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SPACE PROCESSING OF COMPOSITE MATERIALS

FINAL REPORT

GENERAL DYNAMICS
Convair Division

FOREWORD

This report was prepared by the Convair Division of General Dynamics under Contract NAS8-29620, "Space Processing of Composite Materials" for the George Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered by the Space Sciences Laboratory under the technical direction of Mr. I. C. Yates, Jr. (ES-24).

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SUMMARY

This report documents the investigations and results of a study on "space processing of composite materials." The primary objective of this study was the definition of materials and processes for the testing of aluminum-base fiber and particle composites, and of metal foams under extended-time low-g conditions, as achieveable in suborbital rocket flights.

The investigations were preceded by a detailed analysis of candidate materials, resulting in the selection of several promising reinforcement materials for aluminum-base composites and of a suitable matrix material for metal foaming experiments.

For fiber and particle composites, an absolute prerequisite is mutual wettability between reinforcements and matrix during liquid-state processing. It was found that practically all effective reinforcement materials are not wetted by liquid aluminum. This problem was solved by the development of a new wetting and dispersion technique, based on the previously advanced theory that under the absence of a gas phase all solids are wetted by liquids. The process is characterized by a high vacuum environment and a high temperature cycle.

In a specially constructed apparatus, providing these conditions, successful wetting and dispersion experiments were carried out with sapphire fibers, whiskers and particles, and with fibers of silicon carbide, pyrolytic graphite and tungsten. The developed process and facilities permit the preparation of a "precomposite" which serves as sample material for flight experiments. Low-g processing consists then merely in the uniform redistribution of the reinforcements during a melting cycle.

For the preparation of metal foams, gas generation by means of a thermally decomposing compound was found most adaptable to flight experiments. Laboratory experiments with zinc as matrix material and Titanium hydride particles as foaming agent demonstrated the effectiveness of this method. Coalescence is minimized by a partial reaction of the evolving hydrogen gas with the bubble walls. For flight experiments, the use of a compacted mixture of the component materials limits low-g processing to a simple melt cycle.

A flight experiment program was defined, together with the specification of material compositions, sample preparation and experiment performance procedures.

Product applications studies could not arrive at reliable conclusions due to the unknown properties of the end product as obtained by low-g processing. This, in turn, emphasizes the need for early flight experiments.

1. OBJECTIVES AND SCOPE

1.1 STUDY OBJECTIVES

This study represents a developmental program on the preparation of aluminum-base composites and controlled density materials in a low-g environment The original objectives were defined as follows:

Task 1. To establish specific material compositions, processing requirements, and processing techniques for the preparation of reinforced composites and controlled density metals in space.

Task 2. To produce prototype composites and controlled-density metals by processing in ground-based low-g test facilities and to derive from such experiments the properties which may be attained in space-processed composites.

Task 3. To define applications, potential users, and the technical and economic payoff for specific products.

In view of the unavailability of flight opportunities within the performance period of this study, the study scope was amended to the effect to delete Task 2, above, and to place more extensive efforts on Task 1.

1.2 BACKGROUND

The production of composite materials and shaped products by liquid-state processing (composite casting) as a potential application of the weightless environment of orbital flight was first suggested in 1967. In the ensuing years a number of conceptual studies were carried out on materials, products, processes and systems integration which are summarized in Ref. 1. In 1971 the feasibility of composite casting was demonstrated in flight experiments on the Apollo 14 mission (Ref. 2, 3). The substantially increased stability of gas dispersions in liquid metals under low-g conditions, which is the basis for producing metal foams (controlled density metals), was demonstrated in a suborbital (rocket) flight experiment in Oct. 1971 (Ref. 4).

In view of the encouraging results of these studies and experiments, a formal investigation of the "preparation of composite materials in space" was initiated which led to the following conclusions as to further action (Ref. 5): (1) As the next step in process development, to concentrate on one specific base metal for each composite type (fiber and particle composites, foams) in view of the complexity of interactions between liquid metals and solid or gaseous dispersions, peculiar to each material combination, (2) to direct these efforts toward early low-g flight experiments with material quantities which permit the establishment of the product properties by mechanical testing.

These recommendations were implemented in the present study. Aluminum was selected by MSFC as the preferred base-metal and process development was aimed at the preparation of flight samples for suborbital (rocket) experiments.

1.3 DEFINITION OF COMPOSITES COVERED IN THIS STUDY

The objective of the processing of composites in space is to obtain a product characterized by a uniform dispersion and spacing of dissimilar materials. In terrestrial processing, composites with spaced reinforcements can only be obtained by solid-state techniques, such as compaction and sintering, which greatly limits the adaptable materials and the product properties. The preparation by a matrix melt cycle is impossible due to the unavoidable segregation and sedimentation of reinforcements. Segregation is particularly pronounced in metal matrices, in view of the low viscosity of liquid metals which is in the order of water. It has been shown in earlier studies and experiments, that in one-g an unacceptable displacement of the reinforcements in liquid metals occurs at density differences ($\Delta\rho$) as low as 0.1. Preparation in space (or low-g environments) is, therefore, primarily aimed at metal base composites and accomplished exclusively by liquid-state processing.

The space composites which have so-far been identified and pursued by various investigators apply different means of dispersion and may be divided into two groups:

Group 1. Metal-base Fiber- and Particle Composites and Controlled Density Metals (plain and reinforced metal foams)

Group 2. Metastable Alloys (Immiscibles) and Unidirectional Eutectics

In Group 1, the dispersions are introduced as solids or gases and remain in their original state throughout the matrix melt/solidification cycle. In Group 2, the dispersions or second phases are formed from an all-liquid solution by controlled cooling.

This study is exclusively concerned with Group 1 and, specifically, with the following types of composites:

Aluminum-base fiber composites

Aluminum-base particle composites

Foamed metals

1.4 STUDY SCOPE AND APPROACH

The prime objectives of this study were twofold: (1) To demonstrate by gound experimentation the feasibility of producing metal-base composites in space and (2) to develop the techniques and facilities necessary for the preparation of materials for low-g experiments with emphasis on aluminum as base metal.

For fiber- and particle-reinforced castable composites, an absolute prerequisite is a successful immersion and dispersion of the reinforcements in the molten matrix. However, paractically all reinforcement materials which exhibit attractive properties are not wetted by metals. This precludes their dispersion in liquid metals by conventional techniques, particularly in aluminum. Aluminum is a highly reactive metal which dissolves practically all potential metallic reinforcement materials to various degrees. The few metals which are fairly stable as well as all non-metallic reinforcement materials, such as oxides or carbides which are attractive due to their high strength and hardness, are not wetted by aluminum. The solution of this problem represents the prime effort of this study. It was approached in the following sequence of investigations:

1. Evaluation of various metals and nonmetallic materials for their attractiveness as reinforcements
2. Theoretical studies of the wetting mechanism and the related techniques to enhance wettability.
3. Verification of the established theories and techniques in wetting experiments.
4. Development of processes and facilities for the dispersion of non-wetting reinforcements in aluminum.
5. Performance and evaluation of dispersion experiments.

In the course of the study it was recognized that for initial low-g experiments, particularly for suborbital (rocket) testing it is advantageous to perform all not-gravity sensitive process phases on the ground by preparing a "precomposite" in which the reinforcements are segregated, yet wetted and dispersed. The sole gravity-sensitive

process phase is then the transformation of the precomposite into a casting with a uniform distribution of reinforcements, consisting of a re-melting cycle and agitation in the liquid state.

Metal foaming investigations and experiments were aimed at the definition of suitable materials and techniques for flight experiments. Experimental verification was limited by the high sensitivity of the liquid/gas mixture to gravity i.e., the impossibility to maintain a stable mixture under gravity conditions.

The study includes a theoretical assessment of the potential capabilities and applications of metal-base composites. It was based on calculated data, since the introduction of real data has to await the performance of flight experiments.

2. EVALUATION AND SELECTION OF MATERIALS

The discussion in this chapter gives an account of the original considerations for the selection of materials, prior to the development of the new wetting and dispersion technique, as well as of the final selection for processing by this technique.

2.1 CRITERIA FOR MATERIALS SELECTION

Materials selection was based on the evaluation of the criteria applicable to the matrix, those applicable to the reinforcements and interrelated criteria.

2.1.1 Criteria Applicable to Matrix Metals

The selection of specific matrix materials was based on the consideration of the following criteria:

1. Processing temperature
2. Wetting characteristics
3. Strength after solidification
4. Susceptibility to oxidation
5. Availability
6. Cost

The order of the above listing represents the original judgement as to relative importance.

The processing temperature should be high enough to represent a substantial advancement over previous experiments with Indium-base alloys, yet, at the same time, remain within the limitations of existing and planned multipurpose furnaces. These temperature considerations refer to the low-g processing cycle, while higher temperatures can be allowed for the preparation of the primary precomposite.

Wetting characteristics of the matrix were considered equally significant. Although molten metals possess a low viscosity and flow well, they also have a high surface energy in the order of 5 to 10 times that of water which inhibits spontaneous spreading over solid surfaces (wetting). The development of the new wetting technique de-emphasized these considerations.

Even though the strength of the matrix material after solifidication was taken in consideration in the selection of specific alloys, it was considered a secondary criterion for initial experiments.

The stability of controlled density metals (metal foams) is promoted by the formation of oxide films on the surface of the metal composing the foam. Hence, lower priority was given to metals which were least easily oxidized.

The easy availability and low cost of material are not prime requisites for a study material but may be the prime consideration for a practical material.

2.1.2 Criteria Applicable to Reinforcements

The following criteria was taken in account for the selection of reinforcements, listed in the order of relative importance:

1. Physical properties
2. Degradation effects
3. Wetting characteristics
4. Availability
5. Cost

The primary consideration for reinforcements was the physical properties - those qualities which serve to enhance, to the highest degree, the properties possessed by the bulk, unstrengthened metal or alloy. Next in turn was the property of degradation - the loss of the initial properties as a result of exposure to the processing temperature or of reaction with, or solution in, the matrix metal.

Wetting characteristics are of crucial importance for the preparation of composites. They were, however, considered as a secondary criterion, since it was expected that suitable coatings can be found. The necessity for coatings was, however, eliminated by the development of the new wetting technique.

The availability and cost cannot be disregarded, especially when considering reinforcements. Many attractive reinforcement candidates are exceedingly expensive and

very difficult to obtain in quantity. However, with greater use, it is reasonable to expect increased production and lower costs. Increased demand can also be expected to lead to new and more economical industrial processes for production.

2.1.3 Interrelated Materials Criteria

The criteria for selecting the system of matrix and reinforcement comprised the following elements:

1. Density difference, $\Delta\rho$
2. Chemical compatibility
3. Bond strength
4. Product properties

The chief parameter characterizing a suitable product is the density difference between the matrix and the reinforcement. A unique composite resulting from space processing will undoubtedly exhibit a substantial $\Delta\rho$ because on earth it is this specific property arising from gravity and buoyancy forces which defeats the preparation.

Next in importance is chemical compatibility. Reaction, solution, and diffusion at the interface between the metal and reinforcement may proceed too far. The reinforcement may dissolve and decrease in diameter and therefore lose strength. Complete solution of the reinforcement is possible if this proceeds too far. Diffusion may result in a new metal or alloy phase at the interface which may become a source of weakness or failure. The net result of these reactions is that the expected increase in properties will not be achieved.

Poor bonding may be closely associated with the chemical behavior. If the metal and reinforcement can be readily separated from each other mechanically, a poor bond has occurred and a inferior composite will result.

The bond strength may, however,be enhanced by controlled surface reaction between matrix and reinforcement, generating a gradual change of properties in the interface region.

Product properties can only be taken in account qualitatively, pending the availability of low-g experiment results.

2.2 SELECTION OF MATRIX METALS FOR FIBER AND PARTICLE COMPOSITES

Data for the selection of matrix metals are presented in Table1.

The basic metal matrices selected to be used in this study were Al as the primary base material, and zinc which was chosen to be optional for convenient experimentation with regard to specific composite characteristics, or material and processing parameters.

The objective of the evaluation was to define specific material compositions which appear most promising for showing the highest effectiveness, considering the combined effect of all identified criteria. Originally, prime emphasis was placed on the effect of composition on wetting characteristics. As a result of the evaluation of material in Table 1, the following base material compositions were selected initially:

Pure Al

Al 43 Alloy

Al 195 Alloy

Al A108 Alloy

Pure Al is used to establish a reference from which to predict the effect of changes in the variables produced by the alloying elements. Alloy 43 contains silicon which provides good flow properties (lower viscosity). Alloy 195 contains copper which serves to enhance the wetting properties with many reinforcements which are planned for use. Alloy A108 contains both Cu and Si to contribute to wetting and flow properties. Its mechanical properties also lie in a range where changes produced by processing may be easily distinguished.

In the course of the Task 1 experiments it was, however, found 1) that some of the selected casting alloys are no longer available, and 2) that the presence of Si, typical for all Al casting alloys, is neither necessary in the developed wetting/dispersion technique, nor desirable due to excessive vaporization. With the new technique for primary composite preparation there was no reason precluding the use of the readily available Si-free wrought alloys, which are more desirable from the viewpoint of strength. The final selection of experimental materials was, therefore, as follows:

Pure aluminum

Aluminum alloy 2024

Most of the experiments were carried out with pure Al. Only a few experiments were performed with alloy 2024, to verify the applicability of the techniques to Al-alloys.

Table 1. Candidate Base Metals and Alloys

		Al ALLOYS								Zn ALLOYS		
PROPERTY	UNITS	EC	13	43	195	108	A108	B195	356	PURE	AG40A	AC41A
Composition	%	99.5	12 Si	5 Si	4.5 Cu	4 Cu/3 Si	4.5 Cu/5.5 Si	4.5 Cu/2.5 Si	7 Si/0.3 Mg	100	4 Al/0.04 Mg	4 Al/1 Cu 0.04 Mg
Density	g/cc	2.70	2.66	2.69	2.81	2.79	2.79	2.81	2.68	7.17	6.6	6.7
Liquidus Temp	°C	657	582	632	644	527	613	635	613	420	387	386
Solidus Temp	°C	646	574	574	521	521	521	532	557	400	381	380
Processing Temp	°C	660	635	650	680	680	680	680	680	440	410	410
Specific Heat	Cal/g/°C	0.225	0.23	0.23	0.23	0.23	0.23	0.23	0.23	0.092	0.10	0.10
Heat of Fusion	Cal/g	94	93	93	93	93	93	93	93	24	-	-
Thermal Expansion to 300°C	10^{-6} cm/cm/°C	25.6	22.4	24	25	24	23	24	23.5	60	27.4	27.4
Strength as cast	10^3 psi	10	35	19	32	21	28	37	33	20	41	47.5
Yield Strength	10^3 psi	4		8	16	14	16	19	24	-	-	-
Elongation	%	43	3.5	8	8.5	2.5	2	9	3.5	25	10	7%

2.3 SELECTION OF REINFORCEMENTS

Data for the selection of reinforcement materials are presented in Table 2.

The reinforcement data are divided into four groups - filaments, whiskers, chopped wires, and particles. The table shows the values of the important physical, chemical and mechanical properties which were used as criteria for evaluating the materials. Additional tabulations give the availability and cost of experimental and commercial quantities.

In columns 17 and 18 the positive and negative criteria for acceptance are identified by the corresponding (preceding) column numbers. Finaliy, in the last column the tentatively selected reinforcement materials are grouped into two priorities. This initial selection was later revised, as outlined in Section 3.3.3.

2 3.1 Discussion of Individual Reinforcement Materials

Graphite. Two types of graphite are available as reinforcement material. The product from the pyrolysis of organic fibers has very good mechanical properties and is available at an acceptable cost. However, it is not wetted by aluminum. To achieve dispersion by conventional methods, it has to be coated with a wetting metal. Coatings of copper and nickel have been prepared successfully; however, the coatings are dissolved rather rapidly in liquid aluminum.

Research quantities of an alternate graphite fiber in pre-composite form are available at a substantial price from Aerospace Corporation. The materialconsists of graphite yarn embedded in, and wetted by an Al base alloy. A proprietary method of preparation has been used for its production. It was selected as a primary candidate, since it was expected that the pre-coated fibers of the chopped yarn are readily wetted and dispersed in molten Al.

Quartz has the highest tensile strength of all the fibers and is commercially available at reasonable cost. However, it is lacking in wettability. It has been reported that attempts to wet the fiber with aluminum have been attended with unexpected explosive reactions. This is understandable in view of the fact that the free energy of formation of Al_2O_3 is -399 kcal per mole vs. -205 kcal per mole for SiO_2. For this reason, quartz was considered only as a secondary candidate.

Alumina (sapphire) will not react with Al, yet is also non-wetting. Its density is substantially higher than Al and its alloys, so the segregation effects are conspicuous. Although fibers are commercially available, their cost is high. Because of this, Al_2O_3 fibers took originally a secondary priority as a candidate material.

Table 2. Candidate Reinforcement Materials

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
		MATERIAL	DENSITY		MELTING TEMP °C	STRENGTH 1000 PSI		CHEM COMPATIBILITY	WETTING			AVAILABILITY		COST $/CC		ACCEPTANCE CRITERIA (IDENTIFIED BY COLUMN NUMBERS)		SELECTION	
			g/cc	Δ ρ		BEFORE PROC'G	AFTER PROC'G		BARE	COATED	COATINGS	EXPT'L	COMM'L	EXPT'L	COMM'L	POSITIVE (ABOVE AVG)	NEGATIVE (BELOW AVG)	1	2
	FILAMENTS (FIBERS)	GRAPHITE	1.9	0.8	3650	350	350	●	●	●	AEROSPACE	●	○	280	30	11, 13	14, 15/16	1	
		GRAPHITE	1.9	0.8	3650	350	350	●	○	◐	Cu, Ni	●	●	1.5	1.5		10		
		QUARTZ - SiO_2	2.2	0.5	1660	850	(850)	⊘	○	◐	Cu, Ni, Ag	●	●	30	1.0	8, 14	9		2
		ALUMINA - Al_2O_3	3.8	1.1	2053	350	350	●	○	◐	Cu, Ni, Ag	●	◐	500	5	5, 14	15		2
		ZIRCONIA - ZrO_2	5.3	2.6	2650	300	(300)	⊘	○	◐	Cu, Ni, Ag	●	◐	80	10	5	9, 15		
		BORON	2.65	0.05	2300	400	400	◐	○	◐	Cu, Ni	●	●	6	6	15/16	5		
		PYREX	2.2	0.5	815	600	600	⊘	○	◐	Cu, Ni, Ag	●	●	20	0.2	8, 14, 16	(6), (9)	1	
		BN	2.1	0.6	2980	200	200	●	○	◐	Cu, Ni, Ag	●	●	2	0.8	15/16	8		
	WHISKERS	SiC	3.1	0.4	2690	3000	(3000)	●	○	◐	Cu, Ni, Ag	●	◐	160	30	8	14, 15/16		2
		Si_3N_4	3.2	0.5	1900	2000	(2000)	●	○	◐	Cu, Ni, Ag	●	◐	150	30	8	14, 15/16		2
		AlN	3.4	0.7	≤200	2500	(2500)	●	○	◐	Cu, Ni	●	●	150	50	8	14, 15/16		
		SAPPHIRE Al_2O_3	3.96	1.26	2040	3000	(3000)	●	○	◐	Cu, Ni, Ag	●	◐	160	60	5, 8	14, 15/16	1	
	WIRES (CHOPPED)	Be	1.85	0.85	1280	185	185	○	●	—	—	●	●	100	35	10	8		
		STAINLESS STEEL	7.8	5.1	1430	300	200	◉	◐	●	Cu, Ni	●	●	2	0.5	2, 9, 11, 14, 16	8		2
		TUNGSTEN	19.4	16.7	3400	400	300	●	○	◐	Cu, Ni	●	●	6	4	5, 14		1	
	PARTICLES	GRAPHITE	1.9	0.8	3650	NA		●	○	◐	Cu, Ni	●	●	0.01	0.01	14, 16	5, 10		
		QUARTZ	2.2	0.5	1660	NA		⊘	○	◐	Cu, Ni, Ag	●	●	0.01	0.01	14, 16	5, 10		
		ALUMINA	3.8	1.1	2040	NA		●	○	◐	Cu, Ni, Ag	●	●	0.3	0.3	14, 16	10		
		SiC	3.1	0.4	2690	NA		●	○	◐	Cu, Ni, Ag	●	●	0.03	0.02	14, 16	5, 10		
		STAINLESS STEEL	6.3	3.6	1430	50 (SINTERED)		●	◐	●	Cu, Ni	●	●	0.07	0.05	5, 9, 11, 14			
		ZrO_2	5.3	2.6	2650	NA		⊘	○	◐	Cu, Ni, Ag	●	●	0.04	0.03	5, 14, 16	10		

● SATISFACTORY
○ UNSATISFACTORY
◐ PARTLY SATISFACTORY
⊘ POSSIBLE UNCONTROLLED REACTION

Silicon Carbide has properties similar to Alumina. The density is somewhat closer to aluminum (density difference app. 0.5). It is fully compatible with Al and also non-wetting. While basically available, procurement proved to be very difficult and costly.

Zirconia, ZrO_2 has the highest density of all nonmetallic materials. It would therefore be the best choice for demonstrating the advantage of low-g processing. However, its strength is only modest. As with most of the other fibers, wetting is a problem. Comparison of the heats of formation of the oxides show that ZrO_2 is unstable with respect to metallic aluminum, so if enough energy of activation is imparted, the material can be attacked by the Al. Although ZrO_2 fibers can be obtained, their potential cost is high. Because of the disadvantages, ZrO_2 fibers were not considered to be a candidate material.

Boron fibers are fairly strong, but their density is similar to that of Al and its alloys. Boron fibers also can react with molten aluminum. A product AlB_2 may not be wettable The reaction seriously degrades the product. Boron fibers are commercially available for an acceptable but high price. Nevertheless the density value and the reactivity are the factors which overshadow any benefits of this choice.

Pyrex has good strength at room temperature. It is a very low cost fiber which is readily available. Pyrex fibers would require a coating of copper or nickel in order to achieve a wetting system with Al. The melting temperature is 815° which is above the processing temperature. If the fibers do not lose their structural integrity during processing, then the room temperature product will provide an excellent test material.

Boron nitride fibers are the weakest of the filaments. The fibers probably are not wet by Al. On the other hand, a reaction with molten Al is possible. The fibers are available commercially at an acceptable cost but because of the low strength, other choices are better.

Chopped wires. Be wire has the lowest density difference, the lowest strength, the lowest chemical compatibility and the highest price of the wires. It was therefore removed from consideration. W wire has the greatest density difference, the highest strength, good chemical compatibility and acceptable cost. It is therefore the first choice for a wire reinforcement. Stainless steel (SS) has a high density difference and a relatively good initial strength. Some of the strength will be lost as a result of heating to the processing temperature. The chemical compatibility between Al and SS appears excellent. The materials are wetted and a good bond is formed. The cost and availability of stainless wires is the lowest of all the wires. While SS may be attractive as an experimental material, it is of little practical value.

Whiskers. With a few exceptions all the whiskers have similar properties. The density differences between them and Al are of similar magnitude except that sapphire

whiskers have a difference 2 to 3 times greater. The tensile strength of all the whiskers are extremely high, ranging from 2×10^6 psi for Si_3N_4 to 3×10^6 psi for SiC and SiO_2. All of the whisker materials suggested require a coating to allow them to be wet by Al. The cost for each is high and of the same order of magnitude. On the basis of the above, the first choice is sapphire whiskers because of their high strength and relatively high density. A pair of second choices are SiC and Si_3N_4 which may eventually be lower in cost. The strength of the SiC however is much greater than Si_3N_4.

Particles. Because of the large number of similar properties in the criteria for selecting particles it is more convenient to discuss the selection by considering the properties rather than the individual materials.

From the standpoint of density, Al_2O_3, SS and ZrO_2 are superior. All the particles have melting points considerably above the processing temperature. Strength of particles is not a factor for particle reinforcements. Quartz and ZrO_2 are deficient in respect to chemical compatibility because of possible reaction with molten Al. The remaining particles are compatible.

All the materials except SS will require some means to provide wettability. The availability and cost of any of the particles is sufficiently adequate that none can be excluded on this basis regardless of the fact that Al_2O_3 is 30 times more expensive than graphite or quartz.

From the overall aspects, Al_2O_3 is considered the most promising particle material. While ZrO_2 has a similar density, it has been deleted in view of its possible reactivity with molten Al. Very fine SS particles (powder) may be considered as activators for the formation of fine-grain castings, rather than composites.

2.3.2 Final Selection of Reinforcement Materials

In the course of the Task 1 investigations, the reinforcement selection was revised and further narrowed-down.

