STUDY ON DEVELOPMENT OF SATURN MANUFACTURING TECHNOLOGY FOR WELDING METHODS AND TECHNIQUES TO REDUCE HYDROGEN POROSITY

Final Report to

GEORGE C. MARSHALL SPACE FLIGHT CENTER
Huntsville, Alabama

FACILITY FORM 602

N67-26508	
(ACCESSION NUMBER)	(THRU)
57	1
(PAGES)	(CODE)
CR-84152	15
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

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STUDY ON DEVELOPMENT OF SATURN MANUFACTURING TECHNOLOGY FOR WELDING METHODS AND TECHNIQUES TO REDUCE HYDROGEN POROSITY

to

George C. Marshall Space Flight Center
Huntsville, Alabama

Contract NAS8-20307
FINAL REPORT
(Report period 25 February through 24 September, 1966)

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October 28, 1966
8086-1806-VII

ABSTRACT

A literature study and several series of welding experiments were performed to determine the feasibility of using various elements, as getters and removers of hydrogen, to prevent or reduce hydrogen-induced porosity in the inert-gas arc welding of aluminum alloys. The experimental welds were made on specimens of 2014-T6 and 2219-T87 aluminum-alloy plate of 0.375-in. and 0.312-in. thickness respectively.

Arc spot-welding experiments were performed with four getter materials (Ti, Zr, Ce, and Ca) that were chosen as most promising from the results of the literature study on hydride-forming characteristics. Despite several methods of application of the getters, including mixes with various venicles as carriers, compaction in small drilled holes, compaction in shallow depressions, compression between halves of butt joints, and deposition and drying (at 400° F) on the surface in slurry form, the results were essentially negative. Similarly negative or worse results were obtained with a large number of additional elements and compounds.

It was concluded that hydrogen porosity in aluminum welds would not be prevented by the getter technique if conventional welding procedures are used. However, there was an indication that some of the getters did attract hydrogen and might have been effective had they not alloyed and carried the hydrogen into the weld nugget. Therefore, it was recommended that further welding studies be preceded by a study of the comparative hydrogen-attracting properties of molten aluminum and prospective getters of various form and content under heat conditions expected to exist in the arc and at the weld-nugget surface.

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INTRODUCTION

Purpose:

The purpose of this project was to investigate the feasibility of using scavenging elements for eliminating hydrogen porosity in welds made with high-strength aluminum alloys. A preliminary investigation of the literature on the hydride-forming properties of the elements indicated that some elements might have the capabilities of:

(1) attracting hydrogen from the atmosphere surrounding a welding arc and, possibly, from the molten weld puddle,

(2) retaining a higher affinity than aluminum for hydrogen at temperatures above the melting point of aluminum, and

(3) forming hydrogen compounds that would have insignificant effects on the strength, fatigue, and other desirable properties in welds.

Background:

One of the most troublesome problems encountered in welding aluminum alloys for aerospace applications is porosity that sometimes forms in or near the weld bead. It is generally agreed that the cause of such porosity is hydrogen, which is highly soluble in molten aluminum but relatively insoluble in solid aluminum. Therefore, as solidification of a weld bead progresses, any previously dissolved hydrogen tends to be discharged, and some of it becomes entrapped and produces porosity. The porosity, of course, contributes to unsoundness in the weld to a degree depending upon the severity of the porosity. Since the degree of porosity that would be acceptable has not been well defined, any detectable porosity is considered undesirable.

Sources of hydrogen in the welding process include the presence of air, water vapor, grease or oil, and hydrogen previously dissolved in the base metal or filler wire. Removal of these sources of contamination by careful attention to the purity and surface preparation of the materials and environments involved can greatly reduce the amount of porosity produced and makes it possible to produce porous-free welds on a laboratory scale. In production, however, porosity tends to be a problem even under closely controlled conditions and a vacuum environment. Therefore, it would be desirable to develop a welding technique wherein the hydrogen that sometimes eludes all efforts to exclude it could be captured and retained in a harmless form by some material that would have higher affinity than the aluminum base metal for hydrogen.

Approach to Problem:

It was surmised that information on hydride formation would furnish the most valuable indication of the potential hydrogen-getting ability of the elements. Although considerable information on hydrides exists in the literature, none was directly applicable to the pressure and temperature conditions that could be assumed to exist in an aluminum-welding arc. Therefore, it was assumed that the most reliable indicator of an element's promise as a getter would be the magnitude of its negative free energy of formation (ΔF) of its hydride.

The general isothermal equation for the free energy of formation (ΔF) of a compound is:

$\Delta F = \Delta H - T\Delta S$, where

ΔH = heat of formation,
T = absolute temperature, and
ΔS = entropy.

Because of a lack of entropy data for the hydrides, and because of uncertainties about the prevailing temperature in a welding arc, it was not possible to calculate free energies of formation. However, available information pertaining to other alloys indicated that differences in $T\Delta S$ would usually be small and, consequently, the free energies of formation would be mostly dependent upon the negative heats of formation. Therefore, elements with large negative heats of formation for their hydrides would be expected to be promising candidates as hydrogen getters in welding.

A preliminary consideration of possible elements revealed large negative heats of formation to exist for calcium ($\Delta H = -46.7$ Kcal/mole), lithium ($\Delta H = -21.3$ Kcal/mole), titanium ($\Delta H = -32.4$ Kcal/mole), and zirconium ($\Delta H = -46.7$ Kcal/mole). These findings were encouraging because they tended to correlate well with some of the known characteristics of these metals. The alkaline earths, calcium and lithium, are used extensively as purifying agents for many alloys because of their affinity for harmful elements such as oxygen, sulfur, and hydrogen. Titanium is known to attract hydrogen and can absorb as much as 1600 times its own volume of that element. Zirconium was not as well known in these respects, but was known to form stable hydrides at temperatures above the melting point of aluminum.

This project was initiated to determine whether these elements, or others substituted for them after further study, would, in fact, attract hydrogen and remove it from the vicinity of the weld or combine with it to form a harmless inclusion in the weld. The latter phenomenon would be analogous to the role of manganese in combining with harmful sulfur to form relatively harmless manganese-sulfide inclusions in steel.

Scope:

The project was divided into the following four phases:

Phase I: Literature and theoretical study to select the most promising elements to be used as getters.

Phase II: Preliminary evaluation of the selected elements by means of rapid melting operations simulating weld heating cycles.

Phase III: Evaluation of methods for applying the promising elements, using fusion spot welds made with TIG and MIG welding techniques.

Phase IV: Evaluation of the most promising elements and application methods on 36-in.-long welds.

Phase IV was not accomplished because the lack of positive results from Phase III indicated that none of the getters were effective enough to investigate further. Phase II was discontinued shortly after it was begun because the rapid heating methods were found to be destructive to the specimen as soon as melting began to occur. Therefore, this report consists of the procedure and results from Phases I and III, the procedure and difficulties encountered in Phase II, a discussion of the results, and conclusions and recommendations.

PHASE I: LITERATURE AND THEORETICAL STUDY

Procedure:

This phase consisted of a thorough search of the literature on hydrides in order to determine more accurately the relative getting ability of all the relatively stable elements in the periodic table. These elements were then compared on the basis of their hydride-forming ability and other known characteristics to determine which would be most likely to prevent hydrogen porosity in aluminum welds.

Results:

It was determined from the literature (1-4)[a] that hydrogen is chemically able to combine with almost every element in the periodic table to form binary compounds. For convenience, these compounds can be arbitrarily divided into three groups: the covalent hydrides, the saline hydrides, and the transition-metal hydrides.

The covalent hydrides are formed by the elements B, C, N, O, F, Si, P, S, Cl, Ge, As, Se, Br, Sn, Sb, Te, I, Pb, Bi, and Po. The elements Cu, Ag, Au, Zn, and Hg form an intermediate type of hydride that is neither pure ionic nor metallic bonded but tend to have the characteristics of the covalent hydrides. Therefore, they were included with the covalent hydrides for consideration in this study. In their natural state these hydrides are usually in either liquid or gaseous form. Since it was considered likely that liquid or gaseous hydrides would be detrimental if mixed into the weld puddle, these elements were eliminated from further consideration.

The saline hydrides are ionic in their bonding (1-4) and form stoichiometric compounds. The elements included in this classification are: Li, Na, Mg, Al, K, Ca, Rb, Sr, Cs, Ba, and Ra. It is probable that the rare earths would also be included in the saline-hydride group. The characteristics of the saline hydrides are such that these elements could not be eliminated as a group.

The transition-metal hydrides are formed by Ti, Zr, Hf, Th, V, Cb, Ta, Pa, Cr, Mo, W, U, Pu, Fe, Ru, Os, Rh, Ir, Ni, Pd, Co, and Pt. These hydrides exhibit metallic bonding and non-stoichiometric compositions (1-4), depending upon the exposure time to hydrogen, temperature of reaction, and past history of the element. It was not possible to eliminate these elements as a group either.

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[a] Numbers in parentheses refer to the References.

The purposes of the present study require a hydride-forming element that will combine with any gaseous hydrogen present in the weld zone in preference to the hydrogen combining with the aluminum. Although aluminum readily takes hydrogen into solution in the molten state, the possibility for the formation of a binary hydride of aluminum is virtually non-existent because no such hydride has been successfully isolated. To be effective in welding operations, the hydride-forming element should probably combine directly with elemental hydrogen. The usual laboratory procedure, wherein hydrides are produced by a complex series of reductions of organic radicals, would not be applicable in the welding operation. Therefore, it was possible to eliminate Al, Mg, and Ra from the saline group, and Th, V, Ta, Pa, Mo, W, Pu, Ru, Os, Co, Rh, and Ir of the transition-metals group, because they are not included in the group of elements that form hydrides by direct combination (1).

The remaining elements were Ti, Na, K, Ca, Rb, Sr, Cs, Ba, and the rare earths in the saline group and Ti, Zr, Hf, Cb, Cr, U, Fe, Ni, Pd, and the Pt metals in the transition-metals group. Other criteria were then necessary to further screen this group and choose elements with most promise for the intended purpose.

In the welding application the hydrides must coexist with molten aluminum and should not decompose at temperatures below the melting temperatures of the aluminum alloys. Thus, except for Ti, it was possible to eliminate from the saline group the alkali metals Na, K, Rb, and Cs (3, 4, 6). From the transition-metal group, Cb was eliminated because it does not form stable hydrides at temperatures below 1000° F. Uranium was eliminated because it would present a radiation problem.

The mechanism whereby Pd absorbs and rejects hydrogen is not well understood but, in some opinions, it does not involve the formation of a hydride, in which hydrogen would be present as the H^- ion. Rather, it is thought that a Pd-H solid solution is formed with H^+ ions, thereby allowing the hydrogen to slowly diffuse out of solution as gaseous hydrogen. Other elements, Fe, Ni, Cr, and the Pt-group metals react in a manner similar to Pd. They absorb small quantities of hydrogen by endothermic reactions but none from the exothermic reactions exhibited by the other elements remaining in consideration. Since hydrogen could be evolved from the Pd-type reactions, the elements exhibiting that characteristic, Pd, Pt, Fe, Ni, and Cr were eliminated from further consideration.

Among the seven remaining elements, Ca, Sr, Ba, Ti, Zr, and Hf and the rare earths, there was little clear choice from the hydride-forming standpoint. With the exception of Ti (-22 Kcal/mole), the heats of formation of the hydrides of these elements range from -28 to -45 Kcal/mole, and all would be expected to form hydrides with nearly the same degree of facility.

Thermodynamic data was available (6) for calculating the free energies of formation for the hydrides of Ti, Sr, Ba, and Ca in the saline group. These calculations did not provide information on the kinetics or rates of reaction but did show whether the hydride would form at given temperatures. The temperature (T) used in the calculations was 973° K (700° C) because of its proximity to the melting point of aluminum (660° C). In accordance with derived equations (6), the calculations were as follows:

1. $2\,\mathrm{Li} + \mathrm{H_2} \quad - \quad 2\mathrm{LiH}$
   $\Delta G_{973} = -33,870 + 27.82\ T = -6,801$ cal/mole $\mathrm{H_2}$

2. $\mathrm{Sr} + \mathrm{H_2} \quad - \quad \mathrm{SrH_2}$
   $\Delta G_{973} = -42,500 + 31.5\ T = -11,850$ cal/mole $\mathrm{H_2}$

3. $\mathrm{Ba} + \mathrm{H_2} \quad - \quad \mathrm{BaH_2}$
   $\Delta G_{973} = -40,900 + 31.3\ T = -10,445$ cal/mole $\mathrm{H_2}$

4. $\mathrm{Ca} + \mathrm{H_2} \quad - \quad \mathrm{CaH_2}$
   $\Delta G_{973} = -42,280 + 31.52T = -11,611$ cal/mole $\mathrm{H_2}$

The calculations showed that the hydride of Li would be least likely to form and remain stable because its negative free energy of formation is considerably lower than the others. The negative free energies of formation for Sr, Ba, and Ca are quite similar and no preference between these elements was indicated on this basis. However, from the standpoints of availability, cost, and relative handling ease, Ca appeared to be the logical choice.

The free energies of formation for the remaining transition-metal (Ti, Zr, Hf) and rare-earth hydrides could not be calculated because sufficient thermodynamic data was not available. It is doubtful that such data exists because the hydrides of these elements are non-stoichiometric and, therefore, do not have a fixed atomic ratio. Non-stoichiometry might be an advantage, however, simply because the hydrides could form and exist in a variety of compositional ranges and, therefore, be more able to attract hydrogen. Investigators (7) have reported high mobilities of the hydrogen atom in the non-stoichiometric hydrides, lending credence to the possibility of enhanced hydrogen scavenging by these elements. It has been reported (8) that zirconium hydrides will form readily in a magnesium alloy of Mg, Zn, Th, and Zr when the alloy is in the molten state in a wet atmosphere. Titanium hydride has apparently been found in titanium welds (9), showing that the formation of titanium hydride during welding is a reality—at least in pure titanium.

It was decided to select four of the promising elements for experimental investigation of their hydrogen-getting abilities, one from the saline group, two from the transition metals, and a rare earth. Calcium was chosen to represent the saline group because it was more readily available and presented less stringent handling requirements than Ba and Sr. Of the transition metals, Ti and Zr were chosen because of their availability and lower cost in comparison to Hf. Mischmetal, a mixture consisting of approximately 50% cerium and other rare-earth metals (principally lanthanum and neodymium), was chosen to represent the rare earths.

PHASE II: PRELIMINARY EVALUATION IN SIMULATED WELDS

Materials:

The experiments in this and later phases were performed with two aluminum-alloy base metals (the materials to be welded) consisting of 0.375-in.-thick 2014-T6 and 0.312-in.-thick 2219-T87 alloys. These were supplied by NASA in the form of 6-in.-wide x 36-in.-long slabs. All of the subsequent welding operations (Phase III) were of the TIG type performed with 1/8-in.-diameter by 7-in.-long 2%-thoriated tungsten electrodes. Bottled helium of -35° F dew point was employed for the uncontaminated protective gas.

The calcium getter material was obtained in the form of small shot graded between -4 and +80 mesh. It was reported by the supplier to be 99.9% minimum purity. Titanium was obtained in powder form of 94% minimum purity and 6 to 9 micron particle size. Zirconium was obtained in powder form of 94% minimum purity and 1.5 to 3.5 micron particle size. The titanium and zirconium powders were shipped and stored under moisture (20 wt/o for Ti and 30 wt/o for Zr) to prevent excessive oxidation. Mischmetal was obtained in the form of sawings of 97.5% purity and sized at -325 to +10 mesh. This material was shipped and stored under kerosene.

Procedure:

Attempts to simulate weld heating times were made by resistance heating modified tension specimens. The specimen stock consisted of 1-in.-wide by 4-in.-long pieces cut from the original stock. Gage lengths were machined to 1/4-in. widths and to three different lengths: 1/4 in., 1/2 in., and 1 in. Preliminary melting experiments were performed with each gage length and it was determined that the most rapid heating could be accomplished with 1-in. gage lengths.

The specimens were heated in a chamber consisting of a bell jar seated on a rubber gasket on a metal base plate. The base plate contained sealed connections to accommodate two electrical cables from a step-down transformer heating source controlled by a saturable reactor, one gas inlet for introduction of the desired atmosphere, and one exhaust outlet for purging and outgassing purposes. A fixture mounted on the metal plate held the specimen in a horizontal position and non-conducting ceramic supports (made of Transite) supported the gage length portion of the specimen on the bottom and two sides to preserve continuity when the specimens were melted.

It was intended to apply the getters to the top surface of the specimen, heat rapidly until the middle portion of the specimens was molten, and then allow it to solidify. These operations were to be performed with various levels of hydrogen contamination in the protective atmosphere within the bell jar. Specimens so treated, with and without getters, were then to be examined for porosity by metallographic or radiographic techniques to determine the relative effectiveness of the getters in preventing porosity.

