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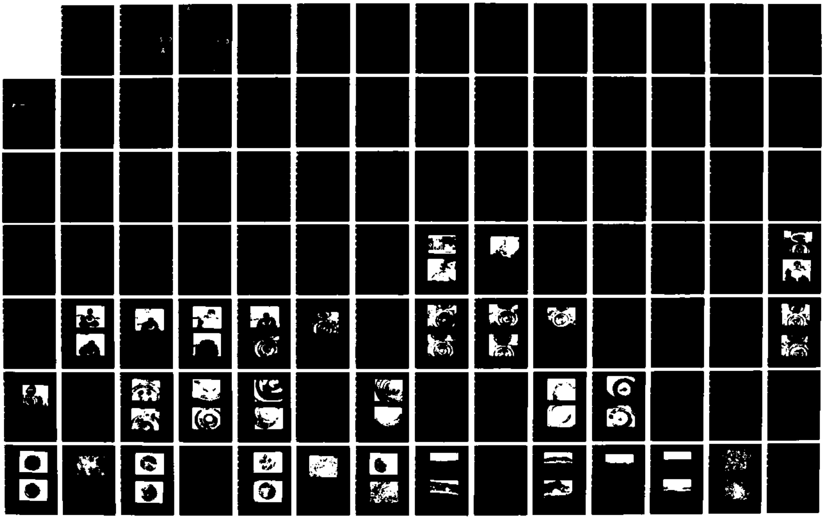

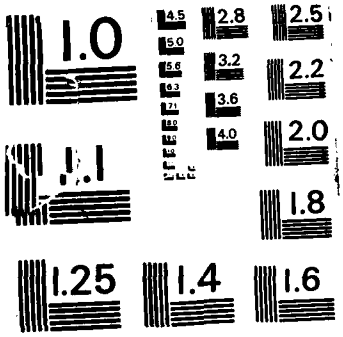

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Title

SURFACE ATTACK ON METALS
IN THE PRESENCE OF LIQUID METALS

AMALGAMATED TECHNOLOGIES, INC.

AMALGAMATED TECHNOLOGIES, INC.

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SURFACE ATTACK ON METALS IN THE PRESENCE OF LIQUID METALS

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April 10, 1986

Final Report

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SURFACE ATTACK ON METALS IN THE PRESENCE OF LIQUID METALS

TOPIC NO. N85-1

1. SUMMARY

A study has been undertaken to evaluate liquid metals as electrical collectors in contact with solid metal alloys. Surface attack of the liquid metal on the solid metal is expected to be a major challenge to the development of a credible system. Low melting temperature metals and alloys of the fusible type are to be utilized for a collector that will operate in the 200-500°F range, with emphasis towards the lower end. Solid metals have been selected for experimental work based on their electrical properties and minimal potential reaction with the candidate liquid metal alloys. Material properties of both liquid and solid metals were reviewed to identify initial material combinations for evaluation. Thorough literature searches were conducted to obtain as much pertinent physical property and metallurgical data as possible, prior to actual experimental work. Process and material modelling was adopted to select candidate materials for both solids and liquids. Consideration of practical requirements for the eventual collectors is an integral part of the study.

Work effort has concentrated on apparatus construction, evaluation and a program of testing to obtain screening data on materials selected and the chosen test method. Results have identified limitations of the

test unit design and maximum current loads under test conditions with experimental current collectors. Candidate electrode materials have been exposed in low melting fusible alloys for direct dissolution data.

Experimental apparatus for collector material evaluation was constructed initially with free flowing argon gas coverage. A pressurized collector system was developed with improved gas protection to alleviate the dominant oxidation problem found in using liquid metals under rotating and power transfer conditions. A total of 49 test runs were made under current flow conditions using mainly tungsten electrodes. The most successful test run was performed under pressurized argon with tungsten electrodes and a 50% tin-50% indium liquid metal at 350°F, with which over 700 hours of operation was achieved. Electrode materials were evaluated by direct dissolution studies and tungsten was determined to be the best candidate with the liquid alloy metals tested. The work has progressed satisfactorily and preliminary device designs suggest that a 10,000 hour operating life is feasible, with promise of further improvements in Phase II of the program.

2. LIQUID METAL PROPERTIES

Minimum oxidation and stable low oxygen absorbtion conditions are paramount to a successful collector system design. Temperature is most critical because reactions generally are exponentially increased with it. The individual components of the system of solid metal and liquid metal conductors are both important in oxidation characteristics. A practically designed collector system can make use of protective atmospheres to lessen or render impotent the oxidation effects of a system. Preferentially, the materials involved should have inherently good oxidation resistant properties to minimize potential problems and degradation, should breakdowns, system leaks, etc. occur during operation.

Liquid metals generally are in equilibrium with their environment as far as oxygen potential is concerned, and effectively reach saturation very rapidly. Low, partial, or absolute pressures of a system can cause localized vapors of the liquid metal to develop. Sublimation on adjacent material occurs when the situation changes. A low vapor pressure system is, therefore, important to obtaining a system that can be repeatedly operated without losing the liquid metal contact material. A dynamic equilibrium will tend to result in all systems to be explored. A sealed system that is slightly tolerant to the oxidation condition can be self-cleaning by quickly depleting the oxygen potential of the environment and converting it to oxides that may not interfere. A good design, therefore, will effectively have a minimum of gaseous environment within which to work and preferably will be satisfactorily sealed from further air ingress to the system.

Alloy systems in the liquid state are known to have a capability of producing composition gradients with preferential elements becoming surface active. A good example occurs in brazing where very small quantities of lithium produce effects far beyond the general composition level because of surface activity. Surface active elements can be useful in retarding the rate of oxidation of a liquid metal by development of a surface heterogeneous layer. Electrical collection, however, usually involves some relative surface movement that can negate such positive effects. Actual experiments are needed to evaluate potentially useful systems with alloy additions considered to be surface active.

Surface defects do occur on liquid metal surfaces and are affected by such factors as surface tension, mechanical vibration or rotation, diffusion, oxide properties, and materials in contact. Some factors only can be evaluated by direct experimentation which will be carried out on promising systems of liquid and solid electrical collection materials. Pressures, temperature, and time are important variables.

The Gibbs free energy of formation (ΔG) per mole of oxide is a definitive measure of degree of oxidation or affinity of a metal for oxygen. Lower free energies are related to more stable oxides.

Oxidation rates generally are suppressed by the additions of aluminum. Chromium, and titanium liquid metals will quickly oxidize. Copper is fairly neutral in aluminum. A useful graph was abstracted from Metallurgical Reviews No. 131.[1]

Bismuth oxidizes by a parabolic law and up to 709°C, solid α-oxide of bismuth is formed. Lead in the temperature range of interest forms PbO by a parabolic law relationship. Silver increases resistence to oxidation of lead. Other suitable oxidation retardants are aluminum between 0.01-0.02%, tin up to 1%, and bismuth 1%. Passage of electrical current is expected to increase oxidation rates and probably requires a neutral gas atmosphere such as argon or nitrogen. Gruhl summarizes the effect of various additions to lead on oxidation in air at 400°C.[2] Aluminum and zinc additions at very low levels reduce the oxidation of tin by a substantial amount. There appears some possibility of using a mercury-copper (0.003) alloy with relatively low oxidation characteristics, some temperature stability, and low reaction with the solid collector material. This raises an interesting possibility of mercury-copper-aluminum alloys if these can be formulated to be liquid at the intended operating temperature of the collectors.

An example of surface tension reduction by elemental additions to a mercury-base is shown in Figure 1. Surface tension also has been shown as

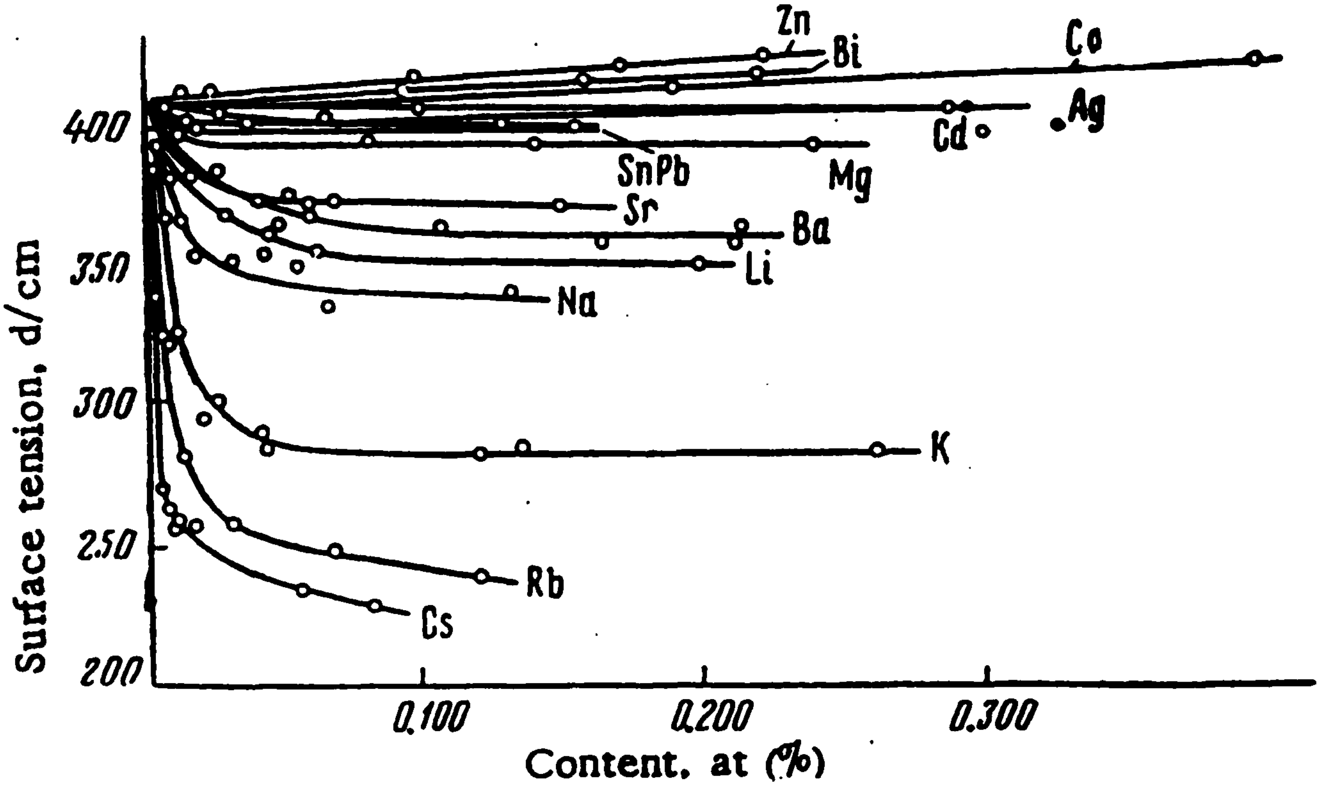


FIGURE 1 - Dependence of surface tension of amalgams on composition.

directly related to atomic volume, indicating that alloy changes can be used directly for control of contact angles between liquid and solid metals. There has been work that shows some relationship between the constitutional diagrams and surface tensions that develop between alloying elements. For example, zinc-bismuth and zinc-lead show minima at the approximate eutectic. The degree of change obtained relates to the differences in atomic volume. The surface active effects and changes in surface tension are not negated in more complex alloys. Thus, it should be possible to construct an alloy system with preferable properties, using solid-liquid relationships to control dissolution and reaction, and liquid metal properties to control surface tensions within the range of interest. Coupled with relative oxidation characteristics, a method of compiling good attributes and potential usable alloys begins to emerge.

Viscosity of a liquid metal appears to be an important factor in considering these materials as collectors. Essentially, a combination of viscosity and surface tension or wetting capacity will indicate the drag forces involved in moving the liquid and selected solid materials against each other. Metals are known to have a lower cohesiveness at elevated temperature in the liquid state, generally producing an inverse relationship between viscosity and temperature. The higher temperatures and lower viscosities appear appropriate to the current task. Therefore, in practice a low oxidation rate, high surface tension, low viscosity and low reaction products by metallurgical interaction or oxidation are desirable. Available data also suggests a direct observable correlation between the liquidous slope on a binary constitution diagram and the viscosities measured. Eutectic alloys in particular seem to produce lowered viscosity values.

Corrosion rates of solid metals in liquid metal flowing systems previously has been investigated for the purpose of working on breeder reactor systems. An example of the corrosion rate of stainless steels in flowing Pb-17Li, is presented in Figures 2 and 3 demonstrate data obtained, and presentation that could be appropriate to the present work. Interestingly, the addition of titanium to lead was found to inhibit dissolution of the solid metal in earlier work. The proposed mechanism of protection was reaction with carbon and/or nitrogen to introduce a protective surface film of titanium nitride or carbide. The lack of much definitive work in the area was expressed by Chopra, et. al.[3] There is a conflict of requirement concerning oxidation or reduction and protection of the metal surfaces in electrical contact. Wetting characteristics demand that a high wetting angle and minimum surface adhesion are important to successful electrical energy transfer without sticking or affecting the interfacial area. A very thin stable oxide film to retain these properties is desirable on the solid metal with no visible oxidation of the liquid metal. A good selection of material, therefore, appears to be a high stability oxide forming material

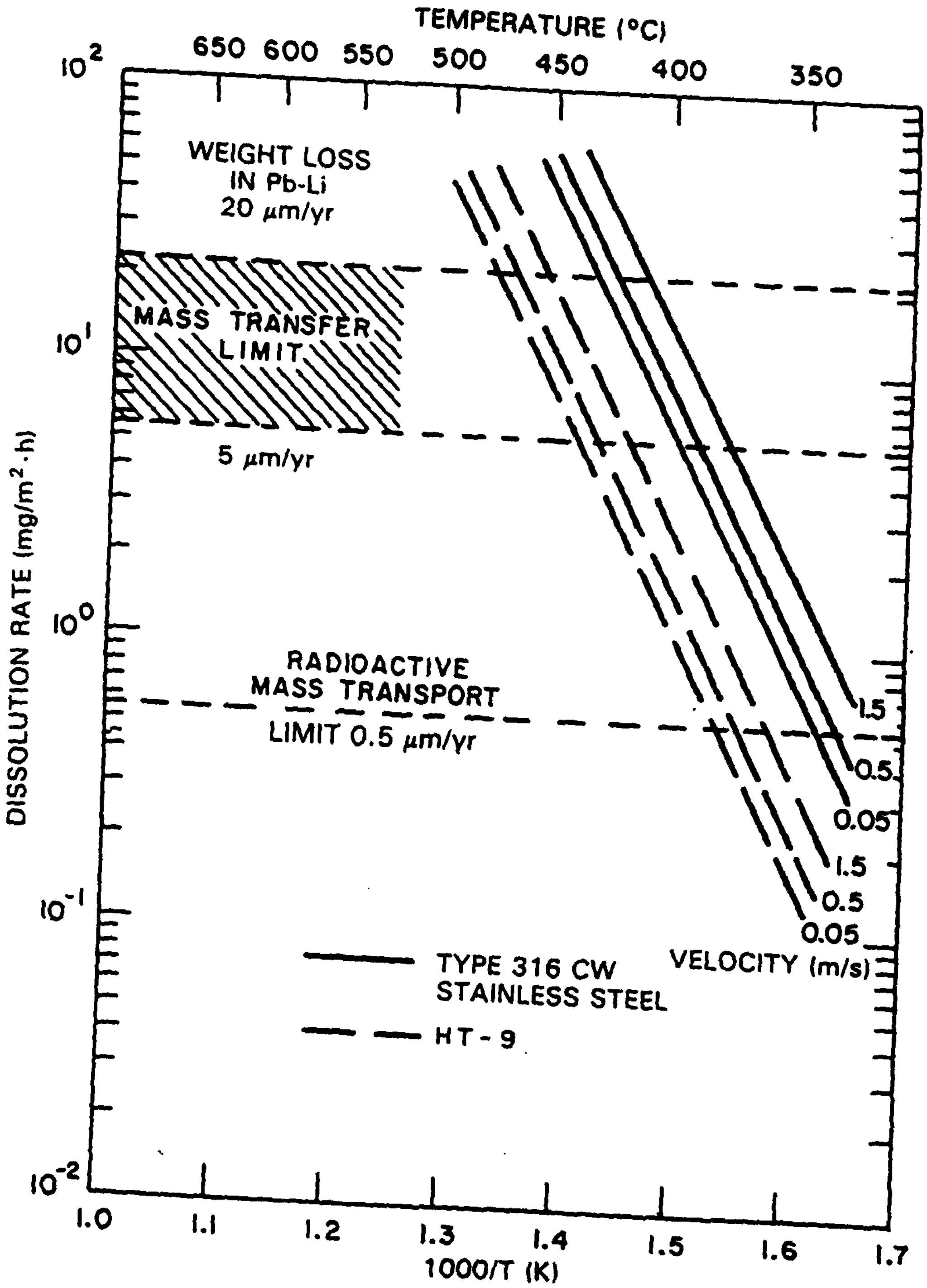


FIGURE 2 - Effect of temperature on the corrosion rate of 20% CW Type 315 stainless steel and HT-9 alloy in flowing Pb-17Li.

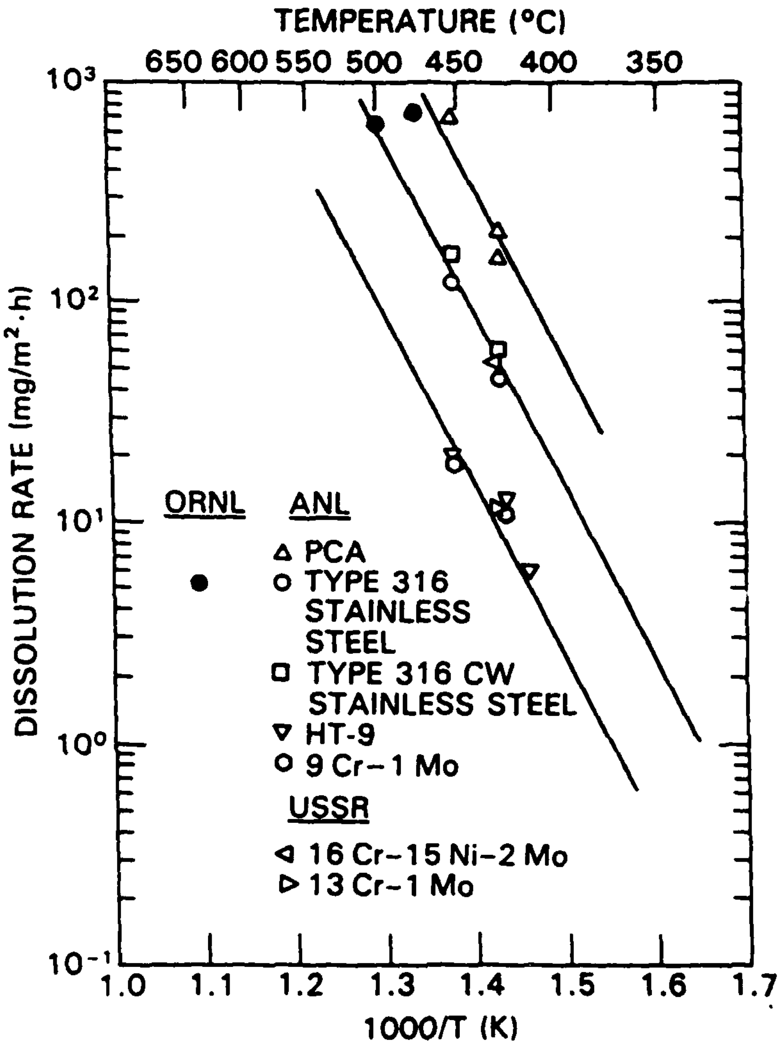


FIGURE 3 - Arrhenius plot of corrosion rate data for austenitic Type 316 stainless steel and ferritic HT-9 alloy, and Fe-9 Cr-1 Mo steel in flowing Pb-17Li. Data are normalized for V=1.5 m/s.

such as aluminum that would be better than copper, which has a relatively unstable oxide. Atmosphere controls will affect the results drastically. A sealed unit designed to transfer the available oxidation potential from that dissolved in the liquid metal to a protective surface oxide film could provide good results.

Interfacial effects are critical to passage of electrical current without localized resistive build-up or breakdown of the alloy materials involved. The appropriate constitutional diagrams are being reviewed, to find material combinations that are metallurgically relatively inactive. Reactions that can take place include alloy formation between liquid and solid metal, diffusion of elements into the solid metal, grain boundary diffusion and embrittlement, formation of intermetallic compounds, and surface complexing of mutually developed oxides or other reaction products. All these interactions, are dependent upon the material, temperature, and time, with the extra requirements of handling electrical energy. Limited solid solubilities and low diffusion rates are important requirements for a long-lived liquid and solid metal interactive system. Using low temperature liquid metal with high melting solid materials is beneficial. The high stability of oxides and carbides can also be useful in minimizing possible diffusion and reaction, providing electrical losses are not a problem.

3. LITERATURE SEARCH IN DATA BASES

3.1 General

The Metadex and Non-Ferrous Metals Abstracts databanks were searched for relevant documents. Several hundred references were located with some indication of usefulness. Some of these references were not retrieved because of overall time and cost. Also, to evaluate information adequately, further restrictive searches will be made where appropriate, when more specific needs are defined. These initial blanket search strategies have yielded data to assist in the modelling concepts and narrow the field of experimental work to areas of projected promising results.

The metals aluminum, antimony, bismuth, cadmium, indium, lead, mercury, tin, and zinc were examined for oxidation properties, surface tension and wetting, and diffusion characteristics into selected solid metals. A limited number of alloy combinations that will be included in base-line experiments were also reviewed.

3.2 Oxidation of Liquid Metals

Slight pressurization in a protective atmosphere is recommended for minimizing oxidation in articles on casting low melting non-ferrous alloys. Lithium is demonstrated to be a poor metal from an oxidation point of view. In an aluminum 3% lithium alloy, rapid air oxidation and thick friable films occur. A comment is made that the latent heat of fusion of an alloy can be important in some applications, such as start-up periods in the electrical collector. Prior solid metal oxidation can occur if protection of the atmosphere is not provided.

Liquid metal embrittlement of the solid metal is to be controlled, and this problem is covered more fully in the section on diffusion characteristics of alloy combinations. Reaction models on oxidation generally show the tremendous affinity of aluminum for oxygen. Any dissolved oxygen in solid or liquid metal would be subject to an almost instantaneous irreversible reaction from aluminum to its' oxide.

A suggestion is made that the solid metal part of the collector could be prepared by deliberate high temperature exposure in selected metals to give a diffusion coating of a desirable composition. The coating is presumably then resistant to further attack by the liquid metal medium. An example is given of a niobium alloy that is diffused with aluminum, silicon, molybdenum, chromium, and titanium, to subsequently resist oxidation and the actions of liquid lead, bismuth and tin.

Data available on liquid metal oxidation of the metals of interest was minimal in the Non-Ferrous Metals Abstracts. A book entitled "Surface Phenomena of Metals" has a limited number of useful papers that will be oftained, if possible. The only direct work was of Russian origin on the oxidation of liquid zinc. Clearly, the data banks currently do not adequately cover subject areas, and information in our library did not show up in our search. Although useful, the data bank searches cannot be considered exhaustive.

3.3 Surface Tension and Wetting

A number of references were located in Metadex, largely related to soldering of metals and consequently were often in connection with metals that were fluxed and good wetting was the objective.

Wetting of molybdenum with aluminum, carbon by aluminum and aluminum alloys, aluminum-magnesium and graphite, aluminum-nitride and titanium-carbide by liquid lead, were interesting references for which full papers are being obtained. The wetting balance equipment normally used for soldering technique evaluations has good experimental possibilities for the program. One paper demonstrates that small quantities of copper and phosphorous in liquid solders comprising tin-lead or bismuth-tin enhance the wetting process.

Work on the compatibility between carbon fiber and binary aluminum alloys showed that aluminum alloys containing small amounts of lead, indium, and titanium produced much better wetting behavior. These alloy elements have significantly lower surface energies and are practically insoluble in aluminum even in the liquid state.

A study on spreading kinetics shows that in low reaction systems the process occurs rapidly and is related to the adhesion work at the solid-liquid metal interface. Where intermediate phases occur, the process is activation energy related and directly results from chemical reaction at the liquid-solid metal interface. Wetting of lead-silver compositions on iron were investigated with a minimum surface tension at 40% silver. Iron wetting was covered in a lead-tin-silver ternary where an intermetallic had been formed with iron before test that contained iron, tin and silver, higher adhesion and better wetting was achieved with a silver-rich material of the lead-tin-silver system.

The formation of a Cu_3Sn intermetallic at the surface between copper and liquid solders can cause dewetting action. The intermetallic generally is considered to be unsolderable and may provide a stable base for electrical collection devices. The intermetallic formed on copper is known to grow faster than that formed on copper alloys with quite small elemental additions of materials such as cadmium and chromium.

Interpretation of work carried out on wetting and surface tension for soldering purposes in a reverse view could be beneficial to the program. Impurities detrimental to soldering used judiciously could provide the necessary stability of liquid-solid combinations.

