CASTAING'S ELECTRON MICROPROBE AND ITS IMPACT ON MATERIALS SCIENCE

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A central theme of modern materials science has been the exploration of the relationship between the microstructure of a material and its macroscopic properties. Beginning in the late 19th century, the developing field of metallography permitted scientists to view the microstructure of metal alloys. Mechanical polishing followed by selective chemical etching produced differential relief on chemically distinct phases or at grain boundaries. With such specimens, reflection optical microscopy revealed structures with micrometer and even finer dimensions. The microstructural world that was found proved to be highly complex, and most alloys were observed to be chemically differentiated into two or more distinct phases. The answer to many materials science questions required knowledge of the specific composition of such fine scale phases. Castaing's research was motivated by these considerations, as evidenced by the title of his first paper, "Application of electron probes to metallographic analysis".[1] The subsequent impact of Castaing's electron probe microanalyzer (EPMA) has occurred across a broad range of the physical and biological sciences. Materials science has been one of the most active areas and chief beneficiaries, as well as a source of researchers who not only employed electron beam microanalysis to solve their problems but who also contributed innovations that advanced the microprobe field. For example, the abstracts of the First National Conference on Electron Probe Microanalysis contain numerous examples of advanced applications of the electron microprobe to materials science, including analysis of (1) refractory metal coatings (P. Lublin and W. Sutkowski), (2) diffusion in the Ti-Nb system (D. Nagel and L. Birks), (3) Au-Al alloys (C. Nealey), (4) various steels (H. Nikkel), (5) Al-V-Mo-Ti alloys (R. Olsen), (6) corrosion of Ni-Co alloy (C. Spengler and R. Stickler), and (7) analysis of metal oxides and carbides (T. Ziebold).[2] Integrated over 50 years, the impact of electron probe microanalysis on materials science has been so broad and varied, especially in its continued development and incorporation within scanning electron microscopy and analytical electron microscopy, that a suitably comprehensive review is beyond the scope of this article. Instead, selected examples of critical applications will be presented to illustrate the impact in materials science.

1. Basic materials science information infrastructure: determining equilibrium phase diagrams.

The equilibrium phase diagram is a basic tool of materials science, relating composition, temperature, and phase for two or more elemental or compound constituents. Determining a phase diagram involves careful studies of the composition-temperature space with a series of alloys that span the full range of composition. To preserve the phase equilibrium established by holding the specimen at a chosen high temperature, a suitably small sample is rapidly quenched, and the resulting microstructure is studied. This treatment often results in micrometer-sized discontinuous particles in a continuous matrix. Only the EPMA (and at even higher spatial resolution, the closely related analytical electron microscope, AEM) can characterize such fine chemical phases with sufficient accuracy to elucidate the phase diagram.

2. Two-dimensional chemical structure

The natural evolution of the Castaing EPMA into the scanning electron probe microanalyzer of Cosslett and Duncumb opened an important new avenue to materials characterization, the technique of x-ray mapping.[4] The ability to visualize the actual distribution of elemental constituents with x-ray maps has proven to be one of the most popular methods of presenting EPMA data. Indeed, qualitative analysis to identify the elements present coupled with x-ray mapping to show their spatial distribution have probably solved many more practical problems than fully rigorous quantitative EPMA. With the further co-evolution of the EPMA and the scanning electron microscope (SEM), the modern composite SEM/EPMA instrument has emerged, incorporating high resolution electron imaging and diffraction techniques with x-ray microanalysis.[5,6]

3. Diffusion studies

Diffusion is a critical rate-defining process in many solid state reactions employed in materials synthesis, fabrication, and processing, as well as a contributing factor to certain kinds of in-service failures. The actual rates of diffusion are often low, resulting in compositional changes that occur over microscopic spatial distances. The micrometer to nanometer spatial resolution of EPMA and AEM is vital to the solution of many diffusion problems. Additionally, although the absolute accuracy of EPMA/AEM may be limited to two percent relative or higher in systems with large matrix corrections, the long-term stability of the EPMA enables the measurement precision to be reduced to well under one percent relative, permitting sensitive measurements of compositional change from one location to another, such as that found across diffusion gradients.[7,8]

4. Solid state reactions: alloy age hardening

An important class of metal alloys are those that undergo age hardening, that is, the mechanical properties can be modified by control of time-temperature variables. For example, fabrication can be carried out while an alloy is in a soft and malleable condition to place it in the desired shape, after which a particular heat treatment or simply time at room temperature results in solid state reactions that result in the precipitation of fine scale phases that serve to strengthen the final object. EPMA and AEM have helped elucidate the compositional changes that occur during these reactions, such as the formation of discrete particles and denuded zones.

5. Coatings and Interfaces

Protective coatings are applied to materials for resistance to mechanical and environmental challenges, particularly for high temperature service. Coatings can range in thickness from nanometers to micrometers, and EPMA has the sensitivity and spatial resolution to span this wide range of thicknesses. For film thicknesses less than the range of the beam, the composition, thickness, and even depth inhomogeneities can be determined. A sequence of measurements (film x-ray intensity normalized by the bulk pure element intensity) is performed over a range of beam energies, effectively depth profiling in a non-destructive manner. Quantitation is based upon $\Phi(\rho z)$ corrections. For thick films, classic metallographic cross sections can be prepared for probe analysis by line traces.

6. Light element analysis

The detection of light elements (Be, B, C, N, O, and F) has become routine with the advent of layered synthetic materials (LSM) as efficient diffractors of low energy radiation in wavelength dispersive spectrometry (WDS). Accurate measurement of these elements has had to take account of pronounced chemical (bonding) effects on the peak position and shape. Bastin and Heijligers have played a leading role in developing a robust methodology to deal with these spectrometric problems.[9]

7. Material failure analysis

Unanticipated changes in the chemical microstructure during service, especially when the environment is highly challenging, can lead to macroscopic failures. EPMA and AEM have been key contributors to the "Sherlock Holmes" approach to solving such failures. Catastrophic failure often destroys large scale evidence that might identify the cause, but microscopic evidence may still be preserved. ■

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