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PROCESSING OF IMMISCIBLE MATERIALS FOR
SUPERCONDUCTORS AND ELECTRICAL CONTACTS
Final Report, 28 May 1975 - 30 Sep. 1976
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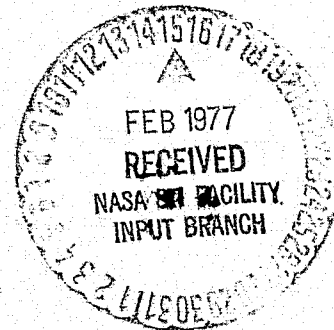
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**ANALYTICAL STUDY OF SPACE PROCESSING OF IMMISCIBLE
MATERIALS FOR SUPERCONDUCTORS AND ELECTRICAL CONTACTS**

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Interim Report

January 1977



Prepared for

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| 16. ABSTRACT <p>This report presents the results of a study conducted to determine the role space processing or materials research in space may play in the superconductor and electrical contact industries. Visits were made to manufacturers, users, and research organizations connected with these products to provide information about the potential benefits of the space environment and to exchange views on the utilization of space facilities for manufacture, process development, or research.</p> <p>Although the advantages that might be gained by utilization of space to aid in the manufacture of current products were not obvious, the interchanges uncovered potentially fertile areas that might lead to improved products made in space or improved space manufacturing processes. In addition, space experiments were suggested which could result in improved terrestrial processes or products. Notable examples of these are, in the case of superconductors, the development of Nb-bronze alloys (Tsuei alloys) and, in the electrical contact field, the production of Ag-Ni or Ag-metal oxide alloys with controlled microstructure for research and development activities as well as for product development.</p> <p>The report also describes a preliminary experimental effort to produce and evaluate rapidly cooled Pb-Zn and Cu-Nb-Sn alloys in order to understand the relationship between microstructure and superconducting properties and to simulate the fine structure potentially achievable by space processing.</p> | | | | | |
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FOREWORD

This report was prepared by Battelle's Columbus Laboratories under Contract NAS8-31445, entitled "Analytical Study of Space Processing of Immiscible Materials for Superconductors and Electrical Contacts" for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. It covers the period May 28, 1975 through September 30, 1976. Mr. I. C. Yates and Dr. L. L. Lacy were the Contracting Officers Representatives.

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FINAL REPORT

on

ANALYTICAL STUDY OF SPACE PROCESSING
OF IMMISCIBLE MATERIALS FOR SUPERCONDUCTORS
AND ELECTRICAL CONTACTS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER

from

BATTELLE
Columbus Laboratories

September, 1976

INTRODUCTION AND SUMMARY

Background

Immiscible Materials and Space Processing

The field of immiscible materials and its relation to space processing has been summarized in a recent publication.⁽¹⁾ Immiscibles represent a broad category of multiphase materials embracing composites, eutectics, monotectics, peritectics, eutectoids, peritectoids, precipitates, and systems with miscibility gaps.

Only materials and reactions that involve fluid phases (liquids or gases) have a special role in space processing. It is only in these that the effects of gravity would be pronounced. The more obvious mechanisms influenced by gravity are:

- Segregation in a single phase liquid or gas due to density differences arising from local variations in composition or temperature

- Segregation in a multiphase system due to density differences between droplet and host phases (Stokes migration)
- Convection currents in both single-phase fluids and those containing liquid or solid droplets due to temperature gradient-induced or composition-induced density variations in the liquid phase
- Segregation of a liquid phase in a porous solid host phase. This mechanism may be applicable to segregation in castings or in liquid-phase sintered compacts.

Our work at Battelle's Columbus Laboratories⁽²⁾ in the area of immiscibles has concentrated in those systems containing a liquid phase miscibility gap, i.e., a two-phase field consisting of two liquids which at sufficiently high temperature become a homogeneous single-phase liquid (see Figure 1). Our efforts in this area have been concerned with the potential usefulness of such materials, the relationship between their microstructure and properties, the evolution of these microstructures at 1-g and at 0-g, and the role of space processing in developing unique properties and microstructures. We have also been active in analyzing a Science Demonstration Experiment performed in Skylab dealing with the stability of oil (Krytox)-water mixtures.^(3,4)

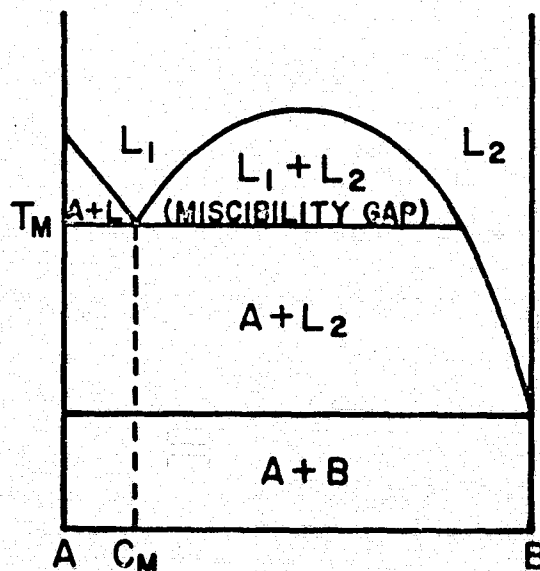


FIGURE 1. SCHEMATIC DRAWING OF LIQUID PHASE IMMISCIBLE SYSTEM

The important findings of our work are summarized in the following section.

Pertinent Prior Results. Computer simulation studies carried out on a previous contract^(2,4) have shown that space processing of liquid phase immiscible materials would be expected to produce a fine droplet size distribution in addition to the anticipated spatially uniform distribution. This results from the fact that in the space environment, gravity-induced coalescence processes should be significantly retarded. Some agglomeration processes such as Brownian motion and interdiffusional growth are essentially independent of gravity. They occur rapidly when the droplet radii are small (1μ) but coalescence is slowed significantly when the radii reach a somewhat larger size ($\sim 10\mu$). The agglomeration mechanisms that occur at longer times involve gravity induced collision processes which involve Stokes migration and/or velocity gradients induced by convection currents. Reduction of the gravitational level should greatly reduce this source of agglomeration and so allow the production of materials with a relatively fine distribution of second phase droplets. It may also be possible to retain a spinodal structure* by processing in space due to the minimization of disturbing convection currents. Experimental evidence for spinodal decomposition in liquid phase immiscibles has been recently reported.⁽⁵⁾

During the course of this study, another characteristic of the space environment offered some promise for producing superior superconductors. The weightless environment of space would allow the processing of materials without a container and, therefore, would avoid contamination and sites for heterogeneous nucleation associated with the container. It should then be possible to obtain significant amounts of undercooling in superconducting alloys or electrical contacts which would foster a finer microstructure and show significantly less microsegregation and a more uniform distribution of shrinkage porosity. Processing in the weightless environment of space also might allow the handling of fine wires or wide films without support and perhaps without the customary handling equipment.

* The spinodal structure results from a decomposition within the "spinodal" of the miscibility gap. The structure which up to the present has only been directly observed in alloys with a solid state miscibility gap consists of a single phase with uniform composition oscillations of wave length usually $< 100\text{\AA}$.

Experimental work has confirmed the lack of segregation and the fine microstructure in microgravity processed alloys. In the case of the Bi-Ga system,⁽⁶⁾ the fine, uniform structure has led to unusual electrical properties (manifestations of semiconducting and superconducting behavior).⁽⁷⁾ In the case of Au-Ge and Pb-Zn-Sb, unexpected X-ray diffraction lines were observed in the microgravity processed samples, but not in samples processed at 1-g.⁽⁸⁾ An attempt to confirm the presence of the unexpected phases, however, has not been successful⁽⁹⁾ and so may be discounted until further supporting evidence is obtained.

In contrast to the findings above, cases have been recently reported in which the fine structure expected has not been observed.^(10,11) This has been tentatively attributed to interfering fluid flows resulting from surface tension effects or convection currents caused by large density differences in the micro-g environment. Agglomeration by Ostwald ripening is a slower process and would be expected to be important in experiments and processes that involve very slow cooling rates at micro-g.

The early work of Reger⁽¹²⁾ and the more recent work performed by Battelle⁽²⁾ have listed a number of potential applications for liquid phase immiscible systems processed in space. Among these were superconductors, electrical contact materials, III-V semiconductors, catalysts, permanent magnets, bearings, and superplastic materials. The present program was motivated by a desire to make an in-depth study of two of the more promising application areas, namely, superconductors and electrical contact materials. Our prime motivation for processing these materials in space would be to produce superconductors or electrical contact materials with superior performance characteristics which might result from a fine distribution of one phase in a host matrix.

Superconductors

Interest in the potential of processing superconducting liquid phase immiscible materials in space resulted from the large number of potentially applicable alloy systems, the microstructural variations possible from processing these systems in space and the unique properties to be derived from these structures.

Cooling a liquid phase immiscible alloy from the single liquid phase field through the miscibility gap (see Figure 1) can result in various microstructural configurations of the two phases, depending on the composition of the material and cooling rate used in its preparation. Thus, it is possible to have a dispersion of A in a matrix of B, a dispersion of B in a matrix of A, an interlacing mixture of A and B with either or both being continuous phases or a spinodal structure. The shape of the dispersed particles is usually spherical, but it is possible that by directional cooling through the monotectic transformation temperature, T_m , for rod or plate morphologies to be obtained. For example, Livingstone and Cline⁽¹³⁾ were able to grow fine lead rods in a copper matrix by directional solidification of hypermonotectic alloys.

A list of potential superconducting materials based on the work of Reger⁽¹²⁾ (see Table 1) presents an ambitious number of systems in which either one or both of the elements has been verified to undergo a superconducting transition, and where selected alloys within the total system have demonstrated superconducting properties. To be sure, not all of the elements listed have demonstrated superconducting properties in normal bulk form; bismuth, for example, has no verified superconducting transition except in very thin films.⁽¹⁴⁾ The inclusion of such special conditions, however, is in keeping with the general direction of this discussion, for it is the unique properties which may be attained only through specialized processes or structures which are of primary interest.

This existence of mixed phases in a superconducting system can produce either detrimental or beneficial effects, depending upon the nature and distribution of the phases. For example, induced superconductivity of normally nonsuperconducting materials (e.g., bismuth, as seen above), whether it be through thin film, granular or deformation effects,

is usually associated with significant perturbations in the local vibration modes of the crystal lattice, and a resultant enhanced phonon contribution to the electron-electron coupling responsible for superconductivity. It would be expected that such enhanced superconductivity (as seen principally through effects on the transition temperature) would result from a configuration in which there was a high surface/volume ratio, as would be the case in systems composed of an interlaced mixture of phases.

Such composite structures have been proposed earlier wherein porous ceramic or glass systems have been infiltrated with liquid aluminum, indium, lead, or other relatively low-melting superconductors.⁽¹⁵⁾ Enhancement (raising) of transition temperatures through applications of this approach offers the potential for creating superconducting materials or systems based almost entirely upon morphological contributions.

Superconducting behavior has also been observed in systems in which fine particles of superconductor are dispersed in a normal conducting matrix. Thus, in the systems Cu-Nb and Cu-Nb-Sn, superconducting behavior results from the fine distribution of niobium or Nb₃Sn particles in a copper matrix. These types of alloys, first suggested by C. C. Tsuei,^(16,17) have typical atom percent formulations, Nb₁₀Sn_{1.5}Cu_{88.5}, V₁₀Ga₁₀Cu₈₀, and Nb₁₅Sn_{1.5}Cu_{83.5}. The superconducting behavior of the as-cast alloys has been explained in terms of a fine superconductor precipitate forming either a continuous path along the copper alloy grain boundaries⁽¹⁸⁾ or in terms of the particles being spaced within the coherence distance so that conduction is by means of a proximity effect.⁽¹⁹⁾

When these alloys are worked into the form of a fine wire and undergo reductions in an area of approximately 600:1, the primary niobium-rich dendrites become elongated fibers and the superconducting properties improve significantly over those in the as-cast form. These materials have transition temperatures close to that of the bulk A15 superconductor compound Nb₃Sn and have critical currents and critical fields that are comparable to those produced by current manufacturing methods.⁽²⁰⁾ In addition, the new Tsuei alloys appear to have the advantage of improved tolerance to damage by repeated bending and potentially lower manufacturing costs.