Results:

Results pertaining to the effectiveness of the getters was not obtained because of problems encountered in the resistance heating of the specimens. As soon as melting at the center of the gage length was achieved, electrical forces expelled the liquid metal and caused the establishment of an instantaneous arc that spattered further metal and destroyed the electrical continuity of the specimen. Attempts were made to overcome the problem by reducing the current supply to the specimen (with a consequent slower heating rate), but the same reaction occurred even at heating rates requiring several minutes to achieve melting. Since such slow heating rates would not simulate practical welding times even if further reductions were successful in overcoming the problem, it was concluded that resistance heating of these specimens was impractical. Therefore, it was decided to incorporate Phase II with Phase III and make the preliminary evaluation of the getters in fusion spot welds.

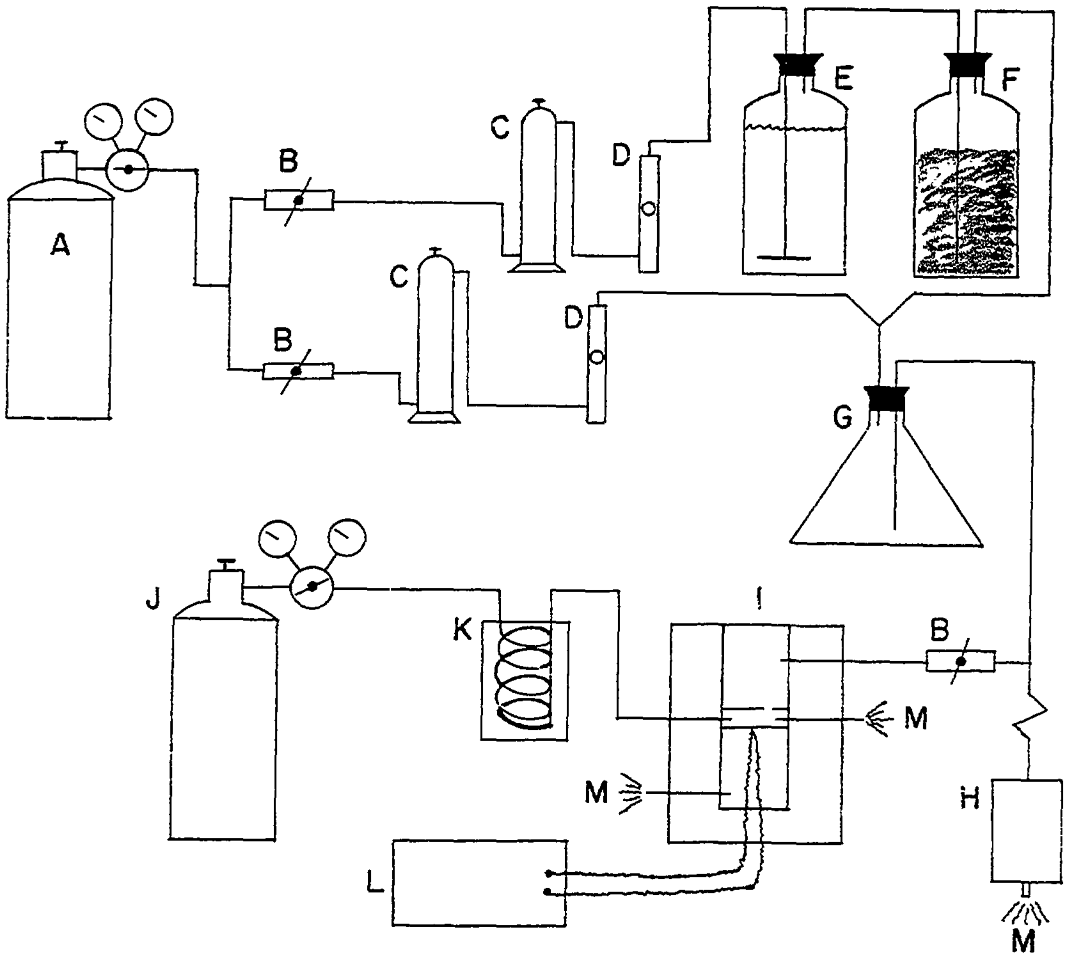
PHASE III: EVALUATION IN FUSION SPOT WELDS

Procedure:

The fusion spot welds were made by the TIG process with helium. The conditioning train for the helium gas is shown in Figure 1. The bottled helium gas (A) with a -35° F dew point was divided into two parallel lines controlled by means of needle valves (B). From the needle valves the gas passed through drying towers packed with Drierite crystals (C) and through tube-type flow meters (D) by means of which the proportioning of the wet and dry gases was controlled. The helium in the wet-gas train was then passed through a water tower (E) for moisturizing and then through a spray trap packed with glass wool (F) to remove any entrained drops of moisture. After passage through these trains, the wet and dry helium gases were rejoined in a mixing chamber (G). From the mixing chamber the helium could be passed either to the welding head (H) or to an apparatus for measuring dew points. When dry gas was desired, the wet-gas train and mixing chamber were bypassed by closing off the wet-gas needle valve and by replacing the Y connector from the mixing chamber with a straight connector from the dry-gas flowmeter.

During welding operations, the needle valve to the dew-point apparatus remained closed. When dew-point determinations were desired, the needle valve was opened. No valve was needed in the line to the welding head because a solenoid valve automatically closed that line when the welding machine was switched off. For the dew-point determinations the helium gas was allowed to flow through a foam-plastic chamber (I) and exhaust to the atmosphere. In passing through the chamber the welding gas surrounded a mirror-polished stainless-steel tube that passed through the chamber. The interior of the tube was connected to a line from a bottle of nitrogen (J). The nitrogen gas, after passing through a cooling chamber (K) packed with dry ice, was used to cool the stainless-steel tube to the temperatures at which moisture would condense from the surrounding helium and produce a fog on the outer polished surface of the tube. The temperature of the tube was monitored by means of a thermocouple flash welded to the tube surface and connected to a potentiometer (L). The dew points were considered to be the temperatures above which no fog would form and below which fog would form. The temperature of the polished tube could be varied by controlling the rate of nitrogen-gas flow throu[illegible] the regulator valve mounted on the nitrogen bottle.

The welds were made with the equipment shown in Figure 2, except that the traveling carriage shown in the photograph was not used for these experiments. The equipment consisted of an Airco Model C Heliweld automatic welding head with its controls and a 400-ampere DC Lincoln motor-generator power source (not shown).



A. Helium Bottle.
B. Needle Valves.
C. Drying Towers.
D. Flow Meters.
E. Saturator Tower.
F. Spray Trap.
G. Mixing Chamber.
H. Welding Head.
I. Dew-Point Chamber.
J. Nitrogen Bottle.
K. Cooling Chamber.
L. Potentiometer.
M. Gas Outlets.

Figure 1. Schematic Illustration of Gas-Preparation Train.

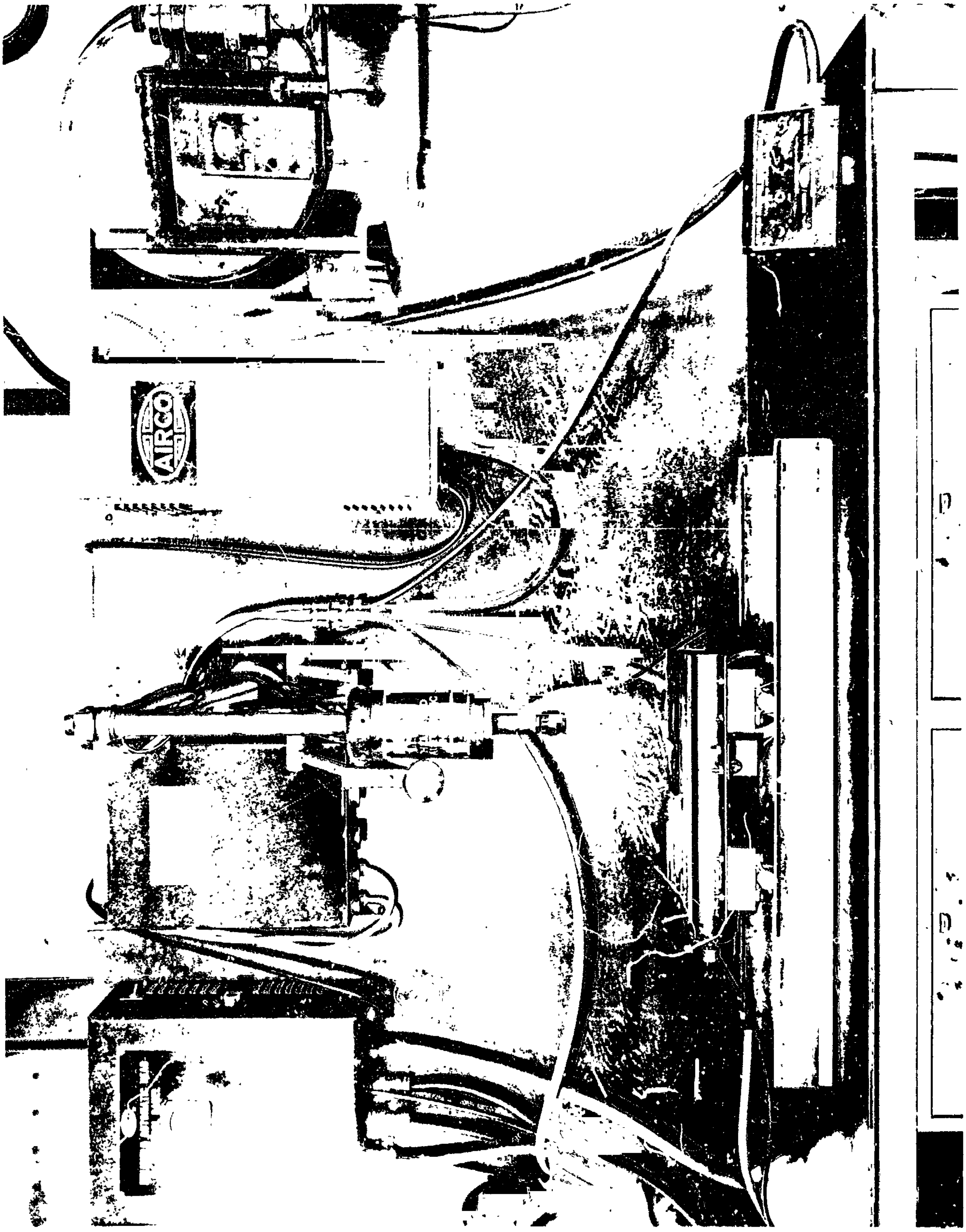


Figure 2. Automatic TIG welding machine

The type of specimen used in most of the experiments and the clamping arrangement are shown schematically in Figure 3. The specimen consisted of 1/2-in. by 3-in. rectangles of the two aluminum alloys. The fusion spot-weld nuggets were made at the point of intersection of the two centerlines shown. When temperature measurements were made, two chromel-alumel thermocouples of 5-mil-diameter wire were flash welded to the bottom side of the specimen on the longitudinal centerline at points 1/4-in. on each side of the transverse centerline. The signal from these two thermocouples was recorded simultaneously on the chart of a 2-pen potentiometric recorder. For welding, the specimen was clamped in a table vise that was separated from the steel bench top with insulating bricks. The ground lead from the welding machine was clamped to a ledge of the vise and the ground lead from the welding head was clamped to one corner of the specimen.

The procedures used in connection with the getters varied depending upon the several methods tried for applying the getters. For convenience, each series of welds made with different application methods have been identified as the vehicle series, the small-hole series, the depression series, the butt-joint series, the first slurry series, and the second slurry series. With the exception of calcium, the getters were received in forms that necessitated drying procedures prior to application of the powders. Cerium (Mischmetal), which was received under kerosene, was given repeated rinses in hexane and allowed to dry following the final rinse. The titanium and zirconium powders were received in a moisturized condition to protect them from oxidation. This moisture was removed by keeping the powders in a continuously evacuated dessicator for a period of 24 hours. The dried powders were stored in dessicators under argon atmosphere. A subsequent analysis of these dried powders showed them to contain 0.02% (200 ppm) moisture in the titanium and 0.03% (300 ppm) moisture in the zirconium.

The vehicle series of welds was made to determine whether some materials that might be used to bond the getter material to the workpiece surface would, in themselves, provide a source of moisture or hydrogen and contribute to porosity. The vehicles examined were epoxy resin, Duco cement, lime paste, and ethyl alcohol. These vehicles, alone and in combination with Ti powder, were applied to the freshly scraped surfaces of a series of specimens and fusion spot welded. The welding conditions used for each specimen are listed in the tabulated results. In general, all specimens were welded at 150 or 200 amperes, 14 volts, and 53 CFH gas flow. Welding times varied depending upon the time necessary to achieve deep penetration into the workpiece. The helium gas in the dry condition (no moisture added) had a dew point of -35° F and consistently produced pore-free spot welds. On the basis of preliminary experiments to produce welds with easily detectable porosity, the moisturized gas was standardized at a +50° F dew point. When the specimens had been welded, they were

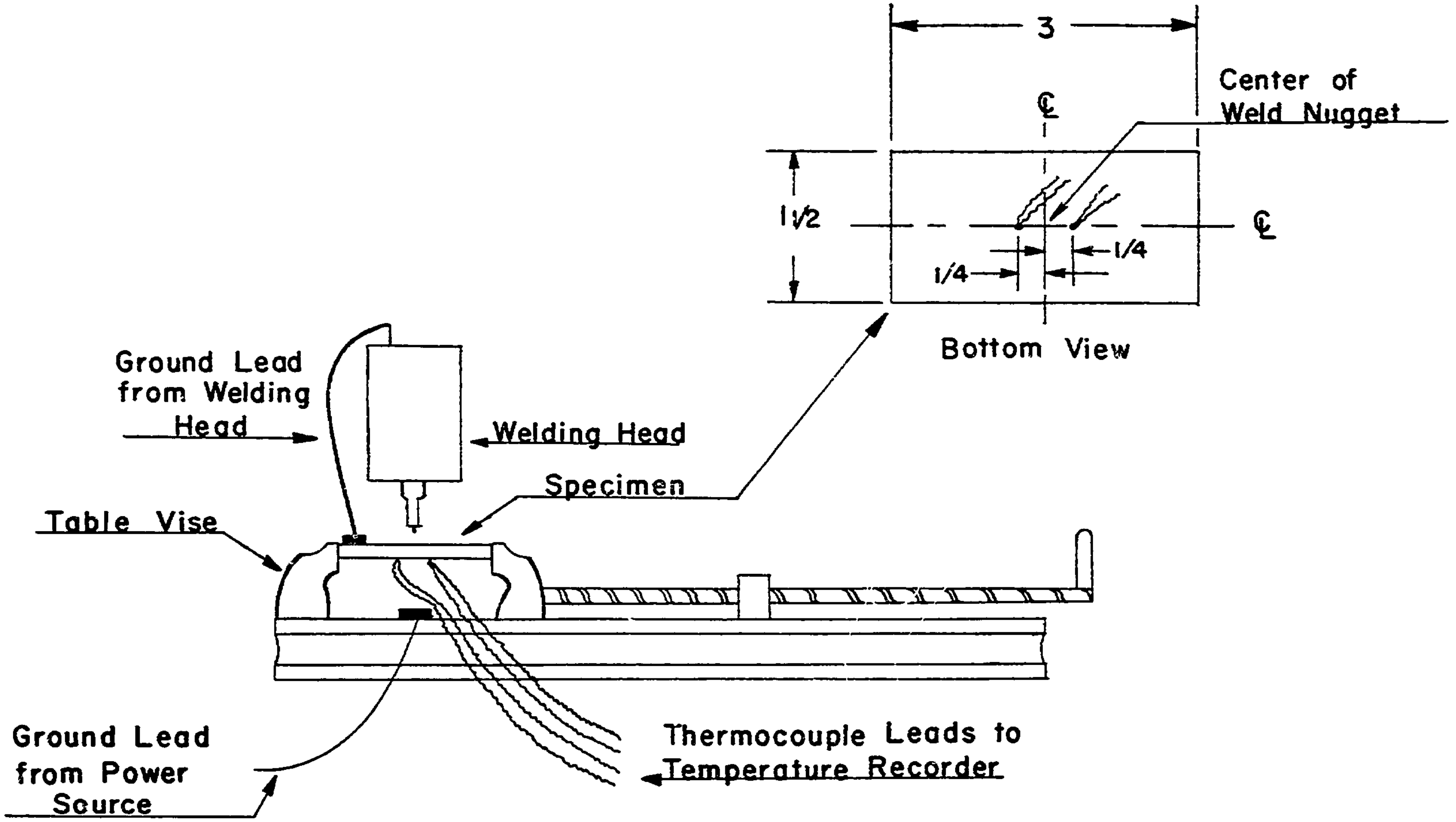


Figure 3. Schematic Illustration of Specimen Clamped for Welding. Nominal dimensions shown in inches.

sectioned through the center of the nugget, wet-ground with silicon-carbide papers through 500 grit fineness, and visually examined for porosity. Since the visual results were negative, it was decided that the vehicle series would not be subjected to quantitative examination.

