THE ULTRAFINE STRUCTURE OF COAL DETERMINED BY ELECTRON MICROSCOPY

L. A. Harris and C. S. Yust

Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830 USA

INTRODUCTION

The technological utilization of coal is dependent upon its physical characteristics as well as its chemistry. The size and spatial distribution of pores; and the size, distribution, and identity of the submicron size minerals are physical attributes of particular interest because of their influence in coal conversion processes such as liquefaction and gasification.

The present paper is one of a series in which electron microscope analyses inincluding transmission, scanning transmission, and scanning reflection methods have been employed in examining bituminous coals (1, 2). These techniques have the advantage of revealing the microstructures of coal at magnifications substantially greater than that available with light microscopy. Consequently, a more detailed direct observation of the pores and submicron minerals within the coal may be obtained.

EXPERIMENTAL

Sample Selection and Preparation

Samples were selected from two high volatile bituminous coals, namely, Illinois No. 6 and Eastern Kentucky splint coal from Perry County. The selection of the above coals was based on the fact that both are of equal rank but of different lithotypes (i.e. maceral contents), microstrucutures, and geographically separated. Consequently some evaluation could be made of the variation in microscale features which could be significant in coal utilization or diagenesis.

Specimens were prepared from the above samples by slicing sections normal to the bedding and subsequently grinding them into optical thin sections approximately 10–15 μm thick. The optical sections were removed from the glass slide by acetone and thinned to electron transparency by ion bombardment (ion milled). The ion milling process was performed on fragments approximately 3 mm on edge using argon gas and a liquid nitrogen cold stage in order to ensure a sample free from thermal damage. The ion milled samples were fixed to electron microscope grids using silver conductive paint.

Analytical Methods

Both a high voltage transmission electron microscope (TEM) (1 Mv) and a scanning transmission electron microscope (STEM) (120 Kv) were used in this study. The STEM was fitted with an energy dispersion system utilizing a Si(Li) detector. Microchemical analyses of particles as small as 20 nm for elements of atomic number 11 or greater could be attained by use of the STEM and EDX.

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RESULTS AND DISCUSSION

Figures 1 and 2 are TEM photomicrographs of specimens from the splint coal and the Illinois No. 6, respectively. The photomicrographs serve to illustrate the differences in microstructures between coals of the same rank. In general, the splint coal contains fragments of exinite, inertinite, and vitrinite closely compacted together, with the former two macerals making up over 70 volume percent of the total material. On the other hand, the Illinois No. 6 coal contains large bands of vitrnite interbedded with inertinite and exinite, where the latter two macerals combined comprise between 10 and 20 volume percent of the total macerals.

EASTERN KENTUCKY SPLINT COAL

Examination of the microstructure in Figure 1 reveals that the exinitic material (E) is essentially featureless in electron transmission. This material however, frequently contains relatively large and irregularly shaped pores (P). Immediately adjacent to the exinite is a region of vitrinite (V), containing a nearly uniform distribution of fine porosity. The boundary between the exinite and the vitrinite contains opaque fragments of mineral bearing inertinite as well as more finely divided inertinitic matter. The coarse porosity associated with the granular inertinite at the boundary is seen by detailed study to be continuous with the finer porosity that is observed in the vitrinite. This gradation of porosity from the inertinite to the vitrinite may be indicative of a transitional zone between the two macerals. The vitrinite bands observed in this field are relatively porous and as would be expected in a low density body, the porosity is highly interconnected.

The porosity associated with the exinitic maceral of the splint coal can be seen more clearly in Figure 3. The large, irregularly shaped pores often form distinct tubular channels which extend from the apparent center of the spore exine to the boundary between the spore and the surrounding inertinite. Commonly, the channels contain spherical mineral particles, which appear to be associated with the formation of the channels. Other studies (3) on the interaction of fine metal particles on graphite surfaces have demonstrated that particulates can catalyze surface reaction and lead to generation of elongated pores of the type shown here. The particles in the exinite were identified by means of EDX analyses and selected area diffraction (see inserts in Figure 3) as the mineral aragonite (calcium carbonate) which presumably enters the exinite from the granular inertinite that typically surrounds the spore exines. Usually, the granular inertinite contains an appreciable amount of mineral matter, primarily as clays.

