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Publication Date

1977-10-01

UC-11

Submitted to Environmental Research

LBL-6283 c.1
Preprint

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October 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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DEFORMATION OF CHRYSOTILE ASBESTOS

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ABSTRACT

The degree of microcrystalline deformation in fibers of chrysotile asbestos may be distinguished using high resolution dark-field electron microscopy. This is demonstrated by comparing undeformed chrysotile with UICC* standard reference samples. The UICC samples are shown to be partially deformed as a result of milling in the mixing process. Using this technique, samples of used and unused brake shoe lining dust were examined; it is shown that chrysotile asbestos in various stages of deformation — relatively undeformed to heavily deformed — survives in automobile brake drum dust. Such dark field images can serve to identify the source of asbestos found in environmental pollution samples.

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*Union Internationale Contre le Cancer (UICC).

INTRODUCTION

There is a controversy in the literature as to whether or not fibers of chrysotile asbestos survive in automobile brake drum dust: two studies (Rohl et al., 1976; Alste et al., 1976) reporting that they do contradict earlier work (Lynch, 1968; Hickish and Knight, 1970) which report that they do not. The latter claim that the chrysotile is converted to forsterite under the high temperatures attained in the braking process.

As high resolution dark field electron microscope images are sensitive to the degree of deformation, they can be used to distinguish between deformed and undeformed fibers and thus to resolve these two differing sets of results. Using this technique, it is shown that chrysotile asbestos fibers in various states of deformation — relatively undamaged to heavily deformed and recrystallized — exist in automobile brake drum dust.

SAMPLE SELECTION AND PREPARATION

Four samples were selected: (A) undeformed chrysotile ore samples from serpentine outcrops of Calavares County (California); (B) slightly deformed UICC reference standards of Canadian chrysotile milled during preparation to reduce fiber size (Timbrell et al., 1969); (C) unused brake lining dust, collected during burnishing prior to installation of new brake shoes; and (D) brake drum dust collected from the front and rear brake drums of a State vehicle obtained during brake shoe service (Seshan and Smith, 1977).

Samples were transferred directly to formvar-coated electron microscope grids and coated with carbon on both sides.

EXPERIMENTAL

As the high resolution dark field method is described in great detail elsewhere (Hirsch et al., 1969), only a very brief description is included here. An electron beam striking a polycrystalline specimen with grains of different orientation (e.g., A and B in Fig. 1) is diffracted into cones, causing the typical polycrystalline ring pattern. The high resolution dark field method consists of tilting the incident beam so that part of the diffracted ring passes through the optic axis of the microscope (Fig. 1b). The tilting is accomplished with the electronic beam tilt device. Then an aperture collects intensity only from those crystallites diffracting into this part of the ring, e.g., B (Fig. 1c).

Various factors involved in the interpretation of the diffraction patterns of chrysotile asbestos fiber bundles are shown in Fig. 2. The actual lattice of chrysotile is a defected, scrolled crystal with fiber axis along a (Yada, 1967). The reciprocal lattice of this crystal should be some form of a spiral, equispaced along the a* axis. Zvyagin (1967) and Whittaker (1966) have studied diffraction effects from concentric cylinders. How deformation and shear will affect the diffraction patterns has not, to the author's knowledge, been studied and is under study here.

The simpler case of an undeformed, defect-free chrysotile fiber, where the fiber is idealized as a series of concentric cylinders, as first proposed by Whittaker (1969) is shown in Fig. 2i. The reciprocal lattice then consists of a series of concentric rings, Fig. 2ii (only the two rings in the 2kl layer are drawn). The electron diffraction pattern represents the intersection of the reflecting or Ewald sphere (ES, Fig. 2ii) with these rings (Hirsch et al., 1969). This ought to result in a series of spots as shown in the -2kl layer line. Streaked patterns are, however, obtained from single fibers of chrysotile (Yada, 1967; Seshan and Smith, 1977).

The explanation for the streaking probably lies in refraction effects and the fiber shape (Yada, 1969); it could also result from the various faults produced during the growth of the crystal. The influence of these faults on the diffraction patterns and their influence on deformation needs further study.

When bundles of fibers are involved the streaks are replaced by arcs (Figs. 2iv and 3b), showing a strong tendency towards a texture, and yielding the typical "arcuate" patterns observed by several researchers (e.g., Rohl et al., 1976). The dark field image obtained by imaging any part of the arc, as in Fig.1 and 3b, should yield uniform intensity, _if_ the crystal is homogeneous. This is the case to be expected _only_ in the case of the undeformed fibers — and is consistent with the experimental observations in Fig. 3a,b.

RESULTS

Bright and dark field images of naturally occurring chrysotile (A) are shown in Fig. 3. The dark field is obtained by imaging a portion of the diffracted intensity as explained above. The result is a uniform contrast as would be expected from an undeformed crystal.

The striking feature of the dark field images is the great intensity along the hollow canals and this needs further investigation. The intensity difference cannot be explained on the basis of differences in absorption alone; it appears that some diffraction processes are operative: notice that the canals are sometimes bright and sometimes dark. However, in the crystalline part, the intensity is uniform and it is clear that these fibers are free of gross deformation.

