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DEVELOPMENT OF A LOW LOSS MAGNETIC COMPOSITE
UTILIZING AMORPHOUS METAL FLAKE

First Semi-Annual Progress Report

For the Period

19 September 1978 - 18 March 1979

Metallurgy Laboratory

Corporate Research and Development

General Electric Company

P. O. Box 8

Schenectady, New York 12301

Principal Investigator: Lyman A. Johnson

Prepared for the

United States Department of Energy

Division of Electrical Energy Systems

Under Contract ET-78-C-01-3205

Project Manager: J. P. Vora

April 1979

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Forward

The contributors to this project have been R. P. Laforce, R. T. Laing and A. C. Rockwood on flake and ribbon casting; S. J. Kelly and P. G. Frischmann on magnetic measurements; and M. A. Byrne and J. H. Lupinski on composite formation. J. J. Becker, F. E. Luborsky and H. H. Liebermann provided helpful discussion and consultation. All are members of the General Electric Corporate Research and Development Center.

I. INTRODUCTION

The objective of this project is to develop and optimize the processes for casting amorphous metal flake and fabricating a magnetic composite material from the flake and a suitable binder. It is expected that the resultant composite will have substantially lower magnetic losses than currently obtainable from electrical steels and, when applied in motor stators, will provide increased motor efficiency and opportunities for innovative motor designs.

To meet the project objective the work has been divided into five tasks whose technical approach is briefly described below.

Task I: Processing of Amorphous Metal Flake

The principal process method to be evaluated for development is the continuous casting of molten alloy onto a patterned rotating wheel. The initial variables to be examined are those which are expected to control the ability to make a uniform flake product nearly 100% amorphous. These variables include the method of patterning the wheel, nozzle geometry, wheel surface speed and surface condition, and ejection angle and pressure. Variables which are expected to control the magnetic properties of the composite are also being examined. These include flake length, thickness and width (and their controlling process parameters), wheel material and surface condition, ejection pressure and angle, melt superheat and casting atmosphere and pressure.

Task II: Initial Magnetic and Physical Properties Assessment

Properties assessment is made during all phases of making flake and in its resultant composite form. Physical measurements include dimensional characteristics, surface and edge irregularities, ductility and degree of uniformity from flake to flake. Magnetic properties are established by measurements of the d.c. hysteresis loop on flake and similarly cast ribbon both before and after annealing and by a.c. and d.c. hysteresis measurements on the composites.

Task III: Forming of the Composite

The composites are formed by combining the flake with a binder and pressing in a die. The principal variables are the binder material, flake

size and shape, and the compacting time, temperature and pressure. Binder materials from the epoxy, cyanoacrylate and polyimide families are being evaluated.

Task IV: Optimization of Unit Processes

When successful processing techniques from Tasks I and III are demonstrated by the evaluations in Task II, their process variables will be optimized with respect to the final composite properties and consideration for future scale-up.

Task V: Final Properties Evaluation

Property measurements established during the individual task developments will be evaluated by comparison with the final product properties. The effects of various anneal cycles, process steps and the suitability of configurations will be evaluated for subsequent motor applications.

II. PROGRESS THIS REPORTING PERIOD

II.1 Summary

This report covers the work done during the first six months of this twenty month project. During this period work was limited to the first three tasks described in the introduction. This section of the report will summarize the approach and results of this work and will be followed by a detailed description of the experimental data.

II.11 Processing of Amorphous Metal Flake

Before the initiation of this project two methods for producing amorphous metal flake or short ribbon segments had been demonstrated on an experimental basis. The first method, called splat quenching, involved the high velocity impact of a milligram size molten alloy droplet onto a cold substrate. While well proven in the laboratory, this method appears to have intrinsic limitations for economic scale up to large production rates.

The second method was a continuous one, called melt extraction and developed by Battelle for the production of short fibers of crystalline alloys. In this method a continuously rotating disc touches the surface of a molten metal pool and extracts a solidified ribbon or wire. If the disc edge is grooved, short fibers are produced. By combining this idea of a patterned casting wheel with the melt spinning method for making amorphous metal alloys, we demonstrated in the laboratory that short amorphous metal segments could be produced on a semi-continuous basis.

The work of this period has been focused on experimentally defining the processing conditions under which this approach could be used to successfully produce a high yield of amorphous metal flake with good physical and magnetic characteristics. Several wheel patterning methods were evaluated. The most successful technique consists of putting axial shallow grooves 0.0005-.004 inches deep on the outer circumference of the wheel, filling these grooves, polishing the wheel and casting. This patterning technique results in the most uniform flake and minimizes the amount of crystalline material in the product.

Most of the other casting parameters were also examined in some detail. From this examination we have arrived at a tentative preferred set of casting parameters. Further optimization in remaining project periods will undoubtedly see modifications of this set which appears in table I.

TABLE I
Preferred Flake Casting Parameters

Composition:	4Si-14.5B-81.5Fe at.%
Atmosphere:	15 Torr He
Nozzle:	Round Hole 0.025" diameter
Ejection Angle:	90°
Wheel-Nozzle Distance:	0.040"
Wheel Material:	Aluminum Bronze
Wheel Surface:	600 grit polish
Grooves:	0.001" deep, 0.003" wide filled with Rapidograph 3072-GLD ink
Ejection Temperature:	1250°C
Ejection Pressure:	3 psi
Wheel Wiper:	Scotch Brite Brush
Wheel Speed:	5500 ft/min

II.12 Magnetic and Physical Properties Assessment

This task is basically one of support for Tasks I and III. Physical property assessment during this period consisted mostly of characterizing the geometrical shape and uniformity of the flake product and occurrence of crystalline material mixed in with the flake. The magnetic property assessment consisted of measuring d.c. hysteresis characteristics of flake, narrow ribbon and pressed composite bars. Under the wide range of casting parameters used there was considerable scatter in both property assessment areas. The results of these studies, however, indicated that the best physical flakes with the lowest fraction of crystalline material are obtained under the conditions listed in table I. Magnetically, a wide range of properties were obtained. The best ribbons in the annealed condition had coercive forces below 0.05 oersteds and a flux density at one oersted field of over 15 kilogauss, substantially better than common motor lamination steels. The best flakes also had coercive forces of about 0.05 oersteds.

II.13 Forming of The Composite

During this period our efforts focused on trying to make composites of high packing factor using epoxy binders. Small samples of flakes were combined with various epoxies and curing agents and pressed in a one inch circular die at various temperatures, times and pressures. It was found that Shell epoxy Epon 828 with MDA curing agent using vacuum impregnation and pressing at 175°C for two hours at 100 kpsi load gave the highest packing factor of 67%. Two reasons prevented the achievement of a higher packing factor. First, the high strength of the amorphous metal tends to create internal delamination of the composite. Second, nonuniform packing of the die also causes the average packing factor to be lower than the maximum attainable in local regions.

The final composite will require a stress relief anneal. Therefore, future work will focus on high temperature binders from the polyimide family. In order to decrease the delamination tendency pressing will be done at somewhat elevated temperatures. Also, methods will be explored to improve the packing uniformity.

II.21 Results - Processing of Amorphous Metal Flake

Based on experience gained before the start of this contract it had been established that ribbons of amorphous metals approximately 0.001" thick by 0.04" wide could be readily cast from alloys in the $\text{Fe}_{75-85}(\text{B},\text{Si})_{15-25}$ family. Compositions in this family hold the most promise for a good combination of properties and cost. Casting can be accomplished under a broad range of casting parameters centered around those shown in table I of section II. Experiments during this period were focused at two objectives: 1) Developing a method of patterning the wheel to produce flake material instead of continuous ribbon and 2) determining the effect of specific casting parameters on the ribbon and flake quality.