Several articles appear of Russian origin in the study of surface tension and wetting of metals. One area covered is the reaction between titanium and the low melting point fusible metals. Wetting of titanium surfaces is achieved in lead, tin or bismuth at gradually increased temperatures. Minimum temperature quoted for wetting to occur is 823 K for lead, which is above anticipated temperatures to be covered on the present program. Titanium appears to be a candidate for liquid metal addition at low levels, or as a solid material provided reaction rates can be minimized.

An article in Surface Science gives some idea of relating experimentally derived surface tension values of binary systems, and those deduced from a theoretical approach. A statistical treatment is necessary to correctly describe results. French work presents some data on aluminum-indium, and aluminum-lead alloys.

Wetting of metals by lead alloys and surface properties of mercury are covered in two additional references obtained from the non-ferrous metals abstracts database.

3.4 Diffusion Between Metals

A sharp contrast in database information available on diffusion and the subjects of oxidation of liquid metals and wetting characteristics was found. Covering interrelated diffusion between metals are several hundred papers. For the purposes of the present study, an initial serach covered ten articles each on the subject with copper as the universal component and aluminum, antimony, bismuth, cadmium, indium, lead, mercury, tin, and zinc as the related diffusion couple.

Several articles on aluminum-copper suggest that copper enriches at the oxide surface of alloys of these elements and some information is available on interdiffusion coefficients for alloys, but not separately coupled metals with a diffusion boundary. Additions of titanium and vanadium increase non-equilibrium and reduce diffusion measured.

Articles on copper refining suggest that antimony and arsenic are stable additions but bismuth removal is rapid by an evaporation mechanism. Antimony provides a stronger creep resistant copper. Binary systems with solutes of silver, magnesium, antimony, indium, and tin, were studied to assess diffusion induced grain migration. No data are given in the summary reference. Antimony and copper can co-exist up to 9% in a copper-1% antimony alloy. Grain-boundary location of antimony can be expected.

Bismuth also is determined to segregate to grain-boundaries in copper. The result is embrittlement and intergranular failure at low stress levels. The problem is related to interfacial energies and stress and could lead to difficulties in rotating electrical machinery where enhanced diffusion can occur because of electromagnetic fields developed.

Cadmium and copper in contact were studied. A low melting eutectic occurs with the formation of an intermetallic compound. The reaction is exothermic and can further lower the apparent melting temperature to 305°C.

The dissolution of solids in molten metals has been studied for several systems. Mechanisms and kinetics were investigated. Unfortunately, none of the combinations of alloys or elements are directly appropriate to the present study, except to indicate that dissolution experiments could be well used as a preliminary evaluation before involving electrical current collector aspects of the program.

Diffusion into copper by indium and tin is slower than in zinc. Small amounts of additive elements were made to study softening and electrical resistance characteristics of pure copper. Indium, lead, tin, and antimony were effective at 200 ppm. Large atomic radii and lower diffusion coefficient are preferable for good results.

Work on metal-metal oxide films can give clues to the most useful metal couples and oxidation characteristics. The natural tendency for metal oxides to reduce diffusion can be utilized if localized resistive effects are not detrimental to the overall system. Materials prepared by sputtering of metal in the presence of active oxygen show a progression from agglomerated columnar-granular and amorphous to the full oxide. Oxide structures and their restriction of elemental diffusion of liquid metal components are seen as a very important aspect of the proposed experimental work on electrical collector systems.

A nickel sub-layer can be completely effective in suppressing the diffusion of tin into copper, provided that it has adequate thickness and that the temperature is not too high. A study indicated that 130-170°C is needed to begin development of copper-tin intermetallics with a nickel barrier present. Ni_3Sn becomes a real problem above 170°C.

A recent book on the liquid metal embrittlement of metals and alloys will be obtained to evaluate the proposed liquid metal/solid metal combinations from this aspect. The United Kingdom Department of Industry commissioned the compilation as a guide to plant engineers after a chemical plant failure in 1974, it is understood that both ferrous and non-ferrous metals are covered.

Copper-indium couples have been used to study the theory of diffusion between solid and liquid metals. Diffusion annealing was carried out in the 200-500°C region. Phases developed were correlated with the copper-indium diagram.

A book on diffusion processes was retrieved from the non-ferrous metals database, but tended to be rather theoretical. A paper on diffusion under mechanical stress, however, may be useful to us. Grain boundary grooving and diffusion processes are covered in another reference.

The effect of relative rotation speed, temperature, and time on copper dissolution in liquid tin was recently investigated. Copper dissolution increases with all factors. An activation energy of four K cal/mol was derived from the work. An increase in the amount of copper in the tin does slow down the reaction rate.

Diffusion characteristics of the copper-zinc couple and the intermetallic compound formation between these elements suggests that zinc is not likely to be as good a candidate as a liquid metal component in the copper or copper alloy solid situation.

Copper is a face centered cubic metal with a density of 8.96 and an atomic weight of 63.54, and represents a group I element. Molybdenum is a body centered cubic metal with a density of 10.2 and atomic weight of 95.95, representing the group VI elements. Reports are that lead, for example, is very limited in solubility and reaction with the Group V and VI elements, such as molybdenum.

Diffusion properties of molybdenum in conjunction with the candidate liquid metals were reviewed in the Metadex and Non-Ferrous metals abstracts databases.

A plasma-sputtered coating of molybdenum was found to be protective of an underlying iron-based alloy in the presence of liquid bismuth, and liquid tin, over a wide range of temperatures from work in the 380-560°C range. Obviously, below that temperature, conditions should be even more favorable to success. The system also appeared to work satisfactorily under a state of stress in the coating surfaces. Surface diffused layers of selected resistant elements on other candidate solid metals and alloys is a feasible approach to electrical collectors. A titanium nitride used for dispersion hardening was found to be highly resistant to diffusion in a molybdenum matrix. It should also be possible to develop molybdenum materials with a rich carbide surface layer in addition to nitrides. These aspects may require fabrication of specially made alloys for the purpose. Very little directly applicable data was retrieved.

Development of literature search strategies more specifically related to the program tend to result in limited, or no articles being recovered from the databases and wider strategies bring up some additional data, but at the expense of many articles and papers of no direct relevance. Further work in the area will assist in definition of the background characteristics of alloys and metals that impact on the development of suitable electrical collector systems. The experimental work combined with the literature searches is expected to yield practical results and directions to proceed.

The very large number of references with diffusion between metals makes the database search more challenging in finding most appropriate articles for the present program. A search strategy was devised to eliminate references involving steels, and then a further restriction was added to include articles with liquid metal references only. Search results are summarized in the appendix for tungsten and nickel. More data is available on nickel than tungsten where no liquid metal couple information was gleaned.

Most of the data available on tungsten coupled to the liquid metals of interest, is related to thick film growth characteristics of vapor deposited materials. An article on surface diffusion of lead in tungsten was unfortunately not practical for our purposes. Thermal conductance at metal interfaces, including copper-tin, copper-lead, and copper-chromium were measured in the presence of magnetic fields. A linear temperature dependence was found in each case. There is a known reaction between tungsten and nickel in tungsten fibre reinforced nickel composites, titanium carbide, and nitride coatings can be used successfully to restrict reaction.

Tin is found to diffuse into nickel at temperatures below 250°C. Long-term embrittlement of the solid electrodes by the respective liquid metals will be a concern for potentially commercial electrical collectors. Liquid mercury was found to cause intergranular embrittlement of a copper-nickel alloy. When candidate materials have been evaluated by other parameters, some experimental work, of possible liquid metal embrittlement factors will be necessary. A book by Nicholes, published through ASME will be obtained to review available data. Work has been carried out in England at the University of Sheffield by Coppleman, G.R. on the dissolution of solids in molten metals, characteristics of several coupled systems have been identified. Operative mechanisms of dissolution have been utilized in many products, however, a study shows that the nickel only slows down diffusion, and the barriers are eventually destroyed, especially above 170°C. Additions of iron, nickel, or tin to a copper alloy can be used to slow diffusion rates with solders. Intermetallic compounds are still formed, that contain some concentration of the added elements resulting in voids. Depending upon the life cycle of a collector, the approach may be useful in some instances, but clearly will result in changes in the liquid metal and gradual disintegration of the system over time. Essentially liquid metals containing tin will be effectively unstable in contact with copper or copper alloys in the temperature range required. The effects are expected to be similar, but at a slower rate when nickel and alloys containing tin are exposed together. Several articles indirectly indicate that liquid indium alloys would diffuse readily into a nickel electrode material. Concerns with the effect of small quantities of a diffusing species on the properties of an alloy or metal has resulted in extensive research in this area, but is not directly applicable at the exploratory stage of this program. The continuing literature search to assist in narrowing the experimental program to those combinations with some chance of success, is revealing the very specific nature of any resulting liquid metal alloy, and electrode combination that is a likely candidate for electrical collection devices. Some experimental work has been done with copper and nickel electrodes with tin and indium bearing solders and results are examined in a later section. Better achievements are suggested with lead-bismuth alloy as the liquid with copper and nickel. There is insufficient data in the literature to indicate so far, that tungsten and molybdenum will develop problems as electrodes with any of the liquid metals being studied.

4. GRAPHICAL DATA ON IMPORTANT PARAMETERS

Reviewing the literature, several graphs were located on oxidation, surface tension, viscosity, dissolution, and intermetallic compound formation. The information given is important in trend as well as specific facts to allowing the development of both a logical modelling of electrical collector requirements, and the experimental studies.

Oxidation of aluminum is presented in Figure 4, showing the effect of alloying additions that generally increase oxidation. The effect of alloying additions on the oxidation of liquid tin at a relatively high temperature is given in Figure 5. A tin-lead solder was stirred under standard conditions to produce a composite temperature and time effect on oxidation as shown in Figure 6. Additional work by the same author also gave results on the effect of speed, but was greatly affected by the chosen experimental conditions. The oxidation of liquid lead with various alloying additions is illustrated in bar chart form in Figure 7. A lead-antimony curve is shown to have a minimum for weight gain at 0.5% antimony in lead as in Figure 8.

Surface tension is found to depend significantly on the atomic volume of the metal concerned as shown in Figure 9. Amalgams of mercury with various elements is presented in Figure 1 for surface tension versus percentage addition. Very small amounts appear to have a large effect if any differences of major import are to be obtained. Viscosity relationships are covered in Figures 10 through 12. Again, an atomic volume dependency is

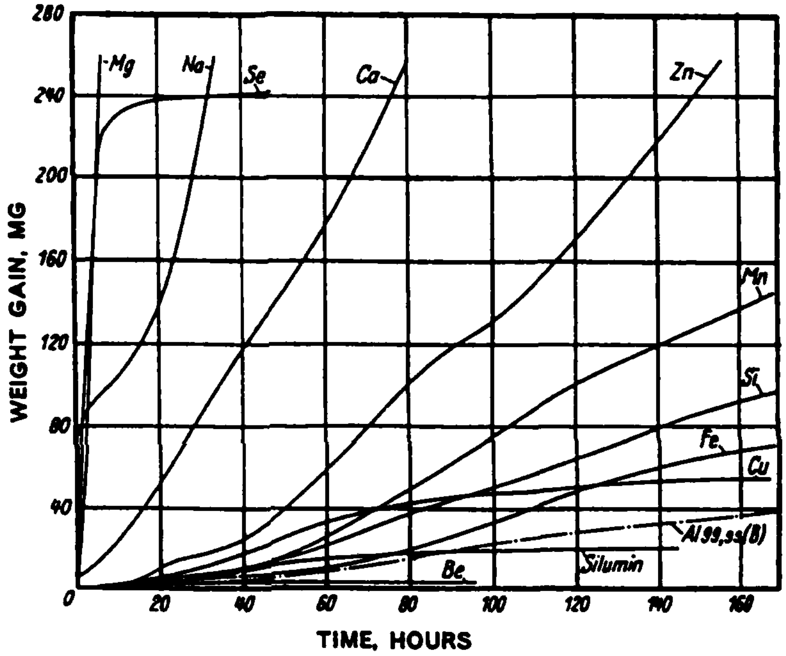


FIGURE 4 - Effect of 1 at.-% alloying additions on the oxidation of aluminum at 800°C. Surface area 8·5 cm^2.

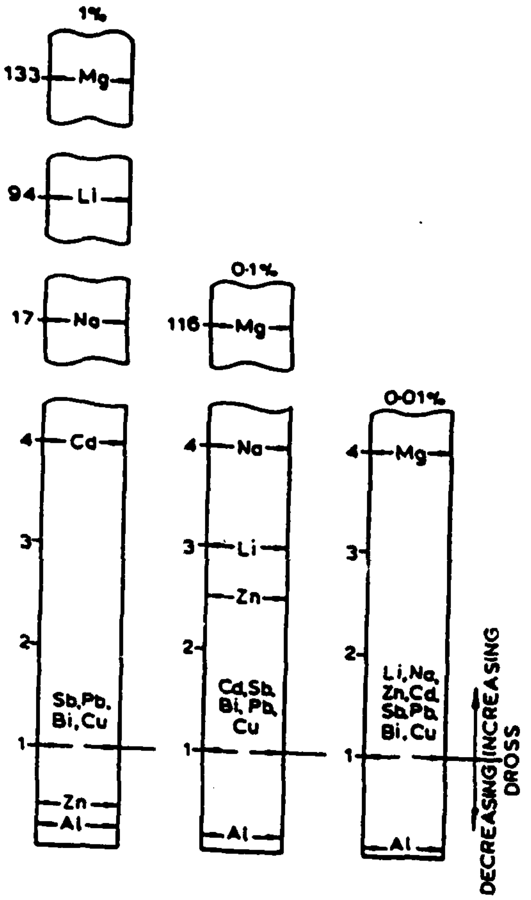


FIGURE 5 - Effect of alloying additions on the oxidation of liquid tin at 425°C.

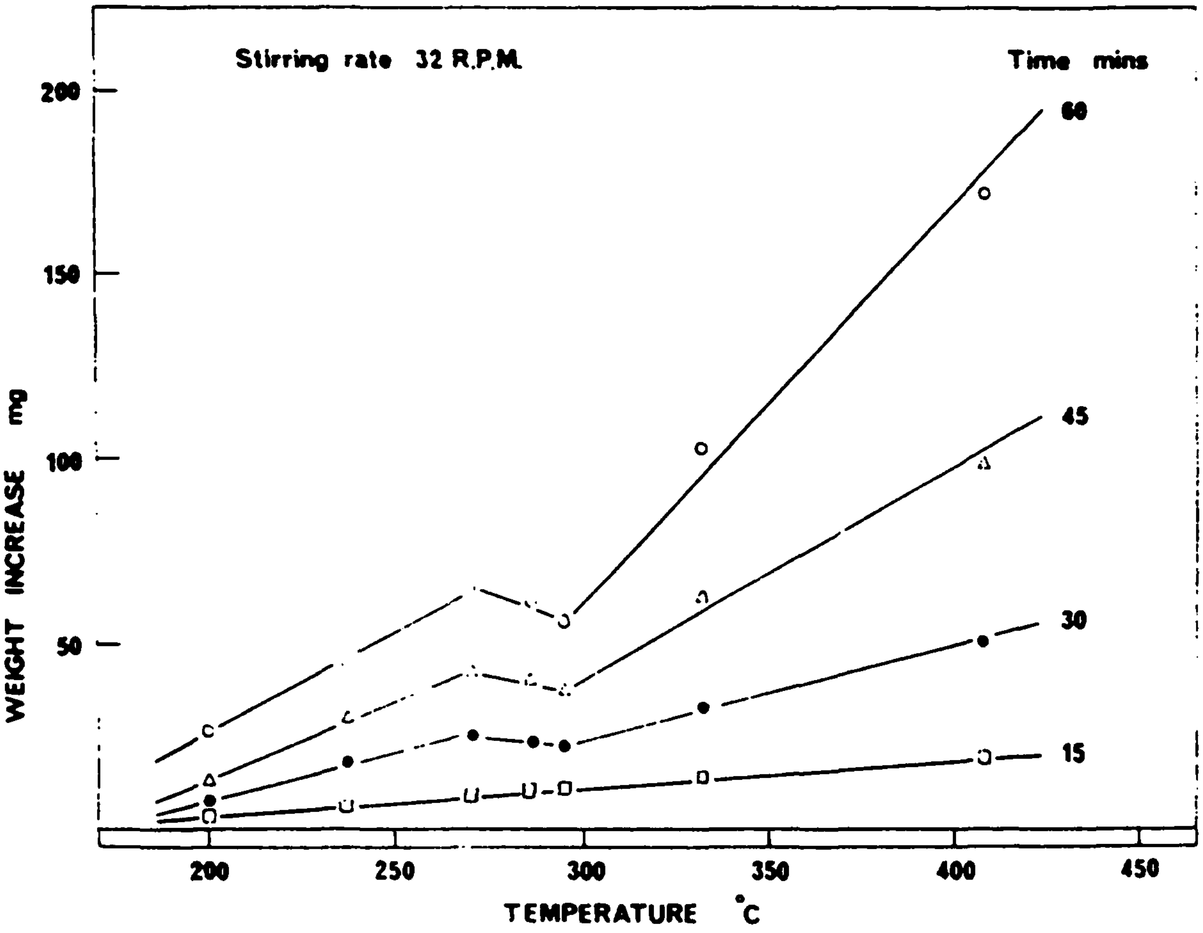


FIGURE 6 - Effect of temperature on oxidation of 60% tin-40% lead under standard stirring conditions.

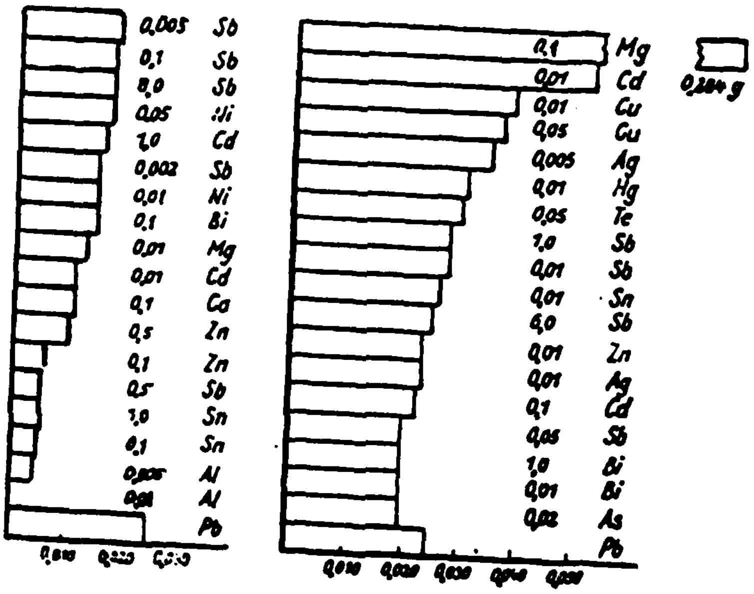


FIGURE 7 - Effect of alloying additions on the oxidation of liquid lead in a 2-h test at 520°C.

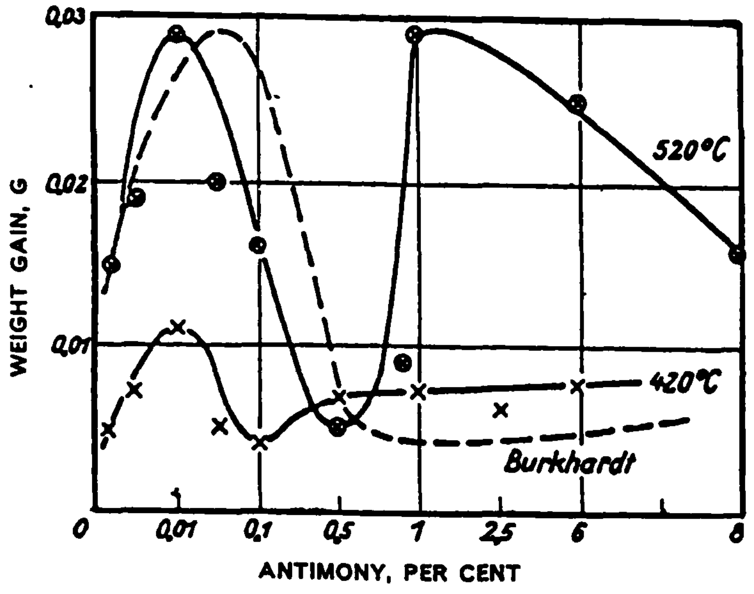


FIGURE 8- Oxidation of lead-antimony baths in 2-h tests at 420 and 520°C. The dotted curve shows the results of Burkhardt on agitated baths.

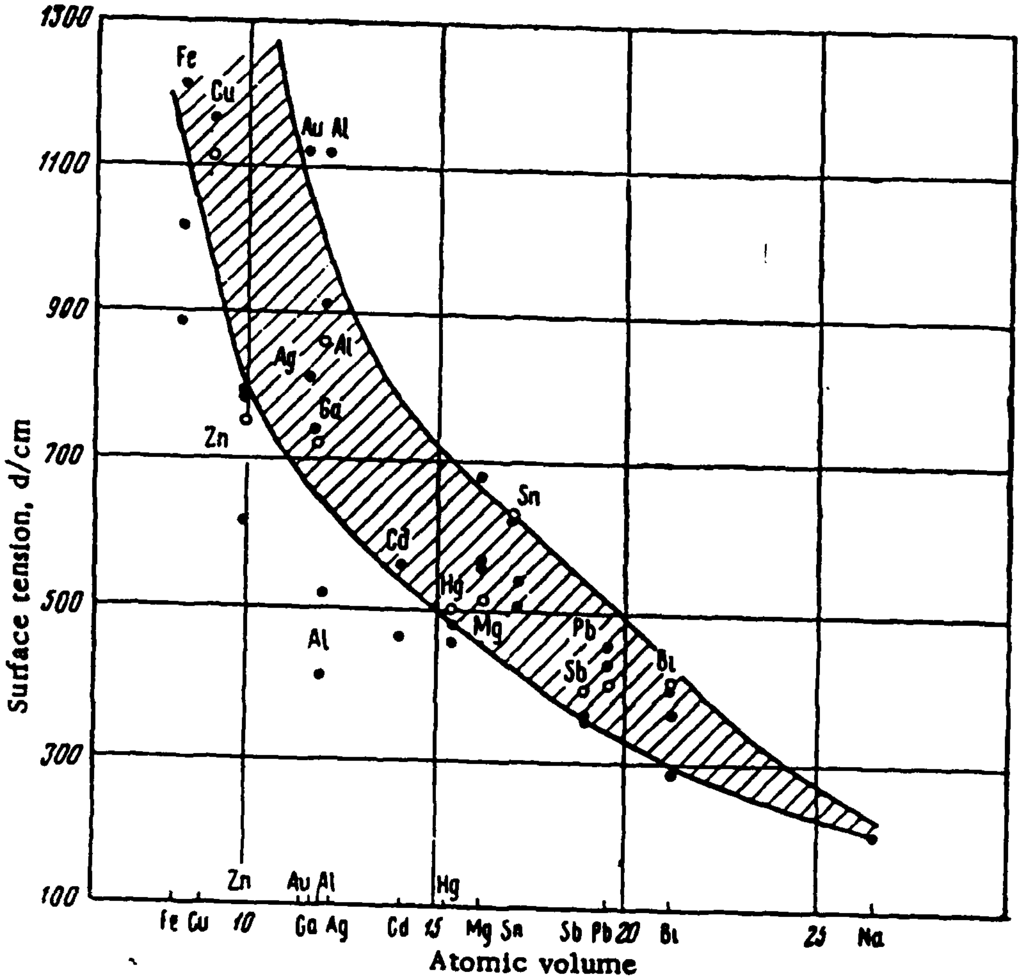


FIGURE 9 - Dependence of surface tension of liquid metals on their atomic volume: Data of various authors; O experimental data of our laboratory.

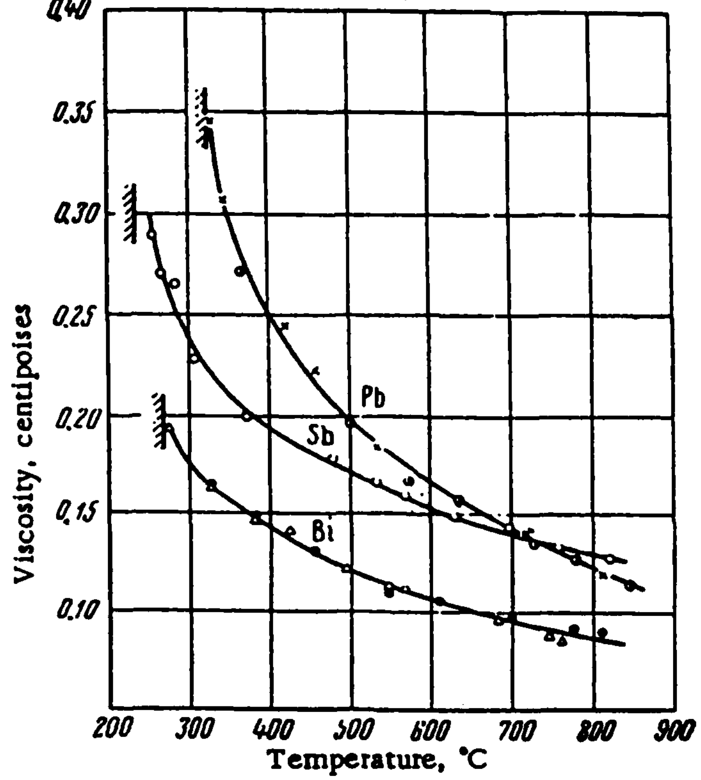


FIGURE 10- Temperature dependence of the viscosity of lead, tin and bismuth.

