INTERFACE ENGINEERING IN CERAMIC COMPOSITES

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Abstract.- In multicomponent composites the morphology of the
phases and the composition and structure of grain boundaries and
interphase interfaces in system which can be designed from a
knowledge of their component phases, are most important factors
to be considered in order to understand and improve the
mechanical behaviour of ceramics.

In the present work this important issue is faced through the
studies carried out in mullite and mullite/ZrO_2 based materials
using TEM and AEM analysis.

1. INTRODUCTION

In previous conference ten years ago,
[1] the introductory papers described
the main principles of transmission
electron microscopy (TEM) and
microanalysis (AEM) applied to ceramics
but few of the remaining 55 or so papers
made significant reference to these
techniques. In the same year a
conference on mineralogy dedicated to
electron microscopy demonstrated many
beautiful examples [2] which are of
direct interest to ceramists, and
techniques were developed to analyze
grain boundaries and intergranular
phases [3]. In the interim electron
microscopy has become firmly entrenched
in ceramics research, as is quite clear
from the papers in this volume. The
availability of new and improved
instrumentation such as microanalysis
and high resolution imaging especially
of interfaces has played a very
important role in the growth of research
activity, [2-5]. A good illustration of
this growth may be found in a recent
symposium on electron microscopy on
electron microscopy of ceramics [5].

The uniqueness of transmission electron
microscopy is the ability to obtain full
morphological, crystallographic and
microanalytical (local composition) data
from the sample. Imaging at the atomic
level to 1.6 A° is now demonstrated and
clearly such high resolution is
essential for studying interfaces.
Analytical microscopy (AEM) by energy
dispersive x-ray (EDX-elements with
$Z > 6$) or energy loss spectroscopy
(EELS), illustrated in Fig. 1, whilst
limited in spatial resolution to about
100 A° can in principle, at least
qualitatively, detect all elements which
may be present in the sample at
concentrations $>10^{-5}$ depending on atomic
number and the very recent introduction
of parallel detection by EELS [6] will
certainly accelerate the utilization of
this sophisticated technique in
ceramics. Likewise, microdiffraction,
especially convergent beam analyses,
provides space group, crystal structure,
strain, thickness, etc., data at similar
levels of resolution as for EDX and
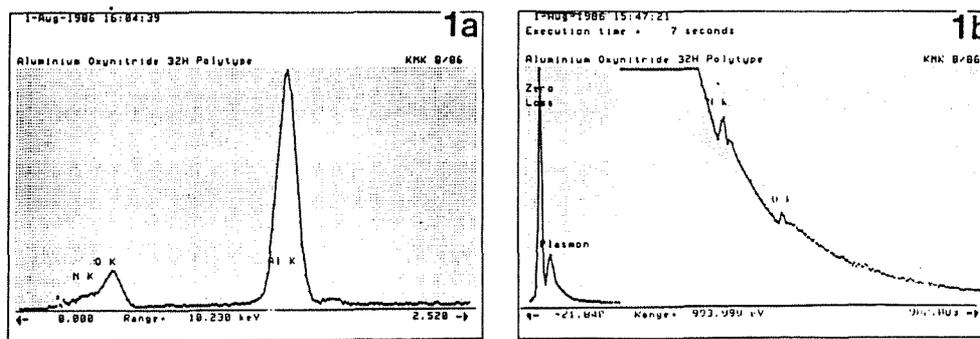EELS. Channelling enhanced microanalysis

Fig. 1.- (a) EDXS spectrum for AlN-Al$_2$O$_3$ 32H polytypoid: thin window but nitrogen barely resolved. (b) Spectrum from same sample showing nitrogen and oxygen k edges. The cation/anion ratios vary from polytypoid to polytypoid.

is a technique that offers information on lattice site occupancy [7, 8]. Specialized instrumentation such as high voltage microscopy with its advantages of resolution, penetration and in-situ dynamic capabilities [3] e.g., the work of Ruhle and his colleagues on fracture and stress induced phase transitions in zirconia ceramics [9, 10], is also being more widely used.

Some problems which should be mentioned include specimen preparation difficulties, e.g., in ion milling. Contamination in the microscope, in-situ phase transitions due to thinning or beam effects, radiation damage, heating and specimen instabilities under small intense probes. High voltage microscopy should be more widely utilized to reduce some of these problems. However, very thin clean specimens are needed for HREM and EELS. Improvements in detectors and electron sources will certainly increase the sensitivity of AEM methods and advances in such instrumentation are especially important in ceramics because of the significance of small amounts of impurities and particularly light elements.