The small-hole series was made in an effort to apply the getters without vehicles and to assure that the getter material would be incorporated in the molten puddle during welding. In this procedure, eight 0.073-in.-diameter holes were drilled to a depth approximately 3/4 of the thickness of the plate at approximately equally spaced locations on the circumference of a 1/2-in.-diameter circle surrounding the center of the location of the subsequent spot weld. Prior to the welding operation, the specimens were scraped and the getter materials packed into the small holes. The welding and inspection procedures were the same as those used for the vehicle series. These results were also negative and no quantitative measurements of porosity were made.

The depression series was made in an effort to avoid the use of vehicles and yet apply the getter without installing it into the deep interior of the specimens. Accordingly, the getters were packed into a shallow depression made with a 1/4-in.-diameter drill to approximately a 1/8-in. depth, or the approximate depth of the chamfer on the end of the drill bit. This depression was located at the center of the subsequent weld location. The same welding and inspection procedures used for the two previous series were used on these welds. Although these results were also negative, four of the specimens, one representing each of the four getters, were subjected to microprobe analysis to determine whether the getters were incorporated into the weld puddle, and whether there would be any correlation between the locations of the pores and the locations of concentrations of the getters. These specimens were metallographically polished and etched for the microprobe surveys but no quantitative measurements of porosity were made.

The butt-joint series was made before the microprobe survey was completed and represents further efforts to incorporate the getters in a practical manner. For this series, the specimens were cut in half along the transverse centerline and then rejoined with a fusion spot weld. The getters were placed on the end faces to be butted together and were held in place by clamping the two pieces tightly together in the vise. An additional getter, barium, was included in this series to determine whether it might react more favorably than calcium. The welding procedures were the same as those used previously except that temperature readings were taken at the locations shown in Figure 3. The resulting welds were visually examined and, since the results continued to be negative, no quantitative measurements were made.

The first slurry series was planned in an attempt to overcome the problems that had prevented the attainment of uniform welding conditions in the previous experiments. As a first criterion, it was decided that the getter should be applied only to the scraped surface and not packed in prepared holes or depressions. Since no suitable vehicle had been found to bond the getters, and since dry getters would not adhere sufficiently, the powdered getters were moistened with distilled water to form a slurry, which was then applied to the specimen surface with a small brush. The specimens were then placed on a 250° F hot plate and heated until all visible traces of moisture were gone. The dried getter-coated specimens were stored in a dessicator while awaiting the welding operation. On the day of the welding run, these specimens were placed in an oven at 400° F and allowed to remain heated for at least one hour before the first specimen was removed for welding. Therefore, the dryness of the getters was assumed with a high degree of confidence. Indeed, no analysis for moisture content was made on these getters because all of the analysis methods available within the equipment, time, and cost scope of the project would be less effective than the 400° F treatment in removing hydrogen for analysis.

Of the four originally chosen getters (Ti, Zr, Ce, and Ca), all were tried in the first slurry series except Ca, which reacts with water to form $Ca(OH)_2$ (calcium hydroxide). Therefore, CaO (lime) was substituted for Ca because it also forms $Ca(OH)_2$ with water but is less violent in its reaction. Because of the possibility that some of the candidate getters were eliminated during the literature study on the basis of assumptions that might be invalid, the study was reviewed and some additional getters were included. The additional getters chosen were S (sulphur), Na (sodium), and B (boron). The elemental form was used for S but the Na and B were applied in the form of the compounds $Na_2B_4O_7$ (anhydrous sodium borate, or borax) and $NaNO_3$ (sodium nitrate). The specimens in this series were all welded under identical conditions consisting of 150 amperes, 14 volts, 7 seconds welding time, and 53 CFH gas flow with at least 1-min. purging prior to welding. Since some getters had interfered with the striking and holding of the arc in the previous experiments, a small area approximately 1/8-in. square was scraped at the arc-striking location immediately prior to welding. The scraping of this small area made it possible to start the arc on bare aluminum and thereby standardize the welding conditions regardless of the getter material. By the time the thermocouples were welded to the specimens and the specimens were installed in the vise and scraped, the temperature of the specimen had cooled from 400° F to approximately room temperature, so all welds were started at that temperature.

Although the welds from the first slurry series were porous (indicating the continuation of negative results), quantitative readings of porosity were taken because it was thought that trends might be indicated when not obscured by the necessity (in previous runs) to change welding conditions. For porosity readings the welds were sectioned through the nugget and metallographically polished. A Filar eyepiece at 1.3X magnification was used to take the measurements. On each specimen, one horizontal traverse across the weld nugget was taken at a position 1/3 of the specimen thickness (measured from the upper, or face, side of the specimen) and one vertical traverse was taken at the center of the weld nugget. The porosity was calculated by the formula:

$$\% \text{ porosity} = \frac{HV - (H-h)(V-v)}{HV} \times 100, \text{ where}$$

H = the total distance of the horizontal traverse,
h = the sum of pore diameters intersected by the horizontal traverse,
V = the total distance of the vertical traverse, and
v = the sum of pore diameters intersected by the vertical traverse.

A second slurry series was made because the quantitative results from the first slurry series indicated a slight reduction in porosity resulting from the use of Ti, Zr, and Ce. Also, a large number of additional prospective getters were included in order to provide representation for all of the different categories of hydride-forming elements discussed in the literature study (Phase I). Since the second slurry series was performed at the end of the allotted time schedule for the project, the choice of additional getter materials was largely dictated by the elements and compounds already on hand at Southern Research Institute. These additional materials are listed in the tabulated results for the second slurry series (Tables VI and VII).

The second slurry series was performed by the same procedure used in the first slurry series except for some minor changes designed to improve the uniformity of the getter coatings and to increase the exposure surface of the getters. Therefore, the following additions were made to the procedure:

1. An approximately 1-in. length at each electrode tip was coated with the same coating used on the corresponding specimens.

2. Identical measured amounts (3cc) of each getter were used for making the slurries.

3. All getters that were not already in fine-powder form, or that would not react with water to form a powder, were ground with a mortar and pestle prior to making the slurry.

4. The amount of distilled water used to make a suitable slurry (by appearance) was measured and recorded.

The welding procedure for each of the series from the time the specimens were installed in the table vise consisted of the following steps:

1. The tungsten electrode was installed in the welding head and allowed to protrude approximately 1/16-in. below the outlet for the protective gas.

2. The welding head was lowered and the position of the table vise adjusted to center the weld at the proper location.

3. The welding head was raised to approximately 3 in. above the specimen.

4. The helium gas flow was started and adjusted to provide 53 CFH. For dry gas (-35° F dew point) the dry flow meter was set to a scale reading of 42. For moist gas (+50° F dew point) the scale readings were 11.5 on the wet flow meter and 30 on the dry flow meter.

5. The motor-generator power source and the chart drive of the temperature recorder were switched on. The M-G set and welding machine had been preset to provide 150 amperes and 14 volts for most welds.

6. The welding machine was switched on, which automatically lowered the welding head, struck the arc, and adjusted the arc length to provide 14 volts.

7. A stop-watch was started at the moment the arc was struck and the welding machine was switched off after the predetermined welding time (7 seconds for most welds).

8. The welding head was raised to its top position and all units were turned off in preparation for setting up the next specimen.

Results:

Vehicle Series - The results from the vehicle series, made to determine the feasibility of using various vehicles as carriers and bonding agents for the getter materials, are shown in Table I. These specimens were examined visually after wet grinding cross sections of the welds through 600 grit silicon-carbide papers. The porosity produced by a +50° F dew point, when used to weld the aluminum alloys without getters or vehicles, was rated as "par." Smaller degrees of porosity were designated as "slight," and greater degrees as "excess."

Table I. Results from Vehicle Series

Spec. No.	Welding Current,[1] Amperes	Welding Time, Seconds	Gas Dew-Point[2] ° F	Getters and/or Vehicles	Porosity Level[3]
			2014 Alloy		
1	150	7	+30	None	Slight
2	200	5	+30	None	Slight
3	200	5	+40	None	Slight
4	200	4	+50	None	Par
5	200	4	+50	Ti + Duco Cement (5-min.dry)	Par
6	200	4	+50	Ti + Duco Cement (overnight dry)	Par
7	200	5	+50	None	Par
8	200	5	+50	Lime paste	Par
9	200	5	+50	Ti + Ethyl alcohol	Par
10	200	5	+50	Duco cement only	Par
11	200	5	+50	Epoxy cement only[4]	Excess
12	200	5	+50	0.5g Ti + ethyl alcohol	Par
13	200	5	+50	1.0g Ti + ethyl alcohol	Par
14	200	5	+50	1.5g Ti + ethyl alcohol	Par
15	200	5	+50	2.0g Ti + ethyl alcohol	Par
			2219 Alloy		
100	200	1	+50	None	Par
101	200	1	+50	0.5g Ti + ethyl alcohol	Par
102	150	6	+50	1.0g Ti + ethyl alcohol	Par
103	150	6	+50	1.5g Ti + ethyl alcohol	Par
104	150	6	+50	2.0g Ti + ethyl alcohol	Par

---

[1] Arc voltage was 14 volts for all welds.
[2] Gas flow was 53 CFH for all welds.
[3] Porosity caused by +50° F dew point on bare aluminum is rated as par.
[4] Epoxy cement used was Epon 828.

The first specimens, Nos. 1 through 4, were used to establish conditions for a desirable porosity level to use as a visual comparison standard with other specimens. As shown in the table, it was necessary to raise the dew point of the helium to +50° F (specimen 4) to produce par porosity. Porosities of this level are illustrated by specimen No. 134 in Figure 18 and specimen No. 143 in Figure 19.

When the conditions for par porosity had been established for the 2014 Alloy, two specimens (Nos. 5 and 6) were welded under the same conditions using Duco cement to bond a Ti-powder coating over the surface to be welded. One specimen (No. 5) was dried for 5 min. before welding and the other (No. 6) overnight, but both produced par porosity and the results were inconclusive.

For the remainder of the 2014 alloy specimens, the welding time was increased to 5 sec to provide deeper penetration. The vehicles alone and four concentrations of Ti with ethyl alcohol were tried. All of the specimens except the one coated with epoxy (No. 11) produced par porosity and the epoxy produced increased porosity. The four concentrations of Ti powder with ethyl alcohol were also tried on the 2219 alloy with par results. Therefore, except for indicating that the epoxy would be a poor carrier or bonding vehicle, the results were inconclusive. The next series was welded without vehicles to determine whether the getter elements could be applied alone and show some effect on the porosity.

Small-hole Series - In this series of welds the getters were applied by packing them in small drilled holes surrounding the center of the eventual nugget. The tabulated results from this run are shown in Table II. All of the welds made with getters were porous even though made with dry gas. Since four of the specimens (19, 21, 109, and 111) retained unfused portions of the original drilled holes, it is likely that much of the porosity was caused by entrapped air from the holes. Longer welding times to produce complete fusion were tried with some specimens (22, 23, and 110) but this only reduced the severity of porosity and did not eliminate it. Since porosity could not be eliminated when the small-hole method was used with dry gas, no moist-gas welds were made by this method.

Depression Series - Table III is a summary of the results from the specimens on which the getters were packed within a depression made by drilling to 1/8-in. depth with a 1/4-in.-diameter twist drill. Welds in this series were made with dry gas first (Nos. 24, 25, 26, 27, 113, 114, 115, and 116), with inconclusive results. Two of the welds (Nos. 24, 26) contained porosity but the others were essentially pore free. The welds made with moist gas were all porous. However, the results could not be considered conclusive because the arcs struck directly on the getters were erratic, and there was some doubt about whether the getters remained in position long enough to be effective.

Table II. Results from Small-Hole Series

Spec. No.	Welding Current,[1] Amperes	Welding Time, Seconds	Getters	Results
			2014 Alloy	
16	150	9	None	Low penetration - Nil porosity
17	200	5	None	Nil porosity
18	200	6	None	Nil porosity
19	200	6	Titanium	Very porous - Holes not all fused
20	200	6	None	Nil porosity
21	200	6	Zirconium	Very porous - Holes not all fused
22	200	8	Cerium	Porous - Complete fusion
23	200	7	Calcium	Porous - Complete fusion
			2219 Alloy	
105	150	6	None	Low penetration - Nil porosity
106	150	8	None	Excessive penetration - Porosity not observed
107	150	7	None	Nil porosity
108	150	7	None	Nil porosity
109	150	7	Zirconium	Very porous - Holes not all fused
110	150	11	Cerium	Porous - Complete fusion
111	150	9	Calcium	Porous - Holes not all fused
112	150	9	Titanium	Very porous

---

[1] All welds: 14 volts, -35° F Dew-point helium, and 53 CFH gas flow.

Table III. Results from Depression Series

Spec. No.	Welding Current,[1] Amperes	Welding Time, Seconds	Gas Dew-Point[2] ° F	Getters	Results
			2014 Alloy		
24	200	7	-35	Titanium	Porous
25	200	8	-35	Zirconium	Nil porosity
26	200	7	-35	Calcium	Poor fusion - Porous
27	200	7	-35	Cerium	Nil porosity
28	200	7	+50	Titanium	Porous
29	200	6	+50	Zirconium	Porous
30	200	6	+50	Cerium	Porous
31	200	8	+50	Calcium	Porous
			2219 Alloy		
113	150	9	-35	Titanium	Nil porosity
114	150	9	-35	Zirconium	Nil porosity
115	150	9	-35	Cerium	Nil porosity
116	150	8	-35	Calcium	3 pores at top only
117	150	8	+50	Titanium	Very porous
118	150	8	+50	Zirconium	Porous
119	150	8	+50	Cerium	Porous
120	150	9	+50	Calcium	Porous

---

[1] Arc voltage was 14 volts for all welds.

[2] Gas flow was 53 CFH for all welds.

The four specimens of 2219 alloy welded with moist gas (Nos. 117, 118, 119, and 120) were metallographically polished and subjected to microprobe analysis to determine whether any of the getter materials were distributed in the weld nuggets. Low-magnification (2X) views of the polished and etched specimens are shown in Figure 4.

The weld made with Ti (Figure 4a) was very porous and contained bright inclusions that appear dark in the photograph. The larger inclusions appear near the bottom of the nugget and two small inclusions at the top surface. These inclusions and other parts of the structure were examined by microprobe. An area containing a portion of the large inclusion near the bottom of the nugget is shown in Figure 5. The inclusion, shown by light-optics display in (a), is also discernible in the specimen-current display (b), and is identified to have a large concentration of Ti in the Ti-X-ray-rate-meter display (c).

Another area, surrounded by large pores and containing a needle-like constituent, is shown in Figure 6. Although the Ti concentration gradients are less definite in this view, it is indicated that small concentrations of Ti and, possibly, a general Ti dispersion existed in the nugget. The needle-like constituent appeared to be associated with Ti content, but did not (in these views) appear to contain higher levels of Ti than the background material. Instead, the Ti concentrations correlated more closely with dark-appearing constituents barely discernible in view (a) and only vaguely indicated in view (b). The concentrations of Ti did not exhibit any detectable relationship to the pores in this area.

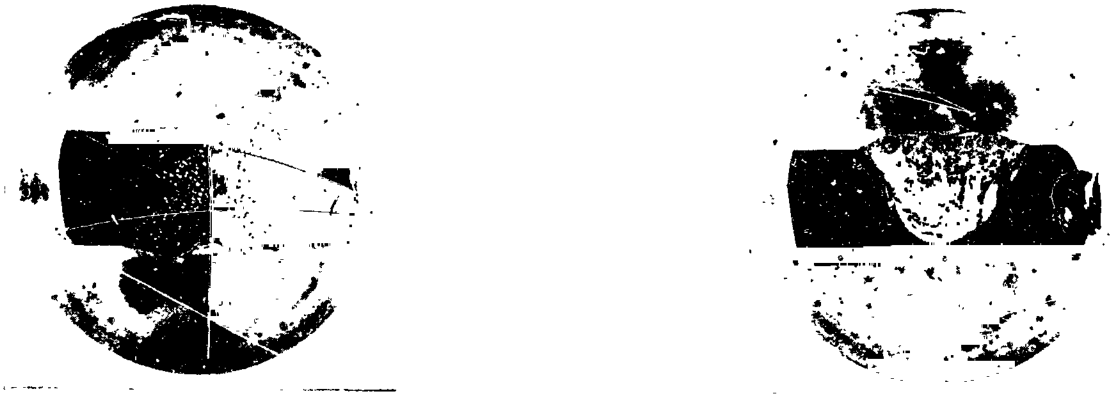
Figure 7 shows a view in which the needle-like constituent is distributed in localized areas rather than generally dispersed through the area as in Figure 6. In this area there is a rather clear correlation between the Ti concentrations and the more prominent needles, both in the specimen-current display (view b) and the light-optics display (view a). There is a slight indication of Ti concentration along portions of the pore boundary, but this concentration also appears to be associated with needle constituents, some of which appear in the specimen-current display.

