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EFFECTS OF THERMAL ANNEALING AND CYCLING ON LIGHT METAL IMPREGNATED GRAPHITE

by

H. BURG, F. LANZA and G. MARENGO

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ORGEL Program

Joint Nuclear Research Center
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Physical Chemistry

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SUMMARY

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KEYWORDS

GRAPHITE
IMPREGNATION
MAGNESIUM ALLOYS
ALUMINIUM ALLOYS
SILICIDES
ANNEALING
THERMAL CYCLING
EXPANSION
STRESSES

Contents

EFFECTS OF THERMAL ANNEALING AND CYCLING ON LIGHT METAL IMPREGNATED GRAPHITE *)

1. Introduction

Graphite is a very good nuclear material, owing especially to its low capture cross-section. Its use as a structural material is hindered mainly by two drawbacks : permeability and porosity. Due to its high porosity a large specific surface (0,2 - 0,4 m^2/g) is exposed to the action of corrosive agents. Permeability makes impossible its use as a canning material for fuel elements.

In order to avoid such drawbacks a method to impregnate has been devised which permits the production of a completely impervious graphite [1]. Magnesium alloys and an Al-Si (13 %) alloy have been used as impregnating metals.

The resulting material has two continuous structures. The metals enter, completely or partially, into the porosity forming a tridimensional network which can be linked to the graphite structure either by a simple mechanical interlocking, if the impregnating material does not react (Mg), or with a true metallurgical bonding, if there is carbide formation at the impregnating temperature (Al).

The impregnating alloys and the graphite have quite different thermal expansion coefficients. Since the impregnation is being obtained by pressure injection of the molten metal, a differential contraction will occur between the two structures on cooling. Due to the different links, between the graphite and the impregnating metal, stresses will appear in both structures. Assuming a simplified model in which the graphite is mechanically in parallel with the impregnating metal, the metal after cooling will be subjected to traction stresses and the graphite to compression.

The elastic modulus of graphite being quite low, these stresses induce measurable dimensional variations. A thermal annealing will reduce this initial state of stress and as a consequence will induce dimensional variations. Thermal cycling will cause

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*) Manuscript received on June 20, 1968.

an alternative loading of the two structures with a possible action on the dimensional stability of the samples.

The composite material obtained using Magnesium as an impregnating medium offers a further interesting possibility. Magnesium has a high vapour pressure at temperature lower than its melting point. A total sublimation of the Mg allows the examination of the graphite structure free from internal stresses.

All samples used in the present study have been prepared using a molded fine grain graphite, grade 3780 produced by Carbone Lorraine.

2. Evaluation of the internal stresses

A detailed calculation of the internal state of stress is practically impossible. The porous structure, filled by the metal, is very complex and no satisfactory models are available. Besides, graphites do not follow Hook's law since the dependence of strain from stress is of the exponential type (2).

Nevertheless it is possible to verify, with a simple calculation, the order of magnitude of the existing internal stresses. The macroscopical effect of such a state of stresses is to induce dimensional variations in the composite material. In magnesium impregnated material the original graphite structure can be obtained by a thermal treatment at 600°C for 12 hours under a vacuum better than 1 torr.

We can thus measure the dimensional changes and from them calculate in a first approximation the originally present stresses.

Assuming that graphite is isotropic and perfectly elastic and that also the graphite porosity filled by the Magnesium is isotropically distributed, we can express the graphite strain ε_1 in the direction of stress σ_1 as follows :

$$\varepsilon_1 = \frac{1}{E_g}\left[\sigma_1 - \nu\,(\sigma_2 + \sigma_3)\right]$$

Due to the assumption of an isotropic structure

$$\sigma_1 = \sigma_2 = \sigma_3$$

and then

$$\sigma_g = \frac{\varepsilon_g\, E_g}{1 - 2\nu}$$

The applied forces on the two structures must be in equilibrium. For any section S composed by a surface area A_g, occupied by graphite, and A_m, occupied by the metal, we can write

$$\sigma_g\, A_g = \sigma_m\, A_m$$

As we have assumed an isotropic material, it follows that the volume ratio is equal to the surface area ratio.