In this brief survey, no attempt is made to be comprehensive, but it is hoped that the examples chosen are representative of typical applications of electron microscopy and microanalysis to research problems in ceramics involving studies of intergranular and intragranular interfaces and phases. The examples have been taken from research in my own group this past decade. The geometrical theory of crystalline interfaces especially grain boundaries is now rather well understood and discussed elsewhere in these proceedings so this aspect will not be discussed in this paper. Suffice it to say that high

resolution imaging is particularly valuable in obtaining direct information on such structures.

2. INTERGRANULAR INTERFACES AND INTER- FACE PHASES.

2.1. Liquid phase sintered ceramics.

One of the most widely studied problems over the past decade or so has been that of grain boundary interfaces in sintered and hot pressed compacts which require sintering aids to allow liquid phase sintering, or dopants to control physical properties. Well known examples are the covalent materials silicon carbide, silicon nitride, as well as alumina, zirconia-mullite, etc., and electronic materials such as varistors, ferrites and ferroelectrics.

Depending on composition and proportion of the additives, which will affect the relative surface energies of the matrix and second phases (s), intergranular continuous, or semi-continuous amorphous and/or crystalline phases have been observed in many systems. Various imaging methods are available for detecting intergranular phases [3, 11- 14, 15]. Since the size and distribution of the phases are similar (morphology) and since very narrow (6-20 A°) glassy regions are detected, geometrical effects alone [16] cannot account for the existence of amorphous phases, although these effects cannot be totally discounted and certainly affect wettability. Glassy phases are subject to ionization damage in the electron beam (especially at low voltages) and this effect [15] ("bubbling") can also be used to detect amorphous phases. Fig. 2 shows a typical example [13].
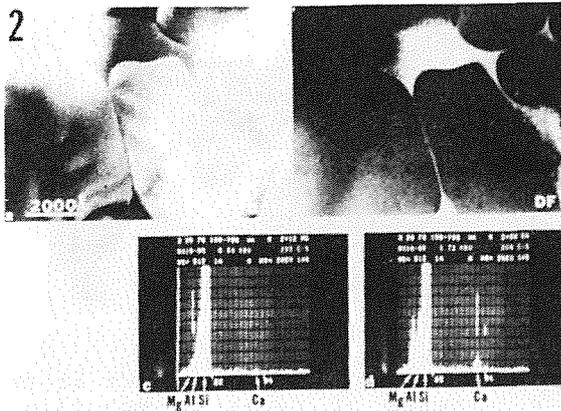
Fig. 2.- Bright and diffuse dark field imaging of Si_3N_4 fluxed with MgO and Al_2O_3 showing extensive glassy phases. Notice ionization damage in the pockets and calcium impurity detected in the EDXS spectrum from these pockets. These glassy phases often act as getters and contain many impurities [13].

Nitrogen ceramics, especially silicon nitride can be taken as an example of extensive investigation. The use of nitrogen ceramics as high temperature structural components has increased dramatically in the past decade. The bulk of this increased usage and the correspondingly increased research has revolved around the use of silicon nitride in gas turbine engine components [17]. The use of silicon nitride for these applications stems from its excellent high temperature properties including very good thermal shock resistance due to a low linear coefficient of thermal expansion (3.0 x 10^{-6}/°C).

Because residual glassy phases reduce creep strength, attempts have been made to obtain glass free interfaces by either controlling the sintering aid, and post treating to crystallise the glass or reaction sintering, or by alloying e.g., sialons, [18], although β11 β¹ sialons also contain glassy phases, the amounts depending on oxygen/nitrogen ratios [19].

3. ZIRCONIA-MULLITE: REACTION SINTERING

An example of multiphase ceramics can be found in mullite/zirconia composites which have been the subject of much research due to their excellent mechanical properties and potentially low production costs. Reaction sintering [20-22] of zirconia and alumina is an economically attractive route for obtaining mullite/zirconia composites, by reactions such as:

$$2ZrSiO_4 + 3Al_2O_3 = Al_6Si_2O_{13} + 2ZrO_2$$

which have mechanical properties (strengths up to 800 MPa and K_{IC} up to 8 MPa√m), which approach more expensive zirconia ceramics such as partially stabilized and tetragonal stabilized zirconia, zirconia toughened alumina etc., [23, 24]. The mullite matrix is particularly attractive because of its strength, chemical resistance, low thermal expansion, low dielectric constant, etc. Processing can be done at around 1550°C and is facilitated with oxide additives.

