

NEW MATERIALS FOR IMPROVED FRACTURE AND FATIGUE  
RESISTANCE

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Abstract. Most new materials are combinations of different ones. Others are the result of new processing techniques. Stopping crack propagation is an efficient way to improve the toughness of brittle material. Bridging the crack surfaces by fibers finds many applications. In other materials the improvement comes from the multiplication of crack initiation sites. In metals a better homogeneity of slip by grain refinement is a good way to reduce the brittleness. Strong high melting point materials, single crystal are developed for high temperature applications. Temperature stable precipitates, small oxide or carbide finely dispersed particles provide good creep resistance. Slip homogenization prevents fatigue crack initiation. The propagation threshold is increased by planary slip and large grains.

WHAT IS NEW MATERIAL ?

A new material comes to existence when a substance, a matter, already existing, or newly created, is put to use. Stone was a matter until man began to fabricate tools with it ; aluminium when first introduced at the Paris exhibition in 1855 was considered as a precious metal and it really turned to a material when the Heroult fabrication process allowed to produce it cheaply ; new polymers keep being invented and in many cases soon enough are used as materials.

Matter transformed in a new fashion gives also birth to a new material : a forged steel is not the same material as a cast steel or sintered steel, even if they have the same chemical composition. An alumina whisker has little to do with an alumina ceramic material.

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Is it possible to provide a clear cut definition of the adjective new applied to a material ? The engineer who claims he has invented a new material, should first accumulate sufficient experience so the demonstration is made of its usefulness. Any new material is doomed to become an old material. But when? After so many years, when the patent expires, when so many tons are fabricated ? It does not seem possible to decide except subjectively and I must be allowed a degree of arbitrariness in my own selection of new materials. In this review my concern is about resistance to damage mechanisms : fracture, fatigue, cavitation, cracking, are the key words.

#### NEW SUBSTANCES

When we come to think of new materials, we envisage firstly combinations of different matters : composite materials mostly, new alloys also. However there are new materials which derive from completely new substances. The extreme example is plutonium, a substance which did not even exist before the first micrograms were isolated during World War II (in August 1942 at Chicago) in the first nuclear reactor. It became a material in a matchless time as it was the essential component of the atomic bomb. The first worry of the engineers who needed to use it for this purpose was its six allotropic forms below its melting point with large transformation volume changes. It soon became clear that the production of a workable part would only be feasible by stabilizing the cubic delta phase with a suitable alloying element. In this way it was possible to obtain metal with good mechanical properties.

Needless to say there are examples of such new materials which are of somewhat easier availability. Whiskers were discovered during World War II, when a few condensators lost their properties in the hot humid atmosphere of the tropics. This was due to thin alumina whiskers growing from the surface of the aluminium plates. These perfect single crystals possess unequalled properties, the elastic limit and the fracture resistance topping near the theoretical value of one tenth of the Young's modulus. Using such whiskers is therefore tempting, would the problem of their loading be solved. Of course the way to do it is to incorporate them in a matrix whose purpose is to transfer the load : aluminium matrix, SiC whiskers composites are available. They provide a fracture stress equal to 500 MPa at room temperature but they are quite brittle, with an extremely low fracture

toughness. This is due to the high stress and strain concentrations which are created in the matrix at the tip of the whiskers. Cavities are easily initiated at these sites and their high density triggers shear instabilities for low overall deformation.

Carbon fibers constitute a new material which has found much wider uses. They are available with a Young's modulus which can reach 500.000 MPa and a fracture resistance of 2400 MPa. Their low density provide extremely high specific properties. They can be incorporated in various matrices, including carbon ones.

A class of matter which allows many new formulae assembles the polymers. New ones are numerous and I concentrate on two of them only. The aramide fibers (poly p phenylene terephthalamide), better known by their commercial denomination Kevlar, can reach extremely high fracture resistance of the order of 3600 MPa. With a density of 1.44, lower than the density of the carbon fibers, they have the best specific resistance and are thus extremely attractive to be incorporated in composites.