In contrast to the above discussion, depression of the transition temperature may result from the presence of non-superconducting particles. In such cases, a lowering of the transition temperature (or complete conversion to the normal state) results from the presence of high densities of particles sized on the order of the coherence length (several hundred angstroms).

The preceding considerations have dealt mainly with the transition temperature aspects of potential materials systems. There are, to be sure, additional effects which can be beneficial, such as flux pinning which can produce a resultant net enhancement of the total superconducting properties. While decreases in transition temperature can result from the inclusion of non-superconducting particles, evenly spaced particles in a superconducting matrix can produce a spreading of the transition over a range of temperatures, particularly where the included phase is ferromagnetic or insulating. These inclusions, which act as effective flux pinners (similar to dislocation pinning in metals) retard the penetration of magnetic flux lines into the superconducting regions of the structure and this can lead to higher critical fields and currents. In addition to the effect upon "intrinsic" superconducting properties, the presence of dispersed phases can also contribute to improved mechanical strength.

In spite of some progress in this area, the relationship between superconductivity and the distribution of phases in a multiphase alloy is only poorly understood. The experimental portion of the present program is aimed at improving this situation. In this case, the microstructure of potential superconductors would be controlled by variations in composition and cooling rate. The product would be a fine wire or ribbon in order to achieve rapid cooling rates and resulting fine structures.

Electrical Contacts

At the present time, immiscible materials are used extensively for electrical contacts. In fact, on a weight basis, such materials comprise an estimated 75-80 percent of total contact material usage.

The material systems of present commercial interest are relatively few. These are (1) Ag-CdO, (2) Ag-Ni, (3) Ag-W, and (4) Cu-W. Several others are used but in low volume. These include Ag-Fe, Ag-Mo, and Ag-WC.

Such materials are used almost exclusively for switch, circuit breaker, and motor control applications above about 5-10 amperes. The objectives in their use are for (1) high conductivity, (2) low arc erosion, (3) resistance to electrical welding, and (4) contact resistance stability.

All of these materials are produced by classical powder metallurgy techniques and in the case of Ag-W and Cu-W, the process also includes liquid infiltration.

While Ag-CdO materials are also produced by powder metallurgy, no more than 10 percent of present usage is in this type of product. Most of the Ag-CdO is produced by internal oxidation of cast silver-cadmium alloys.

One objective in the processing of all of these materials is to obtain a fine, uniform/random dispersion. This feature is generally desired for optimum performance but for reasons which are still not totally understood. Subtle changes in process and microstructural variables are known to result in performance differences of at least a factor of three for a given composition.

While O-g processing offers unique opportunities for producing a uniform distribution of fine particles in a conducting matrix by

- (1) Cooling through a liquid phase miscibility gap
- (2) Introducing stable particles or fibers directly into the molten bath (Al_2O_3 , Ni, etc.)
- (3) Selective internal oxidation of a molten alloy (e.g., Ag-Th \rightarrow Ag-ThO₂),

it is impossible to predict the magnitude of these and other effects on performance. This is due to the fact that the interrelation of variables is imperfectly understood and that studies in this field have proceeded largely on an experimental rather than theoretical basis.

In spite of this, immiscible systems have considerable promise in application. Here there are three factors to be considered. In the first place, absence of miscibility or compound formation will permit maintenance of the high conductivity for which the matrix material was initially selected. Secondly, even in that case where the included second phase (which contributes to mechanical properties enhancement) is an insulator, the volume fraction of the second phase is usually small enough that only insignificant effects upon total bulk conductivity result, and the enhanced mechanical integrity more than compensates for decreased conductivity. And third, the structure which appears to have the greatest promise is that in which the second dispersed phase is metallic and completely noninteractive with the matrix. For it is this latter case that the mechanical integrity is improved, and the losses to electrical conductivity are minimized.

Sixteen systems were listed by Reger⁽¹²⁾ in his compilation of liquid phase immiscible systems as being potentially applicable as electrical contact materials. These are listed in Table 2.

TABLE 2. SUGGESTED ELECTRICAL CONTACT MATERIALS
DERIVED FROM IMMISCIBLE SYSTEMS

| | | | |
|-------|-------|-------|-------|
| Ag-Cr | Ag-Ru | Au-Re | Cr-Cu |
| Ag-Ir | Ag-W | Au-Rh | Cu-Os |
| Ag-Re | Au-Ir | Au-Ru | Cu-Re |
| Ag-Rh | Au-Os | Co-Cu | Cu-Ru |

The rationale for the choice of these systems was the presence of a good conductor (Cu, Ag, Au) and a dispersion of a second phase which adds good wear resistance, corrosion resistance, or strength. Using the same criteria, a few other possibilities could be added to the list among which are the electrical contact materials currently being utilized, Ag-Ni, Ag-Mo, Ag-Fe, and Cu-W, and the as yet unexplored systems, Ag-Cb, Ag-Co, Ag-Mn, Ag-Ta, Ag-V, Cu-Mo, Cu-Ta, and Cu-V. Ag-C and Cu-C are presently being employed where the lubricating property of the graphite improves resistance to sticking.

Part of the motivation for conducting the present program stems from the need to explore the technical benefits derivable from the potentially superior performance of electrical contact materials produced by space processing or from research conducted on these materials in space.

Program Objectives

The objectives of this program are to assess the technology involved in the production of superconductors and electrical contact materials and to evaluate the benefits to be derived from space processing of these materials in terms of enhanced properties and/or more economical production processes.

Program Organization

To meet these objectives, we have carried out a combined analytical and experimental program consisting of the following three tasks.

Task 1. Superconductors

Task 1 is an analytical study to evaluate the status of current technology in the production of superconducting materials and to assess the potential role space processing may play in this technology. This task included visits to superconducting wire manufacturers and, in addition, explored novel methods for producing superconductors through use of space processing.

Task 2. Electrical Contact Materials

Task 2 is an analytical study to evaluate the status of the technology for the production of electrical contact materials and to assess the potential role space processing may play in this technology. This task also included visits to manufacturers of electrical contacts and contact

materials and, in addition, was concerned with novel techniques afforded by the 0-g environment of space for producing superior or novel electrical contact materials.

Task 3. Superconductivity in Immiscible Materials

Task 3 is an experimental study of the relation between the superconducting properties of immiscible materials and their microstructure. This portion of the program originally concentrated on the production of finely structured Pb-Zn alloys by melt spinning. The direction of this task, however, was changed and instead concentrated on preliminary experiments with CuNbSn (Tsuei alloys).

Program Summary

Task 1. Superconductors

Visits were made to five organizations involved in the manufacture of or research in superconductors. In a typical visit, a representative from BCL would first provide a background briefing dealing with the attributes of the space environment that would be of potential interest to the superconductor industry and then a general interchange would follow. This was usually quite beneficial to the organization being visited as well as to the visitors because it provided a new frame of reference to the organization and allowed the visitors to learn in detail about the problems of the industry.

The remainder of each visit was usually devoted to discussion of questions submitted by L. L. Lacy and I. C. Yates of MSFC which dealt with such subjects as trends in superconductor research, problems that space processing might overcome, the relationship between microstructure and superconducting properties, and applications of superconductors. (See Tables 4 and 5).

The highlights of our conversations are summarized as follows:

- The Tsuei materials, Cu-Nb-Sn or Cu-V-Ga, are of interest to the superconductor community in that they offer some

promise of developing into inexpensive highly damage-tolerant superconductors. Space processing has the potential of producing finely structured billets of this alloy which could subsequently be processed on earth into superconductor wire. Processing of wire directly from the melt is also a possibility.

- New materials were discussed such as the Al5 compounds and metallic sulfides. However, there is a reluctance at this time to use advanced materials even if they are fairly well developed (e.g., Nb₃Sn). Instead, most demand is for use of Nb-Ti alloys because of reliability. A "Watson sponge" material⁽¹⁵⁾ consisting of a fine interlacing structure of superconductor with metal rather than glass may have merit as an alloy that could be produced from a liquid phase immiscible in space. Incorporation of flux pinners such as ZrO₂ was another suggested possibility for space processing.
- The cost of superconductors is usually given in terms of performance, i.e., \$0.001 to \$0.010/A-ft (\$0.003 to \$0.03/A-m) which amounts to ~\$100/lb (\$45.00/kg). Even though the cost of the superconductor is a small fraction of the cost of a superconducting system, the large amount of competition in the industry produces extreme pressure on the price. A large fraction of the cost is in the Nb alloy raw materials, however, which is supplied by one or at most two organizations. The cost of the presently available superconductors is not sufficiently high to make present superconductor material a likely candidate for space processing. However, materials with special properties such as the Tsuei alloy or high H_c, J_c materials for magnet applications could be attractive space products if users are willing to pay somewhat higher prices for the specialized properties.

- The potential applications of superconductors are numerous ranging in scope from energy storage devices and CTR containment magnets to transmission lines and magnets for separation processes. Growth in the usage of superconductors has been limited, however, because of user conservatism. Usage of a superconductor in a large scale device should spur further applications.

Task 2. Electrical Contact Materials

As had been the case in the preceding task, visits were made to eight U.S. companies and two German firms engaged in the manufacture and research in electrical contact materials. The following are highlights of the visits, some conclusions, and some recommendations for space experiments:

- The discussions were limited to silver base contact materials, which accounts for approximately 70 percent of the electrical contact usage. The systems of importance are Ag-CdO, Ag-W, and to a lesser extent Ag-Mo, Ag-WC, and Ag-Ni. The thrust of research concerning these materials has been in the area of improving erosion resistance and resistance to welding. Substitutes for the dispersoid materials CdO and W have also been the subject of research efforts.
- Because the cost of electrical contact materials is comparable to the anticipated cost of transportation into and from space, the firms contacted were largely pessimistic about achieving economical space manufactured electrical contacts. This conclusion was moderated by the low but finite possibility that electrical contacts showing much improved performance in arc erosion resistance or anti-welding characteristics could be achieved by space processing.

- The firms contacted were very receptive to the idea of using space facilities as a laboratory to prepare research materials that were difficult or impossible to prepare terrestrially. Since the relationship between microstructure and electrical contact performance is not well understood at the present time, the fertile area for such an effort would be the preparation of research materials which would shed light on this relationship. Research in this area is complicated by the difficulty in controlling a structural variable without altering other important features.
- The microstructural features of interest and that should be controlled are: particle size, particle shape, particle distribution (both in space and in size), concentration of the dispersed phase, amount of porosity in the structure, effect of minor impurities/additions, and thermochemical properties of the dispersed phase.

A number of research areas which involve processing materials in space were suggested. These include:

- The production of electrical contact materials having controlled dispersed size distributions. These experiments could be conducted with Ag-Ni alloys by means of melting and solidification techniques. Control of particle shape in order to ascertain the influence of this parameter may be effected by directional solidification in the micro-gravity environment.
- The production of Ag-metal oxide or silver with various types of compound dispersoids may be produced in space by means of internal oxidation techniques performed directly on the liquid owing to the absence of disturbances from gravity driven convection. The

disadvantages of solid state internal oxidation, such as dispersoid size and concentration inhomogeneties and the excessive reaction times should be minimized by carrying out the process on a liquid at low-g.

