this conclusion, the same anode was transferred to the 40 gallon tank where the temperature of the solution could be controlled. The anode to cathode distance experiments were repeated again with a controlled solution temperature and the results indicated that there was no significant change in voltage and current requirements as the distance between the anode and the cathode changed. Therefore, within the limits stated, the anode to cathode distance has no significant effect on the heating cycle. It is felt however; that once the distance between anode and cathode becomes appreciable, 10" to 15", the distance factor would have an effect due to the increase in resistance of the solution.

6.   Quench Rates of the Electrolytic Heating Process

To determine the quench rate from the solution treatment temperatures for both alloys, the same experimental setup was again used. A chromel-alumel thermocouple was imbedded in the center of the 5/32" thick specimen at approximately 1/4" from the bottom of the specimen. With the temperature trace and a known visicorder feed speed, the quench rate for each specimen could be established quite accurately.

Examination of numerous thermocouple traces indicated the following quench rates were achieved under the given conditions:

TABLE V-7

	Material	Solution Temperature	Conditions	Average Quench Rate
1.	Ti-6Al-4V	190°F 8% $K(C_2H_3O_2)$	No agitation	75°F/sec from 1750°F to 800°F
2.	Ti-6Al-4V	130°F 8% $K(C_2H_3O_2)$	No agitation only pump circulation	260°F/sec 1730°F to 800°F
3.	Ti-6Al-4V	130°F 8% $K(C_2H_3O_2)$	Agitator and circulator + shaking specimen	500°F/sec 1730°F to 800°F

TABLE V-7 (Cont'd)

	Material	Solution Temperature	Conditions	Average Quench Rate
4.	Ti-6Al-4V	130LF 8% K(C$_2$H$_3$O$_2$)	Agitator + circulator + shaking + cold (60°F) solution poured over specimen while submerged	650°F/sec 1730°F to 800°F
5.	2219 Al	190°F 8% K(C$_2$H$_3$O$_2$)	No agitation	60°F/sec 995°F to 250°F
6.	2219 Al	130°F 8% K(C$_2$H$_3$O$_2$)	Circulator only	250°F/sec 1000°F to 250°F
7.	2219 Al	130°F 8% K(C$_2$H$_3$O$_2$)	Agitator and circulator + shaking specimen and cold solution over specimen	550°F/sec 1000°F to 250°F

Table V-7 indicates that with a moderate speed on the agitator, the circulator pump running, a flow of cold solution in the area of the specimen, and a shaking motion of the specimen, very high quench rates can be achieved (500°F to 650°F/sec.). Quench rates of this order would satisfactorly meet commercial requirements for cooling the materials from solutioning temperatures.

C. EVALUATION OF OTHER PARAMETERS WITH RESPECT TO PROCESS MECHANISM

1. Effect of Cathode Size on the Process

As mentioned previously in the discussion on electrolyte temperature, the requirements to start arcing and heat the specimen appeared to increase as the size of the specimen increased. To evaluate this condition a series of heating tests were conducted in which the immersed surface area of the specimen was varied.

All the tests were conducted in the 40-gallon tank using an 8% solution of $K(C_2H_3O_2)$ at 130°F. Figure V-25 is a graphical representation of the data generated by varying the immersed area of the Ti-6Al-4V specimens. After the 4 square inch specimen was heated, the Visicorder circuit had to be altered and recalibrated to record the high amperages encountered. Specimens up to 12 square inches were successfully started and heated with extremely high amperage and voltage requirements. Figure V-25 which is a plot of voltage versus actual amperage shows that 68 KW was required to start the 12 square inch specimens. It should be noted that the D.C. generator is only rated at 30 KW.

A 15 square inch specimen was also tried; however, at full generator output, in excess of 350 amperes and 200 volts, the initial arcing condition could not be attained. It should be noted that between 4 square inches and 8 square inches, the shape of the voltage versus amperage curve changes slightly (see Figure V-25). This change is attributed to the response of generator and the sudden change in load at the very high current level. As the specimen starts to arc, the current requirement drops faster than the generator can respond resulting in a rise in the voltage at this point. Consequently, the Volt versus Ampere curve tends to bow outward during this portion of the cycle. As in previous reports, "A" designates the start of the arcing condition, "C" designates the critical point to start heating, "M" the point at which melting occurs once the specimen has started to heat, and "D" the point at which the arc is extinguished.

Examination of the data from these graphs indicates that as the specimen size increases the power required to start arcing and maintain heating also increase. The current density required during the heating cycle actually decreases with increased surface area; however, it is not a straight line relationship. Table V-8 shows a comparison of the starting requirements and heating requirements at similar points on each specimen size.

The data indicates that between 47 amperes/square inch and 27.5 amperes/square inch are required to start the arcing condition in a 130°F 8% solution of K $(C_2H_3O_2)$ and approximately eleven (11) amperes/square inch is necessary to achieve and maintain heating. With respect to power about 4 KW/square inch is needed to start arcing and about 1.6 KW/square inch is required for heating. It should be noted that with a surface area of 8 square inches the rated capacity of the generator was exceeded during the start of the cycle.

Initial heating trials with 2219 Al alloy were unsuccessful in the large tank set up as described previously. With the automatic timer method described on

page 5-35, samples up to 4 square inches were successfully heated. However, greater surface areas could not be started without melting due to the lag in generator response. In view of these results an alternate method was needed to start the arcing condition. Two possible methods were evaluated, a) preheating the specimen prior to the electrolyte heating cycle, b) use of a capacitor discharge to provide the short, high power pulse needed for starting the arcing condition.

a. Preheating Specimens to Aid Starting

To investigate the effect of preheating a series of 2219 Al specimens were heated on a hot plate to 300°F. The generator was started and preset at a voltage above the "D" point. The specimen was transferred quickly from the hot plate to the holding clamp and immersed in the electrolyte. Arcing started immediately without the high power requirements normally experienced during the heating cycle. Specimens with a surface area up to 8 square inches were tried and successfully heated without melting. Figure V-26 shows the results of this series of tests. These results show the same increasing trend of surface area versus power required as shown with the titanium specimens in Figure V-25. The results also indicate that preheating can be used as an alternate method to achieve arcing and heating without experiencing the extremely high power requirements. The graphs show that about 10 amperes/square inch is still required during the heating cycle.

b. Capacitor Discharge to Aid Starting

At the beginning of the program, it was anticipated that as the specimen size increased, the power requirements would become quite large. To compensate for the high voltage and amperage requirements needed during the starting portion of the cycle, a 27,000 uf capacitor bank was added to the circuit. The capacitor bank was assembled to provide various multiples (2, 4, and 6) of 4500 uf up to 27,000 uf. With the addition of the capacitor bank, it was felt that the generator output could be set at some lower level between the "D" and "M" points similar to the preheat and the specimen started arcing by spiking the voltage with the capacitor bank.

Initial tests with capacitor bank alone, set for maximum output, produced a power spike of 175V and 26 amps. However, when the generator output was added to the system, the increase due to the capacitor bank appeared very low, about 25 volts and 6 amperes. A review of the circuits involved indicated that most of the surge from the capacitor bank was being fed back through the generator circuit. The circuit was modified by adding two IN 3168 diodes in parallel at the generator output, thereby preventing the flow of current from capacitor bank through the generator circuit.

Tests performed with the new setup resulted in a power surge above that of the generator output. However, even with the increased power surge, starting could not be accomplished because the short-time interval of the capacitor bank discharge (about 1/2-second) was destroying the bubble around the specimen. Lower settings on the capacitor bank were tested with the same results. To delay the rapid discharge of the capacitor bank across the specimen, an inductive reactance circuit (an inductance coil) was introduced to the system. Several coils were tried, however,

Voltage Versus Amperage
Curves for Various Size
Ti-6Al-4V Specimens

Electrolyte - 8% $K(C_2H_3O_2)$ at 130°F

2-1/2" x 2-3/8" = 12 sq. in.

2-1/2" x 2" = 10 sq. in.

2" x 2" = 8 sq. in.

1" x 2" = 4 sq. in.

1" x 1" = 2 sq. in.

1/2" x 1" = 1 sq. in.

D.C. VOLTAGE - VOLTS

FIGURE V-25

AMPERES

Voltage Versus Current-Density
Curves to Heat Variables\Size
2219 Al Specimens in 8%
K₂C₂H₃O₂ at 130°F

After Preheating the Specimen

M

M

M

8 sq. in.

4 sq. in.

1 sq. in.

