Symposium on Structure of Jet Fuels V

Presented before the Division of Petroleum Chemistry, Inc.

216th National Meeting, American Chemical Society

Boston, August 23-27, 1998

ANALYSIS OF SOLID DEPOSITS FROM THERMAL STRESSING OF A JP-8 FUEL ON DIFFERENT SURFACES IN A FLOW REACTOR

O. Altin, A. Venkataraman, and S. Eser

Fuel Science Program, Department of Materials Science and Engineering

&

The Energy Institute, College of Earth and Mineral Sciences

209 Academic Projects Building, The Pennsylvania State University

University Park, PA 16802

Phone: (814) 863-1392

Key words: carbon deposition, JP-8, fuel decomposition, deposit morphology

INTRODUCTION

The future high-speed aircraft requires advanced jet fuel with high stability in rigorous thermal environments. The formation of carbonaceous deposits on metallic surfaces of the fuel system is a major concern in the development of advanced jet fuel aircraft in which fuel can be exposed to high temperatures up to 540°C (1). At high temperatures, the fuel thermally decomposes to produce solid deposits on the surface of the fuel lines which can cause serious problems during the operation (2). In addition to homogeneous reactions under supercritical conditions, heterogeneous reactions on metal surfaces can lead to solid deposits in the presence of reactive hydrocarbon species produced by pyrolysis. At high temperatures, nickel based stainless steel surfaces collect large amounts of solid deposit from jet fuel or model compounds (3).

The objective of this research is to study high-temperature solid deposition from a JP-8 fuel on different metal tubes, nickel, copper, and stainless steel, used with and without an inert coating in a flow reactor. Different length segments of the metal tubes were analyzed by a multi-phase

carbon analyzer and scanning electron microscopy to determine the carbon deposition profiles as well as the oxidation reactivity and morphology of the deposit along the tube length.

EXPERIMENTAL

The flow reactor used in this study is a modified Chemical Data Systems (CDS) Model 803 bench scale reaction system which was described elsewhere (4). A new modification in the reactor fittings allowed the use of 20 cm long 1/4-inch (OD) tubes as reactors. Six different tubes were examined: ss316, ss304, nickel, copper, Silcosteel (Restek Co.®) coated stainless steel, and glass-lined stainless steel (Alltech). Before the experiments, all the tubes were washed with hexane and dried. Temperature measurements were made at four different points along the length of the reactors at 5, 10, 15 cm from the top of the reactors, and at the outlet to measure the effluent fuel temperature. Some properties of the JP-8 fuel used in this study are given in Table 1.

In stressing experiments, the jet fuel flowed through the reactor at a flow rate of 1 cc/min for 5 hours. The fuel was preheated to 250°C in the valve oven section and in the influent lines of the reactor. Before each experiment, the reaction zone was maintained at a constant temperature of 500°C and a pressure of 500 psig under flowing UHP nitrogen for two hours. At the end of the experiment, the reactor was cooled down under flowing nitrogen. The reactors tubes were cut into 2.5 cm segments and analyzed for carbon deposit using LECO-RC 412 Multiphase Carbon Determinator. Conventionally, LECO-RC 412 MCD has been used to measure the amount of deposition on tube surfaces (5,6). In this study, we also used the "carbon burn-off profiles" from the analysis to assess the nature of the deposits from their reactivity during oxidation under selected heating conditions. To the best of our knowledge, this is the first attempt to use the carbon determinator to extract information on the nature of the carbonaceous deposits, in addition to the amount of deposition.

The morphology of solid deposits was examined using an ISI-DS 130 Dual Stage scanning electron microscope (SEM). For SEM examination, the reactor tubes were cut longitudinally at the

center. Using carbon burn-off profiles together with SEM examination of the tube surfaces offer valuable information on the properties of the solid deposits and deposition mechanisms.

RESULTS AND DISCUSSION

Figures 1a and 1b show the overall mass of solid deposits on different tube surfaces, and in different tube segments, expressed in $\mu g/cm^2$ of the inner tube surface. As it was expected, nickel deposited more solids, presumably because of its catalytic activity (7). Stainless Steel 316 produced more deposits than the 304 grade. The copper tube showed a small amount of solid deposition, comparable to that obtained on the Silcosteel coated surface. The lowest amount of deposition was obtained on the glass-lined stainless steel tube. Copper, Silcosteel, and glass-lined stainless steel tubes did not show any significant change in deposition along the reactor length.