Like most sheet silicates, chrysotile fibers are beam-sensitive to 100 keV electrons (Langer et al., 1974; Seshan, 1975). Precaution must therefore be exercised while obtaining the high resolution dark field images, because upon focusing the condenser, the fibers tend to become blistered. In the dark field image in Fig. 3a, precaution was taken to <u>prevent</u> any beam damage; the condenser was not focused, and the beam was tilted in the dark field mode. The condenser was then focused to obtain the diffraction pattern shown in Fig. 3b. The resulting beam damage is shown in Fig. 3c. The use of beam sensitivity to distinguish chrysotile from other non-beam-sensitive materials, e.g., the amphiboles has been discussed by Langer et al.(1974).

Dark and bright field images of deformed UICC standards (B) are shown in Fig. 4(a-c). The effects of deformation are clearly seen in the dark field images (a,b) and in the electron diffraction patterns, but not in the bright field images (c). The clear internal canals of the undeformed sample (A) are destroyed; there appears small submicron (100Å) areas which light up as if they were grains or microdomains of different orientations; consistent with this observation, the strongly textured diffraction patterns of the undeformed fibers (Fig. 3) are changed to that of a polycrystal. At the present the crystallographic and microstructural nature of the deformation is not clear and warrants further study. The effect of translating the aperture to a different part of the diffracted ring is shown in Fig. 4a,b. The result is that "grains" in a different orientation "light up," or show diffracted intensity signifying that this is truly a diffraction effect.

In order to isolate the effects of deformation during the braking process, unused brake shoe burnishing dust (C) was examined (Fig. 5a,b). The bright field image (B) is not informative while the dark field image clearly shows some intact internal canals (see arrow, Fig. 5a) resembling the undeformed chrysotile (Fig. 3). There are also small deformation domains which clearly resemble the UICC standard (B) samples. These fibers are therefore deformed less than the UICC standard samples (Fig. 4), as some intact internal canals can still be seen. It is impossible to derive this conclusion from the bright field range.

Samples of heavily deformed chrysotile fiber found in brake drum dust are shown in Fig. 6 in the bright and dark field. Whereas the effects of deformation are not evident in the bright field image, the difference in the dark field image is quite striking. The crystal is inhomogeneous. This is reflected in the electron diffraction pattern, now showing a number of spots (Fig. 6b). The mottled contrast of black and bright areas could arise from one of several causes: severe surface deformation leading to uneven crystal thickness, conversion (or "grain growth" under heat and deformation) to a large grain polycrystal, or transformation of local areas into a new crystalline phase (e.g., forsterite). Further investigation into carefully deformed chrysotile is required to decide which it is. It is, however, quite clear that these identifying effects are associated only with the samples found in the used brake drum dust.

Undeformed and unaltered chrysotile is also found in the brake drum dust collected after use (sample D, Fig. 7). This was confirmed by electron diffraction patterns which were indexed after the camera constant was calibrated using a co-deposited gold standard, with the following results:

Used brake dust	d Å	2.62	2.34	1.49
Yada (1967)	d Å	2.60	2.30	1.46
	hkl	130	220	005

There is also clear dark-field evidence that not all the fibers are deformed. Figure 7 shows the dark and bright field images of fibers found in the brake drum dust; the dark field image resembles that of the UICC chrysotile asbestos (B, Fig. 4) and those in the unused brake lining (C, Fig. 5), the "grain sizes" being the same as in the UICC samples. Based upon this observation, it is concluded that a variety of products ranging from almost undeformed to completely transformed chrysotile products exist in brake drum dust.

DISCUSSION AND CONCLUSIONS

It is demonstrated that high resolution dark field electron microscopy can distinguish the degree of deformation in chrysotile asbestos fibers. In particular it has been shown that UICC standard chrysotile has undergone microdeformation as a result of ball milling in the preparation step. The dark field method may then be used by environmental researchers to trace the origins of asbestos fibers.

The dark field images suggest that there are significant changes in the microstructure of chrysotile upon deformation; the crystallographic and microstructural details of which are complex and are worthy of further study.

There are several references to the beam sensitivity of chrysotile (Yada, 1967; Langer et al., 1974). The utility of using this effect to distinguish chrysotile from other non-beam-sensitive materials could be of value to environmental pollution research.

This preliminary study also shows the need to study details of the growth of the chrysotile asbestos and the nature of the defects involved, if all the diffraction and deformation effects are to be understood.

ACKNOWLEDGMENTS

I thank G. R. Smith of the Air Industrial Hygiene Laboratory (AIHL) Berkeley for bringing this problem to my attention and preparing the samples. I acknowledge useful discussion with him and Dr. Walter John, and thank Professor J. Washburn for encouragement. This work was supported financially by the U.S. Energy Research and Development Administration.

REFERENCES

Alste, J., Watson, D., Bagg, J. (1976). Airborne asbestos in the vicinity of a freeway, Atmospheric Environment 10, 583.

Hatch, D. (1970). Possible alternatives to asbestos as a friction material. Ann. Occ. Hygiene 13, 25.

Hickish, D. E., Knight, K. L. (1970). Exposure to asbestos during brake maintenance. Ann. Occ. Hygiene 13, 17.

