POROSITY AND THERMAL EXPANSION OF CALCINED COKES

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Introduction

The microstructure of coke particles can be considered to consist of their optical texture and porosity [1]. Some studies have been reported on characterization of optical texture of petroleum cokes [2-4] by image analysis to correlate with the coefficient of thermal expansion (CTE), but a few studies addressed the effects porosity on CTE of calcined cokes [5]. This preliminary study investigates the relationships between the porosity and thermal expansion behavior of calcined coke particles. The pores in calcined cokes which can be resolved by optical microscopy (>1μm) was characterized by digital image analysis.

Experimental

Thermal expansion measurements on calcined cokes were performed in an ORTON 1600D dilatometer. The samples were into cylinders about 1 inch in length and 0.3-0.4 inch in diameter. The particles were cut such that their apparent long dimension was parallel to the long axis of the cylinders. For CTE measurements, samples were heated at a rate of 3°C/min in an argon atmosphere and linear changes of samples were recorded from room temperature to 800°C. For comparison with the published literature [2,3], the CTE values were calculated for the same temperature range (300-700°C) for all the particles. When three replicate measurements were performed on each sample, the results show a standard deviation of 1-2%.

To analyze the porosity we used the same coke samples for which CTE measurements were made. The cylindrical CTE samples were placed longitudinally in epoxy resin, and the resulting pellets were polished for microscopic examination. Microscopic images of pores on polished surfaces are two-dimensional projections of a complex three-dimensional pore structure [6]. Therefore, we analyzed the porosity at four different layers of the samples by sequential grinding and polishing of the specimen. An automated microscope stage was used to scan each pellet with a 1.5mm×1.5mm mask in conjunction with the PGT Imagist (Princeton, New Jersey) image analysis system [7]. Generally, around 40 images were used to carry out the feature analysis of the pores in coke particles.

In general, characterization and classification of pores by shape is much less advanced than classification by size [8,9]. A feature analysis technique was used to characterize the size and shape of the pores, which were represented by average diameter and aspect ratio, respectively. The average diameter is calculated as the mean of 12 directed diameters which are the projections of a feature on 12 lines placed every 15° around a half-circle, starting with the x-axis as 0°. The aspect ratio is the ratio of the longest dimension (the longest of the directed diameters) to the breadth (the shortest of the directed diameters). For feature analysis, each gray level image is automatically converted into a binary image.

Results and Discussion

We selected 4 μm^2 as a threshold to filter the electric noise in the image and the 5000 μm^2 as the upper limit to remove very large features which usually had incomplete area in an image. The number of the features whose area is larger than 5000 μm^2 is generally less than 5 in a typical image with approximately 200 features. Figure 1 shows a histogram for the distribution of average diameters for two different coke particles which had rather different CTE. As shown in Figure 1, it has been observed, in general, that cokes with large number of pores tend to have high CTE. To differentiate between two different sizes of pores, we used a randomly selected area of 100 μm^2 to divide the pores into small pores (4-100 μm^2) and large pores (100-5000 μm^2).

Figure 2 shows that CTE of the coke samples tend to increase with the decreasing average diameter of the large pores. The apparent relationship observed between average the pore diameter and CTE can be better explained by analyzing the shape of the pores, as shown below.

Figure 3 plots the aspect ratio versus the CTE for two size fractions of pores in the first layer of pellets. It is seen that as the aspect ratios of the large pores increase, the CTE decreases without much change in the aspect ratio of the small pores. Most of the large pores are actually cracks, which run parallel to texture elements, produced most likely by shrinkage during calcination [5]. Figure 3 shows that the average aspect ratio of the pores does not vary much in different layers of the samples.

Conclusions

An apparent correlation observed between the aspect ratios of the large pores and CTE probably reflects the effect of optical texture, rather than porosity, on CTE. A higher resolution microscopy (SEM and Field Emission SEM) can be useful for analyzing small pores.

Acknowledgments

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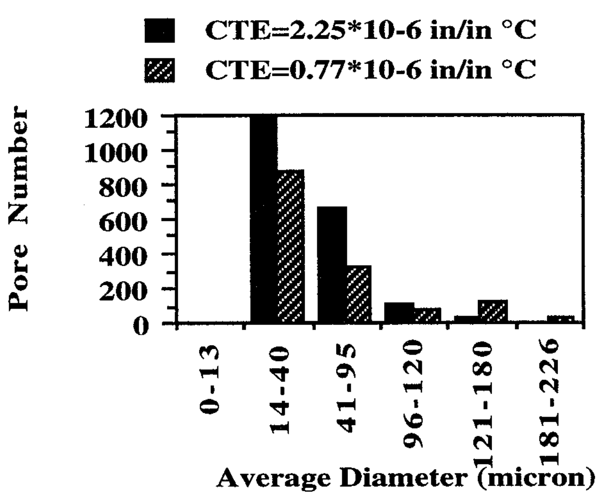

Figure 1. A histogram of average diameters for two different coke particles.

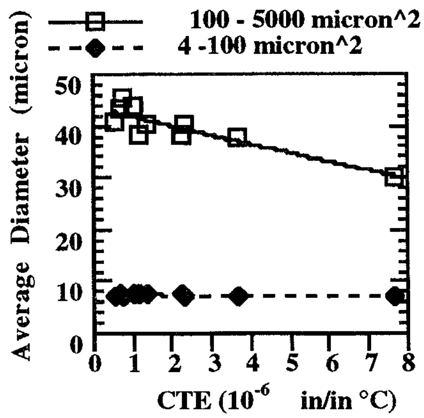

Figure 2. The average diameter versus CTE for two groups of pores in the first layer of pellets.

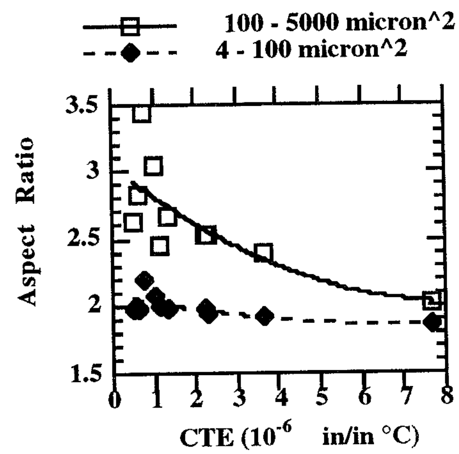

Figure 3. The aspect ratio versus CTE for two groups of pores in the first layer of pellets.

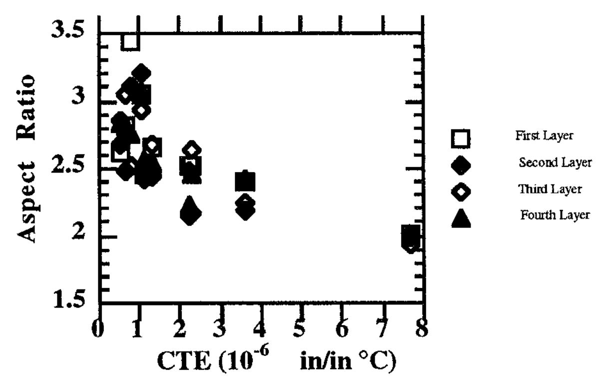

Figure 4. The aspect ratio versus the CTE of the large pores in four layers of the pellets.