Silica in the form of quartz or pyrex was eliminated in view of excessive reaction with molten Al. Also eliminated was the Al-infiltrated graphite yarn, since the individual fibers of the yarn did not disperse (see Section 3.4).

In the preliminary evaluation, a primary restriction of all high-performance reinforcement materials was poor wettability. This problem was resolved with the subsequently developed wetting/dispersion technique, permitting a revision of the initial materials selection and an optimization of choices.

The ultimately selected fiber materials, all in the form of chopped filaments or chopped w.re, and their most significant positive or negative characteristics are as follows:

Sapphire	Positive:	strength, stability
	Negative:	high cost, not readily available in thicknesses below 0.25 mm
Silicon Carbide	Positive:	strength, stability
	Negative:	high cost, not readily available
Pyrolytic Graphite	Positive:	strength, availability, low cost
	Negative:	potential formation of a carbide interface
Tungsten	Positive:	strength, high density difference, availability, low cost.
	Negative:	Alloy formation at high temperatures.

For particle composites. the single choice was alumina, as it exhibits a unique combination of positive characteristics (high strength/hardness, stability, low cost, availability in a wide variety of particle sizes).

Sapphire whiskers were selected for a limited number of experiments. Otherwise, whiskers were deleted from the experimental program for the following reasons: (1) high cost: (2) poor availability (3) unreliable properties in a small quantity procurement; (4) fiber experiments provide the essential processing parameters.

2.4 DISCUSSION AND SELECTION OF MATERIALS FOR METAL FOAMS

The selection of materials for metal foaming experiments was based on the use of a "gas former " In this technique the individual foam bubbles are generated by gas evolving from dispersed solid particles which decompose in the molten matrix.

Most metal (M) salts which would be appropriate for the evolution and dispersion of gases contain oxygen (MNO_2, MNO_3, MSO_3, MSO_4, MCO_3, MC_2O_4, MO). These salts tend to react with Al and Zn to oxidize them, a reaction which may be sufficiently vigorous to be explosive.

The nitrogen (N) oxides and sulfur (S) oxides also tend to be corrosive, especially in moist environments. Salts yielding carbon (C) oxides are not desirable as gas formers because of the reactivity of the C oxides with reducing metals like Al and Zn at elevated temperatures.

Halide Salts (MF, MCl, MBr, MI) are highly reactive so the matrix would be consumed (corroded) by the evolution of halogen gases. Oxides are rather stable so they do not produce gas for use in making foam. The expected reaction is to produce the metal oxide of Al or Zn. Nitrides are formed by Al and Zn even at mild temperatures. Therefore nitrogen gas formers are not desirable foaming agents either.

The most promising materials for producing foam by gas evolution appear to be metal hydrides. TiH_2 and ZrH_2 each decompose at an appropriate rate and at an appropriate temperature. Some of the hydrogen may react to form a compound with Al or Zn; the amount of reaction depends in part on the kinetics involved. This may be of advantage, since it may have a stabilizing effect on the walls of the individual gas bubbles, reducing the danger of coalescence.

The final choice of materials for foaming experiments were Zinc as matrix material and TiH_2 as gas former, since they exhibited the best temperature compatibility with regard to matrix melting and gas evolution.

3. INVESTIGATION OF WETTING CHARACTERISTICS

The condition of free mobility of solid particles in a liquid exists only if the solids are fully wetted by the liquid, since otherwise the solids tend to agglomerate or are entirely rejected by the liquid. Complete wetting is, therefore, mandatory for liquid-state processing as well as for the generation of a satisfactory bond between reinforcements and matrix upon solidification. Unfortunately, practically all desirable reinforcement materials, such as oxides and carbides, are not wetted by liquid metals.

For aluminum it can be stated categorically that all materials which exhibit high strength and stability are non-wetting, while all readily wetted materials also react with, or dissolve in, molten Al. Since only the first type of materials is of interest, the problem of wetting had to be resolved.

3.1 CONCEPTUAL APPROACH

In the initial part of Task 1, preparations were made for the solution of this problem by means of coatings. It was realized that such coatings, in accordance with the statement above, would not be stable. It was hoped that coating materials could be found whose reaction is sufficiently slow to achieve at least the critical initial dispersion. It was, however, questionable whether the dispersion would remain stable and free of coagulations after dissolution of the coating.

In view of these uncertainties, another concept of dispersion was pursued simultaneously, which was based on a theory advanced in the preceding study "Preparation of Composite Materials in Space" (Ref. 5). There it was postulated, on the basis of experiments with simulation liquids, that the conventional theory of wetting is valid only in a three-phase system, or the presence of a gas besides the solid and the liquid. It was further postulated, that under perfectly gas-free conditions, the conventional concept of wetting may no longer apply and any solid can be dispersed in any liquid within the otherwise (temperature, chemical stability) compatible regime.

It was realized that, if this theory can be proven and reduced to practice, it would open up new applications for composites, in space as well as terrestrial production.

3.2 THEORETICAL CONSIDERATIONS

Because force fields extend beyond the boundary surface of liquids or solids, extraneous matter tends to become attached to the surface. Examples are the attraction of gases toward solids (adsorption) or liquids and solids towards solids (adhesion). If a solid is left unprotected, its surface usually becomes quickly coated with a film of gas and other contaminants. For example, Giaever (Ref. 11) simply exposed freshly evaporated aluminum film to air for a few minutes to prepare a 30 Angstrom insulation layer so as to obtain the necessary insulated junction device for investigations of tunneling phenomena in superconductors.

Although any quantitative treatment of the interfacial forces poses considerable difficulties, a large amount of empirical information has been developed.

The work of adhesion of a liquid to a solid may be calculated as the sum of the work performed in generating one unit area of liquid surface and one unit area of solid surface minus the original liquid-solid interface energy (Figure 1). The result may be expressed by Dupre's equation (Ref. 12).

$$w_{s\ell} = \gamma_{sv} + \gamma_{\ell v} - \gamma_{s\ell} \tag{1}$$

where γ_{sv}, $\gamma_{\ell v}$ and $\gamma_{s\ell}$ are the surface tensions at the solid-vapor, liquid-vapor and solid-liquid interfaces, respectively. The difference $\gamma_{sv} - \gamma_{s\ell}$ can in many cases be expressed in measurable quantities by considering a liquid drop resting on the solid (Figure 2). According to Young (Ref. 13). the equilibrium of the forces acting at the drop periphery requires that,

$$\gamma_{sv} = \gamma_{s\ell} + \gamma_{\ell v} \cos\theta \tag{2}$$

Eliminating the immeasurable quantities γ_{sv} and $\gamma_{s\ell}$ from Eqs. (1) and (2) we find,

$$w_{s\ell} = \gamma_{\ell v}(1 + \cos\theta) \leq 2\gamma_{\ell v} \tag{3}$$

The quantity $2\gamma_{\ell v}$ may be set equal to the work of liquid cohesion $w_{\ell\ell}$ (Figure 3). Thus, Eq. (3) shows that the contact angle θ is determined by the relative magnitudes of adhesion of the liquid to the solid ($w_{s\ell}$) and cohesion of the liquid to itself ($w_{\ell\ell}$). The condition for spreading of the liquid on the solid ($\theta = 0$) may then be expressed as,

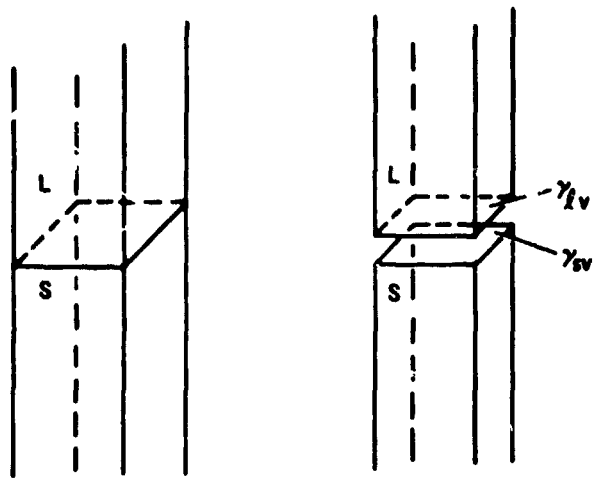


Figure 1. Work of Adhesion

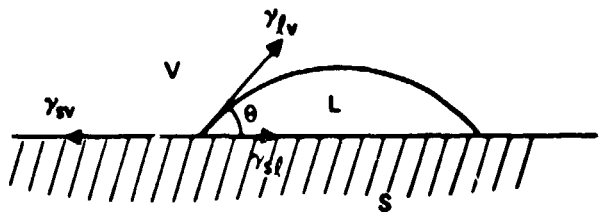


Figure 2. Forces Acting at Periphery of Liquid Drop on Solid Surface

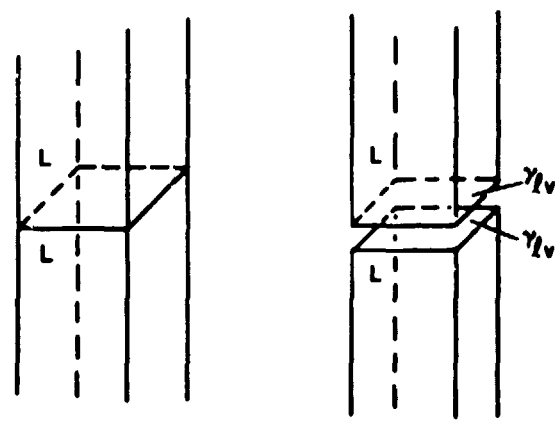


Figure 3. Work of Cohesion

$$w_{s\ell} - w_{\ell\ell} \geq 0 \qquad (4)$$

the difference on the left-hand side being sometimes referred to as the spreading coefficient of the liquid on the solid.

Apart from the difficulties involved in measuring contact angles, the foregoing relations are strictly valid for clean solid surfaces and uncontaminated liquids. These conditions rarely, if ever, prevail on earth. For instance, when the pure solid-vapor interface, shown in Figure 1, adsorbs a contaminant, its surface energy is lowered such that,

$$\gamma_{sv} = \gamma_{so} - \gamma_c$$

where γ_{so} is the surface energy of the pure solid and γ_c is the spreading energy of the contaminant. It is evident from Eqs. (1) and (4) that by lowering $w_{s\ell}$, the contaminant tends to prevent spreading of the liquid on the solid.[+] Sufficiently high values of γ_c will invalidate inequality (4) or even cause dewetting.

It is of interest to note that the meniscus of mercury in a glass container can be changed from convex to concave through extended boiling (Ref.12), baking out (Ref 14) or prolonged electrical discharge (Ref. 15). Langmuir (Ref. 16) showed that a one-molecule thick layer of a fatty substance on a glass plate is sufficient to change the contact angle of water on the plate.

A freshly produced surface or an ideally clean surface in vacuum is actually chemically and/or physically reactive to a high degree because it tends to lower its surface energy by adsorbing gases or vapors that satisfy the structure or force field. Adsorption is mono-molecular up to a vapor pressure of about one-fifth the saturated vapor pressure (Ref. 17), the adsorption layer becoming increasingly thick as the saturated vapor pressure is approached.

The free surface energy of solids ranges from several hundred to a few thousand ergs per cm^2 (Ref. 18) as shown in Table 3.

Generally the higher melting, harder materials (which also tend to have a greater modulus of elasticity) possess the highest free surface energies. These are the kinds of materials which provide reinforcement properties for weaker and softer metals or alloys. It was worthwhile therefore to attempt to produce such reinforced metals by exploiting the surface energy phenomena discussed in the preceding paragraphs. Specifically, the proposed wetting technique involves uncontaminated

+With regard to contaminants, the operations of the wetting technique discussed below, justify the assumption of an unchanging value for $\gamma_{\ell v}$.

reinforcement materials with a high free surface energy, so that inequality (4) is satisfied.

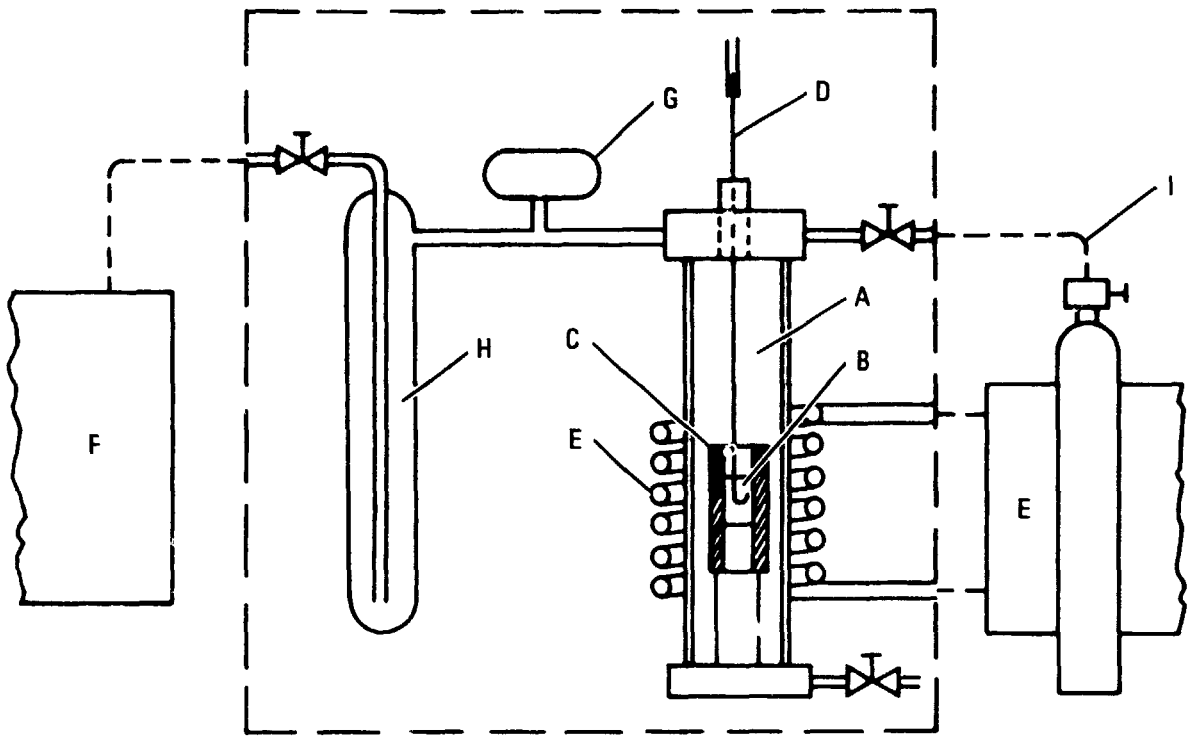
Table 3. Free Surface Energy of Solids in Vacuum

Material	γ_{so} (ergs/cm^2)
Mica	24-5400
Glass	1210
Titanium Carbide (1100° C)	1200
Alumina, Al_2O_3 (1-2000° C)	7-1100
Lime, CaO (0° K)	650-1000
Silver	800
Sodium	170
Sodium Chloride	150-190
Potassium Chloride	160-175
Sodium Bromide	113-175

Generally the higher melting, harder materials (which also tend to have a greater modulus of elasticity) possess the highest free surface energies. These are the kinds of materials which provide reinforcement properties for weaker and softer metals or alloys. It was worthwhile therefore to attempt to produce such reinforced metals by exploiting the surface energy phenomena discussed in the preceding paragraphs. Specifically, the proposed wetting technique involves uncontaminated reinforcement materials with a high free surface energy, so that inequality (4) is satisfied.

3.3 EXPERIMENTAL APPARATUS

In practical terms, the proposed theory calls for the joining (immersion) of the reinforcement with the liquid matrix in high vacuum. For this purpose an apparatus was set-up which permitted melting of the aluminum matrix and joining with the reinforcements in high vacuum. The laboratory-style apparatus is shown schematically in Figure 4. Basic components are the melting chamber A (quartz) with the sample crucible B, a susceptor C, manual stirrer D, and the induction heating system E. The chamber is evacuated with the high vacuum system F. The line from the chamber to the vacuum pump includes an ionization gage G and a metal vapor trap H. To eliminate the prime enemy of liquid metals, oxygen, entirely, an argon flushing system I was added. Sample temperature was measured with an optical pyrometer. The processing section of the apparatus is shown in Figure 5.



A	PROCESSING CHAMBER	E	INDUCTION HEATING SYSTEM
B	CRUCIBLE AND SAMPLE	F	VACUUM PUMP
C	SUSCEPTOR (NOT REQUIRED FOR THICK-WALL CRUCIBLES)	G	IONIZATION GAGE
D	STIRRER	H	VAPOR TRAP
		I	ARGON FLUSHING SYSTEM

Figure 4. Apparatus for Vacuum Wetting Experiments

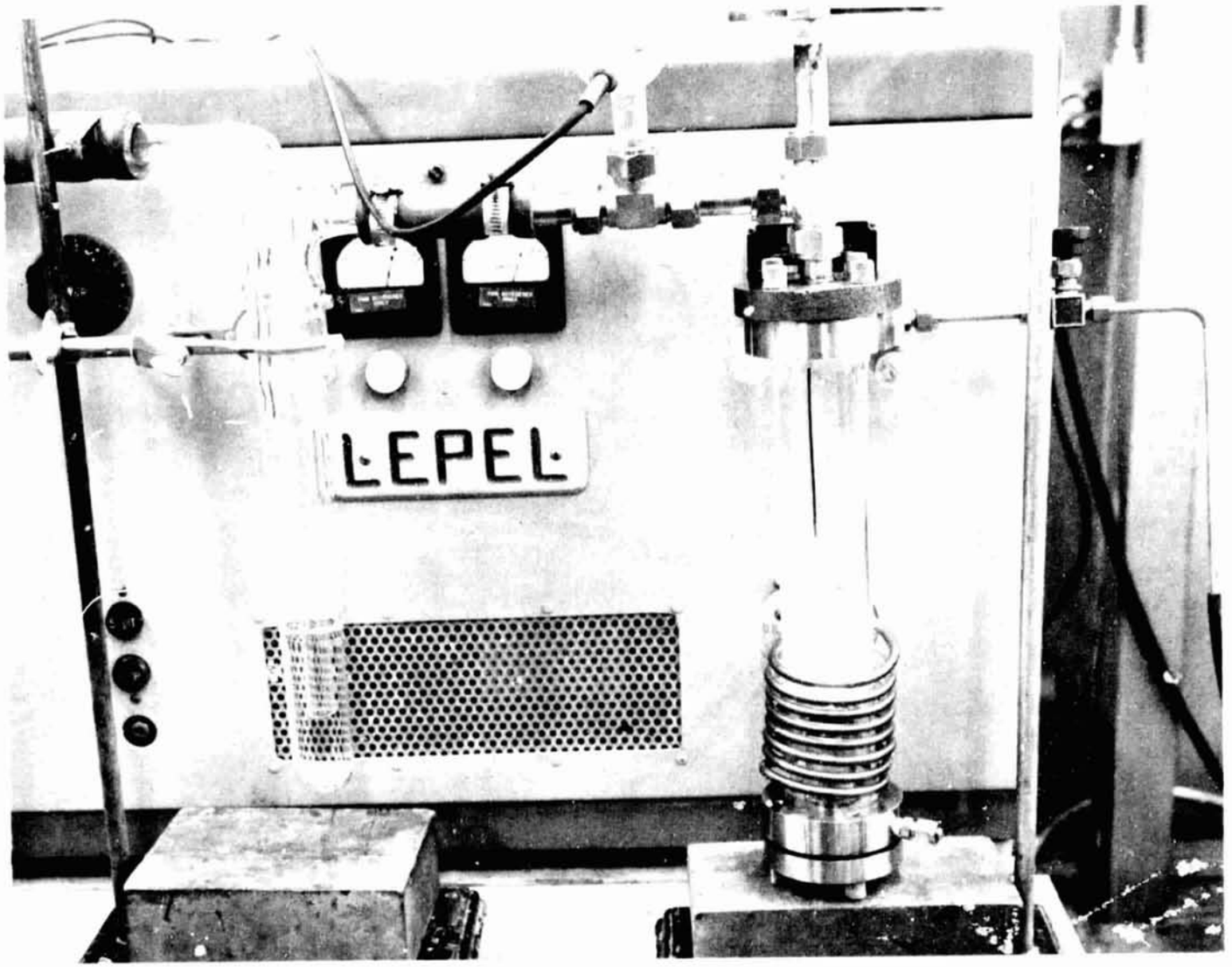


Figure 5. Wetting Apparatus During Experiment Performance

To obtain an oxygen free vacuum, the following procedure is followed:

1. Pump down to $<10^{-3}$ mm Hg.
2. Pressurize with argon and evacuate again $<10^{-3}$
3. Repeat (2) several times.
4. Heat sample to approx. 600° C and repeat step (2).

3.4 WETTING EXPERIMENTS

For the initial experiments, pure aluminum and chopped tungsten wires were used as model materials. They were placed in small pyrolytic graphite crucibles, which served at the same time as susceptors for induction heating. Heating of the sample material was, therefore, primarily by conductive heat transfer. The sample material was arranged so that all surfaces are exposed to the vacuum environment. Exposure for complete gas removal was further enhanced by stirring during heat-up and melting. Preliminary experiments, at a vacuum of only 10^{-3} mm Hg were extremely encouraging, as the tungsten fibers started to join with the liquid aluminum.

In the course of these experiments it was further found that the gas removal is significantly enhanced by increasing the temperature several hundred degrees beyond the melting temperature of the matrix. Experiments carried out with the additional high-temperature cycle were a complete success. The tungsten fibers were wetted spontaneously and dispersed in the matrix. Fibers at the surface were completely covered with aluminum, as shown in Fig. 6.

Another, unexpected and to-date unexplained feature of the high-temperature vacuum cycle is the complete disappearance of the aluminum oxide cover which forms during melting. This phenomenon and the formation of a shiny metal surface serves also as a visible indicator for attaining perfect wetting conditions.

In view of these encouraging results, additional wetting experiments were carried out with other candidate materials. The results were as follows:

Al-Infiltrated Graphite Yarn. Materials obtained from two producers (Aerospace Corp. and Fiber Materials, Inc.) showed wetting of the chopped yarn pieces. However, the individual filaments of the yarn did not disperse under stirring and remained as individual units in the matrix, as evidenced in Figure 7.

Bare Pyrolytic Graphite fibers (0.01 mm diam) exhibited wetting and partial dispersion. The dispersion was somewhat inhibited by mechanical interlocking between fibers. It was however expected that dispersion will be achieved by selecting a more favorable fiber L/D

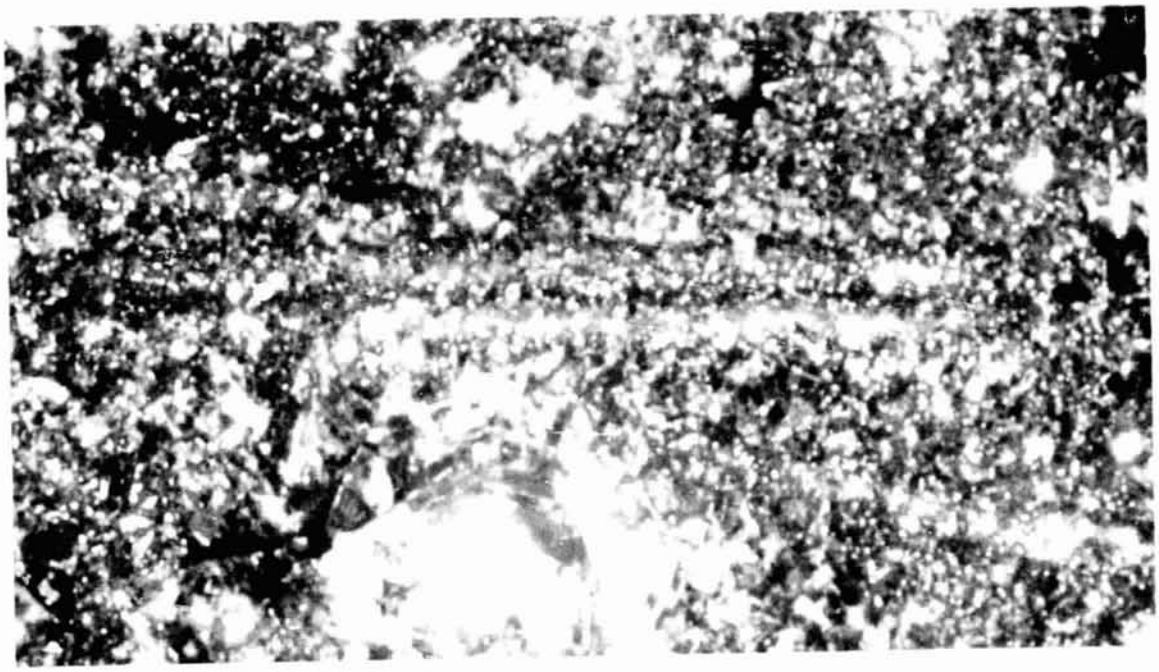


Figure 6. Wetting Experiment: Chopped Tungsten Wire

Figure 7. Wetting Experiment: Al-Infiltrated Graphite Yarn

Silicon Carbide Filaments of 0.1 mm diam. and chopped to an average length of 4 mm exhibited excellent wetting. This can be seen in the left portion of Figure 8, where fibers at the surface and protruding into the vacuum environment are covered with aluminum matrix.