Wheel Patterning

Based on prior work at Battelle on melt extraction of crystalline alloys and prior work at General Electric on melt spinning of amorphous alloys it was known that segmented ribbons or fibers could be produced in the first case by putting notches or grooves into the casting wheel surface and in the second case by patterning non-wetting or low conductivity lines onto the casting wheel surface. Both of these approaches were explored in some detail during this period. A series of different inks and high temperature paints were applied to a copper casting wheel and many casting runs were made. This method did produce flake but two major problems were identified with this approach. First, for long casting runs the wear and deterioration of the lines were extensive enough to indicate that some replenishment system would be required for continuous production. This effect is illustrated in figure 1-2 where 150 grams of melt were ejected from 6 holes. A movie of this casting run showed that for approximately the first half of the run only individual flakes were produced but during the second half of the run many of the flakes did not separate from each other as a result of the deterioration of the lines.

The second and more serious problem associated with casting on an ink-lined wheel was the quality of the product. Figure 3 shows an example of typical flake. In almost all cases at least one end

of the flake is poorly formed and serrated. Additionally, from one to five percent of the product was small crystalline balls as shown in figure 4. Movies show that these balls have their origin in the splashing of small droplets of molten metal off the wheel which then solidify during free flight with a crystalline structure. It has been found during the course of this work that splashing is caused by any sharp geometric perturbations on the casting wheel even ink lines only 30 micro-inches high.

Simultaneous with this early exploratory investigation of ink lines a study was made of casting onto wheels with deep narrow slots cut into the surface. A slotted copper wheel was tried with slots from .010 inch to .030 inch wide across the wheel and .100 inch deep. Poor results were obtained with this design. The jet of molten metal from the nozzle entered the slots, froze and stuck there, leaving small "paddle wheel"-like protuberances which splattered the molten stream and produced very little flake of any uniform dimensions. This is shown in figure 5.

To overcome the problem of metal entering the slots and freezing, various materials were used to fill them. A ceramic cement and an epoxy cement were both tried with similar results. Although a smooth, well-bonded joint was obtained, sticking occurred at the seam between the filler and the copper with enough metal freezing there to again cause splashing of the molten stream. The ceramic filled slots are shown in figure 6.

It appeared that a metallurgical type bond would be necessary to prevent the molten stream from forcing its way into minute cracks and crevices. A copper wheel was constructed with small plates of .008 inch thick stainless steel soft soldered into .010 inch slots. It was believed that this would be the best bond that could be easily achieved and that the stainless steel might be enough of a barrier to separate the flake uniformly. Unfortunately, the soft solder proved to have too low a melting temperature for the run conditions. The solder was eroded easily by the molten jet stream, and sticking and splattering once more occurred as shown in figure 7.

In order to examine in more detail exactly how the molten stream and puddle interact with the lines on the wheel surface wide ribbons were cast from a 1/2 inch wide slot nozzle onto a wheel with various line patterns. In the first several casting runs these lines consisted of several different inks. Figure 8 shows the ribbon ends typically produced by the inks. The arrow in the picture points in the direction of wheel motion. The ink lines were about 50×10^{-6} inches high and about 15×10^{-3} inches wide. As can be seen the tail end is relatively well defined and uniform but the start end is serrated. Movies also showed that several small molten balls left the wheel at each line.

In the next series of runs the lines consisted of grooves scratched into the wheel surface with various sharp tools including a diamond stylus and a hardened steel stylus. Casting onto this wheel resulted in ribbon ends as shown in figures 9-11. The tail ends are again sharp and well defined, but the start ends are badly serrated. A large number of molten balls were thrown off from the wheel at each line. A typical profile of one of these scratches is shown in figure 12. It is 8.6×10^{-4} inches deep and 2×10^{-3} inches wide. However, it has shoulders which rise above the wheel surface about 1×10^{-3} inches and make a total width of 1×10^{-2} inches.

When these shoulders are polished off before casting, the profile of the same groove is shown in figure 13. If the entire wheel is polished with 600 grit paper prior to casting, the ribbon ends look like those shown in figures 14-16 which come from the same grooves as figures 9-11 before polishing. Figure 14 results from a groove that is slightly too deep and wide causing some unstable flow just after the groove passes the melt puddle. Figure 15 results from a groove which is slightly too shallow and narrow causing incomplete separation of the ribbon. Figure 16 is nearly ideal and is cast from the groove shown in figure 13.

Figure 17 shows a 10-1/2" aluminum bronze wheel with these grooves on the circumference which is shown more clearly in figure 18. As can be seen, the grooves on half of the circumference do not extend completely across the wheel. This is done so that when casting from a six hole nozzle one of the holes will produce long segments of ribbon for magnetic testing.

Using this approach of scratched grooves polished before casting, many casting runs were made with a relatively high yield of well defined and separated flake. However, frequently some crystalline balls were still produced and some flakes stuck to the wheel. In order to try to minimize this problem two further refinements of the processing were attempted and are still under development. First, the effect of filling the grooves with ink is being examined. From examination of the movies and the product made, this seems to decrease the tendency of the flake to stick to the wheel and the attendant molten metal splashing. Secondly, wheel wipers of various types are being evaluated to help remove stuck flake before they rotate around to the casting stream. This approach will be discussed in a later section.

Future work on wheel patterning will focus on optimizing the size and shape of the grooves and the method of making them. Additionally, some exploratory work will be done on evaluating wheels with shallow steps on the surface with a profile something like a very low pitched saw. Also flakes of various length, width and thickness will be made to determine the effect of these variables on the packing density and uniformity of composites and their magnetic properties.

Wheel Material

Three different materials have been used for casting wheels. Their compositions and properties are listed in table II. The copper wheel has the highest thermal conductivity, but its low hardness leads to relatively poor surface properties. This is manifest by its relatively rapid wear and pitting and difficulty in maintaining a smooth polished surface.

TABLE II
Wheel Materials

	Thermal Conductivity c.g.s. units	Hardness R _B
OFHC Copper	.93	30
1% Cr-Cu	.40	77
2Fe-7Al-91Cu	.16	84

Our experience with both the chrome-copper and aluminum-bronze wheels has been quite good. Their surfaces are easily maintained and are not easily damaged. It is also easy to make uniform grooves in their surfaces. The poorer thermal conductivity of the harder wheels might be expected to be a problem for continuous production. However, an analysis of the heat flow shows that the dominant thermal barrier is the heat transfer coefficient from the wheel to the cooling liquid and not the heat conduction through the wheel material. In fact at this time it has not been established what the steady state wheel surface temperature should be to achieve the best properties in the product. Other wheel materials such as beryllium-copper and MZC copper have a better compromise between their thermal and mechanical properties and may warrant investigation in the future.

It is not known whether the specific chemical composition of the wheel is of importance. In order for successful casting to be accomplished the molten metal must wet the wheel, but there should be no chemical reaction with or bonding to the wheel. All casting wheels have shown a visual track on their surfaces after casting. This track is more pronounced on copper wheels than on the alloy wheels. It is also more pronounced when casting at high ejection pressures and when casting at 90° to the wheel surface compared to lower inclination angles. Microscopic examination and profilometer traces of the wheel do not indicate any change or damage in the tracked region. It is thought that the track is merely a change of the characteristics of the surface oxide on the wheel which has little or no effect on the casting process.

Wheel Surface Finish

Several different surface finishes on the wheels have been examined for their effect on the flake and ribbon surface roughness, the tendency toward sticking and magnetic properties. The conditions examined have included 600 and 400 grit paper polishing in both the circumferential and axial direction, grit blasted surfaces and surfaces prepared by transverse rotation of wiper brushes made of stainless steel wire and Scotch Brite^R fibers. In general it was found that

ribbon and flake could be easily cast on all these surfaces except for the grit blasted condition where substantial molten metal splashing occurred. There did not seem to be any effect of the surface finish on flake sticking.

