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EXFOLIATION OF MAGNESIUM-GRAPHITE  
COMPOSITES: A COMBINED METALLOGRAPHIC  
AND ANALYTICAL APPROACH.

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Watertown, Massachusetts

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An investigation was conducted to determine and eliminate the causes of localized exfoliation in magnesium and a magnesium alloy (AZ91C) reinforced with graphite fibers. These composites were prepared by liquid phase hot pressing using a titanium intermediate to promote wetting, infiltration, and bonding between the Mg/Mg alloy and the graphite fibers. A multidisciplinary approach involving metallography, scanning electron microscopy, microprobe analysis, electron spectroscopy, infrared spectroscopy and gas chromatography was used to study exfoliated and unexfoliated regions of these composites. The results of these studies indicate that exfoliation in both Mg and the Mg alloy matrix composites occurs when there is poor wetting and bonding and that it can be completely prevented by achieving good wetting and bonding. It was also found that elimination of aluminum as an alloying element improves the suitability of Mg as a matrix material for graphite fibers. (Authors)

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Technical Report by

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER

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An investigation was conducted to determine and eliminate the causes of localized exfoliation in magnesium and a magnesium alloy (AZ91C) reinforced with graphite fibers. These composites were prepared by liquid phase hot pressing using a titanium intermediate to promote wetting, infiltration, and bonding between the Mg/Mg alloy and the graphite fibers. A multidisciplinary approach involving metallography, scanning electron microscopy, microprobe analysis, electron spectroscopy, infrared spectroscopy and gas chromatography was used to study exfoliated and unexfoliated regions of these composites. The results of these studies indicate that exfoliation in both Mg and the Mg alloy matrix composites occurs when there is poor wetting and bonding and that it can be completely prevented by achieving good wetting and bonding. It was also found that elimination of aluminum as an alloying element improves the suitability of Mg as a matrix material for graphite fibers.

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## INTRODUCTION

Magnesium and magnesium alloys reinforced with graphite fibers have been utilized as composite materials because of their very high specific stiffness and specific strength.<sup>1</sup> These properties render them very suitable for such applications as helicopter transmission housings, gyroscope gimbals, rotor hubs, airframe members, and space vehicle structures.

During the development of this composite material the problem of exfoliation was encountered, involving delamination and swelling of the composite. The investigation of the causes and elimination of the exfoliation problem is reported in this paper. The study utilized a combination of metallographic and analytical techniques.

### Composite Material

The composite material being studied was a magnesium or magnesium alloy reinforced with graphite fibers. The magnesium alloy was AZ91C of composition 3.1 to 9.3% Al, 0.13% Mn, 0.4 to 1.10% Zn, and <0.3% Si, <0.1% Cu, and <0.01% Ni. The graphite fibers are either Celion (Figure 1a) or Modmor (Figure 1b). These fibers are produced by various techniques but basically consist of a polyacrylonitrile precursor which has been graphitized at very high temperatures. The graphite fibers are in the form of tows or yarns of many fibers each and some of these have a twist. The description of the various fibers is presented in Table 1. The c-axis of the graphite unit cell is usually aligned perpendicular to the axis of the fiber.

The preparation of the composite is quite detailed but necessarily involves the use of titanium as an intermediate to facilitate wetting and bonding of the matrix to the fibers. The titanium may be applied by physical vapor deposition, chemical vapor deposition, or other proprietary processes. The actual fabrication process may be done by liquid phase hot pressing or liquid phase infiltration of fiber tows at 710 C. These methods have been described in detail elsewhere.<sup>2</sup>

### Exfoliation

Exfoliation occurs in certain areas of composite materials. It involves a delamination and swelling of the affected area of the composite. The process occurs with considerable physical disruption and disintegration of the material. This can be clearly seen in Figure 2 where the exfoliated area is evident.

Exfoliation does not always occur in composites fabricated by the same technique and under the same conditions. Moreover, the disintegration can be very localized and even after a period of years remain confined to only one section of the composite. The process may begin immediately after fabrication or be delayed for several months.

1. LEVITT, A. P., and DICESARE, E. *Aircraft Materials Research*. Army Research and Development Magazine, May-June 1972.
2. LEVITT, A. P., DICESARE, E., and WOLF, S. M. *Fabrication and Properties of Graphite Fiber Reinforced Magnesium*. Metallurgical Transactions, v. 3, September 1972, also, Army Materials and Mechanics Research Center, AMMRC TR 71-44, November 1971.