Sapphire (Al_2O_3) Filaments of 0.25 mm diam. and chopped to an average length of 4 mm exhibited equally excellent wetting characteristics, as evidenced in Figure 9.

Pyrex and E-Glass filaments reacted with the aluminum matrix, forming aluminum silicate crystals. They were, therefore, eliminated from the program.

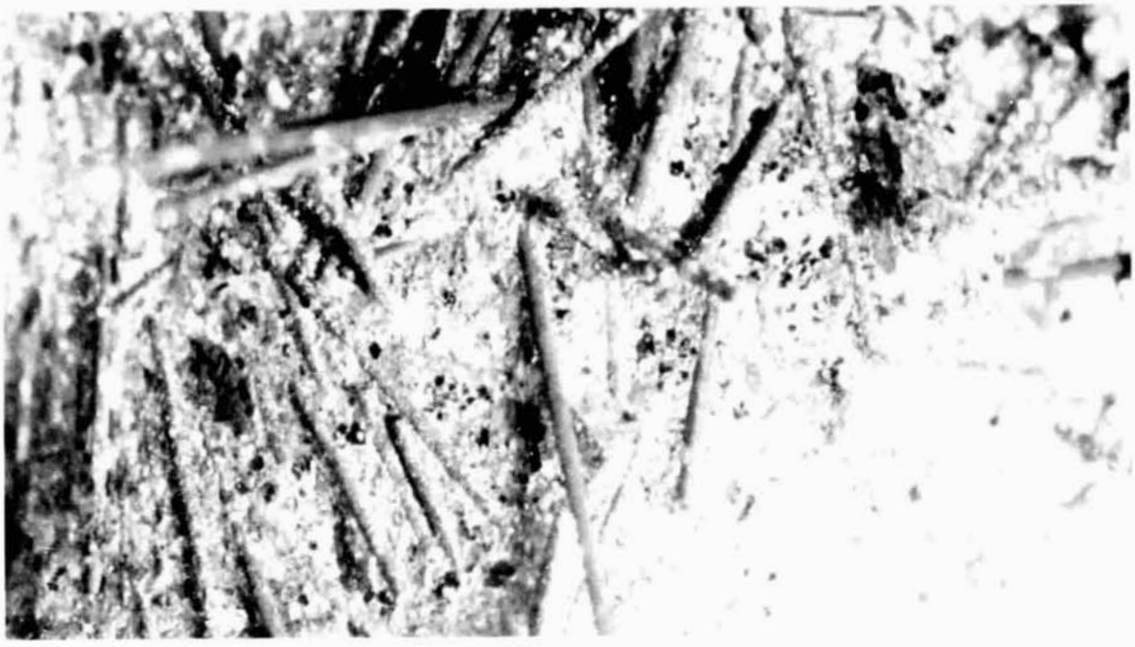


Figure 8. Wetting Experiment: Silicon Carbide Fibers

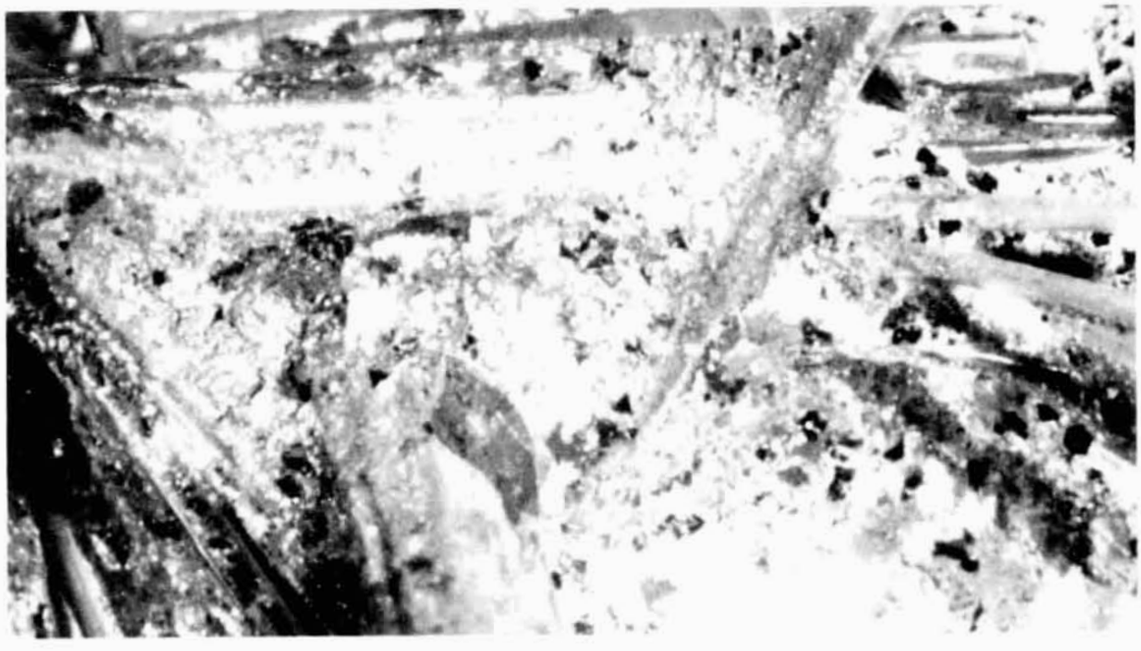


Figure 9. Wetting Experiment: Sapphire Fibers

4. DISPERSION TECHNIQUES

In the course of the wetting and dispersion experiments the processing techniques and the related facilities were gradually improved and refined. The following discussion represents the final state of art, as it was applied in the latter part of the dispersion experiments

4.1 SIGNIFICANT PROCESS ELEMENTS

The process goal was to achieve complete wetting and immersion of the reinforcements through the establishment of a pure two-phase (solid/liquid) system with no interfacial contaminants from either the matrix or the reinforcements. The effectiveness of this principle had been already demonstrated in the wetting experiments. For the dispersion experiments the original procedure (Sect. 3.3) was considerably refined. The essential elements of the perfected process were the following:

a. Substituting Argon for air

b. Vacuum in the order of 10^{-6} mm Hg

c. Repeated preheating close to matrix melting temperature

d. Maintaining a glow discharge

e. Raising processing temperatures significantly beyond the melting temperature

f. Effective stirring.

The substitution of argon for air (a) by means of several argon purge cycles serves two purposes: (1) to reduce the amount of adsorbed gases, since argon is less readily adsorbed than oxygen on most surfaces and (2) to eliminate additional oxidation; any oxygen present reacts with the aluminum matrix and some of the reinforcements, particularly upon heating, producing troublesome amounts of secondary phases.

Low pressure (b) is necessary to reduce the equilibrium amount of gases and contaminants adsorbed at the material surfaces. The lower the pressure, the less

adsorption is encountered; this applies also to chemisorption at aluminum and crucible surfaces at higher temperatures. Low pressure further produces a higher pressure gradient in a batch of reinforcements which, in turn, enhances the rate of gas removal from the reinforcements, as discussed in detail in Sect. 5.7.3.

The required vacuum level depends primarily on the amount and size of reinforcements. For coarse reinforcements or minute amounts of fine reinforcements a vacuum level of 10^{-3} - 10^{-4} mm Hg is sufficient since the surfaces are readily accessible. For substantial amounts of finer reinforcements, such as fibers or particles of less than 100 micron diameter, a pressure of 10^{-6} mm Hg has to be maintained.

The removal of gases from the sample and crucible surfaces is further enhanced by repeated preheating (c) to a temperature slightly below the melting point of the matrix (600° C for aluminum). During experiment performance, the gas removal could be observed at the vacuum gage by a pressure increase in the system. In the initial preheating cycles the pressure rose to 5×10^{-4} and required several minutes to return to 10^{-6} mm Hg. The cycling was continued until the pressure drop became negligible and the recovery was instantaneous.

Maintaining the system for a period of time in a glow discharge (d) as part of the preheating cycles subjects the surfaces to ion and electron bombardment. This causes a further detachment (sputtering) of adsorbed gases and contaminants from various surfaces in the processing chamber.

The most effective and final means of gas removal was an increase of the processing temperature to a level significantly above the melting point of the aluminum (e), since all physical adsorption decreases with temperature. Many oxides also decompose at higher temperatures while organic contaminants decompose and volatilize with other materials of low vapor pressure. The effective decomposition of the oxides in the liquid aluminum could be well observed by the sudden change to a shiny surface. A high temperature further increases the mobility of the aluminum, lowers its surface tension and viscosity and thus provides conditions allowing the liquid metal to surround and adhere to the clean surfaces of the reinforcements. As some of the aluminum vaporizes at the molten surface it may generate a minute liquid coating on the reinforcements, which further enhances wetting and immersion.

Stirring (f) upon melting of the matrix and during the entire high-temperature cycle is necessary for several reasons: First, the agitation of the reinforcements breaks up the batch and exposes a higher percentage of the reinforcements directly to the vacuum environment, enhancing the removal of adsorbed and trapped gases. Second, stirring breaks up any contaminants and scrubs them from the surfaces. Third, it disturbs the surface of the melt and disrupts the orientation of the atoms at the liquid surface which may otherwise form a network strong enough to prevent metal evaporation. Finally, it produces intimate contact between the liquid metal and the reinforcements and, thus, induces immersion and dispersion.

In the course of the experiments it was observed that wetting and immersion of the reinforcements proceeds rapidly only when vapors of aluminum are deposited on the wall of the vacuum chamber; the rate of this deposition serves, therefore, as an indicator for achievement of favorable processing conditions which cannot be measured individually. It was further observed that after wetting takes place, there appears sometimes a film of crystals, presumably aluminum oxides, floating at the surface of the melt. These crystals gradually disappear; it could not be ascertained whether they decompose or are wetted in the same way as the reinforcements and become immersed in the melt. In some Al/sapphire composites, high magnification metallographic examination of the solidified sample showed the presence of perfectly hexagonal single crystals of Al_2O_3. It could not be determined whether they originated from the sapphire reinforcements or from surface oxides.

It is apparent from the foregoing discussion that wetting and immersion of commonly non-wetting materials cannot be related to one specific phenomenon, but is rather the result of a necessary combination of a multitude of phenomena and processing details.

4.2 PROCESS SPECIFICATION

The detailed procedure for the preparation of the primary composite (wetting, joining and dispersion of matrix and reinforcements) in its latest state of refinement consisted of the following steps:

1. Mechanical preparation of reinforcements (if indicated), such as cutting of filaments to the desired fiber length.
2. Cleaning of reinforcements
   a. Fibers: Chemical cleaning with trichloroethylene
   b. Particles: Baking of spread-out particles in a vacuum oven at 104° C for 24 hrs.
3. Preparation of aluminum chips of appropriate size (app. 0.2 cm^3 each) with smooth surfaces and edges. All surfaces to be filed clean immediately prior to Step 4.
4. Filling of the crucible with the cleaned materials. Reinforcements are placed on top of the aluminum, to provide good access to vacuum.
5. Installation of the filled crucible in the processing chamber.
6. Close vacuum system and check for leaks. Adjust mechanical stirrer, so that paddles have a minimum clearance from the crucible bottom.

7. Argon Purge
   a. Evacuate system to 10^{-3} mm Hg
   b. Bleed-in argon to 175 mm Hg
   c. Repeat (a, b) 2 times.
8. Evacuate to 10^{-6} mm Hg
9. Preheating Cycles
   a. Heat crucible/sample to a temperature short of the matrix melting point (600° C for aluminum). This will result in a transient pressure increase in the chamber accompanied by glow discharge. Hold temperature for 15 seconds (or less if vacuum drops below 5×10^{-4} mm Hg).
   b. Wait until vacuum recovers to 10^{-6} mm Hg.
   c. Repeat several times until the pressure increase becomes insignificant and recovers rapidly, yet at least 5 times.
10. Establish working vacuum by leaving system at 10^{-6} mm Hg for 24–48 hours at 200° C or at room temperature. The required time is dictated primarily by the quantity and size of reinforcements; to a lesser degree it also depends on the pumping capacity of the vacuum system.
11. Raise sample temperature to melting.
12. Upon complete melting, start stirring vigorously while raising sample temperature gradually to max. processing temperature (1000 - 1100° C for aluminum). Proper max. temperature is indicated by vapor deposition at chamber wall.
13. Continue stirring at max. temperature until all reinforcements are immersed and the matrix surface has a shiny appearance.
14. Turn off heat, let system cool.
15. Pressurize system, raise upper flange assembly, remove processing chamber and then the crucible.

4.3 APPARATUS FOR DISPERSION EXPERIMENTS

The apparatus used in the dispersion experiments did, in principle, not differ from the original apparatus employed in the wetting experiments as described in Section 3.3. However, the refinements in the processing techniques outlined in Section 4.1 and a gradual increase of the sample size, called for modifications

and improvements, resulting in a much more elaborate, yet at the same time, more capable and reliable facility. The most significant improvements were as follows:

(1) Upgrading of the vacuum system to 10^{-6} mm Hg

(2) Increased sample temperature capability

(3) Increased chamber size to accommodate larger material samples

(4) Improved stirring system.

The original apparatus assembly is shown in Fig. 10. The apparatus in its final configuration, as used in the latter part of the dispersion experiments, is shown in Fig. 11. Its major components are described in the following chapters.

4.3.1 Crucibles

The crucibles in which the sample materials were processed are discussed first, since they dictated the size of other components.

The crucible materials had to meet the following requirements: High electrical conductivity to act as effective susceptors in induction heating; no chemical reaction with aluminum at the max. processing temperature of 1000-1100° C; freedom from any porosity which may contain gases. The ideal combination of these characteristics was found in pyrolytic graphite. Conventional graphite proved to be inadequate, since it was impossible to maintain high vacua (gas evolution from microporosity).

The pyrolytic graphite crucible type A (Fig. 12-A) was used predominantly. It has a net material capacity of app. 1.5 cc (app. 3 grams of Al were commonly used). It has a relatively thick wall which provides good coupling with the induction coil. It is, finally, comparatively inexpensive ($9.50 each as opposed to $21.00 for crucible B). In the choice of crucibles, the price had to be taken into consideration, since one crucible is consumed in each experiment (cracks after cooling). The sole disadvantage of crucible A is the limited height of only 1.25 cm (inside) which cannot prevent spilling of some reinforcements during stirring. For this reason a near-tubular conical pyrolytic graphite crucible of 1.3 cm ID × 5.5 cm high was used in a few experiments; while there was no loss of material, mixing was too difficult and inadequate. The same experience was made with specially fabricated tubular stainless steel crucibles, which were used extensively in initial experiments with small amounts of material.

In the later part of the dispersion experiments the larger crucible B (Fig. 12-B) was used. It has a capacity of 38 cc and a net (sample) capacity of 14-18 cc, depending on the material preparation. The relatively high cylindrical wall prevented spilling, even at high stirrer speeds. A groove ground into the bottom matched the quartz holder, keeping the crucible in place during stirring.

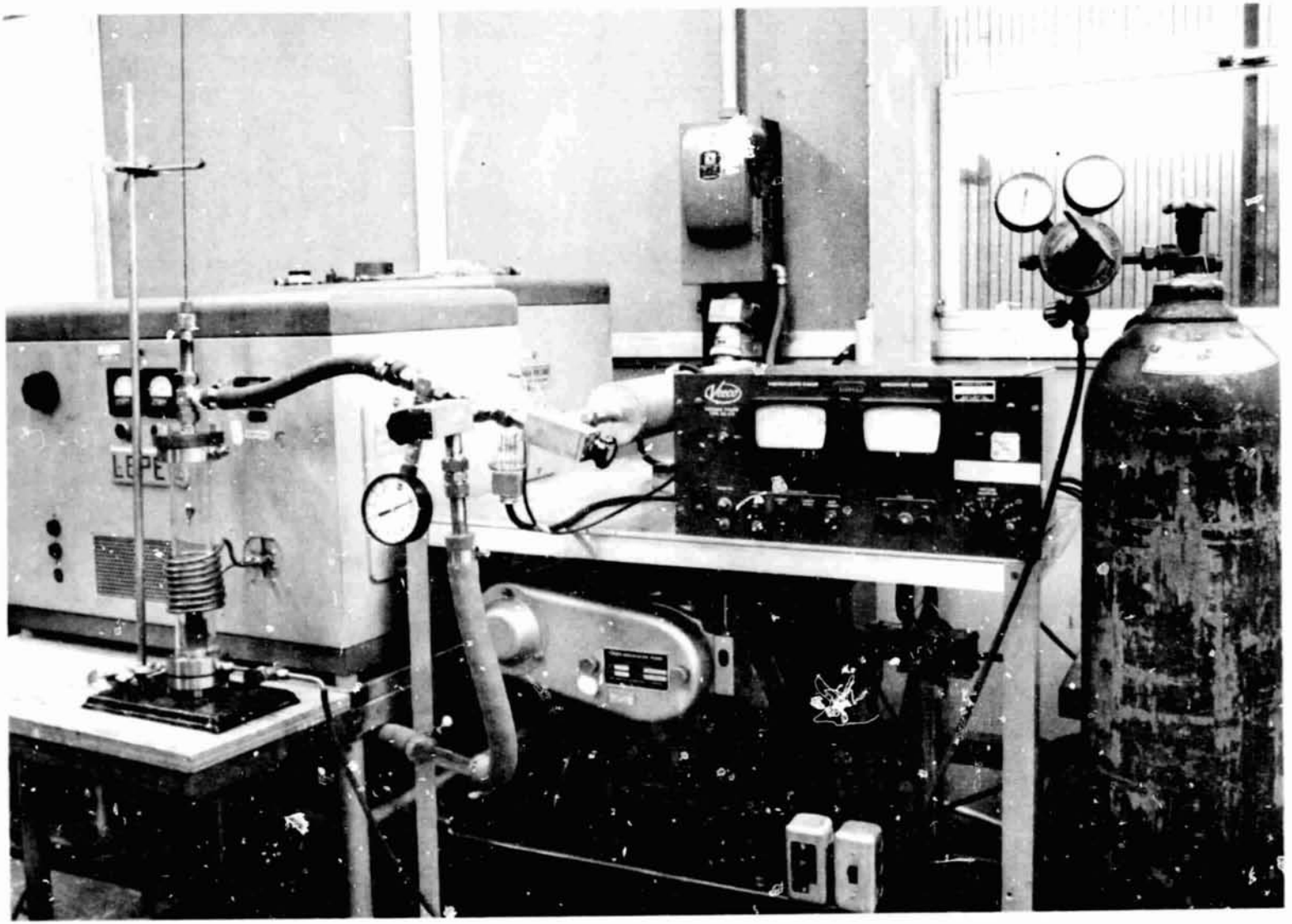


Figure 10. Original Dispersion Apparatus with Chamber A

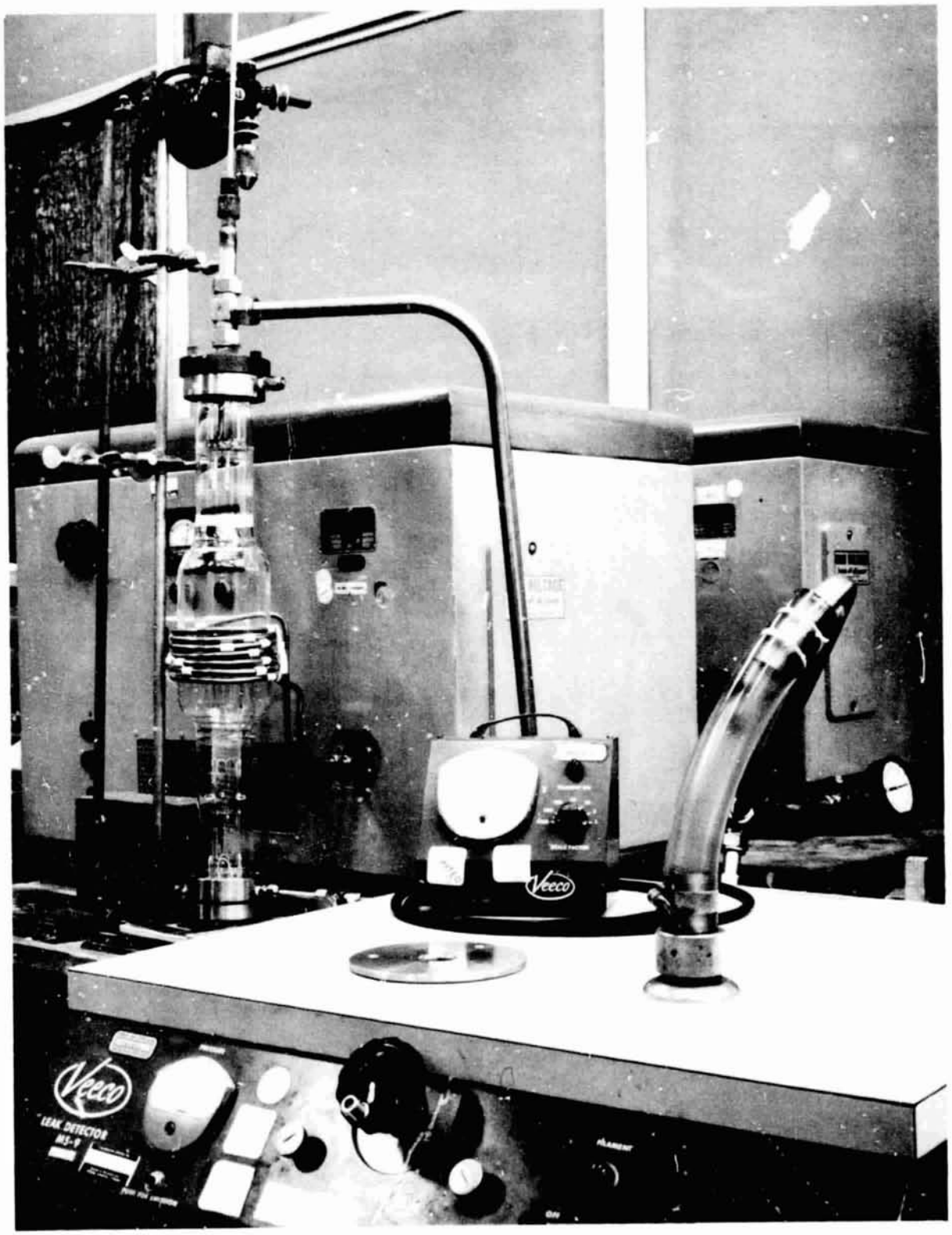


Figure 11. Refined Dispersion Apparatus with Chamber B

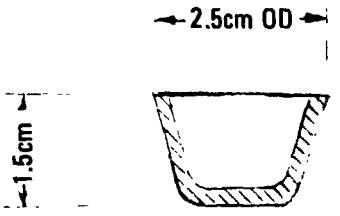


FIG. 1-A

CRUCIBLE A
2.5cc (1.3cc NET)

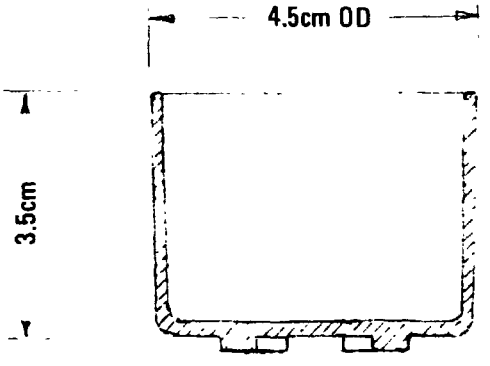


FIG. 1-B

CRUCIBLE B
38cc (18cc NET)

Figure 12. Pyrolytic Graphite Crucibles for Precomposite Preparation

4.3.2 Processing Assembly

The processing section of the apparatus is shown in Fig. 13. It consisted of the vacuum chamber, upper and lower flange assemblies, the sample holder and the stirring assembly.