Hirsch, P. B., Howie, A., Pashley, D. W., Whelan, M. J. (1965). Electron Microscopy of Thin Crystals (Butterworths, London).

Langer, A. M., Mackler, A. D., Pooley, F. D. (1974). Electron microscopical investigation of asbestos fibers. Env. Health Perspectives 9, 63.

Lynch, J. R. (1968). Brake lining decomposition products. J. Air Pollution Control Assoc. 18, 824.

Rohl, A. N., Langer, A. M., Wolff, M. S., and Weisman, I. (1976). Asbestos exposure during brake lining maintenance and repair. Environmental Research 12, 110.

Seshan, K., Smith, G. R. (1977). Characterization of chrysotile asbestos in automobile brake drum dust by transmission electron microscopy. Proc. 35th Annual Meeting of EMSA (Claitors Publishing Div., Baton Rouge).

Timbrell, V. (1969). Characteristics of the international union against cancer standard reference samples of asbestos. Pneumoconiosis. Proc. Interntl. Conf. on Pneumoconiosis, Johannesburg (Oxford University Press, England), p. 28.

Whittaker, E. J. W. (1966). Diffraction contrast in electron microscopy of Chrysotile. Acta Cryst. 21, 4616.

Yada, K. (1967). Study of chrysotile asbestos by a high resolution electron microscope. Acta Cryst. 23, 704.

Zvyagin, B. B. (1967). Electron-Diffraction Analysis of Clay Mineral Structures (Plenum Press, New York).

FIGURE CAPTIONS

Fig. 1. Illustration of the high resolution dark field method:

(a) The bright field image from a selected area of a polycrystal, illustrated with two grains A and B.

(b) The situation after gun tilt; only a portion of the diffracted intensity is collected by placing the objective aperture as shown.

(c) The resulting high resolution dark field image with only favorably oriented grains, e.g., B showing diffracted intensity, or "lighting up."

Fig. 2. Illustration of the real and reciprocal lattice of a defect-free chrysotile fiber (i) and (ii) idealized as a series of concentric cylinders. The actual structure is a defected spiral sheet (Yada, 1967). The reciprocal lattice of the ideal fiber is then a series of equispaced concentric rings along the a^* axis, as in the 2kl layer; when these rings intersect, the Ewald sphere (ES) spots ought to be produced as shown on the -2kl layer line. However, streaks are observed (Yada, 1967) arising probably from the spiral shape of the fiber defects and strains formed during the scrolling process. When a fiber bundle (fibers of different orientations) is imaged, the layer lines are smeared out, yielding a typical "arcuate" pattern as in Fig. 3b.

Fig. 3. Sample (A): natural chrysotile.

(a)(b) Dark field and diffraction pattern. Notice the unusually bright and undamaged internal canals; the crystal is homogeneous and undeformed. A faint outline of the objective aperture is seen in the diffraction pattern of Fig. 3b.

(c) Illustrates the blistering as a result of exposure to the beam.

Fig. 4. Sample (B): UICC Standard Reference Canadian chrysotile. (a)(b) Dark field images that illustrate that the ball milling during the mixing step converts the chrysotile into a fine-grain polycrystal. The aperture is moved from one part of the ring to another resulting in an entirely different set of grains lighting up. (c) The bright field image from which little information can be obtained.

Fig. 5. Sample (C): Burnishing dust from an automobile brake drum prior to installation. (a) dark field, (b) diffraction pattern, (c) bright field. Notice the well preserved canal which shows up (the dark field image) in (a), and indicated by the arrow. This and the well preserved diffraction pattern (b) shows that the fibers are not as deformed as the UICC samples — a conclusion that cannot be inferred from the bright field image (c).

Fig. 6. Sample (D): Brake drum dust after use in State vehicle. (a) bright field, (b) dark field. Although the bright field is not distinctive, the high resolution dark field and the selected area diffraction patterns are remarkably different. The crystal is quite inhomogeneous with very large grain sizes; this can happen for a variety of reasons (see text).

Fig. 7. Sample (D): Automobile brake drum dust after use. (a) dark field, (b) bright field. This shows that relatively undeformed fibers survive in the brake drum dust. The grain sizes in the dark field images (a) are comparable to that in the burnishing dust (Fig. 5a) or the UICC samples (Fig. 4a), indicating little deformation in use.