D

D

D

125   100   75   50   25   0

AMPERES

5-46

0   25   50   75   100   125   150   175   200

L.C. VOLTAGE VOLTS

FIGURE V-26

TABLE V-8

Specimen Size (in.)	Surface Area (sq. in.)	Point "A" Volts	Amp.	KW	Volts/in²	Amp/in²	KW/in²	Point "C" Volts	Amp.	KW	Volts/in²	Amp/in²	KW/in²
1/2" x 1"	1	87	47	3.2	87.0	47.0	3.2	105	15	1.58	105.0	15.0	1.58
1" x 1"	2	107	80	8.6	53.5	40.0	4.30	127	27	3.4	63.5	13.5	1.70
1" x 2"	4	127	140	17.8	31.7	35.0	4.46	137	50	6.9	34.2	12.5	1.72
2" x 2"	8	155	225	34.9	19.3	28.1	4.36	130	72	9.4	16.2	9.0	1.17
2-1/2" x 2"	10	175	275	48.1	17.5	27.5	4.81	155	105	16.3	15.5	10.5	1.63
2-1/2" x 2-3/8"	12	200	340	68.0	16.6	28.3	5.66	152	122	19.0	12.6	10.1	1.58

the time interval could not be extended beyond 0.9 second. From the previous experiments with the large surface areas using the generator, it was determined that a delay of about 2 seconds was necessary to achieve starting. All attempts with the 8% solution of $K(C_2H_3O_2)$ were unsuccessful in starting the specimen arcing.

One additional experiment was tried which was aimed at starting the arcing process with the capacitor bank. The concentration of the electrolyte solution was reduced to 1% which increased the resistance of solution and consequently increased the discharge time. By setting the starting voltage just below the "A" point value (by ~ 10 volts) on small 1/2" x 1" specimens, and discharging the capacitor bank, starting was achieved. This method was not advantageous because the voltage had to be preset too close to the starting voltage without the capacitor bank. On larger sections, 8 to 10 square inches, the preset voltage was too high.

During the cathode size investigation, heating runs were conducted on various shapes of specimens holding the exposed surface area constant. For example, at 8 square inches, specimens 1-inch wide x 4-inches long and 2 inches wide x 2 inches long were heated. These tests indicated that with a 1-inch or more wide specimen, the maximum depth for uniform arcing was 3 inches. With the 1-inch x 4-inch specimen, the bubble only formed around the edges and not in the center of the specimen with the result that the bottom of the specimen was melting on the corners before the entire bubble was generated. This particular condition would probably not hold true if the voltage was increased gradually, permitting the bubble to form. However, with the present equipment and high currents required, the power must be applied very rapidly to prevent burning out the control equipment.

To confirm that the exposed surface area of the specimen was a major controlling factor of the power requirements of the electrolytic heating cycle, two series of experiments were conducted. The first test consisted of heating a single sample of Ti-6 Al-4V .056" thick with an exposed surface area of one square inch (1/2" x 1") and recording the voltage and amperage during the cycle. The second specimen heated was also .056" thick with one square inch of surface area but consisted of two separate areas 1/2" x 1/2", see sketch. The recorded voltage and amperage throughout the cycle for the second specimen was the same as that recorded for the first specimen even through two separate gas envelopes were developed in heating the second specimen. It was also observed that the arcing condition started on both sides of the second specimen at the same time.
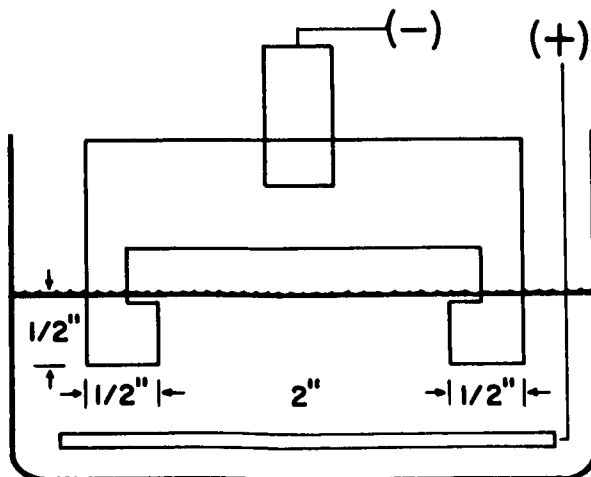
The second series of experiments consisted of heating four different Ti-6Al-4V specimens with an exposed surface area of 2 square inches. The specimens were as follows:
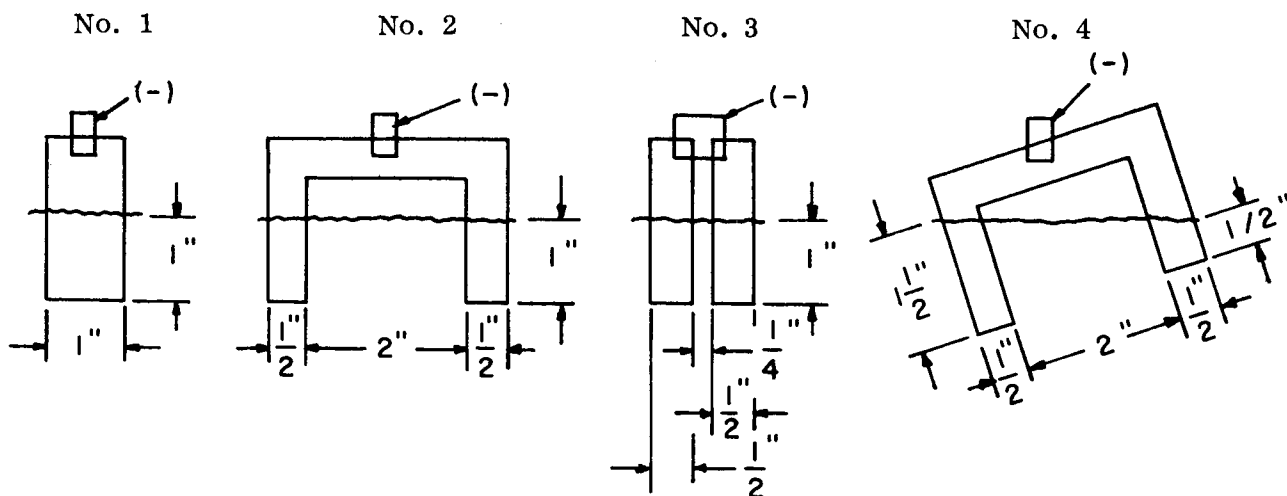
In each of the four cases the same voltage and amperage was required to start arcing and heating of the specimens. On specimen 2 through 4, arcing started at each extremity at the same time. These tests show that the power required to start arcing and maintain it is dependent upon the immersed surface regardless of the shape and spacing of the cathode providing all other conditions are held constant.

2. Investigation of the Gas Envelope Around the Specimen

To gain a better understanding of the heating process mechanism, a series of shadowgraphs were taken during the heating cycle. These photographs provided a means of observing and recording the generation of the specimen envelope and the associated electrical arcing. The system used to produce the shadowgraph image included a specimen suspended in a plexiglas wall tank with a light source on one side and a camera on the other.

A potential was applied at the specimen, which was accompanied by an increase in current as the voltage was increased between points "S" and "A (see sketch on following page).

During this time electrolysis takes place with the migration of hydrogen ions (H^+) to the specimen. The hydrogen ion gains an electron at the specimen and becomes electrically neutral (H°). The atomic hydrogen then combines to form a molecule and is liberated as H_2 gas. During this same period oxygen is being liberated from the anode of the system. The liberation of H_2 at the specimen manifests itself in considerable agitation along the surface of the specimen with boiling, breaking on the surface of the electrolyte. The boiling action becomes more severe
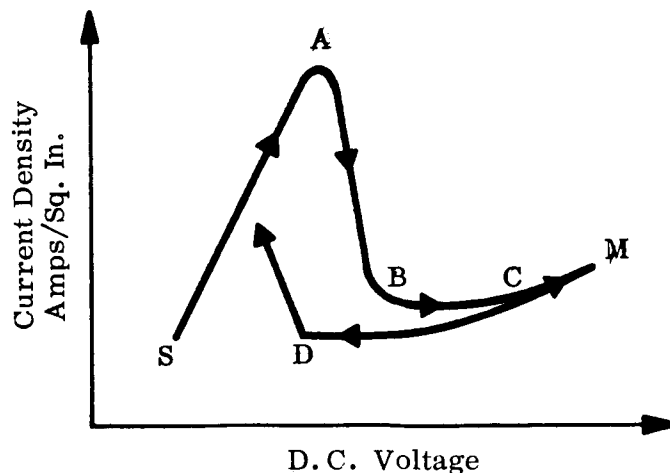
D. C. Voltage

as the voltage and amperage approach the "A" point. The liberation of H_2 is pro-portion to the amount of current flowing according to Faraday's Laws of Electrolysis. Due to the constant quenching action of the electrolyte during electroysis, the speci-men remains cool ($\sim$ 190°F) and there is no electrical arcing.

At point "A", however, this state changes suddenly as the voltage is further increased. The agitation decreases to a relatively even upward flow of gas along the surface, while sporadic arcing begins.