The processing chamber for crucibles A and tubular stainless steel or pyrolytic graphite crucibles was a straight quartz tube of 5.5 cm I.D. and 30 cm in length. The configuration of the larger chamber for crucibles B is identified in Fig. 13; the 16 cm long center section was enlarged to an O.D. of 10 cm, in order to provide sufficient space for the larger crucibles and to prevent overheating of the quartz, yet at the same time assure adequate coupling with the induction heating coil which was as close as possible to the chamber wall. The choice of quartz as chamber material was dictated by the following requirements:

(1) Adequate heat resistance

(2) Dielectric characteristics for induction heating

(3) Transparency to permit observation of the sample

The sample holders were also made of quartz. Specific holders were manufactured for each crucible type, varying in length and in the configuration of the top section. Fig. 13 shows the sample holder for crucible B. The tubular section has a number of openings to assure complete evacuation. The holders were inserted in the lower flange assembly and secured by aluminum spacers and foil. They were further held in position by quartz tips fused to the center of the tubular section which matched the I.D. of the chamber.

The flange assemblies were made of stainless steel, with O-ring grooves for connection with the chamber, and fittings for the argon supply line and argon purge. A fitting assembly at the upper flange provided connection with the vacuum line and seals for the stirrer rod. In all vacuum components a minimum cross-section of 2 cm^2 was maintained.

A manual stirrer was used for the smaller crucibles, such as crucible A. It was a 1.6 mm diam tungsten wire with a specially shaped stirring end. Upon melting of the matrix it was lowered into the sample; stirring was accomplished simply by twisting the end of the wire extending above the chamber between the fingers. The soft vacuum seals permitted sidways movement and oscillatory stirring of the sample. The tungsten stirrer was used extensively because it permitted correlation between sample observation and stirring mode.

For most experiments with crucibles B the mechanical stirring system shown in Fig. 13 was employed. It consisted of a variable speed motor, the stirrer rod and the stirrer assembly. Stirring was accomplished in a rotational mode by two paddles,

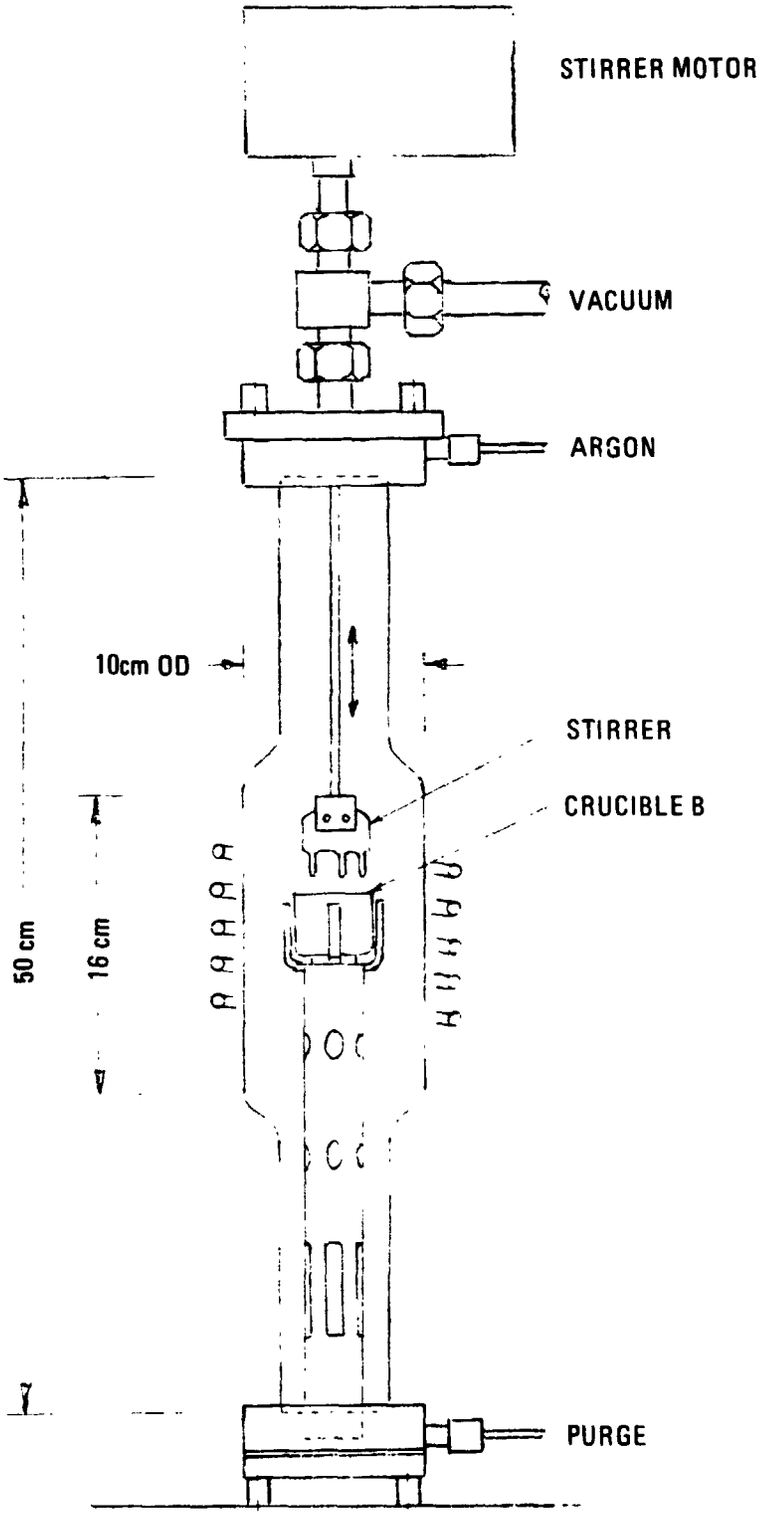


Figure 13. Processing Chamber Assembly B

machined from 0.125 in pyrolytic graphite rods. The ends in contact with the sample were ground flat. The position of the paddles could be varied by insertion in any of the holes in the stainless steel paddle holder, shown in Fig. 14. In the design of the stirrer assembly, as well as any other components in the vacuum chamber, the use of threaded connections was avoided since they may release trapped gases; all connections were either completely sealed (welded or seals with vacuum grease) or deliberately loose so that the gases can readily escape. In the case of the stirrer, therefore, the paddles had a sliding fit in the holder and were held in place by pins rather than screws.

The mechanical stirring assembly could be moved vertically and thus gradually lowered into the sample with a stop for the lowest position providing a safe clearance between paddle ends and crucible bottom.

4.3.3 Vacuum System

In the wetting experiments, a mechanical vacuum pump with a capacity of 10^{-3} mm Hg was used, which proved also adequate for the dispersion of large fibers (over 200 micron diameter and L/D more than 10). For all other dispersion experiments, a vacuum of 10^{-5} - 10^{-6} mm Hg, depending on the size and quantity of reinforcements is required. In earlier experiments, a refrigeration-cooled turbo-molecular pump was used. This system proved too troublesome and was later replaced by an oil diffusion pump (VEECO Model MS-9) with liquid nitrogen cooling. This pump had a lower pumping rate, but proved to be very reliable and accurate. In both cases, an additional mechanical pump was used for pre-pumping. Argon was obtained directly from commercial bottles. It may be mentioned that it is very difficult to obtain high purity argon; the commonly used argon bottles contain traces of oxygen which may affect the dispersion of fine reinforcements.

4.3.4 Heating System

The required combination of high vacuum and high temperatures necessitated heating by induction. A LEPEL high frequency system Model T-25 with max. output of 2.5 KW was used for all experiments. The configuration of the water-cooled coils was adapted to the chamber diameter and the type of crucible. The system proved to have ample capacity for the small chamber and small crucibles and was just adequate for the larger chamber and crucible B. Heating of crucible A to 1050° C could be accomplished within 10 sec, while complete heating of crucible B with 42 grams of sample material took app. 2 minutes. The sample temperature was measured with an optical pyrometer.

Fig. 15 shows the processing chamber B with crucible B during experiment performance; the sample is at 1050° C and mixing has just started; the stirrer is temporarily

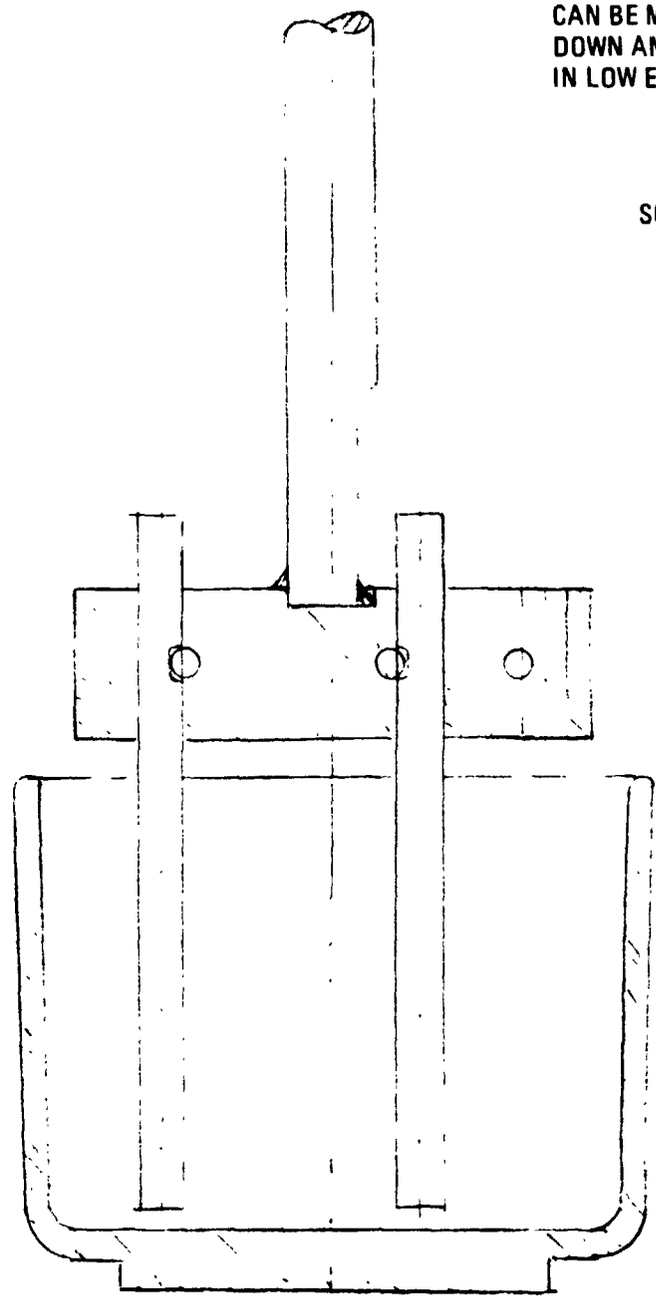


Figure 14. Crucible B Stirrer Assembly

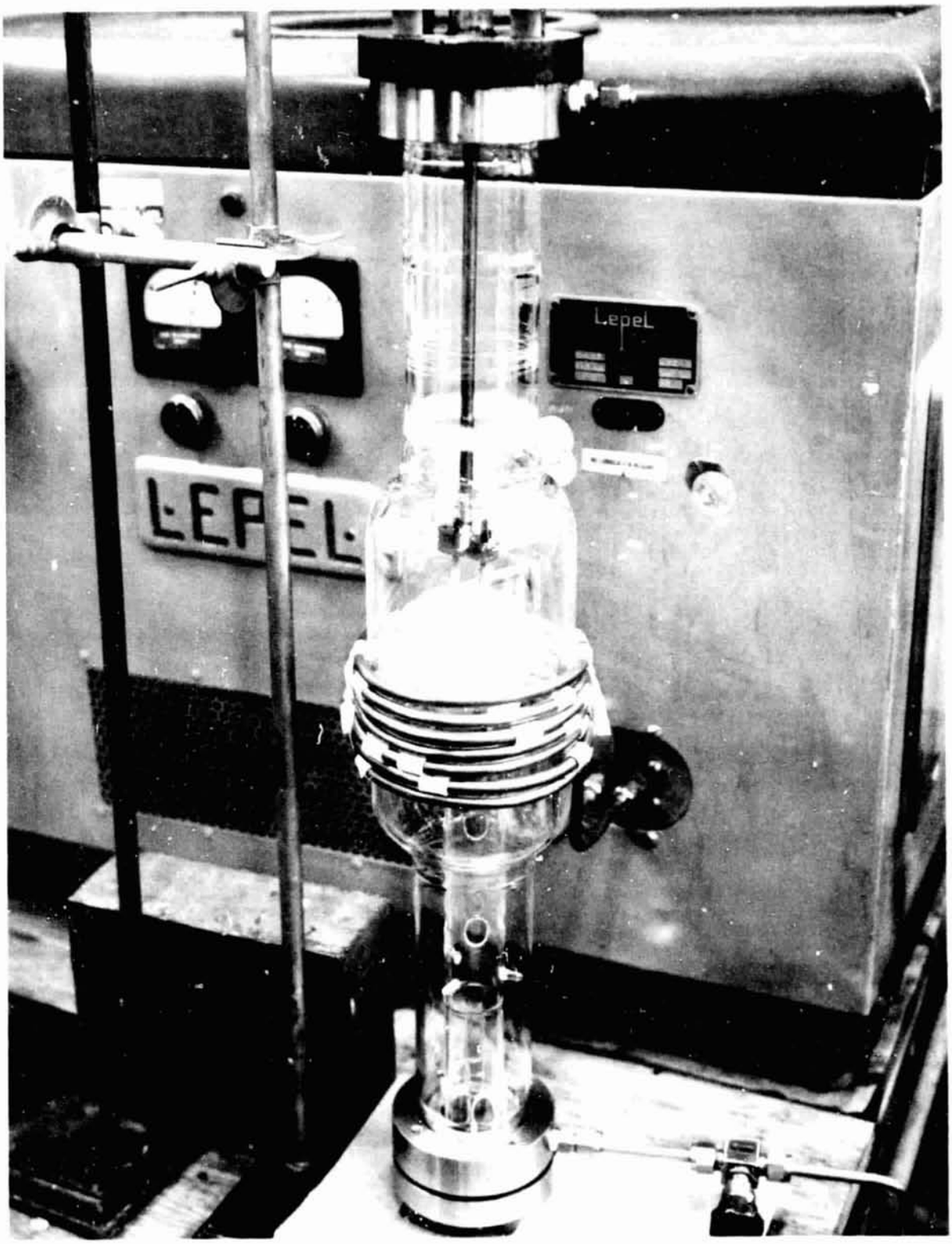


Figure 15. Processing Chamber B During Experiment Performance

raised and coated with wetted reinforcements. As the experiment progresses, the bulb-like part of the quartz chamber becomes increasingly coated with aluminum, so that sample observation and temperature measurement with the optical pyrometer become difficult toward the end of the high-temperature processing cycle. The coating was removed after each experiment by immersion of the chamber in a mixture of hydrochloric and nitric acid.

5. DISPERSION EXPERIMENTS

In ultimate production in space, the preparation of composite castings involves the following four process phases:

1. Preparation of component materials. While the mechanical preparation such as the cutting of fibers and matrix metals to appropriate sizes can be carried out on the ground, the cleaning of the component materials has to be scheduled as close as possible to Phase (2), to preclude excessive surface contamination.

2. Joining of the reinforcements with the matrix metal which is referred to in the following discussion as "Dispersion." The prime objective of this phase is to obtain complete wetting and immersion, while the distribution of the reinforcements is immaterial. This phase requires high vacuum which is readily available in space operations. However, with appropriate vacuum facilities, this preparation of the "pre-composite" can likewise be carried out as part of the pre-flight ground operations since it is not gravity sensitive. The precomposite will then be prepared in a size and shape readily adaptable to Phase 3.

3. Establishment of uniform reinforcement distribution. This consists of matrix melting, agitation of the so obtained liquid-solid mixture by a mechanical, electrogagnetic or ultrasonic mixing system and solidification. In order to maintain mixture stability, low g-conditions are imperative during agitation and solidification. This phase produces the "composite ingot." In many cases, this will be the end-product.

4. Product casting. The ultimate objective of composite casting is the production of shaped products. Casting into one or several molds is accomplished either after re-melting of the composite ingot (3), or by directly proceeding from Phase (3) to (4) without intermediate solidification. This operation, likewise, requires low-g conditions.

For early Spacelab as well as suborbital experiments, Phase (4) can be eliminated since the "composite ingot" produced in (3) serves as sample for evaluation. It will, furthermore, be attempted to confine flight operations to those which necessitate

low-g conditions. Specifically, for rocket experiments it is indicated to prepare the pre-composite (1, 2) in the laboratory and limit the flight operations to Phase (3), resulting in a sample which can be evaluated for composite properties.

The preparation of the precomposite is the subject of the experiments described in this chapter. They comprise the immersion and dispersion of fibers, whiskers and particles in aluminum matrices.

5.1 EXPERIMENTAL MATERIALS

Materials for dispersion experiments were chosen on the basis of the results of the wetting experiments. As matrix, pure aluminum was used in most cases in order to maintain basic and comparable conditions. Exploratory experiments with a typical Al casting alloy and with Al 2024 showed no basic difference in the dispersion results.

Reinforcements comprised three types: Fibers or chopped filaments, whiskers and particles. For the fibers, it was attempted to use a fairly uniform and, therefore, directly comparable reinforcement diameter in the order of 100 microns. This was not possible in all cases due to the unavailability of this size. Sapphire fibers could not be obtained in diameters of less than 250 microns and pyrolytic graphite fibers were available only in sizes of less than 15 microns. The essential characteristics of the selected reinforcement materials are compiled in the following table:

Table 4. Reinforcements for Dispersion Experiments

Material	Diameter (μm)	Length (mm)	Strength (psi)	Density (gr/cc)
Sapphire Fibers (1)	250	3	350×10^3	3.9
Sapphire Whiskers (2)	3-6	0.1-1.0	1.5×10^6	3.9
SiC Fibers (3)	90	3-4	275×10^3	3.1
Carbon Fibers	15	3-4	350×10^3	1.9
Tungsten Fibers	175	3-4	375×10^3	19.4
Sapphire Particles	50-200	-	-	3.9
Sapphire Particles	25	-	-	3.9
Sapphire Particles	15	-	-	3.9

Manufacturers: (1) Sapphicon Division of Tyco Laboratories, Waltham, Mass.

(2) General Technologies Corporation, Reston, VA.

(3) United Aircraft Research Laboratories, Hartford, Conn.

5.2 SAMPLE PREPARATION

Aluminum matrix material was obtained from specially procured cast ingots. The material cut for each experiment was cleaned by filing of all surfaces which was found more effective than chemical cleaning.

Fibers of sapphire and SiC were obtained by chopping of single filaments, and fibers of tungsten by chopping of wire. In view of the large number of cuts required, a special chopping machine was employed. For example, in order to obtain only five volume percent of SiC fibers, approximately 2000 fibers are required for each cc of composite material. For experiments in the small crucible (A) this amount was doubled to provide for a fraction of the fibers lost during the initial stirring process.

Carbon fibers were cut manually from continuous pyrolytic graphite strands. Particles were used as received. All reinforcements were cleaned in Trichloroethylene. This was sufficient, since the thermal treatment in vacuum during the initial part of the experiment performance was a very effective means of final cleaning.

For the filling of the crucibles, the reinforcements were in most cases placed on top of a number of aluminum chunks, approximately $0.7 \times 0.5 \times 0.5$ cm in size. The advantage of this arrangement is the effective exposure of the reinforcements to the vacuum; the disadvantage - at least in the small crucibles - was the loss of some reinforcements due to gases popping-out from the melting aluminum as well as during initial stirring. Several other matrix-fiber arrangements were employed in some experiments. One successful method was the use of a single piece of aluminum, shaped to the configuration of the crucible; the fibers were placed in a hole drilled in the upper part of the aluminum ingot. This method is limited to coarse reinforcements and, particularly, fine particles would not have sufficient access to the vacuum.

5.3 EXPERIMENT PERFORMANCE

The experiments were carried out by the technique detailed in Section 4.2. However, in the course of the progressing experiments, the processing parameters were increasingly refined. Originally, a mechanical vacuum pump with a capability of 10^{-3}mm Hg was used. Later, a vacuum system with a capability of 10^{-6} mm Hg was added, using the mechanical pump only for the Argon purge cycles and initial "pumping down." Other refinements were:

1. Maintaining 10^{-6} mm Hg vacuum for 24 to 48 hours prior to melting.
2. Upon initial establishment of 10^{-6} mm Hg, periodical cycling to a temperature slightly below the matrix melting point in order to enhance gas removal from the reinforcements. The additional outgassing was indicated by a

transient increase of the chamber pressure to approximately 10^{-4} mm Hg. The time for vacuum recovery was reduced in each cycle. Cycling was continued until the pressure drop became insignificant. In most cases this was achieved in 8 cycles.

3. Extended stirring time at maximum temperature (up to 15 min with crucible B and mechanical stirrer).

4. Improved coupling between sample and induction coil. The optimum number of coil turns and spacing, as well as the optimum position of the coil with reference to the sample were determined experimentally. (If the coil is improperly positioned, the bottom of the crucible, particularly crucible B, tends to remain cooler).

Most experiments were carried out with the smaller pyrolytic graphite crucible A or tubular stainless steel crucibles, both using the smaller chamber A (55 mm ID) and a manual tungsten stirrer. The shaped end of this stirrer was dissolved in the aluminum melt to various degrees in each experiment, leaving crystals of tungsten aluminide in the matrix. The presence of such crystals does not affect the dispersion phenomena and was, therefore, considered acceptable.

In the latter part of the program, a number of experiments were carried out with the larger pyrolytic graphite crucible B, the larger processing chamber B and the mechanical pyrolytic graphite stirrer.

The aforementioned apparatus components were described in detail in Section 4.3.

After experiment performance the pyrolytic graphite crucibles fractured during cooling to room temperature due to the thermal contraction differenctial. Consequently one crucible is consumed in each composite batch preparation.

In several cases, one batch of sapphire fibers was re-used in a second experiment in view of their high cost. After evaluation of the first experiment, the aluminum matrix was leached out in a mixture of hydrodiloric and nitric acid and the fibers recovered.

5.4 EXPERIMENT EVALUATION

After experiment performance the sample, including the adhering parts of the crucible, was potted in a plastic compound and then cut in half. One half was evaluated, while the other half was saved for future reference.

Since there is no external indication of the material distribution inside the sample, the first cut was made at a random location. Since, further, the distribution of

reinforcements may be uneven, the randomly selected cross section may represent a reinforcement-ride or a lean part of the sample. In a few cases, one half was cut up further to enhance evaluation. Evaluation of the so obtained cross sections comprised the following:

1. Preliminary surface preparation and visual inspection of the achieved dispersion with a low magnification optical microscope. If this indicated no or poor dispersion, no further evaluation was made. Otherwise, the evaluation proceeded to the following steps.

2. Surface preparation for, and examination in, the scanning electron microscope, using magnifications of 15-25 × for the dispersion pattern and 150-350 × for the analysis of specific sample areas or individual reinforcements. This served three purposes: (1) to obtain a record of the dispersion in a representative section of the sample, (2) to assess the quality of the reinforcement-matrix interfaces and the degree of reaction, (3) to identify individual materials, component materials as well as potentially formed compounds; this was particularly important, since in some cases dispersed phases observed under the optical microscope turned out to be reaction zones (such as Al/W crystals resulting from the tungsten stirrer), rather than reinforcements, Al_2O_3, for example, had to show the same intensity or brightness as the matrix, distinguished only by the contours, since both are basically aluminum. Tungsten aluminide crystals, which often were in the form of needles of similar size as the reinforcements could be clearly distinguished since the appeared by an order of magnitude brighter, due to the high atomic weight of tungsten.

3. If the presence of reinforcements was verified in the SEM examination, the sample was repolished and further analyzed in a metallographic microscope, which produced a better picture of the dispersion pattern than the SEM due to the usually higher contrast. The preferred magnification for display of the dispersion pattern was 15 ×.

For several samples, the COR arranged a more detailed analysis of the interface characteristics by the Natural Bureau of Standards, which is documented in Ref. 19.

Wherever indicated, photographic records were made of the SEM and/or the metallographic examinations, some of which are shown in the following discussion.

All samples and cut pieces were identified by the experiment number to permit correlation with the experiment log.

5.5 EXPERIMENT RESULTS - FIBER COMPOSITES

Some of the microphotographs shown in this section contain Al/W crystals besides

the reinforcements resulting from the dissolving tungsten and recognizable in the SEM micrographs by extreme brightness. As pointed out before, they are considered part of the matrix with no effect upon reinforcement dispersion.