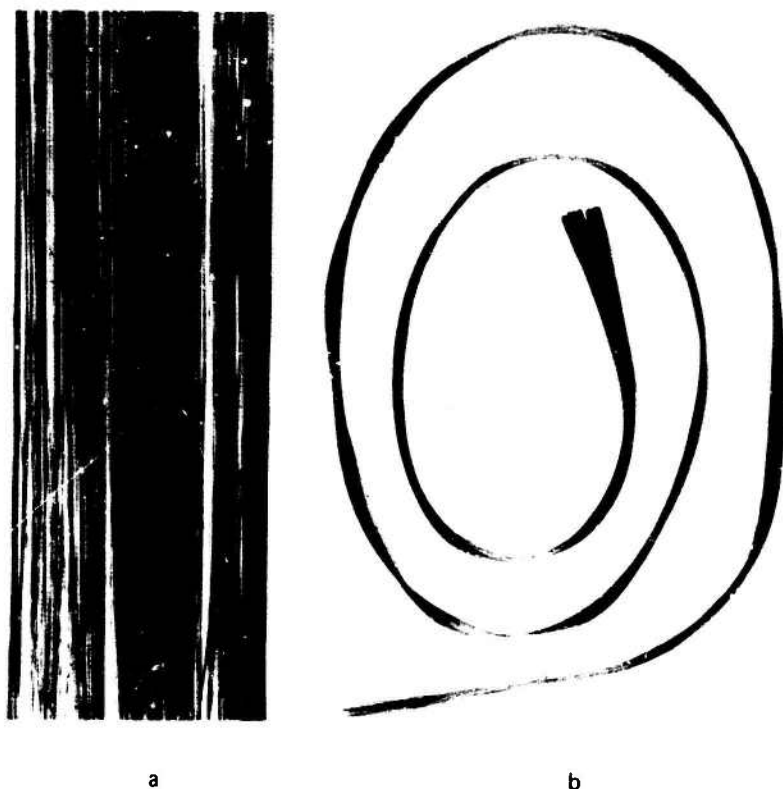


Figure 1. Celion and Modmor I tows



Figure 2. AZ91C Mg-Graphite fiber plate showing localized exfoliation.

Table 1. GRAPHITE FIBER PROPERTIES

Fiber*		T.S. (ksi)	Young's Modulus (psi)	Density		Diameter μ	Fiber Per Yarn†
Type	Trade Name			g/cu in.	g/cu cm		
A	Celion	315	75 to 80 × 10 <sup>6</sup>	0.071	1.96	7 to 8	400
B	Modmor I	250	60	0.073	2.00	7.5	10,000

\*All fibers are graphitized from polacrylonitrile type precursors.

†A yarn is a multifilament fiber bundle, usually twisted to prevent fiber separation.

If its causes are made known, exfoliation can be avoided. This is the purpose of the research described herein.

## EXPERIMENTAL TECHNIQUES AND RESULTS

In the various microscopic techniques, mention will be made of "bad" areas of the sample, those which have exfoliated, and "good" areas, those which have not exfoliated.

### Optical Metallography

Since the fibers are in bundles they tend to preserve their bundle-like morphology even after infiltration. However, infiltration and wetting are much more extensive in the good area (Figure 3a) than in the bad area (Figure 3b). This is further corroborated by the higher magnification photomicrographs of Figures 3c and 3d. Indeed, in Figure 3d each fiber is seen surrounded by a dark phase rather than by the light magnesium alloy matrix.

There is, to be sure, some porosity visible in Figures 3a and 3c, but it is very slight as compared to the total lack of wetting in Figures 3b and 3d.