This process takes place as the current drops from "A" to "B", at which time the arc density changes from a sporadic arc to a continuous arc. At point "C", the specimen begins to heat and thereafter it is a matter of time before it is red hot or, depending on the specimen, it begins to melt. As the arc becomes continuous an envelope of gas is formed around the specimen. Figures V-27 and V-28 are shadowgraphs showing a side view and a front view respectively of two Ti-6Al-4V specimens approaching red heat. These photographs show the general shape of the specimen envelope and the very small arc path at the edge of the speci-mens. The short arc length appears to be associated with the process heating mechanism.

When the power is turned off to quench the specimen, the envelope collapses on the edge of the specimen first and then proceeds to the center of the specimen.

3. Investigation of the Process Heating Mechanism

In an attempt to gain a greater understanding of the process mechanism, a spectroscopic survey system was established to investigate the nature of the arc phenomena occurring at the cathodic element of the bath.

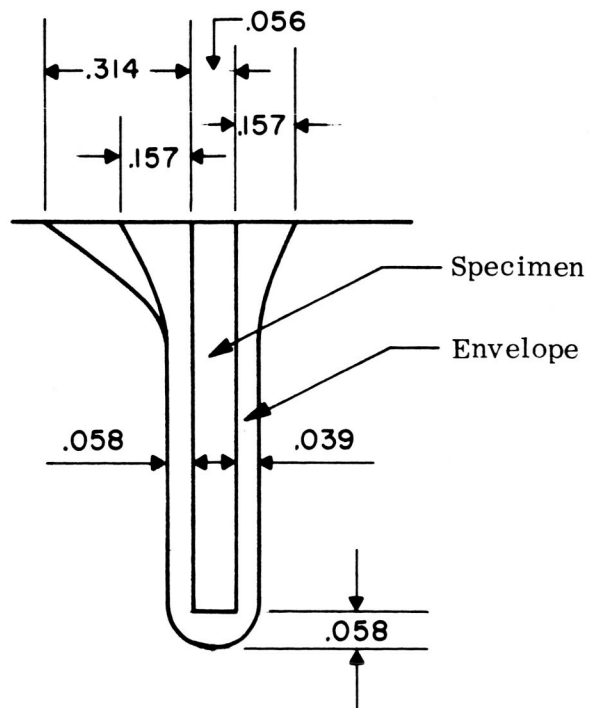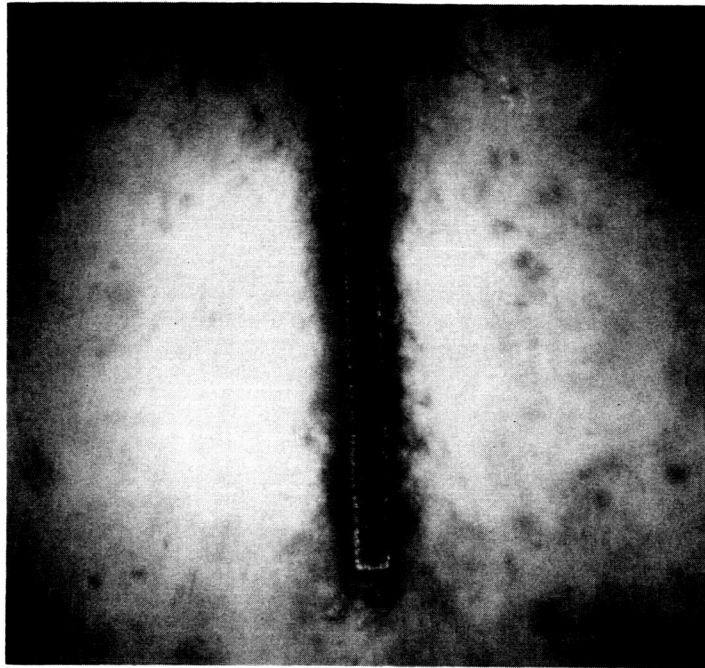Figure V-27. Side View of a Ti-6Al-4V Specimen Approaching Red Heat
Note the arcing condition around the edge of the specimen. The black area
outsie the arc is the specimen envelope.
Measurements in the sketch are taken from photograph. Magnification of
photo is 3.2X
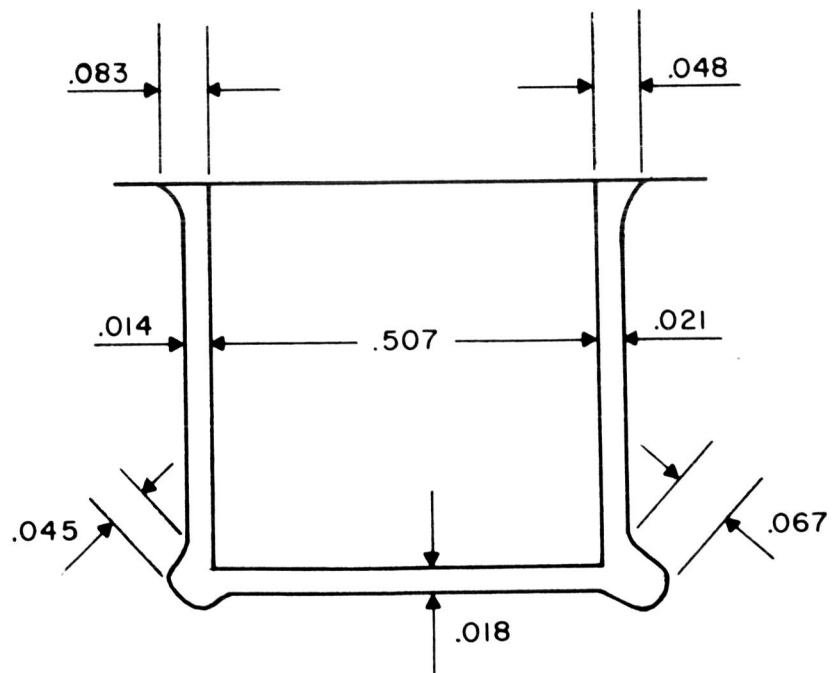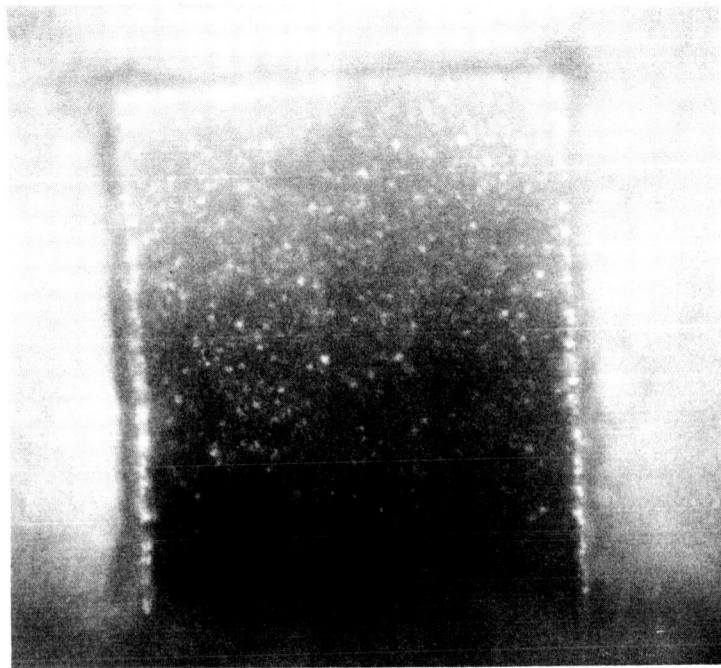
Figure V-28. Front View of Another Ti-6Al-4V Specimen Near Red Heat at 4.5 Magnification. Note the extended envelope at the two corners.

The spectroscopic survey work in emissions was conducted using the equipment shown in Figure V-29. The equipment included:

1) A 5" x 8" x 10" tank with a 4" diameter quartz glass window and a stainless steel anode.

2) A 3" diameter conveying lens and shutter.

3) A Leiss single monochromator utilizing a 14,500 lines/inch diffraction grating blazed for 4000 Å in the first order and mounted in a basic Ebert configuration.

4) A Photovolt Multiplier Photometer (Model 520-M) equipped with a 1P28 photomultiplier.

5) A Minneapolis-Honeywell Visicorder

6) Auxiliary equipment such as spectral calibration devices and optical bench.

To obtain an accurate record of the spectroscopic survey, the photomultiplier tube was positioned at the exit slit of the monochromator. The indicating drum of the monochromator was fitted with a worm gear drive with a 60:1 reduction ratio which was driven by a 60 RPM synchronous motor. With this system, the drum maintained a constant scanning speed of 1 RPM over the entire spectrum. The photo multiplier detects the various emitted bands and transmits a signal to the photovolt photometer. The amplified output of the photometer was fed into a Honeywell Visicorder which projects the signal as a varying galvonometer trace on the paper. The drive switch controlling the paper feed of the Visicorder was wired in parallel with the switch of the drum drive motor to provide a drum scanning speed of one revolution per minute or a spectral scan rate of 555 Å/minute when the Visicorder chart was running at one inch per minute.