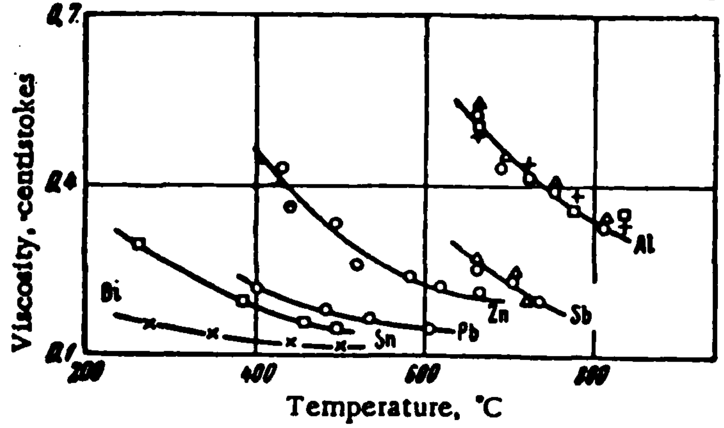


FIGURE 11 - Dependence of viscosity of lead, tin and bismuth.

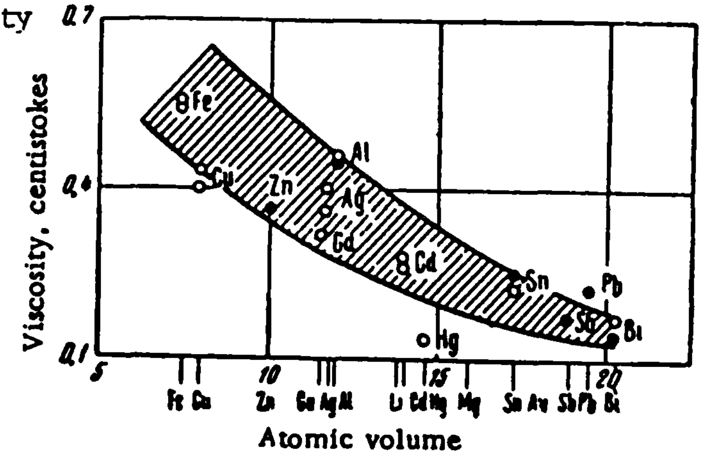


FIGURE 12 - Relationship between viscosity of pure metals and their atomic volume.

observed with generally decreased viscosities in liquid metals with increases in temperature.

Arrhenius plots of different stainless steels showing dissolution effects in flowing lead-17 lithium illustrates a method of presenting the results of experimental work where the relationship holds. Figure 3 indicates better results with ferritic than austenitic steel. Similar graphing approaches will be used if appropriate to interpretation of the experimental studies.

Intermetallic compound formation between the liquid metal and solid metal components will occur where the binary constitution diagram expresses these formations. However, thickness and growth will depend upon each conjoint metal complex. Copper-tin is known to exhibit this effect by creating Cu_3Sn and Cu_6Sn_5 at the interface. General intermetallic growth rates are presented in Figure 13.

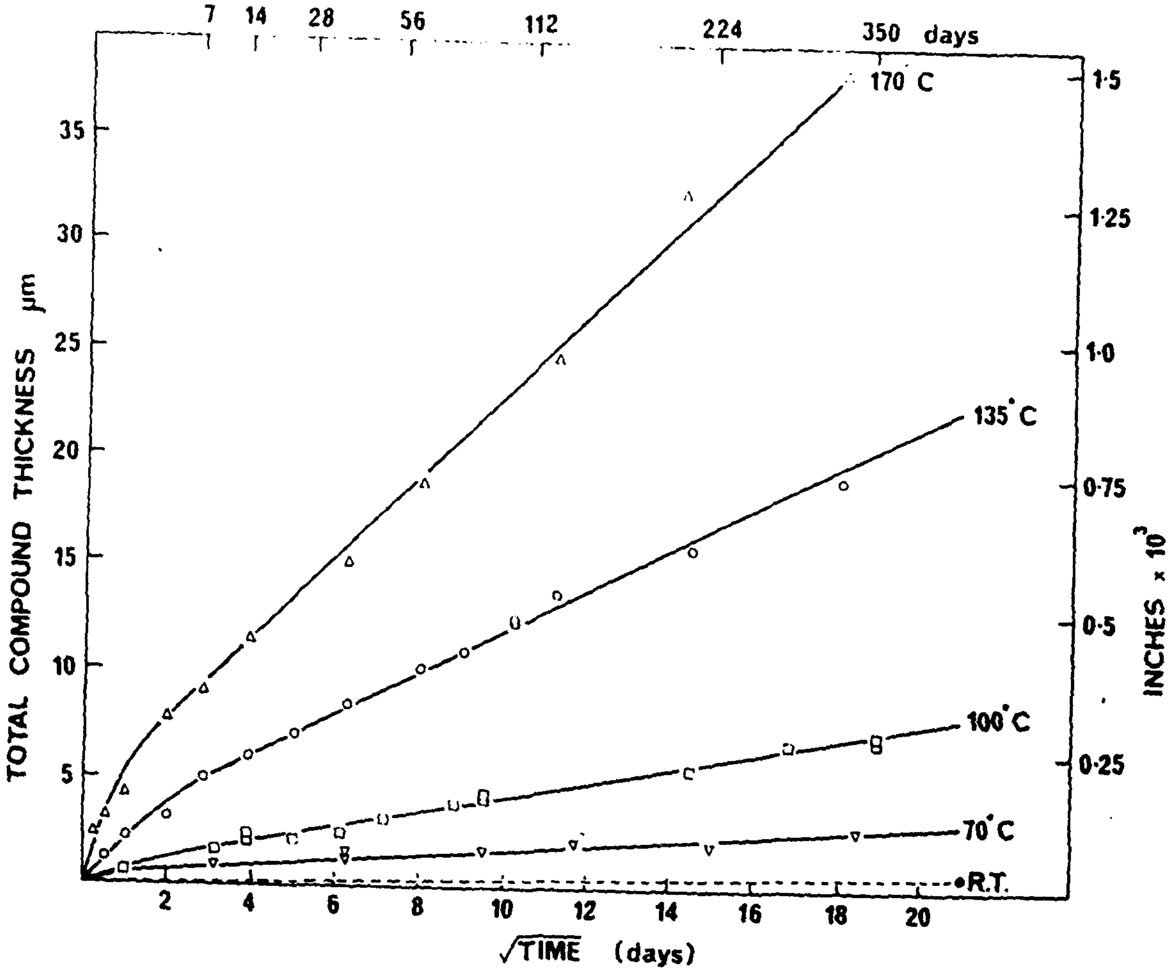


FIGURE 13 - Curves showing rate of growth of layers of intermetallic compound between a 60% tin-40% lead coating and copper at various temperatures.

5. WORK PROGRAM

Electrical conductivities of solid metal and liquid metal materials being considered as candidates for the experimental program are presented in Tables 1 and 2. Nine solid materials and twelve elements that may be used in the liquid metals are included. The list is intended to show direction at this time and not exclude potential materials that may become desirable to use as the work proceeds. For the solid metals, a generally high conductivity level was considered important, although two lower conductivity materials that have other good properties are included. The liquid metal components are limited by the necessarily controlled temperature range in which it is hoped to operate the collector system. Presently, a maximum temperature of 500°F has been arbitrarily set for the collector system. Generally, the conductivities measured in metals for the liquid part of the couple are lower except for silver and aluminum. Mercury, lead, antimony, and especially bismuth show relatively low conductivities. Silver, aluminum, tin and indium have higher conductivities and appear to have other properties useful to collector liquid metals.

Several standard solder alloys are included in the possible alloy selection for the liquid metal and were abstracted from Kohl[4]. Additional alloys that will be used in initial experimental work were obtained from the standard fusible alloy list. These alloys will effectively provide the baseline data on which we can

TABLE 1

ELECTRICAL CONDUCTIVITIES OF CANDIDATE SOLID METAL PARTS

ELEMENT	MICROMHOS	%IACS
Aluminum	0.372	64
Cobalt	0.160	28
Copper	0.580	100
Molybdenum	0.190	33
Nickel	0.146	25
Silver	0.629	108
Tungsten	0.177	31
Titanium Diboride	0.067	12
Graphite	0.003	> 1
SOLDERS		
117 Alloy	-----	3+
136 Alloy	-----	3
158 Alloy	-----	4
160/190 Alloy	-----	4+

TABLE 2

ELECTRICAL CONDUCTIVITIES OF CANDIDATE LIQUID METAL COMPONENTS

ELEMENT	MICROMHOS	% IACS
Aluminum	0.372	64
Antimony	0.026	4
Bismuth	0.0094	>1
Cadmium	0.146	25
Indium	0.120	21
Lead	0.048	8
Mercury	0.0102	2
Nickel	0.146	25
Silver	0.629	108
Tin	0.091	16
Titanium	0.018	3
Zinc	0.169	29
SOLDERS		
117 Alloy	---	3+
136 Alloy	---	3
158 Alloy	---	4
160-190 Alloy	---	4+

build the effectiveness of other elemental additions, such as aluminum, silver, titanium, and nickel, etc. Commonly available alloys are presented in Table 2. Anticipated requirements at the solid-liquid metal interface are listed in Table 3 as a guideline to materials selection.

TABLE 3

ANTICIPATED REQUIREMENTS AT THE INTERFACE

METALLURGICAL FEATURE	PREFERRED CONDITION
Oxidation	Low
S/L Surface Tension	High
Dissolution	Low
Elemental Reaction	Low
Viscosity	Low
S/V Solid Surface Energy	Low
Diffusion	Low
Solid Solubility	Low

*Spreading Coefficient

$$S_{LS} = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$$

6. EXPERIMENTAL WORK

6.1 Apparatus Test equipment in use is presented in Figure 14. A resistance furnace is provided for the heat supply to the collector rings. Power feed throughs are placed beneath the furnace for attachment of welding power unit current supply. Tungsten rods were chosen as the material for electrical connection with the liquid metal in the trough for the initial test series. The collector rings are machined from a dense insulating material and assembled as shown in Figure 14(b). The test electrode materials are 1/4" diameter rods that extend from the upper collector cover into the liquid metal bath. The liquid metal is contained in two concentric rings so that current can be easily passed without slip rings. The collector device is rotated using a D.C. drive motor with infinite speed control up to full motor speed. The furnace bottom is sealed with refractory cement to facilitate argon gas protection during the experiments. Temperature control of the furnace is maintained to the desired temperature, speed of rotation is monitored, current passage is measured, and temperature of the liquid metal is monitored by a glass encased thermocouple inserted in the outer trough. The unit is constructed to turn off in the event of metal loss, current surges, arcing, or failure of the motor to rotate properly. The equipment has proved satisfactory to evaluate some test conditions in a preliminary manner, and will continue to be used throughout the program for the shorter test period material evaluations. Liquid metal oxidation has been revealed as the predominant problem in demonstrating that the liquid metal electrical collector at 200°F is feasible.

A pressurized argon collector was fabricated to provide superior atmosphere protection for collector operation and is shown in Figure 14(c). A feed through device was included for motor rotation and the unit is essentially a closed environment so that gas quality and atmosphere protection can be ensured. Similar assembly and measurement procedures were used with the new system.

6.2 Collector Experiments

Forty-nine experimental runs have been executed during the program. Details are presented in Table 4. Trials were carried out in the apparatus shown in Figure 14. Initially, the equipment was set up to provide a temperature of 200°F, a speed of 250 r.p.m., a current load nominally set at 50 amps, and the test was run in air using an aluminum electrode and 136 alloy liquid metal. This initial test ran for approximately six hours, before the liquid metal turned to a viscous material and the test was stopped. A second run was prepared with liquid Alloy 158 under similar conditions except that the current load was reduced to 30 amps. This test ran for eight and a half hours before an arcing condition occurred between the liquid alloy and the electrode made of aluminum. It was clear from these two preliminary

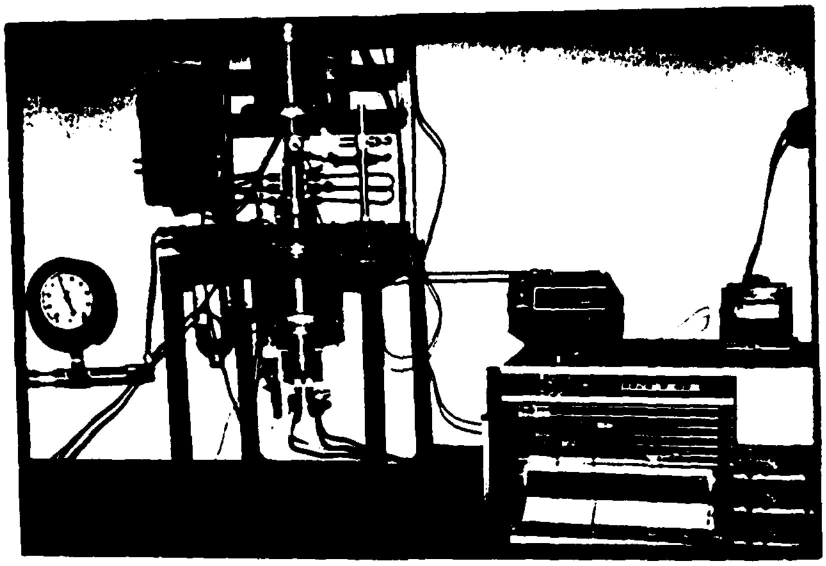


Figure 14(a) - Overall test equipment.

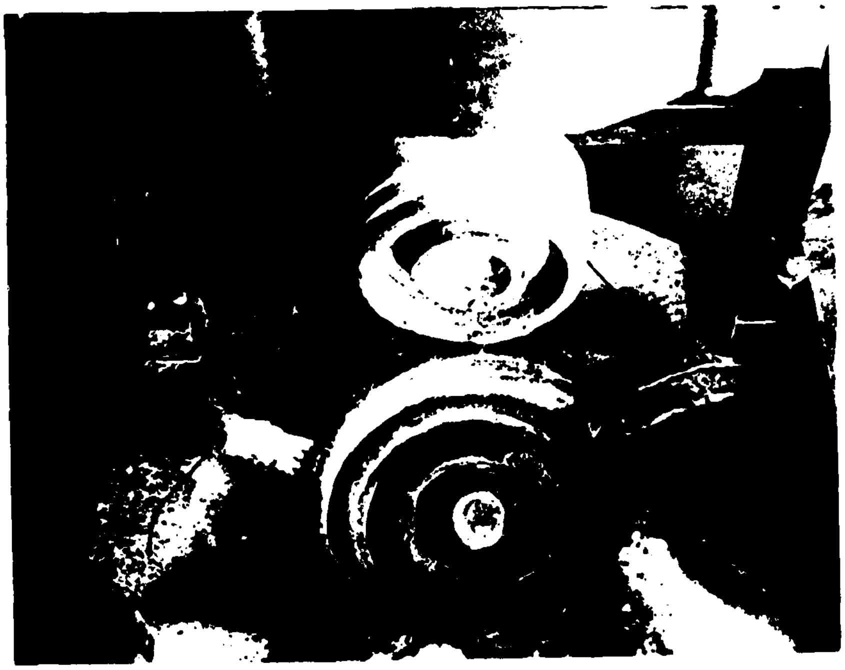


Figure 14(b) - Collector system.

FIGURE 14 - Experimental collector apparatus.

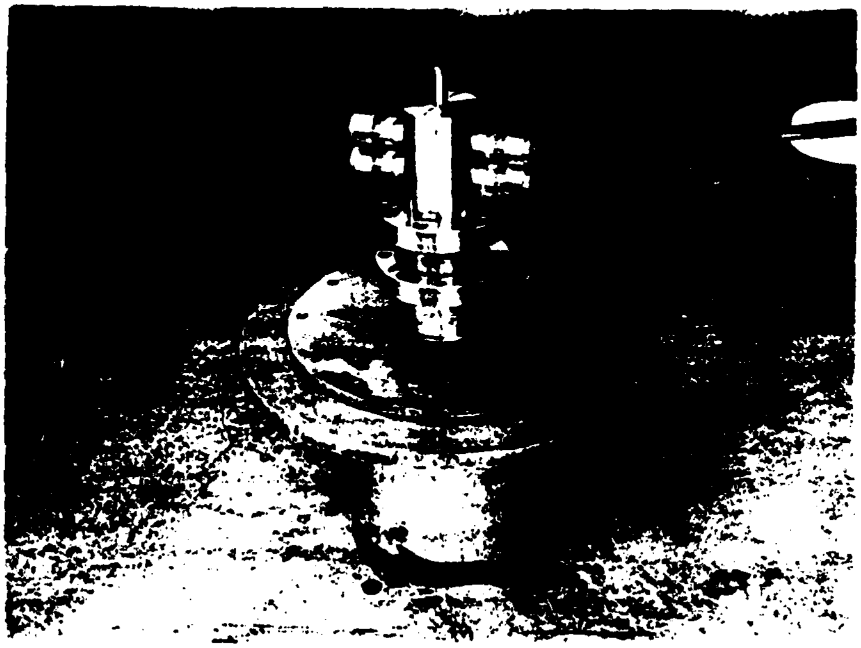


Figure 14(c) - Totally enclosed collector with water cooled feed through.

FIGURE 14 - Experimental collector apparatus.

TABLE 4

EXPERIMENTAL COLLECTOR TESTS

SPECIMEN NUMBER	ELECTRODE MATERIAL	CONDITION AFTER TEST	LIQUID ALLOY	TEST TEMP. °F	SPEED R.P.M.	GAS PROTECTION	CURRENT LOAD AMP.	TIME HRS.
1	Al	V	136	200	250	None	50	6
2	Al	Arc	158	200	250	None	30	8½
3	Al	Poor Contact	255	400	250	S. Argon	20	--
4	Co	V	136	200	325	S. Argon	30	9 1/4
5	Co	P	281	400	250	Argon	30	7
6	Mo	V	136	200	250	Argon	30	5
7	Ag	V	136	200	250	Better Argon	30	1
8	Cu/G	V	136	200	250	" "	30	2½
9	Ag	P	255	400	250	" "	30	9½
10	Cu	V	136	200	250	" "	30	10+
11	W	V/P	136	200	250	" "	None	10+
12	W	V	136	200	250	" "	30	10+
13	Cu	L	136	200	31	" "	30	10+
14	Ni	L	136	200	23	" "	30	10+
15	Cu	L	136	200	25	Argon	30	1+
16	W	L/V	136	200	250	Air	30	1+
17	Ag	L	158	200	25	Argon	30	1+
18	Cu	L	158	200	25	"	30	1+
19	Ni	L	158	200	25	"	30	1+
20	Cu	L	117	200	25	"	30	1+

EXPERIMENTAL COLLECTOR TESTS (continued)

SPECIMEN NUMBER	ELECTRODE MATERIAL	CONDITION AFTER TEST	LIQUID ALLOY	TEST TEMP. °F	SPEED R.P.M.	GAS PROTECTION	CURRENT LOAD AMP.	TIME HRS.
21	Ag	L	117	200	25	Argon	30	1+
22	W	L	117	200	25	"	30	1+
23	W	L	136	200	25	"	30	1+
24	W	L	158	200	25	"	30	1+
25	W	L/V	136	200	25	"	30	10+
26	W	L	158	200	25	"	90	1+
27	W	L	158	200	100	"	30	1+
28	W	L/V	158	200	100	"	30	10+
29	W	L	158	200	25	"	200	1+
30	Cu	L	158	200	25	"	200	1+
31	Cu	L	158	200	25	"	90	1+
32	Cu	L/V	158	200	100	"	30	10+

EXPERIMENTAL COLLECTOR TESTS

SPECIMEN NO.	ELECTRODE MATERIAL	CONDITION AFTER TEST	LIQUID ALLOY	TEST TEMP. °F	SPEED R.P.M.	GAS PROTECTION	CURRENT LOAD AMP.	TIME HOURS
33	copper	L/V	117	200	100	Argon	30	10+
34	copper	L	158	200	25	"	"	10
35	tungsten	L/V	117	200	100	"	"	10
36	tungsten	L/V	136	200	25	"	"	74
37	tungsten	L/V	158	200	25	"	"	96
38	tungsten	L/V	255	400	25	"	"	63
39	tungsten	L/V	99%Sn-1%Al	500	25	"	"	2
40	tungsten	P	136	200	250	Pressurized Argon	"	95
41	tungsten	V	136 + ½%Ag	200	25	Argon	"	108
42	tungsten	P	255	400	25	Pressurized Argon	"	192
43	tungsten	V	50%Sn-50%In	350	25	Argon	"	139
44	tungsten	L/V	Sn/In + 3%Ag	450	25	"	"	52
45	tungsten	V	95%In-3%Ag	350	25	"	"	45
46	tungsten	P/V	136 + ½%Ag	200	250	Pressurized Argon	"	231
47	tungsten	P/V	96%Sn-4%Ag	500	25	Argon	"	96
48	tungsten	P/L	55%Bi-45%Sn	400	25	"	"	45
49	tungsten	L/V	50%Sn-50%In	350	250	Pressurized Argon	"	700+

L = Liquid
P = Powder
V = Viscous

tests that some argon gas protection would be necessary to effectively carry out a test program. The furnace was sealed, and argon gas fed in through a tube and test number three was run. Here, the liquid alloy used was 255, the test temperature 400°F, at the same speed of 250 r.p.m. The graphs monitoring the program suggested poor contact between the liquid alloy and the aluminum electrode, and an examination of the test cell showed that all the liquid metal had turned to a powder. The collector system is shown in Figure 14(b).

Other preliminary tests were run with cobalt as electrode material, using Alloys 136 and 281 for liquid metal collectors. Argon gas protection was provided in both these tests, and the collectors ran for several hours before indications of a deteriorating condition occurred. Test number four when opened up revealed a viscous liquid alloy condition, as shown in Figure 15(a), and test number five had turned into a black powder, as shown in Figure 15(b).

Molybdenum, silver, and copper impregnated graphite electrodes were used in the next three tests, all with liquid metal Alloy 136, at a test temperature of 235°F and speed of 250 r.p.m. A current of 30 amps was utilized with argon gas coverage. All three tests resulted in a viscous condition of the liquid metal alloy after times varying between one and five hours. Indications were that the silver electrodes reacted rather quickly with the environment of liquid metal.

Figure 15(a) - Viscous 136 alloy after 9½ hours.

Figure 15(b) - Powdered 281 alloy after 7 hours.

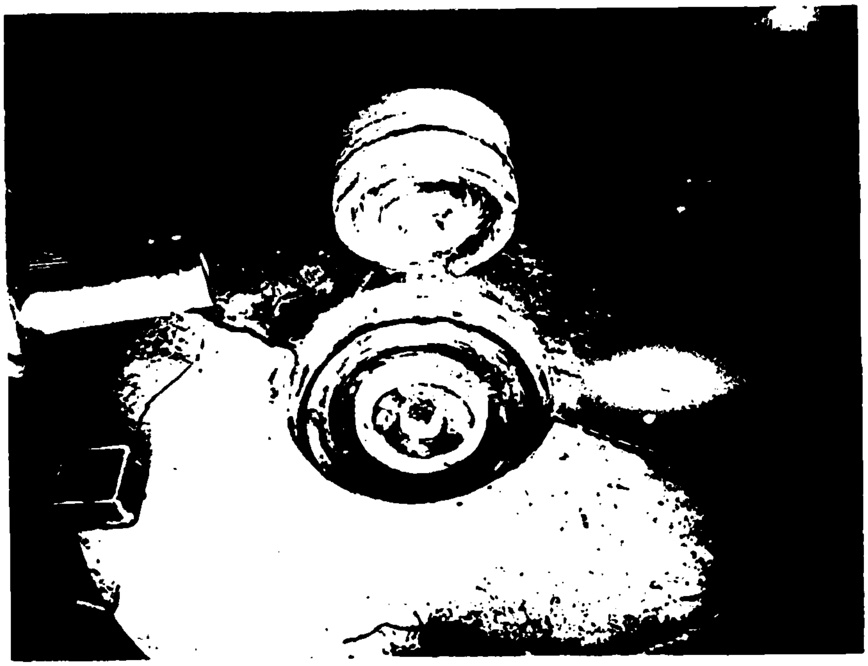
FIGURE 15 - Cobalt electrodes and two liquid metals.

Visual condition of these three tests is presented in Figure 16, showing instability in the liquid metal under all three electrode exposure conditions.

In order to obtain a feel for the range of conditions which may produce satisfactory collection, an attempt was made to expose a liquid Alloy 255 with a silver electrode at 400°F. The result is shown in Figure 17, where the alloy liquid metal completely turned to powder by oxidation, even though very good argon protection was being provided at the time. A load of 30 amps current, and a speed of 250 r.p.m. was being used. The test did last for nine and a half hours before complete deterioration of the liquid metal.