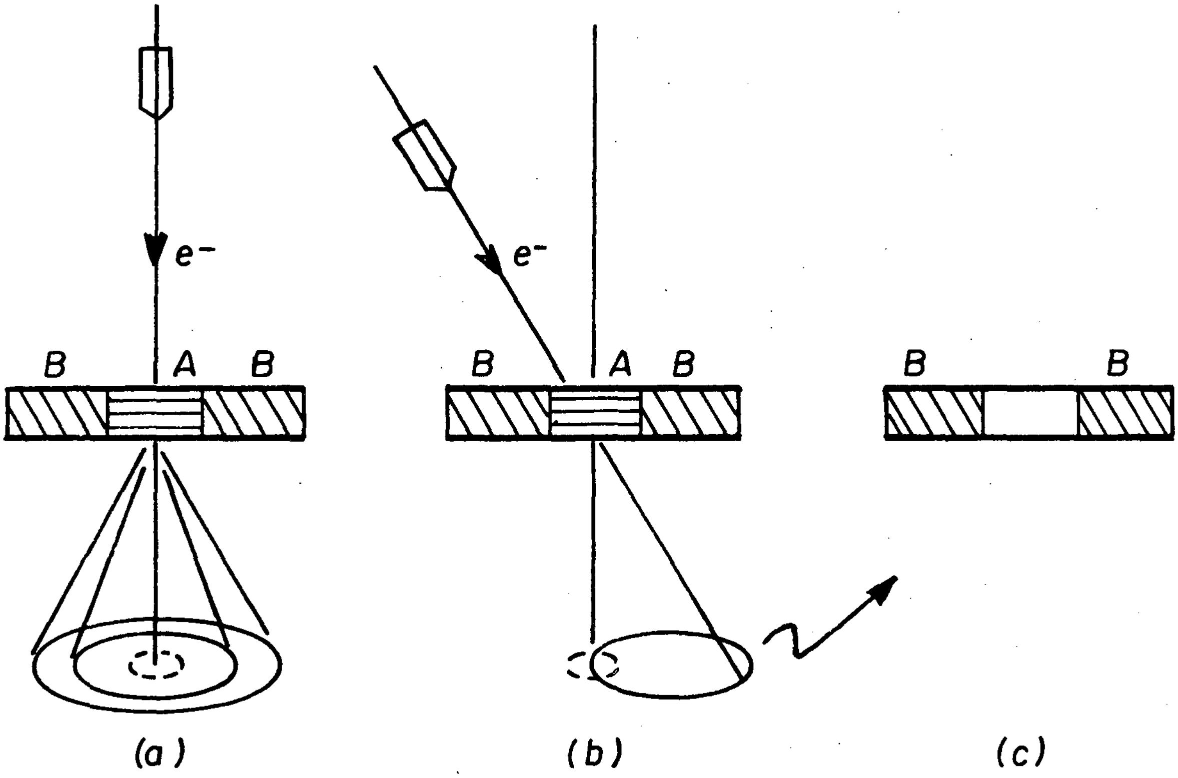

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Fig. 1

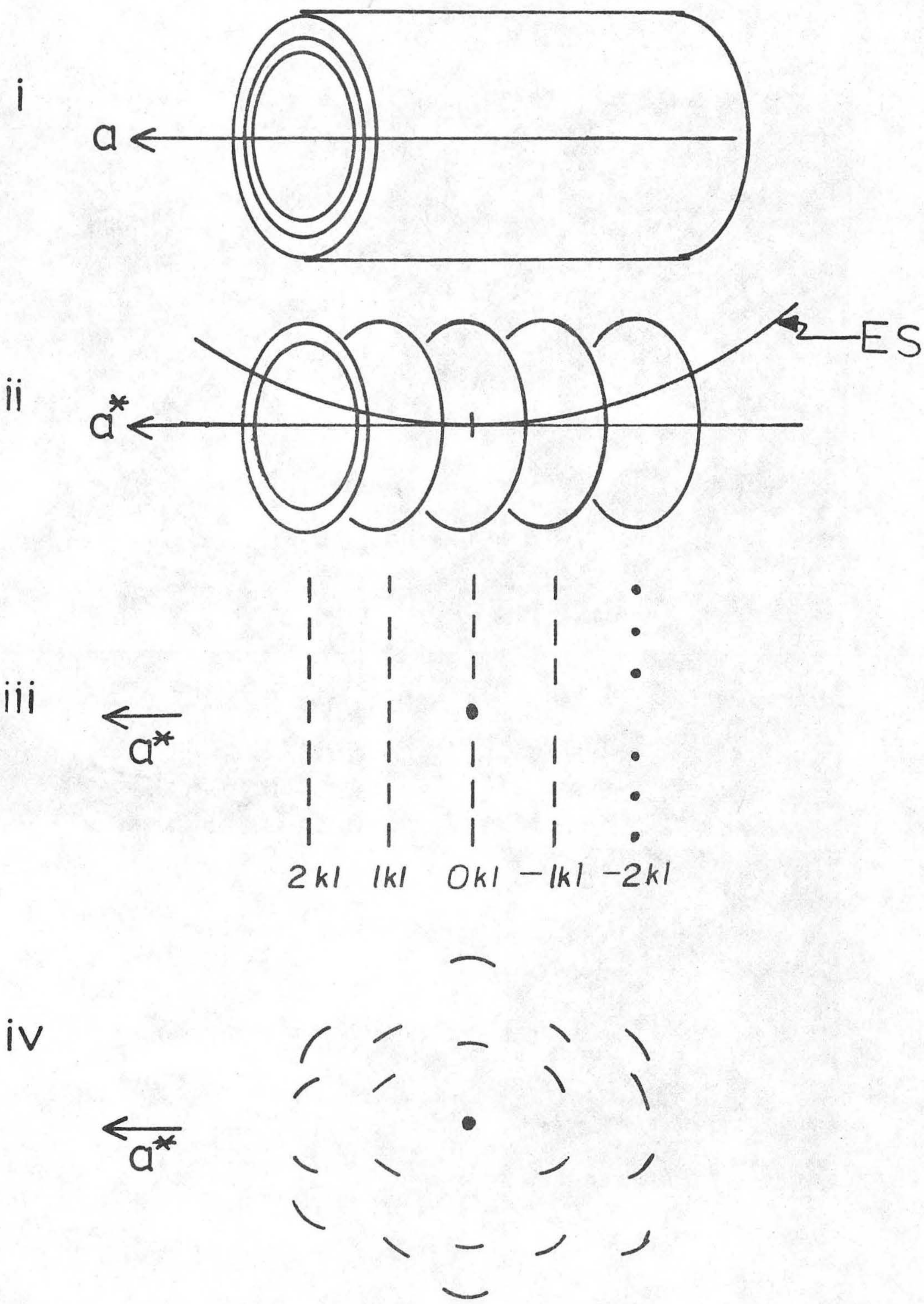