Wave length calibration was achieved using mercury emission lines, calibration points being obtained in both first and second order covering a wave length interval from λ 2536 to beyond λ 8000 Å. A plot of wave length versus grating rotation showed perfect linearity throughout the entire range. Spectral resolution was excellent, the mercury yellow doublet (5770, 5791 Å) being completely resolved using 70 micron monochromator slits. Wavelength assignments for unknown cathodic derived sample spectra were cited by interpolating between two adjacent mercury lines thus minimizing wavelength errors.

Placement and orientation of the cathode relative to the optical system was achieved by mounting the sample immersion chamber on a Palmgren universal head equipped to provide all necessary directional degrees of freedom.

After the calibration was completed, the mercury lamp was replaced with the heating tank and a 3/4 square inch platinum electrode. The platinum cathode was immersed in an 8% solution of $K (C_2H_3O_2)$ and electrolytically heated
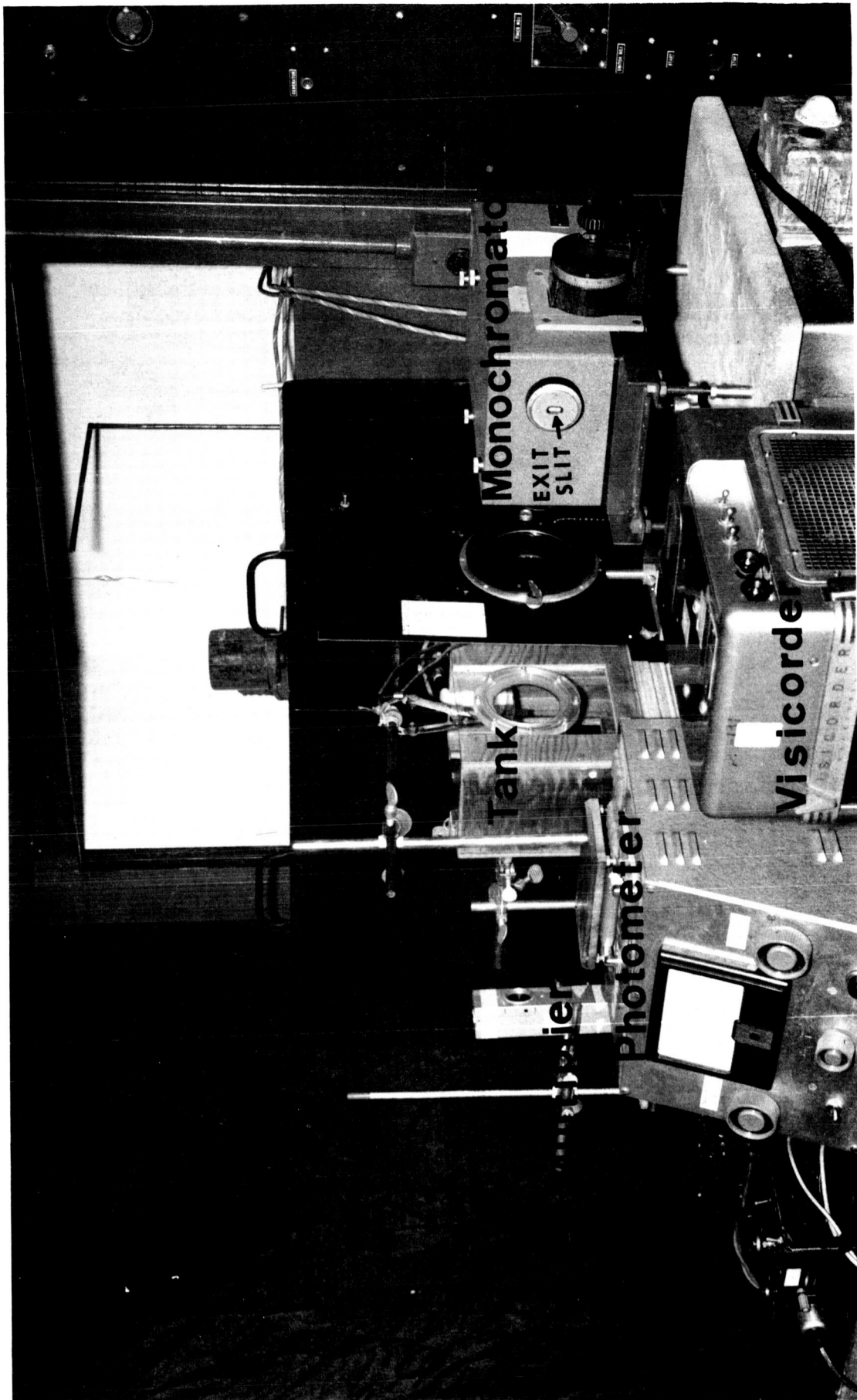
Figure V-29. Photograph shows equipment used in spectroscopic survey. The automatic drive has not been added to the monochromator in this photograph. The motor drive replaces the knob at the right of the monochromator. During operation, the multiplier is positioned in front of the exit slit.

until a uniform arcing condition was produced. Several surveys were run with the platinum cathode to establish repeatability and determine which emissions were being produced as a result of the solution composition. Preliminary runs indicated that the solution degraded rapidly as perceived by various color changes and it was found necessary to use fresh solution for each run. Also, emission intensities appeared quite low and final slits of 400 microns were found necessary to register useful video displays. This reduced the spectral resolution from about 10Å to 50-60Å.

After the platinum surveys were completed, additional surveys were conducted using Ti-6 Al-4V and 2219 aluminum alloy as the cathode. Considerable background emmissions were in evidence on the Ti-6 Al-4V and 2219 Al charts. This was apparently due to the major constituent in each of the cathodes (Titanium and Aluminum).

Because of the high background levels data reduction and interpretation was very difficult. Identification could not be positive in many cases because the second order wave length was obsecured by the high background level.

The following observations were made from the recorded surveys:

1) The 3063 Å OH molecular system seems present regardless of the cathode material used.

2) Atomic potassium lines centering around 4044 Å appear to be present independent of cathode material used.

3) The titanium cathode yields a complex spectra, aluminum less complex and platinum the simplest.

Additional identification work had to be suspended because the length of time needed to evaluate the complex spectras was beyond the financial scope of the contract.

This work did yield one very important fact by establishing the presence of the (OH)- radical and atomic potassium. It indicates that the specimen is not heated in a pure hydrogen atmosphere but that the gas envelope contains many other elements. This also explains the presence of scale on the titanium specimens and the oxygen contamination noted on some of the photmicrographs.

4. Electrolyte Heating Process

Examination of the electrolytic heating process indicates that the heating mechanism is rather complex and consists of several different phenomena. A rigorous treatment of the heating mechanism is beyond the scope of this contract; however, the author offers the following interpretation based on observations and investigations.

If the heating mechanism is examined in relation to the voltage versus current density curve, it has been shown that the current and voltage increase until a point is reached at which an arc appears on the specimen. During this period of

the cycle the temperature of the cathode rises gradually to about 190° to 200°F with an observed bubbling action. Several conditions exist during this portion of the cycle. The electrolyte contains positive hydrogen particles as well as negatively charged particles due to dissociation. As the potential is applied the positively charged hydrogen ions are attracked to the negative cathode where they become electrically neutral and after forming a molecule bubble off as hydrogen gas. This process is known as electroysis. As the potential is increased and the current increases, the bubbling action at the cathode becomes more vigorous. The thin film of solution surrounding the bubbles adjacent to the specimen begins to boil and the gas continues to flow upwards along the specimen. This flow of gas around the cathode establishes a thin viscous boundary layer with zero velocity at the specimen surface. With the establishment of the thin stagnant layer, continuous contact with the specimen is lost and an arc is drawn. As this condition increases, the resistance is increasing with a resulting corresponding decrease in current. The phenomena of a zero velocity layer, as a gas passes over a surface has been studied for many different process and is generally accepted. As arcing becomes uniform over the specimen the gas flow becomes more uniform as it flows to the surface. This point in the cycle corresponds to point "B" on the voltage versus current density curve. The temperature of the specimen would not increase yet because of the flow of gas to the surface would tend to cool it. An additional method of producing heat is needed at this point in the cycle.

This method is supplied when the potential is still further increased to point "C", at which time ionization of the stagnant layer of gas occurs and heat is created by the collision of numerous electrons. The stagnant layer tends to act as a furnace wall to the intense heat generated by the electron collisions and the specimen temperature rises rapidly. Once the ionization level has been reached the reaction tends to be self sustaining. Consequently if the potential is further increased the number of electron collision increases with a resulting increase in temperature. However, if the potential is decreased the number of electron collisions decrease with a resulting decrease in temperature. Becuase the reactions tend to be self sustaining the potential can be decreased below the level necessary to generate it. This explains the "C" - "D" portion of the voltage versus current density curve during which heating occurs at the lower voltage level.