5.5.1 Aluminum/Sapphire Fibers

The Al_2O_3 "fibers" were cut to a length of 3 mm from continuous coiled filament of 0.25 mm diameter, procured from Sapphicon Div. of Tyco Laboratories, Waltham, Mass. In view of the rather high fiber diameter, the number of individual fibers contained in each sample for a given volume fraction was relatively low (at a fiber content of 5 percent each cm^3 of composite contains app. 300 fibers, in contrast to app. 2000 fibers for the finer SiC). It was attempted to obtain finer sapphire filaments; however, this would have required new process and tooling development by the supplier which was precluded by time and fund limitations. It was felt that the use of the thicker fibers is satisfactory for the present dispersion experiments and that the fiber size does not affect the dispersion characteristics. The use of finer fibers becomes only necessary for samples to be evaluated for mechanical properties which, in turn, can only be prepared in low-g experiments. At such time, the expense for custom-made finer filaments may be justified.

A number of experiments were carried out in crucible A, using app. 3.2 gr of aluminum (1.2 cc) and a fiber content of 4-8 percent. Dispersion was achieved without any problem, except in experiments where equipment difficulties (vacuum leak, insufficient temperature) were encountered. The relative ease of wetting and dispersion has to be considered a characteristic of the material combination, even though the large fiber diameter was also beneficial, providing larger interfiber spaces and, consequently more effective gas removal during evacuation. A typical example of the dispersion in crucible A is shown in Fig. 16.

The higher magnification micrograph of individual fibers, Fig. 17 shows a very clean fiber-matrix interface without any sign of reaction. The interface was further analyzed by Dr. Yakowitz of NBS at magnifications up to 10,000 × and termed as "excellent." Even though no firm correlation between interface and bond characteristics exists, it can be expected that the perfect interface represents a high bond strength.

In view of these encouraging results, experiments were also carried out in the larger crucible B with the mechanical pyrolytic graphite stirrer, eliminating the presence of tungsten in the matrix. The material amount was in the order of 42 gr (app. 16 cc), with a fiber content ranging from 3 to 5 percent by volume. The dispersion obtained in the most successful experiment is shown in the optical micrograph, Fig. 18. (Fiber content 3.25 percent). As to be expected, the fibers are concentrated on the bottom of the crucible in view of the density difference between Al (2.69 g/cm^3) and Al_2O_3

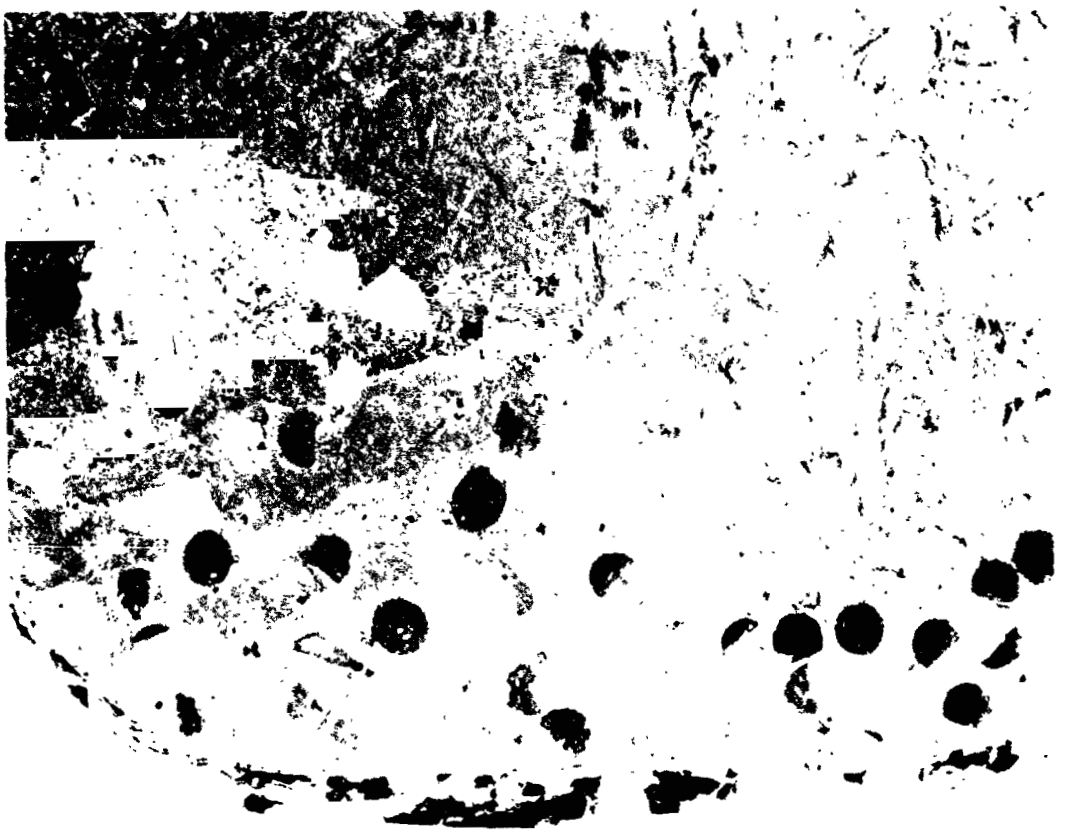


Figure 16. Dispersed Sapphire Fibers, Crucible A (25X)

Figure 17. Dispersed Sapphire Fibers (SEM - 100X)

Figure 18. Al-Sapphire Precomposite, Crucible B (15X)

($3.9\ g/cm^3$) (the black lower section of the photo is the crucible bottom). The inter-fiber spacing indicates perfect wetting. The high cleanliness of the composite is further verified by the SEM micrograph, Fig. 19; the electron backscattering intensity is characteristic of aluminum (including Al_2O_3) and its uniformity indicates the absence of any foreign matter.

5.5.2 Aluminum/Sapphire Whiskers

Several dispersion experiments were carried out with Sapphire (alpha) whiskers produced by General Technologies Corp., Reston, VA. The diameter of the individual whisker varied from 3 to 7 micron and the length from 50 to 4000 micron with an average length of app. 500 micron. The majority was straight, yet some were slightly curved. The whiskers as received clung strongly together, very likely due to electrostatic charges. For experiment preparation, they were carefully separated manually. However, upon deployment in the cold crucible on top of the aluminum, they started to adhere to each other again. During the first seconds of stirring, they assembled into several balls which could not be wetted or immersed. Only the small fraction of individual whiskers which by chance remained separated were wetted and dispersed. They were primarily in the short length regime. The high magnification SEM micrograph (350×) of Fig. 20 shows one whisker intact at the specimen surface, which can be conclusively identified as Al_2O_3 by the degree of brightness which is essentially the same as the aluminum matrix. The two dark oblongs represent whiskers which were pulled-out during surface preparation. The bright areas are, again Al/W crystals resulting from the tungsten stirrer (note the sharp rectangular configuration of the large Al/w crystal).

While the whisker experiments, carried out in crucible A and B, were unsuccessful as to precomposite preparation, they proved that wetting and immersion can be obtained. The achievement of complete dispersion is merely a matter of process refinement, specifically the availability of more perfect whisker material and a mechanical dispensing system in the vacuum chamber which permits gradual addition of the whiskers to the molten and overheated aluminum. The introduction of such a system exceeded the scope of this investigation.

5.5.3 Aluminum/Silicon Carbide Fibers

The SiC fibers were chopped to a length of 3 mm from a continuous coiled filament of 90 micron diameter (3.6 mils) with tungsten core. All experiments were carried out in crucible A with tungsten stirrer. Wetting and dispersion were readily achieved, even at a vacuum as low as 10^{-3} mm Hg. The cross section of one crucible A - precomposite is shown in Fig. 21. In view of the relatively small fiber diameter, the gravity segregation toward the crucible bottom is not as pronounced as in the case of the sapphire fibers, whose mass is by an order of magnitude higher.

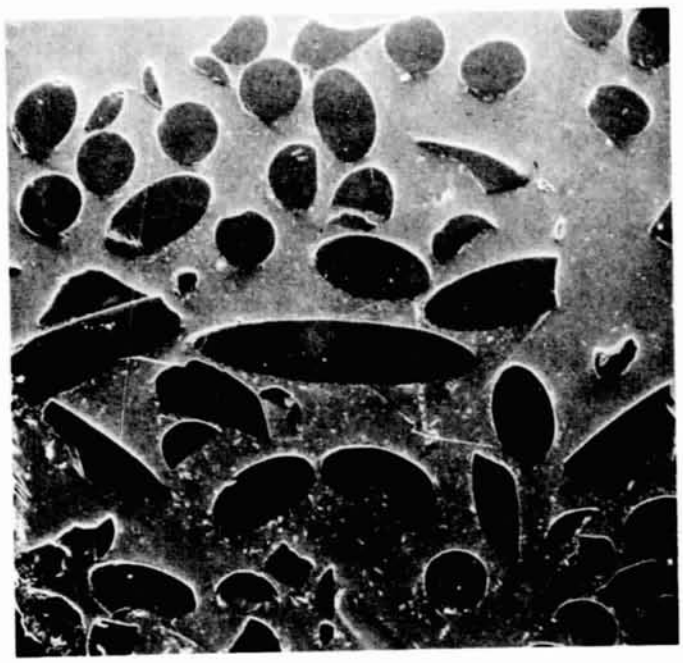


Figure 19. SEM Micrograph of Sapphire Precomposite (35X)

Figure 20. Dispersed Al_2O_3 Whiskers (SEM - 350X)

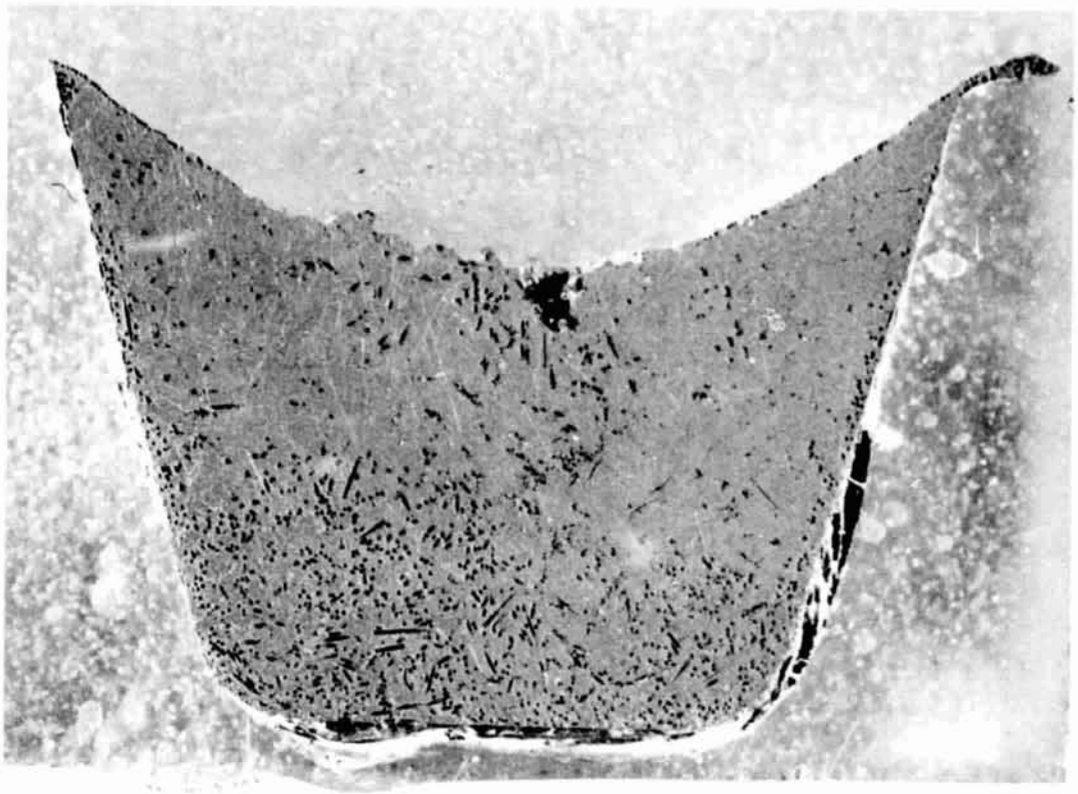


Figure 21. Al-SiC Fiber Precomposite, Crucible A (7X)

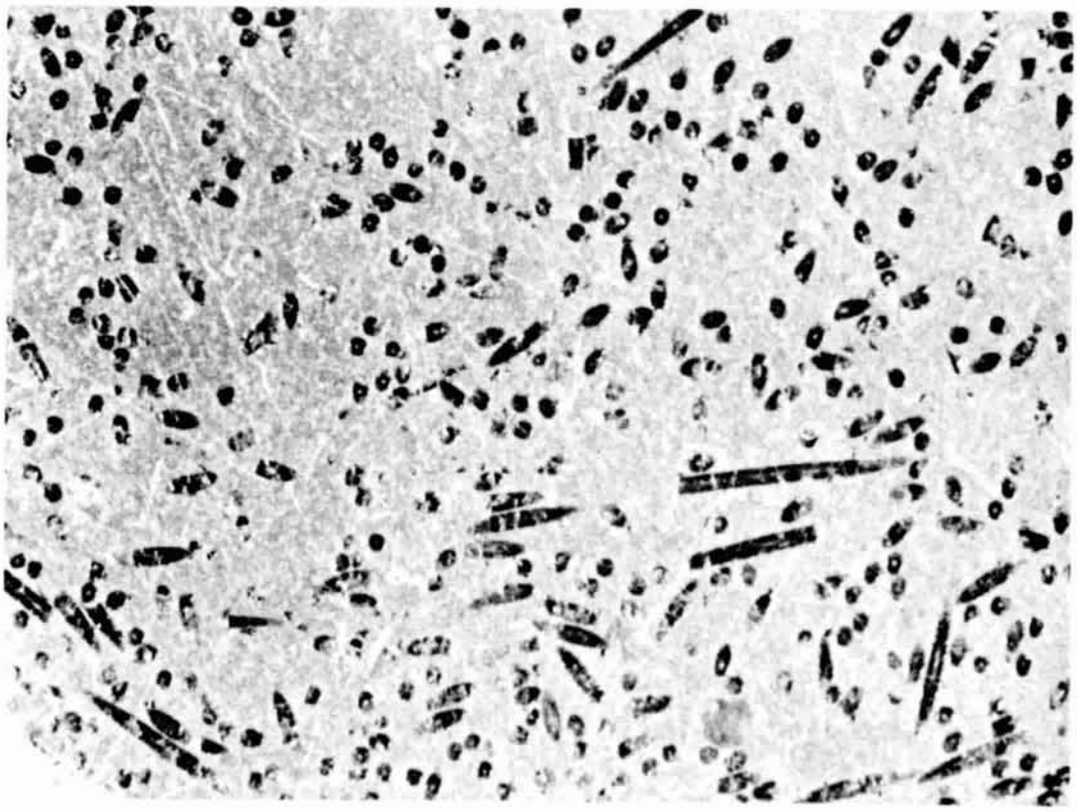


Figure 22. Dispersion of SiC Fibers (25X)

The higher magnification micrograph, Fig. 22 shows perfect dispersion and complete absence of any agglomerations. The analysis of the SiC-Al interface by NBS revealed an "extensive" reaction zone. This zone is, however, limited to a small interface region, leaving the bulk of the SiC fiber intact. From the viewpoint of the end-product, the presence of such a limited reaction zone may be highly desirable, as it represents a gradual changeover from the matrix to the reinforcement material. This may well enhance the interface bonding characteristics and lessen the danger of interface cracks or matrix-reinforcement separation at high mechanical loads.

5.5.4 Aluminum/Carbon Fibers

In spite of the extensive use of graphite as reinforcement material in present technology, filaments of a size comparable with the other reinforcement materials (3-10 mils) are not available. All graphite reinforcement material produced today is in the form of continuous strands whose individual filaments have a diameter of less than one mil. The fibers were, therefore, obtained from purolytic graphite strands procured from two sources. The strands were chopped manually, producing fibers of 15 micron diameter and 3-4 mm in length.

Since the so obtained reinforcement material was inexpensive and readily available in any quantity, it was used for a larger number of experiments, varying crucible configuration and crucible material. Besides crucible A, tubular crucibles of pyrolytic graphite and stainless steel were employed.

Practically in all cases, wetting and dispersion was achieved without any significant problem. The complete dispersion and freedom from agglomerations is evidenced in Fig. 24. The higher magnification micrograph (600×) of Fig. 24 shows an extensive chemical reaction between matrix and reinforcements. The interface was evaluated in more detail by NBS whose findings were as follows:

> "Optical examination indicates reaction between the graphite and the matrix. A core is present in the graphite. In the SEM, the core is black; the reaction zone is grey. Semi-quantitative X-ray analysis indicates the grey region contains about 70 weight percent Al; probably this material is Al_4C_3 (75 percent Al by weight). The black region contains about 26 percent Al by weight, roughly corresponding to something having the formula AlC_6. (No tungsten or other impurity was found in this material.) Not all the carbon bearing particles have the black region. It is likely that an Al gradient exists from the matrix into the core."

The Al/C reaction was somewhat surprising since no visible reaction between the graphite crucibles and the matrix was encountered, even though the interface temperature at the crucible wall was somewhat higher than at the inside of the test material. It can, therefore, be safely assumed that the reaction at the fiber interface is not progressive in nature, but rather self-arresting. This implies that the processing

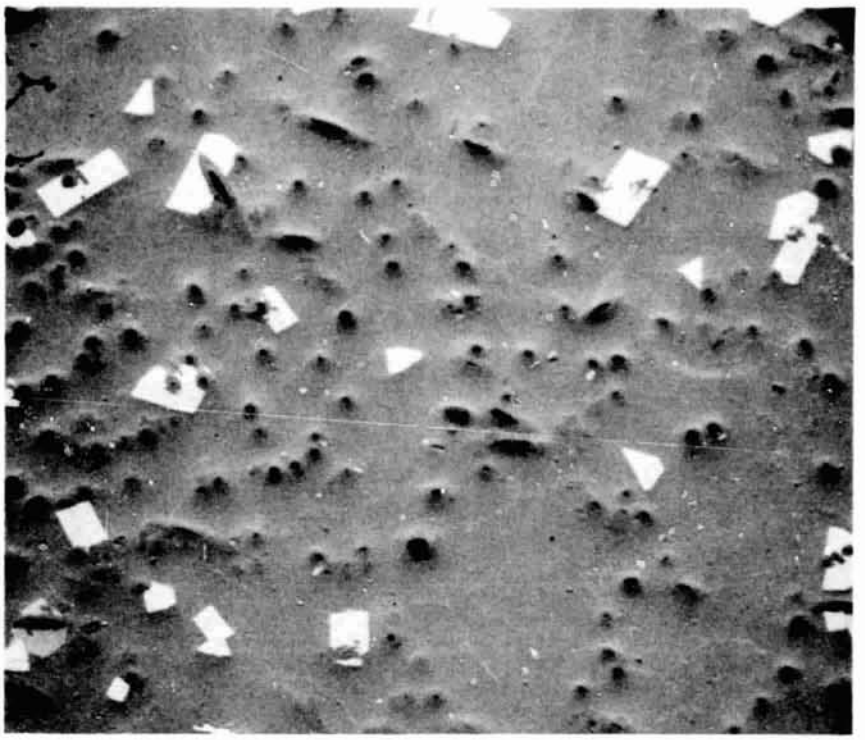


Figure 23. Dispersed Pyrolytic Graphite Fibers, 0.015 mm Diam (150X)

Figure 24. Interface Reaction of Graphite Fibers (400X)

time does not affect the composite quality which may even be enhanced by the presence of an interface reaction zone, as outlined earlier.

5.5.5 Aluminum/Tungsten Fibers

Metallic reinforcements are not as attractive as oxides or carbides in view of their limited strength, comparatively high density and, in most cases, solubility in aluminum. A positive aspect is their higher ductility which precludes reinforcement cracking, very common in nonmetallic reinforcements. The question whether a high differential in deformation resistance between matrix and reinforcement is negative or positive as to the overall performance of a composite is yet unanswered, in view of the complex interface deformation mechanism, particularly in the case of random reinforcement distribution.

It was therefore of interest to include at least one metallic reinforcement in the dispersion experiments. Since all well-wetting reinforcement metals are readily dissolved in the highly reactive aluminum, the use of a stable, yet non-wetting metal was indicated. This provided another test of the wetting and dispersion technique.

Tungsten was selected in spite of its high density (19.4 g/cc) because it proved successful in the initial wetting experiments. It was considered sufficiently stable at the melting temperature of Al, where the solubility is only in the order of 1.5 weight percent, forming $Al_{12}W$. This reasoning proved to be fallacious, since the adopted higher processing temperature led to a substantially higher degree of reaction, as shown below.

The tungsten fibers were obtained by chopping of 175 micron (7 mils) diameter high-strength tungsten wire to a length of 3–4 mm. It may well be of interest to include at this point a few remarks as to problems in chopping. The comparatively brittle nonmetallic fibers could be chopped rather easily, since they break upon contact with the cutting tool. The more ductile metal wires do not break and have to be cut. This proved highly difficult in the case of tungsten due to its high hardness which necessitated extensive modifications of the chopping machine before fibers could be produced in the required quantity.

For sample preparation and experiment performance the same procedures were used as for the nonmetallic reinforcements. Wetting and dispersion were readily achieved in pyrolytic graphite crucibles, while several experiments in crucibles machined from conventional graphite (Type CS-312) were unsuccessful; apparently conventional graphite contains a fair amount of gas which is released during heating. One positive factor was the high weight of the tungsten fibers which essentially eliminated any spilling from the crucible by "popping" gases and during mixing.

Micrographic evaluation of the samples showed a perfect dispersion (Fig. 25), yet at the same time a high degree of reaction as evidenced by the higher magnification micrograph, Fig. 26. At the processing temperature of app. 1000° C two intermetallic compounds, Al_5W and Al_4W are formed with an aluminum content up to 37 weight percent. Evaluation by NBS was reported as follows:

> "Optical examination showed the matrix to consist of dendritic grains whose boundaries contained a eutectic-like material. SEM examinations revealed that the Al and W had reacted during preparation of the composite; all of the W bearing material also contains Al. The interface of the reinforcement with the matrix is variable ranging from straight and sharp to regions where local reaction appears to have occurred. The matrix dendrite boundaries contain eutectic-like material in great profu ion; this material may be Al_3W."

It appears that during the processing period of app. 5 minutes all tungsten fibers were transformed into Al-W intermetallics. However, these intermetallics retained the configuration and position of the original fibers, resulting in a metal-intermetallic rather than a metal-metal composite. This may well represent a new breed of composites and a new technique of composite preparation, as discussed in Section 5.7, below.

5.6 EXPERIMENT RESULTS - PARTICLE COMPOSITES

The objective of this group of experiments was to investigate the applicability of the vacuum wetting technique to the dispersion of non-wetting particles in an aluminum matrix. As in the case of fibers, all attractive particle materials, such as oxides or carbides, are not wetted by liquid aluminum. Alumina was chosen as experimental particle material, since it was readily available in a variety of particle sizes and is rather stable in liquid aluminum.

While the wetting of an individual particle, regardless of size, presents no problem, the dispersion of a batch of particles is considerably more difficult, in view of the large number of particles required for a reasonable bulk volume and the large surface area, resulting in a high amount of adsorbed and trapped gases. This effect increases rapidly as the particle size is reduced. The prime variable introduced in the experiments was, therefore, the particle size. The chosen particle sizes, in the order of progressing experimentation, were as follows:

40-250 (mean 80) micron

15 micron

25 micron

Mixed particles (2-200 micron)

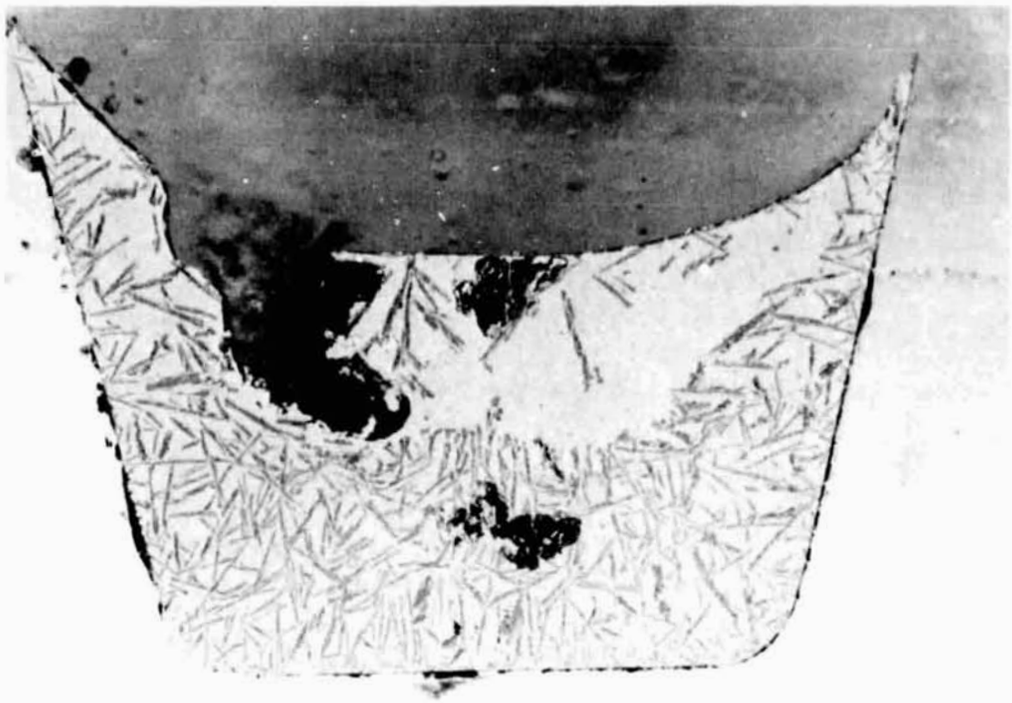


Figure 25. Al-Tungsten Precomposite, Crucible A (7X)

Figure 26. Dispersed Tungsten Aluminide Fibers (30X)

Most of the particles were of irregular shape, in polyhedral form with flat surfaces and sharp edges. Prior to use, each particle batch was placed in a vacuum oven at 104° C for 24 hours to remove any moisture and to reduce the amount of trapped gases. They were then added to the cleaned aluminum chunks in the pyrolytic graphite crucible. Experiment performance followed the procedures detailed in Section 4.2, except that, after argon purge and attaining high vacuum, the samples were kept at a temperature of 200° C for one hour and stirred intermittently to enhance the removal of gases.