The other new polymeric material which I find interesting to mention, was developped as a biomaterial. Surgeons often need to consolidate a fractured bone with metallic implants. These must be taken out after healing, and this of course is a serious drawback. The polylactic, polyglycolic acid polymer is slowly digested by the body, so that, after it served its purpose it disappears by itself (Christel et al. (1) Daniels et al (2)).

#### COMBINATIONS OF DIFFERENT MATERIALS

It is by the new combinations of different substances that new materials are mostly created. This provides a manner to associate quite different properties, and to tailor new materials for specific purposes. Material designers find there a large field for applications. It is interesting to fill a matrix with such new materials.

The diagonal is not empty. Very interesting new materials can be discovered by combining elements of the same class. Most unusual properties can be sought in the boxes at the crossing of different classes. However, as the French saying goes, beware of the carp and the rabbit mating. For instance in metallic composites materials, the large difference of the

thermal expansion coefficients of the components creates problems of ratcheting during thermal cycling.

The question might be raised as to why such combination of different classes of matters were not used sooner to such an extent. There are exceptions. Prehistorical man knew how to mix clay and straw to build a wall, a very interesting composite which was but recently reinvented as soils reinforced with geotextiles. Concrete is a typical aggregate known since the Romans. Metallic alloys are as old as metallurgy. However it is only in recent times that other combinations have been invented. One reason for that is the better knowledge which we have acquired about the physical processes of deformation and thus about the mechanical behaviour of materials. Another one of course is that polymers, elastomers, quite a few covalent materials were only recently developed.

#### NEW PROCESSES TECHNIQUES

Before going to the advantages brought by these new materials as far as resistance to fracture and fatigue is concerned let's examine some processing innovations.

Firstly there are ways to very much reduce the grain size. This can be obtained by extremely high cooling rates. A way to achieve that is to pour the liquid metal on a fast rotating wheel made of copper to remove the calories as quickly as possible. Another one is to use a high power density heating device, such as a laser beam, producing very high heating rates and a strong cooling action by conduction in the interior of the treated part. These processes enable to produce submicronic grains and even amorphous metals with the properties of a glass.

At the other extreme, techniques to fabricate single crystals have been known for a long time, but it is not until recently that such a complicated part as a turbine blade could be produced in this form.

Secondly new surface treatments are experienced. They can bring quite interesting properties such as improved wear or fatigue resistance. One of them is ion implantation. This process consists in bombarding the surface with energetic ions like nitrogen ions which thus penetrate at some depth under the surface. Another new way, which opens the door to many innovations, is the laser treatment. It is characterized, as already stated, by its very high density of energy. It can be applied with or without the simultaneous projection of

a powder, with or without a special gaseous environment, with or without another surface pretreatment to improve the absorption of the beam or to bring elements to be alloyed. Lastly sintering provides ways to combine different phases, or to introduce cavities. It also allows to create materials with a gradient of properties at the surface, opening the way to a completely new material design.

We try now to understand how these new materials bring a new picture in the field of fracture and fatigue.

#### FRACTURE OF BRITTLE MATERIALS

The most efficient way to fight brittle fracture is to reduce the possibilities of crack propagation.

In concrete it is achieved by stopping the cracks on the aggregates (Wittmann (3)). Cement hardened paste is very brittle ; nothing stops a crack from running through an entire specimen. Mortar is less brittle already, because microcracks can arrest at the interface of the gravels, cannot cross them and need to follow the interfaces, not so well oriented to keep propagating. The effective surface area is much increased. This process is even more at work in concrete. This material contains microcracks at the interfaces of the aggregates. Once they broke through an entire face, they propagate in the mortar, often with a change of orientation and they stop at the next aggregate whose interface is in a bad orientation with respect to the tensile axis. New microcracks undergo the same procedure thus multiplying the area of the fracture surface. Damage accumulates, providing for a non linear behaviour, allowing stress concentrations to be somewhat relieved and increasing the fracture toughness.