In the case of the 2219 Al specimen, it was necessary to raise the potential to a very high level to achieve ionization of the gas layer; however, once ionization was achieved the potential had to be reduced quickly to prevent melting. Because of the arcing condition, the stagnant gas layer probably contains some atoms of the base metal or cathode in addition to the electrolyte which would mean that the gas composition would vary for each cathode and consequently require a particular potential to achieve ionization.

As the potential is reduced to the "D" point on the voltage versus current density curve, the velocity of the flowing gas reduces, the stagnant layer becomes thinner, and the arc length also decreases. When the gas flow slows down to the point where the stagnant layer can no longer be maintained, the solution contacts the cathode and the arc is extinguished.

This interpretation of the heating mechanism of the process differs from the Russian literature which indicates that the cathode is heated in a high temperature hydrogen envelope. However, based on the spectrographic survey work and oxide film encountered on the Ti-6Al-4V material it has definitely been proved that the heating environment is not pure hydrogen.

SECTION VI

PHASE IV – DEVELOPMENT OF SOLUTION TREATING CYCLES

Phase IV of the contract involved heat treating tests to determine the feasibility of thermally treating metals in particular the Ti-6Al-4V and the 2219Al alloys by the electrolytic heating process. This was to be accomplished by developing a solution heat treating practice for the Ti-6Al-4V alloy and the 2219Al alloy which resulted in the STA condition for the Ti-6Al-4V alloy and the T-62 condition for the 2219Al alloy after conventional aging. The effectiveness of the developed treatments would be evaluated on the basis of such things as the mechanical properties and oxidation.

A. TITANIUM – 6% ALUMINUM – 4% VANADIUM (Ti-6Al-4V)

1. Metallurgy of Titanium-6Al-4V

The 6Al-4V titanium alloy is an alpha-beta alloy that has been widely applied as an aerospace structural material. The addition of 4 percent vanadium to the basic composition results in considerable beta stabilization and provides a beta transus temperature of approximately 1820°F.

This alloy is used in aircraft in either of two conditions of heat treatment: annealed, and solution treated and aged (STA). A major strength increase is realized when the alloy is subjected to duplex heat treatment. This consists of a solution treatment at a temperature high in the alpha-beta (1750°F), followed by a rapid quench to retain alpha phase and supersaturated metastable beta, and then aging at some intermediate temperature (1000°F). The beta phase is unstable; and upon reheating at lower temperatrues, aging occurs due to the formation of a transition phase, omega. The omega phase subsequently transforms to a stable alpha precipitate, which results in hardening. The severity of the quench in the STA condition is extremely critical, and a rapid (within 4 to 6 seconds) water quench is mandatory to obtain satisfactory strength on subsequent aging. If slower cooling rates are used, some decomposition of the high-temperature beta phase occurs during the quench and reduces the strength level attainable. Cooling rate also affects the maximum section size of the alloy that can be heat-treated for strength improvement.

The following table shows the expected average properties and the normal heat treatment used to obtain them.

TABLE VI-1

Material	Form	Condition	Ultimate Tensile Strength (KSI)	Yield Strength (KSI)	Percent Elongation in 2 inches
Ti-6Al-4V	sheet	annealed	138	128	12
		STA	170	160	8

Ti-6Al-4V -- annealed: 1300°F for 1 hour, with slow cool to 1050°F, then air cool

        -- STA: 1750°F for 30 minutes water quench, plus 1000°F for 4 hours with air cool

2. Development and Testing Procedure

Specimens .750" x 5" x .090" were prepared from the Ti-6Al-4V alloy for heat treatment. Based on previous experiments, described in Section V, it was determined that the most uniform specimen temperature was achieved when the specimen was immersed in a flat parallel plane with respect to surface of the solution. To achieve this condition, a special specimen holder was fabricated (see Figure VI-1).

With the specimen holder, the test piece can be easily inserted, preheated, and quickly immersed entirely in the electrolyte. The specimen is immersed in the electrolyte with the voltage preset by pushing the insulated handle to the left and permitting the clamps to swing down into the liquid. A 350-watt heater is used to preheat the specimen to about 300°F before lowering it into the solution. The preheat operation has eliminated the high initial power requirement previously required to start the arcing condition. As a result, the probability of melting the specimen on starting has been eliminated.

Temperature uniformity over the specimen has been maintained by gripping only the very edge of the specimen with the "C" clamp. This gripping procedure provided good electrical contact but prevented the clamp from acting as a large heat sink. Considerable difficulty was encountered along these lines when heating some of the early specimens. Temperature readings were monitored on a Visicorder employing a shielded chromel-alumel thermocouple embedded in a small drilled hole in the specimen. The exposed metal portion of the thermocouple was insulated with Turco 522 maskant to prevent arcing on the shield. The maskant was also employed on the specimen holder to prevent arcing.

The titanium specimens were electrolytically solution treated in an 8% solution of $K(C_2H_3O_2)$ operating at 130°F. The specimens were heated using the above procedure to 1730°F at a setting of 148 volts and 60 amperes for 40 to 110 seconds followed by a quench with agitation from the circulator and agitator. Additional specimens were furnace treated at 1730°F for 30 minutes and water quenched. Part of the specimens from each solution treated condition were furnance aged at 1000°F for 4 hours and air cooled.

SPECIMEN HOLDER
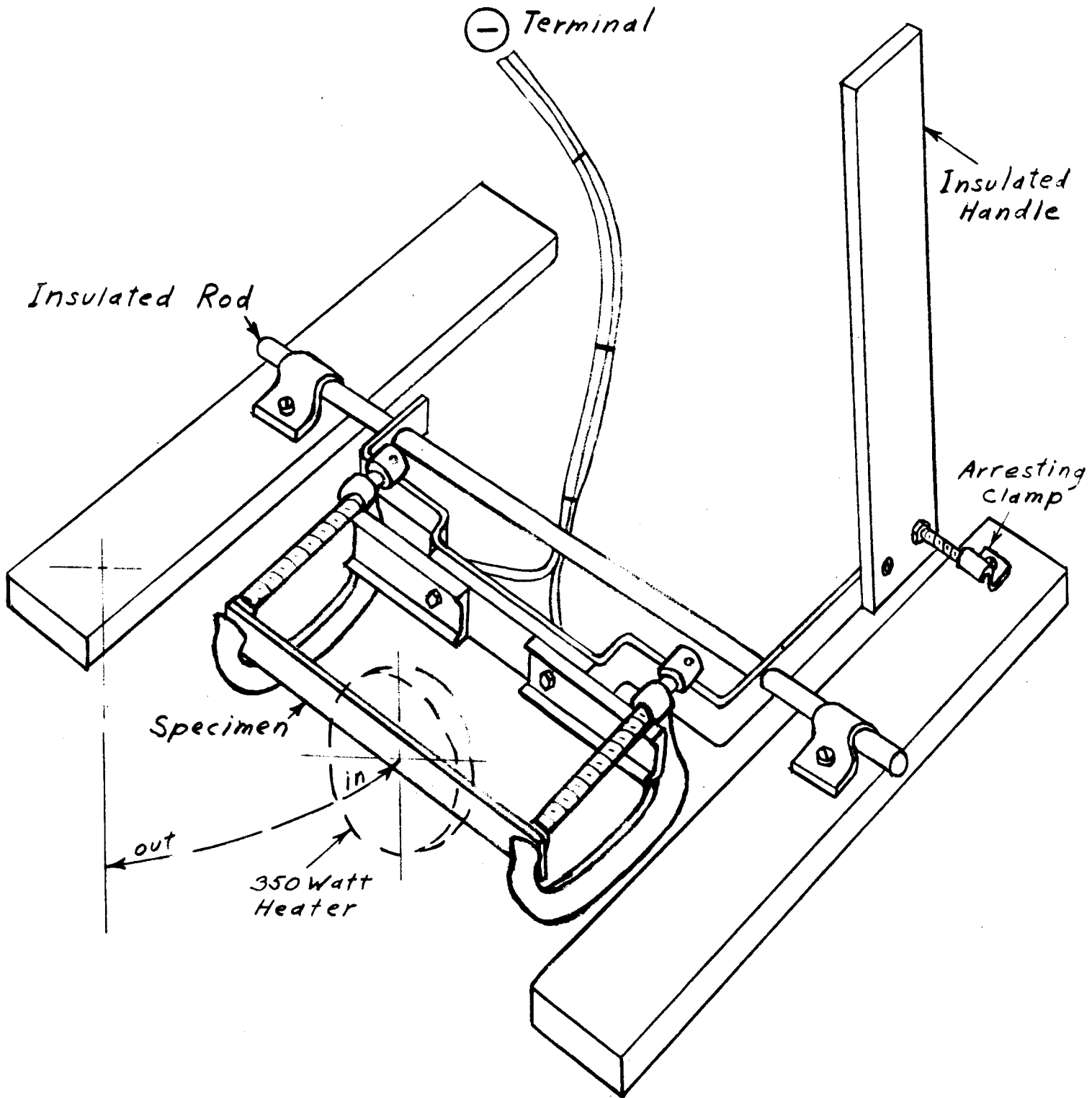
Figure VI-1

During the initial heating trials, the specimen was clamped on both ends by the fixture. During the heating cycle considerable expansion was experienced which resulted in a bulkled specimen. This condition was avoided by clamping the specimen on only one end and using the other "C" clamp only for support. Some distortion in the specimen was still noted probably as a result of the bubbles being trapped on the underside of the specimen. This type of distortion could probably be avoided if the specimens were heated vertically; however, the temperature was not sufficiently uniform to produce satisfactory mechanical properties.