The correlation between the needle constituent and Ti concentrations are also shown in Figure 8, which is a survey of an area in the transition zone between the weld nugget and the heat-affected zone. The needle constituents and Ti concentrations appear in the bottom portion of the photographs.

Figure 9 shows the survey of an area located at one of the large inclusions at the top of the nugget. View (a) shows a light-optics display of the nugget in the upper and left portion of the photograph, an apparent diffusion zone between the nugget and the inclusion, the massive inclusion, and the mounting material in the lower right portions of the photograph. These

(a). 117
Ti.

(b). 118
Zr.

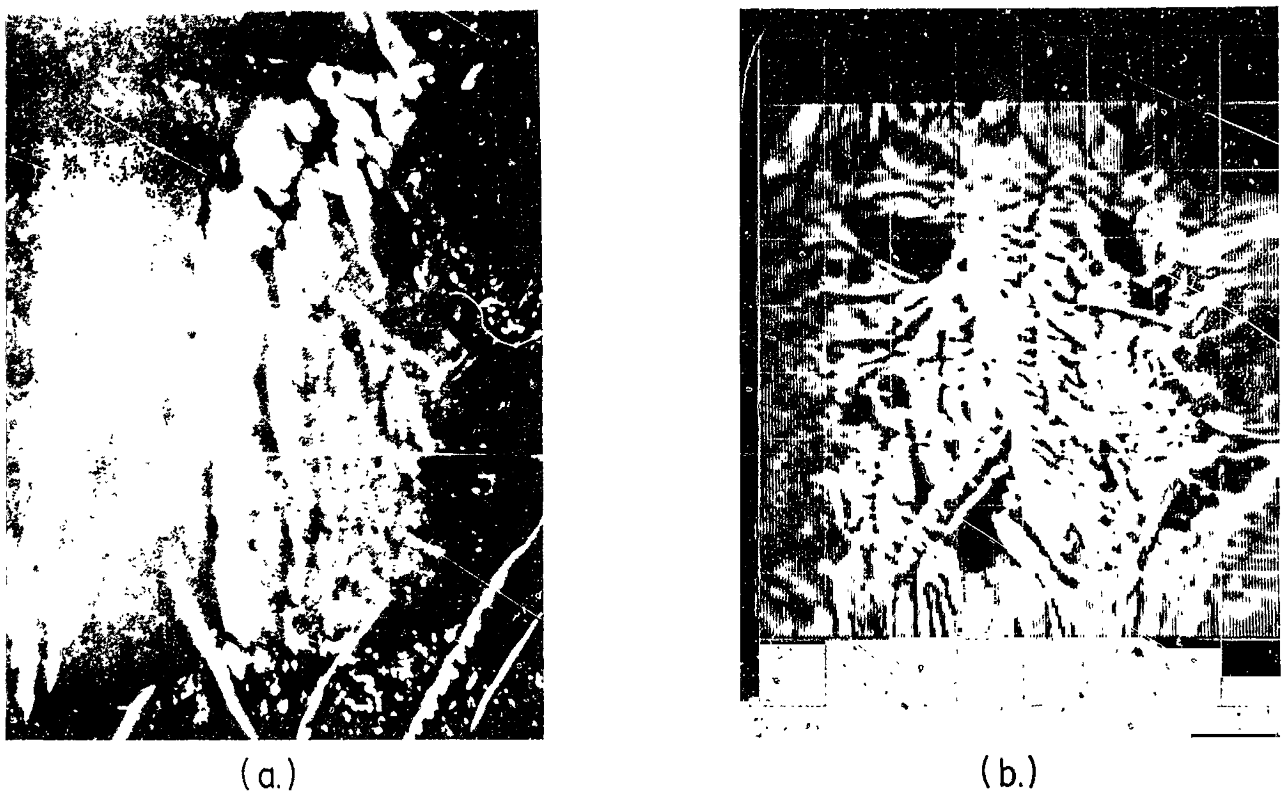


(c). 119
Ce.

(d). 120
Ca.

Figure 4. Welds from depression series.

Specimen numbers and getters employed are shown. Pores appear as either black or white spots within the weld nugget. Etched with 10% NaOH. Magnification: 2X



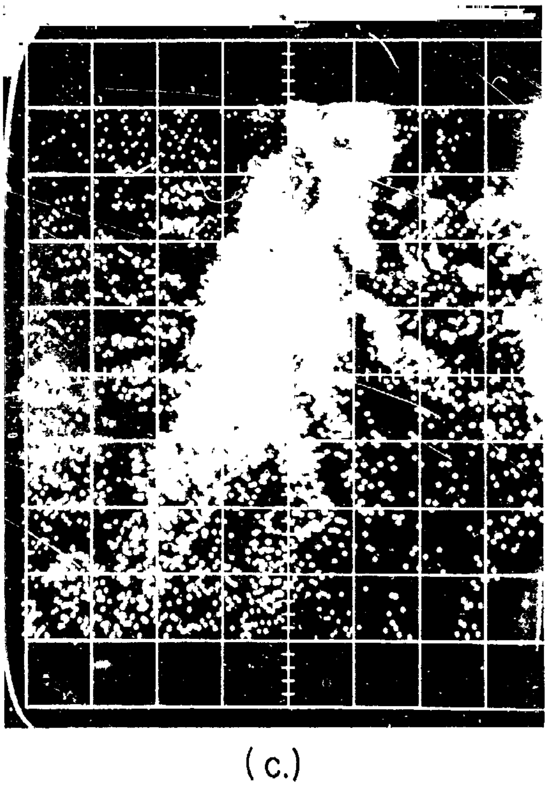
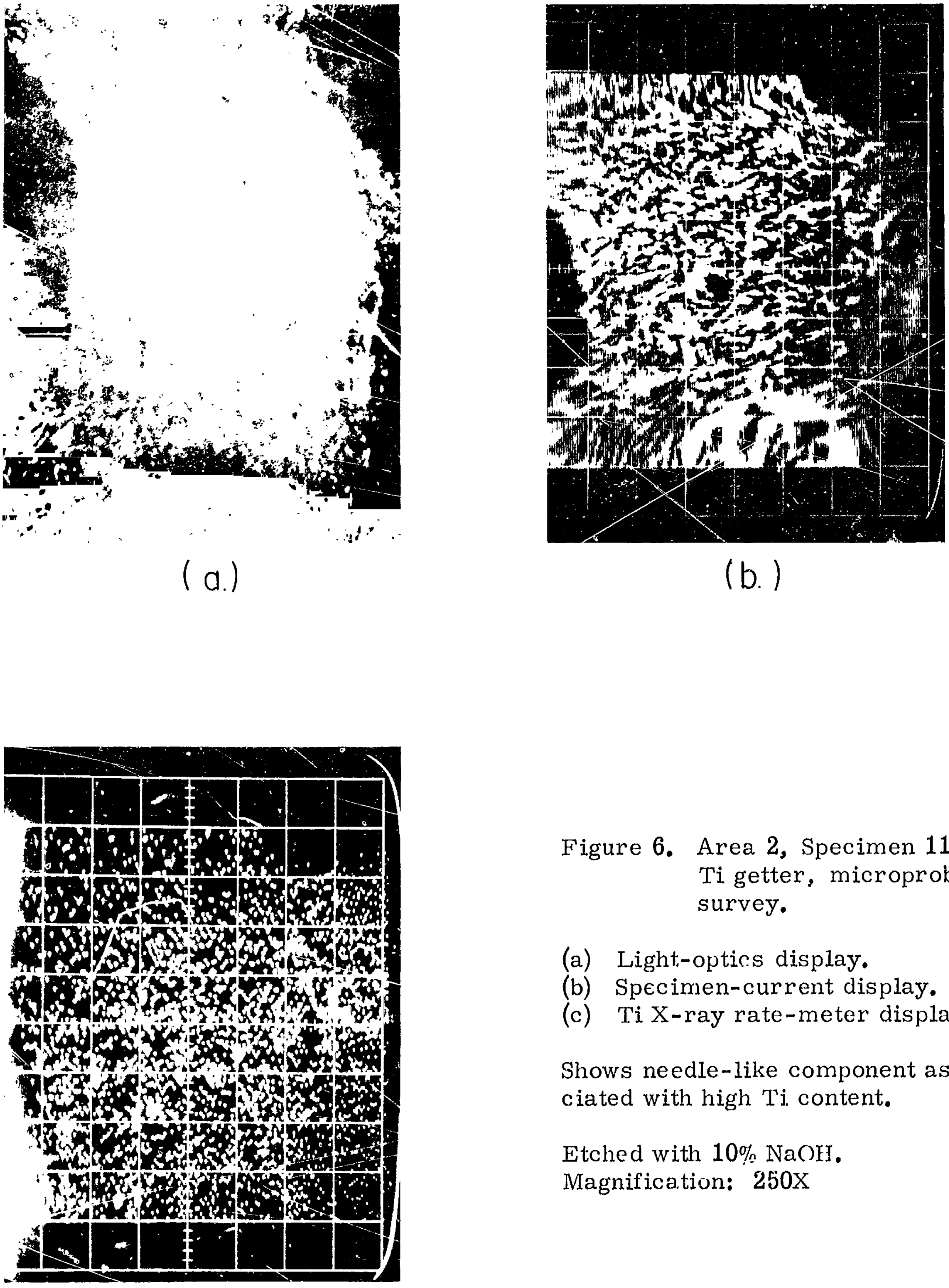


Figure 5. Area 1, Specimen 117,
Ti getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ti X-ray rate-meter display.

Shows portion of massive Ti inclusion near bottom of nugget.

Etched with 10% NaOH.
Magnification: 250X



(a.)

(b.)

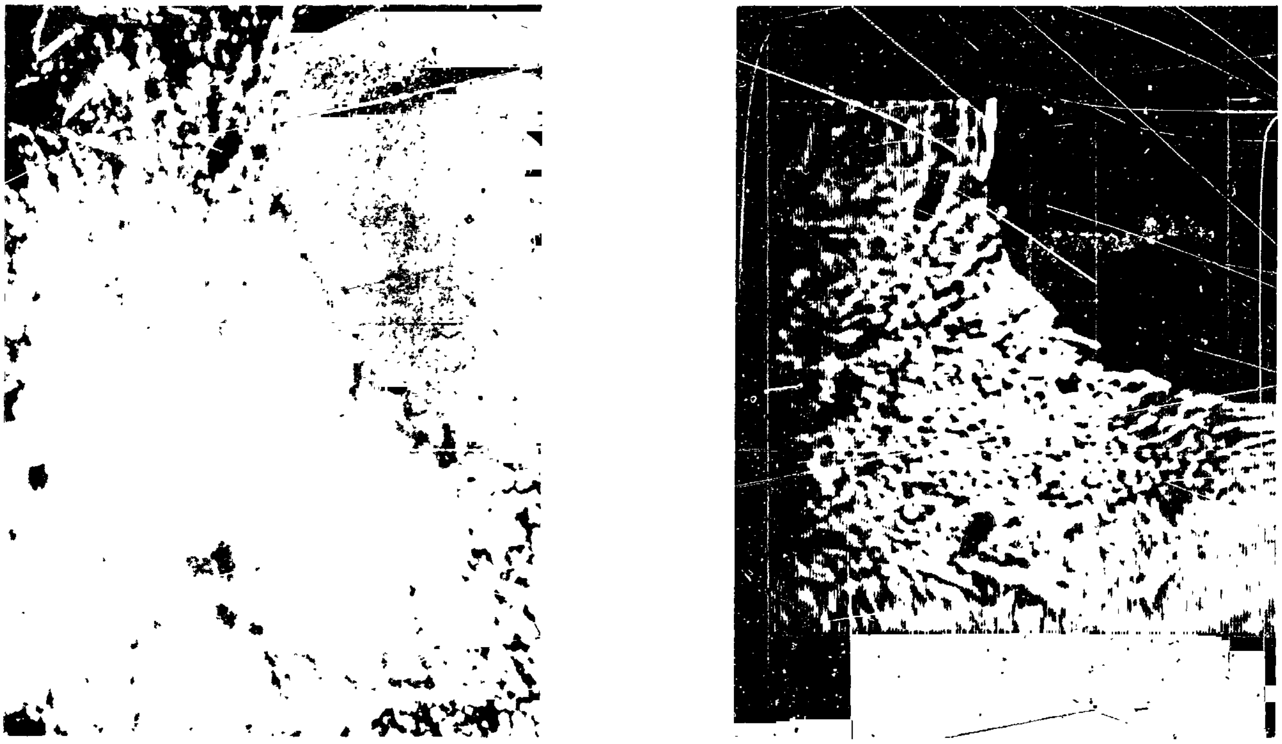
(c.)

Figure 6. Area 2, Specimen 117, Ti getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ti X-ray rate-meter display.

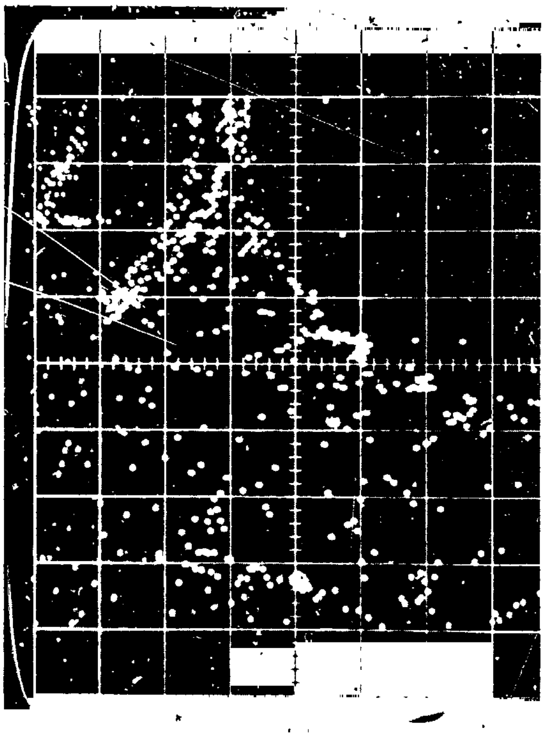
Shows needle-like component associated with high Ti content.

Etched with 10% NaOH.
Magnification: 250X



(a.)

(b.)



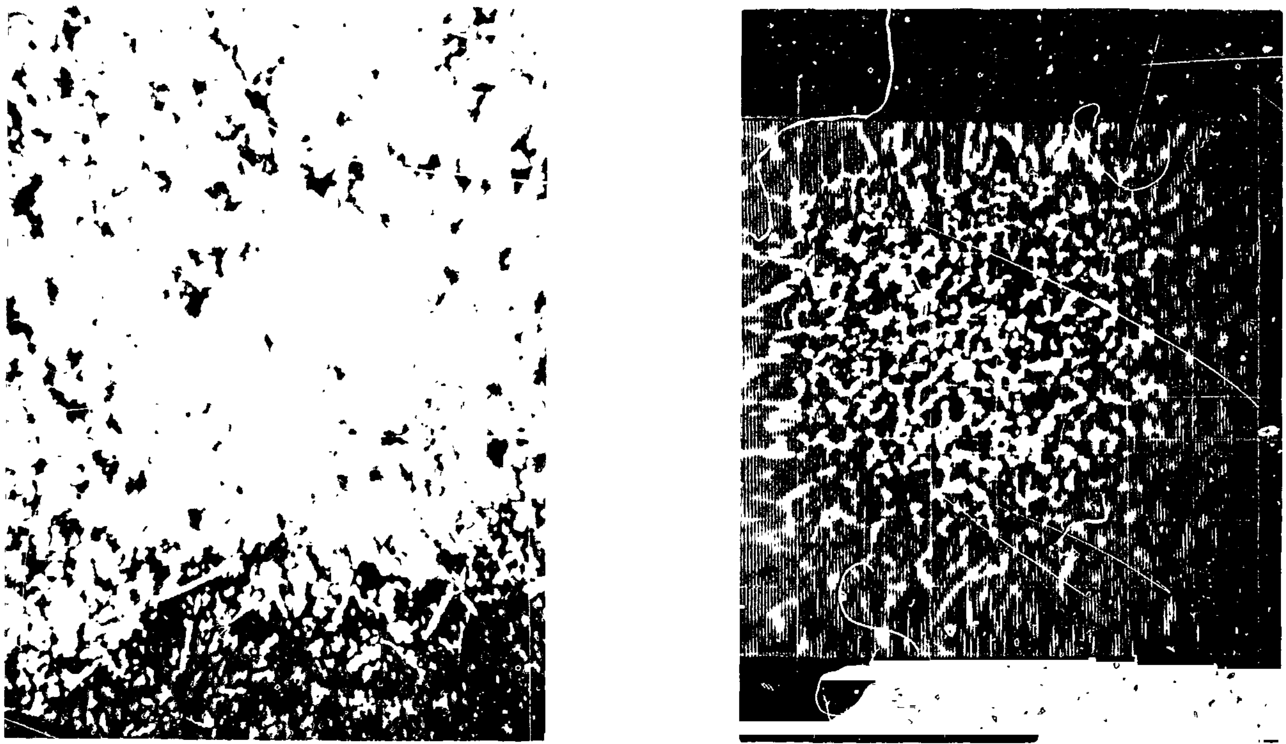
(c.)