Copper and tungsten were next tried as electrode materials, with liquid Alloy 136 at 250 r.p.m. and 250°F, with the first successful test run of 10 hours although the liquid alloy metal in these tests also became viscous in test runs 10 and 12, and where argon gas was used to give good protection against oxidation. Test 11 was run without current and produced some powder in addition to the viscous alloy condition. Visual condition of these tests are presented in Figure 18.

Now that a good number of tests have been run with various electrode materials and liquid metal alloys, at two test temperatures, it was clear that the speed of revolution causing oxidation of the liquid metal was overwhelming any other influence that the test conditions were providing for electrical collection. Essentially, although good argon protection was provided,



mag. 2.2x

Figure 16(a) - Molybdenum electrode tested for five hours.

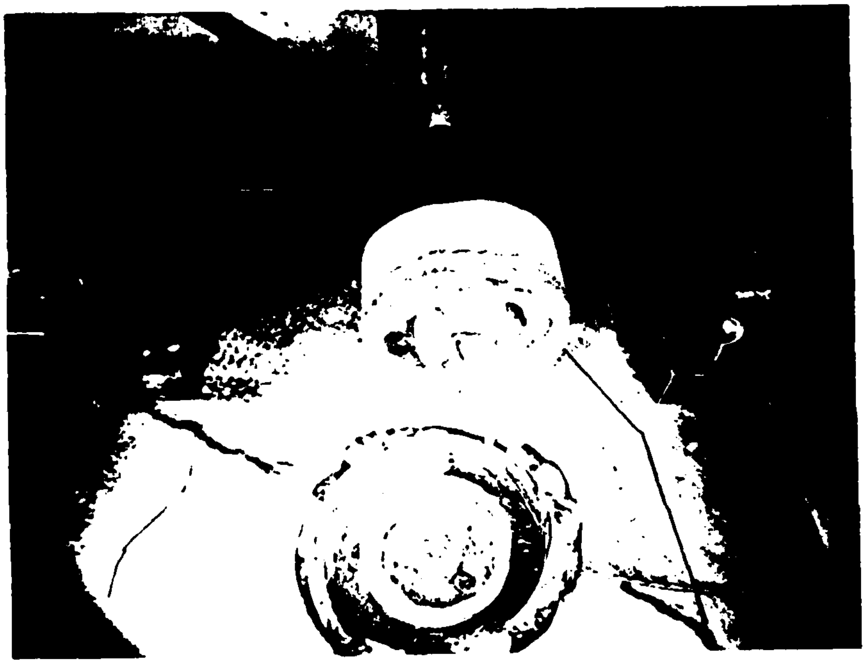


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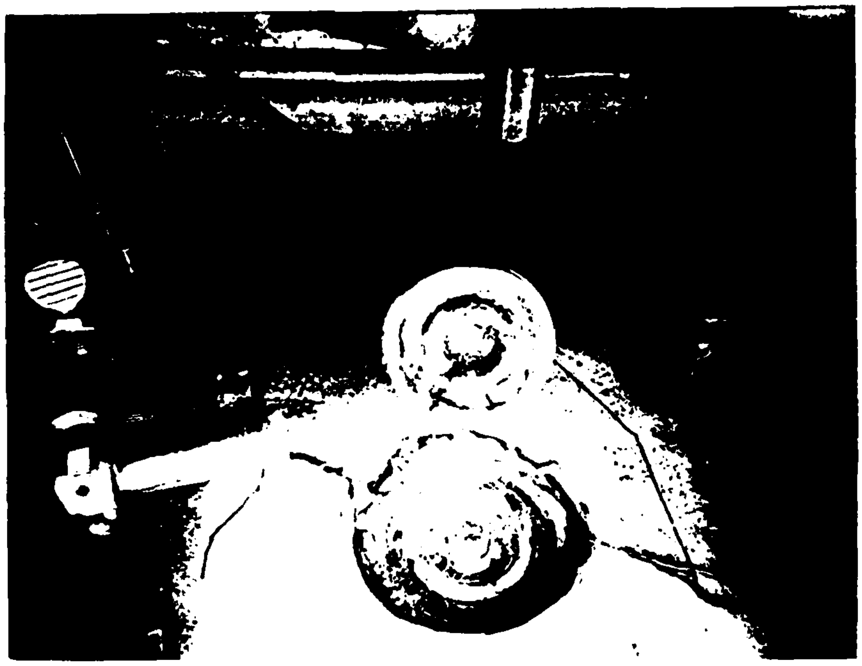
Figure 16(b) - Silver electrode tested for one hour.

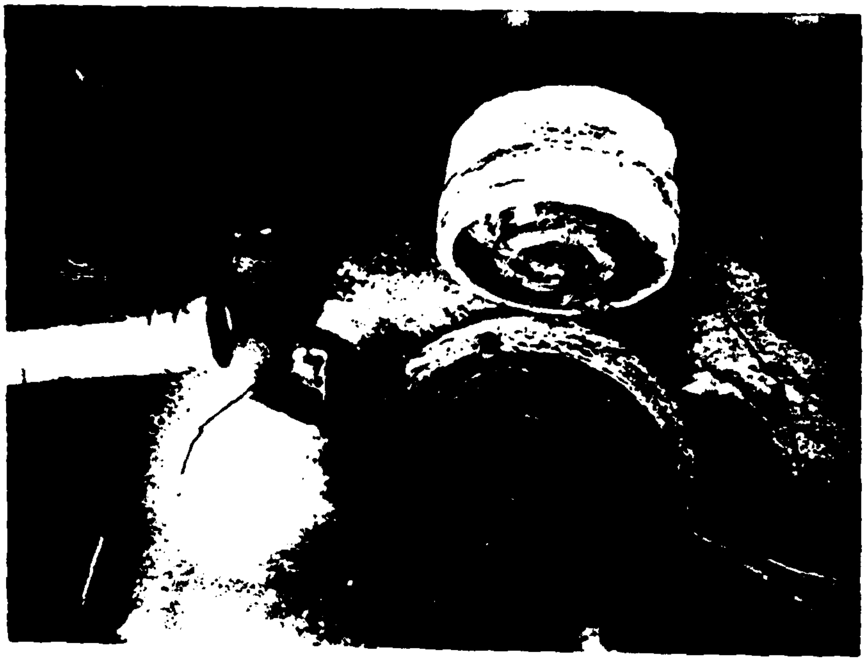
FIGURE 16 - Three electrode materials with Alloy 136.



mag. [illegible]

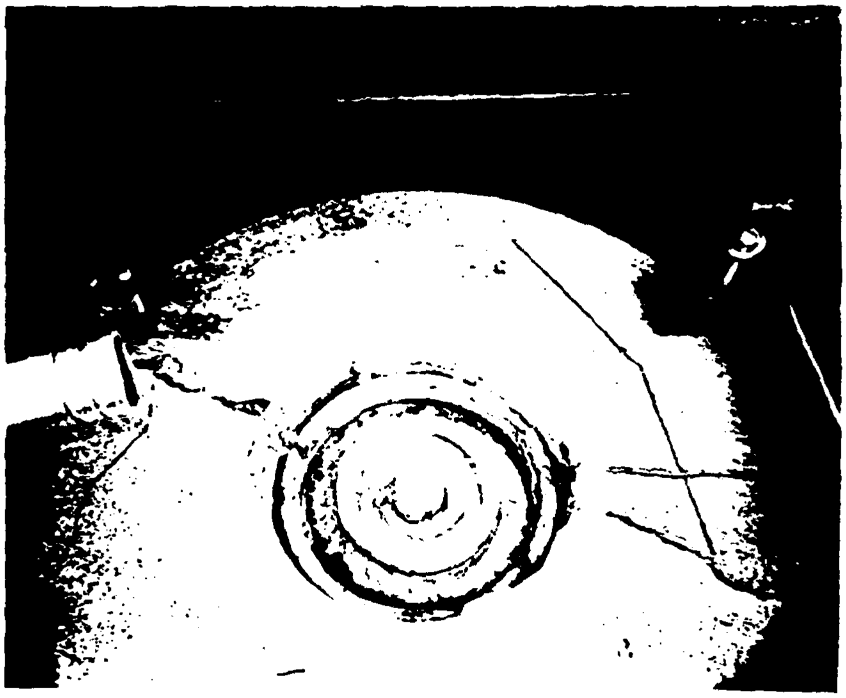
Figure 16(c) - Copper-graphite electrode tested for 2½ hours.

FIGURE 16 - Three electrode materials with Alloy 136.



mag. 1.57x

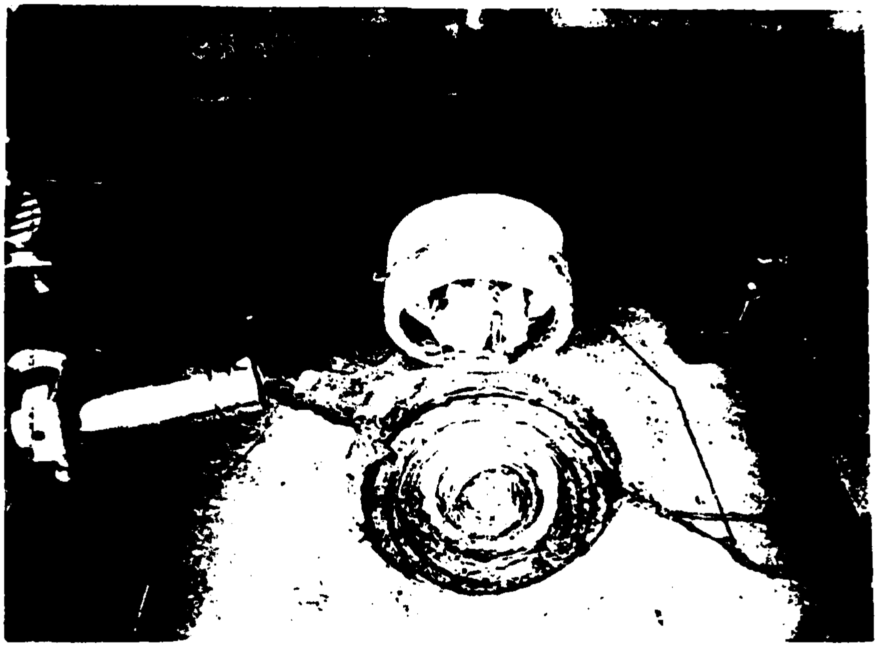
Figure 17(a) - Silver electrode with 255 alloy produced powder.



mag. 1.57x

Figure 17(b) - Liquid metal surface after powder removal.

FIGURE 17 - Silver electrode and Alloy 255



mag.

Figure 18(a) - Copper electrode and Alloy 136.

mag. 1.5

Figure 18(b) - Tungsten electrode and Alloy 136.

FIGURE 18 - Liquid metal condition after exposure tests 10, 11 and 12.

mag. 1.5x

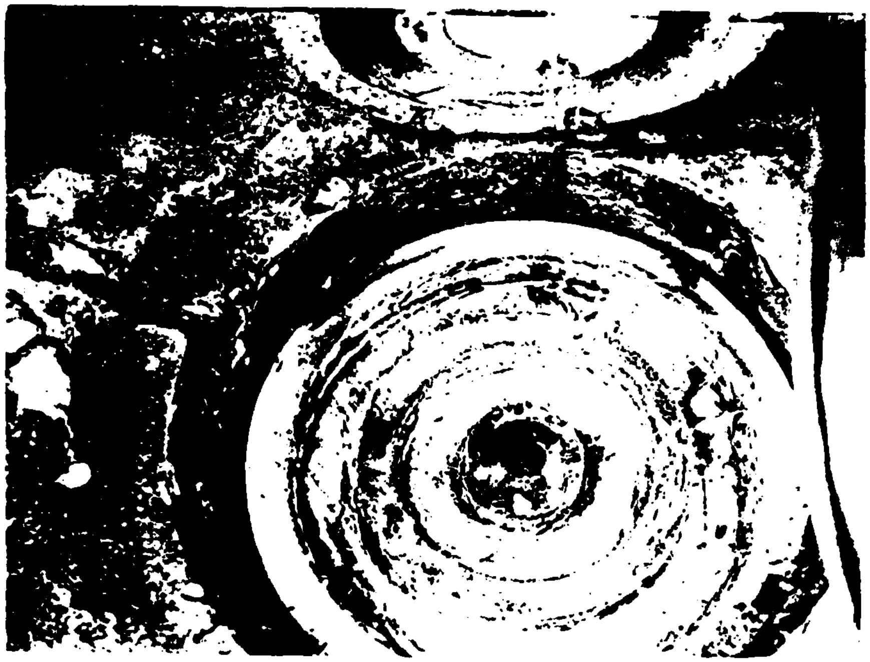
Figure 18(c) - Tungsten electrode and Alloy 136.

FIGURE 18 - Tungsten electrodes and Alloy 136.

a surface speed of 2,500 inches per minute was too high, causing repetitive folding of the surfaces of the fluid, churning and internal oxidation causing instability in the liquid metal alloys. It was decided at this point to back away from the high speed condition in order that some of the other influences, such as alloy and electrode materials could be investigated. Tests 13 and 14 were therefore carried out at a speed fo 25 r.p.m. or 250 inches per minute surface speed against the electrode material by the liquid alloy, which in this case was Alloy 136. Running these tests with copper and nickel electrodes for 10 hours with a current load of 30 amps and argon protection, the liquid metal remained liquid after the test period. As shown in Figure 19, the liquid metal alloys survived the 10 hour test at the lower speed in a much better condition.

One more test was run at the high speed rate of 250 r.p.m. with a tungsten electrode and liquid Alloy 136 for one hour only to obtain some information on how fast these conditions were producing the viscous or pasty liquid alloy. Visual examination of Test 16 indicated that one hour only was sufficient to begin initiating degradation of the 136 alloy under fast speed conditions.

Three liquid alloy metals, namely 117, 136 and 158 were run for one hour periods with different types of electrodes in Tests 17 through 24, at 25 r.p.m., a current of 30 amps, and a test temperature of 235°F. All these tests resulted in a liquid metal alloy condition after the test run. Results are shown in Figure 20.



mag. 1.5x

Figure 19(a) - Copper electrode and Alloy 136.

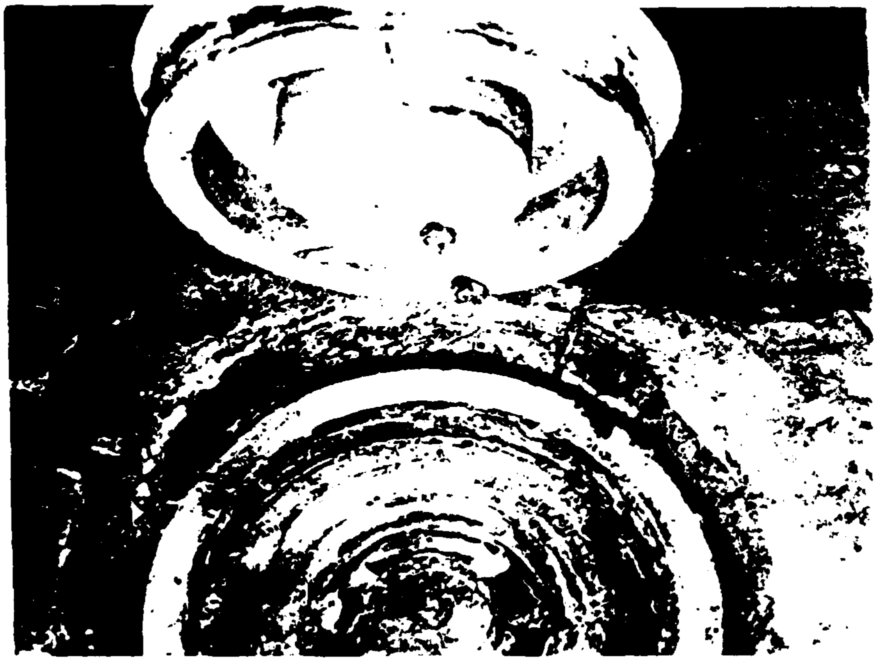
mag. 1.7x

Figure 19(b) - Nickel electrode and Alloy 136.

FIGURE 19 - Effect of lower rotation speed on liquid alloy condition.

mag. 1.

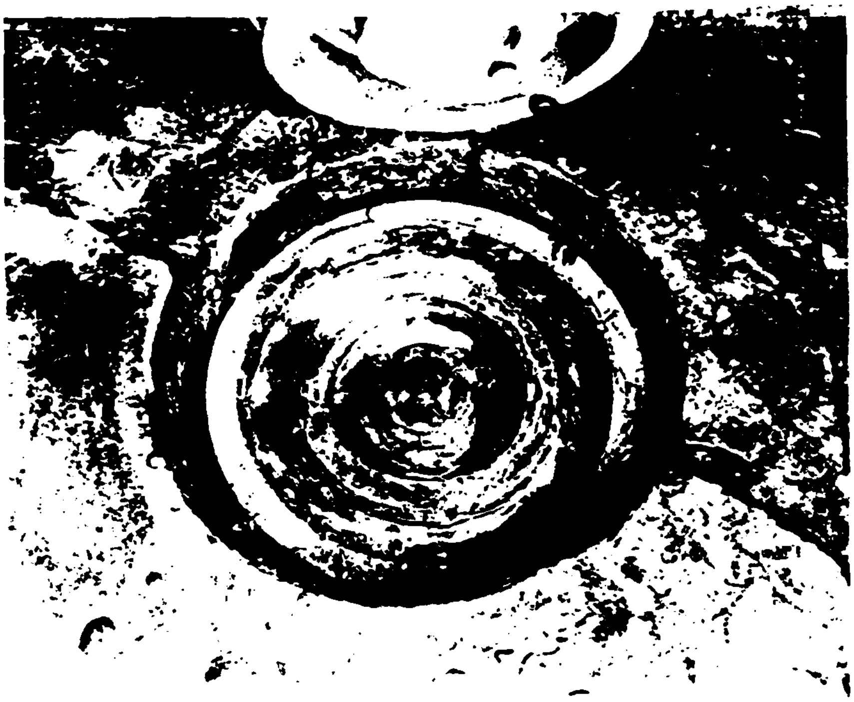
Figure 20(a) - Copper and liquid metal Alloy 117.



mag.

Figure 20(b) - Tungsten and 117

FIGURE 20 - One hour tests at 250 inches per minute surface speed.



mag. 2.1x

Figure 20(c) - Nickel and Alloy 158.

FIGURE 20 - One hour tests at 250 inches per minute surface speed.

Figure 20(a) is for Alloy 117 and a copper electrode, Figure 20(b) is tungsten for the electrode and liquid Alloy 136, and Figure 20(c) is with a nickel electrode and liquid Alloy 158. Noticeable throughout the test series so far, is the influence of speed and then of the alloy liquid metal on results obtained. Essentially, the tests are not yet severe enough to seriously affect the electrode materials being utilized.

The next series of tests from 25 through 32 was carried out to test the influence of speed between the liquid alloy and the solid electrodes, the influence of increasing current load on the system, and limitations of the time periods over which tests were run. Together with results from earlier electrical collector tests the results are graphically presented in Figure 21. The dominating factors are speed of revolution and time of test in obtaining the limitations of the liquid alloy and electrode combinations evaluated. Evaluation of the relative merits of the liquid metal alloys and the electrodes under the test conditions being used, will necessarily be carried out at a speed of 25 r.p.m.s for long periods of time. These results have also prompted the development of a test apparatus with better gas protection so that higher speeds may be feasible without producing the viscous liquid alloy by oxidation in relatively short time periods. Some of the solid metal electrodes used for the test so far are indicated on the graph in Figure 21 for documentation purposes.

Tests with copper and tungsten electrodes with liquid metal Alloy 158 were performed to evaluate the

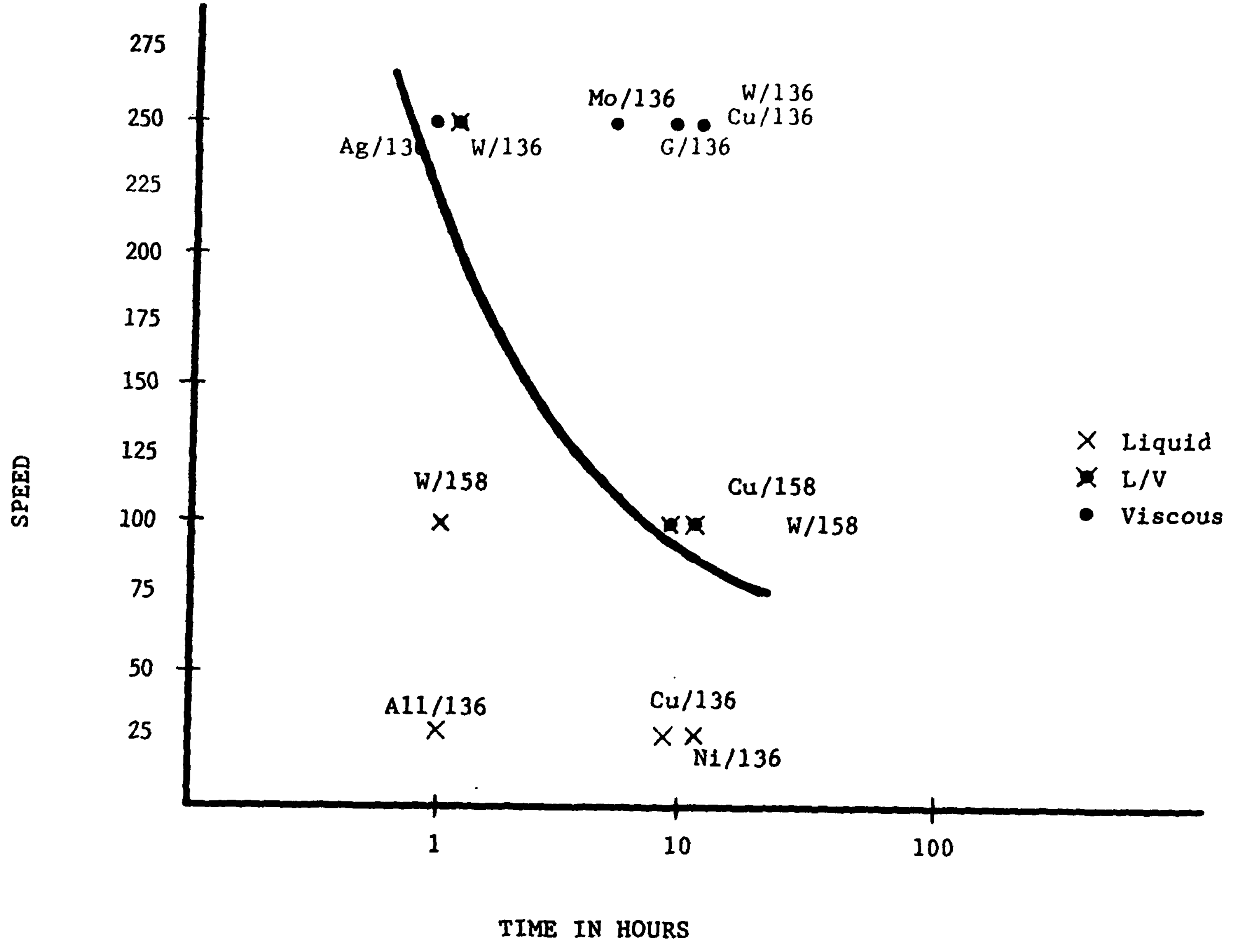
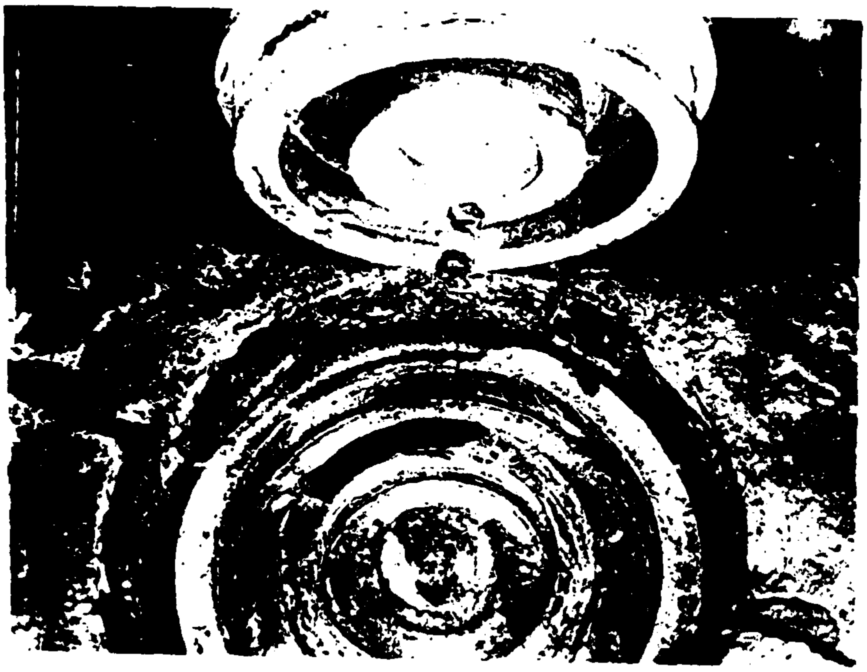


FIGURE 21 - Operation characteristics of experimental collector.

influence of current load on operating parameters of the collectors. One hour tests were carried out at 30, 90, and 200 amps respectively, at a speed of 25 r.p.m. and a test temperature of 200°F. Within these parameters, it was found that the liquid metal alloy remains liquid over the test period, and that the 200 amp setting was essentially the limitation of the collector system as currently designed. Physical condition of the liquid metal after the 90 and 200 amp runs is shown in Figure 22 where tungsten was used as the solid metal electrode. Some slight oxidation of the liquid metal was occurring at the higher amperage level. With both tungsten and copper electrodes at 200 amps, the resistive heating of electrode and liquid metal was sufficient to raise the temperature of the test during the one hour program indicating instability at these particular conditions.