It was found that the smoother the wheel surface is then the smoother are the surfaces of the cast product. The surface of the ribbon or flake in contact with the wheel almost exactly replicates the wheel surface including all surface imperfections such as scratches, pits and surface roughness. Under low ambient pressure casting conditions the top surface is generally smooth, however major imperfections on the bottom surface are apparent on the top surface also. In order for the flake to flow easily into the die when forming a composite it is important that their edges and surfaces be relatively smooth. Also smooth surfaces should provide for better composite packing factors than rough flake.

As was expected from prior work, it was found that wheel surfaces with high roughness resulted in a product with high coercive forces. This was particularly true of the surface prepared with a stainless steel wire brush. High coercive forces will cause higher hysteresis losses. It is currently felt that the surfaces derived from a 400 or 600 grit polish are satisfactory.

Casting Atmosphere

Casting trials have been run in air at full atmospheric pressure and at a vacuum of about 5×10^{-2} torr and in nitrogen, helium and argon at pressures from 15 torr to atmospheric pressure. Both the pressure and the atmosphere composition have an effect on the casting process.

The first and most obvious effect is on the edge and surface characteristics of the cast product. When ribbon or flake is cast in atmospheric pressure of all gases except helium there is a deterioration in the surface roughness and the edge definition of the ribbon or flake. This effect is due to the gas boundary layer on the rapidly rotating casting wheel which perturbs the melt puddle on the wheel. Flake cast in nitrogen at atmospheric pressure is shown in figure 19. Flake cast under identical casting parameters except into a vacuum of 6×10^{-2} torr is shown in figure 20.

In addition to this air boundary layer effect there are other atmosphere effects on the casting process. In a nitrogen atmosphere the metal flow rate out of the nozzles is higher than in air, vacuum or helium indicating that the presence of nitrogen either causes a decrease in the surface tension between molten metal and the nozzle material relative to free surface tension of the melt or decreases the viscosity of the molten metal. As a result of the increased flow rate and its causing effect, ribbon and flake cast in nitrogen are generally wider than castings in other atmospheres under otherwise identical casting conditions. There may be other subtle effects on the physical or magnetic properties of nitrogen cast material which have not yet been determined. For example, nitrogen casting at high melt superheat temperatures seems to produce a more ductile product than low melt superheat temperatures. Further work is required to document and understand these effects.

Another effect of atmosphere is the residence time of the flake or ribbon on the casting wheel. When casting in a vacuum, the product generally departs from the wheel after less than an inch of surface travel. However, in gases at higher pressures the product will generally stay in contact with the wheel for several inches before breaking loose. Thus, under higher ambient pressure conditions the temperature of the product when it leaves the wheel will be lower and the quench rate from the melt temperature down to the departure temperature will be higher. If the ambient pressure is too high however, small bubbles of gas are trapped between the ribbon and the wheel. This is demonstrated by the presence of many microscopic crater-like depressions on the bottom surface of the ribbon. To the extent that the total area fraction of these bubbles increases, the heat transfer to the wheel will decrease and the quench rate will decrease. Thus, under ideal conditions there should be sufficient atmosphere present to increase the residence time on the wheel but not enough to cause significant gas entrapment under the wheel. At present it appears that about 15 torr of helium gas provides the best casting atmosphere. This atmosphere has the added benefit of further cooling of the product after departure from the wheel. Further work is required to determine the best atmosphere conditions for casting.

Gas Jet Hold Down

Another method of increasing the residence time on the wheel without the attendant negative effects of high ambient pressure perturbing the melt puddle and gas entrapment under the ribbon is the use of a high pressure gas jet directed to hold the product on the wheel. Several different designs of gas hold down are under evaluation. Observations of movies made during casting runs using these hold downs indicate that they are effective in increasing the time of contact of the product with the wheel. However, insufficient data is available to determine if this has a positive effect on the properties of the flake.

Casting Wheel Wipers

Not too infrequently small bits or even entire flakes of cast metal stick to the wheel. When this happens, the stuck piece will come entirely around on the next revolution of the wheel and pass under the melt puddle. This event causes molten balls to fly off the wheel and sometimes double casting to occur. If more than a very small percentage of this material is included in the final product, an unacceptably high hysteresis loss will result.

In order to minimize the sticking, various wiper brushes have been rotated against the casting wheel during several of the casting runs. Three types of wipers have been used including a stainless steel wire brush, a Scotch Brite abrasive fiber brush and a soft muslin buffer wheel. All of these have been effective in greatly reducing the wheel sticking. However, each presents its own problems. The stainless steel brush tends to roughen the wheel more than is desirable. The Scotch Brite brush tends to lose small abrasive particles which are difficult to separate from the flake product. The muslin wheel is sometimes not sufficiently effective in removing all of the stuck material. The product of a casting run using a Scotch Brite wiper is shown in figure 21. Further evaluation of wiper systems will be required.

Nozzle Design and Position

Nozzles for casting have been made from clear fused quartz. Tubes about one inch in diameter are pinched down at one end and holes

are drilled into the tube from the closed end. Usually six to eight holes are made in a line on 1/8" centers. These holes have varied from 0.020" to 0.040" in diameter. During casting, the ribbon or flake width and thickness are controlled by the wheel speed, ejection pressure, ejection angle and nozzle orifice diameter. The exact relationships are rather complex, but simplified, the thickness increases with decreasing wheel speed and the width increases with increasing orifice diameter and ejection pressure. Decreasing the ejection angle to a lower inclination to the wheel than 90° decreases the puddle turbulence and likelihood of instability. Increasing the nozzle distance from the wheel increases the instability. In general the exact conditions are found to be relatively unimportant except for determining the product dimensions. In order to make flake wider than about .060" it is better to use a slot nozzle orifice instead of a round hole. Methods for making nozzles with short slots are being explored.

Detailed Casting Conditions

Table III lists processing conditions for the casting runs made during this period. A key to the column heading follows:

Atmosphere composition	- either Air, Helium, Nitrogen or Argon
Atmosphere pressure	- measured in torr
Crucible size	- 6 x .025 means 6 holes each .025 inches in diameter
Angle	- is the angle between the nozzle axis and the wheel tangent
Distance	- is the distance in inches between the nozzle and wheel
Wheel finish	- 600 means polished with 600 paper circumferentially - 600X means polished with 600 paper axially
Pattern	- is a code of what method was used to pattern the wheel for making flake
Speed	- given in rpm, all wheels were approximately 10 inches in diameter

Ejection pressure	- is the pressure used to eject the melt measured in psi above the pressure of the casting atmosphere
Temp	- is the temperature of the melt in degrees centigrade
Thickness	- is the average thickness of the good product made measured in mils
Wiper	- is a code for the types of wiper wheel used
Sample type	- is the type of sample used in the magnetic tests. R = ribbon, F = flakes
As Cast	- are the properties before any anneal
Annealed	- are the properties after an anneal at 320°C for two hours in an inert atmosphere
H _c	- is the coercive force in oersteds after driving to one oersted
B ₁	- is the flux density in kilogauss achieved in a d.c. field of one oersted, reported for ribbon only
Comments	- codes for specific comments about the casting run
F1, P1, W1, C1 etc.	- are codes which are described at the bottom of the table.