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Fig. 2

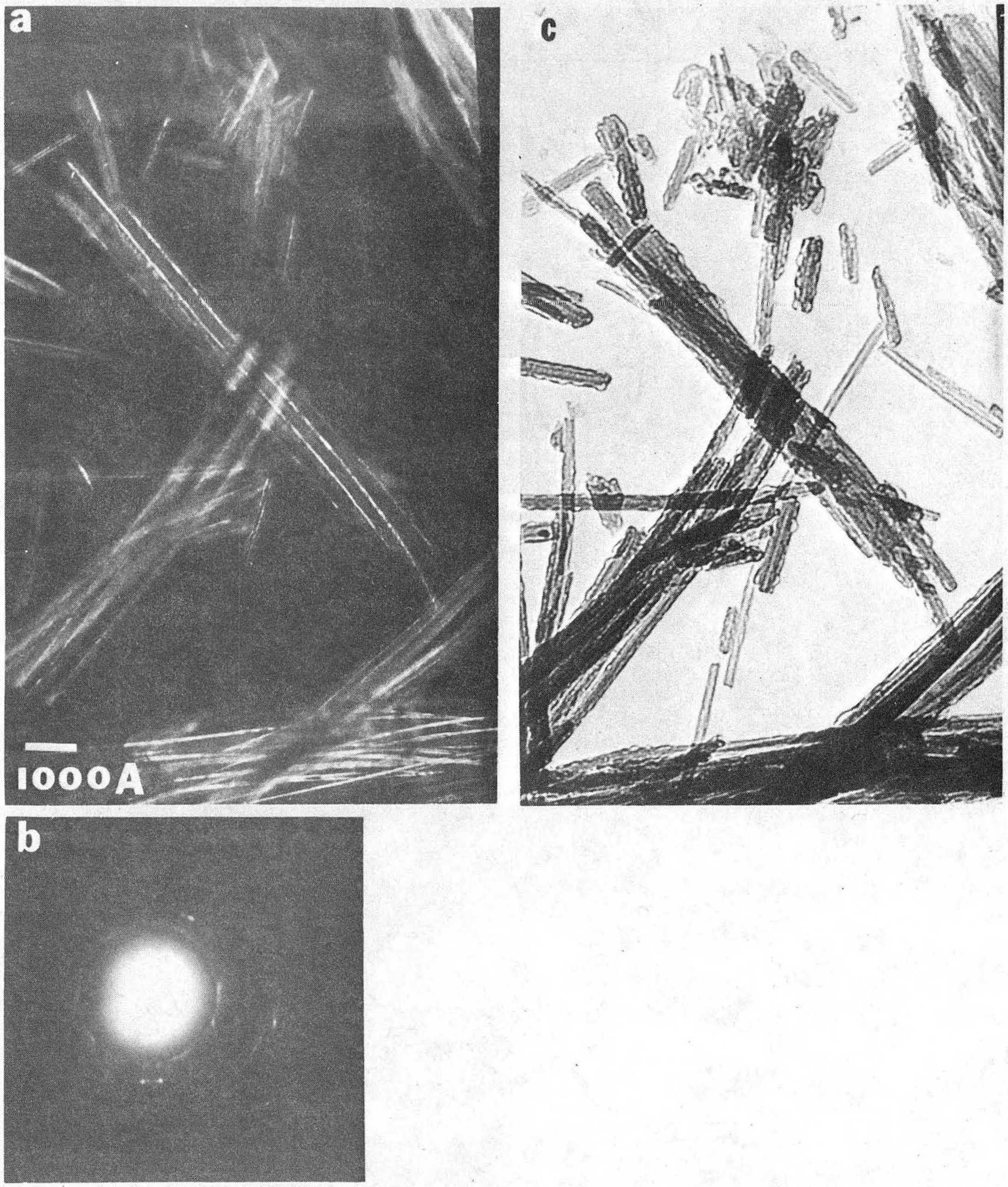

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Fig. 3