- Powder blending in the space environment was suggested as a means for producing uniform distribution of CdO, Ni, C, and W in Ag. Both blending and consolidation need to be conducted in the micro-gravity environment in space to avoid segregation.
- The space environment may offer advantages in the more effective execution of liquid phase infiltration and liquid phase sintering operations used in the production of W-Ag alloys. These materials suffer from excessive porosity, poor wetting characteristics and a propensity for large parts to crack. Carrying out these operations in the space environment is expected to provide some improvements.

Task 3. Superconductivity in Immiscible Materials

This small experimental task was intended to shed light on the relationship between microstructure and superconducting properties in immiscible materials. Initial experiments were performed with Zn-Pb alloys of two compositions, 5 and 50 wt percent of Pb. Ribbons of these alloys were produced by chill block melt-spinning techniques. Preliminary evaluation of these materials by optical and scanning electron microscopy indicated that there were problems associated with our technique but that the basic method of ribbon preparation was applicable.

The direction of Task 3 was changed shortly after the work on the Pb-Zn system was started. The change involved substitution of Cu-Nb-Sn alloys (Tsuei Alloys) for the Pb-Zn and Bi-Ga alloys originally chosen. The decision was prompted to some extent by our visits with

organizations involved in superconductor research and manufacture. This alloy system was deemed to be a more practical one and one which might have both terrestrial, as well as space processing payoffs. Pendant drop melt extraction* was chosen as the most suitable technique in the light of the temperature limitations of our melt-spinning equipment and the need for a protective environment. The feed stock for this preparation technique, 0.5 cm diameter rod, was fabricated by swaging chill cast alloy rod. The pendant drop melt extraction method was then used to produce 80 μ diameter fiber. Optical and scanning electron microscopic examination of both the swaged rod and melt extracted fiber and flake showed that the processing techniques used to prepare the 0.5 cm diameter swaged rod were satisfactory. The microstructure of the cast and swaged rod consists of elongated niobium dendrites about 2.5 μ in diameter. The melt extracted fiber by contrast had a rather nonuniform distribution of niobium which probably resulted from segregation of the niobium and copper within the pendant drop.

It is recommended that further work be conducted in this system but that rapidly cooled fiber or ribbon be produced by chill block melt-spinning or crucible melt extraction. Both these processes start with a homogeneous melt and should avoid the segregation problems we have encountered in the present study.

Recommendations for Further Study

In addition to the specific recommendations for further efforts to conduct specific micro-g experiments with superconductor and electrical contact materials, it is important that studies similar to the present one be extended to other industries which might benefit from incorporation of space processing into their technology. Such industries include those associated with magnetic materials, catalysts, superplastic materials, etc. The interchange that would take place is valuable not only from the direct benefits that might be obtained but also from the standpoint of informing industry of the space program and encouraging industrial scientists and engineers to develop processes that could take advantage of the space environment.

* A Battelle patented process.

DETAILED PROGRAM DESCRIPTIONTask 1. SuperconductorsIntroduction

This task had as a goal the evaluation of current technology involved in the production of superconducting materials and the assessment of the potential role space processing might play in this technology. The task was carried out through a series of visits which included in-depth conversations with manufacturers of superconductors and with research scientists and engineers in the field of superconducting materials.

During the week of August 18, 1975, visits were made to five laboratories and companies engaged in the study, development, and manufacture of superconductive wire (see Table 3). Talks, which occupied the better part of each day, ranged from conventional superconductor manufacturing processes to possible long-term applications of space processing.

The visits usually started with a briefing by one of us dealing with the space program and the unique features of the space environment that might offer advantages in manufacturing processes, in producing research materials, or in carrying out research and development experiments to support terrestrial programs. To a large extent, the special attributes of the space environment were not appreciated before our briefing and from that standpoint much was gained with regard to the development of a potential space facility user. Following the initial briefing, discussions of a general nature took place, but in addition, responses to specific questions posed indirectly by L. L. Lacy (Questions L-1 to L-5, Table 4) and by I. C. Yates (Questions Y-1 to Y-6, Table 5) of NASA Marshall Space Flight Center were sought.

The results of the week's activities are described in the following account, which adheres loosely to the format of the questionnaire. In the interest of anonymity, the corporate sources of the various comments and opinions are referred to by the code letters A through E.

TABLE 3. ORGANIZATIONS AND PERSONNEL CONTACTED
DURING TASK 1 VISITS

| Organization | Contacts |
|--|--|
| Airco, Inc. Murray Hill New Jersey | Dr. E. Gregory Dr. E. Adams |
| Brookhaven National Laboratory Upton, L.I. New York | Dr. D. Dew-Hughes Dr. M. Suenaga Dr. T. Luhman |
| Intermagnetics General Corporation Guildeland New York | Dr. B. Zeitlin Dr. G. Morrow |
| Supercon, Inc. Natick Massachusetts | Dr. W. Larson |
| Magnetic Corporation of America Waltham Massachusetts | Dr. E. Lucas Dr. T. deWinter Dr. Z. Steckley |

TABLE 4. QUESTIONS POSED BY DR. L. L. LACY, MSFC

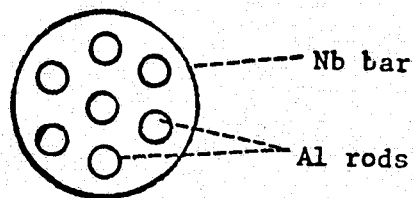
-
- (L-1) - What are the current trends in superconducting materials research that will probably extend into the next 10 years? What are the current research activities? What problems are researchers trying to solve currently?
- (L-2) - What should be the major thrust in space processing research that is connected with superconductivity? Are the major thrusts higher transition temperatures, higher critical fields, or currents?
- (L-3) - On the time scale of 10-20 years, what will be the thrust of superconductor technology? What will be the applications of superconducting devices over this time frame?
- (L-4) - What problems exist today that stand in the way of achieving the technological and application goals? Again, the time frame of 10-20 years should be considered.
- (L-5) - Are there limitations in the present process of making multi-filament superconductor cables in which space processing may offer some advantages? These might be in terms of segregation, contamination, etc.
-

TABLE 5. QUESTIONS POSED BY MR. I. C. YATES, MSFC

-
- (Y-1) - Is liquid-phase processing used in any of the superconductor technology? If so, are there problems imposed by gravity; that is, are there convection and/or segregation problems? If there are, what is being done to overcome these problems, and what are the additional costs associated with the solution of these problems?
- (Y-2) - If the above problems exist, what effect do they have on the structure and resulting properties?
- (Y-3) - How well understood is the relationship between the structure of superconductors and their properties? Do multiphase materials have any application in the superconducting area? Can one predict the superconducting behavior of these materials as a function of microstructure?
- (Y-4) - In the processing of superconductors, is crucible contamination a problem?
- (Y-5) - What future applications have the highest payoff in regard to superconducting devices or alternatively what aspect of superconductivity has the highest present interest?
- (Y-6) - How do the costs of the superconductor influence the cost of the system to which the superconductor is applied? In other words, is there any data dealing with cost trade-offs in the design of systems with superconductors?
-

Results of Visitations

Current Research Activities (L-1)*. (a) Bronze Processes - Contributors B and C. The bronze process continues to be an active area of research and development. In its simple form, this process consists of reacting pure Nb or pure V with Cu-Sn or Cu-Ga to form Nb_3Sn or V_3Ga layers. It was subsequently discovered that starting with dilute Nb-Sn or V-Ga alloys rather than with the pure transition elements resulted not only in enhancements of the rate of diffusion, but also increases in the critical current, J_c , of the final product. During conversations with C, it was suggested that supersaturation of the starting Nb-base or V-base alloys might be achievable during space processing. Also during discussions with C, the subject of Nb_3Al as a superconductor was broached. A recently suggested technique for producing a Nb_3Al conductor is represented by the accompanying diagram (during the reaction, the Al is permitted to melt). It was suggested by C that both the process and its end product could be greatly improved by the addition of ZrO_2 to the Nb. At this point, space processing was invoked as a possible route to the securing of a better dispersion of particulate matter in the Nb.



(b) Tsuei Material - Contributors A, B, and C. During discussion with A, it was considered that the Tsuei material, either in the Nb-Cu or the Nb-bronze formats, might have some potential as a zero-g product. The system Cu-Nb is a member of the group of "immiscible alloys" tabulated by Reger⁽¹²⁾ (see Table 1). Although Cu-Nb is no longer regarded as a true liquid immiscible system, B agreed that Tsuei material would make an

* Question number, see Tables 4 and 5.

interesting and appropriate study. In the initial Nb-bronze work, B pointed out, the composition used was $\text{Cu}_{83}\text{Nb}_{15}\text{Sn}_2$; however, studies were said to be under way on similar systems containing different classes of bronze. It was pointed out by B that, currently, quench rates must be very high in order to obtain a proper dispersion of Nb in the bronze (or copper) matrix. Space processing thus seems to be ideally suited to the melting and solidification of large ingots of Nb-bronze, in that large masses of the ingredients could be melted up and frozen at normal rates without segregation.

It was drawn to our attention by B that recently published studies have shown Tsuei material to contain multiply connected threads of Nb, or multiply connected rosettes, generated by precipitation at granular triple points.⁽¹⁸⁾ In response to this, C commented that if the Tsuei material were indeed multiply connected, precipitation in zero-g would not be helpful, since the resulting fineness of the precipitate would actually be deleterious to its connectivity and consequently to the superconducting performance of the composite. Discussions with A suggested that it would, however, be well worthwhile to pursue Tsuei material with the work taking place in several phases. Initially, further exploration of the 1-g situation should take place, this to include studies of powder-compacted material (in which regard, the suitability of the zero-g environment for producing the starting powder should be considered). Finally, it was recommended during discussions with B that Spacelab be provided with facilities for the melting of bulk samples of alloy. Certainly at the present time, even if the splat cooling of liquid-immiscibles in 1-g produces an acceptable product, large ingots of chilled liquid-immiscibles cannot be handled because of cooling-rate problems.

(c) New Materials - Contributors A, B, and C. As pointed out by B, one important thrust of new materials developments would certainly take the form of continued efforts to depart from the A15 approach to high- T_c superconductivity. Both A and B agree that the metallic sulfides might lead the way into a promising new-materials regime. B pointed out that the best superconducting sulfide produced so far is $\text{PbMo}_{5.1}\text{S}_{6.0}$ and that this material, or compounds like it, should have great potential.

During the meeting with A, the subject of the "Watson sponge"⁽¹⁵⁾ was introduced. This, of course, is a porous glass saturated with metallic phase such as lead. As a "granular superconductor", enhanced T_c 's were noted. C suggested that either the Watson sponge or its equivalent involving a metallic rather than glass matrix might have interesting superconductive properties. A study of this as a new material was considered worthwhile.

Under the heading of "materials advances" should be listed what might be termed "flux-pinning design". The flux lattice spacing is typically 100 to 1000 Å, and for greatest effectiveness, the pinning site lattice should match this. Pinning strength per site tends to be largest the greater the tendency for the pinning center to be nonsuperconducting. Thus, as B has pointed out, submicroscopic ferromagnetic particles, as in a superparamagnet, should make very effective flux pinners (that is, if they don't act to destroy the superconductivity!). Zero-g could possibly provide favorable conditions for the dispersion of a suspension of ferromagnetic particles for designed flux-pinning purposes. On the subject of "new materials", discussions with B indicated that existing materials have not yet met or been exploited to their fullest potential. On this basis there seems to be no pressing need for new materials. On the other hand, since it seems to require a lead time of about 20 years to develop a useful wire from a new superconducting discovery, it is provident not to defer active research into new superconducting materials.

Major Thrusts (L-2 and Y-6) - Contributors A Through E.