3. Test Results

Tensile specimens were prepared and tested in the following conditions:

a) As-received - annealed by vendor
b) Solution treated - electrolytically
c) Solution treated electrolytically and aged
d) Solution treated furnace and aged

The results of these tests are presented below:

TABLE VI-2

Ti-6Al-4V MECHANICAL PROPERTIES

Condition	Heating Time at Temperature	Ultimate Strength psi	Yield Strength psi	% Elong. in 2"
Mill Annealed		138,220	128,860	13.5
		137,450	129,950	13.0
		136,740	129,950	12.5
Solution Treated		151,700	139,390	6.0
1730°F 30 Min. W.Q.		153,950	130,390	8.5
Standard Furnace		154,550	130,120	8.0
Solution Treated	48 sec.	164,630	131,510	7.5
Electrolytically	45 sec.	161,250	131,400	7.0
1730°F for given time	81 sec.	154,090	120,450	5.0
	108 sec.	163,760	120,800	*
Furnace Solution Treated		167,780	157,780	6.0
1730°F Min + 1000°F	Specimen broke in grips - no results			
for 4 hours				
Electrolytically Solution	42 sec.	166,070	140,270	5.5
Treated 1730°F for given time	76 sec.	167,760	140,270	5.0
+ 1000°F for 4 hrs A.C.	114 sec.	161,140	127,280	*

* Broke outside of gage marks

6-4

The results of the mill annealed and the furnace treated specimens are typical, indicating that the heat treatment was properly performed. The results of the electrolytically solution treated specimens indicate a considerably higher ultimate strength by about 10,000 psi; however, the yield strength varies from several thousand psi above to 10,000 psi below the furnace treated specimen. After aging the electrolytic specimens at 1000°F for 4 hours, the ultimate strength appears typical; however, the yield strength is low.

The high ultimate strength of the electrolytic solution treated specimens indicates that the quench time was not fast enough and partial aging occurred in these specimens. The low yield results of the solution treated specimens tends to indicate that the temperature was not high enough to achieve a complete solutioning treatment. After aging in a conventional furnace the yield strength did not respond due to the poor solutioning treatment.

A second set of Ti-6Al-4V tensiles was prepared using the same conditions as the previous trial with the exception of the quench rate. During the quench cycle of the second set of specimens, the sample was vigorously shaken and 200 ml of cold solution (60°F) were poured over the submerged specimen. This method produced quench rates between 650°F and 700°F/second.

TABLE VI-3

Ti-6Al-4V MECHNICAL PROPERTIES IN THE STA CONDITION

Specimen No.	Condition	Time in Sec.	Ultimate Strength psi	Yield Strength psi	% Elong. in 2"
21	Electrolytically heat	47	177,880	165,270	6.0
22	treated at 1730°F for	53	173,000	160,400	4.0
23	given time followed	42	175,160	161,760	4.0
24	by fast quench 650°F	43	175,220	159,290	4.5
25	per second + four	60	175,390	161,860	–
26	hours @ 1000°F in	60	175,110	162,670	–
27	furnace A.C.	120	174,940	162,420	3.0
28		120	175,500	163,030	4.0
29		240	173,400	158,900	–
30		240	174,890	161,110	3.0

The new tests agree with the results obtained on specimens heat treated in the furnace and typical results for STA condition.

Ultimate, psi	–	168,000
Yield, psi	–	158,000
% Elong. in 2"	–	6.0

It should be noted the elongation is slightly below the expected level of 6% in 2"; however, the ultimate strength and yield strength are at a slightly higher strength level than that expected in the STA condition which could account for the lower elongation level.

In addition to the tensile tests, specimens were submitted for gas analysis to determine if heating in an electrolyte changed the gas content of the material. Specimens were submitted to an outside vendor and the average H_2, N_2, and O_2 gas content of duplicate runs was recorded. The results were as follows:

TABLE VI-4

GAS ANALYSIS OF Ti-6Al-4V MATERIAL

Sample No.	Condition	Gas Content Oxygen (%)	Hydrogen (ppm)*	Nitrogen (ppm)*
T2	Mill annealed by vendor	0.115	44	130
23	Solution treated electrolytically for 42 sec	0.110	62	116
13	Solution treated electrolytically for 75 sec	0.160	78	102
28	Solution treated for 120 sec	0.124	83	118
29	Solution treated for 240 sec	0.164	110	117

* ppm = parts per million

The results of Table VI-4 indicate that there is a definite increase in oxygen and hydrogen content which again indicates that the gas surrounding the specimen does contain numerous constiuents. These figures also show that the gas content tends to increase with time.

These two constituents could be very detramental to the metal specimens. The oxygen would probably be present as stabilized alpha (contamination) along the surface of the specimen. The increased hydrogen content would be detramental from an embrittlement standpoint.

Solution treated specimens were sectioned mounted, polished, and microscopicly examine to determine the extent of oxidation on the heat treated material. The investigation revealed that the exposed surface of the Ti-6Al-4V specimens contained small breaks which varied from .0002" to .0016" deep. Figures VI-2 and VI-3 are photomicrographs of the surface breaks at 75x and 500 x respectively in the unetched condition. Figure VI-4 shows that the breaks are associated with a layer of oxygen contaimination of approximately the same thickness as the crack depth. Examination of a series of specimens indicated that the stabilized alpha layer varied from about .0002" to about .0025". The heaviest layers were found on specimens heated for about 120 seconds.
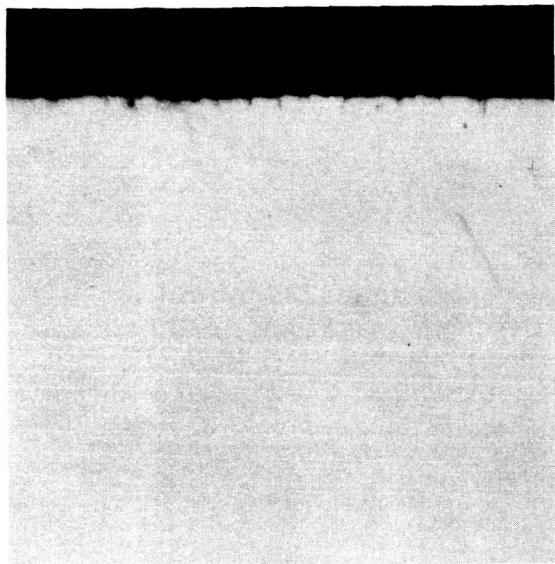
Figure VI-2. Edge of Ti-6Al-4V speci-
men heated to 1750°F electrolytically for
2 minutes and quenched. Note the small
breaks in edge of the specimen.

MAG:75X   Etch: None
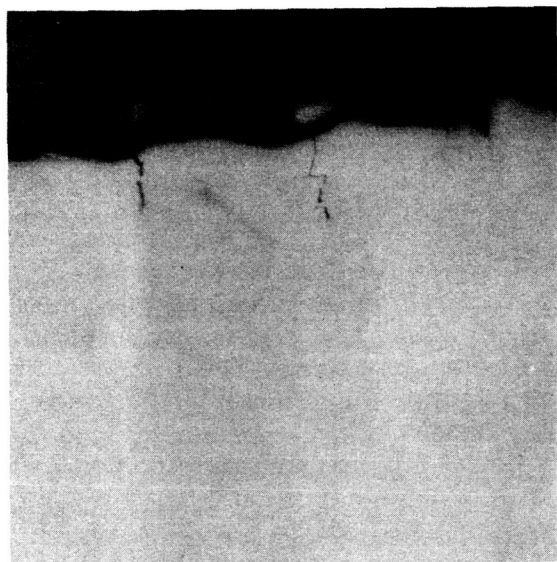
Figure VI-3. Enlarged view of the edge
cracks on the Ti-6Al-4V specimen shown
in Figure VI-2. Crack depth is about
.0008".