Figures 2-6 show the carbon burn-off profiles for different segments of the nickel, 316, 304, and, Silcosteel, and glass-lined stainless steel tubes as a function of temperature with selected SEM micrographs of the deposits on certain tube sections. The different peaks observed in these plots can be attributed to different nature of the deposits with respect their oxidation reactivity under the constant heating conditions used in the carbon analyzer. Broadly, the peaks observed at high temperatures (>500°C) in these plots can be assigned to less reactive (or more structurally ordered) deposits produced most likely by catalytic reactions on active metal surfaces. The peaks at low temperatures, on the other hand, can be assigned to more reactive (or relatively hydrogen rich and more amorphous) deposits. It is very likely that this kind of deposits results mainly from the secondary deposition processes, e.g., pyrolytic carbon formation, on already formed carbon deposits, such as platelets, produced by catalytic reactions. This process of sequential deposition of different kinds of carbonaceous solids is consistent with the mechanism, proposed by Albright and Marek (8). A distinguishing feature of the carbon burn-off profiles for bare metal tubes is the presence of high-temperature peaks shown for nickel, 304, and 316 stainless steel tubes, in Figures 2, 3, and 4, respectively. These peaks are absent in the profiles for Silcosteel coated and glass-lined tubes, as shown in Figures 5 and 6. It appears that the presence of an inert coating on

metal surfaces effectively inhibits the solid deposition from reactions catalyzed by metal surfaces under thermal stressing conditions used in this study. These observations point to the active role of metal surface catalysis on solid deposition which appears to vary depending on the composition of the metal surface. The differences in carbon burn-off profiles for Ni, 304 and 316 stainless steels, especially in the high-temperature region of the plots, shown in Figure 2, 3, and 4 can be attributed to differences in catalytic activity of these surfaces during jet fuel decomposition.

CONCLUSIONS

A combined use of carbon burn-off plots obtained from a multiphase carbon determinator and SEM examination of stressed tube surfaces provides useful information for characterization of solid deposits to elucidate solid deposition mechanisms during thermal decomposition of jet fuel. The experimental results suggest that solid deposition is initiated by catalytic reactions on active metal surfaces and the activity of a metal surface depends on its composition. The formation of catalytic deposits on metal surfaces promotes secondary deposition which proceeds via other deposition mechanisms, such as pyrolytic carbon formation. An inert coating such as Silcosteel or glass on metal surface effectively inhibits catalytic deposition, and, thus, minimizes overall solid deposition from thermal decomposition of jet fuel.

ACKNOWLEDGMENT

This work was supported the Air Force Wright Laboratory/Aero Propulsion and Power Directorate, Wright-Patterson AFB. We thank Dr. T. Edwards of AFWL/APPD for helpful discussions.

LITERATURE CITED

1. Song, C., Eser, S., Schobert, H. H., and Hatcher, P. G., Energy & Fuels, 7(2) 234 (1993).

2. Hazlett, R. N., In Aviation Fuel: Thermal Stability Requirements (Edited by P. W. Kirklin and P. David), ASTM STP, 1138,18 (1992).

3. Li, J., and Eser, S., Carbon'95, Extended Abstracts, 22nd Biennial Conference on Carbon, San Diego, CA, 314 (1995).

4. Li, J., and Eser, S., ACS Symposium Series, 211th National Meeting, 508 (1996).

5. Haneghan, S. P., Martel, C. R., Williams, T. F., and Ballal, D. R., Journal of Engineering Gas Turbines and Power, 115, 480 (1993).

6. Edwards, T., Zabarnick, S., Ind. Eng. Chem. Res., 32, 3117 (1993).

7. Baker, R. T. K., and Harris, P.S., In Chem. Phys. Carbon, 14 (1978).

8. Albright, L. F., and Marek, J. C., Ind. Eng. Chem. Res., 27, 755 (1988).

Table 1. Properties of JP-8 fuel.