(a) Major Thrusts - Costs. Major thrusts in connection with superconductivity are intimately connected with costs. All the commercial contributors agree that advances in T_c , J_c , and manufacturing techniques should all lead to cost reductions. Some contributors regarded the cost of a superconductor as extremely important. It was quite apparent, however, by the end of the week that the pressure to cost-save was imposed by the competitiveness of the market place itself rather than any significant reduction in overall costs that would be reflected in the final system.

(This, of course, is a commercial reality in any major engineering system--generally all components, however insignificant, tend to be procured on a lowest bid basis.) Thus, the ratio between changes in superconductor cost and resultant changes in total system cost is not a meaningful factor.

According to A, cost can be reduced in any of several ways: (1) reduce the cost of presently existing materials; (2) reduce the cost of superconductor fabrication--A made the suggestion that the currently used extrusion-drawing technology may become obsolete in time, and it might well find itself being replaced by some form of continuous casting process; or (3) increase J_c by developing new materials--in so doing, the quantity of material for a given current density would be reduced.

Although, as A pointed out, cost is a very important factor, it may not be of overriding concern when high H_c is absolutely necessary. In CTR applications, the energy of magnetically confined plasma goes as B^4 . There is thus considerable incentive for the development of high- H_c material, even if it turns out to be the most expensive.

Systems cost (specifically refrigeration cost) will decrease as T_c increases. So far, the highest T_c has been obtained with Nb_3Ge ; and B pointed out that working on the principle that T_c would increase if Ge were replaced by a lighter element with similar valence, Nb_3Si should have an even higher T_c . This compound, however, is unstable.

(b) Major Thrusts - Technical. Speaking on the technical side, B pointed out that important new developments in superconductors would be those that yielded higher J_c 's, thus facilitating the ability of a conductor to handle fault currents in high-current-density applications, particularly transmission lines. In magnet applications, particularly for CTR, high H_c in conjunction with high J_c is a necessity. So far, the best high- H_c material available is V_3Ga . Unfortunately, the T_c of this material is lower than that of Nb_3Sn . B pointed out that another important development would be that of a mechanically flexible high- T_c , H_c , J_c conductor--i.e., one that would be forgiving to repeated flexing. In this connection, the Tsuei material is again of interest.

(c) State of Technology. B expressed the opinion, in agreement with A, that superconductivity was already quite an advanced technology; so much so that the catch-phrase "solution in search of a problem" is a fairly appropriate description of the state of the art. B pointed out that Nb-Ti is routinely used at the present time, and that superconductors adequate for most present applications already exist. Sharing this opinion was C, who stated that present-day materials were adequate for current applications. C pointed out that there is a need to develop confidence in superconductors before major advances can be made. This is true, it was claimed, even for that work horse of the superconductor industry, Nb-Ti, let alone anything more exotic.

It was felt that the successful consummation of some notable large scale engineering applications involving Nb-Ti superconductors would do much to engender confidence in superconductors as engineering materials. A forthcoming major application which will make an excellent proving ground for superconductors will be the bending magnets of the National Accelerator Laboratory energy doubler. Another important application will be the interacting storage rings currently being constructed by Brookhaven National Laboratory.

A successful demonstration of the large-scale reliability of Nb-Ti will lead, as a next step, to the acceptance of Nb₃Sn; and other applications will follow. Engineering design of large-scale superconducting machinery is extremely conservative, and at the present time tends to involve cryogenic stabilization and copious amounts of copper to carry fault currents. It is interesting to note that the manufacturers, or product-oriented people, adopted during the interviews a much more pragmatic stance than did the researchers or developers. One might have expected the very opposite, viz., that the attitudes of those with sales interests would have been the more bullish. The conservatism of the producers is, however, quite consistent with their "credibility posture" coupled with an anxiety that superconductivity perform reliably rather than spectacularly.

Properties and Structures (Y-3, L-2) - Contributors A and E.

The primary superconducting property, T_c , does not generally depend on structure (except in the case of granularity, thin-film effects, etc.). H_c (the thermodynamic critical field) is not structure dependent, although H_{c1} and H_{c2} do depend on electronic mean free path. J_c is highly structure dependent--structure in this case meaning flux-pinning elements. During discussions with A it was pointed out that flux-pinning centers in the form of dislocations induced by the cold-working of ductile superconductors would enhance J_c . A pointed out, however, that since superconductive wire elements in a composite might be as small as 5 μm in diameter, particles if introduced must be appropriately small. This condition may rule out all but precipitate-type or dislocation-type pinning defects.

The matter of coring in Nb-Ti was discussed during several of the interviews. This was not regarded as a problem by E; on the contrary, it was suggested that compositional fluctuations resulting from possible coring could be advantageous.

Applications of Superconductivity (L-3, Y-5) - Contributors

A Through E. During discussions with A, it was agreed that future applications of superconductivity will include:

- Energy storage
- CTR containment magnets
- Transmission lines
- Magnets for high-energy physics machines
- Magnets for mag-lev transportation.

B was in general agreement with this, but in addition suggested that magnetic separation was another important application. Magnetic separation can find use in

- Water purification
- Mineral beneficiation
- Desulfurization of coal, etc.

For handling ferromagnetic particles, conventional magnets are satisfactory, especially when used in association with ferromagnetic field concentrators (steel wool, etc.) for ∇B enhancement. On the other hand, since for paramagnetic materials magnetizations are proportional to the applied field, and force is proportional to $M \cdot \nabla B$, very high fields in addition to high field gradients are necessary for effective separation. This calls for the use of superconducting magnets.

The most significant applications according to C would be those which cannot under any circumstances be duplicated by nonsuperconducting materials, rather than those which could be labeled "improvements" of existing technology. Thus, C's criterion includes magnets for CTR, which will not succeed without them, but excludes such applications as transmission lines and magnetic levitation. With regard to magnetic separation, C asserted that for ferromagnetic materials, conventional magnets are satisfactory, but had no real feeling for the need or potential of paramagnetic separation itself. D agreed with all of the above listings and assessments, but in connection with long-range, large-scale applications, stressed the reliability and integrity elements. D pointed out, for example, that it was necessary, on a production basis, to be able to reduce superconducting filaments down to 5-10 μm (in multifilamentary composites) without fear of breakage. D emphasized that reliability was of paramount importance in applied superconductivity and would dominate cost as a requirement, and summarized the applicability of superconductors in the following way:

Principal U.S. applications - CTR

Principal foreign applications - mag-lev trains.

In this connection, it is important to point out that superconductivity appears particularly advantageous when moving high magnetic fields are required, since the use of persistent-mode superconductive magnets obviates the need for high-current-carrying-capacity slip-rings or other such sliding contacts.

Difficulties (L-4) - Contributors C and E. It was asserted by E that no serious technical difficulties plagued the industry today. E and C

agreed that the principal difficulty today might almost be termed psychological rather than technical, and had to do with a general lack of confidence in superconductivity. Thus, as pointed out above, a successful completion of the NAL beam-doubling project would be a turning point for the large-scale engineering applications of superconductivity.

Problems indirectly associated with superconductivity do, however, exist on all levels. One engineering problem, for example, has to do with the selection of "hot" or "cold" reinforcement for the superconducting solenoid and effects associated with differential thermal expansion.

Special Space Advantages (Y-1) - Contributors A, C, D, and E.

During discussions with A, it was suggested that melt-extraction techniques carried out in space, in zero g, could be usefully employed to produce long lengths of very fine wire. The wire would not be spooled but stored in long lengths prior to assembly. C disagreed with this, pointing out that alloy filaments fine enough to be interesting (less than 10 μm in diameter) would always be unhandleable--unsupported brittle compounds would be utterly impossible.

During discussions with D, it was suggested that the undercooling of Nb-Ti by space processing--using a crucible-free technique in which "heterogeneous nucleation" would be eliminated--may reduce the coring often found in the conventionally produced material. On the other hand, E asserted that coring was not a problem--in fact, it may be an advantage from a flux-pinning standpoint. D went on to point out that there seems to be a requirement for unclad (insulated only) Nb/Ti wire for ac applications--thus melt-extraction in space is a real possibility. E felt that space-processing would introduce no special advantages over what is being done in 1-g today, but that space processing would be useful for producing superconductors in situ for subsequent use in space.

Cost (Y-6) - Contributors A Through E.

Costs of superconductors are generally expressed in the units $\$/\text{A-ft}$ or $\$/\text{A-m}$. Thus, one manufacturer (A) claims a figure of about $\$0.01/\text{A-ft}$ ($\$0.03/\text{A-m}$) at 50 kOe and 4.2 K. This is not a firm number since costs seem to vary from 0.001 to

\$0.01/A-ft (\$0.003 to \$0.03/A-m). The utility of this form of expression arises through the parameter J_c and the fact that this is amenable to improvement in any superconductor. Thus, developments which result in an increase in J_c automatically result in a decrease in the ($\$/A-m$) cost parameter.

An alternative way of expressing cost, and one which is useful when making comparisons in the context of space processing, is the per-pound cost. Thus, C suggests that the present cost of superconductor is about \$100 per pound (\$45/kg). With this in mind, it is difficult to envision actual cost savings to accrue from the use of space processing. D would like to see the cost drop below this figure and into the \$20 to \$100 per pound (\$9 to \$45 per kg) range. D pointed out, however, that the base cost is predicated to a considerable extent on that of starting material. In other words, superconductor cost at the present time is dominated by those of Nb and Nb-Ti whose production is in the hands of one or two vendors. A agreed whole-heartedly with this and the manner in which the raw materials market was dominated by a single vendor. It would obviously be helpful for other suppliers to enter the Nb market, but perhaps more importantly, for superconductors to be developed which did not rely on Nb at all. Non-Nb superconductivity has already been referred to in this report.

Superconductor/Systems Costs. Manufacturers agree that the cost of superconductor is between 10 and 25 percent of the cost of a superconducting magnet. Thus, superconductor cost does not figure strongly in the overall systems cost. However, as indicated earlier, the superconductor/systems leverage factor is not in fact meaningful in a business sense. Thus, although the cost of a superconductor appears as a minor component of the systems cost, there is nevertheless strong pressure (harmfully strong, in our estimation) on the manufacturers to trim costs to the bone. As a result, there seems to be absolutely no room for technological improvement, let alone development or basic research, except perhaps in the case where improvements in superconductor properties or behavior may lead to a change in system design to a lower cost version or lower system fabrication costs.

Economic Considerations. With the present cost of superconductor materials at \sim \$100/lb (\$45/kg), it is obvious that superconductors produced by space processing even if they are manufactured more efficiently cannot compete with terrestrially produced material because of the space transportation costs. A space processed superconductor must, therefore, be a unique product, i.e., possess unique properties such as high T_c , J_c , or H_c , or be more reliable. The extra cost may be tolerated if the space processed superconductor is the only one that can do a particular job or if its utilization can lower the overall system costs.

Task 2. Electrical Contact Materials

Introduction

The goal of this task was similar to that of Task 1 but concentrated on electrical contact materials, their production, and properties. Here again, manufacturers and users of electrical contacts and organizations involved in research and development in contact materials were visited in order to learn more about the products and processes involved in their manufacture and to determine where space processing might provide some benefits to the industry. Equally important was the opportunity to obtain industrial reaction, input, and suggestions for future space experiments, the results of which might be of benefit to earth-based applications.

During the months of September-November, 1975, visits were made to the following U.S. major producers and users of electrical contact materials:

- Cutler-Hammer - Milwaukee, Wisconsin
- Fansteel - North Chicago, Illinois
- Square D - Milwaukee, Wisconsin
- P. R. Mallory - Burlington, Massachusetts
- Texas Instruments - Attleboro, Massachusetts
- Handy & Harmon - Fairfield, Connecticut
- General Electric - Plainville, Connecticut
- Gibson Electric - Delmont, Pennsylvania

In addition, two foreign companies were contacted during a visit to Germany by one of the authors. These were DODUCO, Pforzheim, West Germany; and DEGUSSA, Wolfgang, West Germany.