MAG:500X   Etch: None
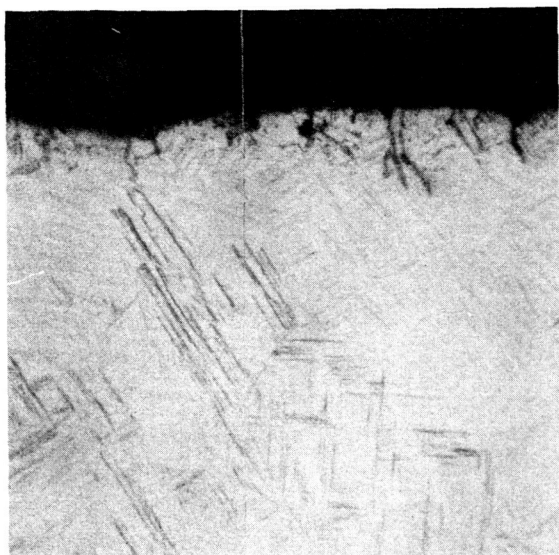
Figure VI-4. Photomicrograph showing
the contamination and edge cracks on an
electrolytically solution treated specimen
of Ti-6Al-4V. Contamination and crack
depth are about 0.0010".

MAG:500X   Etch: Krolls

B. **2219 ALUMINUM ALLOY**

1. **Metallurgy of 2219 Aluminum**

The 2219 aluminum alloy contains copper as the major alloying element and small additions of manganese, zirconium, vanadium, and titanium, which are essential for high strength at elevated temperatures. This alloy differs from other high-strength alloys (Al-Cu-Mg and Al-Zn-Mg-Cu) in that it does not contain either magnesium or zinc. The nominal composition of this alloy is lised below:

1) Copper, 6.3 percent
2) Manganese, 0.3 percent
3) Titanium, 0.06 percent
4) Vanadium, 0.01 percent
5) Zirconium, 0.18 percent
6) Aluminum, balance

The corrosion characteristics of 2219 are similar to those of 2014 and 2024. The influence of quenching water temperature and artificial aging treatments on subsequent resistance to corrosion and stress-corrosion cracking of 2219-T6 is therefore of primary importance. Although an increase in quenching water temperature from 70 to 150°F improves resistance to distortion and does not adversely influence the corrosion behavior of properly aged 2219-T6, it does lower the tensile and yield strength by about 2000 psi. Deviations from recommended aging practice for the T6 temper, however, can lower resistance to corrosion and to stress-corrosion cracking. This is particularly true for material quenched in water at 150°F instead of at 70°F. Because the solution heat-treating temperature is extremely close to the melting range of the 2219 alloy (1010 to 1190°F), it is mandatory that extreme care be exercised during solution treatment (985 to 1005°F) to prevent incipient or catastrophic melting of the alloy.

Table VI-5 shows the typical room temperature properties for the 2219 Al alloy and the standard heat treatments used to obtain them.

TABLE VI-5

TYPICAL ROOM TEMPERATURE TENSILE PROPERTIES OF 2219Al

Alloy	Form	Condition	Tensile Strength Ultimate (KSI)	Tensiel Strength Yield (KSI)	Elongation in 2 inches (percent)
2219	sheet	O	25	10	20
		T-42	53	27	20
		T-62	60	42	10

2219 -- condition O annealed: 775°F; cool at 50°F per hour to 500°F cooling rate below 500°F is unimportant

T-42 solution -- treated: 995°F with cold-water quench

T-62 solution -- treated and aged: T-42 material aged at 375°F for 36 hours

2. Development and Test Procedure

The 2219Al specimens for testing were heated in the same manner as the Ti-6Al-4V specimens using the same holding device.

Specimens 0.750" x 5" x 0.080" were heated in an 8% solution of $K(C_2H_3O_2)$ to 990°F to 1000°F for 30 seconds to 120 seconds followed by a quench. The specimens were preheated to 350°F to eliminate the high power requirements at the beginning of the cycle and held at 110 volts and 59 amps during the heat treat cycle. The temperature of the specimen was monitored by a chromel-alumel thermocouple embedded in the test piece.

In addition, specimens were heat treated in a furnace at 995°F for 45 minutes and water quenched. Part of the electrolytic heat treated specimens and the furnace treated specimens were then aged for 36 hours at 375°F in a standard muffle furnace.

About thirty (30) 2219Al samples were heat treated, prepared for tensile testing, and tested, however, due to a malfunction of the testing equipment the data was unreliable. All of the heat treatments were repeated and the tests conducted again.

3. Test Results

Tensile specimens were prepared and tested in the following conditions:

    a.   As-received – mill anneal
    b.   Solution treated – electrolytically
    c.   Solution treated – standard furnace
    d.   Solution treated electrolytically and aged
    e.   Solution treated standard furnace and aged

All of the specimens requiring a solution treatment were quenched using agitation of the specimen and cold electrolyte poured over the completely submerged specimen. Quench rates of 550°F to 600°F were obtained over the range 995°F to 250°F (1.2 sec). This rate would be considerably faster through the critical range of 850°F to 550°F.

The results of the second series of tensile tests are shown in Table VI-6.

TABLE VI-6

ROOM TEMPERATURE TENSILE RESULTS OF 2219 AL ALLOY IN VARIOUS CONDITIONS

Specimen No.	Condition		Ultimate Strength in psi	Yield Strength in psi	% Elong. in 2"
0	As received-vendor annealed		27,190	13,010	22.0
01	As received-vendor annealed		26,020	18,500	22.5
7	Solution treated in muffle		46,670	19,120	21.5
8	furnace @ 1000°F for 45 min.,		46,700	20,230	21.5
9	water quenched, not aged		46,700	20,230	21.5
10			46,910	17,140	23.0
11	Solution treated in furnace +		63,917	41,620	10.5
12	aged at 375°F for 36 Hrs A.C.		No results		

		Time in Sec.			
63	Solution treated	30	51,050	19,370	21.0
58	electrolytically for	45	51,180	20,000	21.5
66	given time @ 1000°F +	45	50,650	19,430	21.0
62	a solution quench, not aged	60	48,340	22,760	21.5
54	Solution treated	30	60,220	42,490	10.5
55	electrolytically for	30	58,350	40,100	10.0
56	given time @ 1000°F	30	59,740	43,120	9.0
57	+ solution quench +	45	56,700	39,750	–
64	age @ 375°F for	45	59,640	43,060	9.5
51	36 hours A.C.	60	60,360	42,970	8.0
52		60	57,400	38,900	5.5
53		60	59,790	40,590	8.0
60		120	57,510	41,580	–
61		120	57,200	41,260	7.0
65		120	58,860	41,800	8.0

The results shown in these tests indicate a close correlation between the furnace treated specimens and the electrolytically heat treated specimens.

The results of the electrolytically solution treated and aged specimens are well above the minimum values for 2219 Al in the T62 condition.

Ultimate Strength psi - 54,000

Yield Strength psi -   36,000

% Elongation in 2" -   6%

Examination of the heat treating conditions with respect to quench rate, (in excess of 600°F/second in the critical range), control during the conventional aging treatment, (a thermocouple on the part) and the resulting tensile properties tends to indicate that the corrosion resistance of the electrolytically heat treated material would be similar to that experienced with a conventional heat treatment.

Gas analysis tests performed on the electrolytically heated 2219 Al material indicated essentially no change in the oxygen, hydrogen and nitrogen content. Table VI-7 shows the results of this test.

TABLE VI-7

GAS ANALYSIS RESULTS ON 2219 AL ALLOY

Condition	Oxygen[1]	Nitrogen[1]	Hydrogen[1]
As Received	62 PPM[2]	ND 5 PPM[3]	1.5 PPM
Electrolytically heated 60 seconds to 1000°F	64 PPM	ND 5 PPM	1.3 PPM

1) Amounts shown are the average of duplicate runs

2) PPM = parts per million

3) ND = not detected less than

Examination of specimens electrolytically solution treated showed no evidence of oxidation on the exposed surface which also agreed with the gas analysis results. In several cases some incipient melting was detected on those specimens which were inadvertently heated above the 1005°F temperature. Figure VI-5 and VI-6 are photomicrographs at 75X and 500X respectively of a specimen that was heated to 1025°F for 60 seconds. Figure VI-7 is a typical microstructure of a specimen heat to 995°F and quenched.
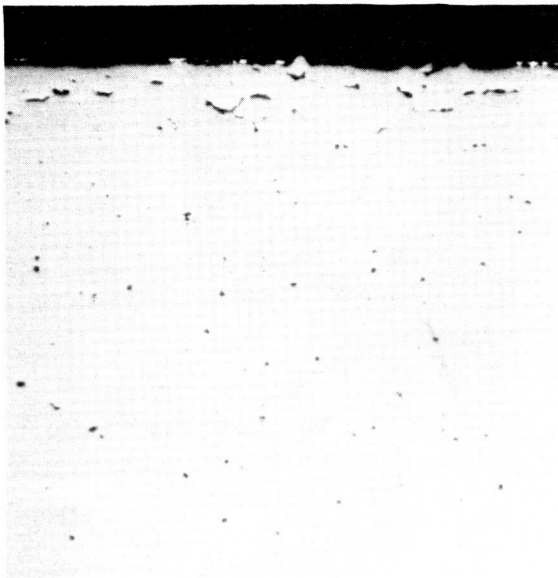
Figure VI-5. This photomicrograph shows the edge of a 2219 Al specimen heated to 1025°F and quenched. Note the incipient melting along the edge of the specimen.