5.6.1 80 Micron Particles

The particles used in this first series of experiments were classified as 60 mesh which defines a maximum size of 250 micron, yet contains a variety of smaller sizes down to 40 micron. The predominant size, by number of particles, was in the order of 80 micron which was adopted as nominal size.

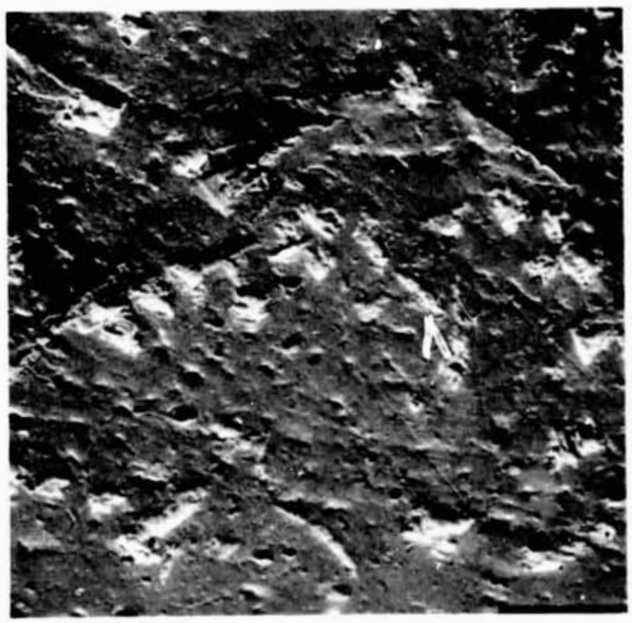
A number of experiments were carried out in the smaller crucible A and two experiments in crucible B. In some of the experiments in crucible A, a fraction of the particles was lost as gas bubbles "popped out" during the initial melting of the aluminum, throwing some particles out of the crucible. This effect was less pronounced in the crucible B due to its higher and vertical walls.

In all experiments the manual tungsten stirrer was used. In spite of this rather crude procedure, complete wetting, immersion and dispersion of all particle sizes was obtained. The SEM micrograph (60×) of a sample prepared in a crubible A (Fig. 27) shows a perfect dispersion, without agglomerations; the uneven distribution was caused by stirring and is immaterial in a precomposite. The darkness of the particles which is essentially the same as the matrix proves that they are clean Al_2O_3. A section of a sample prepared in a crucible type B is shown in Fig. 29. It can be observed that all particles are well embedded in the matrix without any agglomerations, except for gravity sedimentation.

5.6.2 15 Micron Particles

The particles used in the preceding experiments contained sizes down to 40 microns. The ease with which even these small particles were dispersed encouraged to proceed directly to the target size of 15 microns. In contrast to the previous experiments, the 15 micron particles were of uniform size. Initial experiments with crucible A and tungsten stirrer indicated some success, as indicated in the SEM micrograph (100×) of Fig. 28. In this picture, the Al_2O_3 particles are represented by the small dark spots (some of them holes where particles broke-out during surface preparation), while the larger light areas are tungsten aluminide crystals originating from the stirrer.

Figure 27. Dispersed Al_2O_3 Particles, 40-160 Microns (60X)



(The particles are indicated by the small dark spots; the light areas are Al/W crystals.)

Figure 28. Dispersed Al_2O_3 Particles, 15 Microns (100X)

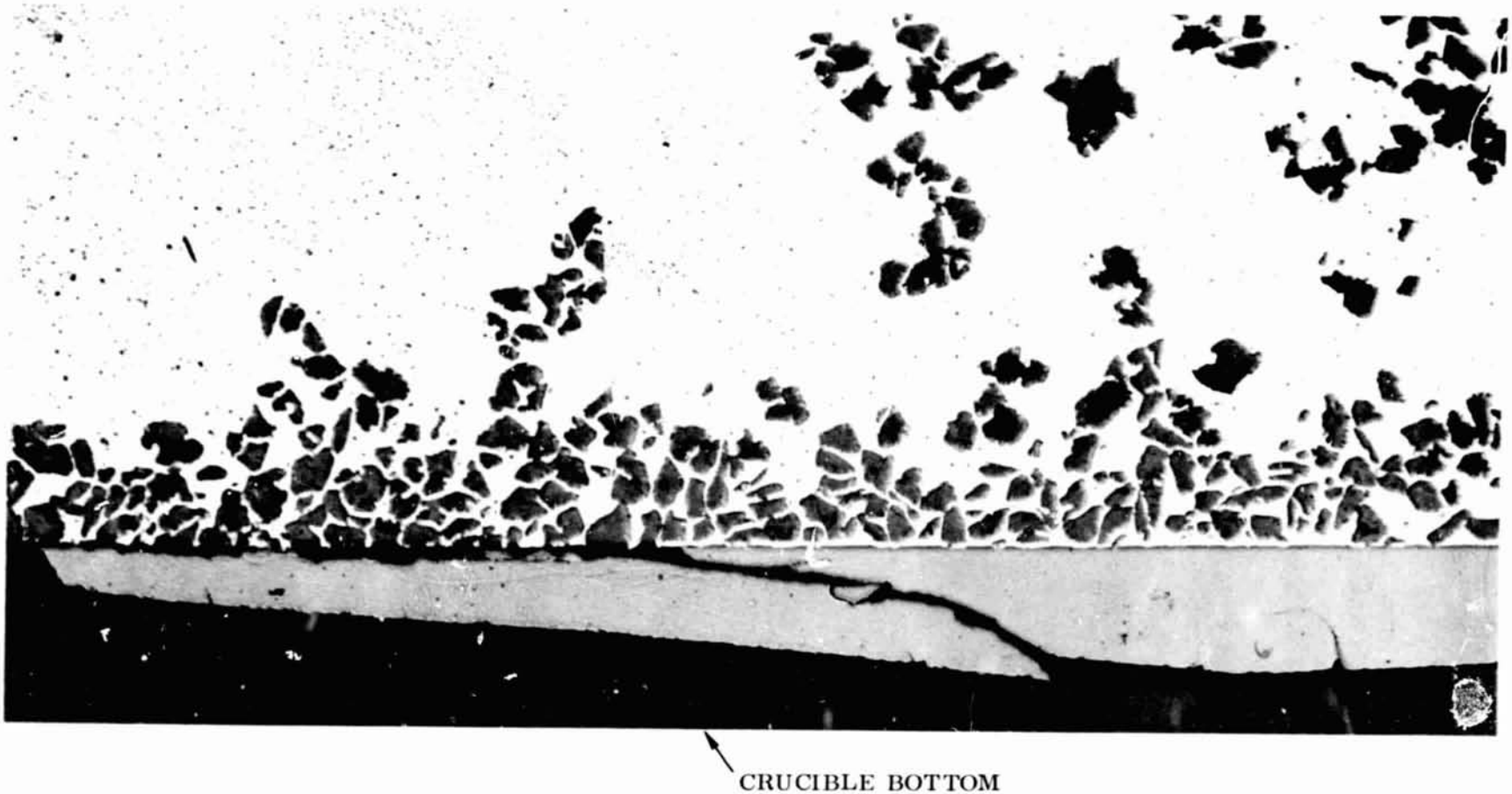


Figure 29. Al_2O_3 Particle Precomposite, 40-250 Micron, Crucible B (23X)

However attempts to disperse a batch of particles in crucible A as well as crucible B with mechanical stirring were unsuccessful. The particle powder, mixed with pure aluminum chunks, remained at the surface of the aluminum upon melting, even after vigorous stirring with the mechanical pyrolytic graphite stirrer. The particles formed small "cakes," very likely held together by trapped gases, which could not be broken up even by vigorous stirring. Some of these agglomerates remained at the surface, while others were wetted as a unit and immersed in the matrix, without releasing any of the particles. Only a few single particles, which by chance remained separate during stirring were found dispersed in the matrix.

Extensive efforts were made to solve this impasse by modifying various details of sample preparation and experiment performance, without success. This appeared at first surprising in view of the small difference in size between the 15 micron particles and the 40 micron fragments readily dispersed in the previous experiments. It was concluded that the decisive factor was the degree of particle size uniformity. In the case of a wide spectrum of sizes, the larger particles generate a wide spaced framework which provides a relatively free path for the gases and, consequently effective gas removal from all surfaces including the smaller particles. In contrast, a batch of particles of uniform size represents a dense and closely spaced network which obstructs the movement of gases. This effect is further aggravated as the particle size and, consequently, the inter-particle spaces are reduced; in a batch of such small particles of uniform size, gas removal is then effective only at the batch surface, while the gases in the bulk remain trapped. This accounts for the formation of clusters which were wetted only at the surface. The problem of gas removal from batches of small particles is further discussed in Section 5.7.3.

5.6.3 25 Micron Particles

In view of the negative results obtained with 15 micron particles, the size was increased to 25 micron. These particles were not quite as uniform in size as the 15 micron particles, ranging from 20 to 30 micron with a small percentage down to 6 micron. They were very irregular in shape; many particles were oblong, with triangular or rectangular cross-sections, measuring 10-15 micron in width and 25-30 micron in length.

In experiments with these particles, a mixed effect was obtained. Approximately 50 percent of the particles were successfully dispersed, as evidenced by the SEM high magnification micrograph (350×) shown in Fig. 30. The experiments were carried out in crucible A with tungsten stirrer which accounts for the presence of large W/Al crystals.

The remainder of the batch formed small clusters, similar to the cakes obtained in the experiments with 15 micron particles. However, all of these clusters were immersed and eveny distributed throughout the matrix.

Figure 30. Dispersed Al_2O_3 Particles, 25 Micron (SEM - 350X)

Figure 31. Dispersed Al_2O_3 Particles, 2-15 Micron (500X)

Comparing the results of the 15 and 25 micron particle experiments, it is apparent that the successful dispersion of a sizeable amount of the 25 micron particles was due to increased interparticle spacing generated by the combination of a larger particle size and a wider size spectrum. The experiments represent, therefore, a marginal condition as to gas complete removal and imply that 100 percent dispersion will be achieved by a refinement of the processing technique.

5.6.4 Mixed Particles

To prove the significance of uniform particle size, an experiment was carried out with a deliberate mixture of large and very small particles, whose average size differed by a factor of 25. Alumina powder was found which consisted basically of particles between 100 and 200 micron, however contained a considerable amount particle debris ranging from 2 to 15 micron. In this experiment, which was carried out by the standard procedure, even the smallest particles were readily wetted and dispersed. Upon immersion, the large particles settled at the crucible bottom, while the small fragments remained suspended throughout the matrix. A high magnification micrograph (500×) of dispersed particles with sizes between 2 and 15 micron is shown in Fig. 31.

This experiment verified the contention that the wetting of very small particles is merely a matter of complete exposure to the high vacuum, achieved in this experiment by the presence of large particles and the resulting wide-spaced batch framework. In the case of small particles only this is prevented by the self-compacting nature of the batch, characterized by an extremely high member of closely spaced particles which represents a high amount of adsorbed and trapped gases whose removal by the mere exposure to a high vacuum environment is impossible. Successful dispersion of such particles is a matter of divising refined techniques which assure at least a transient exposure of all parts of a batch to the vacuum environment. Potential approaches are discussed in Section 5.7.3.

5.7 DISCUSSION OF DISPERSION EXPERIMENTS

In general, the dispersion experiments were successful in verifying the developed wetting/dispersion technique and in defining materials, processes and facilities for the preparation of meaningful flight experiments. They further showed a considerable difference between fiber, whisker and particle composites with regard to processing problems and the related facility requirements. Since these problems reflect inherent differences in the physical characteristics of the three reinforcement types, the results of the dispersion experiments are discussed separately for each reinforcement type.

5.7.1 Dispersion of Fibers

In the course of the experiments the techniques were developed to a degree of refinement which assures the successful dispersion of fibers in aluminum and the preparation of aluminum-base fiber precomposites. On the basis of the experiment results it can be expected that the technique can be adapted to other matrix metals by the modification of specific processing parameters, notably the processing temperatures.

Fibers proved to be most adaptable to dispersion, due to their configuration and absolute size. The combination of a high L/D and a relatively large diameter (in contrast to whiskers) generates a rather wide-spaced framework in the fiber bulk ("dry" fibers) which greatly enhances evacuation. The removal of gases, even in larger fiber batches, is obtained in a relatively short time and is complete, except for negligible gas residues which may be trapped at the contact points between individual fibers. The wide-spaced arrangement further permits matrix vapor to penetrate the dry bulk during the high-temperature cycle, producing a minute liquid coating of the fibers which expedites the subsequent wetting and immersion.

The dispersion experiments further permitted predictions as to some characteristics of the final composite, as produced by low-g processing. They showed that due to the perfect wetting the fibers are independent and free from agglomerations. Even at points of contact the fibers remain separated by a small buffer of matrix. They should, therefore, move freely during low-g agitation for the purpose of establishing uniform distribution.

The experiments showed, however, that the final composite may exhibit a certain amount of reaction between fiber and matrix which is enhanced by the high-temperature cycle of the dispersion process. The degree of this reaction depends on the materials and their inherent mutual solubility. While sapphire fibers remained unaffected by the overheated liquid aluminum, other reinforcement materials showed various degrees of reaction and formation of Al-compounds which may be classified in two categories:

(1) The reaction is slow and confined to a small interface region. In some cases it can even be expected that, once the reaction zone has been generated, it acts as a diffusion shield, preventing its further growth. In this case, the processing time, i.e. the time at which the mixture is in the liquid state, has no bearing upon the degree of reaction.

(2) The reaction is progressive and may eventually consume the entire fiber material, replacing the fiber by a fiber-shaped compound. Since such compounds are usually very stable, further decomposition is not likely and the end product retains a composite structure.

It can be reasoned that the formation of a limited reaction zone (1) is advantageous since it represents a gradual change-over of properties from the matrix to the reinforcements which may well increase bond strength and prevent cracking or separation at imposed high bulk stresses. If this holds true, such mildly reactive reinforcement materials as graphite or SiC may be as attractive as sapphire.

Materials of type (2) can be considered as a new breed of composites with properties which may be attractive for specific applications, such as a significant increase of creep resistance or, in other words, an extension of the useful temperature range of a material. In the context of this study it is important to remember, that even such composites can only be produced in a low-g environment, since the requirement for the dispersion of materials of different density still remains. The final judgement on the properties and the applications potential of reaction composites can only be derived from low-g experiments at extended time, and the preparation of samples of sufficient size to be evaluated by mechanical testing. It is, therefore, suggested that rocket experments comprise three types of fiber composites:

1. Fiber composites which exhibit no reaction between matrix and reinforcements, such as Al matrix - sapphire fibers.

2. Fiber composites with limited reaction, confined to the interface region, such as Al matrix - SiC or graphite fibers.

3. Fiber composites with progressive reaction, transforming the fibers into compounds, such as Al matrix - W fibers.

5.7.2 Dispersion of Whiskers

While the wetting and immersion requirements of a single whisker is not different from a fiber, the immersion of a batch of whiskers is substantially more difficult, as evidenced by the experiment results. The prime reason for this is the smaller absolute size of whiskers whose diameter differs from fibers by, at least, one order of magnitude. For a given bulk volume, this has two primary negative effects:

(1) Significantly increased number of reinforcements and, consequently increased number of enclosed spaces, enhancing the trapping of gases.

(2) Increased reinforcement surface area and, consequently, increased amount of adsorbed gases.

In order to obtain the same reinforcement content by volume with smaller reinforcements, the surface area increases proportional to the diameter reduction, and the number of individual fibers increases by the square of the reduction factor. If we compare, for example, a batch of whiskers with an average diameter of 4 microns

with a batch of fibers of 80 microns diameter, representing a diameter reduction by a factor of 20, the number of whiskers required to obtain the same volume increases by a factor of 400, while the surface area is increased by a factor of 20.

The high number and close spacing of whiskers accounts also for the encountered tendency of the whiskers to cling together, presumably due to electrostatic charges or dipole effects. The agglomeration in the dry state is further aggravated by a high fraction of short whiskers or whisker debris, as was the case in the whiskers used in the experiments. For effective gas removal as prerequisite for dispersion, "clean" whiskers with a well defined and limited range of lengths are required, which could not be obtained at the time of the experiments. The range of whisker diameters is less significant with regard to agglomeration.

Considering the successful immersion of a small fraction of the low-grade whiskers, it can be safely assumed that the dispersion of a complete batch of whiskers can be achieved by the use of custom made, clean whiskers together with an improved dispensing technique as suggested for particles in Section 5.7.3.

5.7.3 Dispersion of Particles

The particle dispersion experiments showed that larger particles (> 50 micron) as well as mixtures of large and small particles can be readily dispersed by the employed process and with present facilities, since the relatively large interparticle spacing provides adequate gas removal for effective wetting.

For small particles of uniform size, i.e. without the presence of larger particles the experimental facility proved inadequate for effective evacuation of particle batches. The problem is basically the same as in the case of whiskers. It is, however, more severe since for a given reinforcement diameter the number of particles required for a batch of a given net (solid) volume exceeds the required number of whiskers by an order of magnitude. The number of particles for a given volume increases by the third power as the particle size is reduced, generating an equal number of close inter-particle spaces in which gases remain trapped.

This effect is further aggravated by the high packing density of particles which is three times as high as in the case of fibers and whiskers. The fraction of solids for a given bulk volume is 45-65 percent for particles, depending upon their configuration, in contrast to 14-22 percent for fibers, depending upon the L/D ratio. The difference in the number of fibers, whiskers and particles for a given bulk volume is best illustrated by a numerical assessment: The data of Table F shows that a reinforcement batch of 1 cm^3 bulk volume contains 2000 to 10000 fibers, app. 1 million whiskers and over 100 million fine particles.

Table 5. Contents of Reinforcement Batches

(Data for a bulk volume of 1 cm^3)

	Fibers	Whiskers	Particles
Reinforcement Diam (μm)	100	20	20
L/D Ratio	30	30	1
Packing Density	0.16	0.16	0.50
Number of Reinforcements	6.8×10^3	8.5×10^5	1.2×10^8
Number of Reinforcements and Spacings Radially from Center	9.5	4.7	245

Table 6. Mean Free Path of Argon at Various Pressures and Temperatures

(Values for air differ by less than 5 percent)

Temp (°C)	Pressure - mm Hg			
	760	1	10^{-3}	10^{-6}
	(μm)	(mm)	(cm)	(m)
0	0.063	0.048	4.8	48
25	0.071	0.054	5.4	54
600	0.24	0.19	19	190
700	0.28	0.21	21	210
1000	0.38	0.29	29	290
1100	0.41	0.31	31	310

In order to assess the significance of reinforcement refinement upon gas removal, it is necessary to analyze the mechanism of gas transfer more accurately. Let us assume a batch of fine particles with a bulk volume of 1 cm^3 has been prepared in the laboratory under atmospheric pressure; the inter-particle spaces are, therefore, at a pressure of 760 mm Hg. Let us further assume that the batch has been heated to a high temperature, as in the dispersion process, so that the gases originally adsorbed at the particle surfaces are detached or, at least, have a very weak surface bond. If we expose this heated batch to a vacuum environment of 10^{-6} mm Hg, the gas molecules at the surface of the outermost layer of particles will be removed at a high rate, considering their high mean free path in the order of 300 m, as listed in Table 6. The gas removal at the surface is for all practical purposes instantaneous, even though a percentage of gas molecules will bounce back and forth in the crevices between particles for a short time.

In the first layer of interparticle spaces underneath, the gas molecules will bounce between the particle surfaces somewhat longer until they find their way through an opening in the first particle layer. The pressure in this layer of spaces is, therefore somewhat higher. As a result of the small pressure gradient, more particles will move to the outside than to the next interparticle layer. This process continues to the inside of the batch, generating a pressure gradient which provides a directionality for the movement of gas molecules. At a certain depth, the pressure reaches a magnitude where the mean free path of the gas molecules is of the same order as the interparticle spacings, so that near-equilibrium exists between two adjacent spacings. From this point on inward there is essentially no pressure gradient; consequently there is no preferred direction for the movement of gas molecules and the gas is retained, referred-to previously as "trapped gases." This condition prevails, until substantial pressure gradients are progressively generated in the interior as the outer part of the batch is gradually evacuated.

From these considerations it is apparent that the time for complete evacuation of a batch, or the decrease of the pressure at the center of a batch to at least 10^{-3} mm Hg depends exclusively on the size and number of particles or interparticle spaces radially from the center of the surface of the batch (for the same batch temperature and pumping capacity of the vacuum system). As can be seen in Table 5, the number of particles is 10^3 times as high as fibers of the same diameter ("whiskers" in Table 5) for a batch of the same bulk volume. The number of 20 micron particles and interparticle spaces in a radial line from the center of the batch to its surface, representing the path for the movement of gases, is 245, in contrast to 47 for whiskers and app. 10 for larger fibers. It is, then, apparent that complete evacuation of a batch of such particles takes considerable time, if it is at all possible.

For this reason stirring is an important element of the process, as it breaks the batch up into smaller pieces. But even in these smaller segments the number of fine particles is still in the order of millions. While the evacuation rate is enhanced, the achievement of pressures in the order of 10^{-3} - 10^{-4} mm Hg at all particles is

impossible within reasonable processing times, such as evacuation for 24 hours. One possible solution is continued stirring of the particles during the entire time of evacuation; this would require a further refined stirring system and sample arrangement. Another method, which would assure exposure of each particle to the high vacuum environment and, therefore, reduce the processing time substantially is a gradual addition of minute amounts of particles to the matrix by the following procedure:

(1) Solid aluminum in crucible, particles in a separate container positioned several cm above the crucible.

(2) Heating of matrix and reinforcements to the max. processing temperature.

(3) While stirring the melt, gradual release of the particles into the crucible.

It is expected that during the free fall of the particles in the high vacuum environment (Step 3) the adsorbed gases are effectively removed. This procedure calls for extensive equipment sophistication which exceeded the scope of this investigation.

6. METAL FOAMS

The production of metal foams is not possible in the terrestrial environment since metals, unlike polymers or glass, do not exhibit a high-viscosity state in the solid/liquid transition, necessary for the retention of a dispersed gas. The preparation of metallic foams or "controlled density metals" in space employs the principle of liquid/gas mixture stability postulated for zero-g conditions. Evidence for the validity of this principle was obtained in rocket experiments in which a metal alloy with predispersed gas bubbles was subjected to a melting cycle under low-g conditions (Ref. 4).

The preparation of metal foams is still a very attractive application of the low-g environment. It requires, however, considerable developmental work as to the methods of foam generation, cell size control and uniform distribution.

6.1 METHODS OF FOAM GENERATION

The potential techniques for foam generation and the related theoretical considerations have been discussed in Ref. 5. The following methods have been identified:

1. Dispersion of gas-filled microspheres
2. Gas generation by a dispersed "foaming agent."
3. Gas injection
4. Ultrasonic foaming
5. Nucleate foaming
6. Cavitation foaming

6.1.1 Discussion of Methods

The dispersion of gas-filled microspheres (1) is a rather simple method to obtain a material of reduced bulk density. Several types of the required high-temperature resistant microspheres are commercially available (carbon, silica). They present, however, the familiar problem that they are not wetted by most liquid metals including aluminum, unless the wetting technique described in section 4 is applied. This may be feasible if the entire process of wetting and dispersion is carried out under low-g conditions. The preparation of a precomposite in one-g, as in the case of solid reinforcements, is not possible since the buoyant microspheres would remain at the surface of the melt.