The basic idea of the processing is to allow a transitory liquid phase to form during the reaction [22] to facilitate densification (Fig. 3) and then this liquid phase is taken into solid solution or forms new compounds. In such materials, over 80% of the zirconia (both inter and intragranular) is monoclinic. The monoclinic phase has characteristic multiple micro-twinning [10, 25] to relieve the martensitic transformation strains. An example is shown in Fig. 4. Since cubic or tetragonal ZrO_2 may transform to monoclinic on specimen thinning for electron microscopy, x-ray analysis of bulk samples should be done to determine the fraction of phases present. Also the use of HVEM is preferred because thicker samples may be used and this effect can be minimized. Microstructural and toughness property correlations indicate that transformation toughening is unimportant in these ceramics but discontinuous microcracking around particles may be an important contributing mechanism, [24]. An example of microcracks is seen in Fig. 5 -they appear to be associated with the tips of microtwins in the ZrO_2 and these may be the initiation sites. Similar effects are known in twinned martensite plates in carbon steel. Care must be exercised in identifying such cracks e.g., by careful tilting and contrast experiments such as fresnel fringe imaging and defocussing. Also they can be enlarged during thinning and handling of the foil.

Another important result which has been found by AEM is the partitioning of Zr into mullite and Al, Si from mullite into zirconia (Fig. 6). When additives such as CaO, MgO, TiO_2 are used, the cations, whilst concentrated near the intergranular interfaces, are also partitioned. These results strongly suggest interdiffusion by interphase grain boundary migration leading to such solid solubility.
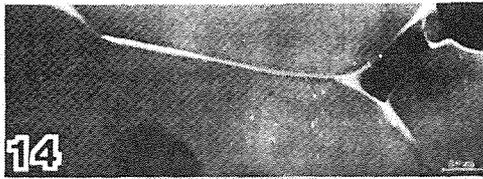
Fig. 3.- Interphase and intergranular glassy phase (transitory) in zirconia mullite with 0.25% Ti (as TiO_2) additive after 2 hours at 1550°C. Prolonged reaction time consumes all liquid phase.
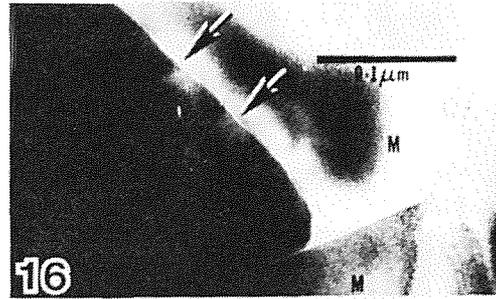

Fig. 5.- Interphase microcracks at the ends of twins in monoclinic zirconia and the mullite matrix. There are no cracks at interfaces lying parallel to the microtwins.

Fig. 6.- STEM-EDXS results showing partitioning of Zr into mullite and Si, Al into zirconia across the interfaces.
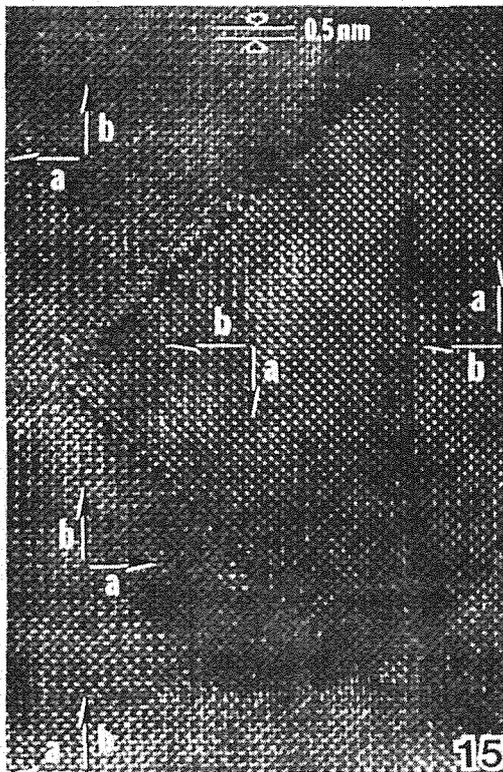
Fig. 4.- High resolution electron micrograph showing the microtwinned structure of martensitically transformed monoclinic zirconia. These twins form in such a way as to relieve the transformation strain from tetragonal to monoclinic phase.
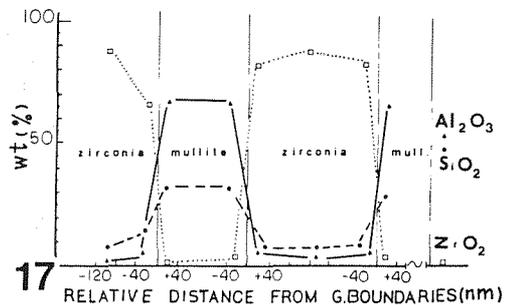
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