TABLE IIIa - Flake & Ribbon Casting - Copper Wheel

Run #	Atmosphere		Size	Crucible		Finish	Wheel Pattern	Speed rpm	Ejection		Product Thick. (.001")	Wiper Type	Hold Down Type	Sample Type	Magnetics				Comments
	Comp.	Pressure (torr)		Angle	Distance				Press. (psi)	Temp. (°C)					As Cast	As Cast	Annealed	Annealed	
1109781	Air	.06	6x.025"	75°	.15	600	P1	3000	4.5	1250	1.3	None	None						
1110781	"	.12	"	80	.20	F1	"	"	4	"	1.3	"	"						C1
1110782	"	"	"	90	"	600	P2	"	"	"	1.3	"	"						C1,C2
1113782	"	.06	"	"	"	F1	"	"	3	1250	"	"	"						C1,C4
1113784	"	.09	"	"	"	600	"	"	"	"	1.9	"	"						C3
1114781	"	.08	"	"	"	"	"	"	"	"	"	"	"						C1,C4
1114782	"	"	"	70	.07	600X	None	"	"	"	1.1	"	"						C3
1115781	"	.06	"	"	"	"	"	"	"	"	1.0	"	"	R	.143	6.4	.16	4.2	
1115782	"	"	"	"	"	"	P2	"	"	"	1.0	"	"						
1115783	"	"	"	"	"	"	"	"	"	"	1.3	"	"						C1,C2,C4,C5
1115784	"	"	"	"	"	"	"	"	8	"	1.1	"	"						C1,C4
1115785	"	.05	"	"	"	"	"	"	15	"	1.3	"	"						C1,C2,C4,C5
1113781	"	760	6x.030	90	.20	600	P2	"	4	1350	2.0	"	"	F	.66		1.1		C1,C2,C4,C5
030979W2	"	"	6x.040	80	.10	"	P4	2000	2	1270	1.4	W1	"						C4
030979W3	"	"	"	"	"	"	"	"	2.4	1165	1.5	"	"						
030979W4	"	"	"	"	.05	"	"	"	"	1270	1.2	"	"						
031279W1	"	"	"	"	.025	"	"	"	2	1285	1.3	"	"						
031279W2	"	"	6x.030	"	.20	"	"	"	"	1265	1.6	"	"						
031979W1	"	"	"	90	"	"	None	"	3	1270	1.2	"	"	R	.106	6.1	.043	12.2	
031979W2	"	"	"	"	"	"	"	"	"	1245	1.7	"	"	R	.12	5.4	.050	12.5	
031979W3	"	"	"	"	.05	"	"	"	"	1270	1.3	"	"	R	.012	11.1	.031	12.9	
1204782	"	"	6x.025	70	.014	"	P4	2700	5	1300	2.5	None	H1						C2,C5,C4

P1 - Mars Staetder 745 ink lines
 P2 - Rapidograph 3072 GLD ink lines
 P3 - Shallow polished grooves
 P4 - " " " , ink filled
 P5 - Shallow grooves unpolished
 P6 - Deep grooves polished
 P7 - " " " , ink filled
 P8 - Deep grooves unpolished
 P9 - Angled groove polished
 P10 - " " " , ink filled

F1 - Not repolished after previous run
 F2 - Lathe turned
 W1 - Muslin wiper
 W2 - Scotch Brite Wiper
 W3 - Nylon wiper

C1 - Molten balls splashing from lines
 C2 - Some flake sticking
 C3 - Melt did not wet wheel
 C4 - Significant fraction of product brittle
 C5 - Some double cast product
 C6 - Flake did not separate
 C7 - Crucible broke
 C8 - Bad edges on product
 C9 - Serrated ends

H1 - Slot hold down
 H2 - Multiple hole hold down

TABLE IIIb - Flake & Ribbon Casting - Aluminum Bronze Wheel

Run #	Atmosphere		Size	Crucible		Finish	Wheel Pattern	Speed rpm	Ejection		Product Thick. (.001")	Wiper Type	Hold Down Type	Sample Type	Magnetics				Comments
	Comp.	Pressure (torr)		Angle	Distance				Press. (psi)	Temp. (°C)					As Cast H _c	B ₁	Annealed H _c	B ₁	
1208781	Air	.06	6x.025	90	.014	600	P3	2000	3.5	1250	1.1	None	None						C6,C4
1208783	"	.08	"	"	"	"	"	"	3	"	1.1	"	H1						C2,C5,C7,C4
1211781	"	.05	"	"	.040	"	P4	"	"	"	1.1	"	None						C1,C4
1211782	"	.04	"	"	.030	F1	"	"	"	"	1.2	"	"						C1,C2,C4,C5
1211783	"	.05	"	"	.040	600	P3	"	"	"	1.1	"	"						C1,C4
1211784	"	.05	"	"	"	600X	"	"	"	"	1.1	"	H1						C1,C2,C4
1211785	"	.05	"	"	"	600	"	"	"	"	1.2	"	H2						C1
1211786	"	.04	"	"	"	"	"	"	"	"	1.1	"	"						C2,C5,C4
1214781	"	.12	"	"	"	"	"	"	"	1200	1.3	"	None	R	.022	7.7	.028	11.4	
1214782	"	.10	"	"	"	"	"	"	"	1250	1.1	"	"						C2
1214783	"	.13	"	"	"	"	"	"	"	1300	1.1	"	"						
1214784	"	.08	"	"	"	"	"	"	"	1350	1.0	"	"						
1214785	"	.08	"	"	"	"	"	"	"	1400	1.0	"	"	R	.096	8.6	.105	9.1	C2,C5
1214786	"	.08	"	"	"	"	"	"	"	1200	1.0	"	"	R	.050	8.5	.032	11.1	
0115791	"	.06	3-1/8x.010	"	.025	"	P3	2100	"	1250	1.2	"	"	R	.044	9.1	.035	9.9	C6
0116791	"	"	"	"	.040	"	"	"	2.5	"	1.6	"	"	R	.058	8.5	.053	15.3	C6
0116792	"	"	"	"	.014	"	"	"	3	"	1.2	"	"	R	.030	9.5	.057	15.2	C5
0118791	"	"	"	"	.040	"	"	3000	"	"	1.1	"	"	R	.065	9.1	.070	12.8	C4
0117792	"	"	6x.025	"	"	"	"	2100	"	"	1.0	"	"	R	.050	8.5	.052	14.4	C2,C5,C6
0117793	"	"	"	"	"	"	"	2500	2.5	"	1.0	"	"	R	.070	8.5	.060	13.8	
0118793	"	.05	"	"	"	"	"	2100	3	1350	1.0	"	"	R	.055	9.1	.045	13.2	C1,C2,C4
0118794	"	"	"	"	.014	"	"	"	"	1250	1.0	"	"	R	.055	9.4	.060	13.6	C2,C6,C4
0119791	"	"	"	"	.20	"	"	"	"	"	1.1	"	"	R	.045	8.2	.044	15.4	C2,C6,C4
1212786	"	.06	"	"	.040	"	"	2000	"	1350	1.0	"	"	F	.06		.062		C2
0123791	"	"	6x.020	"	"	"	P6	2100	"	1250	1.0	W1	"	R	.055	9.3	.062	13.7	C1,C4
0123792	"	"	"	"	"	"	"	"	"	"	1.1	None	"	R	.049	8.0	.042	14.3	C1,C2,C5,C4
0123793	"	"	"	"	"	"	"	"	"	"	1.1	W1	"	R	.064	9.7	.074	12.5	C3,C1,C4
0123794	"	"	"	"	"	"	"	"	"	"	1.0	W2	"	R	.052	9.3	.045	15.1	C6
0123795	"	"	"	70	"	"	"	"	"	"	1.2	"	"	R	.066	8.5	.045	14.3	C6
0124791	"	"	"	90	"	"	P7	"	"	"	1.0	None	"	R	.037	8.3	.053	12.4	
0124792	"	"	"	"	"	"	"	"	"	"	1.0	"	H2	F	.06		.047		