Tests 33 through 35 lasted approximately 10 hours with some attack on the copper electrode, causing a viscous liquid metal. A tungsten electrode allowed rotation at 100 r.p.m., but at that speed the alloy was being whipped into a viscous condition as shown in Figure 23.

It was decided to limit further testing on the remainder of the Phase I program to the use of tungsten electrodes since it appeared more important to evaluate the liquid metal capabilities in relation to oxidation characteristics. Oxidation was clearly a severe limitation to success of the operation.



mag. 1.7x

Figure 22(a) - 90 amps with liquid Alloy 158.

mag. 1.8x

Figure 22(b) - 200 amps with Alloy 158.

FIGURE 22 - Effect of current level on liquid metal.

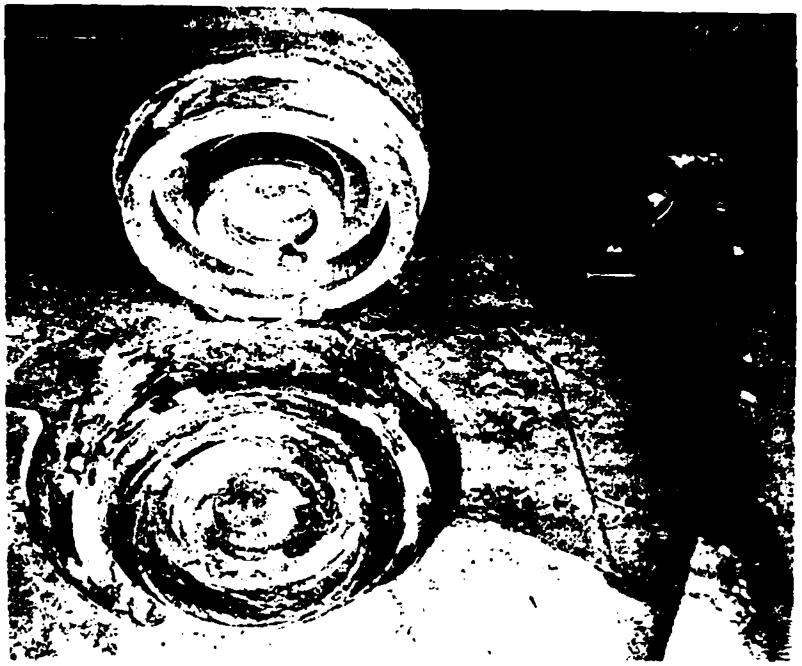


FIGURE 23- 10 hour test at 100 rpm with Alloy 117.

Tests 36 and 37 were run with tungsten electrodes at 25 r.p.m. and 200°F using Alloy 136 and 158 respectively. Under these conditions with argon gas flow at 300 cc/minute, the runs were 74 and 94 hours. Alloy 136 survived in a better condition than 158 as shown in Figure 24. Both alloys were becoming viscous with Alloy 158 in a more advanced state. Note how clean the tungsten electrodes are after the test run.

The oxidation problem suggested that alternate alloys to the fusible range should be tried, and at the same time the new pressurized collector unit was available for test runs. Test 38 was performed at 400°F and Alloy 255 as shown in Figure 25. A good operation of 63 hours was achieved, but severe powdering of the alloy occurred. A high temperature tin-aluminum alloy tested at 500°F only lasted two hours with severe powdering of the liquid alloy metal surfaces as shown in Figure 25(b). This series of tests was performed at 30 amp current, 25 r.p.m., and the test temperatures were adjusted according to the alloy, allowing margin above the liquidous.

Tests 41, 43, 44, 45, 47, and 48 were carried out with differing alloy combinations. The best performing fusible alloy was modified with a silver addition for test 41, and the material ran for 108 hours, the best run so far, or a 40% improvement. In this way, it was clearly shown that a silver addition was very useful to the fusible alloy. Condition of test 41 after the run is shown in Figure 26(a). A 50%tin-50% indium binary alloy was formulated and exposed as test 43.

mag. .

Figure 24(a) - Alloy 136 after 74 hours.

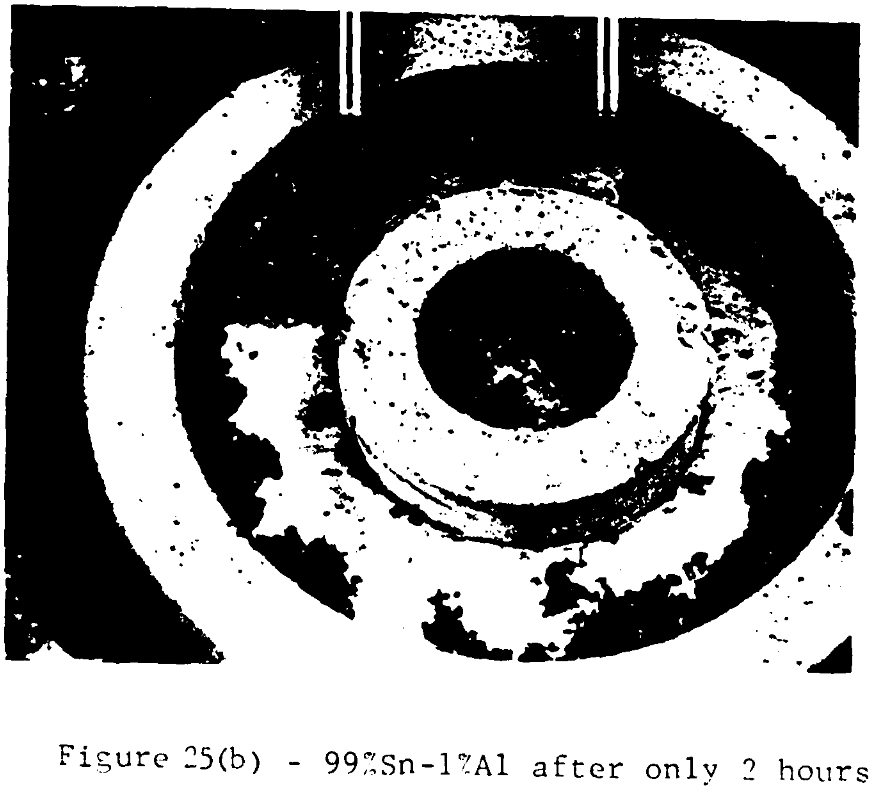
mag. .

Figure 24(b) - Alloy 158 after 96 hours.

FIGURE 24 -- Extended tests with tungsten electrodes and 900°F alloys.

mag. .79x

Figure 25(a) - Alloy 255 after 63 hours.



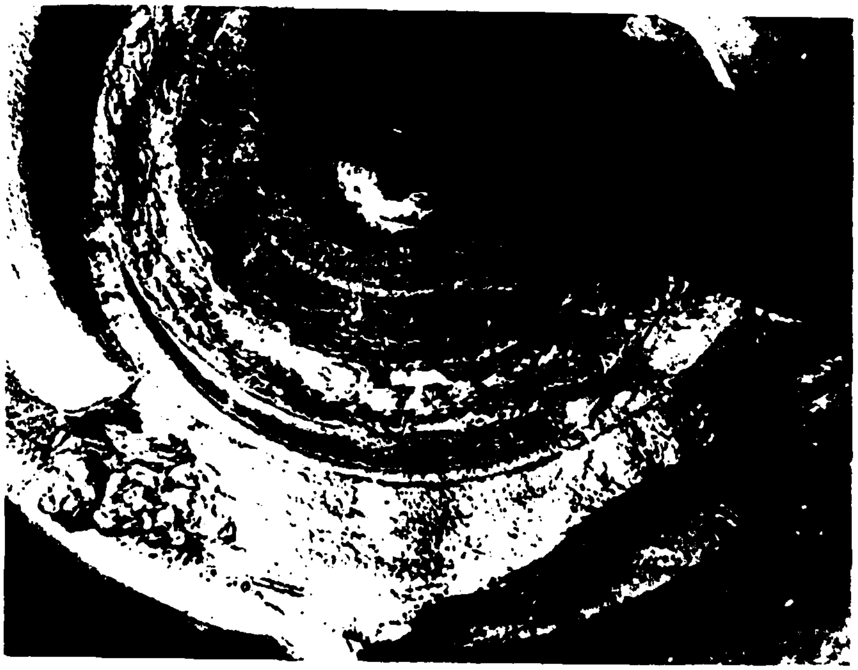
mag. 1x

Figure 25(b) - 99%Sn-1%Al after only 2 hours.

FIGURE 25 - Test with high temperature alloys and tungsten electrode.

mag. .83x

Figure 26(a) - 136 + 1/2%Ag after 108 hours.



mag. .83x

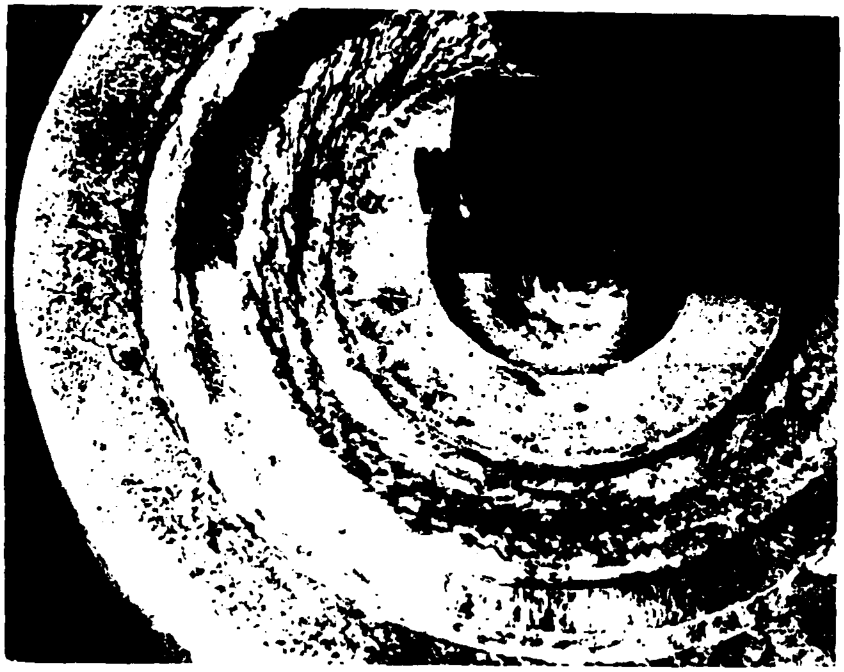
Figure 26(b) - 50%Sn-50%In after 139 hours.

FIGURE 26 - New alloys tested with tungsten electrodes.

After operating at 400°F successfully for 139 hours, again an alloy change was showing the way to improved performance and possible useful material. This alloy became severely affected by increased viscosity. The test was stopped under the condition pertaining to Figure 26(b), when the alloy had stiffened by oxidation, but still was satisfactorily conducting current. The binary alloy was converted to a ternary with a silver addition and run in test 44. The alloy now has a freezing range rather than being a eutectic, which is felt contributed to the deterioration of the liquid metal condition and cessation of testing after only 52 hours as shown in Figure 26(c).

An indium-silver alloy at 97% indium-3% silver lasted approximately 45 hours before a very viscous condition developed preventing further use. A bismuth-tin binary alloy with 55% bismuth-45% tin converted itself almost completely to powder that was very fine and black as shown in Figure 26(d) in test 48. A tin-silver binary alloy performed much better in lasting 94 hours and deteriorated by internal oxidation, stiffening the liquid into a paste, that was pushed ahead of the rotating electrode.

A summary of binary alloy data for life under argon is presented in Table 5. In the range of alloys tested using 500°F as the maximum permissible operating temperature, best performance was obtained by the tin-indium eutectic alloy. Next best results were achieved with a modified fusible alloy 136 adding some silver to it.



mag.

Figure 26(c) - Sn-In alloy with silver added lasted only 52 hours.

Figure 26(d) - 55%Bi-45%Sn alloy after 45 hours.

FIGURE 26 - New alloys tested with tungsten electrodes.

TABLE 5

SELECTED BINARY ALLOYS USED AS LIQUID METALS IN THE COLLECTOR EXPERIMENTS

(All tests at 25 rpm, 30 amp
with argon coverage, W electrode)

ALLOY W/O	TEMPERATURE OF TEST °F	END CONDITION	PERFORMANCE LIFE HOURS
99%Sn-1%Al	500	Viscous	2
50%Sn-50%In	350	Viscous	139
97%In-3%Ag	350	Viscous	45
96%Sn-4%Ag	500	Powder/Viscous	96
55%Bi-45%Sn	400	Powder	45

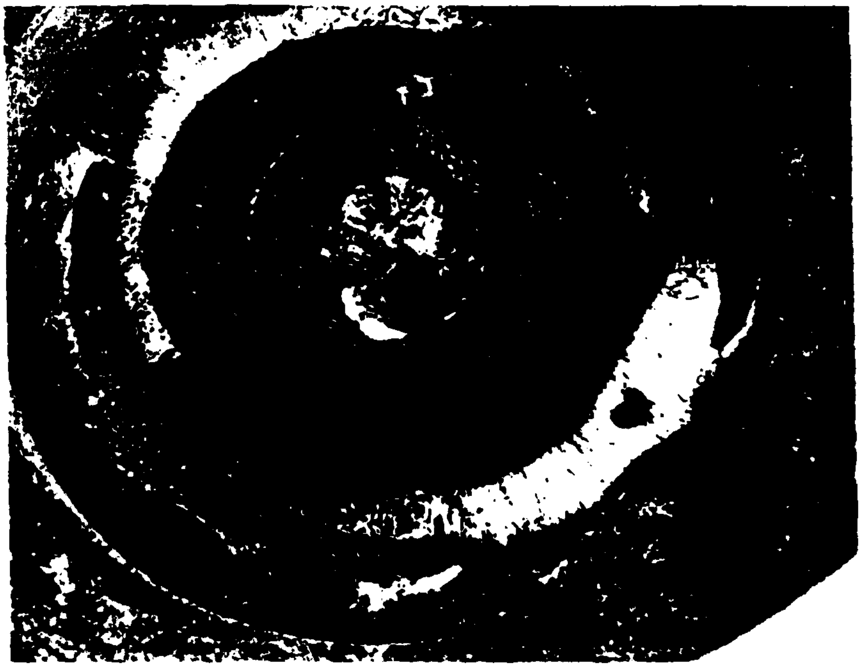
The pressurized collector system was utilized for a critical test series and efforts to proceed in this direction were quickly vindicated, and test hours were much improved. Alloy 136 was selected for the first run of the pressurized unit in test 40, which ran for 95 hours for a 30% life improvement over a similar test in free flowing argon over a collector bath. Interestingly, the mode of deterioration changed from the viscous build-up to the development of a fine powder as shown in Figure 27(a) taken after the test was complete. Alloy 255 was tried in the pressure vessel using a five pound argon gas pressure after suitable purging. The test was run at 400°F and lasted 192 hours, failure took place by formation of powder, observed in Figure 27(b). The modified fusible Alloy 136 with silver added ran for 231 hours, in the pressurized argon atmosphere more than doubling previous test results, failing by partially viscous and powder conditions as in Figure 27(c).

The final test in the Phase I program has been run with the tin-indium eutectic alloy and has achieved 700 hours plus, the test being stopped with the material in a slightly pasty condition and capable of some additional hours, as photographed in Figure 27(d). A summary of the pressurized collector results is presented in Table 6 and graphed in Figure 28.

Tests carried out within the scope of experiments to determine the most important physical and metallurgical characteristics of electrode and liquid metal couples under flowing current conditions have been very informative. Clearly oxidation of the liquid metal is dominant unless some

mag. 0.7x

Figure 27(a) - Alloy 136 after 95 hours at 250 rpm.



mag. 8.3x

Figure 27(b) - Alloy 255 after 192 hours.

FIGURE 27 - Tests in a pressurized and argon protectant collector.

mag.7.5x

Figure 27(c) - Alloy 136 plus ½% silver after 231 hours at 250 rpm.

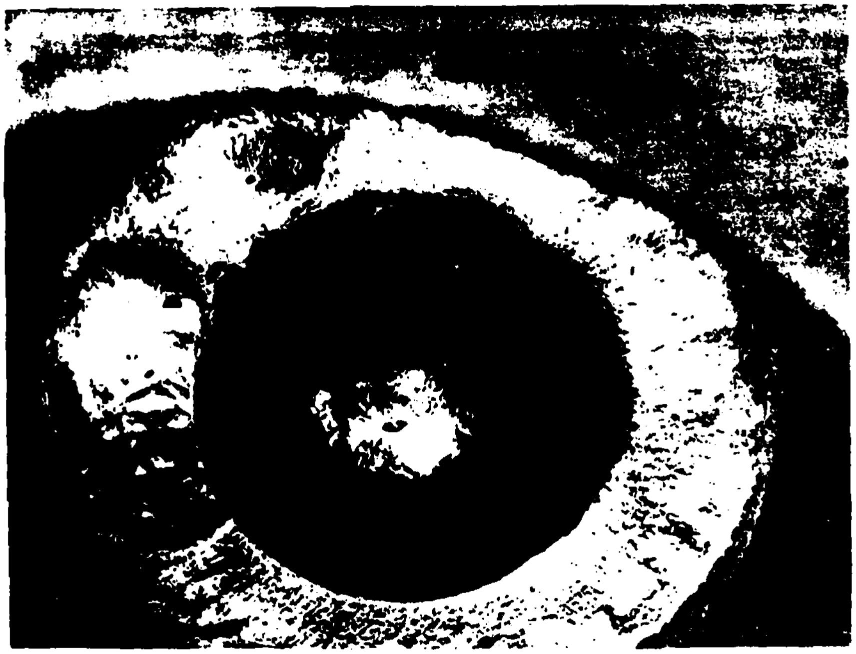


Figure 27(d) - 50%tin-50%indium after 700 hours at 250 rpm.

FIGURE 27 - Tests in a pressurized and argon protected collector.

TABLE 6

PERFORMANCE OF LIQUID METALS IN A PRESSURIZED AND GAS PROTECTED ENVIRONMENT

(Five pound Argon, welding quality)

ALLOY W/O	TEMP. OF TEST °F	SPEED R.P.M.	END CONDITION	PERFORMANCE LIFE HRS.
136	200	250	Powder	95
255	400	25	Powder	192
136 + 1/2% Silver	200	250	Powder/ Viscous	231
50%Sn-50%In	350	250	Viscous	700+

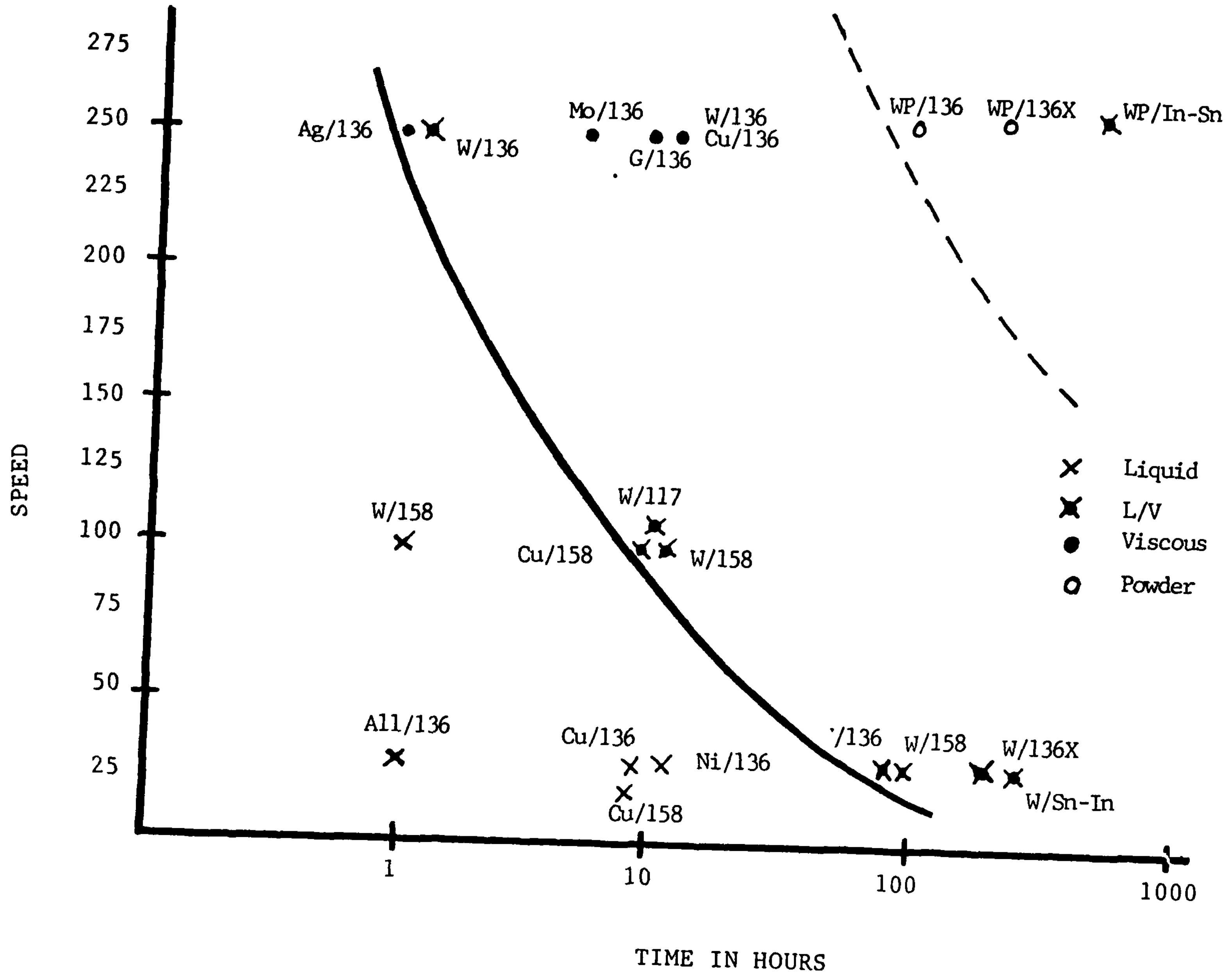


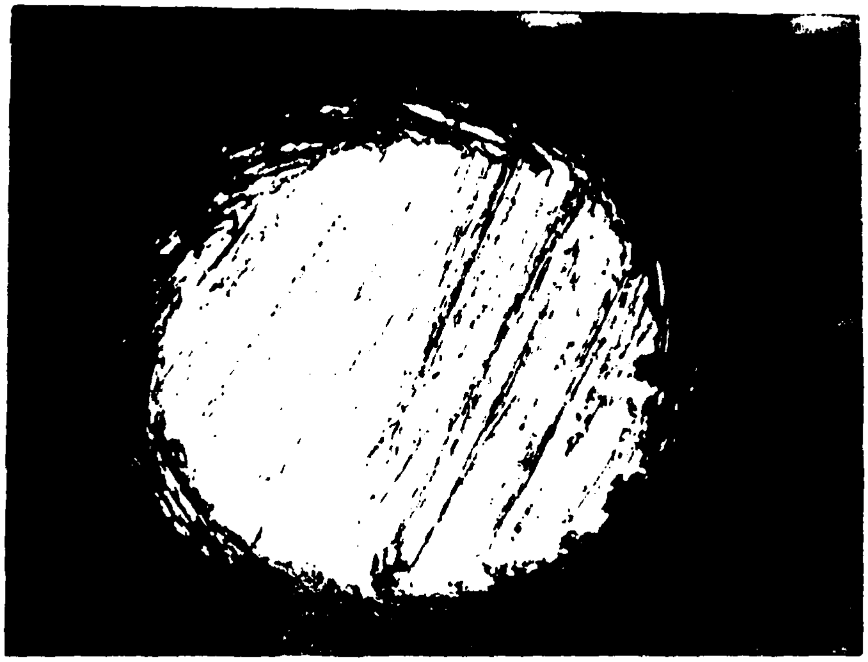
FIGURE 28 - Operation Characteristics of experimental collector.

form of protection is provided. A pressurized collector system enabled several hundred hours of operation to be achieved with an electrode and liquid metal combination. Separate dissolution studies of material interactions is reported elsewhere, but tungsten electrodes have proven satisfactory up to the temperatures and times utilized without visible problems. The results of tests are plotted in Figure 28 to show data obtained and progress made in Phase I of the work. Sufficient data has been collected to put together an initial design concept for a device that with a much reduced surface area and possible active gas environment should be capable of handling moderate currents with extended life. A 10,000 hour operating device appears a reasonable goal for the next part of this effort.