Figure 7. Area 3, Specimen 117, Ti getter, microprobe survey.

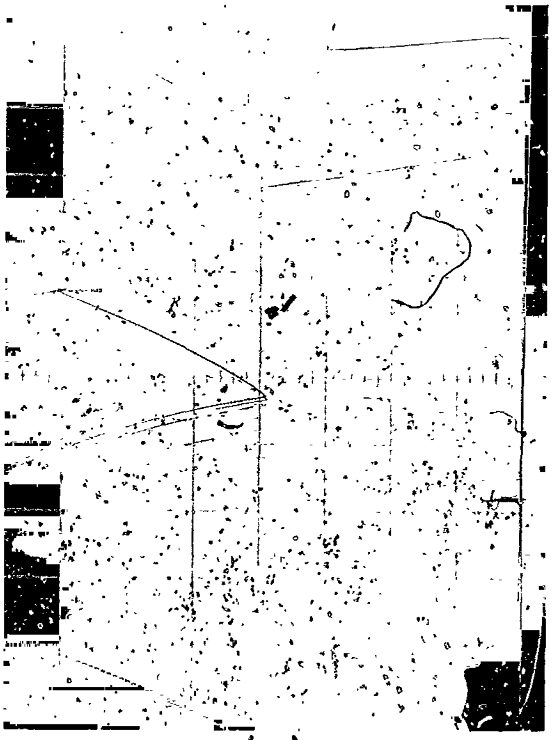
(a) Light-optics display.
(b) Specimen-current display.
(c) Ti X-ray rate-meter display.

Shows Ti content associated with needle-like constituent.

Etched with 10% NaOH.
Magnification: 250X



(a.) (b.)



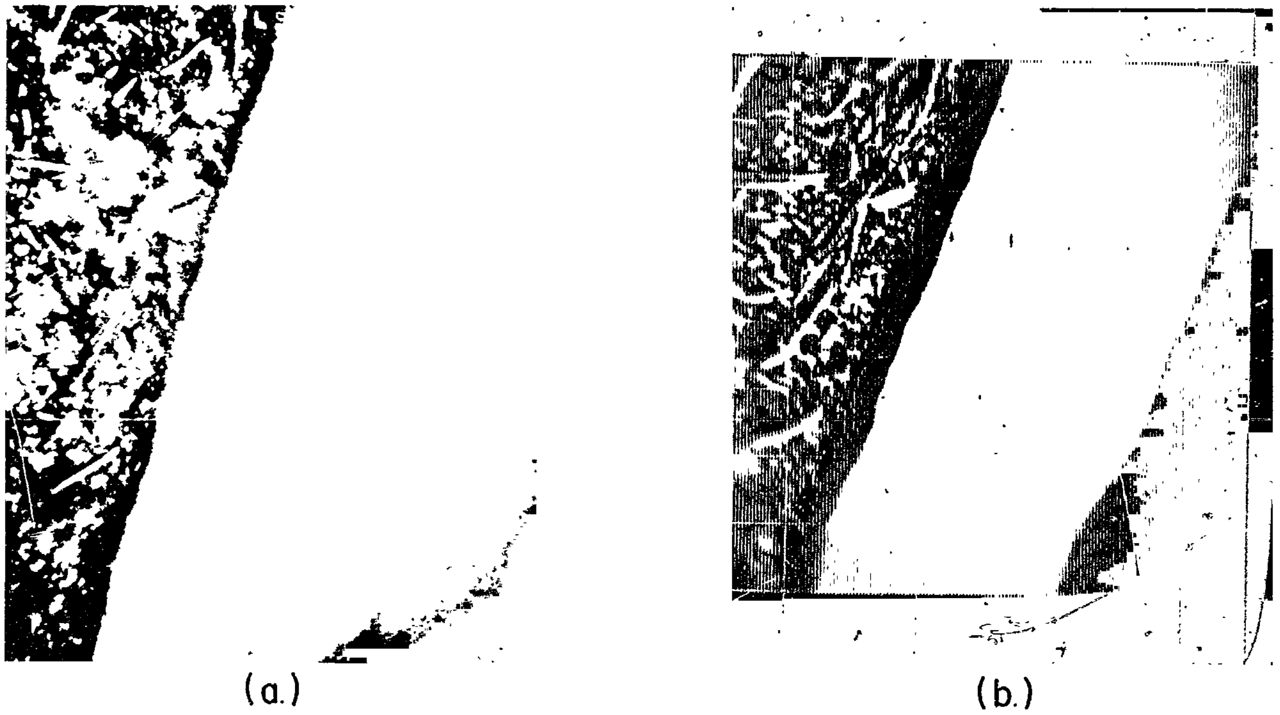
(c.)

Figure 8. Area 4, Specimen 117, Ti getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ti X-ray display.

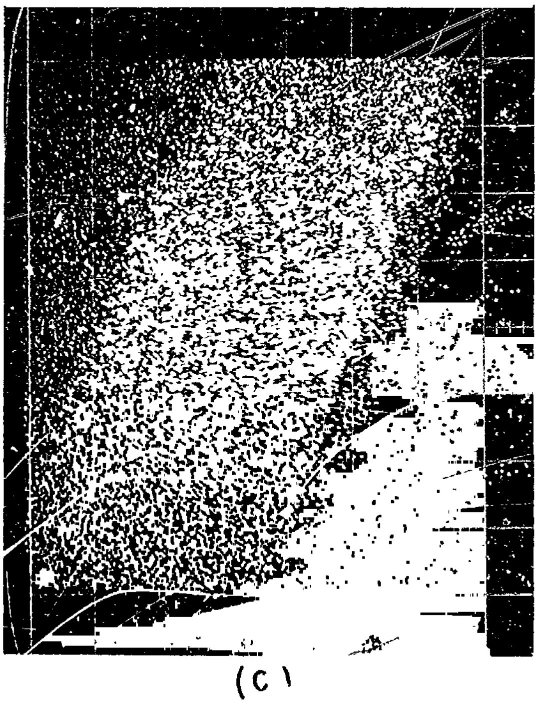
Shows transition between weld (bottom of photographs) and heat-affected zone. Ti concentration is greater in weld zone along with needle-like constituent.

Etched with 10% NaOH.
Magnification: 250X



(a.)

(b.)



(c)

Figure 9. Area 5, Specimen 117, Ti getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ti X-ray display.

Shows massive Ti particle at top surface of weld.

Etched with 10% NaOH.
Magnification: 250X

structures also appear in the specimen-current display of view (b). The Ti X-ray display in view (c) shows heavy concentrations of Ti in the inclusion but less clear correlation with the needle-shaped constituent. View (c) was inadvertently inverted when mounted for reproduction, so the nugget area with the needle-shaped constituents is shown in the lower right portion of the photograph. Although there is a pattern of Ti concentrations in this area, there is no close correlation with the needle pattern. This view also shows some Ti signals emanating from the mounting material. There are several possible causes for these signals, among which are the spreading of some Ti-containing particles into the mounting material during metallographic polishing, the recording of some "noise" because the signal was not refined through the ratemeter channel of the microprobe, or the pick-up of signals from specimen material underlying the surface of the mounting material.

In summary, the microprobe survey of the specimen welded with the Ti getter indicates strongly that Ti was incorporated into the weld nugget, both in the form of massive inclusions and alloyed constituents. Correlation with a needle-shaped constituent appearing in the nugget structure was indicated but not consistently shown in all views in which that constituent appeared. It has been shown, therefore, that concentrations of Ti within the weld nugget did not prevent porosity.

Zirconium concentrations within two different areas of the nugget from the specimen welded with Zr as the getter (No. 118 in Figure 4) are shown in Figures 10 and 11. Both show random spots of Zr concentration in excess of the background concentration or "noise." These concentrations, however, could not be definitely correlated with any of the structural constituents shown in the light-optics, specimen-current (view b in Figure 10), or back-scattered-electron (view b in Figure 11) displays. The Zr concentrations appeared to have no particular relationship with the pores. Both X-ray displays contained considerable "noise" in addition to the concentration signals. Some indication of the signal obtained from an area supposedly free of Zr originating from the getter material is shown in Figure 12, which contains views of the heat-affected zone.

In comparison with the microprobe results from Ti, the Zr getter was present in the weld nugget in considerably less concentration than the Ti. Nevertheless, comparison of views (a) and (b) in Figure 4 indicates that much less porosity was present in the Zr specimen. It was indicated, therefore, that alloying of the getter with the nugget would be detrimental, although other interpretations are possible.

Microprobe surveys of two areas of the specimen welded with Ce (No. 119 in Figure 4) are shown in Figures 13 and 14. These surveys show Ce to

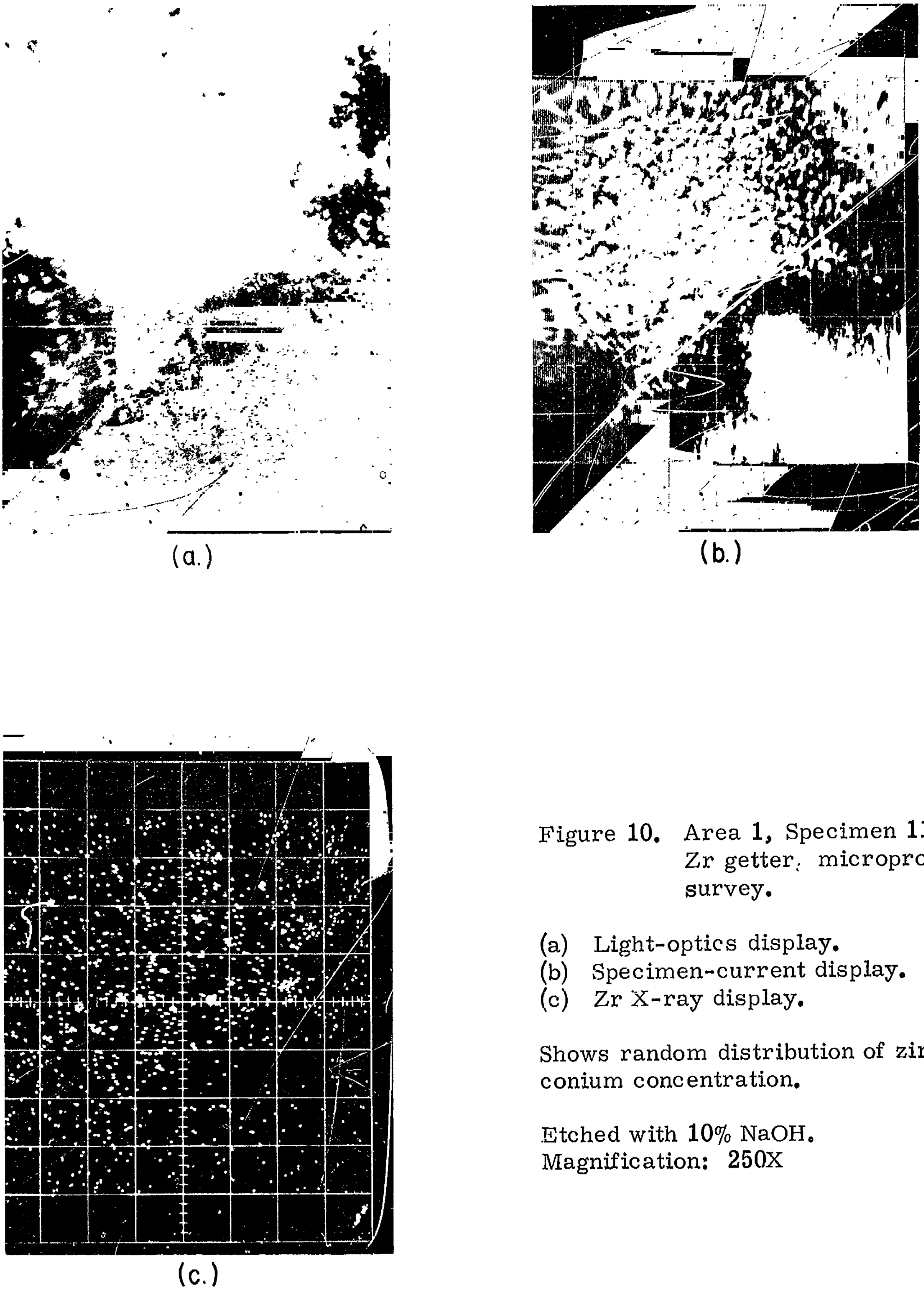
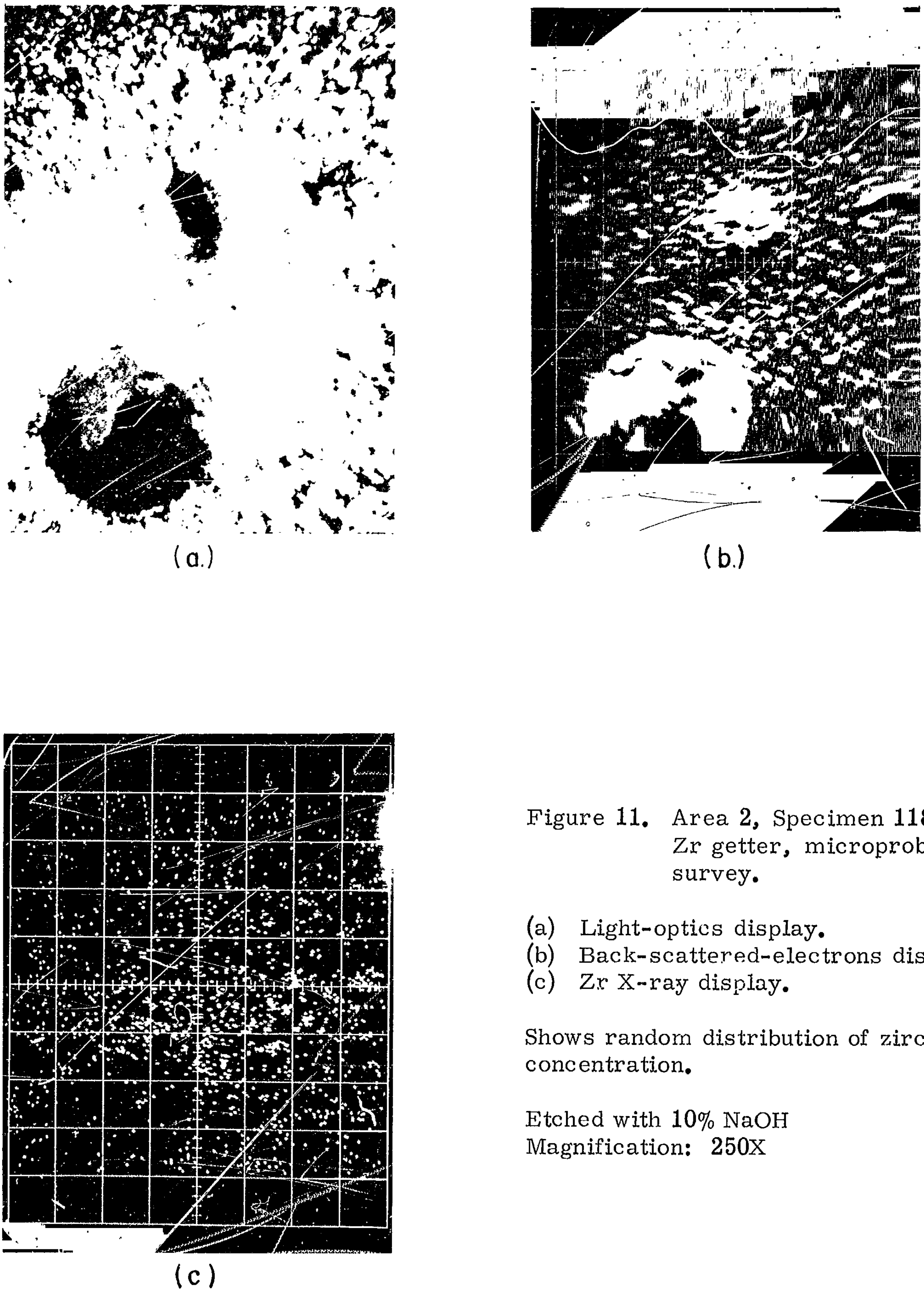


Figure 10. Area 1, Specimen 118, Zr getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Zr X-ray display.