MAG:75X   Etch: None

Figure VI-6. Enlarged view of the edge of the specimen shown in Figure VI-5.
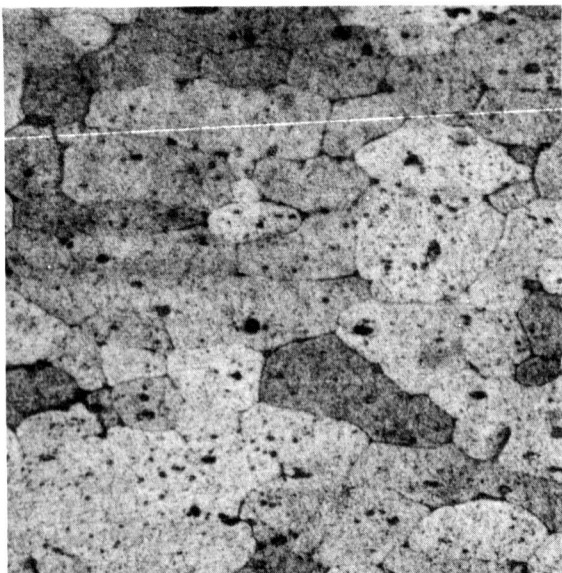
MAG: 500X   Etch: None

Figure VI-7. General microstruction of a specimen heated to 995°F electrolytically and quenched.

MAG: 250X   Etch: Kellers

SECTION VII
CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The following conclusions are based on the work performed during this contract.

1. Both the Ti-6Al-4V alloy and the 2219 Al alloy can be heated to their respective solution treating temperatures and be rapidly quenched without removing the material from the electrolyte. Mechanical properties achieved after conventional aging meet the typical room temperature requirements in both cases and are well above the minimum design limits.

2. Advantages of the process include a rapid heating rate and a fast quench rate. Heating rates on the order 150°F/second to 300°F/second were experienced depending on potential applied between the electrodes. High quenching rates were achieved with the process even though the quenching media was maintained at 130°F. Quenching rates on the order of 500°F/second to 600°F/second over the entire temperature range were achieved; however, in the critical temperature range for the 2219 Al alloy, for instance, (850°F to 550°F) quench rates were probably on the order of 1000°F/second.

3. Several factors previously believed to be advantageous of the process were never achieved. These factors include elimination of distortion during quenching and scale free heating due to the atmosphere of the process. Tests indicated that little distortion was experienced when the specimens were heated vertically, however, this was at the expense of uniform specimen temperature. When heating the materials horizontally, temperature uniformity was experienced but considerable distortion was also encountered due to the bubbling action of the process mechanism. Scale free heating was not achieved because the gas envelope generated around the specimen is not a pure hydrogen atmosphere. Tests conducted indicated that the gas envelope contained many constituents and these varied as the material to be heated varied. A scaled and oxygen contaminated surface up to .0025" in depth was experienced on the Ti-6Al-4V alloy during a two minute heating period.

4. Temperature uniformity of the heated part was very difficult to attain. Heating with the specimen completely submerged and parallel to the liquid surface produced the most uniform heating condition. Specimens

7-1

longer than 3" which were heated vertically, tended to overheat and melt near the bottom of specimen before the gas envelope was completely formed at the top of the specimen.

5. Power requirements experienced during heating were very high but not unreasonable. The power density was comparable to that experienced with induction heating. About 1.6 KW/square inch of surface area was required during heating for the electrolytic process and about 1.5 to 7 KW/square inch is required for induction heating. The current density required during the electrolytic process is about 10 amp/sq". About 5 KW/square inch is required to start the electrolytic process without preheating the material. Process efficiency for the electrolytic process varies between 9.5 and 12%.

6. The major factors which effect the electrolytic heating process are:

   a. Electrolyte composition

   b. Electrolyte concentration

   c. Electrolyte temperature

   d. Cathode or specimen material

   e. Cathode size

   f. Cathode temperature

   All of these factors are inter related and a change in one could affect another. The electrolyte composition tends to determine the power required during the cycle and the degree of operational control. By varying the concentration of the electrolyte the actual voltage and amperage requirements for the heating cycle can be changed. In general voltage decreases and amperage increases as the concentration of the electrolyte increases. Electrolyte temperature also effects the process from the standpoint of required amperage and voltage to achieve heating. The electrolyte temperature effects the degree of temperature control, a cold solution provides less temperature control than a hot solution. The temperature of the electrolyte will also effect the quench rates that can be achieved.

   The cathode material in conjunction with the electrolyte controls the voltage and amperage needed to achieve heating of the specimens. Cathode size with respect to the exposed surface area actually determines voltage and amperage that will be required for a given system of variables. Cathode preheating can eliminate the extremely high power requirements to start the heating cycle. All of these factors can be related by the voltage versus current density curve for the process.

7. The system selected for heating the Ti-6Al-4V alloy and the 2219 Al alloy consisted of an 8% solution of potassium acetate as the electrolyte operating at a temperature of 130°F. Solutioning was achieved for Ti6Al-4V alloy at 148 volts 60 amperes for 45 seconds. The solutioning treatment was achieved for the 2219 Al alloy at a voltage of 110 volts and 59 amperes for 30 to 60 seconds.

B. RECOMMENDATIONS

The following recommendations are made based on the results and conclusions of this program.

1. The electrolytic heat treating process can be used as a method of heat treating; however, this process has limited application due to the power density requirements and temperature control limits.

2. The 2219 Al alloy should not be solution treated by this method because the solutioning temperature is too close to the melting temperature of the material and incipient melting in the grain boundaries could occur very easily.

3. Ti-6Al-4V material could be solutioned treated by this process providing some surface removal operation is used in conjunction with the process. Part size would be a major evaluation point to determine possible use.

4. This process would have greater application as a heating method for a fabrication operation instead of a finish heat treating operation. However, the process should not be discarded as a possible heat treating method. The process should be considered for surface hardening applications and large quantities of small parts requiring a short cycle.

5. Additional work on this process should be aimed at greater temperature control and methods to increase the size of the part that can be heated.

APPENDIX A

Material List for Figure III-2

Location	Switch
Station I	Local control push button station plus key switch
Station II	Local control push button station
Station III	Local control push button station
Switch 4	DPDT
Switch 5	DPST (for repeat or single)
Switch 6	DPDT
Switch 7	SPDT Momentary switch
Switch 8	DPDT
Switch 9	DPDT
Switch 10	SPDT Momentary switch

	Potter Brumfield Relays
R_1	KL17A
R_2	KL17A
R_3	KL17A
R_{4A}	KL17A
R_{5A}	KL17A
R_4	PM17AY
R_5	PM17AY
R_6	PR11AL5
R_7	PR11AL5
R_8	KL17A
R'	GA17D
R''	GA17D

Material List for Figure 1 continued

Location	Industrial Timer
T_1	H-65
T_2	H-15S
T_3	H-30S
T_4	CH-1M

0-500V Spellman Power Supply - for capacitor circuit

3 capacitor banks of 9000 uf each

Motor Generator - Empire or Spellman - 100 amp 300V DC
with starter, field control, main breaker and meters

2 additional similar field rheostats for program voltage control

G. E. 0-250 - 500V DC Voltmeter

G. E. 0-250 - 500 AMP Ammeter plus Shunt

APPENDIX B

REFERENCES

1. N. H. Polakowski, "Contemporary Metal Processing Techniques in Russia," Metals Progress, January 1955, p 103.

2. I. Z. Yosnogordski, "Electrolytic Hardening-Heating of Metals and Alloys in Electrolytes," Russian text published in 1949 - translated into German by F. Krantz in 1952.

3. Kogyo Gijutsu, "A Study of the Electrolytic Hardening Process," Fujimoto Printing, 1959.

4. H. Frankel, "The Heating of Metals in an Electrolyte," Technical Report WVT6528, 1965, Benet Laboratories, Watervliet Arsenal.

5. Robert G. Mahorter, "Investigation of Electrolytic Heat Treatment," Technical Report No. NAEC-AML-1835, Aeronautical Materials Laboratory, Philadelphia, Pa. , December 1963.

6. J. D. Cobine, "Gaseous Conductors" Theory and Engineering Applications, Dover Publications, Inc. , New York, 1958.

7. J. W. Cable, "Induction and Dielectric Heating," Reinhold Publishing Corporation, 1954.