TABLE IIIC - Flake & Ribbon Casting - Aluminum Bronze Wheel

Run #	Atmosphere		Size	Crucible Angle	Distance	Finish	Wheel Pattern	Speed rpm	Ejection		Product Thick. (.001")	Wiper Type	Hold Down Type	Sample Type	Magnetics				Comments
	Comp.	Pressure (torr)							Press. (psi)	Temp. (°C)					As Cast H _c	B ₁	Annealed H _c	B ₁	
1212781	N ₂	745	6x.025	90	.040	600	P3	2000	3	1250	1.0	None	None	F	.11		.052		C1,C4,C8
1212782	"	"	"	"	"	"	"	"	"	1350	1.0	"	"	F	.13		.16		C1,C8
1212783	"	"	"	"	"	"	"	"	"	"	0.9	"	"	F	.05		.015		C1,C8
1212784	"	"	"	"	"	"	"	"	"	1250	1.0	"	"	F	.10		.09		C1,C4,C8
1212785	"	320	"	"	"	"	"	"	11	1350	1.0	"	"	F	.016		.057		C1,C2,C5,C7,C8
1218781	"	745	"	"	"	"	"	"	3	1200	1.0	"	"	R	.083	5.4	.053	10.3	C8
1218782	"	"	"	"	"	"	"	"	"	1300	0.9	"	"	R	.047	8.4	.057	13.4	C8
1218783	"	"	"	"	"	"	"	"	"	1400	1.0	"	"	R	.038	8.8	.075	14.2	C8
1218784	"	"	"	"	"	"	"	"	5	1300	1.1	"	"	R	.036	9.9	.053	13.9	C8
0118792	"	15	6x.020	70	"	"	P4	2100	3	1350	1.1	"	"	F	.065		.060		C8
														R	.092	6.7	.077	12.7	
0206793	"	"	"	"	"	"	"	2500	14	1250	1.4	"	"	F	.035		.045		
0212791	"	"	"	"	"	"	"	"	3	1250		"	"	F	.07		.06		C4
1220781	He	745	6x.025	90	"	"	P3	2000	3	1300	0.8	"	"						
0124793	"	15	6x.020	"	"	"	P7	2100	"	1250	0.9	"	H2	F	.065		.035		
0125791	"	"	"	"	"	"	"	"	"	"		"	H2	F	.055		.042		C1,C2
0125792	"	"	"	"	"	"	"	"	"	"		"	"						C4
0126791	"	"	"	"	"	"	"	"	"	"	1.1	"	"	F	.065		.052		C2,C4,C5
0126792	"	"	"	"	"	"	"	"	"	"	1.1	"	"	F	.055		.050		
0126793	"	"	"	"	"	"	"	"	"	"	1.1	"	"						C2,C5
0201791	"	"	"	"	"	"	"	"	"	"	1.1	W2	None	F	.052		.080		
0202791	"	"	"	"	"	"	"	"	"	"		W3	"	F	.055		.052		
0321791	"	"	"	"	"	"	P9	"	"	"		None	"						C1,C2,C4,C5
0321792	"	"	"	"	"	"	P10	"	"	"	1.2	"	"	R	.06	9.1	.042	13.2	C1
														F	.045		.035		
1218785	Argon	745	"	"	"	"	P3	2000	"	1300	1.0	"	"	R	.041	9.1	.062	12.7	C8

TABLE IIId - Flake & Ribbon Casting - Chrome-Copper Wheel

Run #	Atmosphere		Size	Crucible		Finish	Wheel Pattern	Speed rpm	Ejection		Product Thick. (.001")	Wiper Type	Hold Down Type	Sample Type	Magnetics				Comments
	Comp.	Pressure (torr)		Angle	Distance				Press. (psi)	Temp. (°C)					As Cast	As Cast	Annealed	Annealed	
															H _c	B ₁	H _c	B ₁	
1116781	Air	.05	6x.025	75	.040	600	None	3000	8	1250	1.0	None	None	R	.099	10.0	.058	7.0	C1,C2,C4,C5
1117781	"	"	"	"	"	"	P2	"	"	"	"	"	"	"	"	"	"	"	"
1117783	"	"	.5x.007	"	"	"	"	2000	5	"	1.0	"	"	"	"	"	"	"	C9
1117784	"	"	"	"	"	"	"	1500	2.5	"	1.9	"	"	"	"	"	"	"	C9
1117785	"	"	"	"	"	"	"	2000	5	"	1.0	"	"	"	"	"	"	"	C9
1117786	"	"	6x.025	90	.025	"	"	"	"	"	1.1	"	"	"	"	"	"	"	"
1121785	"	"	.5x.007	"	.014	"	"	"	8	"	1.0	"	"	"	"	"	"	"	C9
1121786	"	"	"	"	"	"	"	"	5	"	0.8	"	"	"	"	"	"	"	C9
1128781	"	"	"	"	"	"	P5,P8	"	"	"	0.8	"	"	"	"	"	"	"	C9
1128782	"	"	"	"	"	"	P5,P8	"	"	"	0.8	"	"	"	"	"	"	"	C9
1129781	"	"	"	"	"	"	P3,P6	"	"	"	0.8	"	"	"	"	"	"	"	C9
1220782	"	.03	6x.025	"	.040	"	P3	"	3	1300	1.3	"	"	R	.070	7.6	.066	13.9	C6,C2
1220783	"	.05	"	"	.030	"	"	2200	3	1250	1.0	"	"	R	.074	7.3	.095	13.0	C2,C5
1220784	"	.05	.5x.008	"	.014	"	"	2100	5	"	1.1	"	"	"	"	"	"	"	"
1221781	"	"	5x.020	"	.040	"	"	"	3	"	1.1	"	"	R	.091	6.8	.104	13.1	C2,C5
1221782	"	.09	"	"	.014	"	"	2150	"	"	1.1	"	"	R	.12	6.3	.095	13.4	C2,C5
1221783	"	.05	"	70	.040	"	"	"	"	"	1.2	"	"	R	.072	6.8	.107	12.2	C2,C5
1221784	"	"	"	90	"	600X	"	2500	"	"	1.0	"	"	F	.13	"	.23	"	C2,C5
1221785	"	"	.5x.008	"	"	600	"	2500	"	"	1.0	"	"	"	"	"	"	"	"
0222793	"	"	6x.025	"	"	"	None	2100	"	"	1.1	"	"	"	"	"	"	"	"
0221791	He	15	"	"	"	F2	"	"	"	"	1.0	"	"	R	.12	5.1	.052	11.6	C2
0222791	"	"	"	"	"	600	"	"	"	"	1.1	"	"	R	.13	3.9	.21	8.7	C2
0222792	"	"	"	"	"	"	"	"	"	"	1.2	"	"	R	.065	6.6	.082	16.5	"
0222794	"	"	"	70	"	"	"	2500	14	"	1.1	"	"	R	.098	7.1	.20	9.7	"
0223791	N ₂	"	"	"	"	"	"	"	"	"	1.1	"	"	R	.092	8.6	.17	11.7	C2
0227792	"	"	"	"	"	"	"	2000	"	"	1.2	"	"	R	.117	5.0	.17	10.1	C2

II.22 Results - Magnetic and Physical Properties Assessment

The end product of the project is a formable composite magnetic material. The usefulness of the product will depend upon its magnetic characteristics. Therefore, once the ability to make flake has been established, magnetic measurements are used as the major feedback for further process development and optimization. To minimize expenditure of labor, the measurements made in this task have been selected to give the critical information on a fast turn around basis. More detailed engineering magnetic characterization will not be done until task V is started and the processes are near optimization.