Molecular weight : 167 (mean)
Boiling point : 205-300 °C (401-572°F)
Freezing Point : -56 to -50°C (-69 to 58°F)
Vapor pressure : 0.4 mmHg @ 20°C
Vapor density (air=1.0) : 4.7
Specific gravity (water=1.0) : 0.775-0.840
Viscosity : 8.0 cSt
Flash Point : 38°C (100°F)
Lower flammibillity limit : 5.0%
Upper flammibility limit : 0.7 %
Autoignition : 99°C (210°F)

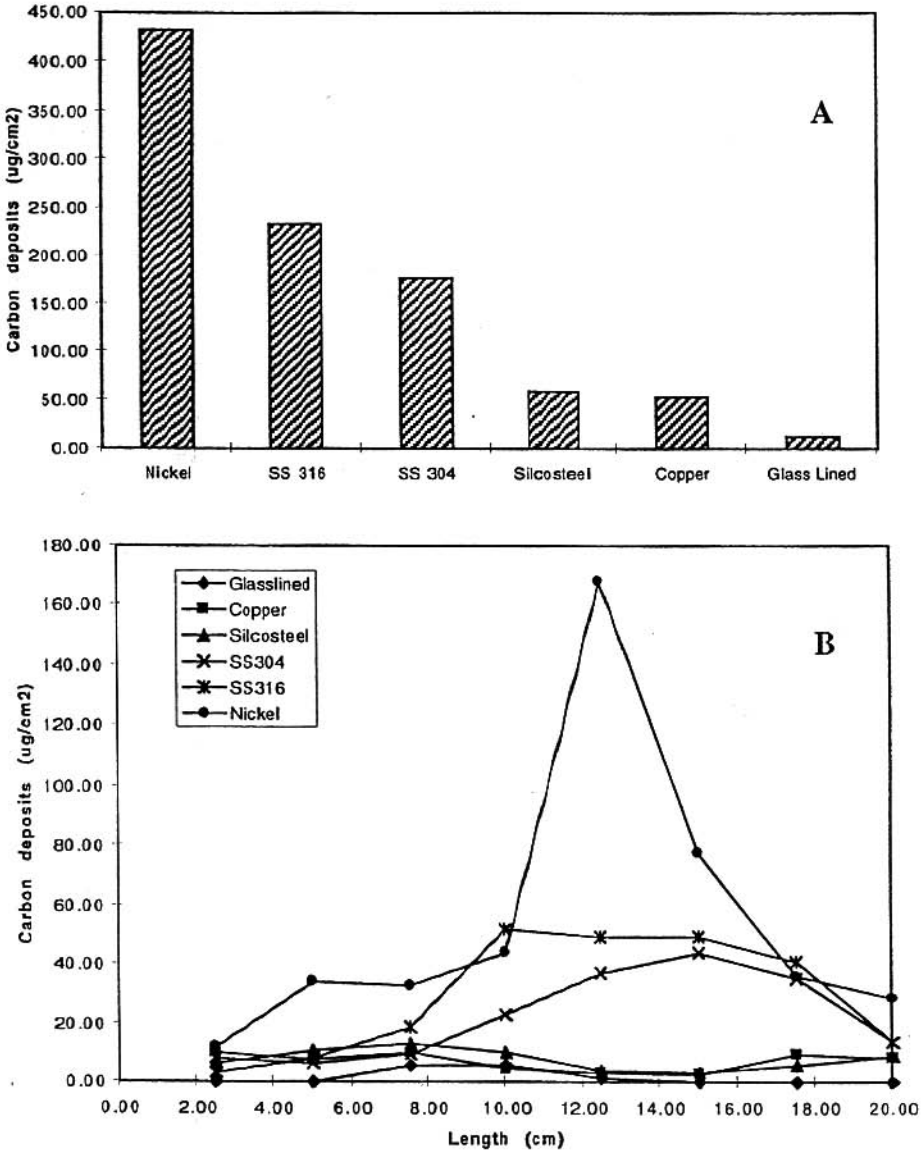

Figure 1. Carbon deposits from JP-8 fuel on different metal tubes at 500°C, 500 psi, and 1 cc/min flow rate. A) Overall deposition on the tubes, and B) Deposition profiles along the tubes.