This process requires a very good balance between the fracture properties of the mortar and of the aggregates. In light weight concrete, in which the aggregates contain small porosities, the microcracks are able to cross them, and the fracture toughness is decreased. The same happens if, on the contrary, the toughness of the mortar is increased, as in silica fume cement paste (Zaitsev et al. (4)).

This same principle is the one used in glasses in which small metallic particles are incorporated (Krstic et al. (5)).

In order to fully understand this mechanism, what is mostly needed is a good criterion for microcrack propagation including branching. It could be that the maximum stress criterion of Erdogan and Sih could be the right one, but this needs confirmation in such materials and fundamental experiments are missing. Another problem is the statistical distribution of sizes and shapes of the aggregates. Numerical concrete (Wittmann (3), Zaitsev et al. (4)) can help to optimize the material design, but this numerical material is only two dimensional so far. Otherwise damage mechanics looks to be the right tool. Methods exist to evaluate the influence of a distribution of microcracks on the compliances, and thus to quantify damage parameters.

Another way to hinder crack propagation is to bridge the crack surfaces by fibers. They act as crack closing forces, thus reducing the effective stress intensity factor at the tip. The application of this principle are numerous. It works in carbon, carbon composites in which the matrix is a brittle amorphous carbon phase ; in concrete containing metallic fibers ; it has long been used in asbestos cements (Deschryver (6)) which must now be replaced by other fiber cement composites because of the obnoxiousness of asbestos. It is also the toughening mechanism in glass fiber-epoxy resin composites. The difficulty there is to know the value of the closing force which a fiber exerts on the crack tip. It is related to the resistance of the fiber-matrix interface, the origin of which is difficult to ascertain and it is difficult to measure.

A similar idea leads to the reinforcement of soils with geotextiles, made of aging resistant polymers such as polypropylene, or polyester.

The other principle for improving the toughness of brittle materials is to react on the initiation of cracks. The first manner is to multiply the sites of crack initiation : this multiplies the number of cracks and thus the energy absorbed by fracture. If we observe how fracture occurs in a syntactic foam (fig. 1) a material made of hollow glass microspheres imbedded in an epoxy resin, we see that cracks are initiated in the largest microspheres. If they were large enough they would propagate at once in the epoxy resin and in the rest of the material which would be very brittle. But as they are smaller than this critical size, the microcracks do not propagate, the compliance of the material increases, and so do the stress concentrations in the unbroken glass microspheres. New ones are then cracked, and in this way damage accumulates and

fracture toughness increases.

We observe the same kind of phenomenon in an epoxy adhesive which contains elastomeric particles (fig. 2).

The tools exist to optimize these materials. Using either finite element modelling with three phases : the particle, the surrounding matrix and the surrounding composite equivalent material, or the inclusion analysis of Tanaka and Mori, it is possible to calculate the stress in the particle or at the interface, and thus to evaluate the initiation of the microcracks as a function of the distribution of shapes, sizes and local volume fraction (a most important parameter in that case) (fig. 3).

In metals it is inhomogeneous deformation which triggers cleavage. Reducing the grain size is the most efficient way to prevent harmful localized slip. Very strong quenching achieves that. This can be obtained either by high pressure gas atomization and centrifugal gas atomization, or by meltspinning-ribbon comminution. These techniques give successful results in the production of very fine grain magnesium alloy with aluminium, zinc and yttrium in which a uniform dispersion of 20 nm intermetallic  $Al_2Y$  stabilizes the grain, and provide obstacles to the motion of dislocations. A yield strength of 425-460 MPa is thus obtained, with a 5-14% elongation (Kim and Das (7)). The same technique can produce ultrahigh strength structural steels (0,25 C, 4 Mo) with improved fracture toughness and lower brittle-ductile transition temperature.

#### PREVENTION OF CREEP RUPTURE

Many of the new materials were designed to obtain a better resistance at high temperatures. The important mechanisms of deformation and fracture under those conditions are diffusion of vacancies and gliding of grain boundaries.

The coefficient of self diffusion being related to the absolute melting temperature, one way of course to obtain creep resistant materials is to turn to refractory elements. The carbon-carbon composites are an example of such materials. They take the advantage of the great strength of carbon fibers, up to high temperatures and the binding of these fibers together is achieved by amorphous carbon.