Shows random distribution of zirconium concentration.

Etched with 10% NaOH.
Magnification: 250X



(a.)

(b.)

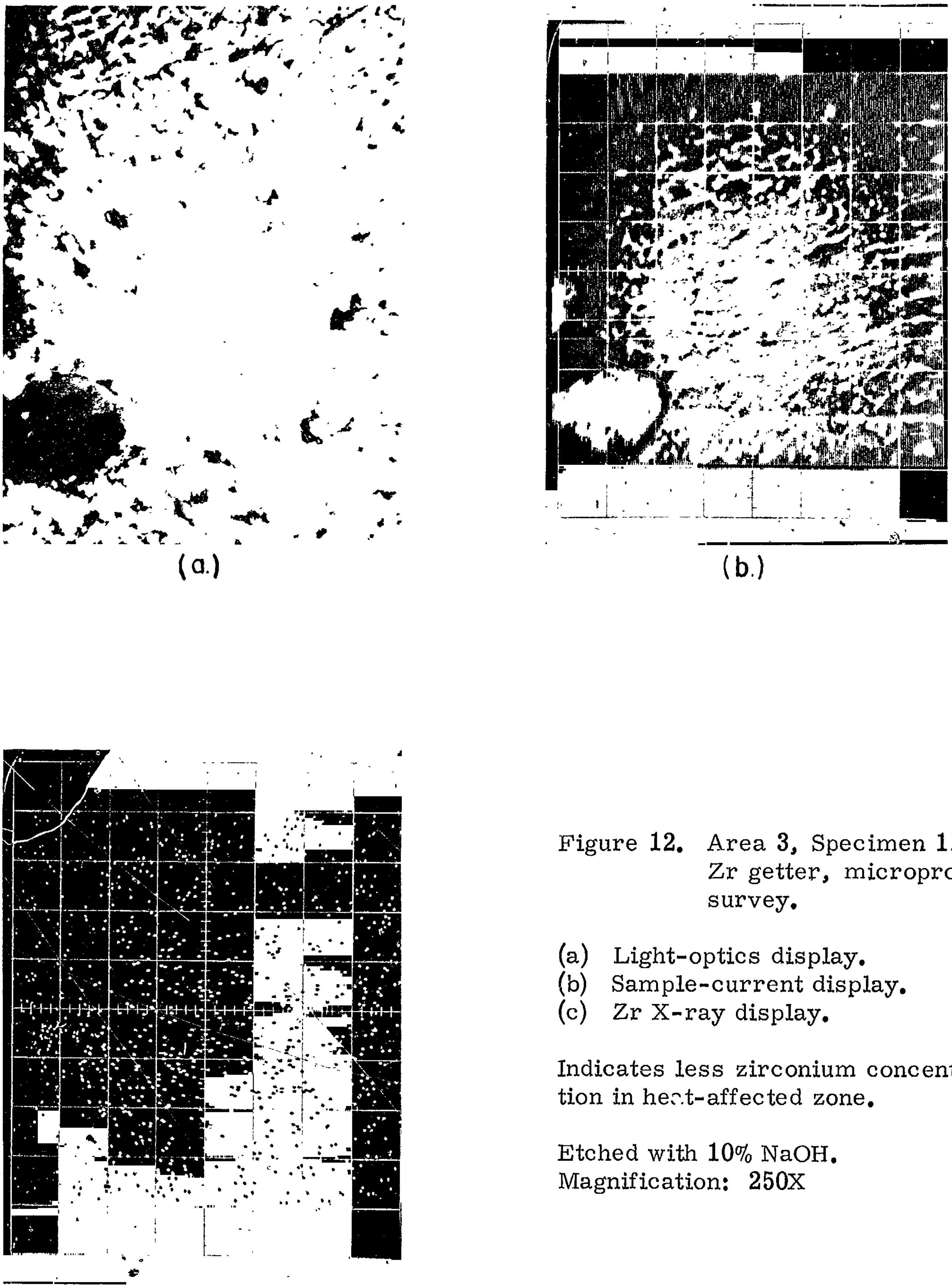
(c)

Figure 11. Area 2, Specimen 118, Zr getter, microprobe survey.

(a) Light-optics display.
(b) Back-scattered-electrons display.
(c) Zr X-ray display.

Shows random distribution of zirconium concentration.

Etched with 10% NaOH
Magnification: 250X



(a.)

(b.)

(c.)

Figure 12. Area 3, Specimen 118, Zr getter, microprobe survey.

(a) Light-optics display.
(b) Sample-current display.
(c) Zr X-ray display.

Indicates less zirconium concentration in heat-affected zone.

Etched with 10% NaOH.
Magnification: 250X

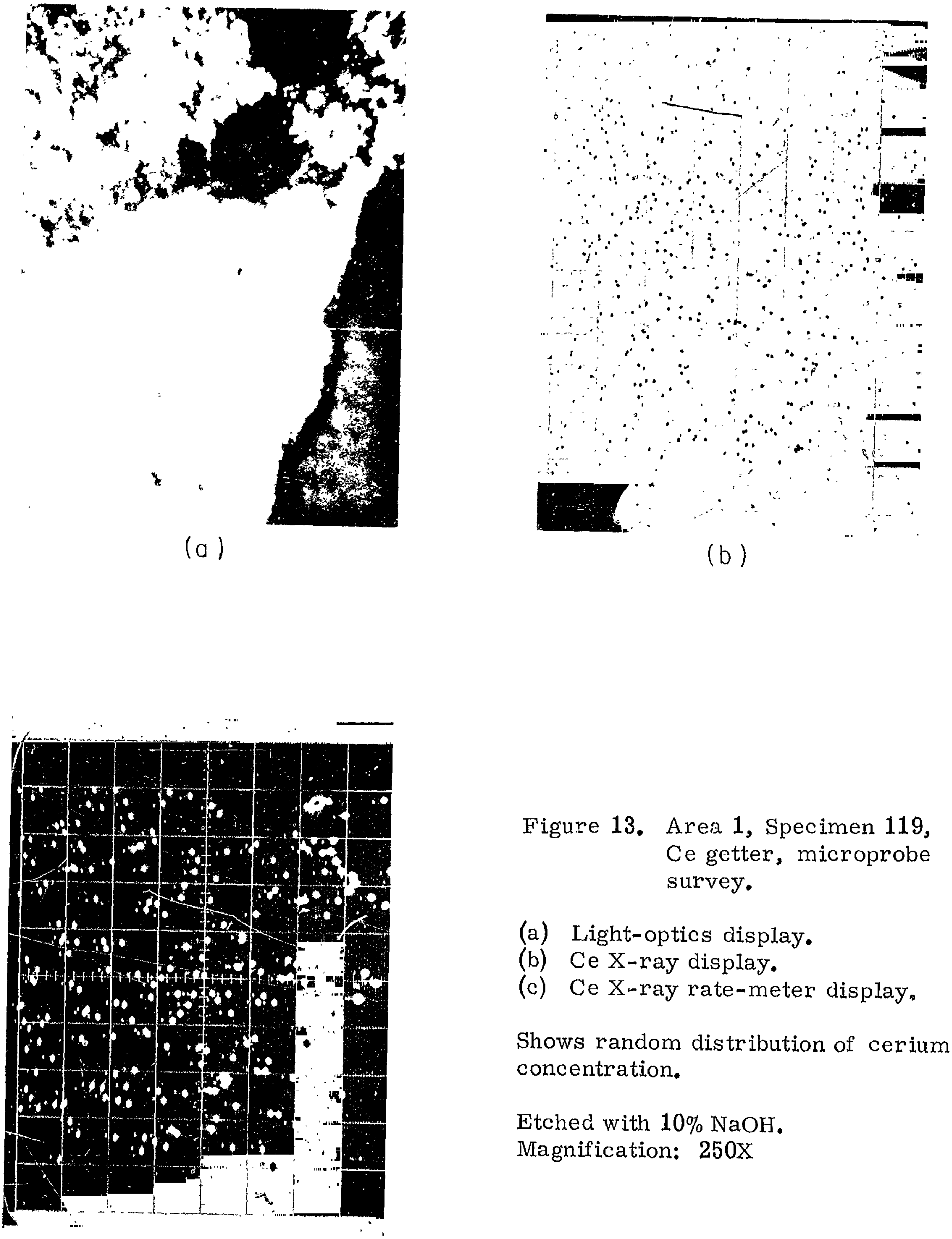
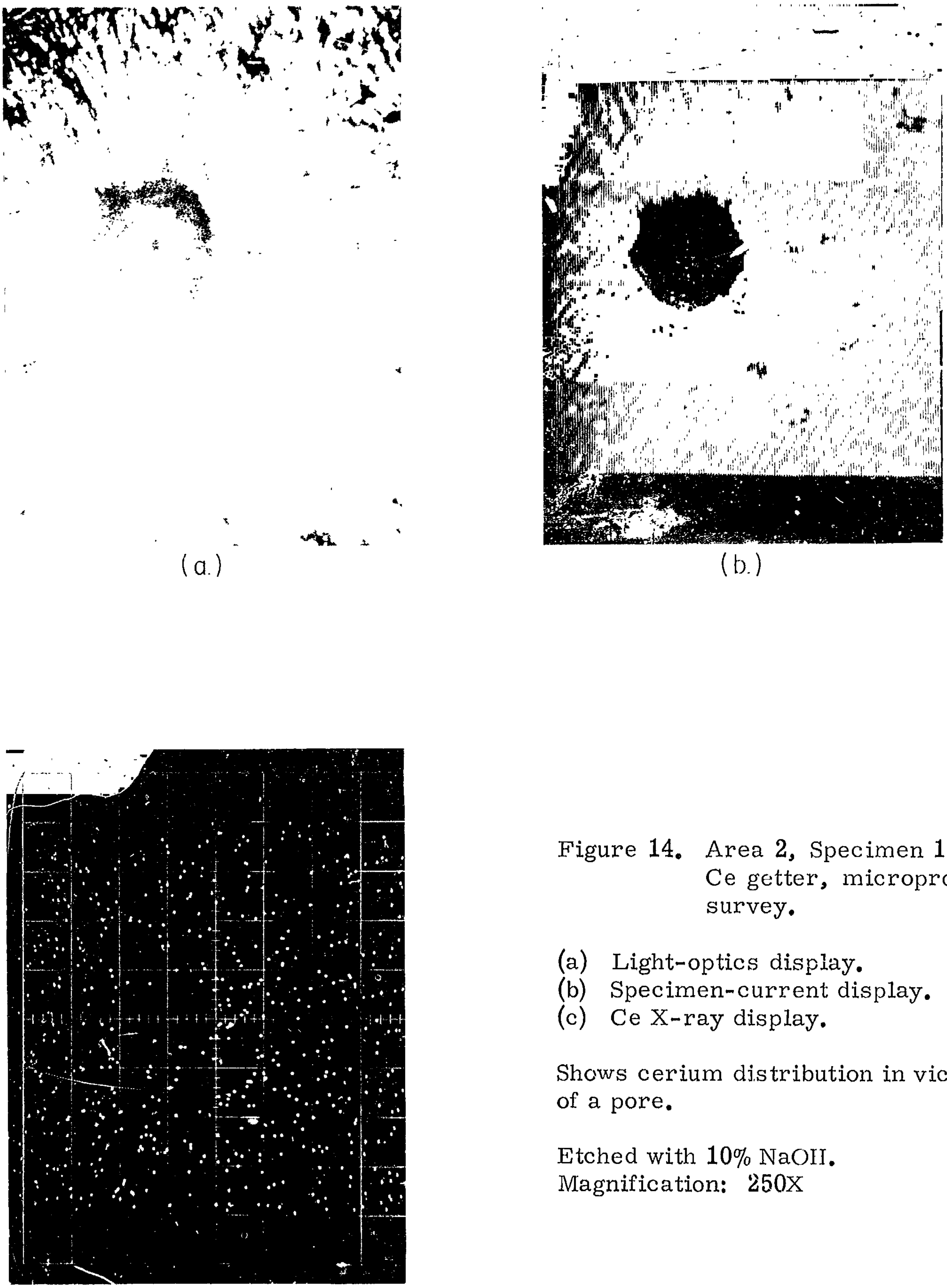


Figure 13. Area 1, Specimen 119, Ce getter, microprobe survey.

(a) Light-optics display.
(b) Ce X-ray display.
(c) Ce X-ray rate-meter display.

Shows random distribution of cerium concentration.

Etched with 10% NaOH.
Magnification: 250X



(a.)

(b.)

(c)

Figure 14. Area 2, Specimen 119, Ce getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ce X-ray display.

Shows cerium distribution in vicinity of a pore.

Etched with 10% NaOH.
Magnification: 250X

be distributed through the nugget structure but no segregated concentrations are evident, either in the vicinity of pores or otherwise. The appearance of the Ce-gettered nugget in Figure 4 indicates that the Ce furnished least resistance to the action of the arc in melting the nugget and, therefore, might have been more uniformly distributed than the more resistant getters.

The surveyed areas on the specimen welded with Ca are shown in Figures 15, 16, and 17. The photographs in Figure 15 show a transition area in which the nugget structure at the bottom of the photograph joins with the heat-affected zone. Heavier concentrations of Ca are shown in the nugget area. Figure 16 shows an area in the vicinity of some of the larger pores. This area shows some concentrations of Ca but the concentrations do not correlate with any of the structures revealed in the light-optics or specimen-current displays. Figure 17 shows the survey across a portion of one of the lighter-toned areas shown in Figure 4(d). As suspected, these areas are shown to be high in Ca content.

In general, the results from the microprobe surveys indicate the following:

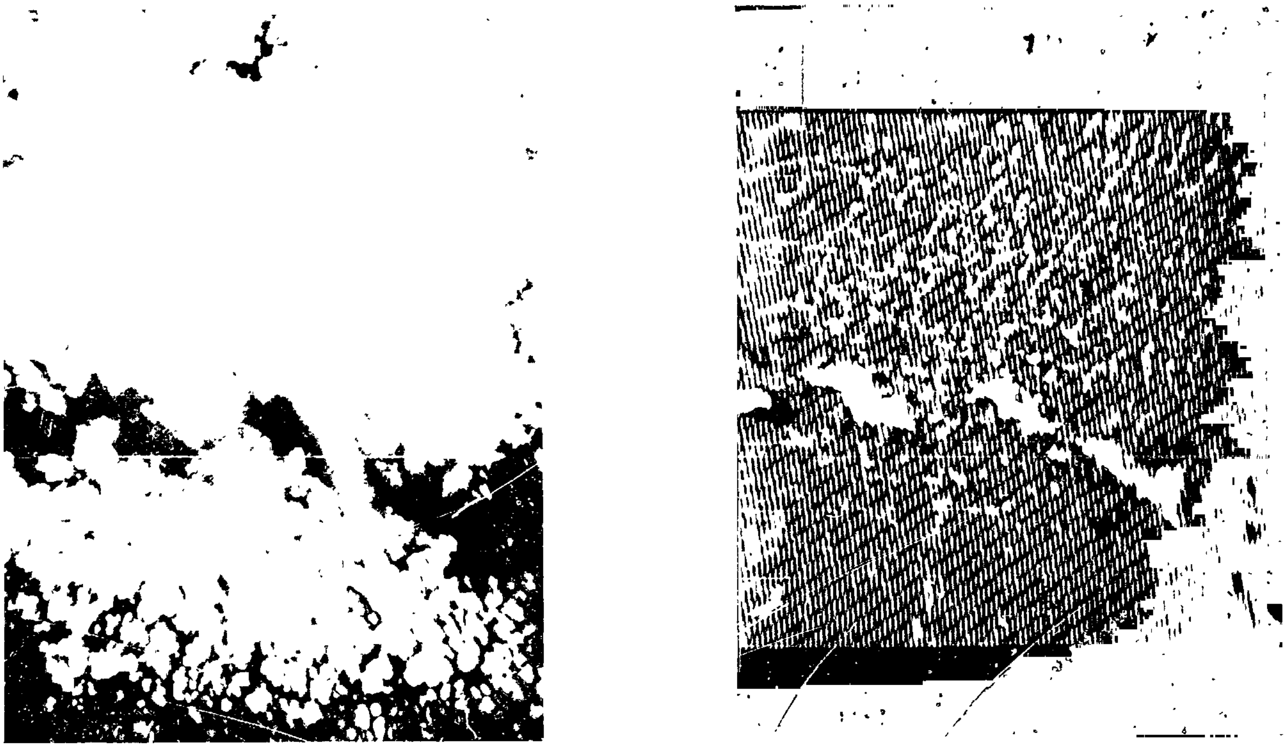
1. All getters were incorporated and alloyed with the weld nugget when applied by the depression method.

