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# Applications of the Scanning Electron Microscope in Materials Science

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The commercial manufacture of scanning electron miscroscopes and their introduction into experimental research programmes has led to an increasing appreciation of the application of this type of instrument in materials science. Some account of their employment is presented here, the varying applications indicating clearly the importance of the instrument and its potential for both research and control.

## 1. Introduction

The scanning electron microscope is primarily a tool for the observation of surfaces, with the advantage of a depth of focus approximately an order of magnitude greater than that of the optical microscope, and with the possibility of direct viewing of complicated surfaces without replication. It has thus been possible to note phenomena in crystal growth hardly amenable to investigation by other methods. The facility of experimental study of phenomena occurring at surfaces, or features of surfaces characteristic of flow and fracture, appears to indicate the importance of the microscope in studying oxidation and corrosion phenomena and in diagnosing mechanical failure modes, e.g. fatigue, ductile and brittle fracture. The applications discussed extend across the field of materials and include metals, oxides, glass, textile fibres, wood and paper, and cement. In the field of semiconductors, applications include the fabrication and inspection of devices and the detection of defects.

## 2. Description of the Instrument

The scanning electron microscope has been described in a number of publications [1-3]. In this type of instrument, electromagnetic lenses are employed to focus an electron beam onto the specimen surface, which is then scanned in a raster in synchronism with the beam of a cathode ray tube. Secondary electrons emitted from the surface are collected by a grid and accelerated towards a hemisphere of plastic scintillator, the video signal from which is converted and amplified to modulate the signal on the cathode ray tube. The differences in signal intensity provide the modulations of brightness of the image on the screen. These intensity differences may result from changes of surface orientation in which case the screen image gives the surface topography, or differences of composition in the specimen enabling observation of different phases. Differences in contrast due to voltage enable observations of p-n junctions in semiconductors.

## 3. Comparison with Other Instruments

The scanning electron microscope has a resolution and depth of field approximately an order of magnitude greater than the light microscope. In principle, therefore, it extends considerably the range of observations allowed by the latter instrument, enabling the direct observation of material surfaces where previously the transmission electron microscope used with replica techniques was primarily employed. Since replication of surfaces is not required, it enables direct observations to be made conveniently of complicated features and forms not always amenable to investigation by the other techniques.

Resolutions at present obtainable with the scanning microscope are in the range 200 Å, while the optical microscope has a resolution limit of 2000 Å. The advantage of higher resolution (7 to 8 Å) with the transmission electron microscope must be weighed against the ease of observation in the scanning instrument. When resolution alone is important, the former instrument would be employed. In the scanning microscope, the design of the instrument and the

large focal length of the second lens allow large specimens to be inserted in the specimen chamber.

In general, the ranges of application of these instruments tend to be complementary, and the introduction of scanning electron microscopy should be looked upon as extending the possibilities of observing phenomena in materials science. Hence current research may employ a number of instruments, among which the scanning electron microscope should occupy an important position.

An example of the particular properties of the scanning electron microscope in surface observations is illustrated in figs. 1a, 1b, and 1c, which also illustrate the remarkable depth of field of the instrument at high magnification. These figures show views of the surface of a graphite crystal in which holes are present [4]. The magnification has been progressively increased and it is seen that, at approximately ×14 000, one can more or less see into the hole, observing its internal features and the structure of steps in the interior. The width of the hole is approximately 5 μm and the spacing between steps is approximately 500 Å. Focus is easily obtained over the entire depth of the hole. It is unlikely that this type of observation could be obtained by replication techniques in the conventional electron microscope.

## 4. Fields of Research Application of the Scanning Electron Microscope

In the Sorby Centenary Lectures, 1963, Melford [5] briefly reviewed the instrument and assured its potential in materials science, stressing that intensive effort was still required to develop its applications.

Wells [6] has recently listed approximately 150 published papers on the instrument, mostly written since 1960. With the commercial manufacture of instruments and their incorporation into research programmes, it is expected that there will be a large increase in published results and fuller evaluation of its possibilities.

The present review covers only some of the research, selected to typify the applications.