6.3 Examination of Electrode Tips After Test

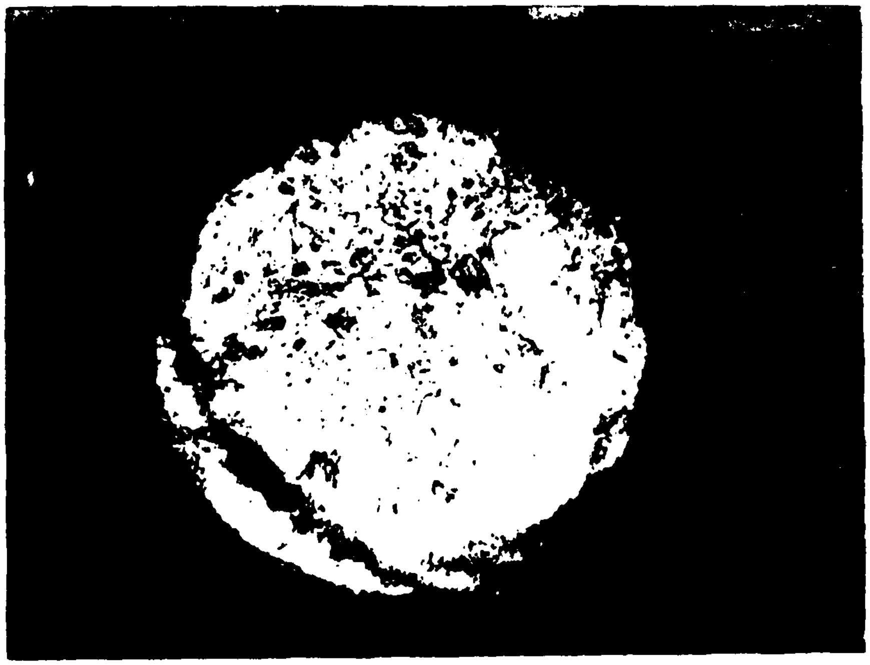
Tests carried out so far have enabled a preliminary evaluation of the separate effects of speed amperage and alloy on the survivability of solid metal electrodes. Examples are given using copper and tungsten electrode materials.

Test runs 10 and 13 were used to compare the effect of speed on electrode condition, using a copper electrode tip. Figure 29(a) shows a tip after 10 hours in Alloy 136 at a speed of 25 r.p.m. Essentially, no change has taken place, with a very slight adhesion of the liquid metal alloy. A very noticeable difference is observed with the copper electrode tip shown in Figures 29(b) and (c). This tip has operated for 10 hours at 250 r.p.m. The electrode is completely wetted by the liquid metal alloy with some reaction beginning with the copper material. Tungsten electrodes are used as the second example of the effect of speed on the condition of electrodes after use as an electrical current collector in liquid metal. Figure 30(a) shows a tip after



mag. 12x

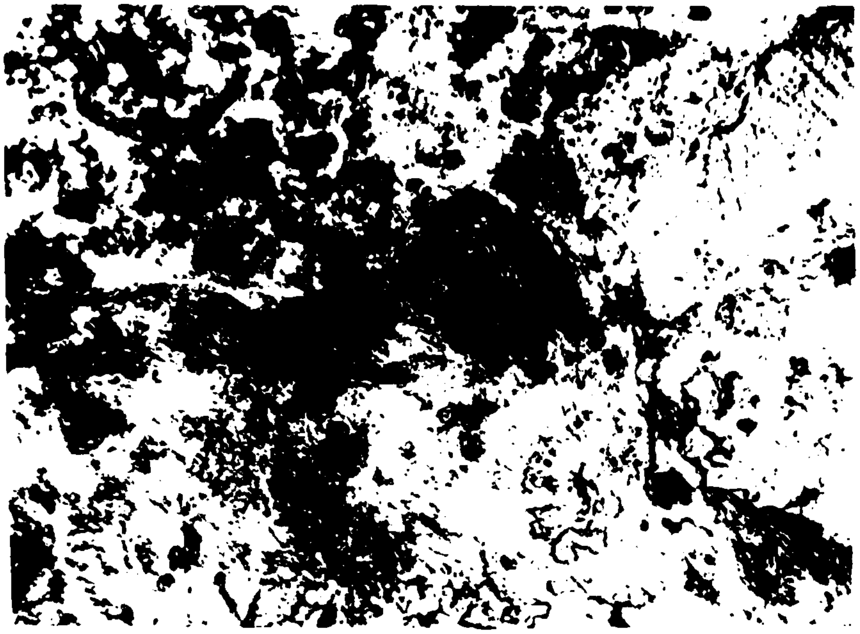
Figure 29(a) - Copper tip after 10 hours at 25 rpm with Alloy 136.



mag.

Figure 29(b) - Copper tip after 10 hours at [illegible] rpm.

Figure 29 - Effect of rotation speed on copper electrode.



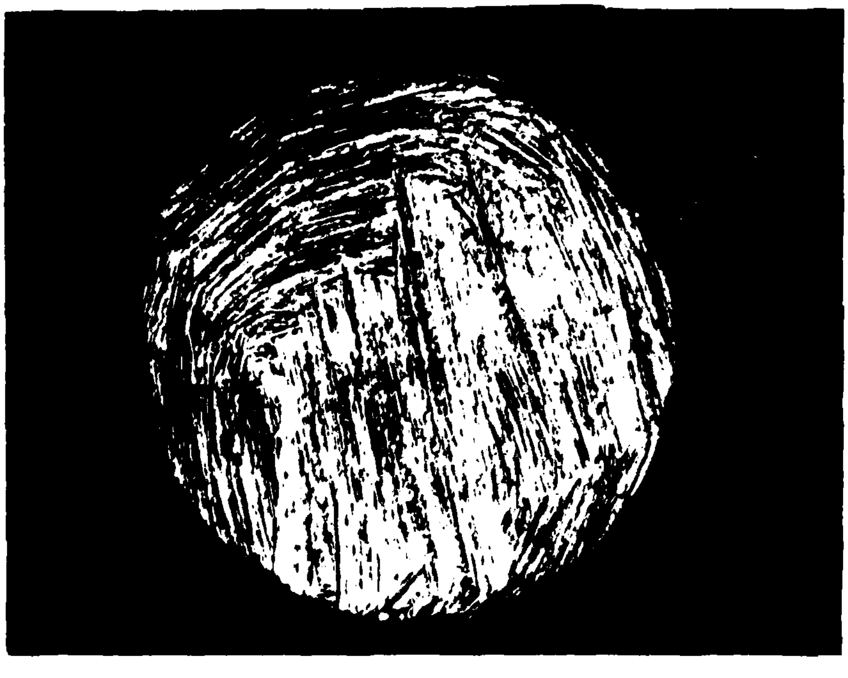
mag. 50x

Figure 29(c) - Copper tip after 10 hours at 250 rpm.

FIGURE 29 - Effect of rotation speed on copper electrode.

mag. 12x

Figure 30(a) - Tungsten tip after 10 hours at 250 rpm.



mag. 12x

Figure 30(b) - Tungsten tip after 10 hours at 25 rpm.

FIGURE 30 - Effect of speed on a tungsten electrode.

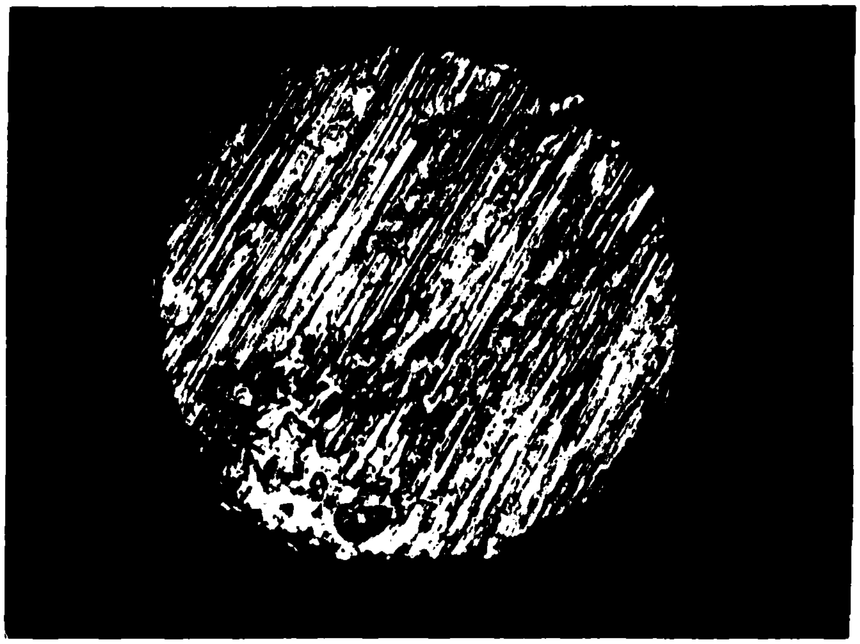
10 hours at 250 r.p.m., and 30(b) at 25 r.p.m. for the same time period. Difference noted is some adhesion of the liquid metal to the tip after 10 hours at the higher speed, however, it was found that the liquid alloy was becoming viscous and this alone can account for the formation observed. Essentially, no changes were seen in either tungsten tip after these tests were performed.

The test set-up will allow a current variation up to 200 amps. The condition of copper tips after exposure with Alloy 158 at 30 and 90 amps respectively are shown in Figure 31. Increasing current appears to result in some increase in adhesion, although in the tests carried out so far, amperage within the range tested does not seem to be as strong an influence as speed and time parameters. The main limitation with current occurs from the resistive loading obtained on both electrode and liquid metal alloy.

Examination of copper tips after exposure to the three fusible alloys used as the liquid metal part of the collection system, indicates that the lower temperature 117 alloy is capable of wetting a copper surface even when no fluxing agent is present, as shown in Figures 32(a) and (b). Results were much better with Alloy 158 and copper, where for 25 r.p.m. did not produce any change in the copper electrode. Surface wetting of copper with a liquid metal containing tin and indium occurs under electrical collector conditions.

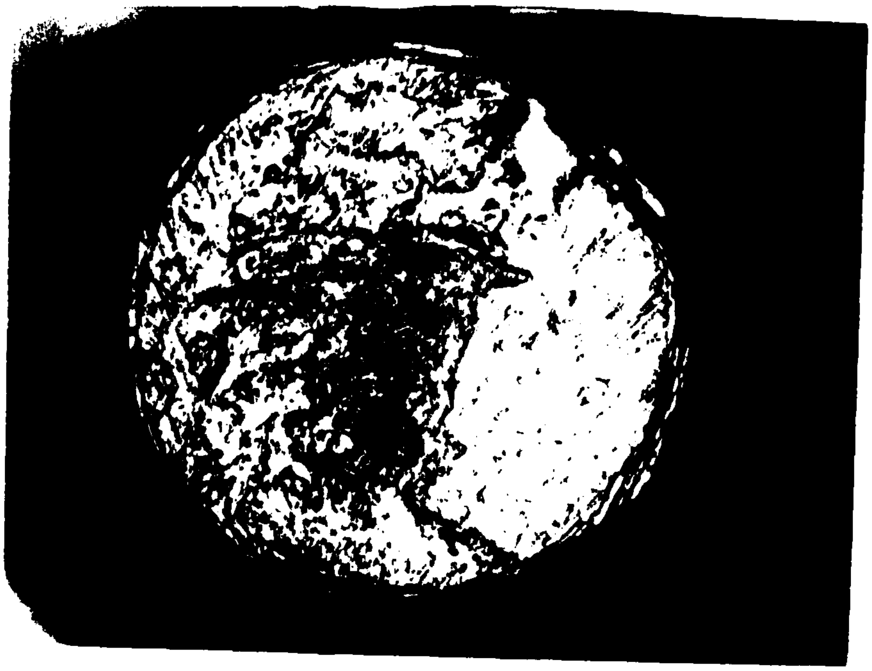
6.4 Metallographic Examination of Tips and Liquid Metal

Metallurgical cross-sections were made of some of the tips from the test runs to identify any reaction between the liquid metal alloy and the electrodes. The effect of rotation speed on tip condition is illustrated in Figure 33 where a low speed copper electrode in 33(a) is shown to have no reaction with the



mag. 12x

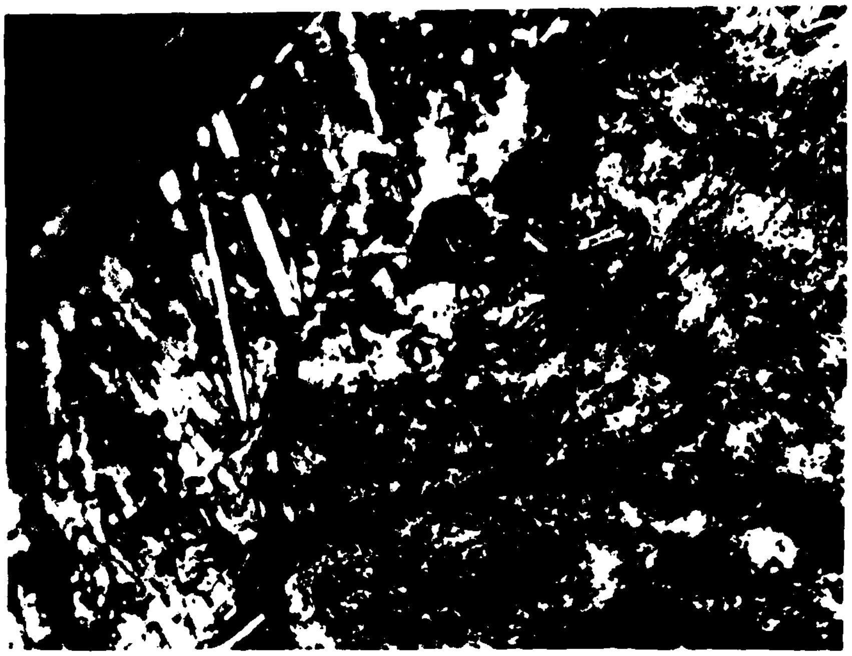
Figure 31(a) - Copper tip at 25 rpm with Alloy 158 for 10 hours at 30 amps.



mag. 12

Figure 31(b) - Copper tip after 90 amp test.

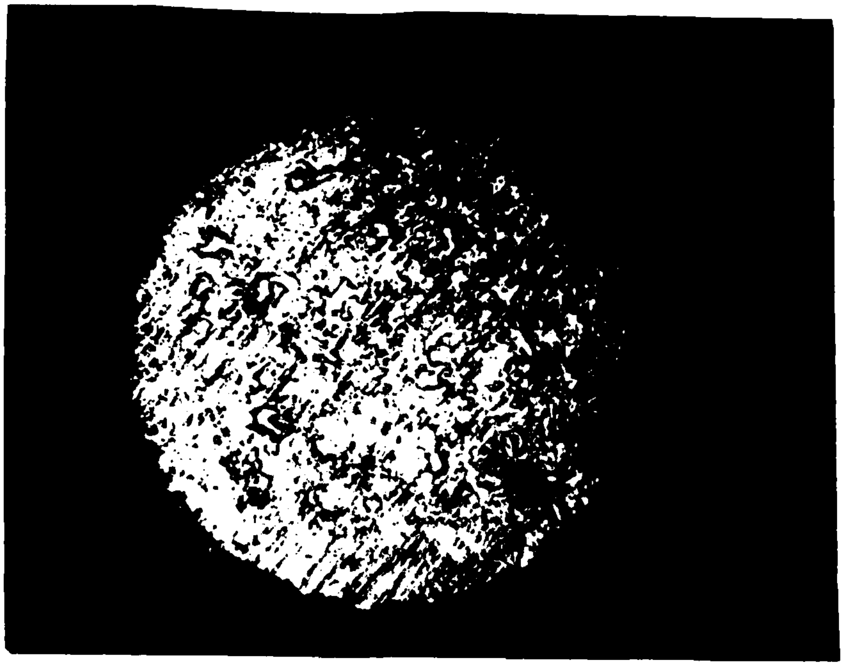
FIGURE 31 - Effect of increased amperage on a copper electrode.



mag. 50x

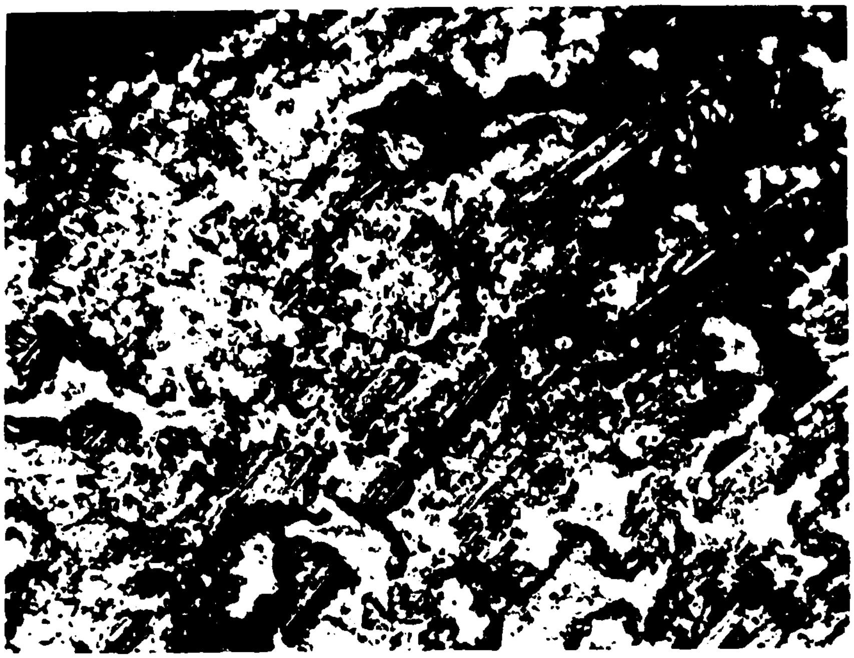
Figure 31(c) - Copper tip after 90 amp test.

FIGURE 31 - Effect of increased amperate on a copper electrode.



mag. 12x

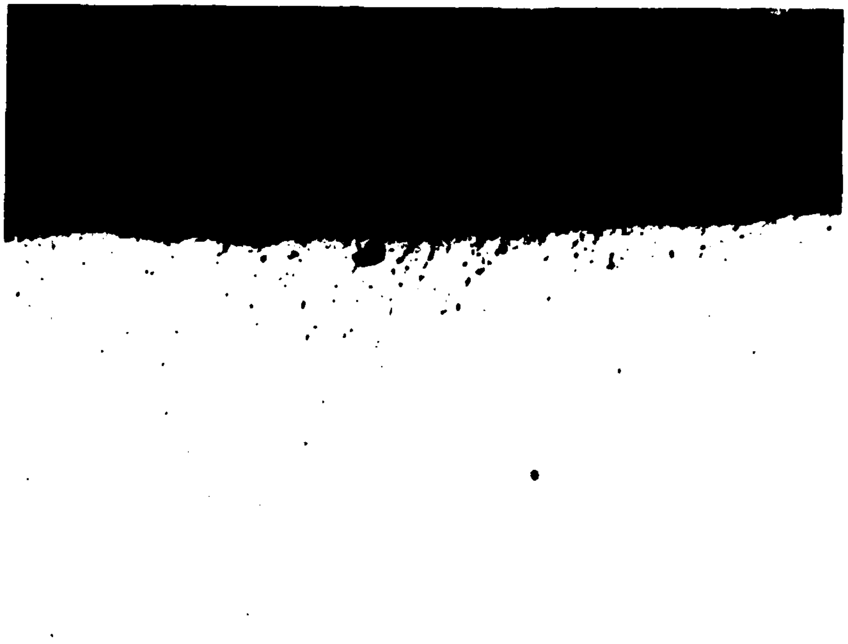
Figure 32(a) - Copper tip and Alloy 117 for 10 hours at 25 rpm.



mag. 50x

Figure 32(b) - Copper tip and Alloy 117 at higher magnification.

FIGURE 32 - Effect of alloy on copper electrode.



mag. 40

Figure 33(a) - Low speed.

mag. 400

Figure 33(b) - High speed.

FIGURE 33 - Effect of rotation speed on tip condition.

liquid metal in the collector. Increasing the speed to the 250 r.p.m. condition, produced wetting of the copper surface, formation of intermetallics between the copper and the liquid metal alloy resulting in some degradation of the electrode. The effect of increase in current on tip condition is shown in Figure 34. The only noticeable effect was a very slight surface attack on the copper by Alloy 158, increasing slightly with the increased amperage. There is a sharp contrast, however, between these photographs and that shown in Figure 35(a), which represents cross-sections of tungsten tips. Under all conditions tested, the tungsten was completely unaffected by any of the fusible alloys or any of the speed or time conditions. A comparison is made in Figure 35 between a tungsten and copper tip used under similar conditions, showing how the liquid metal alloy has reacted with the copper surface and no reaction at all has taken place with the tungsten material. These tests were both under current loaded conditions in the collector rings.

Commentary has previously been made on the condition of the liquid metal alloys after circulation in the collector for the tests carried out. Samples of the liquid metals were taken and cross-sections made to evaluate general condition after test, with results presented in Figure 36. The main effect on the liquid metal alloys was the generation of oxides that became entrapped in the liquid metal as the tests proceeded. Figure 36(a) shows a very heavy oxidation condition after a high speed run, with many air pockets and internal

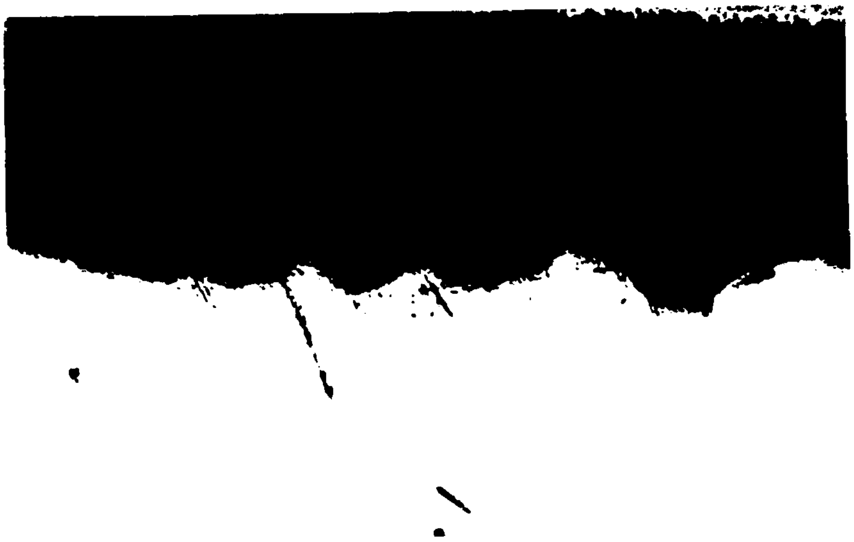
mag. 400x

Figure 34(a) - 30 amp.

mag. 400x

Figure 34(b) - 90 amp.

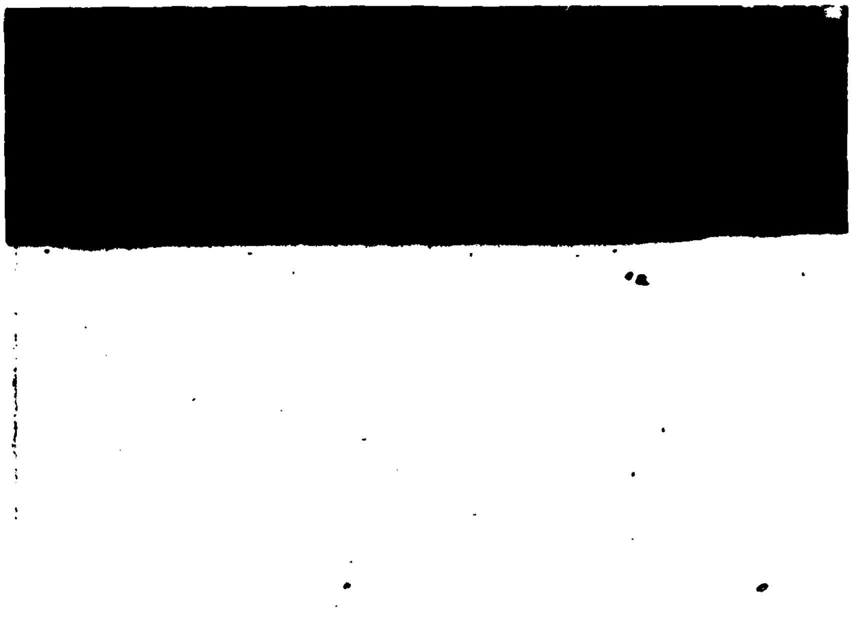
FIGURE 34 - Effect of current level on tip condition.



mag. 400x

Figure 34(c) - 200 amp.

FIGURE 34 - Effect of current level on tip condition.