Discussions were generally restricted to immiscible material systems. More specifically, they centered on silver-base or silver-containing materials of the silver-refractory or silver-metal oxide types. These are the materials which on a weight basis comprise 70-80 percent of electrical contact usage. They are also the materials with which industry is familiar in terms of contact design, fabrication, cost reduction, and research to obtain improved performance.

Overview of Survey Results

It was recognized from the beginning of this work that the potential benefits of space processing could be derived in two ways. One would be from the actual processing in space of advanced contact materials. Presumably, the degree of processing would only be through the ingot or initial consolidation stage after which the material would be transported to earth and processed to end-use form by conventional techniques. There may be advantages, however, to complete processing in space in order to minimize transportation costs by directly recycling the scrap from the process. Also, unusual techniques such as forming directly from the liquid may be possible.

Present estimates of transportation costs for space processing range from \$440-\$1100/Kg (\$200-\$500/lb). This compares with present costs of silver-base contact material on the order of \$132-\$154/Kg (\$60-\$70/lb).

Assuming that silver prices remain in the \$129-\$160/Kg (\$4.00-\$5.00/oz.) range, these numbers reflect the major and almost universal source of industrial pessimism over the commercial use of space-processed materials, namely, cost. In order for such materials to become economically viable, space processing would have to effect one or both of the following improvements in performance characteristics resulting from unique or "unexpected" material properties:

- (1) A minimum of a three- to fourfold decrease in arc erosion rates, thus allowing for use of substantially less material

- (2) Exceptionally low electrical welding tendency or temperature rise characteristics not attainable in conventional materials which might permit unique device capability and offsetting cost benefits.

Industrial consensus is that Item (1) probably cannot be achieved by space processing. This is also the opinion of BCL electrical contact specialists on the basis of earlier research and a best estimate of effects of performance on those properties that can be controlled by space processing. A similar prognosis has to be given for Item (2). However, for both items these forecasts must be qualified by the low-but-finite possibility that space processing alone might result in a totally unique set of properties and performance. Experiments at low-g to investigate this possibility are deemed worthwhile.

There is a second and perhaps more important means by which space processing could provide benefits on earth. Viewed as an experimental technique providing a unique opportunity to prepare materials with controlled properties and structure, the concept of space processing was well received by industry. According to this approach, critical experiments in materials preparation might be conducted in space to obtain materials which may be difficult or impossible to prepare on earth. For example, the zero-g environment might be used to obtain both a finer and more uniform distribution of nickel particles in a silver matrix than has previously been possible by conventional powder metallurgy processing. Or it may be possible to closely control and vary particle size over a wide range.

Materials prepared in this manner could then be used for experimental performance studies on earth. These results might, for the first time, provide a clear understanding of the relationship between structure, properties, and performance. At a minimum, this could serve to direct future research, development, and manufacturing effort and provide some indication of the benefits to be gained if an "idealized" structure could be approached by processing on earth.

In summary, space processing of selected materials systems for experimental use in electrical contacts does appear to be worthwhile. Benefits are possible which could have major effects on both performance and costs of future materials.

Details of Survey

Materials. The relatively few systems which comprise the bulk of the immiscible materials used in electrical contacts are: (1) Ag-CdO, (2) Ag-W, and (3) much smaller amounts of Ag-Mo, Ag-WC, and Ag-Ni. Table 6 gives BCL estimates of U.S. annual usage of these materials for the period 1972-1973. Excluded from this table is the important material silver-graphite which is used in substantial quantities as a brush material but reliable figures on usage are not available.

The immiscible electrical contact materials can be further categorized by composition and methods of manufacture. Ag-CdO is used at compositions of 5-15 wt percent CdO although in the last year some interest has emerged in CdO contents as high as 25 percent. BCL estimates are that about 85 percent of Ag-CdO materials used in the U.S. are the 90 Ag-10 wt percent CdO composition. Two primary manufacturing methods are used; internal oxidation of Ag-Cd solid solution alloys and powder metallurgy processing.

The remaining materials in Table 6 fall into two groups with respect to silver content and processing. The Ag-Ni materials which have been more popular in Europe than in the U.S. have competed in application with Ag-CdO. Although nickel contents up to 40 wt percent have been produced, the Ag-10 wt percent Ni is probably the most common alloy. These materials are presently produced by powder metallurgy and all compositions are fabricable.

The silver-refractory materials (Ag-W, Ag-WC, Ag-Mo) have found their greatest commercial use in the low-silver compositions of 25-50 wt percent Ag although materials are produced with compositions as low as 10-15 wt percent Ag. All of these compositions cannot be fabricated by mechanical working but must be produced by a variety of powder metallurgy, liquid-phase sintering, and infiltration techniques.

Other than these "standard" materials, relatively few systems have found commercial use. Only the Cu-W system particularly at the 90W-10Cu composition has found use in high current, protected environment applications such as vacuum or oil immersion breakers.

TABLE 6. USE OF SILVER ON ELECTRICAL CONTACTS FOR THE PERIOD 1972-1973

| Material | Kg x 10 ⁴ (a) | Tr. Oz. x 10 ⁶ (a) |
|----------|--------------------------|-------------------------------|
| Ag-CdO | 34-37 | 11-12 |
| Ag-W | 5.0-5.6 | 1.6-1.8 |
| Ag-Ni | 3.1-4.7 | 1.0-1.5 |
| Ag-Mo | 0.3-0.6 | 0.1-0.2 |
| Ag-WC | 0.03-0.06 | 0.01-0.02 |

(a) Weight of precious metal only.

Small amounts of an Ag-Fe alloy have been used in specialized applications involving very slow make-and-break action. The Ag-10 wt percent Fe composition is claimed to have good anti-sticking/welding properties but for reasons which are not clear.

Past and current research has been directed toward both improving performance of these materials and finding alternatives for tungsten and CdO. The impetus for this is:

- (1) The limitation to improved performance of Ag-W caused by the poor chemical/oxidation characteristics of tungsten
- (2) The real or imagined environmental problems associated with cadmium-containing alloys, particularly in overseas markets.

Toward these objectives some work has been performed on the use of TiC and Si_3N_4 as alternatives to tungsten. Substitutes for CdO have also been sought in a variety of metal oxides including CuO, ZnO, SnO_2 , In_2O_3 , and mixtures of these. To date, however, these studies have been rather inconclusive and somewhat negative and have not led to new commercial materials.

In summary, only two systems are prominent among the immiscible materials; Ag-CdO and Ag-W. Both have their limitations and improved performance from existing materials and/or the use of alternatives are needed. Experimental studies in space may aid the development of these materials.

Relation of Properties to Performance. In spite of a considerable amount of published research on the Ag-CdO, Ag-W, and Ag-Ni materials, there is, unfortunately, no clear understanding of the relationship between structure, properties, and performance. This is due in part to the practical difficulties in the preparation of these materials with controlled structure for study.

As one important example, there is good evidence that the particle size of the dispersed phase (CdO, Ni) has a first order effect on arc erosion and possibly welding. There are, however, conflicting data on this point. One study indicates that the finer the particle size the better the

performance. Another indicates that there is an optimum particle size for best performance while a third indicates that there is no effect of particle size at all.

These differences are due in part to difficulties in varying one structural feature (particle size for example) without changing one or more of the other features such as material chemistry.

Based on the present state of knowledge, the following characteristics of the immiscible material may be regarded as most important with respect to electrical contact performance:

- (1) Particle size
- (2) Particle shape
- (3) Particle distribution
- (4) Volume percent of dispersed phase
- (5) Density of the material (percent of theoretical)
- (6) Presence of impurities or intentional additives
- (7) Thermochemical properties of the dispersed phase.

The tensile strength and ductility of the contact material may be of importance to the manufacturing process but they are believed to be of secondary importance to contact performance.

A discussion of specified material characteristics follows.

Particle Size. Considerable interest was expressed in the preparation and study of immiscible materials with particles in the submicron range--possibly down to about 0.1 micron diameter. For comparison with commercial materials, it would also be desirable to obtain space-processed materials with particle sizes up to about 3-10 microns in diameter. Presumably, space processing would also allow such materials to be prepared with:

- (1) A highly uniform size and spatial distribution
- (2) Nearly spherical particles
- (3) Low porosity
- (4) High purity.

The material system of particular interest for such studies is silver-nickel at a composition of ~ 10 wt percent Ni. Particle size control might be effected in either of two ways. One would simply involve additions of carefully sized nickel powder to molten silver followed by cooling to the solid state in the zero-g environment. One potential problem

with this approach, however, may be the agglomeration of nickel particles during the homogenization step. A possible variation on this could be the blending of silver and nickel powders followed by melting and cooling with all operations taking place at zero-g.

A more desirable approach would be to heat above the miscibility gap in the Ag-Ni system to form a homogeneous liquid solution. Cooling back through this gap at controlled rates in zero-g should produce the desired results but it is difficult to predict the particle-size/cooling-rate relationship.

Another problem is that the extent of the miscibility gap in the Ag-Ni system is not known but is probably in excess of 2000 C at the Ag-10 wt percent Ni composition. It is suggested that experiments be conducted to define this boundary.

Similar experiments should also be considered in the silver-chromium system. It is of potential commercial interest but also suffers the disadvantage of high miscibility gap temperatures.

Particle Shape. Emphasis in most earlier work has been on dispersed phase contact alloys having spherically-shaped particles. Recent work, however, has indicated that in at least one system (Ag-Ni), rod- or fiber-shaped particles oriented normal to the contact surface may significantly lower erosion rates. Only limited experimental work has been reported, however, on the effects of fiber diameter, spacing, or length-to-diameter ratio.

It seems possible that directional solidification through a miscibility gap may be one means of producing a fibrous dispersed phase in a controlled manner. Investigation of the achievable structures is recommended for the Ag-10 wt percent Ni and/or Ag-10 wt percent Cr composition.

Particle Distribution. General industry opinion is that a uniform microstructure is desirable. However, there are conflicting views as to whether the most desirable structures are those with (1) a uniform particle size (narrow distribution) or (2) a wide particle size distribution.

It may be possible to resolve this question by materials preparation at zero-g. Heating above the miscibility gap as described above for an Ag-10 wt percent Ni alloy may result in a narrow but controlled particle size distribution.

A structure consisting of a mixture of fine and coarse particles may be produced at low-g by first heating the alloy into the homogeneous liquid region at a temperature above the miscibility gap and then cooling to a relatively high temperature within the gap and holding at this temperature until particle coarsening takes place. Finer particles could subsequently be formed in the structure by cooling through the remainder of the miscibility gap at a moderately rapid rate. A major advantage of the zero-g environment would be the possibility of obtaining a highly uniform or random structure.

The zero-g environment could also present a unique opportunity to prepare material analogous to internally-oxidized Ag-CdO but without some of their microstructural disadvantages. For example, when a solid solution silver-cadmium alloy is oxidized, the resulting structure has:

- (1) A large particle size gradient ranging from very fine near the surface to quite large toward the center
- (2) A depletion/unoxidized zone near the center consisting mainly of pure silver.

The latter feature obviously limits the useful or erodable volume of the material. The former interferes with the characterization of the material and analysis of performance data. Other limitations on this process include the maximum alloy contents which can be oxidized and the type of solute additions which can be used. There are a number of silver-metal oxide (or other compounds) systems which could be prepared by internal oxidation (or similar reaction) and would be of interest if a uniform particle size could be produced throughout the material.

The possibility exists that these materials could be prepared by space processing. Specifically, it may be possible to effect direct internal oxidation of a molten alloy with control of particle size and microstructural homogeneity.