## 5. Decomposition of Crystals

One of the first reported applications of the scanning electron microscope was by Bowden and McAuslan [7], observing the slow thermal decomposition of silver azide. The crystals were allowed to separate from ammoniacal solution onto a silver plate, which was then mounted on a heating stage in the microscope. Both needles and plates of silver azide were prepared in this way, the needles varying from 1 to 10 μm in diameter. Changes in the crystal during stages of the decomposition could then be conveniently followed in the microscope.

The disintegration of the crystal into pebble-shaped units about 0.3 μm in diameter was noted. It was suggested that the observations were consistent with a preferential reaction (formation of silver and liberation of nitrogen) on a fine network of dislocations existing within the parent crystal.

## 6. Growth of Crystals

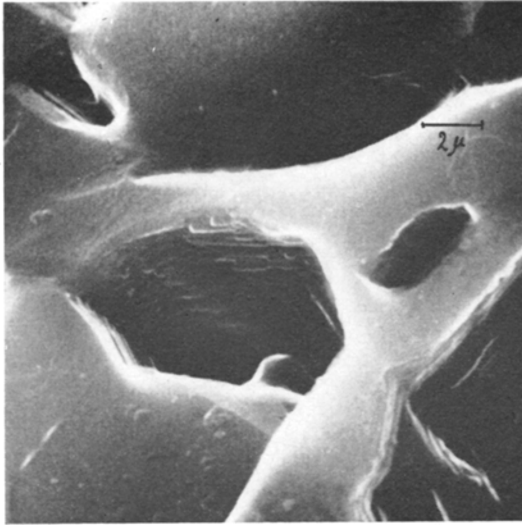
Several aspects of interest in the growth of crystals have been shown to be exceptionally amenable to investigation in the scanning electron microscope.

(*a*) Study may be made readily of the growth forms of crystals under varying conditions. This is particularly applicable to complicated growth forms or complicated features of growth. As an example, the study of whiskers and spherulitic crystals may be cited.

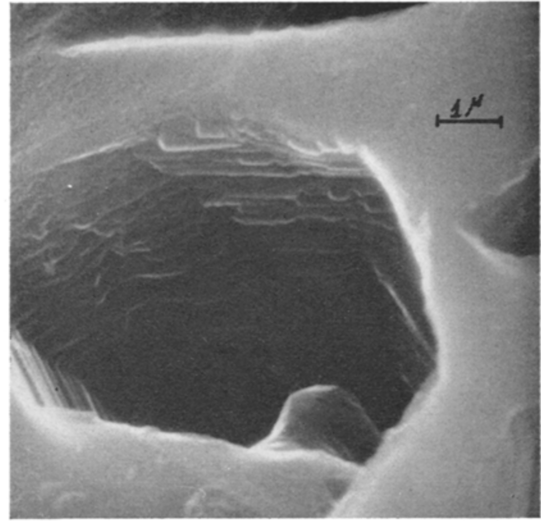
(*b*) Observation may be made of the three-dimensional features of the phases extracted from solids, which normally may be observed only in two dimensions in a prepared section.

The growth of crystal whiskers has been reported by Thornton *et al* [8] and by Gardner and Cahn [9]. The former investigators studied the growth of silicon crystals grown by the vapour-liquid-solid (VLS) process. A number of complementary techniques could be used for this type of investigation. The conventional techniques employed for studying whisker growth were used, i.e. optical microscopy and transmission electron microscopy using replicas, together with shadow micrographs, to reveal internal structure, and, in reflection, to obtain diffraction patterns. The scanning electron microscope was used specifically to study the morphology of the grown crystals and the change of morphology with variation of experimental conditions. The authors confirmed the ability of the scanning instrument to examine whisker structures with a resolution and depth of focus impossible by other techniques.