The best way to avoid grain boundary sliding is to

suppress it altogether and to use single crystals, as it is achieved for turbine blades.

However important are vacancy diffusion and grain boundary sliding in creep, dislocations displacements remain a controlling mechanism in a large temperature and strain rate field. Precipitates can provide strong obstacles to the dislocations, especially ordered ones, because a dislocation which glides across them must create a high energy antiphase boundary. These precipitates must remain stable at high temperatures in order to improve the resistance to creep. It is the case with the  $Ni_3Al$ , gamma prime precipitates, which are the basis of the metallurgy of the heat resistant nickel base super alloys (fig. 4).

Why not turn to pure  $Ni_3Al$  ? The trouble with this intermetallic compound is its great brittleness at room temperature owing to very weak grain boundaries. It was found that small additions of boron, which segregate in the grain boundaries, drastically improves the ductility (Stiegler and Liu (8)). Intermetallics are very interesting prospective materials for high temperatures applications, and improving their ductility, and further increasing their creep resistance is a challenge which inspires much research, centered on the mechanisms of grain boundaries strengthening.

Other obstacles to the displacement of dislocations are non metallic inclusions, such as oxides or carbides. Their efficiency is the greater, the finer their dispersion. This is the idea which forms the basis of the development of metallic matrix composites. One can quote aluminium with alumina particles (SAP), with SiC particles, steel containing a fine dispersion of alumina (ODS). The small particles can be replaced by fibers, such as carbon fibers or SiC fibers or whiskers. There are problems to incorporate them in a metallic matrix. C for instance reacts with liquid aluminium. By dispersing the fibers in the solid state an excellent material can be fabricated (fig. 5).

#### INCREASING THE RESISTANCE TO FATIGUE

The ways to fight fatigue crack initiation and fatigue crack propagation are completely opposite (François (9)). Fatigue cracks initiate by irreversible slip at the surface of parts, and to improve the fatigue resistance this slip must be prevented. The usual strengthening mechanisms such as solid solution hardening or precipitates hardening are efficient.



However some precipitates favor planar slip as the ordered delta prime precipitates in Al Li alloys. The reason is that once a dislocation has created an antiphase boundary by crossing the precipitate, the following ones find there an easier path. Repeated planar slip is very harmful in fatigue.

A very good way to reduce slip is to refine the grain and the fatigue limit is found to follow the same dependency on the inverse of the square root of the grain size, as it is the case for the yield stress.

If we turn to fatigue crack propagation we find on the contrary that planar slip and large grains increase the fatigue threshold. This is due to a misfit between the crack surfaces on unloading which creates a very large closure effect and a small effective stress intensity factor. This is well demonstrated in AlLi.

#### CONCLUSION

These few examples demonstrate that improvement of the properties of materials can be achieved by a judicious combination of phases, of elements, of materials. This requires a good understanding of the basic mechanisms of deformation and fracture. It is a science which combines metallurgy, its extension to other classes of materials than the metals, and solid state mechanics. The tools to predict the macroscopic behaviour from the microstructure are being developed. More and more they rely on a good description of the statistical distribution of the components. Some of these tools require heavy computer work. In the end it seems that it is really the fabrication of the material which is the limiting factor. It is the technical area which requires the broadest knowledge and the best experience and judgement and imagination.