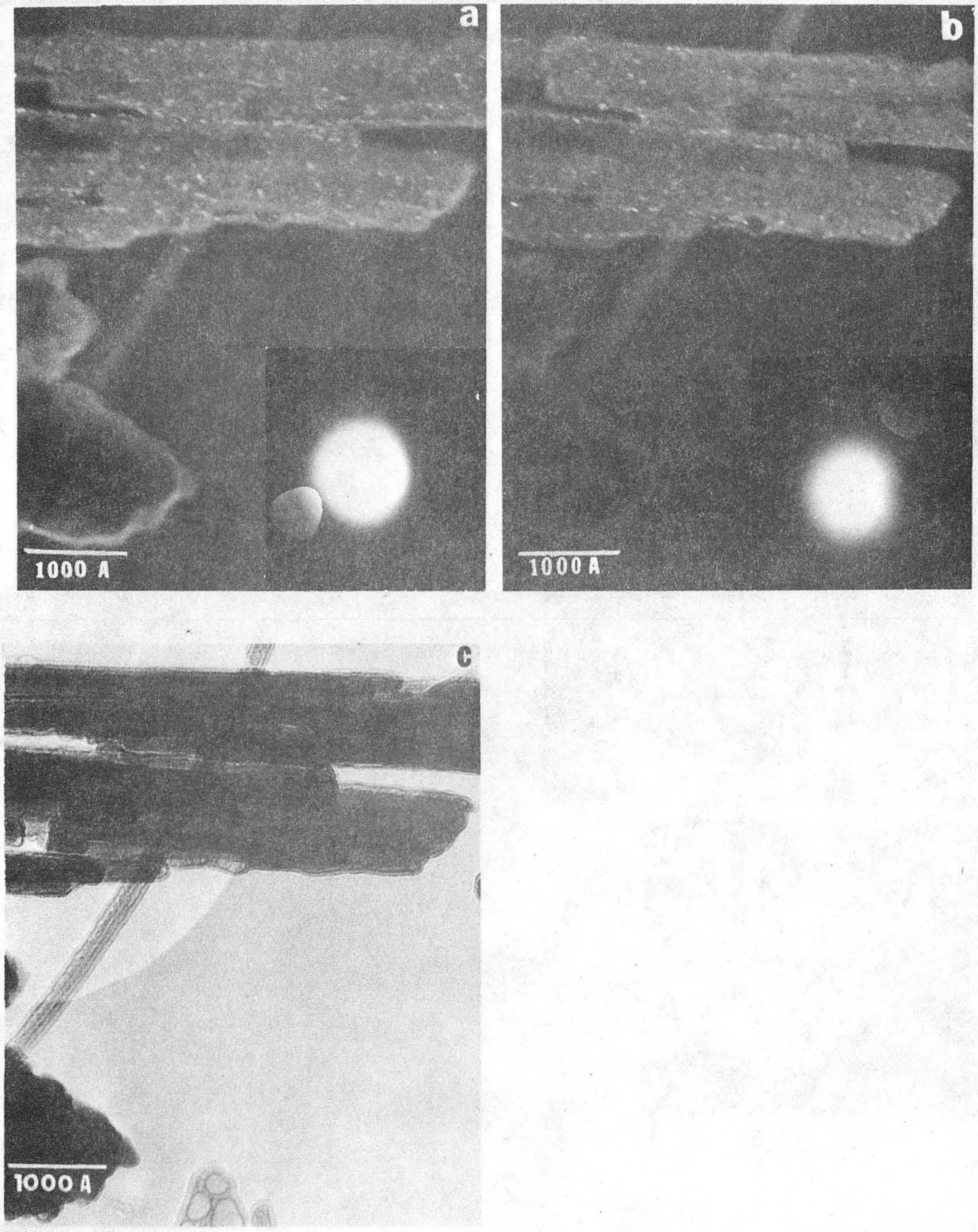

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Fig. 4

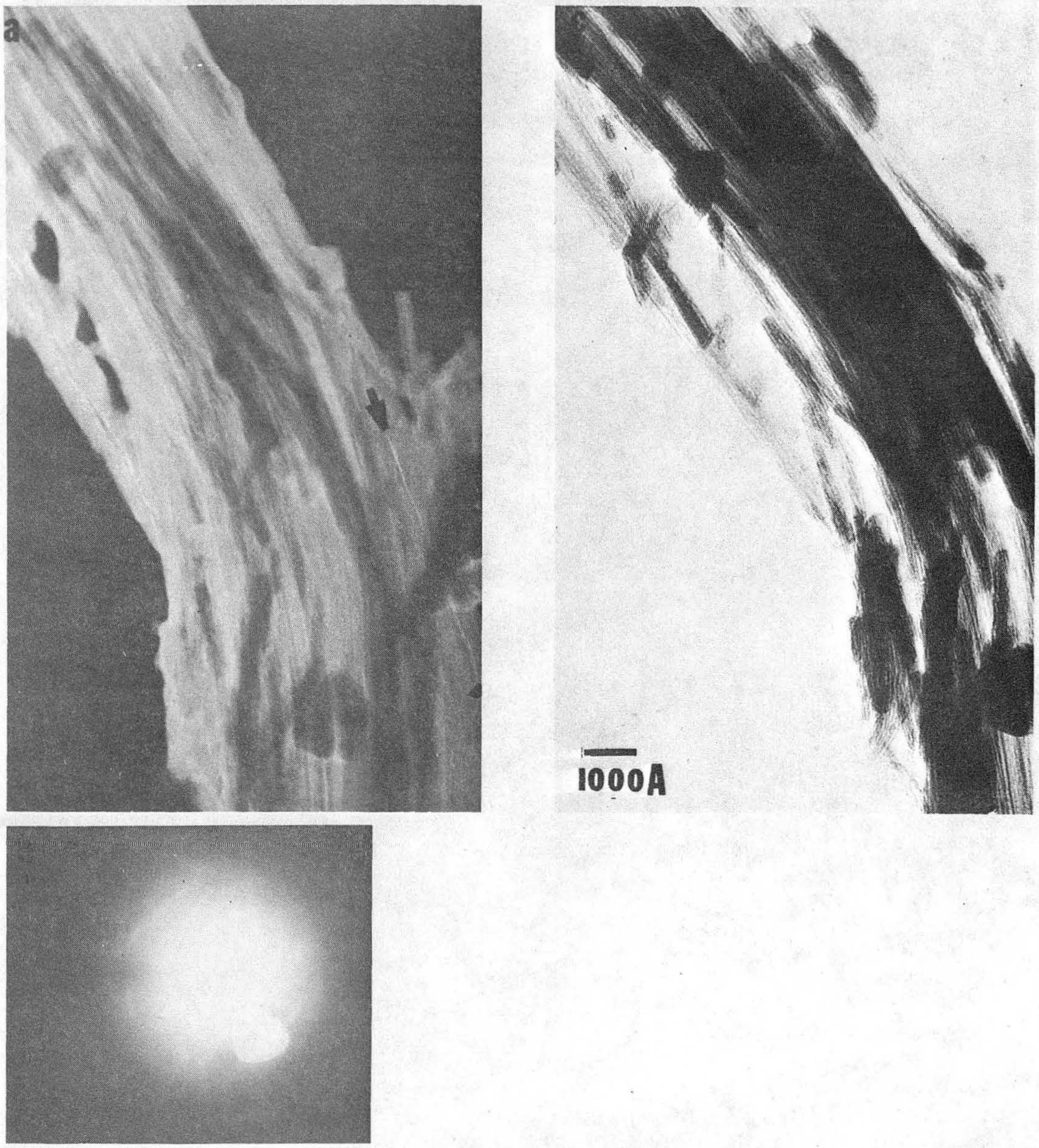