Previous porosity studies of coal by gas absorption methods (4) reveal a direct relationship between the fine porosity and the vitrinite content of a coal. These observations are confirmed by this study for both the splint and Illinois No. 6 coals in as much as all the vitrinite observed by TEM was found to contain large regions of fine porosity. In Figure 4, a TEM photomicrograph of a vitrinite fragment in the splint coal, the pore sizes range from approximately 2 nm, to greater than 20 nm. The smallest pores, some of which may even be less than 2 nm, appear to be related to connecting channels or irregularly shaped pores that cannot be described as spherical. Stereo pairs of these vitrinite fragments indicate a connecting network of pores suggesting high permeability.

ILLINOIS NO. 6 COAL

The granular constitutent shown in the Illinois No. 6 microstructure (Fig. 2) contains a broad range of interconnecting pores (∿40–50 nm in dia.) which may be classified as predominantly macropores (<50 μm). The exact identity of this constituent is not clear, however, it is thought to be a mixture of inertinite and exinite. The microstructure of this coal is dominated by large vitrinite bands

(V) which are separated by the highly porous regions. Areas of apparently interconnected fine porosity can be observed in both vitrinite bands (see arrows). Also noteworthy in this microstructure are the opaque (OP) fragments that have been found to contain minerals. The opacity of the mineral regions may be due to a greater thickness of the face caused by the greater resistance minerals have to ion milling.

Figure 5 is a TEM photomicrograph of a region of vitrinite in the Illinois No. 6 coal obtained at higher magnification (50K) in order to perform a more detailed analysis of the porosity associated with this maceral. Pore dimensions range from approximately 1 to 10 nm which classifies them as a mixture of micropores (<2 μm) and mesopores (2–50 μm). The detection of porosity in the 2 dimensional image becomes more difficult as the specimen thickens. However, when viewed in 3 dimensions via a stereo pair, the porosity in the thicker regions remains clear. Three dimensional viewing also reveals that the porosity is irregularly shaped, and is often present as volumes of highly interconnecting pores. In regions of locally high porosity as is observed in the center of Fig. 5, the degree of interconnectivity is relatively great whereas in the surrounding region the pore volumes are largely isolated.

Several vitrinite fragments were found to contain bands of minerals, aligned parallel to the bedding plane of the coal (Fig. 6). Many of the minerals exhibit well developed growth habits. A size analysis of the minerals (5) by direct measurement from the TEM photomicrographs reveals that the majority of minerals were under 30 nm in diameter with the average diameter being approximately 10 nm. Larger mineral fragments up to 300 nm on an edge were recorded but comprised only a small fraction of the total observable mineral matter. Subsequent analyses of small angle x-ray scattering (6) (SAXS) from a similar sample of Illinois No. 6 coal showed a multimodal size distribution (Fig. 7) which essentially confirms the TEM observations. For example, the peak at 3 nm relates to the fine pores observed in the vitrinite component whereas the peak at 10 nm fits the average mineral diameter, and finally the peak at 25 nm accounts for the larger mineral fragment plus the larger pores observed in the granular constituent.

In addition to the microstructural studies of these two bituminous coals an effort was also made to do EDX analyses via STEM on microareas of the macerals in order to obtain data related to the composition of the coal macromolecule. However, typically, the observation of detectable elements (i.e., of atomic number 11, Na or greater) always correlated with the presence of minerals, except for sulfur. These observations, though limited, do suggest that chemical analyses of coal which report the existence of heavy metals (>Na) in coal macerals as part of the organic constituent may be suspect. As witnessed in Fig. 6, the size range for minerals can be exceedingly small, e.g. less than 2 nm in diameter thus their detection by standard techniques very improbable.

CONCLUSIONS

The shape and size of pores in two high volatile bituminous coals of differing lithotypes have been directly observed by means of transmission electron microscope (TEM). The distribution of the porosity with respect to their maceral associations were ascertained as were the sizes and distributions of the micro minerals. The use of stereo pairs reveals the interconnectivity of the pores in micro volumes of the macerals indicating a high degree of permeability within those regions.