### Scanning Electron Microscopy

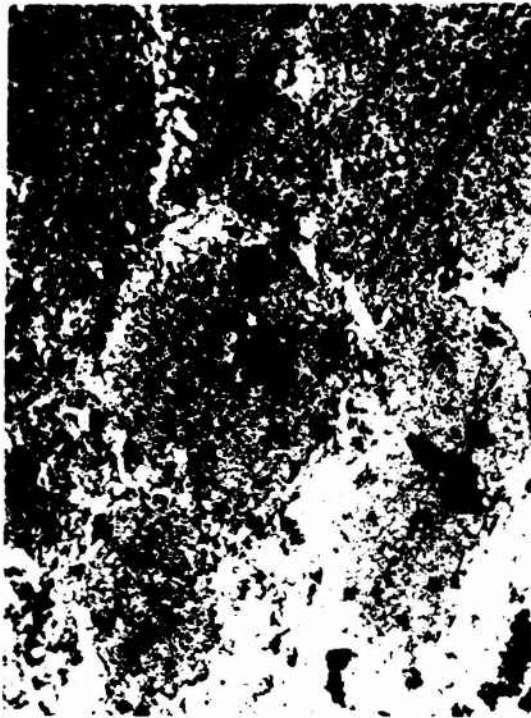
The surfaces at two sites are shown at two different magnifications in Figures 4a and b and 5a and b. From these scanning electron micrographs it is evident that there is little if any infiltration of the matrix alloy into the fiber bundles. This results in considerable porosity and lack of wetting of the graphite fibers by the magnesium alloy matrix. Indeed, in Figure 5a a very large void is clearly evident. This sparsity of magnesium alloy matrix adjacent to the fibers and the large voids suggest, as did the optical micrographs, that exfoliation either produces voids and debonding or is caused by them.

To verify that the already exfoliated surfaces were representative of bad matrix-fiber interaction, the composite plate was fractured (sheared) perpendicular to the fiber direction. The fractured surfaces of the good and the bad regions of the composite are shown in Figures 6 and 7.

It is easy to see that there is very little evidence of internal porosity or voids in the good region of the composite and that the wetting and bonding is extremely good. In Figure 6b the fibers break off cleanly at the fracture surface while considerable plastic deformation of the matrix has occurred. There is also clear evidence that the intimate bonding of the matrix to these fibers remains even after fracture. It should be noted that despite the convoluted shape of the Celion fibers, excellent infiltration has been obtained.

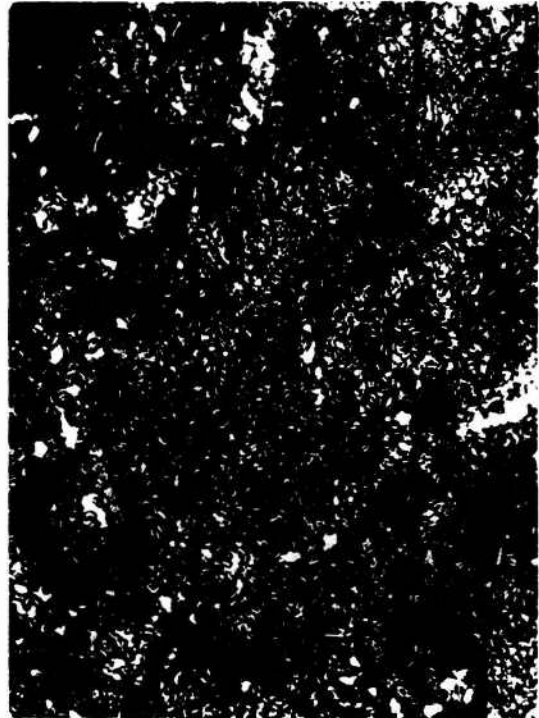
In contrast to the good area of Figures 6a and b, the bad regions of Figures 7a and b show little or no wetting and bonding. The fibers are virtually devoid of matrix metal and are fractured at various points along their lengths. Scattered small particles of matrix metal may be seen in Figure 7b adhering to some fibers.





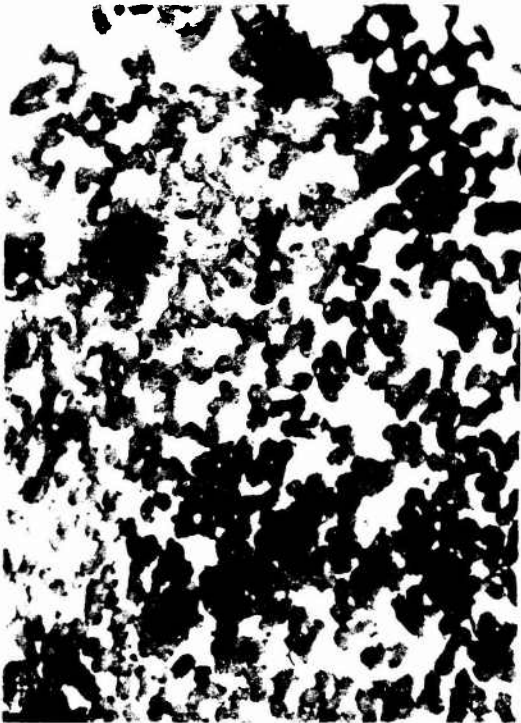
19-066-1638/AMC-72

a. Good area. Mag. 100X



19-066-1635/AMC-72

b. Bad area. Mag. 100X



19-066-1636/AMC-72

c. Good area. Mag. 500X



19-066-1634/AMC-72

d. Bad area. Mag. 500X

Figure 3. AZ91C Mg-Graphite fiber composite (cross sections)