The basic samples made on this program are narrow continuous ribbons, narrow flakes of various lengths and pressed and compacted flake. To meet the objective of minimizing labor and turn around time, the samples are measured in the geometry in which they are cast, reducing sample preparation time. Samples are taken from the total product formed in a casting run on a random basis. Physically poor samples, e.g., lacy, brittle, rough edges, are not selected as the purpose of the measurement is not to obtain data on the total distribution of properties during a run but to determine the better properties a run is capable of producing. For narrow ribbon, 4 pieces each 16" long are selected and sealed in an evacuated glass tube. The selection of 4 samples helps to minimize the probability of measuring a small volume in a single sample of atypical properties. Sixteen inch lengths are chosen to keep demagnetizing fields low, approximately 0.2 oersted for high quality amorphous metal in this range of dimensions. The less than 0.5 oersted demagnetizing field allows simple determination of induction at one oersted.

When spherical particles are part of the cast flake product, they are not included in the sample to be measured as they are invariably crystalline, of poor magnetic quality and will not be a significant fraction of the finally optimized casting process. Removal of the balls is accomplished by vibration and separation through settling or double sieving. The flake is then loaded into a glass tube with the aid of a simple funnel and tweezers. Packing is accomplished

by simple acceleration forces. The tube is then evacuated and sealed. Since packing density of such a sample will generally be below 10%, magnetic measurements have evolved which tolerate low densities.

During several process runs, both flake and ribbon were formed by marking the wheel around only part of its periphery. Thus, both ribbon and flake are made during one run. This allows a comparison of properties when flake and ribbon are cast under identical conditions. Such measurements are used to determine any degradation of properties of flake properties due to end effects such as geometric irregularities or partial crystallinity.

Dies for flake compaction and bonding were dimensioned to accomodate press limitations as well as magnetic measurements. Properties of both bars and small toroids can be evaluated.

Measuring equipment for d.c. hysteresis loops consists of a pair of 24" long x 1-3/8" I.D. cylindrical coils capable of operating to 500 oersted and a pair of companion pick up coils, each with 3100 turns over the center 1/2" of length with a one inch I.D. The two excitation coils are connected in series-aiding while the two pick-up coils are connected opposing. With an adjustment for area balance, this type of connection eliminates air flux and allows for the exact determination of induction. The two solenoids are placed at right angles to each other and some distance apart to minimize mutual interactions. A further refinement is a set of 3 mutually orthogonal pairs of coils in the form of a two foot cube which are excited to buck out the earth's field at the sample measuring location. A schematic circuit diagram of this system is shown in figure 21c.

Samples are measured in the as cast state and then annealed and remeasured. To calibrate for flux density, the cross sectional area of the sample must be known. To determine this, the physical density of the particular composition is accurately determined. The average cross sectional area of the samples is then obtained by weighing the sample and dividing the weight by the density and length of the ribbon. This method of determining area is more accurate than mechanical measurements when sample dimensions are small and surfaces may not be smooth and parallel.

To quickly evaluate samples, three d.c. hysteresis loops are taken at maximum fields of one, ten and 100 oersteds on straight ribbon samples and one, ten and 500 oersted on flake samples. The one oersted loop gives an accurate measure of coercivity which is proportional to losses and for ribbon the value of B at one oersted is inversely proportional to the excitation required in a device. This is also true for compacted flake.

The 10 oersted loop is drawn to see if the coercivity as determined at one oersted is essentially the saturated coercivity. The value of B at 10 oersted also gives an accurate measure of the approach to saturation and the general hysteresis loop shape is an indication of properties as they might be used in a motor. The 100 oersted loop shows approach to saturation and also a saturation value. If this value is significantly different from intrinsic values determined for this material by other means, the sample may not have a uniform cross sectional area. Since the method used to determine cross sectional area gives an average area, this may vary locally giving rise to apparent variations in saturation flux density. To circumvent this problem, if the 100 oersted loop appears to have reached saturation, the data taken for B at one and ten oersted can be ratioed. In fact, the ratio of B at one oersted to B at 100 oersted is a more convenient means of evaluating excitation requirements for this material in a practical device.

Since losses and excitation are the most significant properties in applying this material, a quality factor has been developed which evaluates the material by combining both. This quality factor is

$$Q = \frac{B_1}{B_{SAT} \times F(H_C)} .$$

The value of B at one oersted compared to the saturation value will be high and increase Q when low excitation is required. Since coercive forces as low as .005 and as high as several oersted have been observed, a factor to cover ranges of coercivity has been selected. A low value of F, implying low losses, will also increase Q.

<u>F(H_C)</u>	<u>H_C</u>
1	<.03
1.1	.03<H _C <.05
1.2	.05<H _C <.07
1.3	.07<H _C <.1
1.4	.1 <H _C <.15
1.5	H _C >.15

A value of Q below .65 for narrow ribbon material in flake form will probably not be competitive with present magnetic material. With loosely packed flake a flux measurement indicative of the excitation requirements cannot be made. In this case the only meaningful measurement that can be made is the coercivity. This value, however, is a screening test to indicate the quality of the casting run. In all cases, measurements are taken in the as-cast condition and compared with the annealed data.

Initially, many samples were annealed both with and without magnetic fields. The effect of magnetic annealing was not significant in early phases of process development and has since been eliminated. A recheck of its effect will be done as part of process optimization.

Figure 22 is a typical set of 3 hysteresis loops on narrow ribbon in the as cast condition, and figure 23 is the same sample after a stress relief anneal at 330°C for 2 hours. The steps in the sides of the loop in the annealed condition are due to the 4 separate samples reversing magnetization at slightly different fields. Note the increase in the sharpness of the knee of the 100 oersted curve after anneal.

Figure 24 and 26 are loops taken on as cast flake and ribbon segments cast on the same run. This confirms that identical magnetic properties can be obtained with flake and ribbon. The shearing of the loop obvious with the flake sample is due to the demagnetizing field generated by the short, loosely packed flake samples. Figures 25 and 27 are the same samples in the annealed condition.

Magnetic properties of flake and ribbon cast at the same time are not always the same, as is shown in figures 28 and 30. Figure 28 shows

the loop for flake. When the sample is driven to high fields, a "cobra head" hysteresis loop results. The characteristic of this type of loop is a wider width at the knee of the loop than at zero field. This is characteristic of a composite sample made up of some magnetically soft material and some magnetically hard material. To examine the origin of this hysteresis loop in more detail, several individual flakes from this casting run were measured one at a time in a vibrating sample magnetometer. Figure 32, curve A shows a hysteresis loop from this measurement on one of the flakes. This flake which is typical of most of the flakes from the total casting run product has the characteristic of being very smooth and uniform and highly ductile. The magnetic curve shows that this is good soft magnetic material with a very low coercive force and high permeability typical of a flake which is 100% amorphous.

Figure 32, curve B shows the vibrating sample hysteresis loops of another flake from the same casting run. This flake which is shown in figure 33 is typical of a significant but smaller fraction of flake from this casting run. It is poorly formed, brittle and probably 100% crystalline. The hysteresis loop curve B shows that this is hard magnetic material with a coercive force of 36 oersteds. These results demonstrate that the "cobra head" loop of figure 28 results from the sample containing two different kinds of flake. Some are good, magnetically soft amorphous flake and some are bad, magnetically hard crystalline flake.

Figure 34 is a hysteresis loop of the same sample of figure 28 after having been driven to 500 oersted. The zero offset between applied and internal field confirms that there is a source of field internal to the sample which did not change when subjected to an externally applied reverse field of 10 oersted.

Comparing figures 28 as cast and 29 annealed, the value of B reached at any field is higher, and the low field coercivity is lower after anneal. Both of these are to be expected due to the relaxation of strains by the anneal. The cobra head did not change as the anneal time and temperature were too low to substantially increase the amount of crystallization.

Figures 30 and 31 loops on ribbon made at the same time as flakes of figures 28 and 29 do not give any indication of crystallized material. Hence, there is no cobra head loop. The steps in the side of the loops at low field are again the property of the separate ribbons of the sample.