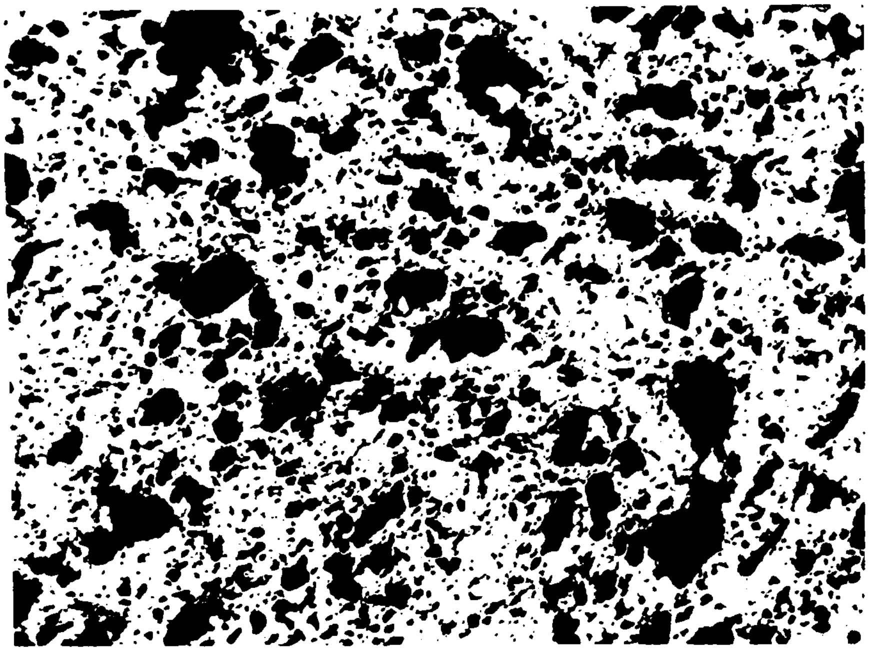
mag. 400x

Figure 35(a) - Tungsten.

mag. 400x

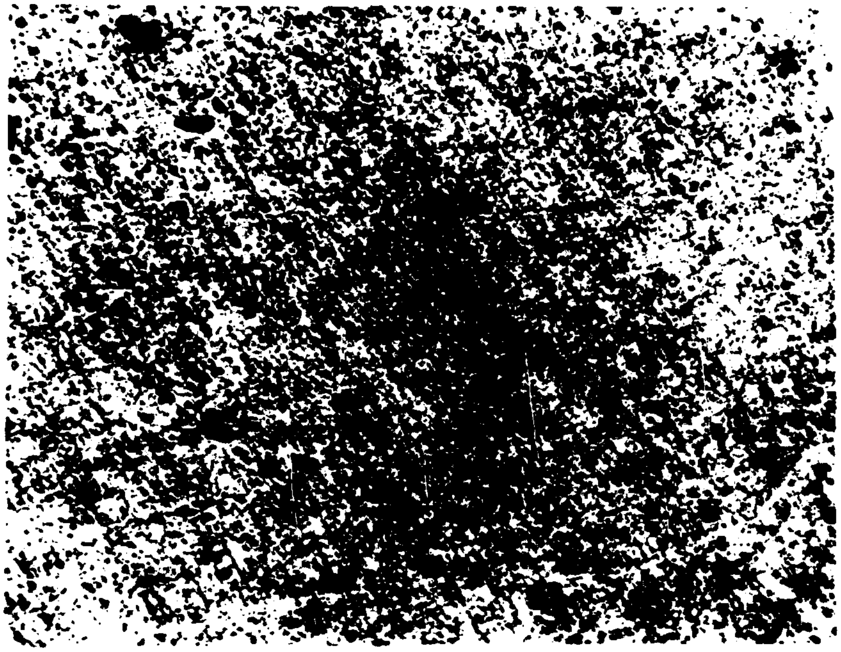
Figure 35(b) - Copper.

<u>FIGURE 35</u> - Electrode selection.



mag. 100x

Figure 36(a) - Heavy oxidation after high speed run.



mag. 100x

Figure 36(b) - Oxidation after moderate speed run.

FIGURE 36 - Effect of rotation speed on occluded oxide.

oxides that resulted in the liquid metal being very viscous, although current was still being passed under this unstable condition. Much less oxidation was revealed internally in the liquid metals when a moderate speed of 100 r.p.m. was used, and Figure 36(b) shows a test after 10 hours at that speed. Compared to Figure 36(a), much less oxide has been entrapped into the liquid metal. Finally, at the low speed of 25 r,p,m, condition, essentially some surface oxidation of the liquid metal was occurring but the liquid metals remained in good condition after 10 hour test runs as shown in Figure 36(c).

Metallurgical cross-sectioning of the electrodes and of the liquid metal alloys after the test runs has proved to be a very satisfactory way of evaluating the results obtained in addition to the monitoring of current, speed, and temperature during the test run. Results are indicating directions in which the program should go to examine the feasibility of producing practical electrical collection devices using fusible metal alloys to operate at temperatures of 200°F and above.

AD-A167 403 SURFACE ATTACK ON METALS IN THE PRESENCE OF LIQUID METALS(U) AMALGAMATED TECHNOLOGIES INC SCOTTSDALE AZ R E BEAL 10 APR 86 N00014-85-C-0848 2/2

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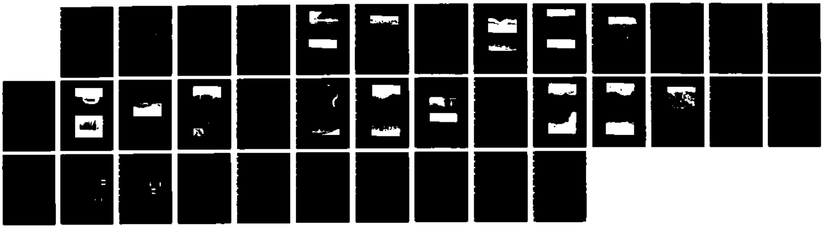
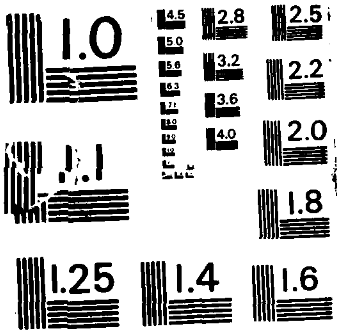




MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

mag. 100x

Figure 36(c) - Low speed run.

FIGURE 36 - Effect of rotation speed on occluded oxide.

7. ELECTRODE DISSOLUTION STUDIES

Eight electrode materials were exposed to four liquid metal alloys in the 117 to 200°F melting temperature range, as detailed in Table 7. Test temperature was held at 200°F for a period of 20 hours with the solid material placed in the liquid. Solid metals were removed after the time period, sectioned and examined under the microscope for any reaction with the liquid metal. Under the test conditions utilized, silver and copper were found to react with all of the alloys to some extent, with silver reaction more than the copper. Copper and Alloy 158 showed some promise, since the reaction was only limited to slight surface notching effects. No reaction at all was measured with aluminum, nickel, tungsten, cobalt, molybdenum and titanium specimens. Further dissolution trials will be run for longer time periods and at higher temperatures, since the results obtained appear beneficial in helping determine suitable materials for the electrical collectors.

Cross-sections were taken through copper electrodes exposed to the various liquid metal alloys and are presented in Figure 37. The 117 and 136 alloys reacted with the copper to produce a tunneling into the surface with formation of modified alloys as shown in Figure 37(a). Examination of the surfaces suggested that the liquid metal found defects in the copper surface sufficient to provide the initial penetration followed by the rapid tunneling action beneath the metal surface. Copper performed much better with Alloy 158,

TABLE 7

EXPOSURE OF ELECTRODE MATERIALS IN LIQUID METALS AT 200°F FOR 20 HOURS

ELECTRODE MATERIAL	LIQUID METAL
Aluminum	Alloy 117
Copper	Alloy 136
Nickel	Alloy 158
Silver	Alloy 160/190
Tungsten	
Cobalt	
Molybdenum	
Titanium	

mag. 200x

Figure 37(a) - Copper and Alloy 136.

mag. 200x

Figure 37(b) - Copper and Alloy 158.

<u>FIGURE 37</u> - Dissolution studies with copper electrodes.

mag. 200x

Figure 37(c) - Copper and Alloy 160/190.

FIGURE 37 - Dissolution studies with copper electrodes.

as shown in Figure 37(b), where negligible surface attack was to be found. However, Alloy 160-190 reacted with the copper alloy as shown in Figure 37(c). These direct dissolution studies with copper electrodes suggests that only Alloy 158 of this series has any chance of being a reasonable candidate for electrical collection. Silver electrodes proved to be very reactive with all of the low melting point liquid metal alloys. Typical examples of this reaction effect is shown in Figures 38(a) and (b). Silver electrode and Alloy 136 in Figure 38(a) reveals a penetration-type attack, whereas Alloy 160/190 has thoroughly wetted the silver surface and formed an intermetallic layer between the silver electrode and liquid metal as shown in Figure 38(b). From these early tests, it would appear that silver electrodes do not have the potential for providing good electrical collection with the low melting liquid metal alloys. Much better results were obtained with the other electrode materials as previously stated. Examples of these results are given in Figure 39, for tungsten, cobalt, and copper impregnated graphite. Each of these materials survived the 20 hour test at 200°F without any visible reaction at all between the electrode and the liquid metal in all four alloys tested.

The dissolution studies were continued for longer time periods at 200°F, and with alternate liquid metals at 400°F. Results of the 200 and 1,000 hour exposure tests are presented in Table 8, for the 200°F temperature. The copper and nickel electrodes

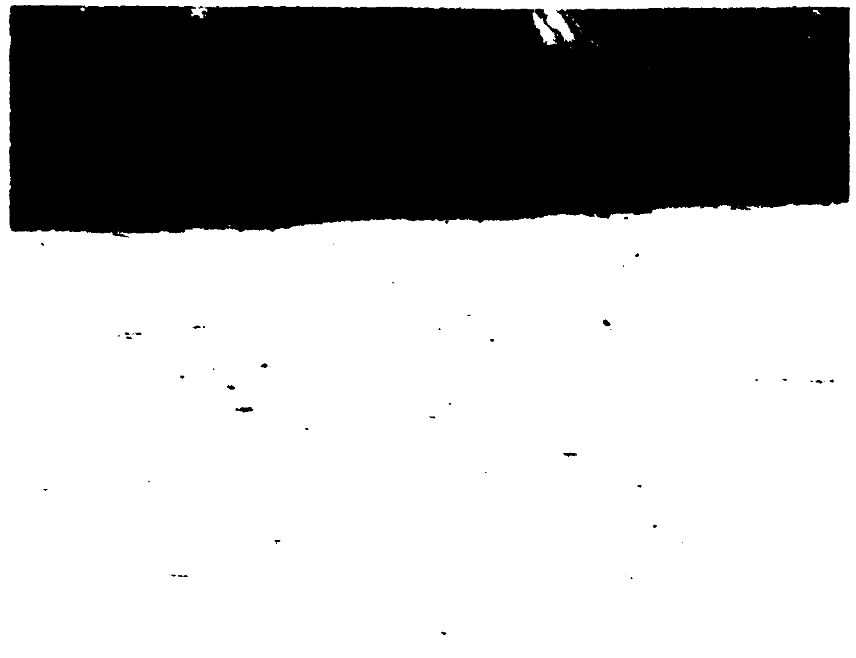
mag. 200x

Figure 38(a) - Silver and Alloy 136.

mag. 200x

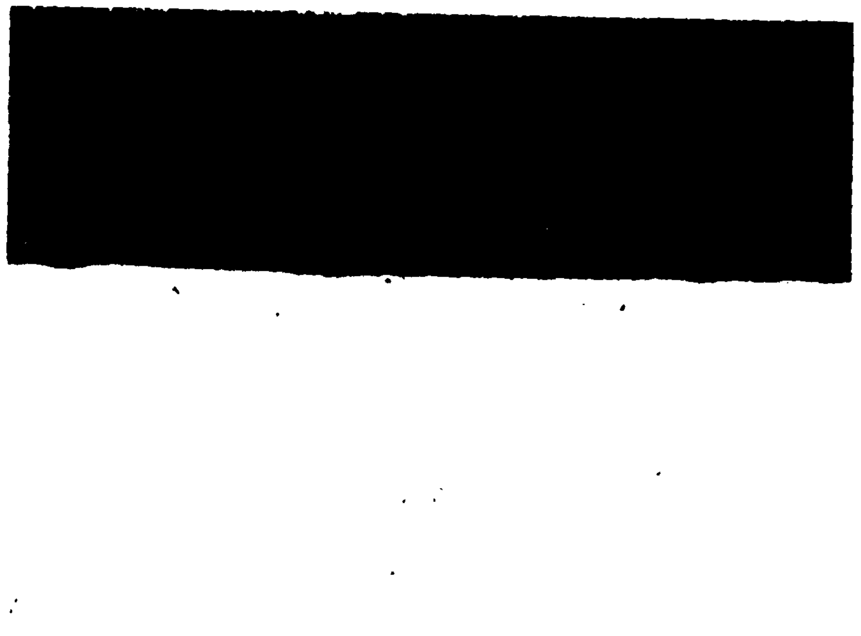
Figure 38(b) - Silver and Alloy 160/190.

FIGURE 38 - Dissolution studies with silver electrodes.



mag. 200x

Figure 39(a) - Tungsten and Alloy 117.



mag. 200x

Figure 39(b) - Cobalt and Alloy 158.

FIGURE 39 - Materials with no test reaction with 20 hours at 200°F.

mag. 200x

Figure 39(c) - Copper impregnated graphite and Alloy 117.

FIGURE 39 - Materials with no test reaction after 20 hours at 200°F.

TABLE 8

EFFECT OF EXPOSING CANDIDATE ELECTRODE MATERIALS IN LOW TEMPERATURE LIQUID METALS AT 200°F

ELECTRODE MATERIAL	LIQUID ALLOY	EXPOSURE PERIOD, HOURS	
		200	1,000
Aluminum	117	No Reaction	No Reaction
	136	"	"
	158	Some Reaction	"
	160/190	No Reaction	"
Cobalt	117	No Reaction	Attachment
	136	"	No Reaction
	158	"	"
Copper	117	Slight Attack	No Reaction
	136	"	"
	158	No Reaction	"
	160/190	"	Slight Attack
Molybdenum	117	No Reaction	No Reaction
	136	"	"
	158	"	"
	160/190	"	"
Nickel	136	No Reaction	No Reaction
	158	Slight Attack	"
	160/190	"	"
Tungsten	117	No Reaction	No Reaction
	136	"	"
	158	"	"
	160/190	"	"
Copper/Graphite	117	No Reaction	No Reaction
	136	"	"
	158	"	"
	160/190	"	"
Titanium	117	Slight Diffusion	No Reaction
	136	No Reaction	"
	158	"	"
	160/190	"	"

were the only materials showing reaction and dissolution. Some slight diffusion was observed with the titanium material. Four liquid metal alloys, namely 117, 136. 158, and 160/190 performed well with aluminum, cobalt, molybdenum, tungsten, and carbon impregnated with copper. These direct dissolution tests have effectively eliminated copper, nickel, silver and possibly titanium from consideration as suitable electrode materials.

Liquid metal alloys and electrode materials demonstrated increased interactions at the higher exposure temperature of 400°F. Results are presented in Table 9. Three alloys were utilized for these tests, Alloy 255, which is a lead-bismuth eutectic, Alloy 281, a lead-bismuth alloy, and 50% tin-50% indium. Tungsten electrodes were found to be the only material universally resistant to the liquid metals tested. Alloy 255 showed no reaction with cobalt, molybdenum, or tungsten for the 1,000 exposure period at 400°F. Alloy 281 reacted more strongly, and molybdenum and tungsten were apparently immune to dissolution in the liquid metals over the duration of the test.

Work with the 50% tin-50% indium alloy included a titanium electrode that worked satisfactorily over 1,000 hours. Good results were also achieved with aluminum and tungsten electrodes. Copper and cobalt suffered badly with dissolution attack and would be totally unacceptable.

A dissolution study of candidate electrode materials has been undertaken to study interaction effects with candidate liquid metal collector alloys.

TABLE 9

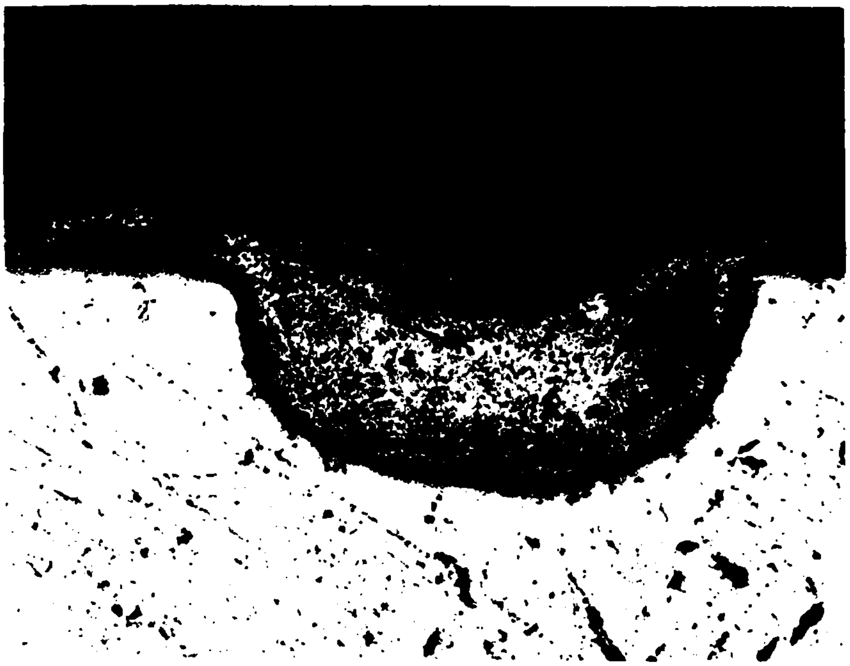
EFFECT OF EXPOSING CANDIDATE ELECTRODE MATERIALS IN LOW TEMPERATURE LIQUID METALS AT 400°F

LIQUID ALLOY	ELECTRODE MATERIAL	EXPOSURE PERIOD, HOURS	
		200	1,000
255	Aluminum	No Reaction	Slight Dissolution
	Cobalt	"	No Reaction
	Copper	Slight Oxidation	Oxidation
	Molybdenum	No Reaction	No Reaction
	Nickel	Some Reaction	Dissolution
	Tungsten	No Reaction	No Reaction
	Copper/Graphite	"	Infiltration
281	Aluminum	Local Dissolution	Dissolution
	Cobalt	Dissolution	Massive Dissolution
	Copper	"	"
	Molybdenum	No Reaction	No Reaction
	Nickel	Slight Dissolution	Dissolution
	Tungsten	No Reaction	No Reaction
	Copper/Graphite	"	Infiltration
50%Sn/50%In	Aluminum	No Reaction	No Reaction
	Cobalt	Slight Dissolution	Deep Finger Attack
	Copper	Dissolution	Severe Dissolution
	Molybdenum	No Reaction	Slight Dissolution
	Nickel	Reaction Growth	No Reaction
	Tungsten	No Reaction	"
	Copper/Graphite	Infiltration	Infiltration
	Titanium	No Reaction	No Reaction

The only material that was found universally applicable as an electrode with unequivocal success was tungsten. Other electrodes could be used as alloy specific materials for particular situations. For example, tungsten, molybdenum, and cobalt worked with Alloy 255, and tungsten and molybdenum only with Alloy 281. The tin-indium alloy worked well with aluminum, titanium, and tungsten. At 200°F, a much wider range of candidate alloys is available from the dissolution work with aluminum, cobalt, molybdenum, tungsten and copper impregnated graphite all surviving a 1,000 hour exposure period.

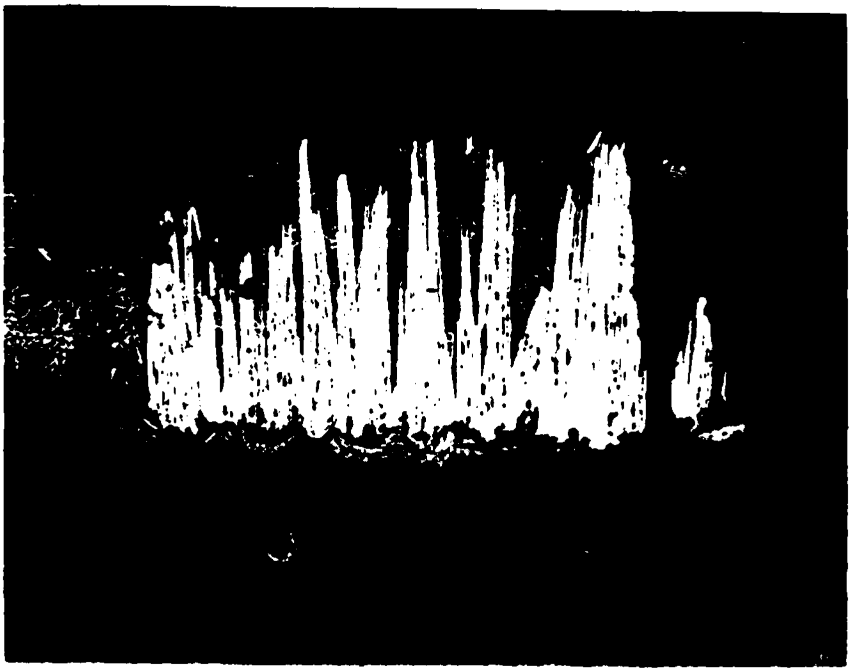
Metallographic examination was carried out on all electrode materials exposed to the liquid metals used at 200°F and 400°F. Some of the alloys that were found to react in liquid metal Alloy 281 are presented in Figure 40. Localized dissolution of an aluminum electrode is shown in Figure 40(a), and a surface activated alloy growth is depicted between cobalt electrode material and Alloy 281 in Figure 40(b). Even after only 200 hours at 400°F, the copper electrode in Alloy 281 showed significant dissolution of the solid material with a series of localized surface intrusions as shown in Figure 40(c).

The same electrode materials were exposed for 1,000 hours in Alloy 281 and are presented in Figure 41. Similar attack of the metals was obtained with aluminum illustrated in Figure 41(a) where localized dissolution of the electrode has occurred. In this series, the cobalt alloy broke down and produced serious dissolution and alloying as shown in Figure 41(b). The original surface of the electrode is observed to the left with



mag. 50x

Figure 40(a) - Aluminum in Alloy 281 after 200 hours.



mag. 50x

Figure 40(b) - Cobalt in Alloy 281 after 200 hours.

FIGURE 40 - Electrode condition after 400°F exposure

mag. 50x

Figure 40(c) - Copper in Alloy 281 after 200 hours.

FIGURE 40- Electrode condition after 400°F exposure.

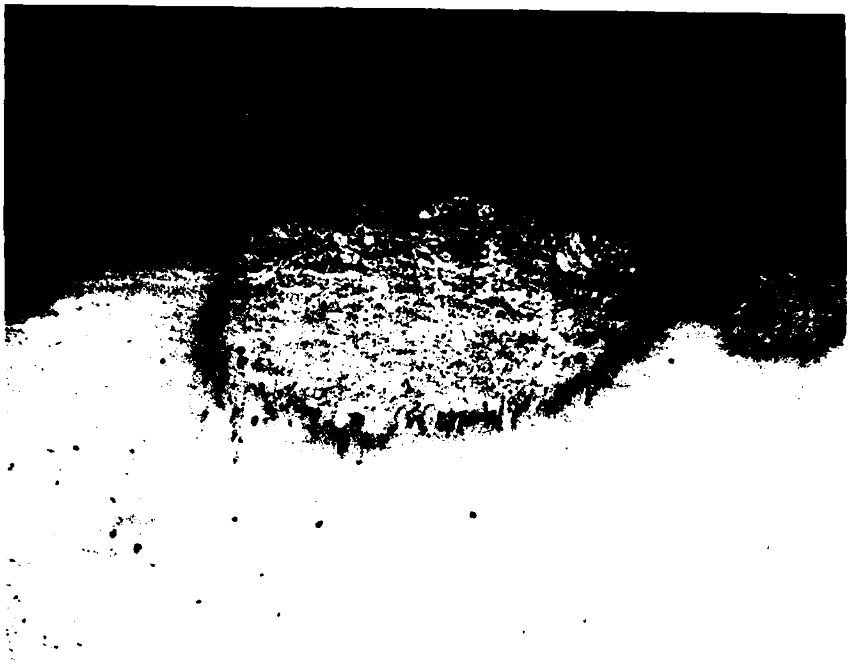


Figure 41(a) - Aluminum in Alloy 281 after 1,000 hours.

Figure 41(b) - Cobalt in Alloy 281 after 1,000 hours.

FIGURE 41- Condition after exposure at 400°F for 1,000 hours.

reaction causing considerable penetration into the surface. The level of dissolution of copper increased with similar patterns of localized attack and layered growth of the reaction formed alloy. The number of attack initiation sites has increased causing severe electrode damage as shown in Figure 41(c). Reaction, dissolution, and growth of a modified alloy at the surface is illustrated in Figure 41(d) for nickel electrode material with Alloy 281. A nickel rich material is formed that sloughs off into the liquid metal.