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Fig. 5

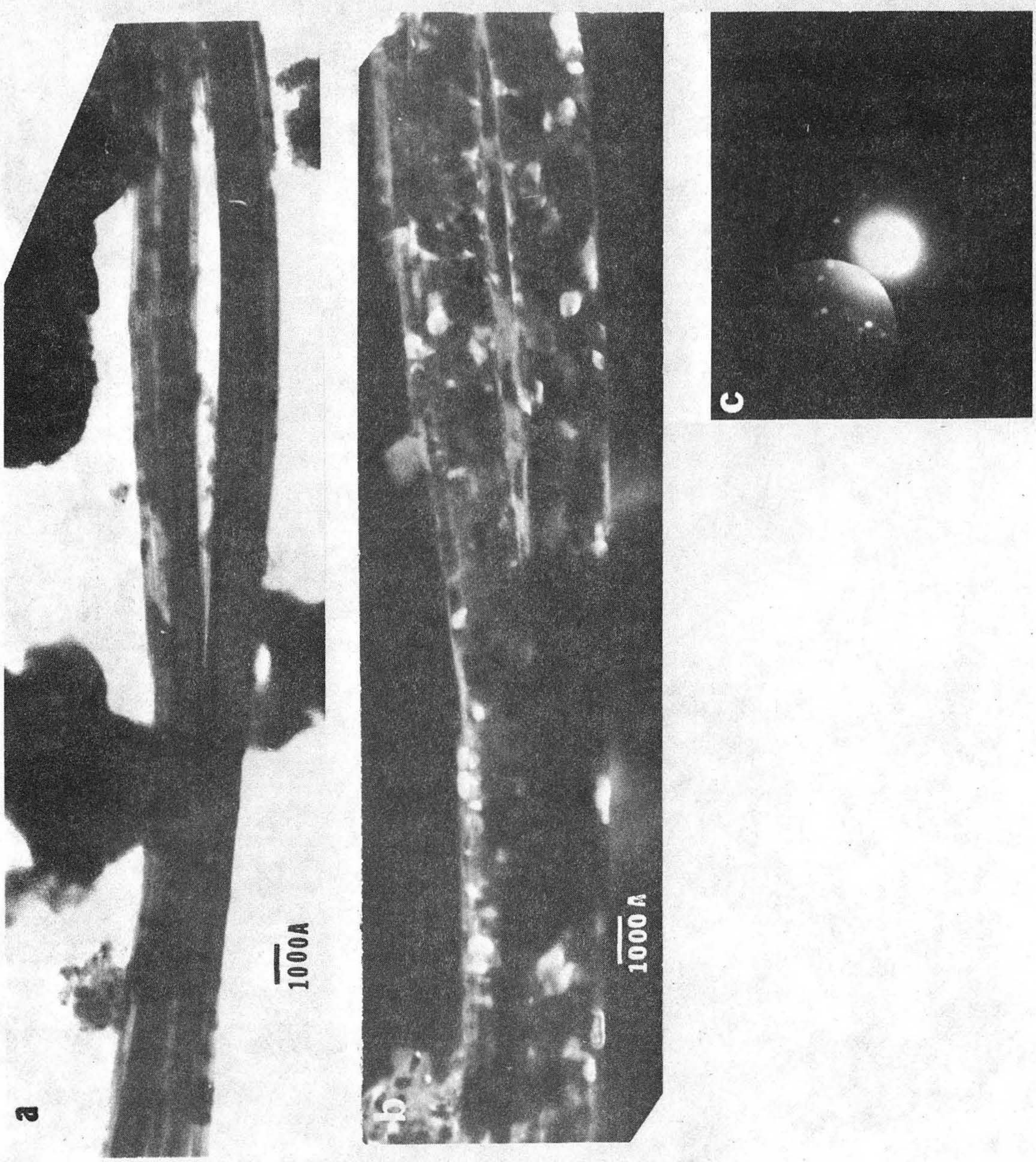

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Fig. 6