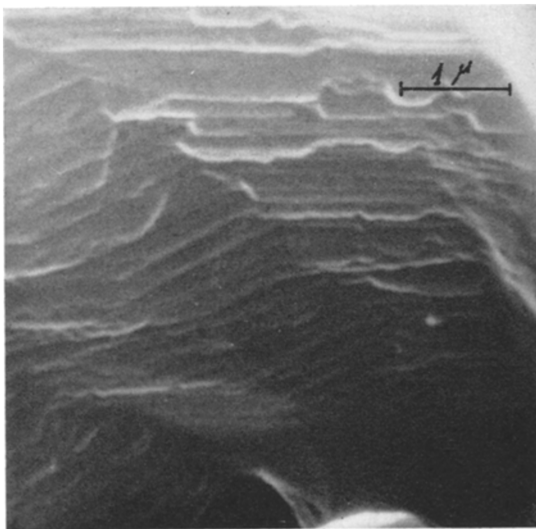
An application in a widely differing field, where the observation of crystal form is required, is shown in a recent note on hydration products in set cement paste by Chatterji and Jeffery [10].




(a)




(b)




(c)

*Figure 1 a, b, and c* Scanning electron micrographs of a hole in a graphite crystal. Approximate linear magnification of fig. 1c is ×14 000. (Courtesy of *J. Appl. Phys.* [12])

These authors note that previous attempts at studying the three-dimensional arrangement of hydration products could be made only by cutting ultra-thin sections (about 200 to 300 Å thick) and viewing them in a transmission electron microscope. The difficulties involved are the cutting of thin sections and the reconstruction of the three-dimensional model. Scanning electron micrographs of fractured cement paste show clearly the structural arrangements of crystals in the set paste, and demonstrate the possibility of further study of the dependence of physical structure of different types of cement on chemical composition. An illustration of a set cement paste is shown in fig. 2.

The use of the microscope in metallurgical systems, and in particular the study of growth forms of graphite in cast iron, has been demonstrated by Minkoff [11] and Minkoff and Nixon [12]. The observation of complicated growth forms of graphite in cast iron is normally limited to two-dimensional metallography of polished sections, from which growth form and growth behaviour may be surmised.

*Figure 2* Fracture surface of cement after hydration. (Courtesy of Dr S. Chatterji and *Nature* [10])

It was possible to photograph the branching of extracted crystals and the effect of adsorbed impurities blocking the thickening of graphite crystal growth. Figs. 1a, 1b, and 1c were taken from this research. Spherulitic crystals examined in the instrument showed surface protuberances which appear to be a characteristic feature of this type of growth.

## 7. Deformation and Fracture

The scanning electron microscope should lend itself admirably to the study of fracture surfaces, as a means of diagnosing failure mechanisms, thus furthering "fractography" with its aims of being able to identify the type of failure, the nature of the loading, and the direction of crack propagation.

McGrath *et al* [13] investigated the use of scanning electron microscopy to study fatigue and impact fracture of metallic materials, and compared the results obtained with replica techniques in the transmission electron microscope. The materials investigated were copper in fatigue, and 24 ST aluminium alloy in fatigue and impact.

The very fine striations (microbeach marks) associated with fatigue could be readily observed, as could the dimples associated with ductile failure in the impact specimens. These observations are comparable to replica photographs. As

the scanning electron microscope would represent a more convenient approach to the examination of fractured surfaces than replica techniques in the transmission microscope, it is expected that this will become a standard tool in the diagnosis of failure.

Tipper *et al* [14] had previously reported comparison between scanning electron microscopy and replica methods in examining the cleavage fracture of iron. The convenience of direct observation of cleavage faces was noted, as well as the use of stereoscopic techniques in the scanning instrument to determine the angles made by projecting surface irregularities (flakes) with the (001) plane of iron. These measurements were made by employing a holder to rotate the specimen about a vertical axis. The angle was calculated from photographs taken with the electron beam scanning the specimen from two directions at 90°.

## 8. Oxidation and Corrosion

Pease and Ploc [15] studied the oxidation of iron in the scanning electron microscope. The experimental method adopted was to heat the specimen on a heating stage in the specimen chamber of the microscope, oxidation proceeding at atmospheric pressure at 500 and 630° C. After each period of oxidation, the specimen chamber was evacuated and the specimen examined in the electron beam. By this method, it was possible to observe the progress of oxidation and to study the kinetics. The research was performed with iron specimens of varying purity. It was possible to observe oxidation at grain boundaries and on different grains of the specimen, so that some idea could be obtained of the dependence of oxidation on crystal orientation.