19-066-1641/AMC-72 a. Mag. 50X



19-066-1640/AMC-72 b. Mag. 1000X

Figure 4. AZ91C Mg-Graphite fiber composite exfoliated surface, area A



19-066-1632/AMC-72 a. Mag. 100X



19-066-1630/AMC-72 b. Mag. 2000X

Figure 5. AZ91C Mg-Graphite fiber composite exfoliated surface, area B.



19-066-1629/AMC-72

a. Mag. 100X



19-066-1628/AMC-72

b. Mag. 1000X

Figure 6. AZ91C Mg-Graphite fiber composite, good area (fractured)



19-066-1627/AMC-72

a. Mag. 100X



19-066-1626/AMC-72

b. Mag. 1000X

Figure 7. AZ91C Mg-Graphite fiber composite, bad area (fractured)

These scanning electron micrographs clearly indicate a lack of any wetting or bonding between fiber and matrix in the exfoliated regions of the composite while in the good regions there is excellent wetting and bonding.

### Microprobe Analysis

Microprobe analysis was conducted on the cross-sectioned samples of good and bad areas. Spectral patterns of the elements present in the range magnesium through uranium revealed the presence of only magnesium and aluminum in the matrices of the good and bad areas and also of the dark phase (see Figure 3b) around fibers in the bad areas. A light element study revealed that the dark phase at the interface between fiber and matrix contained sufficient oxygen to be an oxide type of compound.

A quantitative microprobe analysis was made for the concentration of aluminum at various points in the structure. From this it was determined that the good matrix contained 1.0 weight percent (w/o), the bad matrix 1.2 w/o, and the dark phase adjacent to the fibers in the exfoliated regions 17.0 w/o of aluminum. This indicates that the normal matrix content of AZ91C alloy was depleted of aluminum from 8.1 to 9.3 w/o to 1.0 to 1.2 w/o while the dark phase at the fiber/matrix interface was rich in aluminum (17 w/o). This data would indicate that the dark phase was a compound of aluminum with oxygen.

### Effect of Immersion of Composite Panels in Water

An exfoliated panel and a good panel were immersed in tap water and heated to 100 C. The exfoliated panel began to decompose with the emission of a gas as soon as it was immersed. The evolution of gas continued and further exfoliation occurred for about 20 minutes. No gas emission, exfoliation, or decomposition was observed for the good panel. The experiments were repeated using distilled and deionized water with the same results.

### Electron Spectroscopy

Using electron spectroscopy, exfoliated composites have been examined to determine the nature of the surface of the fibers and, especially, whether there was evidence at that surface of magnesium, aluminum, titanium, and oxygen. The surface of the graphite fibers showed a high percentage of magnesium and slightly less aluminum to be present. This is in good agreement with the microprobe analysis which indicated that the aluminum had been depleted from the matrix and was concentrated at the interface between fiber and matrix.

From the oxygen peak, it was evident that the oxygen present at the surface of the fibers is not in the form of an oxide, i.e.,  $Al_2O_3$  or  $MgO$ . Rather the shifts in binding energies of the magnesium and aluminum suggest that the interface may be in the form of a magnesium-aluminum spinel or a hydroxide.

### Infrared Spectroscopy of Evolved Gas

The gas generated during exfoliation as a result of aqueous immersion of a magnesium alloy (AZ91C) matrix was identified by infrared spectroscopy as

consisting entirely of CH<sub>4</sub>. When composites had been fabricated under a protective atmosphere of nitrogen, the only gas observed by infrared spectroscopy to have evolved during exfoliation was NH<sub>3</sub>.

### Gas Chromatography

The sample composites prepared under a protective layer of nitrogen were subjected to exfoliation by aqueous immersion and the resulting gases analyzed by chromatography. The only gas found to be present was NH<sub>3</sub>, thus confirming the infrared spectroscopy results.