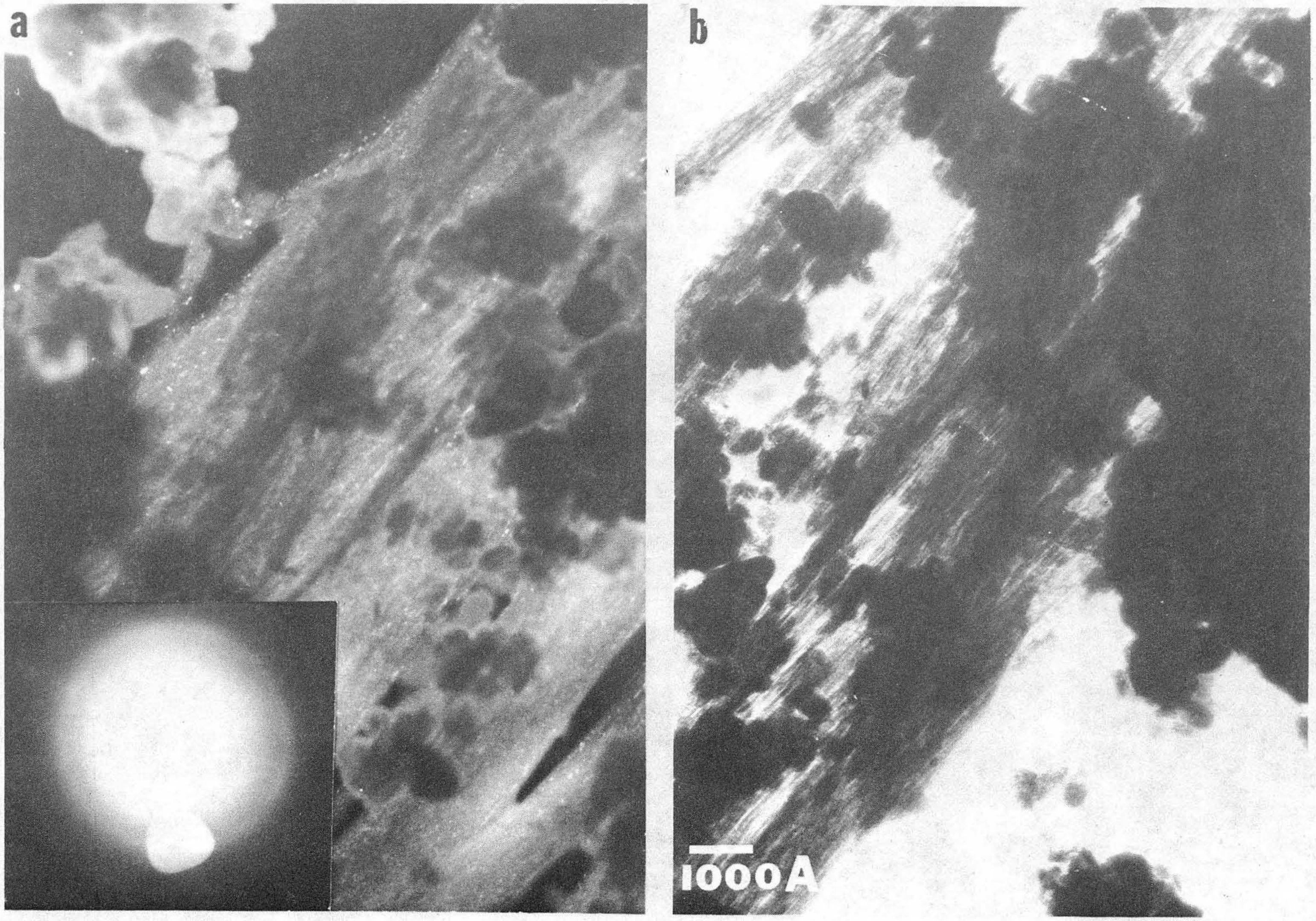

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Fig. 7

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