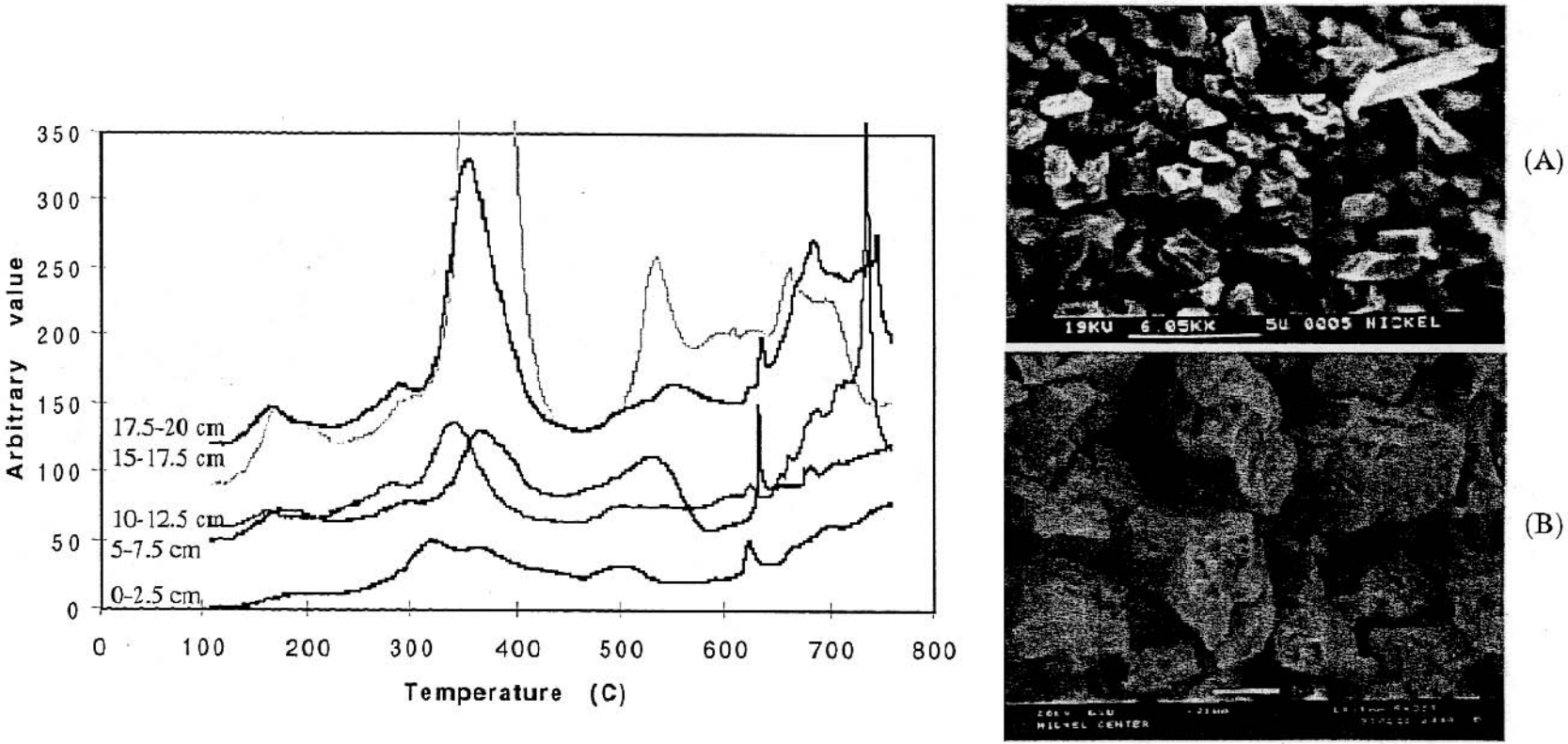

Figure 2. Carbon burn-off profiles for a 2.5 cm segments of a stressed nickel tube, and the SEM micrographs for the 15-17.5 cm (A), and 10-12.5 cm (B) segments.