2. Incorporation of the getters within the weld nugget did not prevent porosity and might have contributed to the increased porosity exhibited by these welds.

3. Concentrations of the getters were not shown to be directly associated with the pores.

4. Concentrations of the getters could not be consistently associated with metallographic structure except for massive inclusions of the getters.

Butt-Joint Series - This series of welds was made before the completion of the microprobe surveys, which indicated that incorporation of the getters might be detrimental to porosity prevention. Therefore, the getters were applied in a layer clamped between two halves of a specimen to form a butt joint. It was assumed that this application method would insure the presence of getter material in the molten nugget. The results from this series are recorded in Table IV. Although all but the last two specimens were welded with dry helium, only one specimen (No. 130) appeared to be relatively pore free. Welds No. 131 and 132 were made with the same conditions used for No. 130 except for the substitution of moist gas and both



(a) (b)

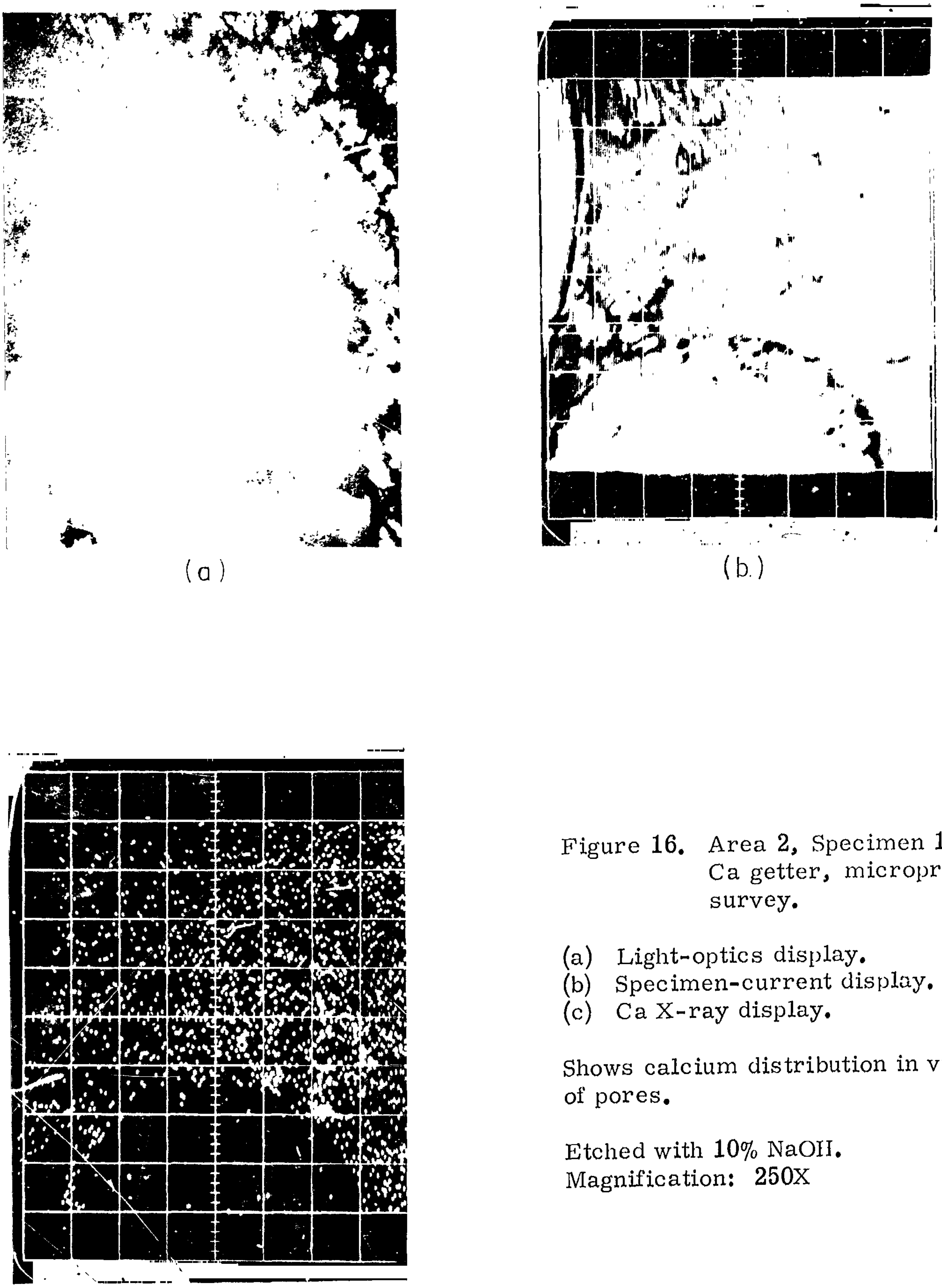
(c)

Figure 15. Area 1, Specimen 120, Ca getter, microprobe survey.

(a) Light-optics display.
(b) Specimen-current display.
(c) Ca X-ray display.

Shows calcium concentration toward weld zone (bottom of photograph) in comparison to heat-affected zone.

Etched with 10% NaOH.
Magnification: 250X



(a)

(b.)

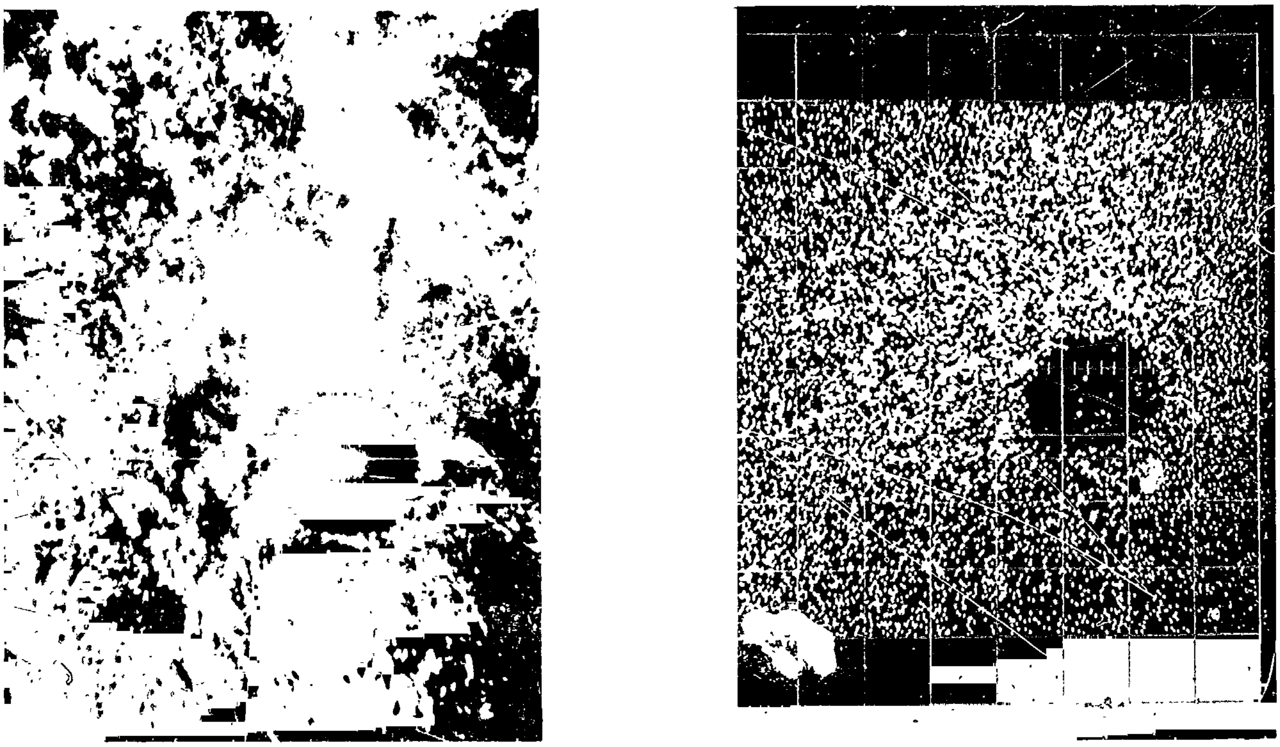
(c)

Figure 16. Area 2, Specimen 120, Ca getter, microprobe survey.

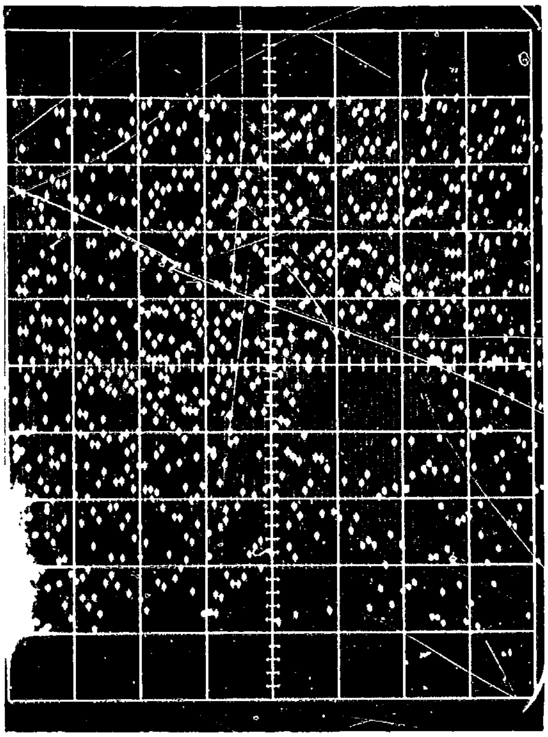
(a) Light-optics display.
(b) Specimen-current display.
(c) Ca X-ray display.

Shows calcium distribution in vicinity of pores.

Etched with 10% NaOH.
Magnification: 250X



(a.) (b.)



(c.)

Figure 17. Area 3, Specimen 120, Ca getter, microprobe survey.

(a) Light-optics display.
(b) Ca X-ray display.
(c) Ca X-ray rate-meter display.

Shows large calcium concentration in light-toned zones shown in Figure 4(d).

Etched with 10% NaOH.
Magnification: 250X

Table IV. Results from Butt-Joint Series

Spec. No.	Welding Time,[1] Seconds	Gas Dew-Point[2] ° F	Getters	Results	Joint Temp,[4] ° F
121	7	-35	Titanium	Joint did not fuse[3]	814
122	8	-35	Titanium	Joint did not fuse - Porous[3]	936
123	9	-35	Calcium	Joint partially fused-large cavity	887
124	13	-35	Calcium	Complete fusion - Porous	–[5]
125	11	-35	Calcium	Complete fusion - Porous	1001
126	10	-35	Barium	Joint partially fused-very porous	–[6]
127	7	-35	Titanium	Joint did not fuse[3]	869
128	7	-35	Zirconium	Joint mostly fused - Porous	875
129	8	-35	Cerium	Joint partially fused - Porous	899[7]
130	8	-35	Titanium	Complete fusion - Nil porosity	919
131	8	+50	Titanium	Joint partially fused - Porous	924
132	8	+50	Titanium	Complete fusion - Porous	940[7]

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[1] All welds made with 2219 material, 14 volts, and 150 amperes.

[2] All welds made with 53 CFH gas flow.

[3] Aluminum fused on each side of titanium layer but joint did not fuse.

[4] Average temperature from two thermocouples on bottom of nugget 1/4 in. from centerline.

[5] Thermocouples became detached during welding.

[6] Temperature not recorded.

[7] Readings from one thermocouple only. Other thermocouple became detached during welding.

were porous. In addition, it was found to be difficult, especially with Ti, to fuse the joint together. The arc tended to melt the aluminum on either side of the getter layer but the molten material would not penetrate through the unmolten getter to form the joint. One specimen (No. 126) was welded with barium instead of calcium, and although apparent fusion was achieved, the joint was extremely porous and allowed the two halves to be broken apart by hand pressure after the specimen had been removed from the clamp.

First Slurry Series - In this series, the getters were applied only on the surfaces of the specimens in an attempt to prevent the apparently detrimental effects of deeply incorporated getters. Small spots directly underneath the electrodes were scraped free of getter material in order to provide good arc-starting characteristics. As a further caution against extraneous moisture, all specimens were heated to 400° F for at least one hour immediately prior to welding. The series included three getter materials other than the original four. The degrees of porosity in the resulting welds were measured quantitatively by means of a Filar eyepiece used at 1.3X magnification.

Photographs of cross sections of the welds are shown in Figure 18 and the results of the porosity measurements are shown in Table V. All of the gettered welds contained general porosity similar to that in the ungettered weld (No. 134), and most contained one or more pores larger than the size of the general porosity. Each of the three additional getters (Nos. 139, 140 and 141) produced greater porosity than the original four, except that Ca (applied as lime) also had high porosity. Although the relationship was not visually evident, the quantitative measurements showed the welds made with Ti, Zr, and Ce (Nos. 135, 136, and 137) to have less porosity than the ungettered specimen welded with moist gas (No. 134). These results indicated that some benefit was derived from Ti, Zr, and Ce even though porosity was not eliminated but only slightly reduced.

Second Slurry Series - The second slurry series was performed to check the previous results with Ti, Zr, and Ce, and to investigate a large number of other elements and compounds for their capabilities as getters. This series was performed in the same manner as the first slurry series, except that equal volumes of the getter materials were used in making the slurries, and the slurries were applied to the electrodes as well as to the specimens. Although some of the materials failed to make a good slurry, all were sufficient to deposit a coating on the electrodes and specimens. Data on the application procedure are recorded in Table VI.

Photographs of the cross sections of the welds are shown in Figures 19 and 20, and the results from the porosity measurements are recorded in Table VII. The porosities developed by Ti (No. 150), Zr (No. 151), Ce (No. 147) and Ca (No. 146) were approximately the same as in the first slurry

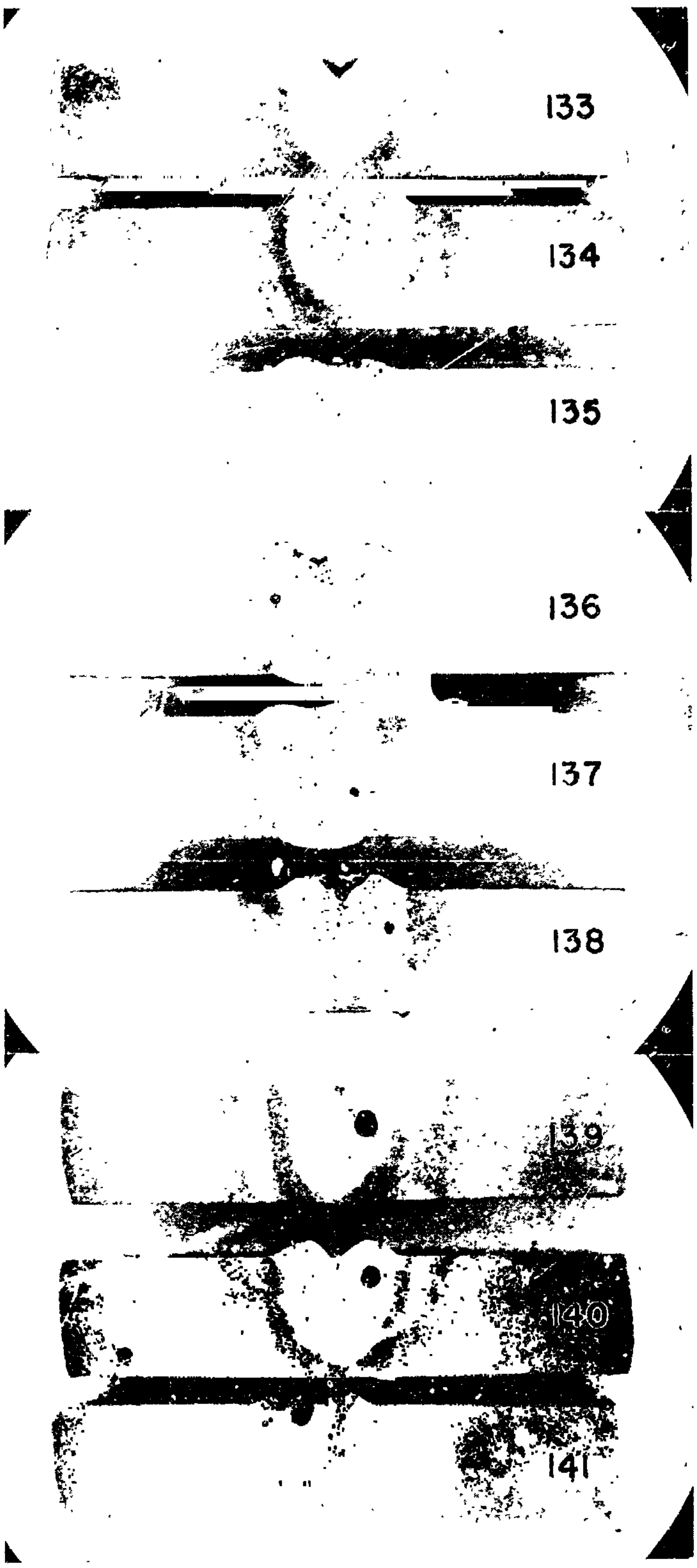

Figure 18. Porous conditions of first slurry series. Specimen numbers refer to those in the tabulated results. Black and white spots both indicate pores within the weld nugget.