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|                                   | Metals                           | Covalents                        | Ceramics                            | Glasses                   | Cement paste          | Geo-materials         | Cellulose woods textiles papers | Polymers                | Elastomers     |
|-----------------------------------|----------------------------------|----------------------------------|-------------------------------------|---------------------------|-----------------------|-----------------------|---------------------------------|-------------------------|----------------|
| Metals                            | Alli, superalloys intermetallics | Metallic matrix composites (MMC) | Oxide dispersed strengthening (ODS) |                           |                       |                       |                                 |                         |                |
| Covalents                         |                                  | Carbon-carbon composites         |                                     |                           |                       |                       |                                 |                         |                |
| Ceramics                          |                                  |                                  | Alumina-Zirconia                    |                           |                       |                       |                                 |                         |                |
| Glasses                           | Glass with metallic inclusions   |                                  |                                     |                           |                       |                       |                                 |                         |                |
| Cement paste                      | Fiber reinforced concrete        |                                  |                                     | Cement fiber composites   | Silica fumes concrete | Light weight concrete | Cement fiber composites         | Cement fiber composites |                |
| Geomaterials                      | Nailed earth                     |                                  |                                     |                           |                       |                       |                                 | Reinforced soils        |                |
| Cellulose : woods, textile papers |                                  |                                  |                                     | Textiles                  |                       |                       |                                 | Textiles                | Textiles       |
| Polymers                          |                                  |                                  |                                     | Syntactic foam Composites |                       |                       |                                 | Polymeric alloys        | Shock polymers |
| Elastomers                        | Tires                            |                                  |                                     |                           |                       |                       |                                 |                         |                |

Table I : New Materials

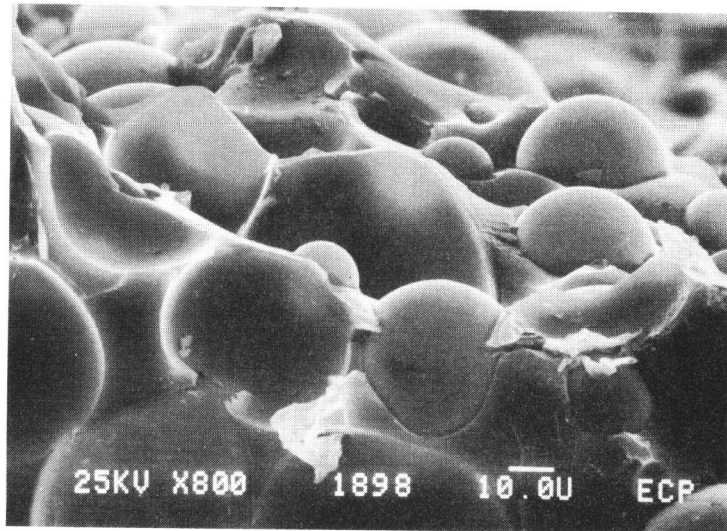


Figure 1 : Fractograph of syntactic foam.  
(Dan Wei. Theses Ecole Centrale de Paris).

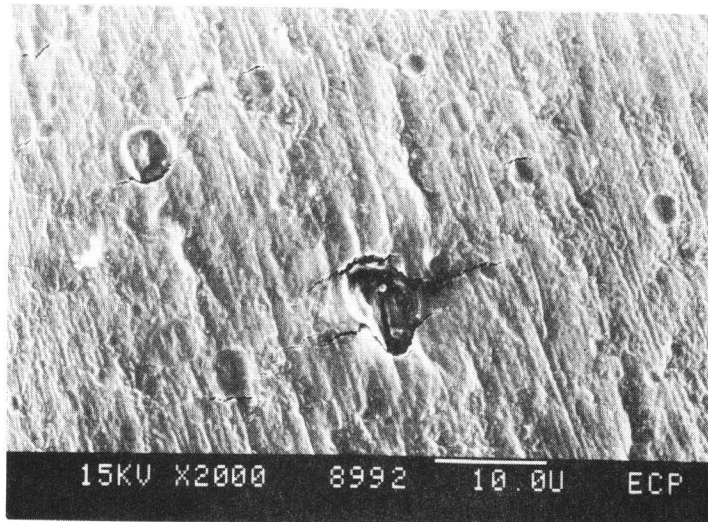


Figure 2 : Cracks initiated at elastomer particles interface in an epoxy adhesive.  
(Hu Geng Kai. Ecole Centrale de Paris).