In the case of an aluminum matrix, the reactivity of the microsphere material has to be considered. While the reaction of carbon is limited to the interface (see Fig. 24), silica reacts vigorously with aluminum. If dispersion can be accomplished while the microspheres are still intact, the progressing reaction may be beneficial, as the generated compound may act as a wall stabilizer for the ultimately resulting gas bubbles. This is, however, not assured.

In view of these problems, the use of microspheres appears not advisable for initial flight experiments. The potential merits of the method may, however, well justify a separate R & D task. Methods (3) through (5), above, were likewise not considered at this time since they are rather complicated, and since the processing equipment involves extensive developmental efforts.

Cavitation foaming (6) has been attempted in Apollo flyback experiments. While these experiments, described in detail in References 2 and 3, indicated that the dispersion of gases from a single ullage is basically feasible, it requires a mechanical agitation system in the melt which poses a number of problems, such as the determination of effective agitation modes or the sealing of a mechanical drive against liquid metals.

6.1.2 Foam Generation by Particle Decomposition

The most promising method for initial low-g experiments is the dispersion of a solid foaming agent which decomposes during melting, resulting in a dispersed gas phase (method 2, above). It was, therefore, chosen for laboratory experiments.

In this method ideal conditions would be obtained with a foaming agent which decomposes at a discreet temperature slightly above the melting point of the matrix; the amount of gas produced would then be merely a matter of the amount of dispersed material and independent of time. However, for all practical foaming agents,

such as various hydrides, the amount of produced gas or the foaming rate is a function of temperature and time: Gas evolution starts at relatively low temperatures and the evolution rate increases with temperature.

There are two ways of combining the foaming agent with the base metal:

(a) Matrix and foaming material, both in the form of particles, are mixed and compacted; foam is produced by heating beyond the melting temperature. This method calls for a high heating rate, to preclude excessive gas generation in the solid state and explosive action at the moment of melting. Gas content and dispersion are primarily determined by the amount and size of the predispersed foaming particles and to a lesser degree by the time the mixture is held in the liquid state. The unavoidable surface oxides at the matrix particles are expected to move to the bubble walls, enhancing wall stabilization.

(b) The foaming material, in particle form, is added to the molten matrix and dispersed by agitation (stirring). The fineness of gas dispersion and the bulk density of the foam are controlled by the relative amount of matrix and foaming material, by particle size and by time at temperature.

Even though both techniques are equally suitable for low-g experiments, method (b) was selected for laboratory investigations since it permitted a better observation of the foaming activity and is rather convenient. It was also taken into consideration that this method is most attractive for the production of controlled-density metal ingots and castings in manned space operations.

6.2 EXPERIMENTAL INVESTIGATIONS

The objective of the experimental investigations was to demonstrate the feasibility of the selected method of foam generation and to obtain an answer to the critical question of bubble stability, whether the bubbles remain intact or coalesce gradually into a few large bubbles.

6.2.1 Experimental Materials

All experiments were carried out with pure zinc as matrix material and Titanium hydride as foaming agent for the following reasons: (1) Availability of data on the gas evolution of TiH_2 from previous efforts (Ref. 5); (2) perfect compatibility of the gas evolution profile of TiH_2 with the melting temperature of zinc (420°C); (3) relatively

low processing temperature, convenient for laboratory and flight experiments; (4) low oxidation sensitivity of zinc as compared with aluminum.

6.2.2 Gas Evolution Experiments

The amount of hydrogen gas generated by complete decomposition of TiH_2 is 448 cc/gram (theoretical maximum). The actual amount obtained depends on the following factors:

Temperature)
) Temperature profile
Time at Temperature)

Gas Pressure

Reaction of the hydrogen with the matrix

Incomplete decomposition

The processing (foaming) temperature for zinc is 450-500°C. In gas evolution experiments with TiH_2 (without the presence of a matrix) at 500°C, 90-110 cc of gas per gram were obtained in three minutes. It can be assumed that approximately half of the gas reacts with the zinc (bubble surface), so that the effective amount is approximately 50 cc/gr. If the gas pressure is allowed to increase, as in the case of an expanding container, the gas or bubble volume is further reduced.

In practice, the temperature is not constant, increasing gradually to the max. processing temperature. A part of the gas is, therefore, generated at lower temperatures with lower evolution rates resulting in a lower total gas volume for a given processing time.

Taking in account a temperature profile applicable to flight experiments at which the temperature increases from 400 to 500°C over a period of 3 minutes, and taking further in account a partial loss of gas due to reaction with the bubble surface, a net gas volume of approximately 30 cc/gr. at a pressure of 1 atm. can be expected for TiH_2 and zinc. In order to reduce, for example, the bulk density of 100 gr. (= 13.96 cc) of zinc to 50% of its original value, an equal amount of gas or 0.47 gr. of TiH_2 particles would be required.

6.2.3 Foaming Experiments

In the laboratory experiments, particles of TiH_2 of various sizes were manually stirred into molten zinc. Gas generation and foaming time were monitored by observing the expansion of the melt.

The prime difficulty of foaming experiments under 1-g conditions is the spontaneous segregation or buoyancy of the gas bubbles. To minimize this and to freeze the foam in the nascent state, the activity of the mixture was observed and at the proper moment the mixture was spilled over a short trajectory into a pail of water. During the free-fall, the sample assumed the shape of a slender drop whose tail solidified rapidly enough during water immersion to arrest the bubbles in the free-fall position. Numerous experiments have been carried out with this technique.

The cross-section of a sample tail-end is shown in Fig. 32. The bubbles are fairly uniform in size and do not exhibit any coalescence which indicates an effective stabilization of the bubble walls due to surface reaction with the foaming gas (hydrogen). The bubble distribution is imperfect as is to be expected in view of the rather crude initial mixing process. The gas content of this sample is approximately 40 percent, which is equivalent to a 40 percent bulk density reduction.

Experiments with higher rates of gas evolution (higher foaming temperature or longer foaming time) showed that the bubble walls remain stable and resist coalescence even under intimate contact where the bubbles press against each other. In many cases, even paper-thin and perfectly plane intersecting walls remained stable, as can be observed at several points in Fig. 32. (This effect is much more discernible in 3-D observation). The cross-section of a sample with approximately 70 percent gas content is shown in Fig. 33. While the configuration is irregular, the individual bubbles remained intact and did not coalesce, forming the classic foam network.

6.2.4 Discussion of Results

With the foam stability in zero-g practically assured, the remaining problem is the refinement and automation of the process. In manned operations it is expected to be less critical since the dispensing of the foaming agent into the molten matrix, mixing and temperature control can be monitored by the crew. For automated (rocket) experiments process control is more complex. Most desirable would be an exact reproduction of the laboratory experiments, consisting of (1) melting of the matrix, (2) dispensing and dispersion of the foaming particles and (3) rapid (active) cooling after a pre-set foaming time.

Figure 32. Gas Bubbles in Zinc, Generated by Decomposition of TiH_2 Particles (15X)

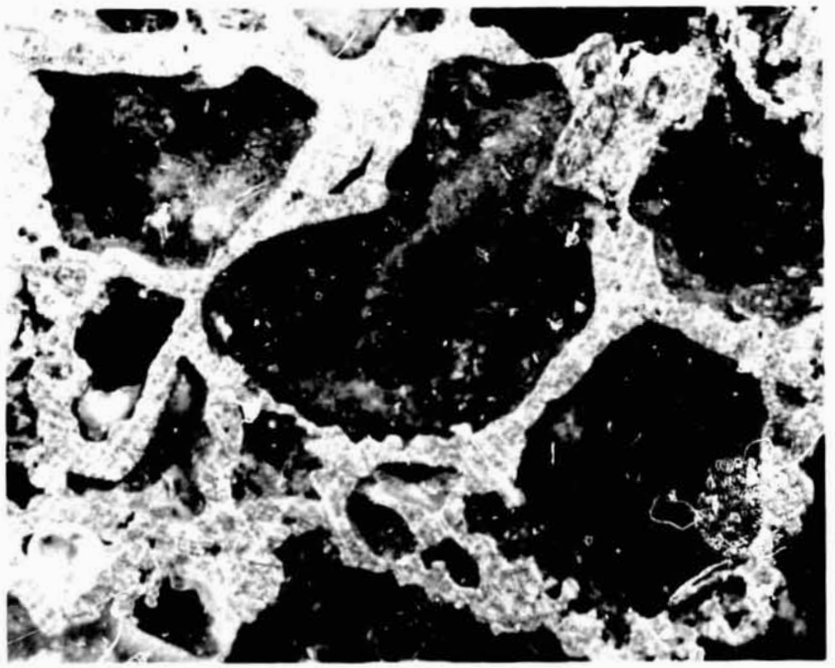


Figure 33. Zinc Foam, 70 Percent Bulk Density Reduction (15X)

Another alternative is the use of a compacted mixture of matrix granules and foaming particles, which is subjected to a melting/foaming cycle under low-g conditions (method (b) above). For this method, induction heating is desirable, since thermal gradients are minimized. However, radiation heating, as in the multipurpose furnace, is also acceptable. The formation of an irregular foam due to thermal gradients could be minimized by the use of a flat sample.

In all cases of zero-g experiments, provisions have to be made for material expansion. Most desirable would be a mechanical system with an expandable capsule (bellow-wall). Collapse of the foam in the initial cooling phase is avoided by arresting the end-volume. This may be accomplished either by rapid cooling, forming a solidified shell, or by mechanical locking of the capsule in its end-position by means of a ratchet system, as indicated in Ref. 5, Vol. II, Page 4-9, Fig. 4-3.

The use of a fixed-shape capsule with an inert gas ullage for expansion appears at first most attractive, as the bubble size can be controlled by inert gas pressure or the equilibrium pressure between foam and ullage. The difficulty is that under low-g conditions contact between the molten sample and the capsule wall and, consequently, effective cooling are not assured.

The laboratory experiments and the foregoing discussion of low-g experiments imply the following conclusions:

1. Bubble coalescence, considered previously a major obstacle in metal foaming, can be completely eliminated by the use of an appropriate gas which reacts with, and stabilizes the bubble surfaces. Even thin bubble walls remain stable.

2. Further development of metal foams calls for low-g experiments, since laboratory evaluation is limited by the instantaneous gas segregation.

3. For initial low-g experiments, the most effective and least expensive method of foam generation is the use of a foaming agent. The usefulness of this technique has been proven in laboratory experiments. It is proposed to use zinc and TiH_2 particles as initial experimental materials.

7. LOW-G EXPERIMENT DEFINITION

The processing of the concerned composite materials calls for a low-g time in the order of several minutes which exceeds the low-g time capability of drop towers or aircraft by at least one order of magnitude. The following discussion of low-g experiments is, therefore, exclusively based on the use of suborbital rockets ("research rockets") and related experiment facilities which are presently either existing or in the state of hardware development.

7.1 ROCKET EXPERIMENT CAPABILITIES

The capability of sounding rockets for the processing of composite materials has been demonstrated in flight tests carried out by MSFC with the assistance of Convair several years ago (Ref. 4, 8). On the basis of the encouraging results of these tests, a detailed planning study for rocket experiments was conducted (Ref. 6) which led to the inauguration of a flight test program in November, 1974 (Ref. 7). The preparation of the carrier rockets and the basic experimental facilities are presently in the hardware phase. Flight operations are expected to start in mid 1975 and to continue throughout the pre-shuttle years.

Flight experiments will initially be conducted with Black Brant VC rockets, augmented later with Aries rockets providing a higher payload capability. Both rockets provide a maximum low-g time of 7-8 minutes (land recovery). Low-g levels in the order of 10^{-4}g are assured and may be further reduced to 10^{-5}g. Extensive instrumentation for in-flight measurements is available (Ref. 8, 9).

The experiment apparatus applicable to the processing of composite materials is a multi-purpose furnace (Ref. 9), similar to the one used in Skylab experiments. Its maximum temperature of 1000° C is ample for the processing temperatures of 440-700° C required for the discussed composite materials. The samples are contained in capsules of 2 cm I.D. and 16 cm (max) in length. The furnace provides for preheating in the pre-launch period and gas cooling for solidification; an alternate water cooling system may become available later in the program.

After flight processing, the samples are recovered and returned, together with flight measurement data, to the principal investigator for evaluation.

7.2 FIBER AND PARTICLE COMPOSITE EXPERIMENTS

As indicated by the results of the investigations discussed in Sections 3 to 5, the two essential processing phases for metal/solid reinforcement composites are: (1) Joining (wetting) of the reinforcements with the matrix and (2) establishment of uniform dispersion. In ultimate space production, both phases would be carried out in one operation or the melt cycle. For rocket experiments it is expedient to perform the first phase in the laboratory, as it is not g-sensitive, and to confine the flight experiment to the second phase only. Rocket experiments consist, therefore, of the following two processing phases:

(1) Laboratory: Preparation of the precomposite; filling of the flight capsule.

(2) Flight: Low-g reinforment dispersion.

7.2.1 Materials Selection for Flight Experiments.

The results of the dispersion experiments described in Section 5 are summarized in Table 7 which includes a relative rating of various reinforcements for the preparation of low-g experiment samples. Sapphire (Al_2O_3 - alpha) fibers of 100-250 and particles of > 50 micron diameter are considered most promising due to the combination of the following positive aspects:

(1) Assurance of dispersion; precomposite for flight samples can be prepared with existing facilities.

(2) Perfect interface characteristics - no reaction with the matrix

(3) Attractive reinformcement properties (fairly high strength/density ratio for fibers, high hardness for particles).

(4) Availability and moderate cost (particles inexpensive, fibers 35 $/gr).

Sapphire fibers of smaller diameter than the 250 micron (10 mil) used in the experiments are presently not available, can however be prepared by the supplier at higher initial cost. The ideal size for flight experiments would be 100 micron (4 mil).

Sapphire particles of less than 50 micron diameter are readily available, however will require additional processing facilities to achieve complete dispersion. They are, therefore rated lower (3).

Sapphire whiskers are difficult to obtain in perfect condition. They, likewise require additional processing facilities. Their most positive aspect is the combination

Table 7. Summary of Dispersion Experiment Results

Reinforcements			Experiment Results			Relative Rating
Type	Material	Diam. μm	Wetting	Dispersion	Reaction	1 = Highest
Fibers	Al_2O_3	250	+	+	None	1
	SiC	90	+	+	Limited	2
	C	15	+	+	Limited	2
	W	175	+	+	Total	4
Particles	Al_2O_3	60	+	+	None	1
	Al_2O_3	25	+	(+)*	None	3
	Al_2O_3	15	+	(+)*	None	3
Whiskers	Al_2O_3	3-7	+	(+)*	None	3

*Feasibility demonstrated by dispersion of a limited fraction of the reinforcements; complete dispersion requires more extensive processing facilities.

of perfect interface characteristics with a high strength/density ratio. The overall rating is comparable with the small particles (3).

Silicon carbide fibers are available in the exact desired size regime. They are rated somewhat lower (2) than sapphire fibers (1) in view of the encountered interface reaction. If the presence of a reaction zone should prove beneficial, they would be even preferable to the sapphire fibers. This can, however, only be determined by mechanical testing which requires a sample of apprecialble size which, in turn, can only be obtained by low-g processing.

The same considerations apply to carbon (pyrolytic graphite) fibers. The most advantageous aspects are low cost and availability. This is offset by the size limitation of commercially available filaments to 10-20 micron diameter, demanding more exacting processing conditions.

Tungsten is rated lowest in spite of perfect dispersion characteristics due to the complete reaction with the matrix. Whether the fiber-like dispersion of Al/W intermetallic compounds represents an attractive and useful composite material can, again, only be determined in low-g experiments.

For all solid reinforcement experiments a baseline reinforcement content of 5 percent by volume is recommended, since it is low enough to assure effective low-g mixing and high enough to yield meaningful property data. If the rocket program permits, additional experiments with 12 percent fibers, 20 percent particles and with 0.5 percent whiskers are recommended. Another interesting composition would be a mixture of 8 percent sapphire fibers and 5 percent alumina particles. The suggested scheduling of experiments is discussed in Section 7.4.

7.2.2 Sample Preparation

The preparation of a flight sample consists of (1) the preparation of the precomposite material and (2) the filling of the flight capsule.

The preparation of the precomposite follows the procedures defined in Section 4.2. With the present apparatus and related facilities, described in Section 4.3, app. 18 cc of precomposite material can be produced in one heat, which yields app. 13 cc of "clean" material after removal of the void-containing top section of the casting.

The flight sample should have a size of 2 cm OD × 8 cm long. The use of the full diameter of the standard multipurpose furnace capsule is necessary for the preparation of a tensile test sample whose gage length diameter is a multiple of the max reinforcement length and thus provides a fair representation of a random-oriented composite. The length of 8 cm is adequate for tensile testing. This sample size requires 25 cc of clean precomposite material, or two batches prepared in crucible B

of 13 cc net. For particle composites, a smaller sample size could be used, if desirable.

The essential sample data are summarized as follows:

Original Precomposite Batch	18 cc (app. 50g)
Cleaned Precomposite Casting	13 cc (app. 36g)
Flight Sample Size	2 OD × 8 cm
Material Required for Flight Sample	25 cc (app. 70g)
Batches Required for Flight Sample	2

For filling of the flight capsules, the two cleaned precomposite batches are remolten in a high-purity argon atmosphere and cast into the stainless steel capsule. Remelting experiments showed that this operation does not affect the integrity of the precomposite. (Reinforcements remain dispersed).

7.2.3 Experiment Performance

The flight experiment consists of two distinct processing phases: A non-g-sensitive and a g-sensitive phase. In Fig. 34 the g-sensitive phase is identified by bold frames.

The melting of the sample prior to mixing is not g-sensitive and can be carried out at the launch pad with ground-supplied power. As indicated in the flight time diagram, Fig. 35, the max.processing temperature of 700° C is then maintained through the count down, lift off and boost periods. Upon attaining coast and low-g conditions the second processing phase is initiated which consists of agitation to achieve uniform dispersion, passive stilling (deceleration of the mixture to near-zero motion) and active solidification with a coolant.

The total low-processing time is app. 100 sec, including 20 seconds for active water cooling. Four samples can be conveniently processed in one flight, preferably scheduled in two pairs as indicated in Fig. 35. If solidification is to be accomplished by gas cooling, the required cooling time is app. 300 seconds, increasing the total low-g processing time to 400 sec. In this case, all samples have to be processed concurrently to make full use of the total available low-g flight time of app. 420 sec.

The necessity of low-g agitiation for the establishment of uniform reinforcement dispersion calls for appropriate attachments to the multipurpose furnace. Three agitation methods have been considered:

(1) Mechanical Stirring
(2) Electromagnetic Agitation
(3) Ultrasonic Agitation.

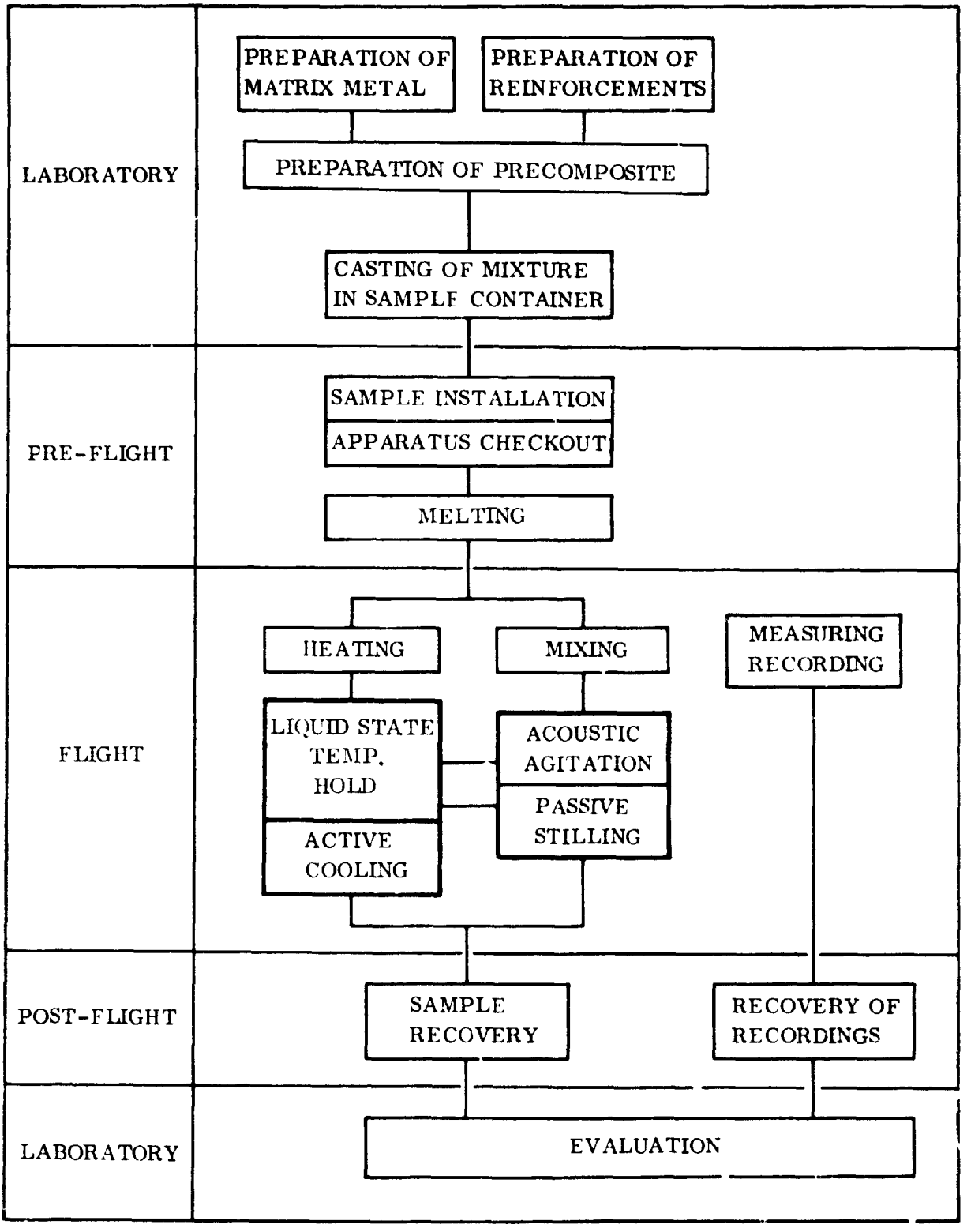


Fig. 34. Experiment Flow Diagram - Fiber and Particle Composites

EXPERIMENT PROGRAM – TRAJECTORY A

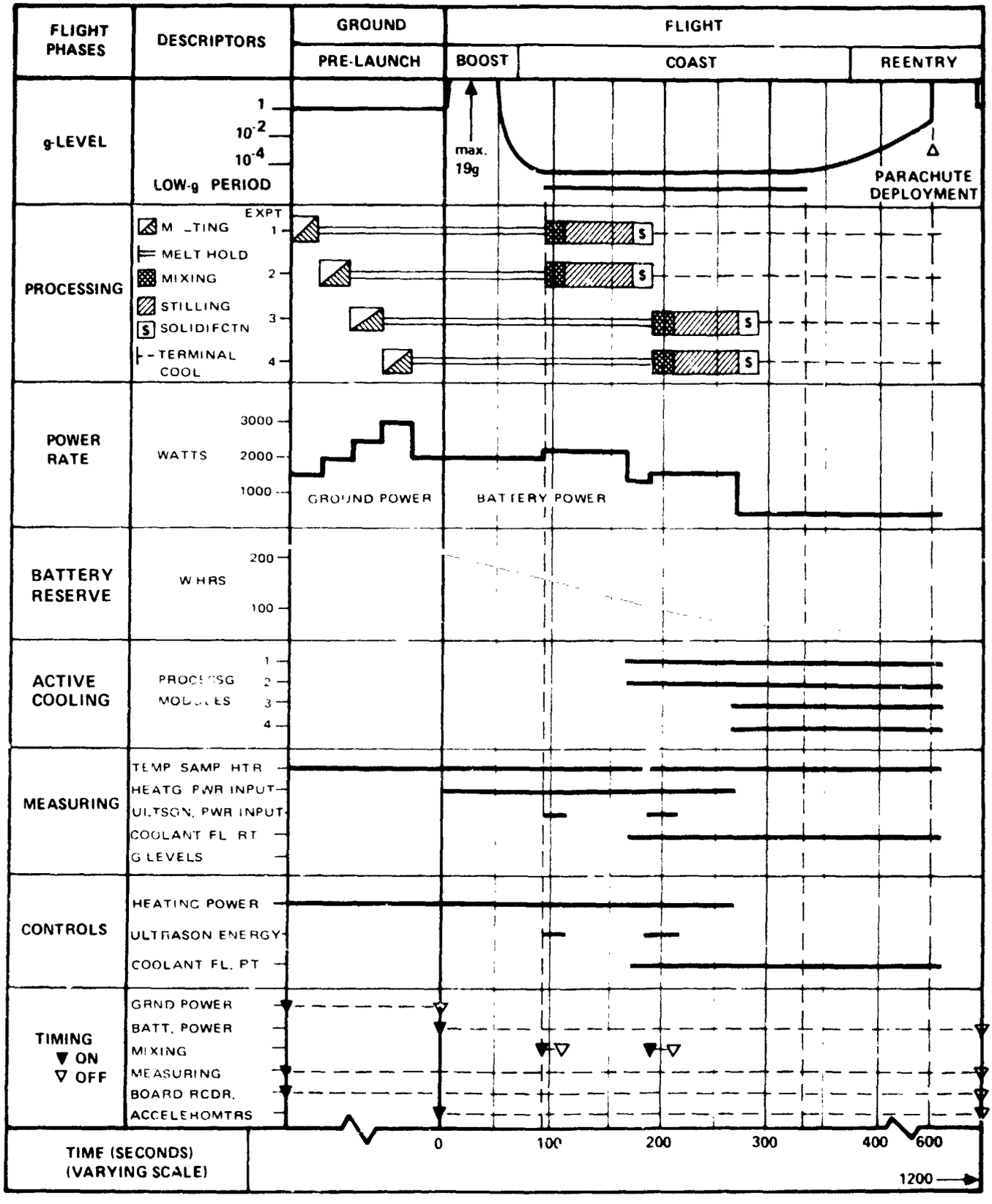


Fig. 35. Flight Diagram - Fiber and Particle Composites

Mechanical stirring is the most effective, yet also the most complex technique; the primary problem is the seal for the drive shaft operating in liquid metals at a fairly high temperature; it further has the disadvantage of a small stirrer cast in one end section of the sample which should, however, not affect tensile testing.