If V is total volume and I the impregnation coefficient

$$V_m = V.I$$

If d_t is the theoretical density of graphite and d its apparent density

$$V_g = V\,\frac{d}{d_t}$$

We obtain then

$$\sigma_m = \frac{\varepsilon_g\, E_g}{1 - 2\nu}\;\frac{d}{I d_t}$$

The samples were measured, the impregnating Magnesium evaporated, and then measured again in order to obtain the dimensional variations.

Two series of samples have been tested, the first one was impregnated with pure Mg, the second one with an Al-Mn alloy, ATESIA T (*). As a matter of fact, the graphite used is slightly anisotropic : in order to experimentally approach the assumption of isotropic material, the values of dimensional variations have been taken as the arithmetical means of 6 samples of which three were machined parallel to the forming direction and three perpendicularly. Table I shows the mean values of the stresses in the metal and graphite.

Table I

Imp. Mat.	$\varepsilon.10^3$	σ_m (kg/mm²)	$\sigma_{0.2\%}$ (kg/mm²)	σ_g (kg/mm²)	F
Mg	2,5 ± 0,4	9,7 ± 1	9,2	2,8 ± 0,2	0,22
ATESIA T	3,7 ± 0,5	13,9 ± 1	13,5	4,4 ± 0,3	0,37

The stresses in the metal are compared to the conventional yield stresses (0.2 % plastic strain). The calculated values are very close to the conventional yield stresses. Such a concordance gives rise to a simple model. The metal structure reacts elastically against the dimensional differences up to the yield point. The metal flows then plastically under constant stress.

The fourth column of table I shows the value of the stresses acting on graphite. In order to compare such a value with the mechanical resistance of graphite we have to introduce a correction factor taking into account the graphite porosity. Since the compression strength of the graphite used had the following dependance from porosity P [4].

$$\sigma = 12,3 \quad (1 - 2,1 \text{ P})$$

The fraction F of the applied stress to the ultimate compression strength will be

$$F = \frac{\sigma g}{12,3}$$

(*) Composition of the Mg alloy ATESIA T ; Al 8 % Zn 0.7 % Mn 0,2 %

We can see from table I that this fraction has a significant value. We note, however, that it is a triple state of compression stress due to which there should be no influence on the mechanical resistance of the composite material.

We can expect, on the contrary, an effect on the dimensional variation since graphite exhibits hysteretic effects giving rise to large permanent deformation after removal of the applied stress [3].

3. Annealing tests

Annealing tests have been conducted in a furnace under Argon atmosphere. Samples were supported by a capsule made of nuclear grade graphite. Thermal gradients in the experimental zone at the highest used temperature were lower than ± 3°C. The temperature was controlled in a range of ± 0,5°C. Four cylindrical samples with the axes parallel (//) to the forming direction and four perpendicular (⊥) have been treated for every annealing temperature.

The cylinders have a diameter of 8 mm. Preliminary tests have shown that dimensional variations are insensitive to the diameter value, at least up to 30 mm.

3.1. Magnesium alloy impregnated graphite

Impregnation was performed with Magnox Al 80, a Magnesium alloy containing 0,8 % Al, 0.05 % Be. It presents a very good oxydation resistance but a rather low creep resistance [5]. Annealing effects can be obtained also at temperatures as low as 250°C.

Fig. (1) shows the mean dimensional variation of samples, annealed for 24 h, as a function of temperature. We can see that a dimensional increase is obtained at 250°C increasing slightly up to 400°C, where it remains practically constant. The dimensional increase depends on the graphite orientation, parallel samples showing higher values than perpendicular ones. We remember that the used graphite is a molded one ; therefore in the parallel direction the elastic modulus will be lower. The anisotropy in the dimensional variation confirms, therefore, the inverse proportionality between the dimensional variation and the elastic modulus obtained in the preceding paragraph.

Fig. (2) shows the dimensional variation obtained at 250°C as a function of annealing time. The positive dimensional variation increases with time tending to an asymptotic value which is reached practically after 14 days of annealing. The obtained value is of the same order of magnitude which was reached by Magnesium sublimation.

If dimensional variation has undesirable effects at room temperature, we can use long term annealing as a stabilisation treatment. The annealing time required at 250°C is too long. However, it is not possible to reduce the annealing times by increasing the temperature, because the stresses to be annealed are caused by dimensional difference due to the thermal expansions of the two structures ; as a consequence, increasing the annealing temperature decreases the existing annealable stresses. Therefore a higher annealing temperature gives lower annealing effects. An annealing test performed at 400°C for 4 days gives practically the same dimensional variation as was obtained at the same temperature in one day. From fig. (1,2) we can see that this value is about half of the asymptotic value at 250°C.