Figures 35 and 36 are hysteresis loops taken on samples of compacted flake. The samples were made as part of the program to develop a process for compacting and bonding and were made from flake selected for physical rather than magnetic properties. The loops were drawn principally to check out our measuring technique. It is interesting to note that in figure 35 the coercivity is reasonable, a factor of 4 better than common iron. Also, both samples show the cobra head loop suggesting the partial crystallinity of the material. A photograph of one of these bars appears in figure 39.

II.23 Results - Forming of the Composite

The objective of this task is to identify a suitable binder which can be used to fabricate amorphous metal flake composites. Many classes of materials are available which can be used as adhesives for metal substrates, for example epoxies, cyanoacrylates and polyimides. Our initial efforts concentrated on the use of epoxy resins as these readily available materials offer a range of formulations¹⁻² that would be useful for studying fabrication techniques. Epoxies, however, do not offer the solution to long range objectives of the program, which require a high temperature resin, preferably capable of enduring a 300°C annealing treatment after composite formation.

Although epoxies are lacking in high temperature capabilities, they are generally recognized as having good overall adhesion performance on many substrates, especially in its adherence to metal substrates.³

Metal flake composites have not received much attention in structural applications,⁴ but are generally used as automotive finishes, maintenance paints and decorative coatings. The objective of this program is to fabricate a high metal density composite which will retain a rigid structure after composite formation. Thus the task is to adhere amorphous metal flakes which have very high strength and thus a springy character. The adhesive chosen must be able to overcome this resiliency, yet be used in a minimum quantity since a high metal fraction is needed for optimum magnetic properties. The result is that the composite fabricator is dealing with glue lines thinner than recommended for maximum adhesion.

Studies of Metglas^{R*}, an amorphous metal ribbon, in a plastic matrix have been reported by Goldwasser⁵ for use in structural applications. This is not directly related to flake composite formation but this work gave metal densities of ~40% and also mentioned the problems of adhesion of the Metglas^R material.

*Trademark of Allied Chemical Co.

Epoxies

Epoxy formulations can be varied on the basis of many different epoxy type polymers and curing agents as well as through the use of flexibilizers, diluents, and fillers. Listed in table IV are several epoxides that were used to study the fabrication of amorphous metal composites. This list is not intended to be a comprehensive tabulation; many more epoxy resins can be used to fabricate composites. An attractive epoxy resin to start with is derived from the reaction of Bisphenol A and epichlorohydrin and is the resin of choice for our studies. One such epoxide is Epon 828 (I)* and it is used in this study because it is widely recommended for its adhesive performance. DEN 431 (II) is an epoxy novolac resin which can produce tightly crosslinked cured systems with good elevated temperature performance and adhesion. DER 736 (III) is used as a flexibilizing agent and it can also act as a diluent for the more viscous EPON 828. DER 736 is a polyglycol diepoxide.

TABLE IV

<u>Epoxide</u>	<u>Manufacturer</u>	<u>Viscosity (CPS @ 25°C)</u>	<u>EEW^a</u>
Epon 828	Shell	10,000-16,000	185-192
DEN 431	Dow	1100-1700 ^b	172-179
DER 736	Dow	30-60	175-205

a. epoxy equivalent weight

b. @ 52°C

Curing Agents

Many curing agents are available to catalyze the crosslinking of epoxy resins; some of which are listed in table V. As a general rule, aliphatic amines (IV) and polyamides (V) cure under mild curing conditions and give only moderate strength at elevated temperatures. Aromatic amines (VI) are more difficult to react but give better elevated temperature strengths. Anhydrides (VII) give fair overall properties and are used when amines are incompatible with certain substrates. Latent curing systems such as Boron trifluoride monoethylamine (BF₃MEA) and dicyandiamide (DICY) were not used as these are slightly inferior to aromatic amines in bonding performance.

*Structural formulas are shown at the end of this section.

TABLE V

<u>Curing Agent</u>	<u>Type</u>	<u>Curing Temperature Range</u>
TETA	aliphatic amine	15-150°C
V-40	polyamide	15-150°C
MDA	aromatic diamine	60-200°C
NMA	anhydride	80-260°C

Preparation of Compactionsa. Discs

A 1 inch circular die was chosen because this requires a relatively small quantity of flake. Amorphous metal flake (.560x.026x.0011 inches) was added to the die and then impregnated with a low viscosity epoxy resin. The impregnation of the flake cluster in the die could be affected in several ways; either by dropwise addition of the resin at different stages of the flake loading or by saturation of the flake cluster by filling the mold cavity with resin. The excess resin was removed during compression of the die contents.

Our initial compactions were made with an epoxy blend of Epon 828 and DER 736 (70/30). This was done to reduce the viscosity of the epoxy resin so that good impregnation could be obtained. Table VI shows the effect of pressure during compaction using the Epon 828/DER 736 (70/30) epoxy resin cured with an aliphatic amine curing agent (TETA).

TABLE VI

<u>Pressure Effect</u>			
Epoxy Curing Agent Cure	Epon 828/DER 736 (70/30) TETA (13 phr) 95°C/90 minutes		
<u>#</u>	<u>PSI</u>	<u>Packing Factor (%)^a</u>	<u>Flake</u>
11496-78-4	141,000	48	12/11/78-4
11496-77-3	128,000	48	"
11496-79-5	45,000	48	"
11496-82-9	16,000	49	12/11/78-2

a. Vol Metal/Vol sample X 100
Vol sample - avg. of 5 thickness measurements

For this system, pressure changes from 16,000-140,000 psi appeared to have little effect on the packing factor at constant cure time and temperature. The relatively low packing factor is the result of the composite's relaxation as soon as the pressure is released and the sample is taken from the mold. Amorphous metal flakes of this type are sufficiently resilient to spring back regardless of the adhesive present. From these experiments it became apparent that this binder system was not strong enough to retain the springy nature of the amorphous flake. Discs produced from these trials showed internal delamination as well as poor homogeneity in dispersion of the flake. Figure 37 of sample 11496-79-5 gives clear evidence of this internal delamination. Packing inhomogeneity is clearly evidenced by the radiograph of sample 11496-78-4, shown in figure 38. Despite the apparent disadvantage of using this circular die with regard to uniform flake loading, we continued to make samples as this was a convenient mold for screening resins.

Referring to table VI, calculations showed that since ~48% by volume of the disc was metal, there was between 10-20% by volume of residual resin, leaving 42-32% of voids or air gaps in the sample.

A vacuum impregnation apparatus was devised to remove air which could become entrapped in the sample. The device consisted of a vacuum desiccator which was modified to adapt a pressure equilibrated addition funnel in its cover. The mold, filled with flake, was placed in the desiccator and the resin added to the addition funnel. A vacuum was applied to remove air in the chamber as well as to degas the resin. During degassing the resin was heated gently. It was subsequently added, saturating the flake before the vacuum was released. Next, the plunger was set in place and excess resin was squeezed out during compaction and before cure.

Table VII illustrates the advantage of vacuum impregnation. Sample 77-3 was made without evacuation and yielded a packing factor of 48% while a similar compaction (sample 94-13) prepared with vacuum impregnation yielded a packing factor of 59%.

TABLE VII
Effect of Vacuum Impregnation

#	Epoxy	Curing Agent	Cure	KPSI	Packing Factor (%)	VI*
11496-77-3	70% Epon 828 30% Der 736	TETA (13phr)	95°/60'	128	48	No
11496-94-13	" " "	"	"	100	59	Yes
11496-107-20	Epon 828	MDA (29phr)	125°/60' + 175°/120'	100	51	No
11496-106-18	Epon 828	"	"	"	67	Yes

* VI = Vacuum Impregnation

Epon 828 without flexibilizer and an aromatic amine as curing agent (MDA) turned out to be a better performing binder. The higher viscosity of this formulation did not seem to prevent complete impregnation of the cluster of amorphous metal flakes.