The finest porosity was observed in vitrinite fragments of both coals and ranged in size from under 2 nm to 20 nm in diameter, with the majority in the smaller end of the size range. On the other hand, inertinite appears to be the most porous maceral and typically contains a broad range of pores from 5 through 50 nm. Much of the inertinite is granular material varying from fine to coarse grained particles with the former corresponding to micrinite.

Finally, the least porous maceral is exinite which generally appears as a featureless material except for the presence of irregular and tubular pores thought to be initiated by the catalytic action of minerals. The intimate relationship between exinite and inertinite such as exists in durains, where the inertinite contains large amounts of fine mineral matter, may therfore promote the generation of porosity in exinites.

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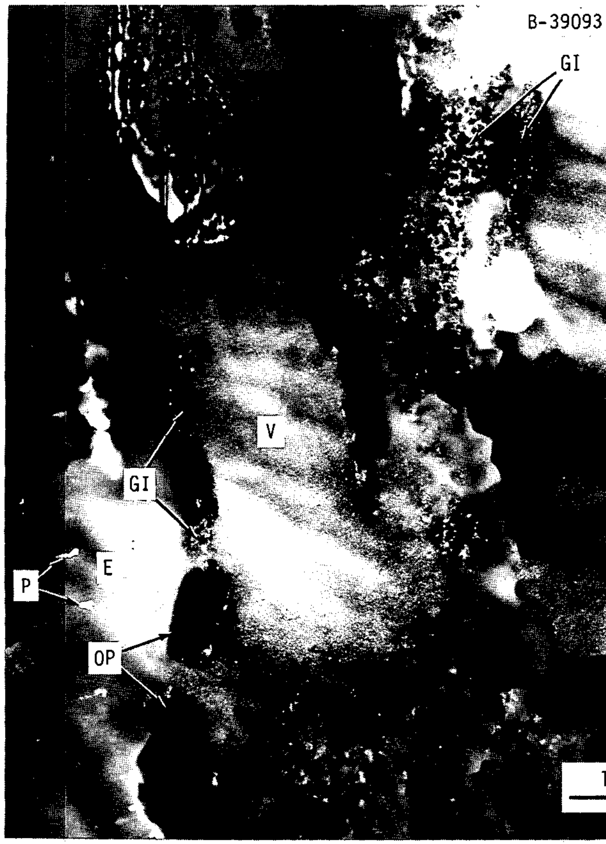

Fig. 1. TEM Splint Coal (Where E = Exinite, V = Vitrinite, GI = Granular Inertinite, OP = Opaque Particles, and P = Pores in Exinites).

Fig. 2. TEM of Illinois No. 6 Coal (Where V = Vitrinite and OP = Opaque Particles).

Fig. 3. TEM of Tubular and Irregular Pores in Exinite Showing the Location (See Arrows) and Identity (See Insets) of Spherical Particles.

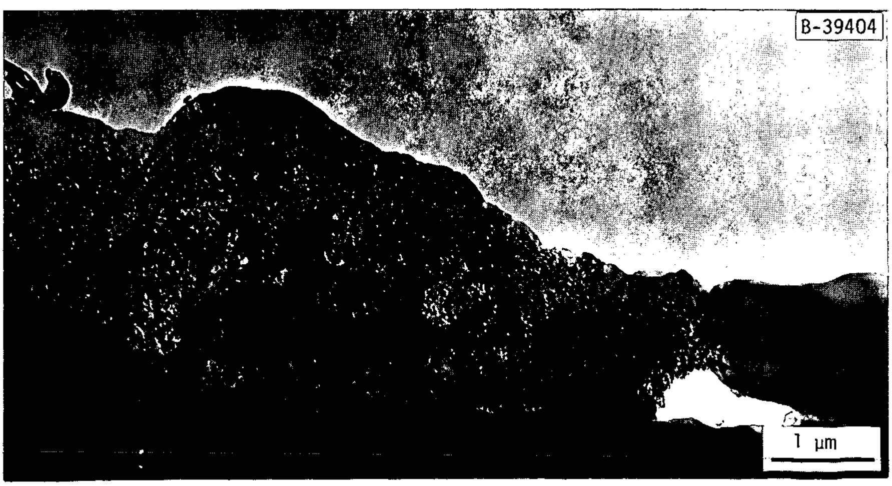

Fig. 4. Fine Porosity Observed in Vitrinite Fragment in Splint Coal by TEM.