Experiments showed that electromagnetic rotation the liquid matrix without any components in the capsule can be easily achieved;adaptation of the electromagnetic drive unit to the processing temperature of 700° C may, however, pose severe problems; further, the rotational mode may not be adequate for effective mixing. Other electromagnetic agitation techniques, such as the combination of an electric field and a permanent magnet, or the rotation of an iron rod immersed in the liquid sample pose equally difficult problems.

Ultrasonic mixing appears most attractive for two reasons: (1) all components can be located outside of the high-temperature environment by means of an attachment to the multipurpose furnace (2) developmental work is in progress, partly under MSFC sponsorship.

The definition of optimum mixing modes and the related modification of the agitation device requires additional theoretical and developmental effort. Preliminary theoretical assessments are documented in Ref. 5 (Appendices A, B, C and D).

7.2.4 Experiment Evaluation

Upon recovery, the flight capsule is removed from the sample by the method developed by MSFC in connection with earlier rocket experiments. The sample is evaluated for reinforcement distribution, mechanical properties and metallurgical characteristics by the following sequence of operations and tests.

(1) Surface examination

(2) X-ray radiographs in radial directions for the possible presence of voids.

(3) Preparation of a tensile test specimen (diameter reduction of the central portion by grinding) and performance of a tensile test.

(4) On one-half of the fractured tensile specimen, cutting of the 2-cm diam end end section for a compression test.

(5) On both parts of the same half-specimen, preparation of radial slices for the evaluation of reinforcement distribution.

(6) Lengthwise cutting of the second half specimen in a center plane; evaluation of the reinforcement distribution along the cut surfaces.

(7) From one of the two sections (6), lengthwise cut of a slice (0.3 cm thick for fibers, 0.2 mm thick for particles and whiskers) for final evaluation of reinforcement distribution by x-ray or neutron radiography.

(8) Metallurgical and metallographic evaluation of selected radial slices (5) for matrix microstructure, reinforcement interface characteristics and degree of reaction.

The remaining longitudinal quarter-section is saved for further reference or display. All essential stages of the evaluation are recorded photographically at appropriate magnifications. Results are correlated with recorded flight data, particularly temperature and g-level vs. time.

7.3 METAL FOAM EXPERIMENTS

A comparison of various methods of foam generation and the reasons for selecting the use of a foaming agent for initial flight experiments were presented in Section 6. As pointed out there, the foaming material can be added to the matrix either by mixing with the liquid matrix as part of the foaming process, or by solid-state mixing and compaction of matrix and foaming particles, followed by a separate foaming cycle. The first technique, used in laboratory experiments, is not suited for early flight experiments since the entire process has to be carried out under low-g conditions and necessitates a rather complex apparatus.

In the "compact" technique the mixing phase is carried out manually on the ground, while low-g processing consists merely of a melt cycle without any active mechanical controls.

7.3.1 Materials Selection for Flight Experiments

On the basis of the laboratory experiments, the use of Zinc as matrix metal is recommended for initial flight experiments due to its thermal compatibility with Titanium hydride (TiH_2) as foaming agent. There is no doubt that suitable foaming agents for aluminum can be found; this would, however, require additional developmental effort. Besides, another method of foam generation, such as gas injection foaming, may be preferable for aluminum; again, this would necessitate additional efforts for the development of the rather complex flight equipment.

The objective of the initial flight experiments is to gain experience and data on the generation and the properties of metal foams which can only be obtained in extended-time low-g processing. The advantage of the Zinc/TiH_2 system is that it serves this purpose at a minimum of side problems irrelated to the preparation of foam.

The compact method is readily adaptable to the addition of fibers for the preparation of reinforced foam. However, the choice of reinforcement materials is somewhat limited for zinc as well as other metals. High strength oxide or carbide reinforcements are not wetted by practically all metals and are, therefore, not considered for initial experiments. The majority of metallic reinforcement materials with positive wetting characteristics, such as copper alloys, are readily dissolved in zinc as well as aluminum. The best choice are high-strength steel fibers (chopped cold-drawn wire) which are wetted by zinc after surface cleaning in hydrochloric acid. Steel wire with a tensile strength of 450,000 psi is readily available in a variety of thicknesses. Recrystallization and loss of strength at the relatively short time at the foaming temperature of 450°C are minimal.

7.3.2 Sample Preparation

The matrix and foaming particles in the proper ratio, determined by weight, are first chemically cleaned and deoxidized under atmospheric conditions; the cleaned particles are stored in alcohol to preclude surface contamination and transferred into an argon glove box. All subsequent laboratory operations are carried out in a high-purity argon atmosphere.

After removal from the alcohol beaker, the particles are spread out on a flat glass pan, dried and then mixed manually. The mixture is filled into the bellow-wall flight capsule and compacted in the capsule with proper tooling. Upon sealing, the capsule is removed from the glove box and the top secured by electron beam welding. A similar procedure has been practiced successfully in the preparation of the samples for earlier rocket flight experiments (Ref. 4, 10).

The recommended sample size is 1.7 (mean) cm diam × 5.4 cm. The diameter is based on commercially available (3/4in.) stainless steel bellow-wall tubing. Upon foaming, the sample length is app. 8.1 cm (33 percent bulk density reduction), adequate for tensile testing.

During the process of expansion, the capsule volume increases from 12.25 to 18.37 cc, calling for a gas volume of 6.12 cc. The stretching of the capsule bellows causes a pressurization of the gas to 2 atm. According to the data on gas evolution in Section 6.2.2, the volume of generated gas at this pressure in 15 cc/gr. The amount of Ti H_2 particles required for expansion is, consequently, 6.12/15 or 0.41 gr. At a deliberately low compaction factor of 0.97 the volume and weight of zinc and Ti H_2 (densities 7.17 and 3.9 gr/cc, respectively) and of the complete sample are as follows:

	Vol. (cc) Compacted	Vol. (cc) Net	Weight (gr)
Zn	12.142	11.777	84.44
Ti H_2	0.108	0.105	0.41
Sample	12.250	(11.882)	84.85

7.3.3 Experiment Performance

A previous investigation of various foaming agents (Ref. 5 P. 3-92 to 3-102) showed that the decomposition of Ti H_2 or Zn H_2 at a pressure of 1 atm. (capsule pressure) starts above 200° C. The samples can, therefore, be preheated at the launch pad with ground power to 200° C, as indicated in Figs. 36 and 37. This temperature is maintained through lift-off and boost phase. Upon reaching coasting (low-g) conditions, the sample is heated to the matrix melting temperature at a high heating rate to preclude excessive gas evolution in the solid state. As the foaming particles decompose, the sample and the bellow-wall capsule expand. A ratchet device (such as shown in Ref. 5, Fig. 4-3) locks the capsule in the expanded position, preventing collapse of the foam during cooling.

Solidification should be carried out at a high cooling rate to terminate gas evolution. While this calls for water cooling, the experiment may also be adapted to gas cooling by a careful dosaging of the foaming agent

Some of the hydrogen gas, generated by hydrides, will react with the bubble walls. As pointed out before, this is expected to enhance bubble wall stabilization.

7.3.4 Experiment Evaluation

Upon recovery and removal of the capsule, the sample is evaluated for bulk density, foam distribution and structure, metallurgical characteristics and physical properties by the following sequence of tests:

(1) Measurement of bulk density

(2) Center of gravity determination as rough measurement of gas distribution.

(3) X-ray radiograms in various axial directions

(4) Tensile test for strength and fracture pattern (enlargement of tensile specimen ends by cast-on matrix material according to earlier developed method).

The following tests are performed on one half on the fractured tensile sample:

(5) Compression test on one end section after removal of cast-on material by machining.

(6) Radial slicing of the gage length of the tensile sample for evaluation of foam distribution and structure.

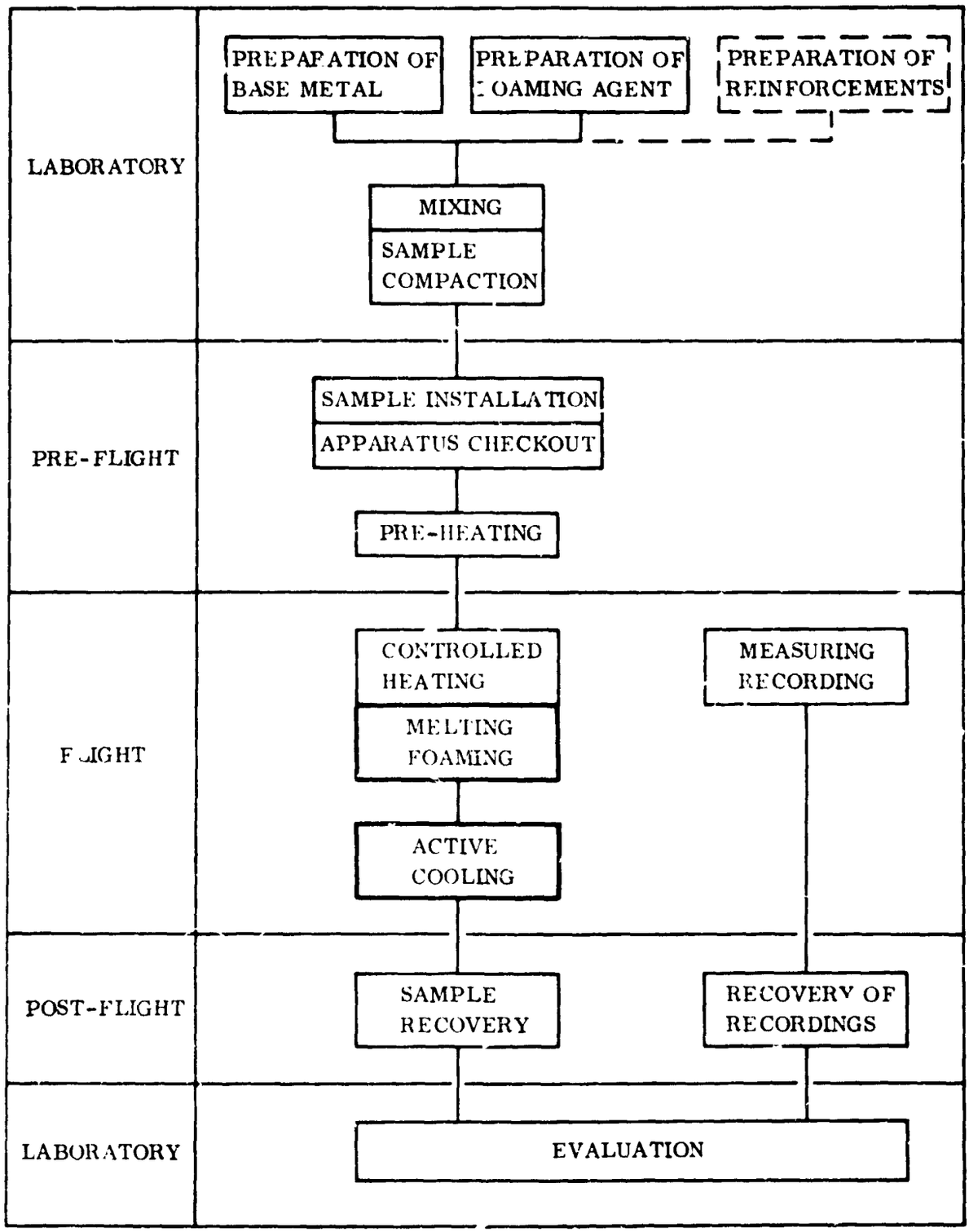


Fig. 36. Experiment Flow Diagram - Metal Foams (Predispersed Compact)

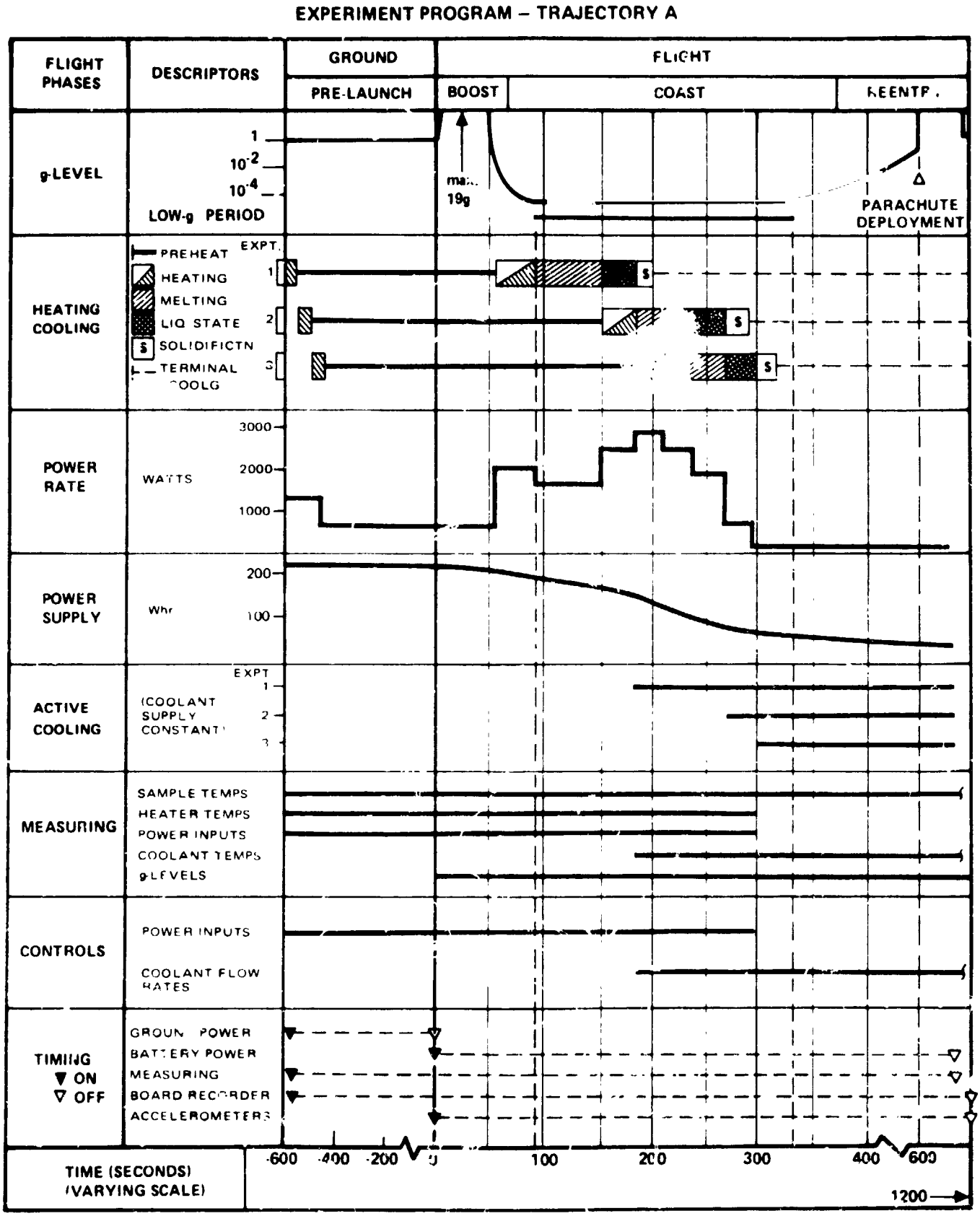


Fig. 37. Flight Diagram - Metal Foams (Predispersed Compact)

(7) Metallurgical evaluation of two selected slices.

(8) Determination of bubble gas composition by axial slicing of sample (5) immersed in an inert liquid.

The second half of the tensile specimen is cut in half axially for the following tests:

(9) Foam structure along axial plane.

(10) Refined determination of foam structure by cutting a 3-mm thick axial slice off part (9); x-ray shadowgraph.

The remaining quarter section of the sample is saved for further reference or display. All essential stages of the foregoing evaluation are recorded photographically at appropriate magnifications. Results are correlated with recorded flight data (temperature profile, g-level etc.)

7.4 PROPOSED ROCKET EXPERIMENT PROGRAM

The selection of experiments for rocket flight tests is based on equal consideration of the following criteria:

(1) Assurance of success
(2) Scientific and/or technical value
(3) Availability of materials
(4) Additional developmental requirements.

The assurance of success (1) is primarily based on the state-of-art achieved in the investigations discussed in this report. Criteria (2) and (3) are self-explanatory. Additional developmental requirements (4) refer to modifications of existing ground and/or flight processing equipment. They are divided into two groups: (A) Minimum requirements, consisting of relatively simple and inexpensive modifications of existing equipment; (B) more extensive requirements, which involve more complex equipment modifications or additions.

In accordance with this distinction of developmental requirements, the first priority experiments are divided into two groups (A, B). A third group (C) comprises other desirable experiments of secondary priority, also with "minimum developmental requirements." Sample configurations and experiment performance are as specified in Sections 7.2 and 7.3.

A. Minimum Developmental Requirements

a. Fiber and Particle Composites. Developmental requirement: Ultrasonic mixing attachment to multipurpose furnace. Max. processing temperature (flight): 700° C.

(1) Al - 5 percent sapphire fibers, 100-250 micron diam.
(2) Al - 12 percent sapphire fibers, 100-250 micron diam.
(3) Al - 20 percent $Al_2 O_3$ particles, 50 micron diam.

b. Metal Foaming Experiments. Developmental requirement: Ratchet-type capsule arresting device located in the multipurpose furnace. Max. processing temperature: 500° C.

(4) Zn - 0.41 gr Ti H_2 particles
(5) Zn - 0.80 gr Ti H_2 particles
(6) Zn - 0.41 gr Ti H_2 + 5 percent steel fibers.

B. More Extensive Developmental Requirements

Particle and Whisker Composites. Developmental requirement, in addition to Aa, above: Addition of a reinforcement delivery system to the ground pre-processing facility. Max. processing temperature (flight): 700° C.

(7) Al - 8 percent sapphire or SiC whiskers
(8) Al - 0.2 percent sapphire whiskers
(9) Al - $Al_2 O_3$ particles, 15 micron diam.

C. Other Desirable Experiments

Additional Fiber Composites. Developmental requirements identical to Aa, above. Max. processing temperature (flight): 700° C.

(10) Al - 8 percent SiC fibers, 50-90 micron diam.
(11) Al - 8 percent carbon fibers, 15 micron diam.
(12) Al - 8 percent W fibers, 100 micron diam.

8. CONCLUSIONS AND RECOMMENDATIONS

8.1 GENERAL CONCLUSIONS

The dispersion characteristics of solids and gases in liquid metals can be well investigated in the terrestrial environment. However, the properties of castable metal-base composites and metal foams can only be derived from material processed under low-gravity conditions. Research efforts have now reached a point, where low-g experiments are needed in order to obtain data necessary for process perfection and for a realistic assessment of the product applications potential. Suborbital rockets provide the exact low-g time for the processing of a material quantity adequate for evaluation of the mechanical properties. The earliest possible scheduling of such experiments in the recently activated rocket test program is, therefore, indicated.

In the present absence of flight experiment data, no conclusive definition of the applications potential can be made. Tentative studies indicate that applications will be primarily characterized by high performance requirements rather than cost effectiveness. This places emphasis on military applications and on large, permanently deployed space structures. In the latter case, the products may be directly introduced in space assembly without return to earth.

8.2 CONCLUSIONS - FIBER AND PARTICLE COMPOSITES

1. A prerequisite for the dispersion of solid reinforcements in metals by liquid-state processing is mutual wettability. Practically all attractive reinforcement materials, such as oxides or carbides, are not wetted by liquid metals.

2. Theoretical and experimental investigations indicated that the conventional concept of wetting, where wetting characteristics are expressed by the contact angle, appears to be valid only in the three-phase liquid/solid/gas system and that in a perfect two-phase liquid/solid system or in the complete absence of a gas all materials are mutually wetting.

3. On the basis of this theory, commonly non-wetting reinforcements were successfully dispersed in molten metals by a new process developed in this

investigation, characterized by a high vacuum environment and a processing temperature substantially above the melting point of the matrix metal.

4. Wetting and dispersion of fibers and particles over 50 micron diameter presents no problem. The achievement of a gas-free environment becomes increasingly difficult as the size is further decreased. For particles and whiskers below 25 micron diameter a mechanical dispensing system is required to achieve complete gas removal.

5. For rocket experiments it is expedient to divide the entire process into two phases: (1) Joining of the reinforcements with the matrix (preparation of the "precomposite") which is not g-sensitive and can, therefore, be carried out in the laboratory. (2) Establishment of uniform dispersion by a melting and agitation cycle under low-g conditions. In ultimate space production with crew assistance, both phases can be performed in one operation (one melt cycle).

6. Pure aluminum or aluminum alloys are equally suitable as matrix material. The preferred reinforcement material is sapphire ($Al_2 O_3$) as it exhibits the most perfect reinforcement/matrix interface. Reinforcement materials which react slightly with the matrix, such as graphite or silicon carbide, may even produce a higher composite bond strength. An entirely new breed of composites may be obtained by the use of highly reactive reinforcement materials, such as tungsten, which are transformed into a high-strength aluminum compounds without loss of their fiber-like configuration.

8.3 CONCLUSIONS - METAL FOAMS

1. Metal foams are produced by the dispersion of a gas in the molten metal. Coalescence of the gas bubbles can be minimized by the use of a gas which reacts with the matrix, resulting in a stabilization of the bubble walls. By this technique, even paper-thin dividing walls between bubbles remain intact, permitting the production of foams with high gas contents and high bulk-density reduction.

2. Various methods of gas dispersion have been defined. For initial low-g experiments the preferred method is the generation of gas bubbles by thermal decomposition of dispersed metal hydride particles. A compacted mixture of matrix granules and gas-forming particles is prepared in the laboratory; foam generation consists then merely of a melt cycle under low-g conditions.

3. For initial flight experiments, pure zinc as matrix material and $Ti H_2$ as gas former have been selected in view of their perfect thermal compatibility.

For reinforced foam, the addition of high-strength steel fibers is proposed, as they combine a fair strengthening effect with adequate wetting characteristics.

8.4 RECOMMENDATIONS

It is recommended to concentrate continuing efforts on the performance of rocket flight experiments, since gound-based evaluation has arrived at a point where low-g processing results are needed for process refinement and for the definition of product applications. Preparation of flight experiments comprises the following efforts: (1) Preparation of flight samples; (2) development and fabrication of an ultrasonic material agitation attachment for the multi-purpose furnace; (3) design and fabrication of a capsule-arresting device for metal foam experiments. A proposed flight experiment program is defined in Section 7.4 of this report.

In support of this program it is recommended to promote the somewhat neglected field of whisker research, particularly the preparation of high-quality sapphire and/or silicon carbide whiskers.

It is further suggested to investigate potential terrestrial applications of the new wetting and dispersion process developed in the course of this study.

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