An experiment was performed to observe the influence of impurities on oxide whisker growth. This could be performed conveniently in the microscope by doping the surface of an iron sample with bismuth evaporated through a grid. On subsequent oxidation, whisker growth occurred only in regions exposed through the grid. In comparing the scanning electron microscope with other techniques, these authors pointed out that replica techniques are liable to be imperfect in examining these specific growth phenomena on surfaces. Discrepancies were observed between conventional electron microscopy of the surface replicas and scanning microscopy of similar surfaces.

Corrosion studies by Castle and Masterson [16] used the scanning electron microscope to investigate the oxidation of mild steel in high-temperature aqueous solutions, studies related to corrosion in boiler tubes. The particle size in the various oxide formations was measured by fracturing the metal oxide specimens while they were immersed in liquid nitrogen. The scanning electron micrographs obtained were used to estimate the internal area of oxide and to establish whether pores provide an interconnecting system of channels between the reaction surface and the aqueous environment.

## 9. Semiconductor and Solid-State Devices

The scanning electron microscope is used in electronics both for research and for the fabrication and inspection of devices. Reviews of these applications have been given by Mackintosh [17] and by Thornton [18], describing the instrument as a reliable means for checking circuitry and for the accurate determination of faults in microelectronics.

One of the important features of the microscope is the ability to observe a p-n junction in a non-destructive manner. The trajectories of slow secondary electrons leaving the surface are dependent on the potential existing between the specimen and the final lens, and between the specimen and the collector. The collection efficiency of secondary electrons will be higher for one area of a semiconductor device separated from an adjacent area by a reverse-biased p-n junction, and appears as contrast.

Another effect of importance in application of the scanning electron microscope to electronics is the conductivity induced by the electron beam. Valence electrons are excited by the beam into the conduction bands, generating hole-electron pairs. This electron-beam-induced conductivity is quite noticeable in semiconductors, especially if the carriers are generated near a reverse-biased junction or in its depletion layer. The current may be used after amplification to control the brightness of a cathode ray tube being scanned in synchronism with the primary beam. The combination of visual and voltage topography together with the detection of photovoltage (or current) increases the diagnostic power of the instrument.

Czaja and Patel [19] used these techniques, but with the electron beam of a microprobe analyser, to observe edge dislocations in silicon, and suggested that contrast is most likely to be

due to a decrease in response current, because of the additional recombination of injected carriers at edge dislocations. These techniques may be conveniently operated in the scanning electron microscope to provide surface topography of the specimen together with the resolution of defects in the bulk [20, 21].

Shaw, Hughes, Neve, and Thornton [22] have used the effect associated with electron-beam-induced conductivity to observe diffusion spikes in gallium arsenide when zinc is diffused into a crystal, an effect related to mosaic structure.

## 10. Paper Technology and the Observation of Fibres

One of the first fields in which the scanning electron microscope was consistently applied in research was in wood and paper technology, and results have been described in a number of publications. Buchanan and Smith [23] have described the use of the instrument for the examination of damage in papermaking wood chips. Rough wood specimens were examined in relating the strength of paper to damage in the wood during chipping. Forgacs and Atack [24] used scanning electron microscopy to observe the surface of newsprint, in particular to examine the distribution of short ground-wood particles sticking out through the long fibre layer of the paper. These observations were reported to support a theoretical approach relating a geometrically defined arrangement of fibres to properties of the resultant sheet. The requirement of a choice of model depends on a knowledge of the structure of real paper.

The application of the instrument to the study of polymers and other fibres has been reported extensively in publications by Sikorski [25]. This research is also based on the exclusive use of the instrument to the study of a particular technology.