It is expected that such a process would be very rapid compared with conventional internal oxidation of solids. Experimentally, the process might consist simply of holding the molten alloy in an atmosphere of controlled oxygen potential for a fixed time period, followed by cooling in zero-g. This process was disclosed as a "Report of Invention" at Battelle's Columbus Laboratories on February 5, 1975, and is considered a Battelle proprietary process. It can equally well be applied to other systems involving dispersoids such as dispersion-strengthened materials and high critical current superconductors.

While the Ag-Cd alloys might appear to be most attractive for these studies because of their commercial use, they would present great experimental problems. These include (1) the high vapor pressure of cadmium and (2) a decomposition temperature of CdO close to the melting point of silver.

These features would preclude relatively simple experiments. Instead, some form of enclosed or high pressure experiments would be required.

While this is possible, it is recommended that initial work be conducted in one or more "simple" system(s) but which also have commercial interest. The systems suggested for consideration are:

- (1) Ag-Cu₂O
- (2) Ag-SnO₂
- (3) Ag-ZnO .

Of these, first priority for testing the feasibility of the process might be given to Ag-10 wt percent Cu alloy. The objective of any initial work should be to determine if a fine (1-3 micron), uniform, oxide dispersion can be obtained by internal oxidation of the liquid alloy at zero-g. If this is possible, electrical performance tests should be carried out to compare space-processed and conventional solid state internally oxidized or powder metallurgy material.

Impurity/Additive Effects. Up to this point, the discussions have assumed studies on materials of relatively high purity levels. Commercially this is not the case; in fact, with material such as the internally-oxidized alloys, intentional additives are used. These include Co, Ni, Al, Ti, Ca, and others at levels well below 0.1 percent.

These additives are known to effect large modifications of the microstructure and electrical contact performance. While it is assumed that they do so by affecting the nucleation and growth of the oxide phase, there is no clear proof of this.

Neither is it known whether the amount of additive affects performance. This is due to the practical difficulties of retaining in the melt either of the two most common additives--Co and Ni--because of their low solubilities and density differences with the silver.

Particular interest was found in the potential of space processing for the experimental preparation of Ag-Co and Ag-metal oxide-Co alloys at varying cobalt levels. Ag-Co binary alloys with, for example, 0.001-0.1 wt percent Co would prove useful in defining whether cobalt also serves in any way to modify the performance of silver.

Ag-Cd-Co alloys with similar levels of cobalt might also be prepared by some form of encapsulated melting in zero-g to retain a uniform cobalt distribution. Both alloys could also be processed on earth by conventional techniques. Electrical contact performance results could then be compared directly with those for more conventional alloys.

Thermochemical Properties. There is increasing evidence, although far from conclusive, that the thermochemical properties of the dispersed phase have major effects on both contact erosion rates and welding. In this context the relevant properties include:

- (1) Decomposition or melting temperature
- (2) Heat of decomposition or melting
- (3) Decomposition rate and products

- (4) Redistribution of oxide phase and/or impurity segregation at surfaces resulting from above
- (5) Surface tension between liquid silver and dispersoid

Unfortunately, none of these effects have been quantified. However, one experimental fact may provide added justification for some of the proposed experiments, particularly in the silver-metal oxide systems. This is that the method by which CdO is formed does have a major effect on performance. Space processing could be viewed as yet another way in which oxide and controlled structures may be produced. Potential benefits are unknown but if differences are found compared to conventional materials these "new" materials might provide important clues to guide future research.

Other Suggested Experiments. These fall into two broad categories where current manufacturing problems are present. These are:

- (1) Powder blending
- (2) Liquid-phase infiltration.

Powder Blending. It is reasonably well established that a uniform microstructure is desirable. However, the question of advantages from a performance standpoint has gone unanswered because of the difficulties in preparing such materials by powder techniques.

Considerable interest was found in the experimental use of zero-g for powder blending for purposes of comparing the resultant structures and performance. Presumably, powder of closely controlled particle size would be blended and consolidated in space and returned to earth for subsequent processing.

The following systems are recommended for study:

- (1) Ag-10 wt percent CdO
- (2) Ag-10 wt percent Ni
- (3) Ag-5 wt percent C
- (4) Ag-50 wt percent W.

A related question was raised by several manufacturers regarding the manufacture of tungsten carbide for use on Ag-WC contacts. The problem area, however, may not be unique to electrical contacts. This is the

difficulty in producing stoichiometric WC even for experimental study. While there is evidence that stoichiometry does affect performance, the optimum composition is unknown.

Questions were raised whether space processing could be used to prepare such materials. One possibility suggested was that of powder blending and consolidation of tungsten and carbon powders should be performed in zero-g to provide a far more uniform distribution for subsequent sintering and to avoid gravity-induced segregation.

Liquid Phase Infiltration/Sintering. Frequent mention was made of problems associated with the manufacture of silver-refractory metals and compounds. These include:

- (1) Porosity after infiltration
- (2) Poor wetting characteristics
- (3) Shrinkage cracking in large parts.

Considerable interest was found in space processing studies of the Ag-W materials. Our recommendation is to combine the advantages of zero-g for both powder blending and liquid-phase sintering. The Ag-50 wt percent W composition would represent an excellent starting point. A further recommendation is that tungsten particle sizes over the range of about 0.1-5 microns be included in the study. This could provide a unique opportunity to resolve questions of particle size effects in materials having exceptionally uniform structures.

One additional experiment is recommended in the Ag-W system. This is infiltration of 90W-10Ag composition with the objective of comparing porosity and shrinkage cracking relative to similar parts produced on earth. Typical pore-size limitations for infiltration are in the range of 4-5 microns. It is further recommended that the work be extended to finer powders in order to obtain a pore size of ~ 1 micron so as to determine if the zero-g environment offers any advantage for producing these difficult-to-fabricate structures.

Task 3. Superconductivity in Immiscible Materials

Introduction

This task was an experimental study aimed at determining the effect of microstructural variations on the superconducting properties of liquid phase immiscible materials. An understanding of this relationship should aid in the selection of alloys and processing conditions for achieving desired superconducting properties. Two model systems were originally chosen for this portion of the study; Bi-Ga and Pb-Zn. They were chosen because of their relatively low processing temperatures which allow the melt spinning technique to be conveniently used. A small amount of work was carried out on the Pb-Zn alloys, but the direction of the effort was changed as a result of the visits to superconductor manufacturers and research organizations coupled with discussions held with personnel at MSFC. It was decided to stop work on the original alloys and to substitute the Tsuei alloys for the model materials originally proposed. The motivation for this change was the feeling that these alloys would yield much more practical results in addition to our basic goals of understanding the microstructure-property relationship.

The samples in this study were prepared by two different rapid cooling techniques, chill-block melt spinning and pendant drop melt extraction.* The chill-block, melt-spinning technique which is shown in Figure 2 was used to produce Zn-Pb ribbon. In the variation of the process we used, the alloy sample was melted in a 1 cm inside diameter graphite crucible containing a 0.25 mm orifice. When the sample reached the desired temperature (650-900 C, in our case) argon gas pressure was exerted on the surface of the molten metal and caused a liquid stream to be extruded from the orifice. The molten stream was directed onto the surface of a rotating copper drum where it rapidly solidified in ribbon form.

The pendant drop melt extraction technique shown in Figure 3 was used to prepare filaments of Cu-Nb-Sn alloys. In the present work we used an

* A Battelle-patented process.

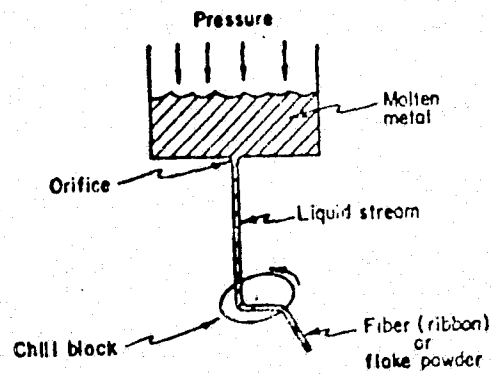


FIGURE 2. SCHEMATIC OF THE PRESSURIZED-ORIFICE, CHILL-BLOCK MELT-SPINNING PROCESS

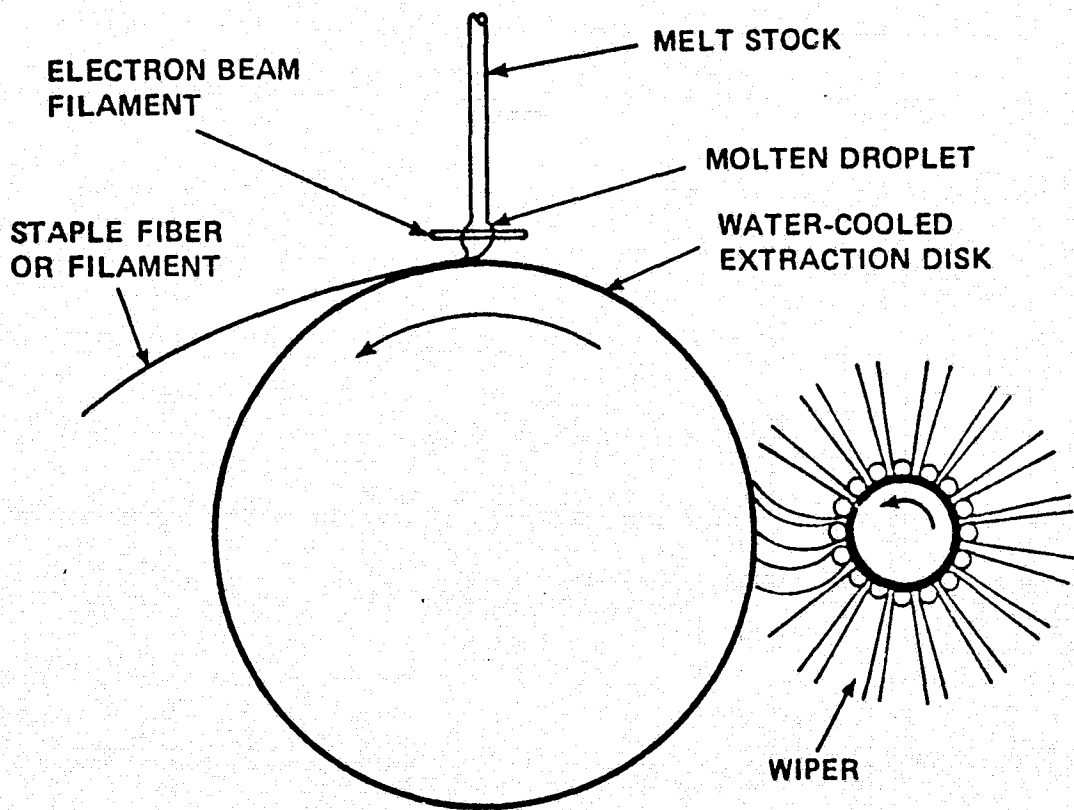


FIGURE 3. SCHEMATIC DIAGRAM OF PENDANT DROP MELT EXTRACTION

alloy rod approximately 0.5 cm in diameter by several cm long. The end of the rod was melted (in our case, by an electron beam) so as to form a pendant drop of molten metal. The water cooled rotating brass disc was brought into contact with the base of the pendant drop and as the periphery of the disc passed through the molten metal the metal solidified onto and adhered to the disc. The solidified metal was extracted from the melt still clinging to the disc periphery and continued to cool. As a result of thermal contraction and centrifugal force, the metal in the form of a fiber or filament was spontaneously released and thrown free after a short residence time.

Both the spinning and pendant drop melt extraction techniques were chosen because they can produce rapid cooling rates with resulting fine structures. This factor has the advantage of simulating what might be expected from bulk alloys processed in space.