On the same plots has been reported, with black dots, the dimensional variation due to the sublimation of Mg after thermal treatment The values on the ordinate are referred to dimensional variations due to sublimation alone. Annealing plus sublimation gives an effect slightly higher than sublimation alone.

We think that such an effect is due to the permanent deformation, caused by the high thermal dilatation of Mg, on the graphite structure. As a matter of fact at the end of annealing we are in a situation of no stress atthe annealing temperature. Now, as the evaporation is performed at 600°C, during heating at a temperature higher than the annealing one, the state of stress is reversed ; graphite is now under traction and Mg under compression. The evaporation, during which the Mg structure disappears, recovers the deformation due to stresses but not the permanent one. Permanent strains can be annealed only at temperature higher than 1000°C [3].

3.2. Al/Si impregnated graphite

The alloy used for impregnation is the Al/Si eutectic containing 12,7 % in weight of Si having a melting point of 577°C. We remember that the resulting material shows a metallurgical bonding between Al and graphite due to the formation fo an Al_4C_3 layer. As a consequence the material presents a higher mechanical strength [4]. Furthermore the alloy used has better creep resistance than Magnox Al 80. We can then foresee that annealing effects will be lower.

Fig. (3) confirms that this is the case. The values obtained by annealing for 24 hours are decidedly lower than what was obtained previously. Also in this case we found an anisotropic effect but in the opposite direction of that obtained with Mg.

Parallel samples show a lower elongation than perpendicular ones. This can be attributed to the presence of Al_4C_3 deposited on the pore surface which alters deeply the elastic characteristics and the anisotropy of graphite. The experimental values present an elevated dispersion. In the samples tested the carbide content was varying from 0.1 to 0.4 %. We can say as a first approximation that higher dimensional variations are obtained for samples with lower carbide content.

4. Thermal cycling tests

Thermal cycling is obtained by putting the sample in a capsule which can be moved between an oven and a cooler. To control the cycling, a thermocouple, connected with a recorder, is fixed at the bottom of the capsule.

Cycling was effected between 50 and 450°C. A complete cycle was performed in 20 min. at an initial cooling velocity of 100°C/min.

Also in these tests the obtained values are the arithmetical mean of 4 samples for each direction.

4.1. Mg alloy impregnated graphite

Thermal cycling causes a dimensional variation (fig. 4) initially rapid, tending then to an asymptotical value. Such a value is practically reached after 500 cycles. In such a condition the structure of the composite material has become insensitive to the differential thermal expansion between the two components.

We can see that the thermal cycling effect produces roughly the same dimensional variation as obtained by sublimation. This leads to the conclusion that the effect of thermal cycling acts only on the Mg structure. Such a conclusion is confirmed by the negligible dimensional variations obtained by evaporation of Mg from samples previously 500 times cycled.

The rearrangement of the Mg structure could cause some detachment between the two structures and as a consequence a loss of the impermeability of the material.

To control this some tests have been performed on cycled samples using an helium leak detector type "Atlas gas detector". The samples were hollow cylinders connected on the open side to the helium leak detector. The other side was closed and a helium pressure of about 1 atm was applied on it. The sample was considered impervious when the leak was lower than the sensitivity of the apparatus ; this condition, due to the sensitivity of the apparatus and the geometry of the sample corresponds to a permeability lower than 10^{-11} $cm^2 sec.^{-1}$.

Four samples have been cycled up to 500 cycles. Up to 100 cycles no leaks have been detected. After 500 cycles only one sample developed a small leak corresponding to a permeability of 10^{-10} cm^{2}sec.$^{-1}$. The rearrangement of the structure due to cycling, therefore, has a negligible influence on the impermeability of the composite material.

4.2. Al/Si impregnated graphite

The Al/Si impregnated graphite is less sensible to the action of the cycling. The asymptotic value is obtained rapidly, fig. (5). If we compare such a value to the dimensional variation obtained at 450°C we can see that the effect due to the cycling alone is really small. Also in this case as in annealing, dimensional variations in the perpendicular direction are higher than in the parallel direction.