Results obtained with Alloy 255 are presented in Figure 42. Similar localized dissolution of the aluminum electrode is obtained as shown in Figure 42(a). Copper reaction has a different pattern with this alloy as depicted in Figure 42(b). A narrow band of closely arranged surface cells have developed an oxide that appears to be partially protected with the solder alloy. A break-out and dissolution would be expected, however, under dynamically operated test conditions. The surface of the nickel specimen is seen in Figure 42(c). The depth of reaction is not high, but clearly some dissolution is occurring that is attacking the nickel and removing material from the electrode surface. Considerable solder alloy oxidation also was noted on this specimen after removal from the liquid. In contrast to all the dissolution attack examples presented in the last few photomicrographs, no reaction at all was found with tungsten electrodes, as shown in Figure 42(d) for Alloy 255. The photomicrograph is typical of all tungsten electrodes after liquid metal exposures up to 400°F and

mag. 50x

Figure 41(c)- Copper in Alloy 281 after 1,000 hours.

mag. 100x

Figure 41(d) - Nickel in Alloy 281 after 1,000 hours.

FIGURE 41 - Condition after exposure at 400°F for
1,000 hours.

Figure 42(a) - Aluminum in Alloy 255 after 1,000 hours.

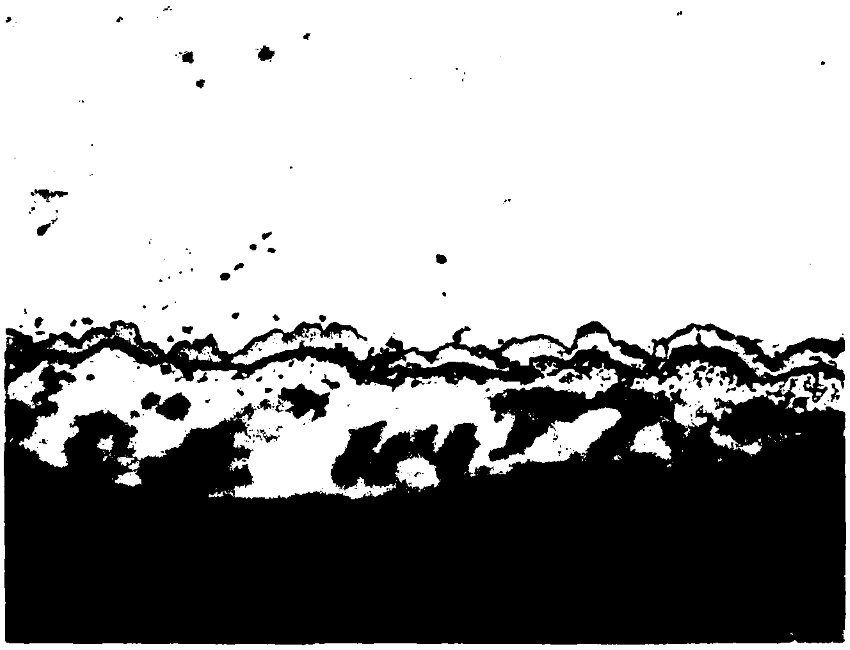
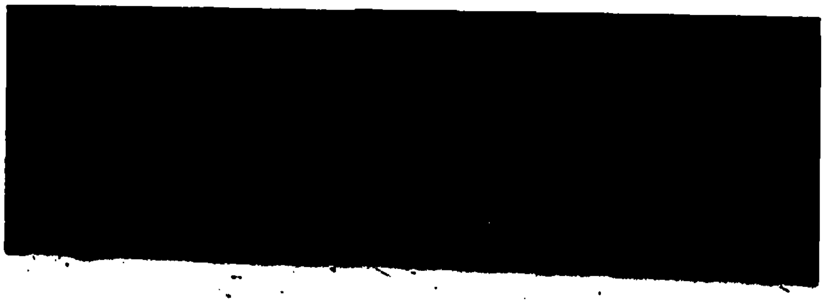


Figure 42(b) - Copper in Alloy 255 after 1,000 hours.

FIGURE 42 - Condition after 400°F and 1,000 hours
with Alloy 255.

mag. 200x

Figure 42(c)- Nickel in Alloy 255 after 1,000 hours.



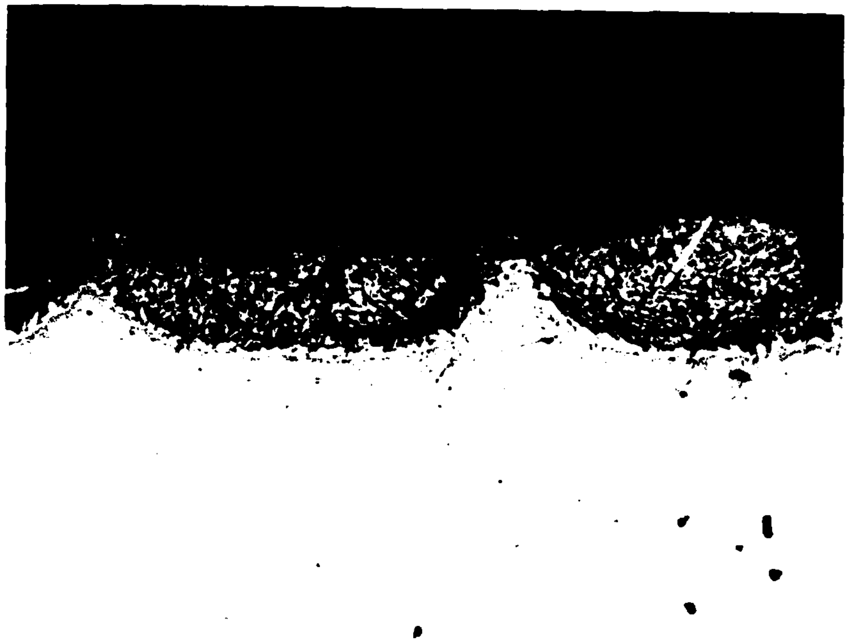
mag. 100x

Figure 42(d) - Tungsten in Alloy 255 after 1,000 hours.

FIGURE 42 - Condition after 400°F and 1,000 hours with Alloy 255.

1,000 hours, and correlates well with the good experience obtained in actual collector experiments where a tungsten electrode is used.

The 50% tin-50% indium alloy reacted with copper and nickel after only 20 hours exposure at 400°F. The copper specimen is shown in Figure 43(a) with a reaction interlayer and localized dissolution of the copper metal. The nickel alloyed with the tin-indium liquid metal producing a reaction growth layer as presented in Figure 43(b). Further attack of the copper is observed after 200 hours with more dissolution of the surfaces, as shown in Figure 44(a). A finger-like deep penetrating attack was found with cobalt electrodes in tin-indium alloy as shown in Figure 44(b). Copper-graphite was found to be infiltrated by the tin-indium alloy after a 200 hour exposure, as in Figure 44(c).



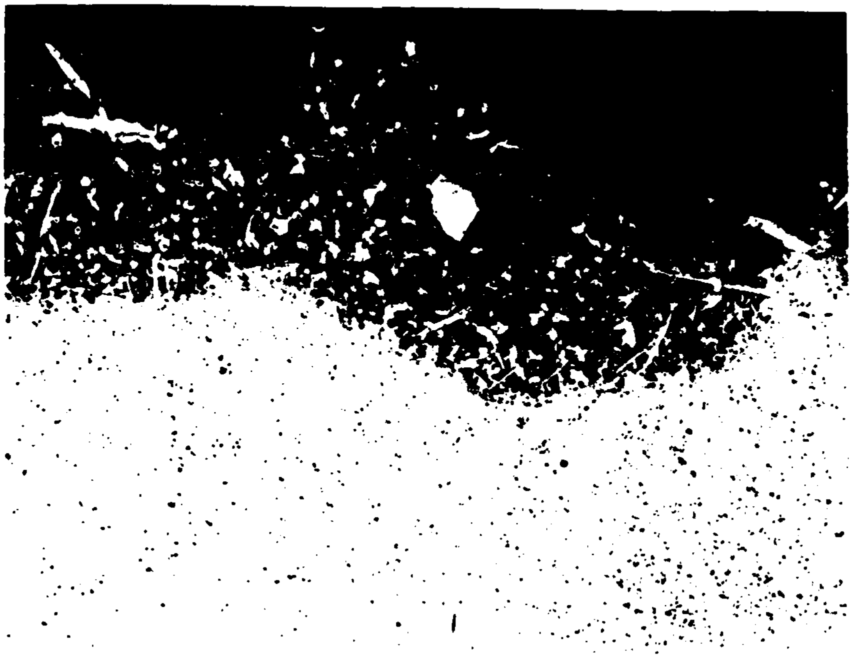
mag. 200x

Figure 43(a) - Copper in tin-indium alloy after 20 hours.

mag. 100x

Figure 43(b) - Nickel in tin-indium alloy after 20 hours.

FIGURE 43- 50%Tin-50%Indium alloy after 20 hours at 400°F.



mag. 50x

Figure 44(a)- Copper in 50% tin-50% indium after 200 hours.

mag. 200x

Figure 44(b) - Cobalt in tin-indium after 200 hours.

FIGURE 44- Condition of electrodes after exposure
at 400°F.

mag. 200x

Figure 44(c)- Copper-graphite in tin-indium after 200 hours.

FIGURE 44- Condition of electrodes after exposure at 400°F.

8. COLLECTOR DEVICES

The test program in Phase I has concentrated on the materials for electrodes and materials for liquid metal alloys. Electrical collection at 200-500°F has proven feasible with no difficulties found in actually passing the current. Maximum collector currents can be related directly to the total resistance in the system and the thermal heating that results. Thermal limits can be imposed on a system for protection purposes from the electrical and collector overheating aspects of usage.

Materials for the solid electrodes are limited by the test results to essentially refractory metals. Devices can utilize tungsten or tungsten alloyed for fabrication that is clad to a copper or friction welded to produce an effective current lead. Standard feed through devices can be adapted for the project that already are capable of handling current levels presently envisaged.

The liquid metal containers for Phase I were made from a lightweight insulating material, which from results obtained now is felt to have been a possible contributor to oxidation due in part to the large surface area within the material and absorption on the material. Current ideas are leaning towards glass-ceramic materials for the liquid metal container or cup area. These materials generally are machinable and can be fired to shape and are anticipated to be non-reactive with the liquid metal alloys to be used.

Liquid metal alloy can be supplied for electrical collection from an external reservoir source. The use of this approach will allow replenishment of the liquid metal part of the system without compromising effectiveness of the collector, by using a pumped circulation of the liquid metal with a ceramic oxide filter system that can have replaceable cartridges. Alternatively, the reservoir could be used as the contact for initiating current flow by a pressure arrangement with a drain plug for replacement of the liquid metal at prescribed intervals to ensure collector longevity. Finally, it is possible to create sealed replaceable collector units with a known life cycle. Some development work on seals would be required for this approach that may be considered effective for small sized collectors or those for remote operations, where simplicity and single usage are the key.

Three alternate design concepts are presented in Figures 45, 46, and 47, using some of the ideas proposed. Figure 45 promotes the protective atmosphere approach with low surface speed electrodes and larger liquid metal baths to accomodate movement in the system. The reduced surface area concept with large volume to surface area ratio of the liquid metal is presented in Figure 46 with the closely machined toleranced close fit electrode. The concept in Figure 47 demonstrates the use of seals between two liquid baths which may prove important in systems that must allow orientations other than vertical or as an aid to reduction in possible oxidation effects.

Electrodes used so far for convenience have been post type that stirred around the collector trough. The stirring action was good to evaluate comparative properties of materials, but in a prospective device, this action should be minimized. A good way to accomplish the interfacial movement reduction is to make the electrode a ring for the outer electrode, retaining a post only for the centrally placed electrode. The liquid metal in the trough is then encouraged to develop a rotation momentum to keep pace with the electrode so that most interfacial movement will be against the glass-ceramic cup.

The electrode system should be designed with the very minimum of clearance between the container wall and the electrode, allowing for necessary expansion changes with temperature. The close wall design will reduce the liquid metal exposed surface area by an order of magnitude, producing a much better liquid volume to surface area aspect that is beneficial in reducing potential oxidation.

A protective atmosphere will be provided. Pressurized high quality argon has been used under five pounds per square inch pressure. Higher pressures can readily be designed into collectors and the oxidation potential can be further reduced by using an active atmosphere with possibly a filter system and suitable monitoring equipment. The level of effort here depends upon the intended degree of sophistication of the finished collector unit.

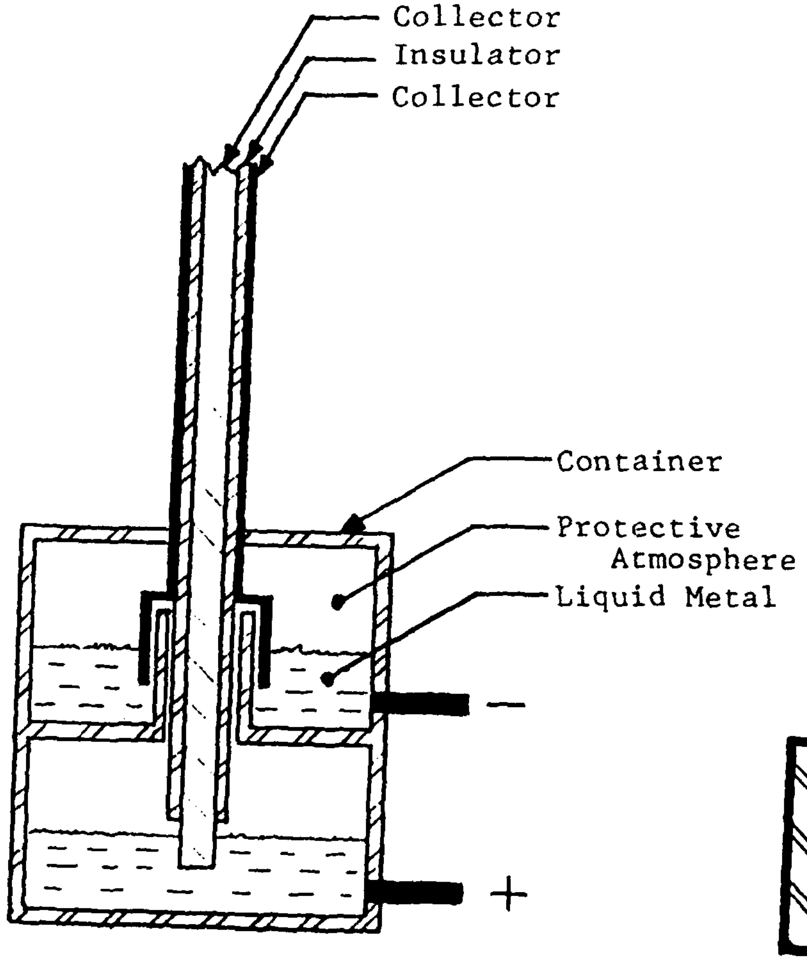


FIGURE 45

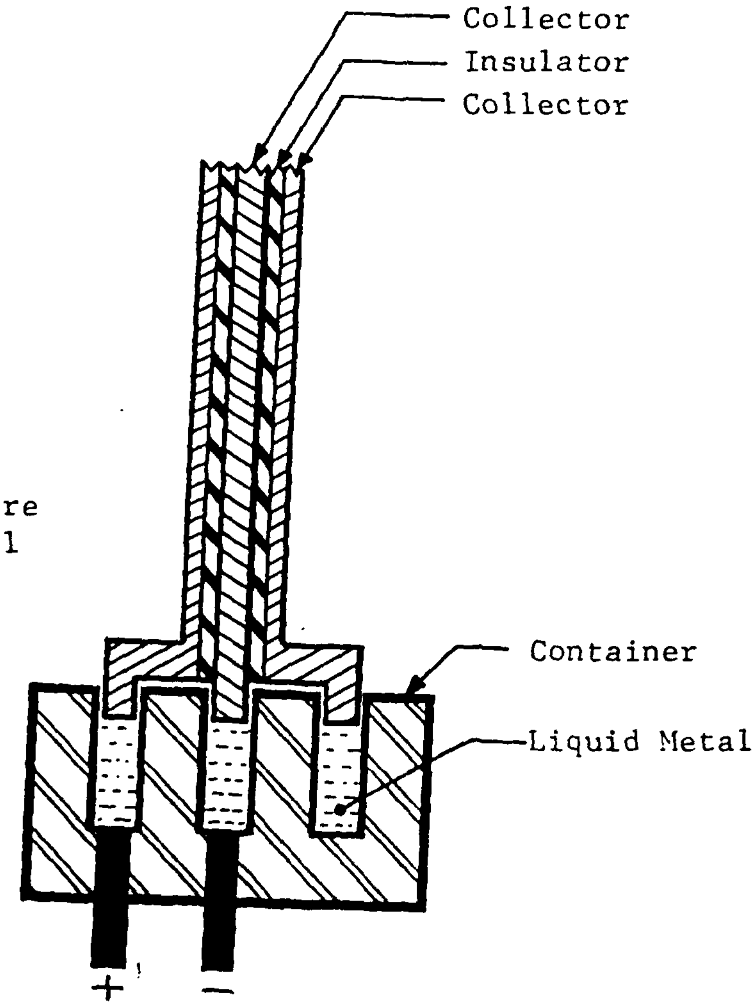


FIGURE 46

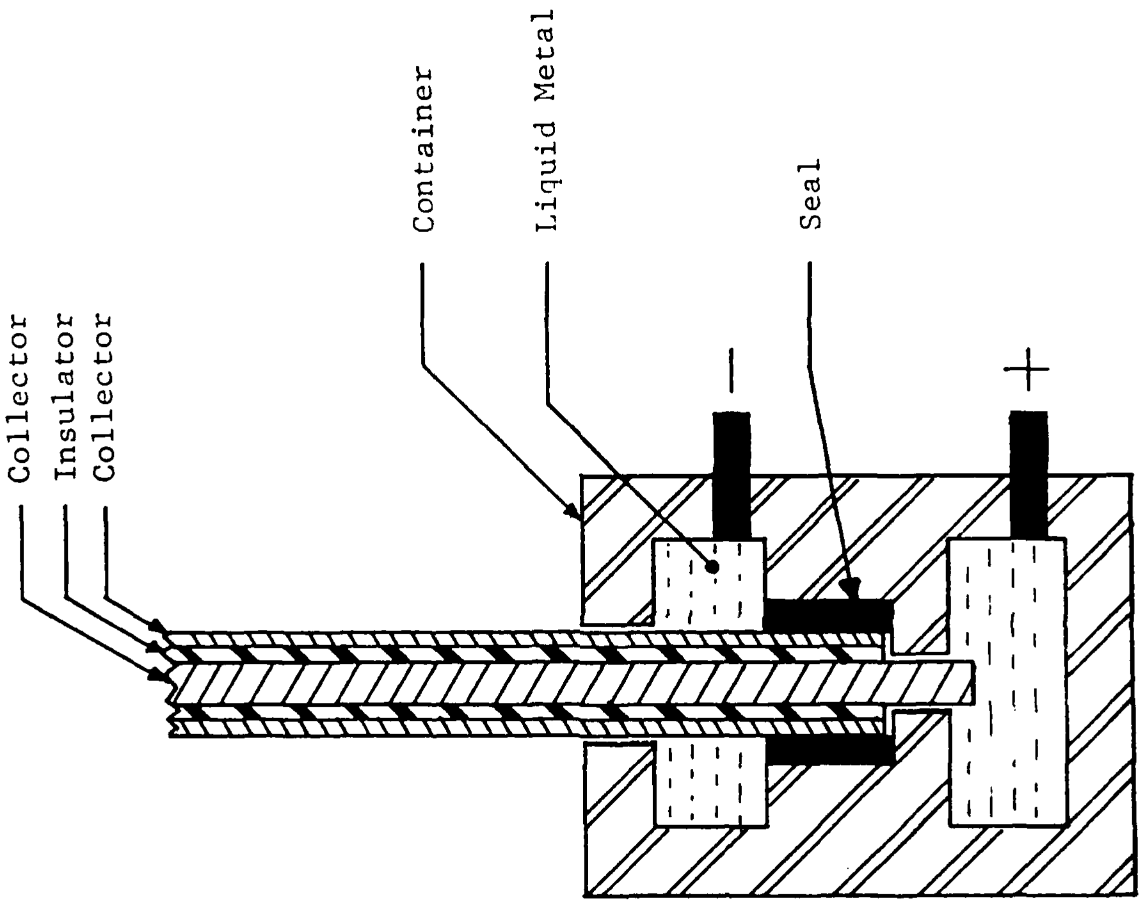

Collector
Insulator
Collector
Container
Liquid Metal
Seal
−
+

FIGURE 47

Several important technical factors can be implemented into a device design to dramatically lengthen operating life over results obtained in the Phase I material evaluation experiments. Conservatively, effort in Phase II of the project can improve the effectiveness of a liquid metal alloy by a factor of two based upon Phase I experience. The oxidation of the liquid has been a severe limitation, further work should readily improve gas protection effects by a factor of two using an active atmosphere. The large surface areas exposed in the material experimental work are not necessary in a device and represents a high potential gain with improvements of an order of magnitude appearing to be quite reasonable. Physical design of the unit by using rotating ring electrodes, glass-ceramic and graphite seals can provide conservatively another factor of two. Overall, therefore, it is not unreasonable, based on this feasibility study, to consider a goal of a 10,000 hour operating unit at 200 amp, with a possibility of much better performance as more design features are understood and implemented.

Electrical collection devices operating at 200-500°F are an exciting possibility and can be achieved with the pursuit of the development phase of the work.

9. DISCUSSION

A total of forth-nine collector test runs was performed in Phase I and evaluated in conjunction with dissolution tests on various electrode metals and low melting liquid alloys. The program has enabled a much clearer picture of collector requirements to emerge in material terms with indications of some important features in designs of devices.

Superior atmosphere protection is paramount to combat the real problem of elevated temperature oxidation of the liquid metal alloys. Most low melting point metals are made up of various percentages of a small family of metals and react very similarly in oxidation. High bismuth containing liquid metals show a propensity to form black powders and alloys containing lead and tin were subject to internal oxidation. Alloys 117 and 136 fusible material were particularly affected by internal oxidation and tended to expand quite noticeably as oxidation proceeded while keeping a metal appearance at the surface. Lead-bismuth for example, was completely converted to a powder condition. Various degrees of powder formation occurred with the other alloys. Best results so far were clearly obtained with the tin-indium alloy. Using aluminum as a protection agent, and silver as a dispersing agent for oxidation did not appear to provide any advantages. The work should be expanded to include other potential low melting alloys to benefit from the tin-indium alloy example by further modifications for improved oxidation resistance.

The pressurized argon experimental collector device was effective in substantially reducing oxidation using a good quality low oxygen level argon gas. A review of possible alternate active gases that will provide oxidation protection will be necessary in Phase II of the work and could result in a life in hours increase of up to an order of magnitude.

The large surface area to volume ratio used in the Phase I experiments was excellent in ranking the oxidation resistance order of merit of the liquid metal alloys. Significant increases in collector operating hours can be accomplished by reducing the exposed surface area to a minimum. A reasonable expectation is to use one-tenth the surface area for a similar liquid volume, and thus probably improve service life of a particular alloy and electrode combination by a factor of ten. Other design implementations are expected to improve life with lower outgassing from the refractory cups chosen and a monitoring system for oxygen levels in the collector zone.

The final test run in the pressurized experimental collector produced over 700 hours of operating time using a tin-indium eutectic alloy, showing great promise. The best results therefore, were achieved with a higher melting temperature.

The metallographic examination of solid electrode materials of various metals exposed to a number of liquid metals gave varying results. The liquid metal appeared to have severe effects or no reaction at all. Almost invariably, the mechanism of attack was a localized penetration of the solid electrode surface with accelerated alloying at that specific location. The time period before onset of the attack varied due to possible surface oxidation acting as a protectant with the absence of any flux to wet the metal-to-metal interfaces. It can be postulated that a break in an oxide film, tunnelling beneath the surface, or transport across the metal interfaces were some of the failure initiation mechanisms. Clearly, the metal interface provides a natural barrier to reaction, but once broken proceeds rapidly depending upon the particular metallurgical relationship between solid and liquid metals.

Metallurgical features appear to dominate any physical relationships such as wetting angles, viscosity, or surface tensions, etc. resulting in very few possible candidate electrode materials considered useful.

Also, it was found difficult to model the data obtained because of the localized and penetrative nature of the liquid metals, rather than gradual attack dissolution or reaction growth at interfaces. Tungsten electrodes were consistently superior in all the work executed by dissolution studies, and generally were used for current collection work.

Sufficient data has been collected to put together initial design concepts for a device that, with a much reduced surface area, and possible active gas environment should be capable of handling moderate currents with extended life. A 10,000 hour operating device appears a reasonable goal for the next part of this effort.

10. CONCLUSIONS

A study has been undertaken to test the feasibility of using low melting temperature liquid metals in electrical collection devices to operate in a range of 200-500°F.

Results of forty-nine collector runs and many dissolution tests on candidate electrode and liquid metal alloys have given positive direction and identified materials of construction for the first actual device.

A tin-indium eutectic alloy in liquid form used in conjunction with tungsten electrodes has operated as a liquid metal electrical collector for over 700 hours in a pressurized collector system.

Results of the program have enabled proposals of collector designs to be made with the objective of a 10,000 hour device as the goal of Phase II of the project.

The concept of liquid metal electrical collectors in the 200-500°F range is feasible and sufficient progress has been made to provide a basis for design of actual devices.

Roy E. Beal

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