### DETERMINATION OF MECHANISM OF EXFOLIATION OF THE ALLOY COMPOSITES

Armed with the data generated by the various metallographic and analytical techniques outlined above, it is now necessary to determine exactly what reactions are involved in exfoliation and why some composites fail by this means and others do not.

If we consider the gas evolved during exfoliation to be methane (CH<sub>4</sub>), then the most probable reaction leading to such gas evolution would be



This is the normal reaction which occurs when aluminum carbide decomposes in water.<sup>3</sup> The reaction satisfies the condition that the only gaseous product is methane — this agrees with the results of infrared spectroscopy where only methane was observed in exfoliating composites. The formation of aluminum carbide would also justify the increase in aluminum content observed by microprobe analysis at the fiber surface and especially in the dark phase surrounding fibers from bad areas of the composite material.

The problem would then be how does the Al<sub>4</sub>C<sub>3</sub> layer at the fiber in the interior of the composite come into contact with water or water vapor. This can be explained by the differences in thermal expansion between the aluminum carbide and the matrix. If the fabrication process allows Al<sub>4</sub>C<sub>3</sub> to form on the surface of the graphite, it will contract at a rate sufficiently different from that of the magnesium alloy matrix so that separation will occur and nonwetting will result. This is shown in Figure 3b. Once there are nonwetting, and therefore nonbonding conditions in the composite, moisture can penetrate and reaction (1) can proceed so that what was formerly Al<sub>4</sub>C<sub>3</sub> becomes Al(OH)<sub>3</sub>. This is the phase that appears as the dark layer surrounding the graphite fibers in Figure 3b. The presence of the hydroxide is borne out by the results of microprobe analysis which detected oxygen present at the fiber surface in bad areas and by the outcome of the electron spectroscopy which predicted oxygen in the form of the hydroxide.

If one argues the case for composites prepared under a protective nitrogen atmosphere and the subsequent evolution of NH<sub>3</sub> as a result of exfoliation, one need only consider the formation of AlN at the fiber surface in preference to Al<sub>4</sub>C<sub>3</sub> and its subsequent decomposition in moisture

3. WEAST, R. C., ed. *Handbook of Chemistry and Physics*, 49th Edition, 1968-1969. Chemical Rubber Company, Cleveland, Ohio.



which results in the same aluminum hydroxide at the fiber surface.

It is the evolution of considerable gas and the attendant volume changes in the solid products that result in the exfoliation of the composites.

### EXFOLIATION IN PURE MAGNESIUM COMPOSITES

If, then, it is the presence of aluminum in the magnesium alloy which gives rise to reactions leading to exfoliation, the logical step is to eliminate all traces of aluminum from the matrix.\* Such a move would involve determining whether exfoliation does or does not occur in a composite material fabricated with a pure magnesium matrix.

Exfoliation, unfortunately, does occur even with a pure magnesium matrix. However, there is no gas evolution and the reaction responsible is found to be



Where, then, does the MgO come from and how does the formation of Mg(OH)<sub>2</sub> cause disintegration of the composite?

The magnesium oxide occurs by the natural oxidation of magnesium during fabrication; the process is not carried out in a reducing atmosphere and there is always some oxide on the "magnesium" powder particles. The formation of Mg(OH)<sub>2</sub> results in a disintegration of the matrix into a white powder, rather than an explosive or bursting exfoliation where graphite fibers "pop" out of the composite.

### CONCLUSIONS AND METHODS OF PREVENTION OF EXFOLIATION

While the above discussion indicates that magnesium-graphite should not be worthwhile as a composite system, all danger of exfoliation can be removed if good wetting and bonding are achieved. This holds for both magnesium and magnesium alloy matrices. This can be clearly seen by studying the scanning electron micrographs of the good areas in Figure 6 or the optical micrograph of Figure 3a. If such wetting and bonding can be achieved, there is no danger of exfoliation. This has, indeed, been observed in practice in both the pure magnesium and the AZ91C alloy matrices. There is also ample evidence that the elimination of the aluminum from any alloy renders the material more suitable as a matrix metal for this composite system.

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\*One might question how aluminum can be the culprit in view of the fact that aluminum-graphite composites are widely used commercially. The explanation lies in the various proprietary methods of establishing wetting and bonding between aluminum and graphite. These methods involve intermediate active metals which avoid the possibility of aluminum carbide formation if fabrication is performed properly.