INTRODUCTION

Nondestructive evaluation, as practiced in the 1960's, attempted to detect (but was often unable to characterize) the existence of defects in engineering structures. Qualitative criteria were used in the assessment of defect significance and the determination of accept/reject decisions. Advances in elasto-plastic fracture mechanics during the 1970's focused attention upon the defect size and orientation— if these could be measured, then fracture mechanics was capable of quantitative structural integrity evaluation. The papers presented in this conference series during the 1980's trace the considerable advances of quantitative nondestructive evaluation in satisfying this measurement need. Nowadays, for monolithic materials with well defined fracture toughness, the overconservative rejection criteria of the past are beginning to be replaced by "retirement for cause" concepts.

Implicit in all of these approaches to structural integrity evaluation is a singular valued fracture resistance. It is assumed that a material's resistance to crack growth at a particular temperature is homogeneous within the body and does not change during the life of a structure. Then, Griffith criteria of the form:

$$r_c = \frac{2\gamma E}{\pi c}$$

where $2c$ is the defect diameter, $\gamma$ is the crack surface energy (Jm$^{-2}$), $r_c$ is the body's fracture stress, and $E$ is Young's modulus, can be used to predict fracture under load. $(2\gamma E)^{1/2}$ can be associated with fracture resistance and thus singular values for $\gamma$ and $E$ lie at the heart of this structural integrity strategy.

Some of the materials in service today, and many of the advanced materials being considered for service during the 1990's do not have homogenous and time independent values for $\gamma E$. It is to be anticipated that the coming years will witness an increasing preoccupation with the determination of the spatial distribution of these quantities— particularly in regions where they are likely a minimum. This, it turns out, is often at interfaces such as grain boundaries, and boundaries between dissimilar materials (in composites for example). The issues for
Quantitative Nondestructive Evaluation (QNDE) in the 1990’s may thus be increasingly concerned with the evaluation of interfaces, and it is the purpose of this overview to attract attention to a selection of problems that may become of increasing future concern.

GRAIN BOUNDARY PHENOMENA

Grain boundaries are frequently found to be the preferred path for brittle fracture and stress corrosion cracking. In some systems, such as intermetallic alloys, the boundaries may be intrinsically weak while in others, such as low alloy steels, grain boundary segregation can weaken otherwise strong boundaries. In some advanced ceramics, glassy films at grain boundaries can significantly affect crack resistance behavior.

a) Low alloy steels

Low alloy steels (for example those with 4 wt%Ni and 1 wt%Cr, or 9 wt%Cr and 1-2 wt%Mo) are used for pressure vessels and turbine rotors. Some of these steels are found to suffer an increase in ductile to brittle transition temperature (DBTT) upon prolonged exposure to temperatures in the 300 °- 600 °C range. The shift is also associated with a change in the low temperature fracture path from trans-to intergranular. The shift in transition temperature, Fig. 2, is dependent both upon the time and temperature of exposure, and is indicative of a diffusion controlled embrittlement process. Examination of the freshly fractured grain boundaries by Auger spectroscopy indicates increased concentrations of trace impurities such as P and Sn cosegregated with Ni to the grain boundaries after embrittling treatments, Fig. 3. These impurities are found to have been enhanced in concentration only within a few atomic spacings of the grain boundary. Heating above 650 °C and rapid cooling through the embrittling temperature range to room temperature is found to reverse all the effects of lower temperature tempering, and thus the phenomenon is referred to as reversible temper embrittlement.

The phenomenon can be thought of as reducing the local (grain boundary) value of $2\gamma E$ in a Griffith-like fracture criterion Fig. 4. One way this can be achieved is if the segregated elements reduce $\gamma$ for grain boundary fracture i.e. if the chemical potential of a solute impurity atom on the fracture surface is less than the chemical potential in an unseparated boundary. Then, it is possible for defects to extend intergranularly at lower stresses along segregated boundaries compared to those with no impurity segregation.

![Figure 1. Impact energy verses testing temperature curves for a low alloy steel before and after prolonged tempering to cause reversible temper embrittlement.](image)
Figure 2. Variation of ductile brittle transition temperature (DBTT) and hardness as a function of ageing at 450 °C, 500 °C, and 550 °C.