The melt-spinning technique has the additional advantage of starting with a homogeneous liquid alloy and thus providing some insurance that a homogeneous alloy will be produced. However, the system, as presently set up at Battelle's Columbus Laboratories, can only be used to process moderate melting temperature alloys and those in which crucible contamination is not a problem. The pendant drop melt extraction technique, which is carried out without a crucible and with the application of electron beam heating, has a much wider temperature capability. However, as previously found, there is a great tendency for immiscible alloys to segregate in the pendant drop.

Preliminary Work on Zinc-Lead Alloys

Four different samples of Zn-Pb alloys were prepared by the melt-spinning technique. Some of these were given a preliminary examination by optical and scanning electron microscopy. The results of this work are summarized in Table 7 and indicate that segregation in the ribbon is a problem. This may be due to insufficient homogenization of the liquid prior to spinning. This issue, however, was not resolved due to curtailment of work after only a few preliminary observations had been made.

TABLE 7. SUMMARY OF PRELIMINARY WORK CONDUCTED ON THE MELT-SPINNING OF Zn-Pb ALLOYS

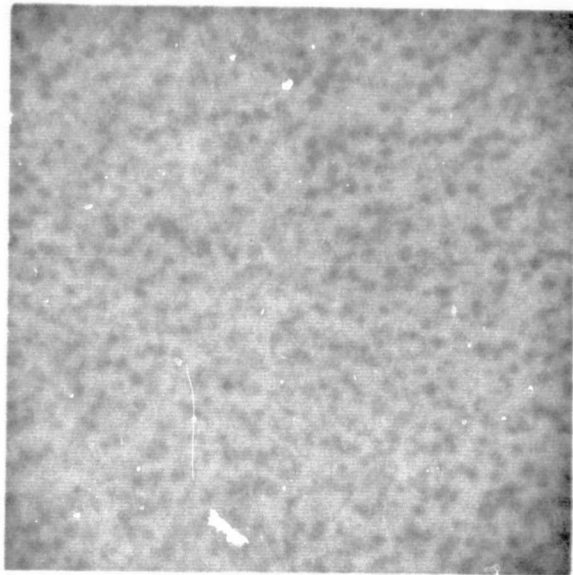
| Alloy Designation | Composition | Spinning Conditions | | Remarks |
|-------------------|-------------|---------------------|---------------|--|
| | | Temp., C | Pressure, MPa | |
| A | Zn-5wt%Pb | 649 | 0.1 | -- |
| C | Zn-5wt%Pb | 704 | 0.1 | Free surface of ribbon examined structure consists of Zn grains ~12 μ in size. EDAX reveals only a trace of Pb. |
| D | Zn-5wt%Pb | 649 | 0.14 | Polished section examined. Structure consists of Zn grains ~12 μ grain size. No evidence of Pb. |
| E | Zn-50wt%Pb | 900 | | Alloy difficult to prepare because of high vapor pressure. One ribbon shows Zn droplets in Pb. Size of droplets varies with cooling rate. Large differences in structure noted in different samples of ribbon. |

One interesting result shown in Figure 4 for Zn-50 wt percent Pb is the difference in the size of Zn particles observed in the region next to the chill block compared to that near the free surface. The particles near the free surface ranged in size between 1 to 4 μ , whereas those abutting the chill block were much more uniform and finer ($\sim 0.4 \mu$ in diameter). This work shows promise of meeting the original objectives of the task, namely, to produce and evaluate liquid phase immiscible materials of varying microstructures. Additional work, however, is required to perfect the techniques used.

Copper-Niobium-Tin Alloys (Tsuei Alloys)

A Cu-Nb-Sn alloy corresponding to the formulation on an atomic basis of $\text{Cu}_{93}\text{Nb}_5\text{Sn}_2$ was prepared by induction melting and swaging from OFHC copper, 99.9⁺ percent pure Nb and 99.997 percent pure Sn. The raw materials were induction melted in a ZrO_2 crucible under an atmosphere of helium. They were cast into a massive copper mold containing 1.9 cm diameter channels, thus producing a rod of this size. The rod was then swaged to 0.5 cm diameter, a size suitable for the pendant drop melt extraction process. Fine wire was produced by the latter technique as previously described.

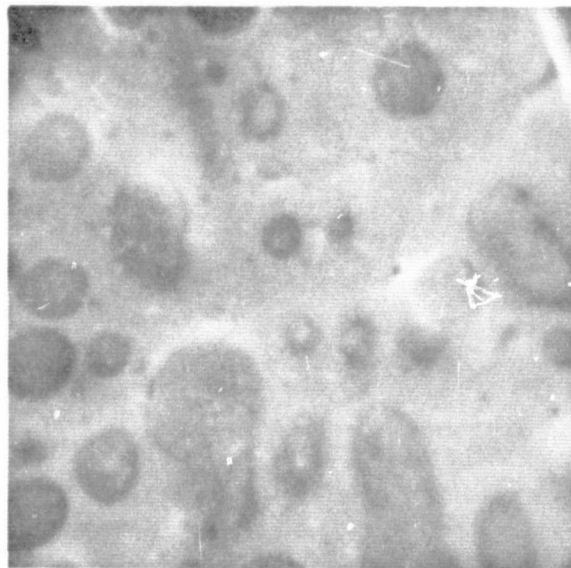
Structural Examination. Examination of the Cu-Nb-Sn alloys was limited to optical microscopy, scanning electron microscopy and energy dispersive X-ray analysis (EDAX). Cross sections of the 0.5 cm diameter swaged rod perpendicular to the rod axis are shown in Figure 5 at 100 and 500 X magnification. The photomicrographs show ends of elongated niobium fibers which are $\sim 2.5 \mu$ in diameter. The uniformity of the microstructure is quite good, certainly sufficient to use the rod as feed material for the melt extraction process. Examination of the as-swaged rod was limited since most of our effort was focused on the melt extracted product. The structure revealed in the as-swaged alloy is typical of what has been previously observed. The niobium particles observed in Figure 5 result from the elongation by swaging of niobium dendrites formed during the cooling of the molten alloy.



B-10

(a)

4600X



B-8

(b)

4700X

FIGURE 4. SEM PHOTOMICROGRAPHS OF MELT-SPUN ALLOY E Zn-50 Wt % Pb
(a) Region in contact with chill block (b) free surface.
As-cast surfaces.

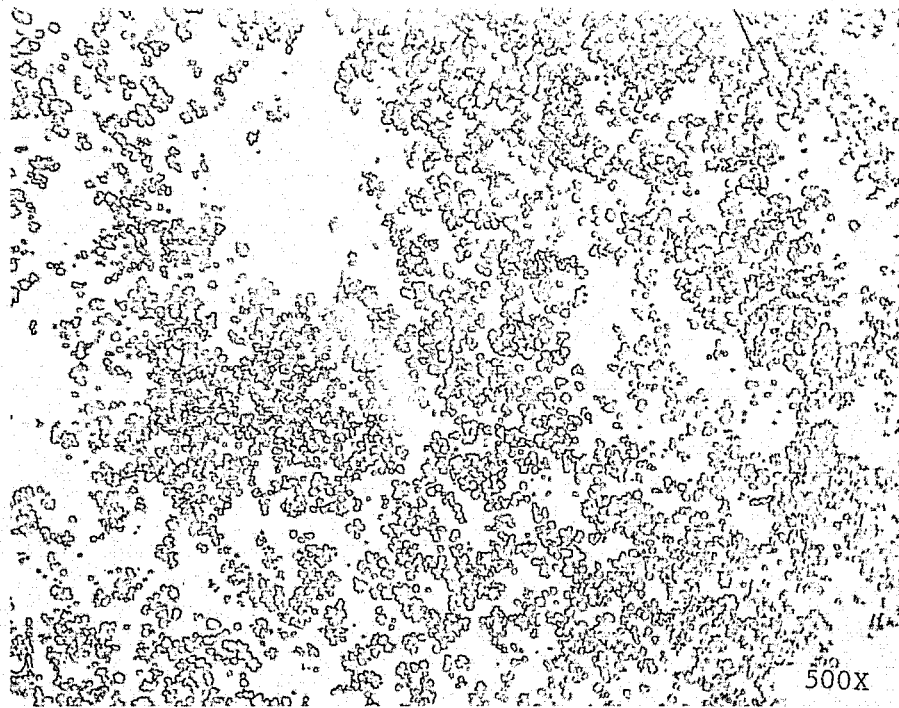
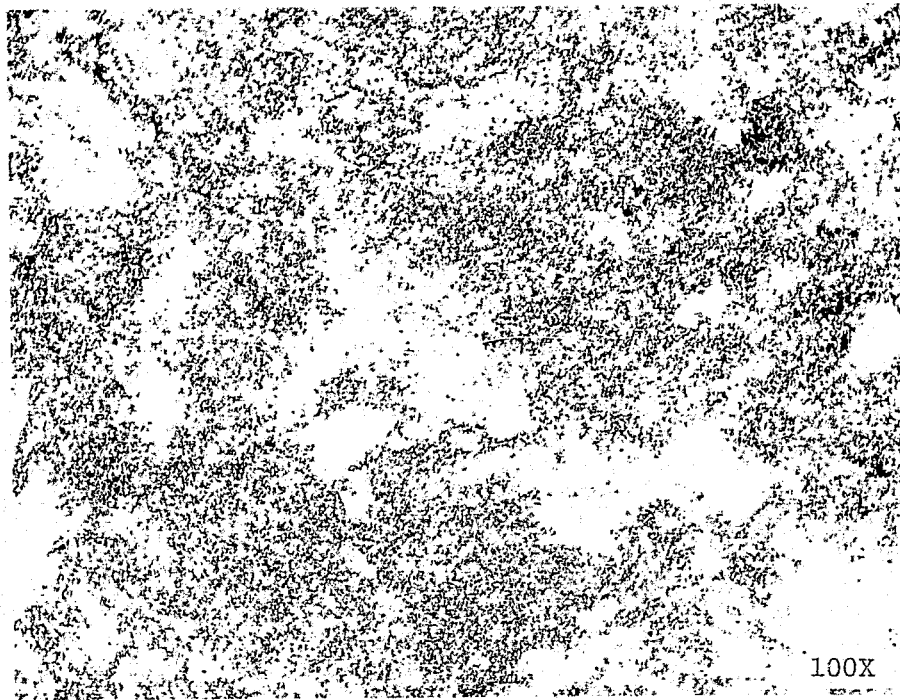


FIGURE 5. OPTICAL MICROGRAPHS AT 100X AND 500X AS CAST-AND-SWAGED $\text{Cu}_{93}\text{Nb}_5\text{Sn}_2$ 0.5-cm DIAMETER ROD

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OF POOR QUALITY

During the melt extraction process, some flakes were occasionally produced along with the fine wire. Figure 6, which is a photomicrograph of a cross section of one of the flakes shows a structure which is similar to that seen in the transverse section of the swaged rod (Figure 5).