Conclusions

The effects produced by thermal treatment on Magnesium (Magnox Al 80) impregnated graphite are quite well understood. The two structures evolve in a different manner. The annealing and the thermal cycling affect mainly the Mg structure. Thermal cycling causes a rearrangement of the Mg structure so that the composite material is no longer sensible to the difference in the thermal expansion coefficient existing between the two continuous structures.

Dimensional changes of the graphite structure are due to the fact that graphite not only reacts elastically to the different state of stress existing in the Magnesium structure but is subjected also to plastic deformations.

The maximum dimensional increase in the composite material is less than 3°/oo. The change of the graphite grade can lead to different values, the dimensional variations being indirectly proportional to the elastic modulus.

The behaviour of the Al/Si impregnated material is more complex due to the formation of an Al_4C_3 layer on the pore walls. The presence of this layer alters the graphite structure and probably the elastic modulus anisotropy ; as a consequence the biggest elongation is obtained not in the parallel direction as with Mg but in the perpendicular one.

Dimensional increase is lower than with Mg and ranges around 1.5°/oo at maximum. A better comprehension of the behaviour of this material asks for a series of tests with constant Al_4C_3 content.

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FIG.1 EFFECT OF ANNEALING ON Mg IMPREGNATED GRAPHITE

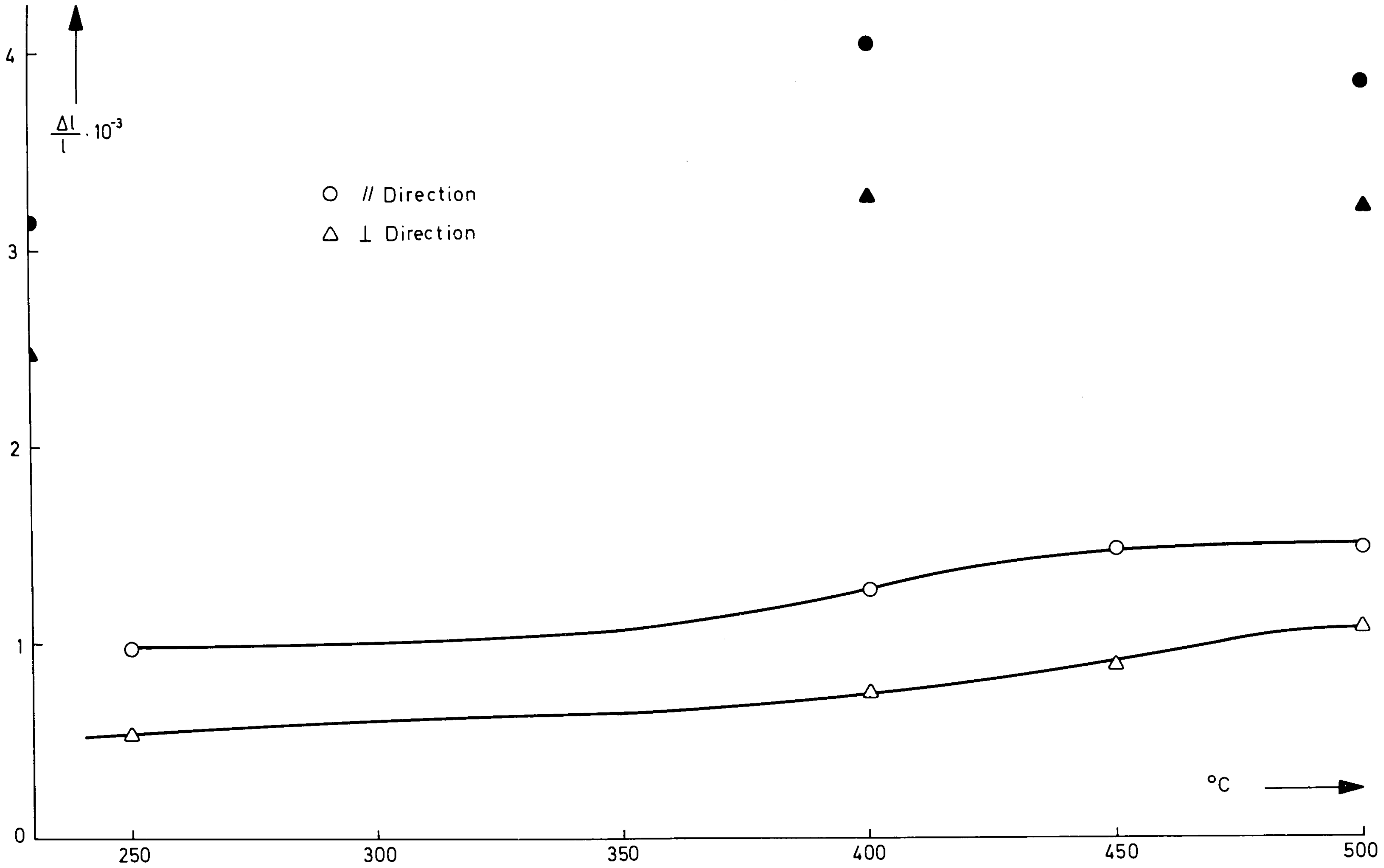


FIG. 2 EFFECT OF ANNEALING AT 250°C ON Mg - IMPREGNATED GRAPHITE

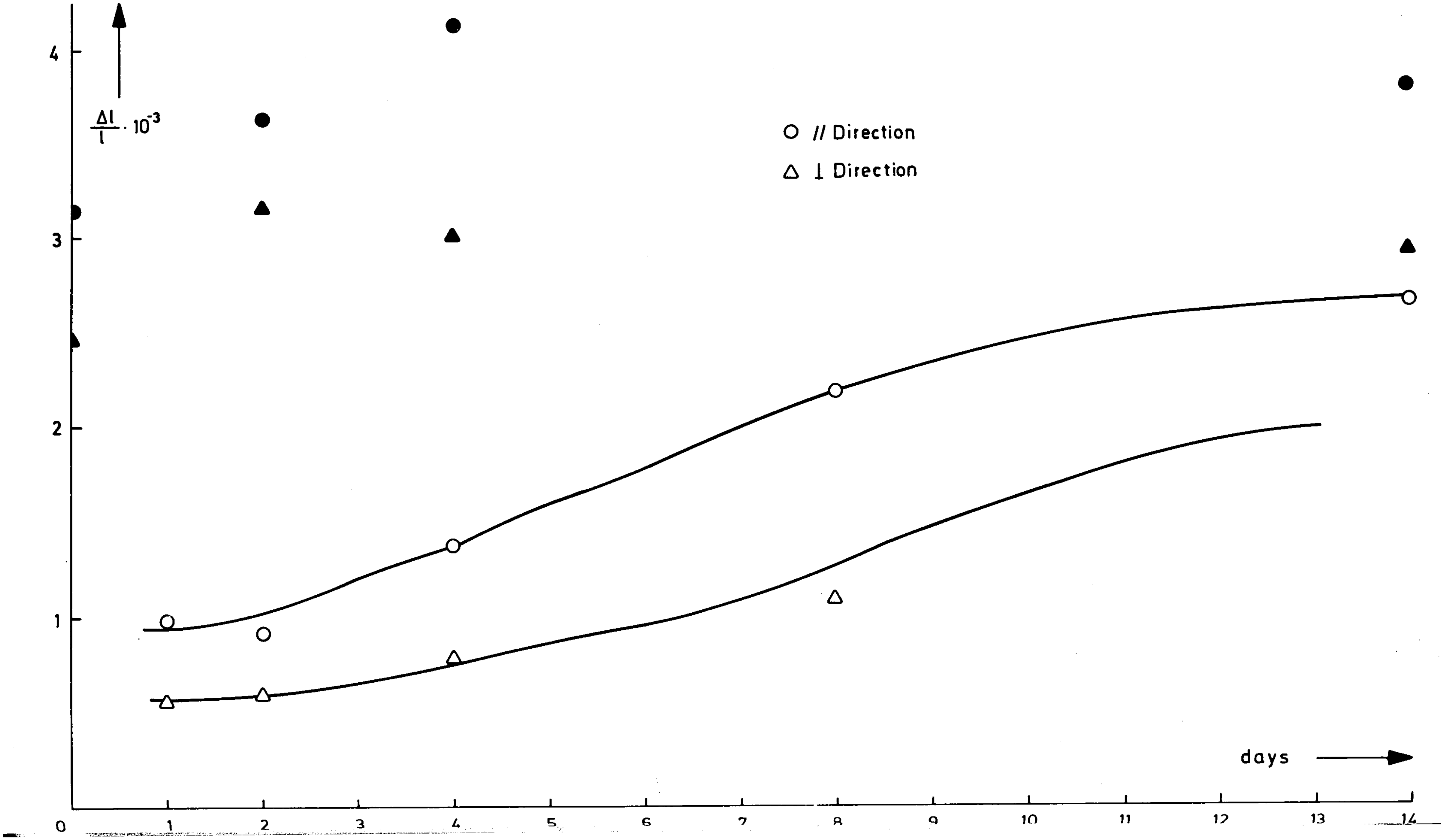