Figure 3. Grain boundary composition as a function of ageing time at 500 °C.
The consequence of this is that a defect considered too small to cause fracture at the beginning of the life of a structure may become a significant defect later, even though it had not necessarily changed its size, due to a service induced loss of crack growth resistance. Much of the electrical generation capacity installed in 1960's and 1970's has, or will soon have, experienced a sufficient integrated thermal cycle to have begun the segregation process. Those regions of a structure that initially contained higher than normal trace impurities (As, Sb, Sn, P etc) will be experiencing an increase in DBTT and thus a decrease of critical flaw size. Faced with the possibility of expensive repairs or plant retirement, utilities will soon be looking for nondestructive techniques capable of detecting grain boundary segregation to ensure that defects present in the structure do indeed still pose no risk to integrity.

Figure 4. A grain boundary Griffith crack under tensile load.

b). Intermetallic alloys

The aerospace gas turbine engine continues to be the target application for many advanced materials development programs. For example the thrust to weight ratio and high temperature capabilities required of the engines in the National Aerospace Plane (NASP) cannot be achieved with available superalloys. Conventional superalloys are reaching maturity, and significant improvement of gas turbine engines is dependent upon the emergence of elastically any stiffer, lower density and higher melting point materials. Amongst the most promising of these are intermetallic aluminides, Fig. 5.

Interest in the aluminides stems from their lower densities, reasonably high melting points and absence of strategic elements such as cobalt. Titanium aluminides look particularly attractive for engine applications because of very low densities, good modulus, oxidation resistance, and creep properties (see Table 1), the latter stemming in part from the ordered structure that can be retained to high temperature.
Table 1. Properties of Intermetallic Compounds

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Structure</th>
<th>Young's Modulus (GPa)</th>
<th>T_m (°C)</th>
<th>T_c (°C)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAl</td>
<td>Ll_o</td>
<td>175</td>
<td>1460</td>
<td>1460</td>
<td>3.91</td>
</tr>
<tr>
<td>Ti_3Al</td>
<td>D0_19</td>
<td>145</td>
<td>1600</td>
<td>1100</td>
<td>4.2</td>
</tr>
<tr>
<td>NiAl</td>
<td>B_2</td>
<td>294</td>
<td>1640</td>
<td>1640</td>
<td>5.86</td>
</tr>
<tr>
<td>Ni_3Al</td>
<td>Ll_2</td>
<td>178</td>
<td>1390</td>
<td>1390</td>
<td>7.50</td>
</tr>
<tr>
<td>FeAl</td>
<td>B2</td>
<td>260</td>
<td>1250-1400</td>
<td>1250-1400</td>
<td>5.56</td>
</tr>
<tr>
<td>Fe_3Al</td>
<td>D0_3</td>
<td>140</td>
<td>1540</td>
<td>540</td>
<td>6.72</td>
</tr>
<tr>
<td>CoAl</td>
<td>B2</td>
<td>294</td>
<td>1648</td>
<td>1648</td>
<td>6.14</td>
</tr>
<tr>
<td>Zr_3Al</td>
<td>Ll_2</td>
<td>135</td>
<td>1400</td>
<td>975</td>
<td>5.76</td>
</tr>
<tr>
<td>Fe_3Si</td>
<td>D0_3</td>
<td>271</td>
<td>1270</td>
<td>1270</td>
<td>7.25</td>
</tr>
</tbody>
</table>

N.B. T_c is the order-disorder transition temperature

Historically intermetallic alloys have been by-passed for engineering applications because many were inherently brittle at ambient temperature and some undergo grain boundary fracture. Recent alloy additions and rapid solidification processing \(^7\) are showing promise of overcoming this for some systems. For example, the tensile ductility of polycrystalline Ni_3Al can be made to approach that of single crystal material by the addition of small concentrations (≤0.1 wt%) of boron, Fig.6\(^8\)
Boron can segregate during solidification processing resulting in regions of low boron content. The existence of these in components could prove very deleterious because even nominally elastic loading may then be able to fracture the unsegregated boundaries creating, early in a component's life, defects that might then grow to cause catastrophic failure. The emergence of QNDE techniques capable of sensing grain boundary segregation throughout the volume of a component may become an urgent need if these intermetallic compounds do indeed become tomorrow's turbine engine material of choice.