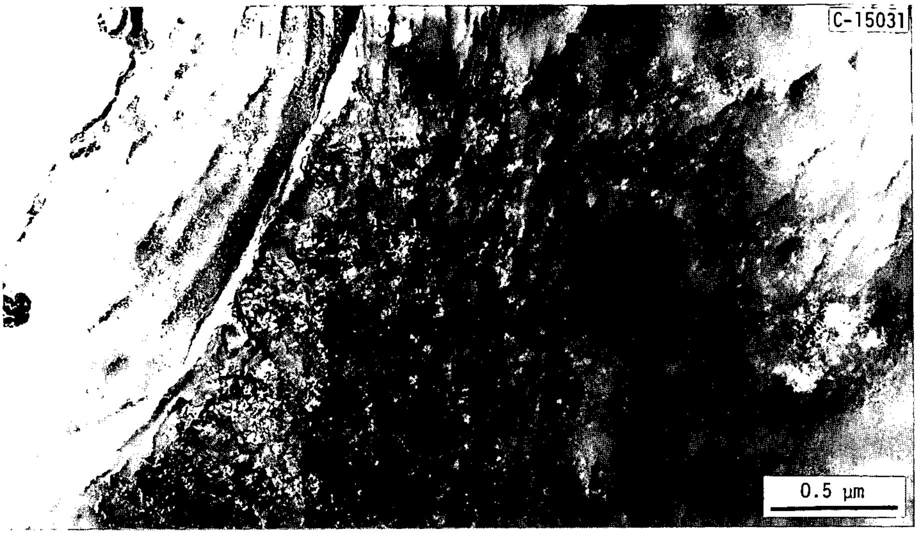

Fig. 5. Fine Porosity Observed in Vitrinite Fragment of Illinois No. 6 Coal by TEM.

Fig. 6. TEM of Vitrinite of Illinois No. 6 Showing Bands of Minerals.

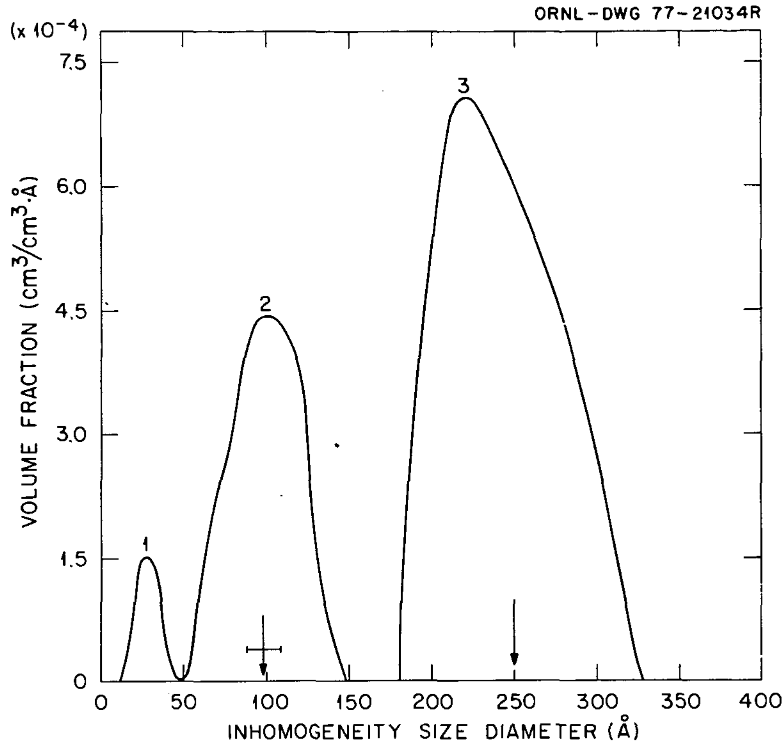

Fig. 7. The Size Distribution of Pores and Minerals from Vitrinite (Illinois No. 6) Obtained by Small Angle X-Ray Scattering (SAXS).