Sample 107-20 is an example of this formulation applied without vacuum impregnation, and sample 106-18 was made with the vacuum technique. An important question in the compaction work is the determination of the maximum obtainable packing factor. Experimental compaction studies without the use of a binder indicate that the amorphous metal flakes can be compacted to a maximum of ~87% under pressure. Addition of the binder reduces this maximum compaction, under pressure, to ~78%. These numbers were generated under pressure of 50,000 PSI and indicate maximum packing factors that might be expected. Various parameters should be investigated such as shape of the mold, size of the flake, alignment of flake, packing homogeneity, molding temperature and pressure, etc. to find experimental maximums.

Another important feature in obtaining maximum packing factor is the shape of the flake. All of the data mentioned thus far in this report were obtained with flake ~9/16" long.

Preliminary results using 3/8" flake seem to show a decrease in the packing factor for the shorter flake. As seen in table VIII the 3/8"

flake gives packing factors slightly lower than the longer flake when compared in compactions containing identical resin systems. The use of the best epoxy system with vacuum impregnation yielded a sample with a packing factor of ~59%. These results are preliminary and further work must be done to identify the role of flake dimension with regard to the packing factor.

TABLE VIII
Effect of Flake Size 3/8" Length

<u>Sample #</u>	<u>Pressure PSI</u>	<u>Packing Factor (%)</u>	<u>Epoxy-Curing Agent</u>	<u>VI*</u>
11496-91-12	100,000	49.0	Epon 828/DER736 - TETA	No
11496-98-15	100,000	52.5	Epon 828/DER736 - TETA	Yes
11496-111-23	100,000	59.0	Epon 828-MDA	Yes

*Vacuum Impregnation

As mentioned previously, the 1" circular mold was used as a screening device to study various resin formulation and techniques. Tabulated in Table IX are epoxies and curing agents used for compaction studies and the results obtained.

TABLE IX
Epoxy Formulations

<u>Sample #</u>	<u>Epoxy</u>	<u>Curing Agent</u>	<u>Packing Factor (%)</u>	<u>VI*</u>
11496-77-3	Epon 828/DER 736 70/30	TETA (13phr)	48	No
11496-102-2	Epon 828/DER 736 70/30	V-40 (33phr)	55	No
11496-81-8	Epon 828/DER 736 85/15	TETA (13phr)	51	No
11496-90-11	Epon 828	V-40 (33phr)	51	No
11496-106-18	Epon 828	MDA (29phr)	67	Yes
11496-107-19	Epon 828	NMA (90phr)	40	Yes
11496-107-21	DEN 431	MDA (28phr)	56	Yes
11496-85-10	DER 736	TETA (13phr)	~10	No

*Vacuum Impregnation

b. Rectangular Bars

Several larger scale compactions (i.e. 20g) were made in a rectangular mold (5" x 1/2"). Our initial attempt (11496-69-2) early in the program yielded a sample with a 45% packing factor. The only rectangular sample made to date on a large scale using the best formulation and technique gave a packing factor of 57.5%. Data for these samples are listed in Table X. This bar is shown in figure 39.

TABLE X
Rectangular Bar Compactions (5" x 1/2")

<u>Sample #</u>	<u>Flake^a Length</u>	<u>Epoxy</u>	<u>Curing Agent</u>	<u>PSI</u>	<u>Packing Factor (%)</u>	<u>VI^c</u>
11496-69-2	9/16"	Epon 828/BGE	TETA (13phr)	34,000	45	No
11496-112	3/8"	Epon 828	MDA (29phr)	84,000	57.5	Yes

- a. width and thickness are fairly constant
- b. BGE-Butyl glycidyl ether (30%bw)
- c. Vacuum Impregnation

These samples were submitted for magnetic measurement and are discussed in section II.22 of the report.

Future Work

Further studies need to be done to determine the effect of flake alignment and size to obtain the highest and most uniform packing factor in the composite. Long range goals require the use of high temperature binders (preferably with 300°C capability) and work has begun with polyimides and polyamideimides. The coating of the flakes and compaction of the coated flakes will be more difficult because the polyimides have relatively unfavorable melt flow characteristics.

I. Epon 828

II. DEN 431

III. DER 736

IV. Triethylenetetramine (TETA)

VI. 4,4'-methylene dianiline (MDA)

V. Fatty Polyamide

VII. Nadic Methyl Anhydride (NMA)

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Fig. 1. Wear of Stabilo 96P ink lines.

Fig. 2. Wear of GLD 3072 ink lines.

Fig. 3. Flake cast on wheel with ink lines.

Fig. 4. Crystalline balls made with flake of figure 3.

Fig. 5. Wheel with 0.010 inch slots after casting.

Fig. 6. Ceramic filled 0.010 inch slots after casting.

Fig. 7. 0.008 inch stainless steel soldered in .010 inch slots after casting.

Fig. 8. Ribbon ends formed by ink line.

Fig. 9. Ribbon ends formed by unpolished deep groove.

Fig. 10. Ribbon ends formed by unpolished deep groove.

Fig. 11. Ribbon ends formed by unpolished shallow groove.

Fig. 12. Profile of unpolished groove in wheel.

Fig. 13. Profile of groove from figure 12 after wheel polishing.

Fig. 14. Ribbon ends from deep polished groove.

Fig. 15. Ribbon cast over shallow polished groove.

Fig. 16. Ends of ribbon formed over groove shown in figure 12.

Fig. 17. Grooved and polished aluminum bronze wheel.

Fig. 18. Grooved and polished aluminum bronze wheel.

a

b

Fig. 19. Flake cast in nitrogen, run #1212784.

a

b

Fig. 20. Flake cast in vacuum, run number 1211783.

a

b

Fig. 21. Flake cast with Scotch Brite Wiper run #0201791.

SCHEMATIC DIAGRAM

Figure 21c

$A_k = .00453$

022179-1A 00

Figure 22. Ribbon 0221791
as cast.

$A_x = .000453$

022179-1 G

10

H_m	H_c	B_m
1	.055	12.4
10	.060	15.4
100		16.1

Figure 23: Ribbon 0221791
annealed.

25

2F 3-22-79 R

FLAKE

011879-2 00

Figure 24. Flake 0118792
as cast

3,1

3F

3-15-79

Figure 25. Flake 0118792 annealed.

$$A_r = .000728$$

011879-2 00 R. 1966V

Figure 26. Ribbon 0118792
as cast.

sf

sf

3-15-79

Nom. Flake $\ell = .35''$

032179-2 1F00

H_m	H_c	B_m
1	.045	2.2
10	.08	7.0
100		~14.5

Figure 28. Flake 0321792
as cast.

7F

3-2379

032179-2 1F10

$A_x = ?$
Nom. $5/16$ Hc $l = .35"$

Figure 29. Flake 0321792
annealed

SF

3-27-79

$A_r = .000819$

032179-2 00

Figure 30. Ribbon 0321792
as cast.

9F

3-23-77

$Ax = .000819$

032179-2 Segments 10

H_m	H_c	B_m
1	.042	13.2
10	.045	15.9
100		16.2

Figure 31. Ribbon 0321792 annealed.

+1.3

+1.7

+1.64

10 F

3-27-79

Fig. 33. Crystalline Flake

Figure 34. Flake 0321792
annealed.

11496-69-2
FLAKE COMPACTED 12-11-78-3

3/16/79

Byrne Pressing 11496-112

FLAKE 01-26-79-3 pressed

13F

3-15-79

Fig. 37. Cross section of composite 11496-79-5.

Fig. 38. Radiograph of composite 11496-78-4.

Fig. 39. Composite 11496-112.