The ductilization of Ni$_3$Al by boron is accompanied by a transition from brittle intergranular to ductile transgranular fracture. Field ion microscopy, Fig. 7, has shown that boron segregates to many (but sometimes not all) grain boundaries. In contrast to the situation above in steels, grain boundary segregation in Ni$_3$Al is beneficial to fracture resistance. This can be understood if the chemical potential of a boron atom at an unseparated grain boundary site is lower than that on a free (fracture) surface. In that case, segregation increases $\gamma$ and the stress to cause fracture may then exceed that to commence plastic deformation.

Figure 6. A plot of room temperature tensile properties as a function of boron concentration for Ni$_3$Al (24 at%Al). All samples recrystallized for 30 min at 100 °C.

Figure 7. Field Ion Microscope images of two grain boundaries illustrating that some boundaries have significant boron segregation while others do not.
Figure 8. Inert strength verses indentation load of three aluminas, single crystal (sapphire) and polycrystalline with and without glassy grain boundary phase (PC-glassy and PC-pure, respectively).

c). Advanced Ceramics

There is a growing realization that the resistance to crack growth in non-transforming ceramics is a function of crack size and is affected by grain boundary properties. Lawn et al.\(^{(10)}\) have used indentation techniques to produce flaws of controlled size in Al\(_2\)O\(_3\) and measured the fracture strength, Fig. 8. Single crystal (sapphire) samples are found to exhibit classical "Griffith-like" behavior. However, polycrystalline material departs from the classical prediction.

In terms of toughness (T), Fig. 9 shows that for small flaw sizes, comparable to the scale of the microstructure, T is an intrinsic quantity representative of the weakest fracture path.\(^{(10)}\) As the flaw size increases, the toughness increases. The T-curves for the three aluminas shown in Fig. 8 also cross over. Thus, for the small flaw size regime, the fracture resistance of sapphire exceeds that of polycrystalline material but the reverse is the case for large flaws.

The origin of T-curve behavior has been found to be crack-face bridging in the wake of the crack tip, Fig. 10. As an intergranular crack advances, it encounters boundaries that are difficult to separate (possibly because they are under compressive residual stress). These regions are by-passed by the crack and then act to pin the crackfaces and inhibit stress intensification at the crack tip. T-curve behavior can

Figure 9. Toughness as a function of crack length for Al\(_2\)O\(_3\).
then be understood as an increase in the number of bridges to a dynamic equilibrium where the number being created near the crack tip equals those eventually destroyed further behind.\textsuperscript{(11,12)}

There are important implications for materials that exhibit strong T-curve behavior. The failure of such materials is independent of initial flaw size. Thus, the prospect of a service induced reduction of strength is avoided. However, there is then no validity to critical flaw size determinations - the foundation of structural integrity evaluation in brittle materials.\textsuperscript{(10)}

The strength of the T-curve behavior depends upon microstructure. In particular, impure alumina's with glassy grain boundary phases do not show as strong a behavior as pure alumina, Fig. 9. This may possibly be due to relaxation of some of the compressive grain boundary stress by the glassy grain boundary phase. The coverage of grain boundaries by glassy phases thus becomes a central parameter in determining fracture resistance, and may be more important to measure than initial flaw size in the gauging of strength.

THIN FILM INTERFACES

Techniques such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) have created the opportunity to produce heterostructures consisting of a silicon semiconductor substrate with thin opto-electronic film overlays with film thickness extending down into the subnanometer range.\textsuperscript{(13,14)} Enormous opportunities for new devices have emerged.\textsuperscript{(15-19)} For example, by co-depositing In, As and Sb, thin films of InAs\textsubscript{1-x}Sb have been deposited on InAs substrates which have the capability of detecting infrared signals in the 8-12\textmu m range.\textsuperscript{(15)} Other research is attempting to couple GaAs and Si technology by depositing GaAs superlattice films on Si substrates. Significant performance enhancements are anticipated if the high speed and opto-electronic properties of the III-V devices could be coupled with the high-density circuit capacity of Si technology.

The opto-electronic properties of these devices of the 1990's are critically dependent upon the attainment of a defect free film. However, defects can readily form at the interface between substrate and film, and between heterostructures within the film itself (e.g. strain layer superlattices).\textsuperscript{(20)} Many of these defects arise because of strain induced during film growth due to lattice constant mismatch.\textsuperscript{(21)} For example, there is a 4\% lattice mismatch between Si and GaAs. As one assesses the prospects for future devices, Fig. 11, one realizes that to achieve
Figure 11. Energy gap versus lattice constant and lattice mismatch to silicon.

smaller bandgap devices on Si substrates ways are going to have to be found to cope with increasingly larger lattice mismatches.