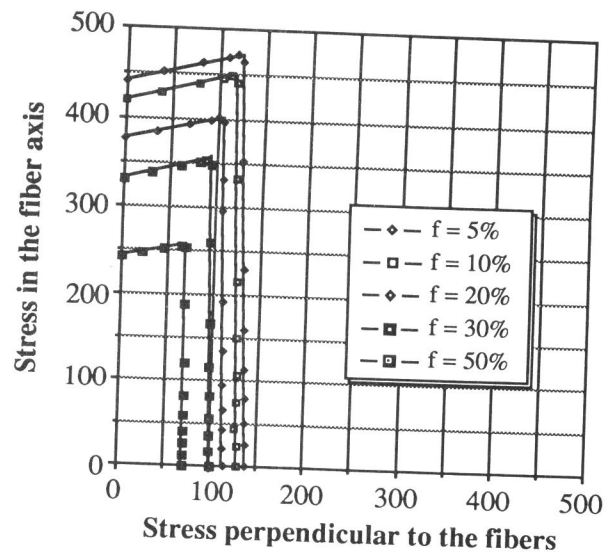


Figure 3 : Damage initiation locus in Al-C composite for various volume fractions of fibers. (Ph. Breban, Ecole Centrale de Paris).

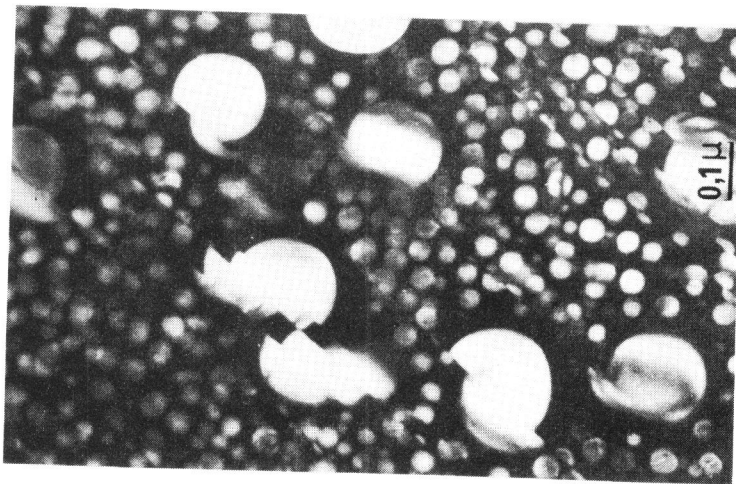


Figure 4 : Shearing of  $Ni_3Al$  precipitates in Waspaloy. (M. Clavel These, Ecole National Supérieure des Mines de Paris).

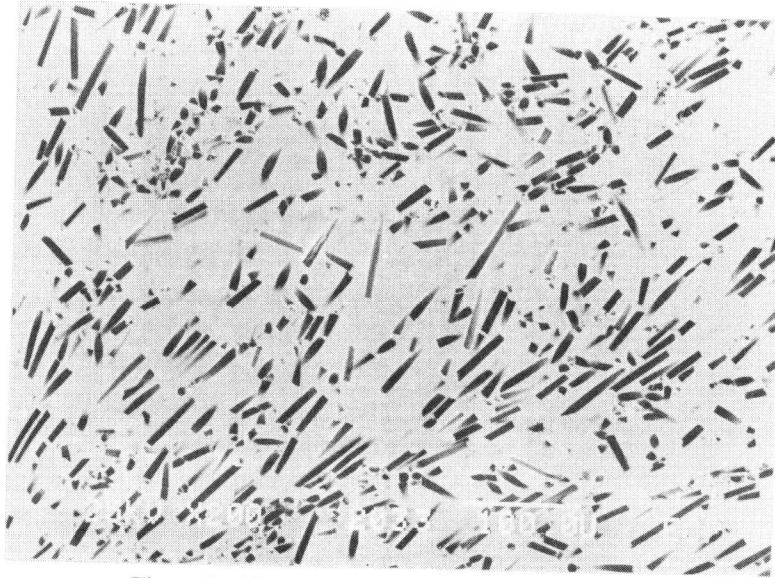


Figure 5 : Aluminium matrix-carbon fiber composite.  
(Ph. Breban. Ecole Centrale de Paris).