Etched with 10% NaOH and Keller's concentrated etch.
Magnification: 2X

Table V. Results from First Slurry Series

Spec. No.[1]	Getters[2]	Porosity, %	Largest Pore Dia., In.	Joint Temperature,[4] ° F
133	None (dry gas)	3.2	0.00275	869[5]
134	None	39.8	0.0159	791
135	Titanium	35.4	0.0205	851
136	Zirconium	33.4	0.0291	890
137	Cerium	29.4	0.0370	874
138	Lime	43.8	0.0376	812
139	Sulphur	45.5	0.0615	789
140	Sodium borate	45.0	0.0511	827
141	Sodium nitrate	50.0[3]	0.0199	715

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[1] All welds made with 14 volts and 150 amperes for 7 seconds.

[2] All welds made with +50° F dew-point helium except No. 133 made with -35° F dew point. Gas flow was 53 CFH for all welds.

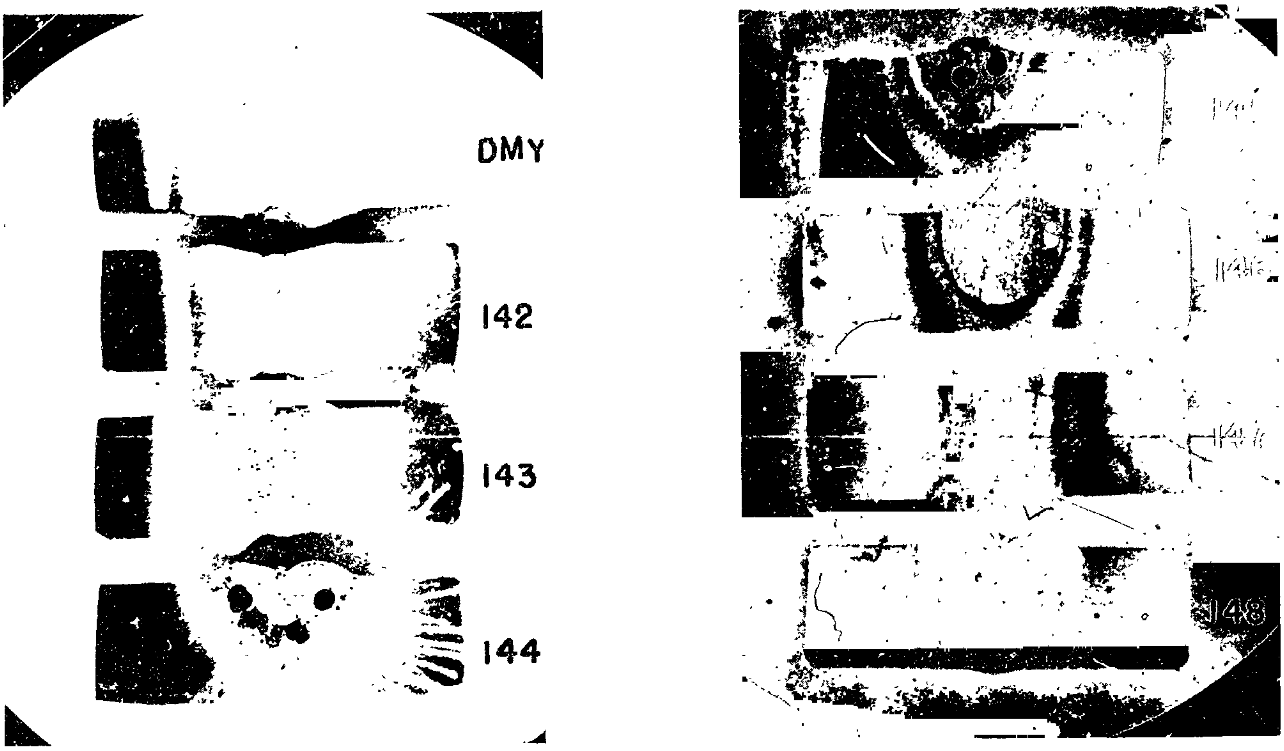
[3] Average of one reading of 25.6% porosity at centerline vertical traverse, and one reading of 74.3% porosity with vertical traverse made at the area of maximum porosity.

[4] Average temperatures from two thermocouples on bottom of nugget 1/4 in. from centerline.

[5] Reading from one thermocouple only. Other thermocouple became detached during welding.

Table VI. Application Results from Second Slurry Series

Spec. No.	Getters	cc H_2O with 3 cc Getter	Results
142	None (dry gas)	–	–
143	None (moist gas)	–	–
144	Aluminum	2	Good paint-type slurry.
145	Barium	6	Foamy solution. Stained Al black.
146	Calcium	20	Thin solution because tap water from cooling water bath accidentally spilled in. White solution.
147	Cerium	5	Solution foamy at first, then thinned out, then foamy again. Poor coating on electrode.
148	Iron	3	Poor coating on electrode.
149	Manganese	2	Good slurry. Similar to aluminum.
150	Titanium	2	Good slurry.
151	Zirconium	2	Good slurry.
152	Lithium carbonate	2	Good slurry.
153	Barium chloride	1	Crystalline paste.
154	Cupric chloride	1	Reacted with Al and turned from green color to dark maroon.
155	Lithium chloride	2	No slurry. Clear solution with some crystals. Poor coating on electrode.
156	Potassium chloride	2	Same as lithium chloride.
157	Sodium chloride	2	Same as lithium chloride.
158	Al-Na fluoride (cryolite)	1	Poor coating on electrode.
159	Manganous oxide	2	Good slurry.
160	Nickel oxide	3	Thick slurry but good.
161	Phosphorous pentoxide	2	Viscous liquid - no slurry.
162	Titanium dioxide	2	Thick slurry but good.
163	Calcium silicide	2	Good slurry.



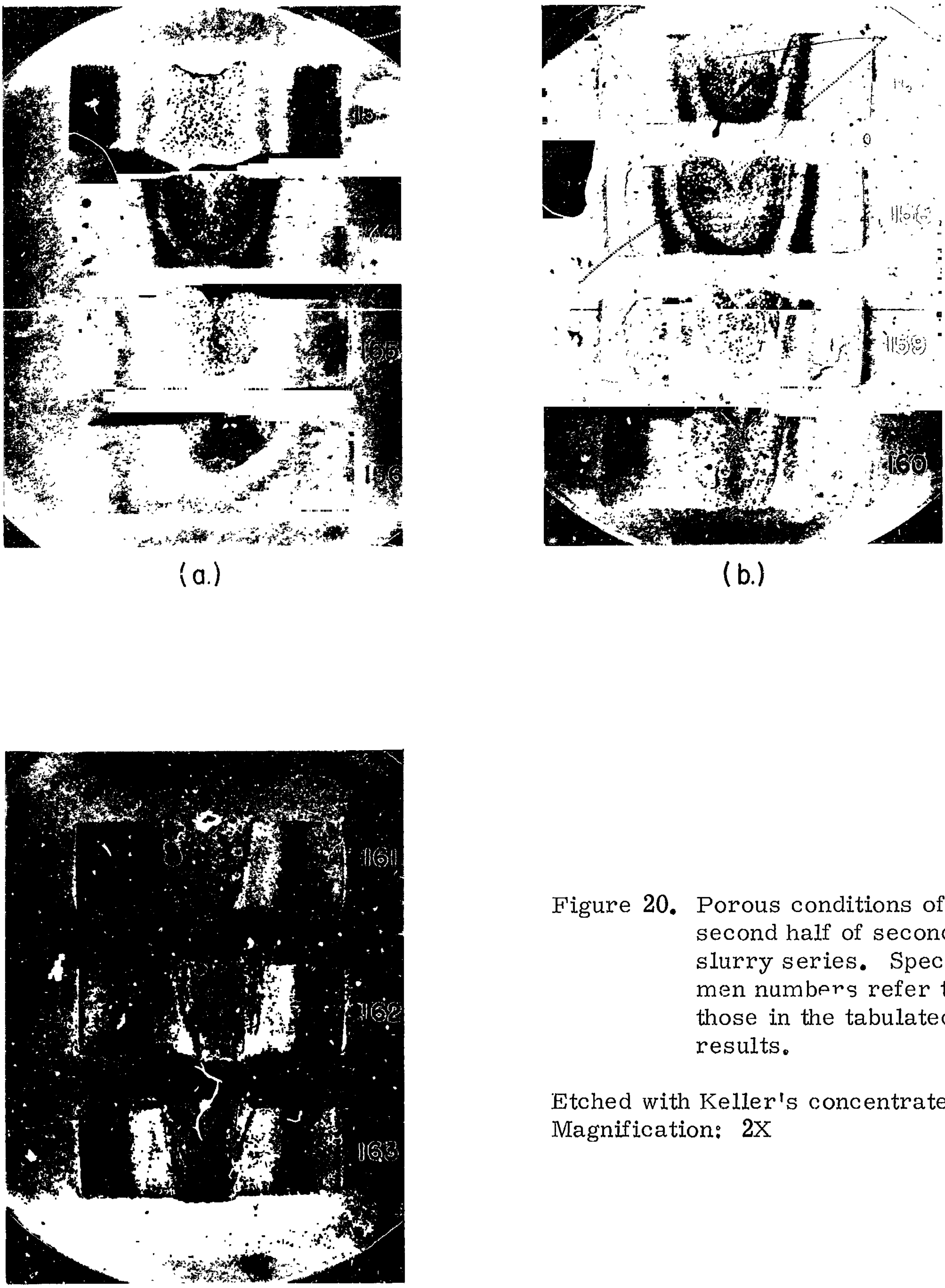
(a.)

(b.)

(c.)

Figure 19. Porous conditions of first half of second slurry series. Specimen numbers refer to those in the tabulated results.

Etched with Keller's concentrated etch.
Magnification: 2X



(a.)

(b.)

(c.)

Figure 20. Porous conditions of second half of second slurry series. Specimen numbers refer to those in the tabulated results.

Etched with Keller's concentrated etch. Magnification: 2X

Table VII. Porosity Results from Second Slurry Series

Spec. No.[1]	Getters[2]	Porosity %	Largest Pore Dia., In.	Joint Temperature,[3] ° F
DMY	None - unscraped (dry gas)	Nil	—	–[4]
142	None (dry gas)	Nil	–	902
143	None	15	0.0082	907
144	Aluminum	73	0.0597	739
145	Barium	47	0.0636	788
146	Calcium	49	0.0351	771[5]
147	Cerium	26	0.0180	936
148	Iron	27	0.0279	855
149	Manganese	30	0.0308	823
150	Titanium	38	0.0207	854
151	Zirconium	34	0.0358	827
152	Lithium carbonate	45	0.0712	789
153	Barium chloride	42	0.0148	927
154	Cupric chloride	35	0.0187	777
155	Lithium chloride	32	0.0092	877
156	Potassium chloride	87	0.1519	800
157	Sodium chloride	32	0.0105	839
158	Al-Na fluoride (cryolite)	35	0.0118	831[5]
159	Manganous oxide	33	0.0174	856
160	Nickel oxide	30	0.0197	861
161	Phosphorous pentoxide	55	0.0659	861
162	Titanium dioxide	32	0.0394	910
163	Calcium silicide	30	0.0148	899

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[1] All welds made with 14 volts and 150 amperes for 7 seconds.

[2] All welds made with +50° F dew-point helium unless otherwise shown. Dry gas was -35° F dew point. Gas flow was 53 CFH for all welds.

[3] Average temperatures from two thermocouples on bottom of nugget 1/4 in. from centerline.

[4] Temperature not recorded.

[5] Readings from one thermocouple only. Other thermocouple became detached during welding.

series but, because of a reduction of the porosity measured in the ungettered specimen (No. 143), none of the gettered specimens appeared to have reduced porosity. Several of the elements and compounds had similar porosities and were within the same range of porosities as the Ti, Zr, and Ce specimens. These materials included Fe (No. 148), Mn (No. 149), $CuCl_2$ (No. 154), LiCl (No. 155), NaCl (No. 157), $AlF_3 \cdot 3NaF$ (No. 158), MnO (No. 159), NiO (No. 160), TiO_2 (No. 162), and $CaSi_2$ (No. 163). All of the other getters produced greater porosities, and two of them, Al (No. 144) and KCl (No. 156) produced extremely high porosities.

The high porosity resulting from the use of Al powder as a getter was probably caused by hydrogen contamination already present in the powder. Aluminum powders have been found to contain large amounts of hydrogen, which requires baking under vacuum for its removal. The welding arc on this specimen (No. 144) was unstable and caused the welding head to oscillate up and down (hunting) during most of the 7-second welding period. Of course, original hydrogen contamination was also a possibility with the powders of other getters, but the Al-coated specimen was the only one that exhibited discernible instability of the arc.

Temperature Measurements - The temperatures developed on the bottom sides of the specimens in the butt-joint series and the two slurry series are recorded for their respective specimens and corresponding welding durations in Tables IV, V, and VII. These temperatures did not correlate with any of the other results so no attempt was made to calculate the energy inputs or input rates to the specimen.

DISCUSSION

The negative results obtained throughout these experiments indicate that hydrogen porosity in aluminum welds will not be reduced or eliminated by means of powdered getters placed in the vicinity of the welding arc. Since all possible materials were not included in the experiments, the possibility still exists that some materials heretofore untried might provide effective protection. However, among those included in these experiments, three of four prospective getters chosen as most promising on the basis of the literature study of hydride formation (Ti, Zr, and Ce) produced results that were among the best obtained. It is likely, therefore, that discovery of more effective getters in conventional welding operations will only be made on an empirical or fortuitous basis.

The experiments in which getters were applied to specimens welded with dry gas indicated, for the most part, that the getters themselves would not cause porosity unless the application method interfered with arc conditions or allowed the entrance of extraneous contaminates. On the other hand, when welds were made with moist gas, even the better getters often appeared to increase porosity. If such is the case, there is a possibility that the better getter materials do attract hydrogen and might protect the aluminum if they could be included in the arc but prevented from becoming incorporated into the weld nugget. Application of the getters in this manner would require the development of altered, and probably much more complex, welding techniques. It is likely that the development of appropriate techniques will not be attempted until the getting abilities of some material in the presence of aluminum has been more definitely indicated.

In view of the results of these experiments, it would appear that any continuation of the search for getters should be made on a fundamental basis. A laboratory procedure should be devised to determine the relative attractions for hydrogen that exist between aluminum and prospective getters (in physical form as well as content) at temperatures in the vicinity of the aluminum melting point (660° C) and higher. If possible, the comparisons should be made at extremely high temperatures approaching those that exist in the welding arc. When the temperature conditions and forms under which other materials will attract hydrogen in preference to molten aluminum have been determined, it will then be possible to attempt to adjust welding procedures to incorporate the required conditions.

CONCLUSIONS

Under conventional inert-gas arc-welding conditions for aluminum alloys, hydrogen porosity was not eliminated or significantly reduced by the getter materials, which had been chosen as most promising on the basis of literature describing hydride formation. Although the best of the getters did not appear to be primary sources for porosity, they frequently increased the severity of porosity arising from other sources of contamination, such as moisture in the inert gas. With the exception of Ca, which was difficult to apply in its elemental form, the four most promising getters on the basis of the literature study (Ti, Zr, Ce, and Ca) were among the most effective getters in the experimental work. However, other transition elements (such as Fe and Mn) and some compounds were equally as effective in the one group of experiments in which they were included.

RECOMMENDATIONS

It is recommended that fundamental studies of the comparative hydrogen-attracting propensities of molten aluminum and other materials be performed prior to further welding experiments. These studies should include considerations of the form of the materials (finely divided powders, "atomized" liquids, ionized compounds, etc) as well as the elemental content.

ACKNOWLEDGEMENTS

Several staff members other than the author participated in this project and their valuable assistance is hereby acknowledged. The literature study and the microprobe surveys were performed by Dr. Joel Solomon. The welding experiments up to those in the slurry series were performed by Mr. J. O. Honeycutt. Some of the metallographic work and porosity measurements were performed by Mr. Harrell Moyers and Mrs. Imogene Baswell.

October 28, 1966
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