A consequence of the lattice mismatch is the generation of dislocations during thin film growth, Fig. 12. These dislocations form to relieve the large elastic strains at the interface. As the film thickness increase those dislocations inclined perpendicular to the substrate may grow through the film. The presence of these threading dislocations within active regions of a device can be very deleterious, and a variety of approaches are being explored to trap dislocations close to the interface.

Figure 12. Misfit dislocations growing in a 2μm thick GaAs MBE deposited film on a Si substrate.
Techniques are needed to non-invasively probe the interface during thin film deposition and characterize the dislocation structures and point defect populations. Of particular importance is the need to determine the density of dislocations that extend from an interface into active regions of a device, and methods of measuring the concentration of electrically active dopants in situ during deposition. It is natural to look to internal friction methods for this since dislocations and point defects can have large effects upon damping.

**COMPOSITE INTERFACES**

Composite materials are increasingly becoming the materials of choice for structural applications where stiffness and low mass are important. For components that are subject to only moderate temperature (200 °C), polymer matrices reinforced with glass, carbon, or SiC fibers are already available. For high temperature applications, and in situations where exceptionally high specific stiffness is needed, researchers are intensively exploring ways to produce advanced composites using light metal (e.g. aluminum, magnesium, and titanium) or intermetallic (e.g. titanium-aluminide) matrices. For the very highest temperature uses, ceramic matrix composites (e.g. carbon/carbon) are also under development.

The bulk properties of a composite, such as its strength and toughness, depend on many factors, Fig. 13. To attain optimum strength, the elastic modulus of the fiber reinforcement needs to be as high as possible, and the fiber needs to be well bonded to the matrix. To achieve high crack growth resistance is less easy to assure. In order to encourage maximum energy dissipation during fracture, strong fibers are needed along with optimum interface strength, so that fiber pullouts (and thus frictional dissipation of energy) are encouraged. If the interface is too weak, however, the interface provides little resistance to transverse crack growth.

\[
\begin{align*}
\sigma_f &= E_f \varepsilon_f \\
\sigma_m &= E_m \varepsilon_m \\
E_t &= \frac{E_f V_f + E_m (1-V_f)}{V_f} \\
\text{For perfect interface strain in fiber & matrix is constant (} \varepsilon_c) \\
E_f &\gg E_m \\
\end{align*}
\]

Figure 13. Composite Interface Measurement Needs.
It is clear that the interface between ceramic reinforcement and matrix is a key factor controlling composite properties. These properties are in turn controlled by the surface coatings applied to fibers and the effect of process pathway on interface reactions. In metal matrix composites featuring (reactive) light metal matrices the possibility exists of extensive deleterious interphase formation during solidification processing. Even when melt temperatures are held low (enough only for metal infiltration), temperature gradients result in some regions being exposed to sufficient heat to cause extensive reaction between matrix and reinforcement and concomitant local loss of fracture resistance. Thick reaction layers, with their unknown elastic properties, may also adversely affect the load transfer between matrix and reinforcement and thus be detrimental to strength. Even when layers are thin, if excessive dissolution of fiber coatings occurs during processing, the load transfer capability of the interface may still be affected, and the toughness of the composite reduced. In ceramic and metal matrix composites, residual stresses at the interface can also be very large and frictional dissipation during fiber pull-out (the principle toughening mechanism) and in metal-ceramic systems it results in extensive dislocation generation and local matrix workhardening which may contribute to the strength of the composite.

If these advanced composites are to be fully exploited tomorrow, new measurement methods are needed today to non-invasively probe interfaces and characterize the state of cohesion, the elastic moduli of interphases, and the frictional resistance to pull-out. Ideally, techniques amenable to interior imaging of these quantities (such as acoustic microscopy) would be preferred to those giving only a bulk average value, since it is going to be important to ensure that properties are homogeneous in the advanced composites of tomorrow.

SUMMARY

Interfaces play a central role in controlling the properties of structural and electronic materials. As we extend the performance of materials, it becomes increasingly important to be able to measure and then optimize local properties of interfaces. The measurement techniques needed for this do not exist today, though the basis for new ones has emerged from the QNDE research of the past decade. As our expertise in bulk materials characterization matures the next challenge for QNDE will come from the need to measure interface properties.

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REFERENCES

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