## 11. Summary

A short account has been given of some applications of scanning electron microscopy in the study of materials. At present, contributions are being made in crystal growth, semiconductor technology, wood and paper, fractography, and fibre technology. Phenomena occurring at surfaces, requiring a resolution higher than that capable with the light microscope or which are not readily amenable to replication techniques for transmission electron microscopy, may be readily investigated. Provided the resolution required is not that of the transmission electron microscope, particular advantages are provided by the scanning instrument, and the viewing of specimens is very much facilitated. Bulky specimens may be inserted, and an initial macroscopic view at low magnification may be obtained over a large area before selecting the feature required for observation at higher magnification and bringing this into the field of view. It is also possible to rotate and view the specimen from different angles. Stereomicrographs may be taken from which angular measurements of surfaces and height measurements may be made.

Some research has been described in which experiments have been performed in the instrument and the specimen viewed *in situ*. Attachments employed have been for heating and cooling and for ion bombardment [26]; this indicates an interesting potentiality in which fixtures may be employed for observing phase transformations, growth, wear of surfaces, and surface effects on fracture.

A wide range of materials has been examined as evidenced by experiments currently performed on metals, ceramics, glass, textile fibres, wood and paper; a versatility which would assure its place in materials research.

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## References

1. R. F. W. PEASE and W. C. NIXON, *J. Sci. Instr.* **42** (1965) 81.
2. K. C. A. SMITH, "Encyclopedia of Microscopy" (Reinhold, New York, 1961), p. 241.
3. C. W. OATLEY, W. C. NIXON, and R. F. W. PEASE, "Advances in Electronics and Electron Physics", Volume 21 (Academic Press, New York, 1965), pp. 181-247.
4. I. MINKOFF, *Phil. Mag.* **12** (1965) 1083.
5. D. A. MELFORD, *Special Report Iron and Steel Inst.* **80** (1964) 214.
6. O. C. WELLS, "Bibliography of the Scanning Electron Microscope" (IBM, October 1966).
7. F. B. BOWDEN and J. MCAUSLAN, *Nature* **178** (1956) 408.
8. P. R. THORNTON, D. W. F. JAMES, C. LEWIS, and A. BRADFORD, *Phil. Mag.* **14** (1966) 165.

9. G. A. GARDNER and R. W. CAHN, *J. Matls. Sci.* **1** (1966) 211.
10. S. CHATTERJI and J. W. JEFFERY, *Nature* **209** (1966) 1233.
11. I. MINKOFF, *Acta. Met.* **14** (1966) 551.
12. I. MINKOFF and W. C. NIXON, *J. Appl. Phys.* **37** (1966) 4848.
13. J. T. MCGRATH, J. G. BUCHANAN, and R. C. A. THURSTON, *J. Inst. Metals* **91** (1962) 34.
14. C. F. TIPPER, D. I. DAGG, and O. C. WELLS, *J. Iron and Steel Inst.* **193** (1959) 133.
15. R. F. W. PEASE and R. A. PLOC, *Trans. Met. Soc. AIME* **233** (1965) 1949.
16. J. E. CASTLE and H. G. MASTERSON, *Corrosion Sci.* **6** (1966) 93.
17. I. M. MACKINTOSH, *Proc. IEEE* **53** (1965) 370.
18. P. R. THORNTON, *Sci. J.* (November 1965) 66.
19. W. CZAJA and J. R. PATEL, *J. Appl. Phys.* **36** (1965) 1476.
20. N. F. B. NEVE, K. A. HUGHES, and P. R. THORNTON, *ibid* **37** (1966) 1704.
21. I. G. DAVIES, K. A. HUGHES, P. R. THORNTON, and D. V. SULWAY, *Sol. State Electron.* **9** (1966) 275.
22. D. A. SHAW, K. A. HUGHES, N. F. B. NEVE, D. A. SULWAY, P. R. THORNTON, and C. GOOCH, *ibid*, p. 664.
23. J. G. BUCHANAN and K. C. A. SMITH, *Proc. European Reg. Conf. Electron Microscopy* (1961), edited by Houwink and Spit.
24. D. L. FORGACS and D. ATACK, *Trans. Oxford Symp. Brit. Paper and Board Makers Assoc.* (1961), edited by Bolam.
25. J. SIKORSKI, *Int. Conf. Roy. Microscopical Soc.* London (1966).
26. A. D. G. STEWART, *Proc. 5th Int. Cong. Electron Microscopy* Philadelphia (1962).