FIG.3 EFFECT OF ANNEALING ON Al/Si IMPREGNATED GRAPHITE

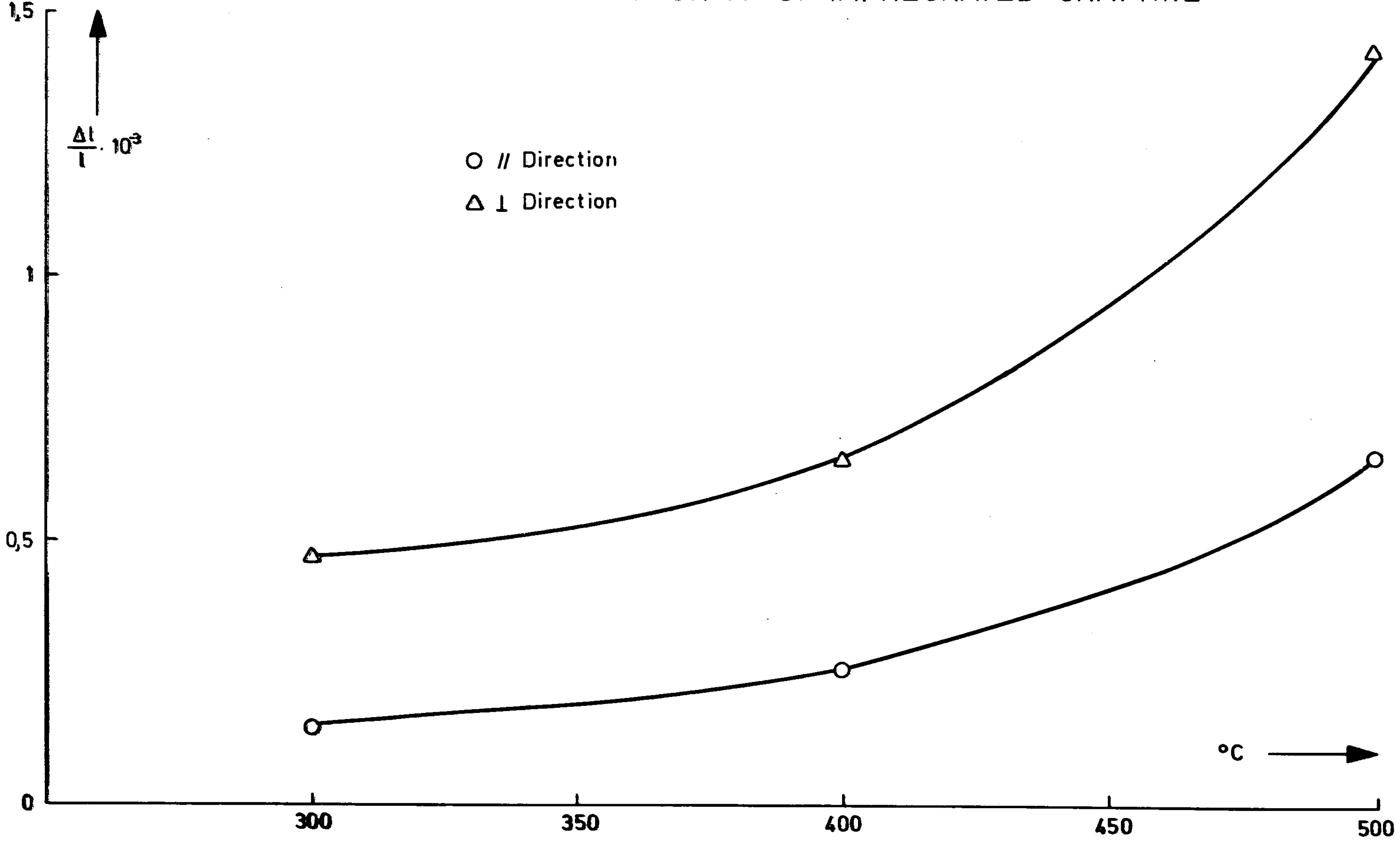


FIG.4 EFFECT OF THERMAL CYCLING ON Mg IMPREGNATED GRAPHITE

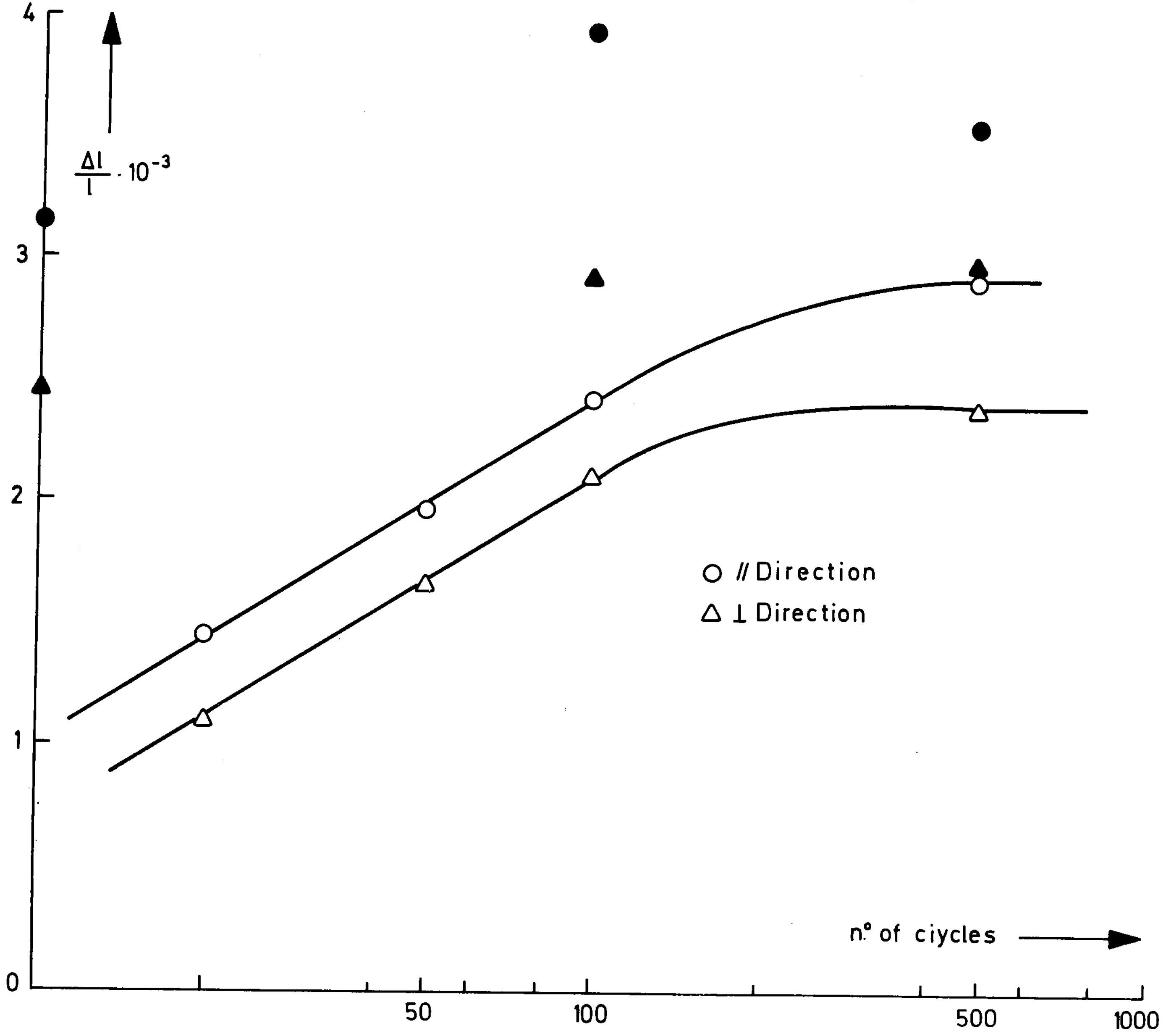
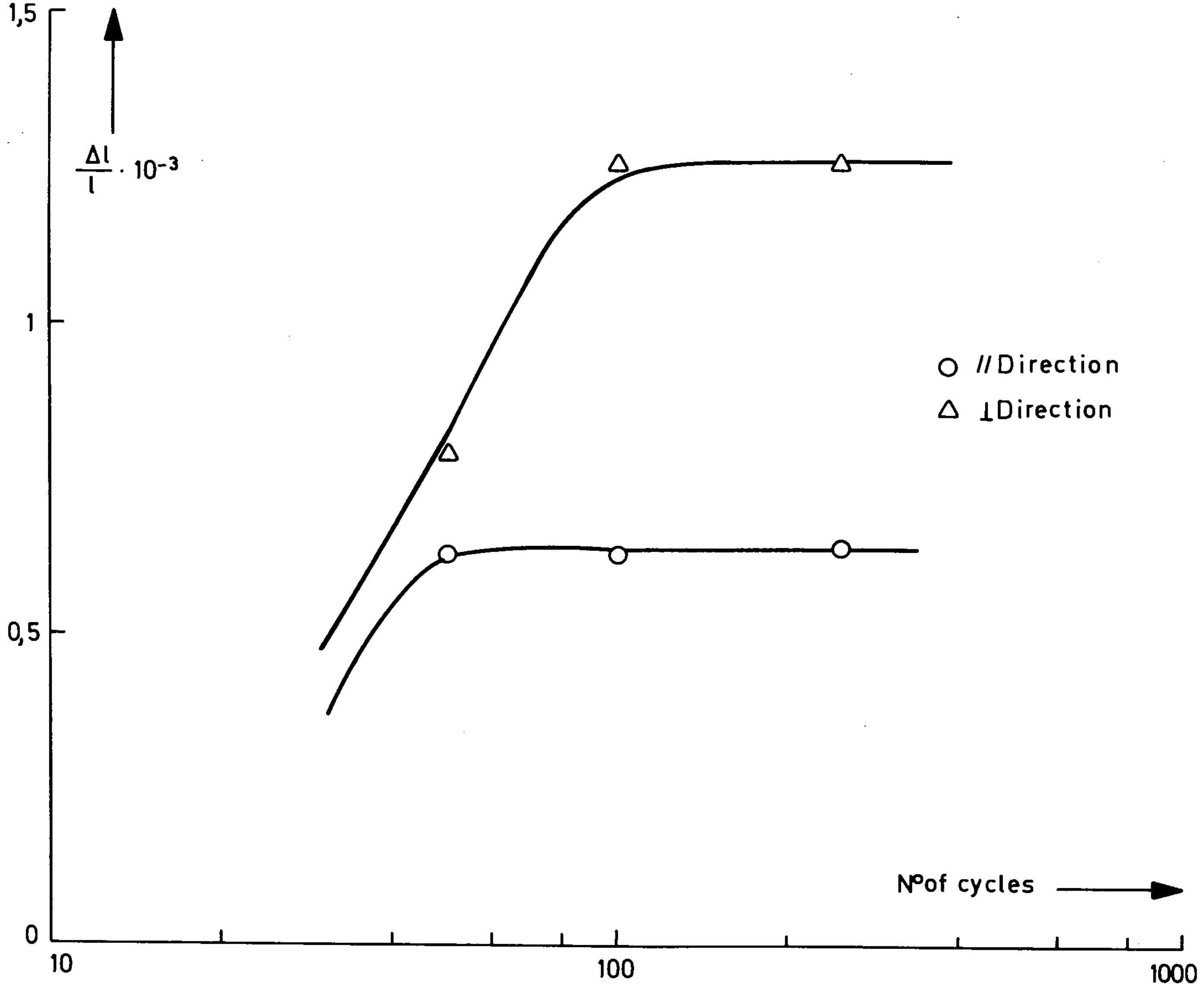


FIG.5 EFFECT OF THERMAL CYCLING ON Al/Si IMPREGNATED GRAPHITE



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>
> Alfred Nobel

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