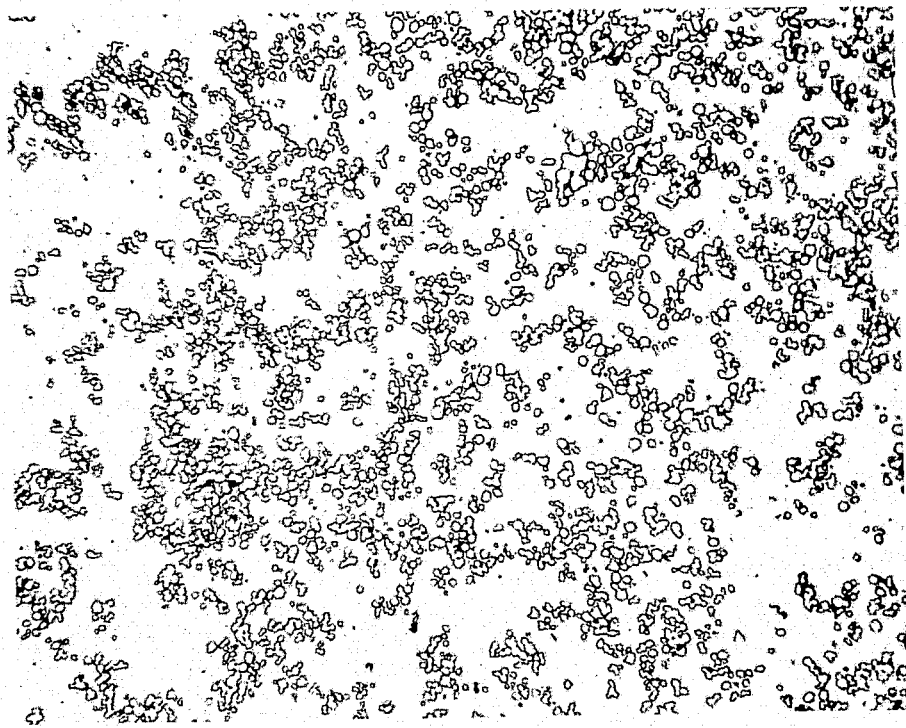
Figure 7 shows SEM photomicrographs of fibers produced by melt extraction. The fibers have somewhat irregular surfaces which contain numerous protuberances. The details of the cast structure are shown in Figure 7d where evidence of a fine dendritic structure is revealed. The wire diameters are approximately 80μ .

Cross-sectional views of the fibers are shown in the optical photomicrographs of Figure 8. The fibers approximate the shape of circular segments and have a width of $\sim 100 \mu$ and a height of $\sim 30 \mu$.

The precipitated phase shown in the top photomicrograph of Figure 8 is niobium which is distributed quite inhomogeneously both within a given cross-section and from one cross-section to another. (Compare the top and bottom photos in Figure 8). Energy dispersive X-ray analysis conducted on the surfaces of different wires also reveal the non-uniformity of the niobium distribution. In a few cases the distribution of the niobium on the fiber surface has been observed by EDAX techniques and correlated with the position of surface protuberances and fine surface features. Figure 9 shows such a comparison. Figure 9a is the SEM secondary electron image of a filament surface and Figure 9b shows the corresponding EDAX image of the Nb distribution. It may be seen from this illustration that some of the rougher bumps on the wire surface are relatively rich in niobium.

Conclusions. Our studies in the Cu-Nb-Sn system have led us to the following conclusions:

- (1) $\text{Cu}_{83}\text{Nb}_{15}\text{Sn}_2$ can be prepared by melting in ZrO_2 crucibles. Induction melting and casting of 1.9 cm diameter rod produces a fairly uniform microstructure.
- (2) Pendant drop melt extraction tends to produce an inhomogeneous structure which is probably caused by segregation within the pendant drop during heating or cooling within the solid plus liquid phase field.



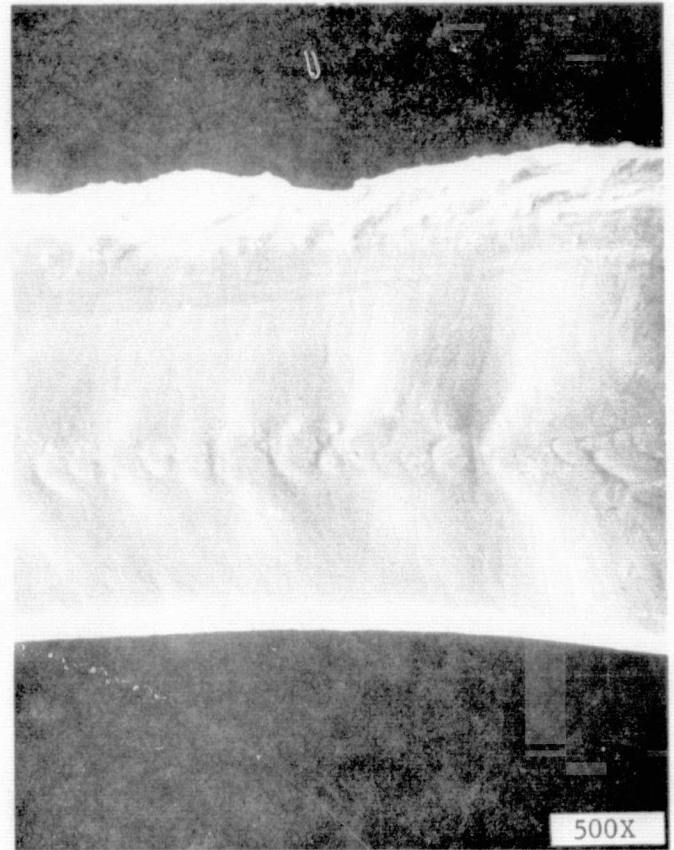
Melted-Extracted Flake

500X

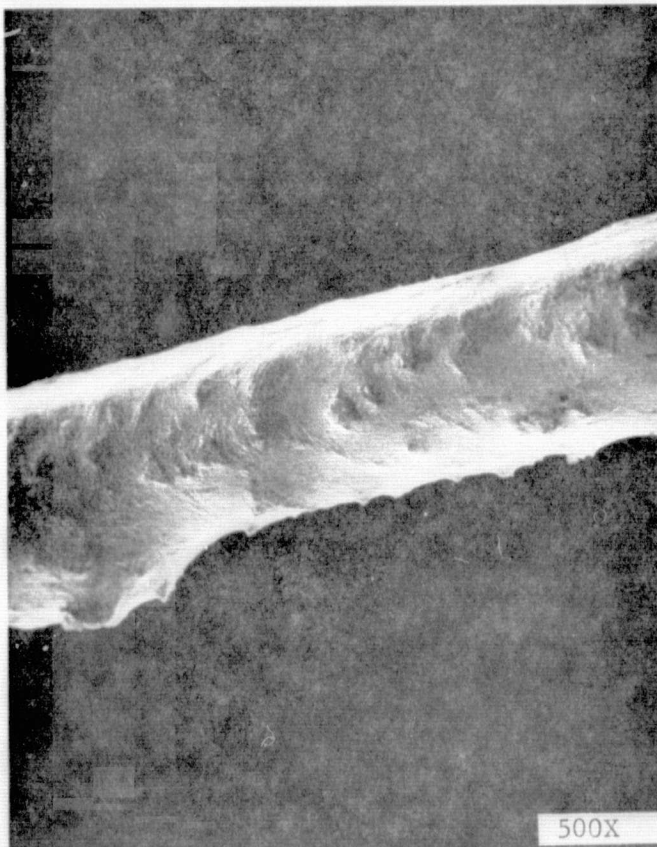
FIGURE 6. OPTICAL MICROGRAPH (500X) OF ME FLAKE
Microstructure is similar to that of
starting rod material (cf. Figure 5).



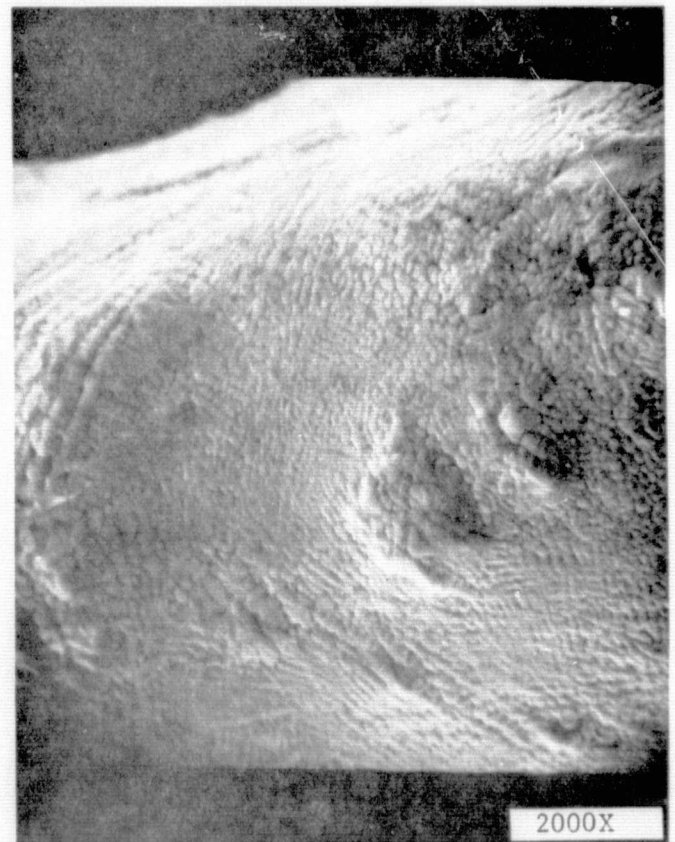
(a)



(b)

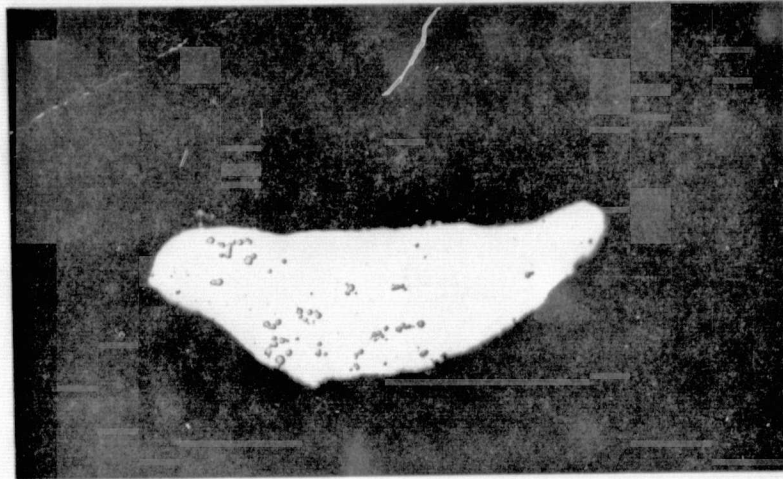


(c)



(d)

FIGURE 7. SEM PHOTOMICROGRAPHS OF MELT EXTRACTED Cu-Nb-Sn FIBER



500X

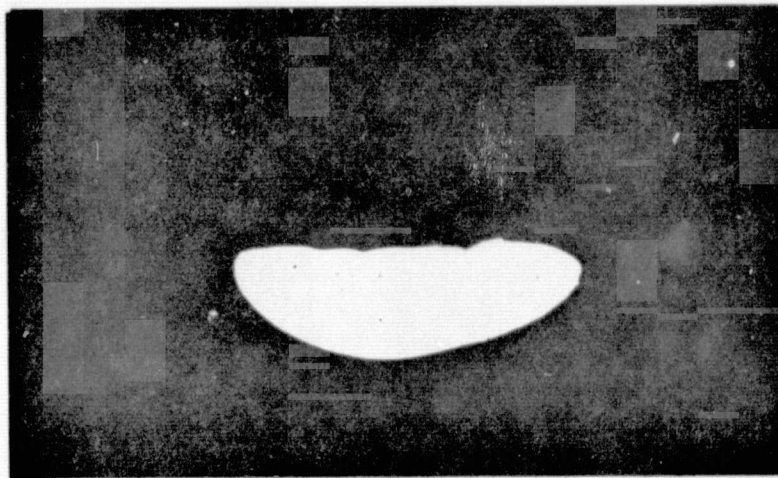


FIGURE 8. OPTICAL PHOTOMICROGRAPHS OF POLISHED CROSS-SECTION EXTRACTED FIBER

These views show uneven distribution of Nb precipitates both within a given cross-section (upper figure) and from one cross-section to another (compare upper and lower figures).

It is recommended that in further work on this subject melt-spinning onto a chill block or melt extraction from a crucible be substituted as methods for preparing these alloys. Both these techniques have the advantage of starting with a homogeneous molten alloy. The chill block technique is expected to provide a somewhat higher cooling rate and thus finer and more uniform structures are expected from this technique.

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