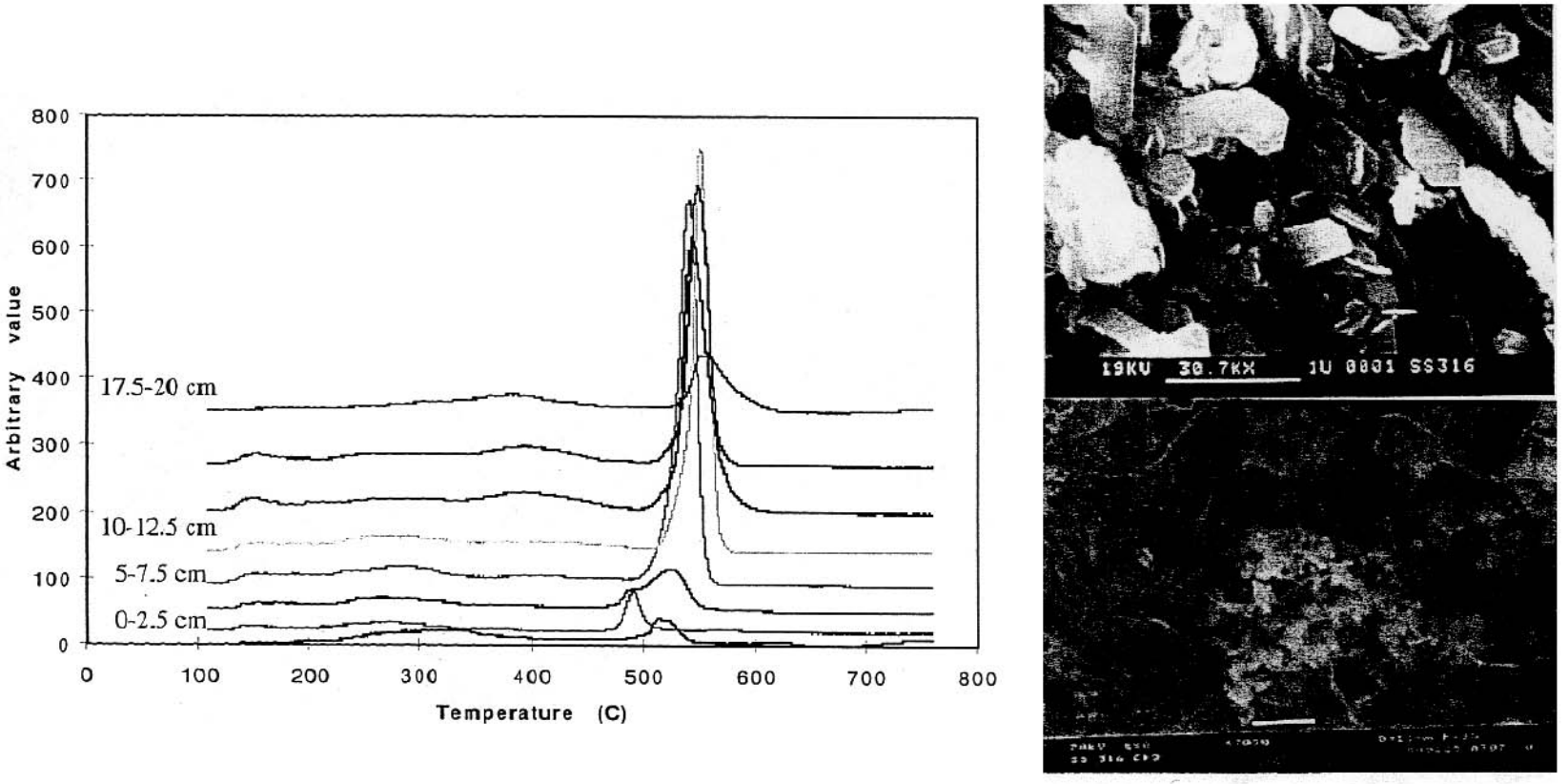

Figure 3. Carbon burn-off profiles for 2.5 cm segments of a stressed ss316 tube and SEM micrographs for the 17.5-20 cm segment.

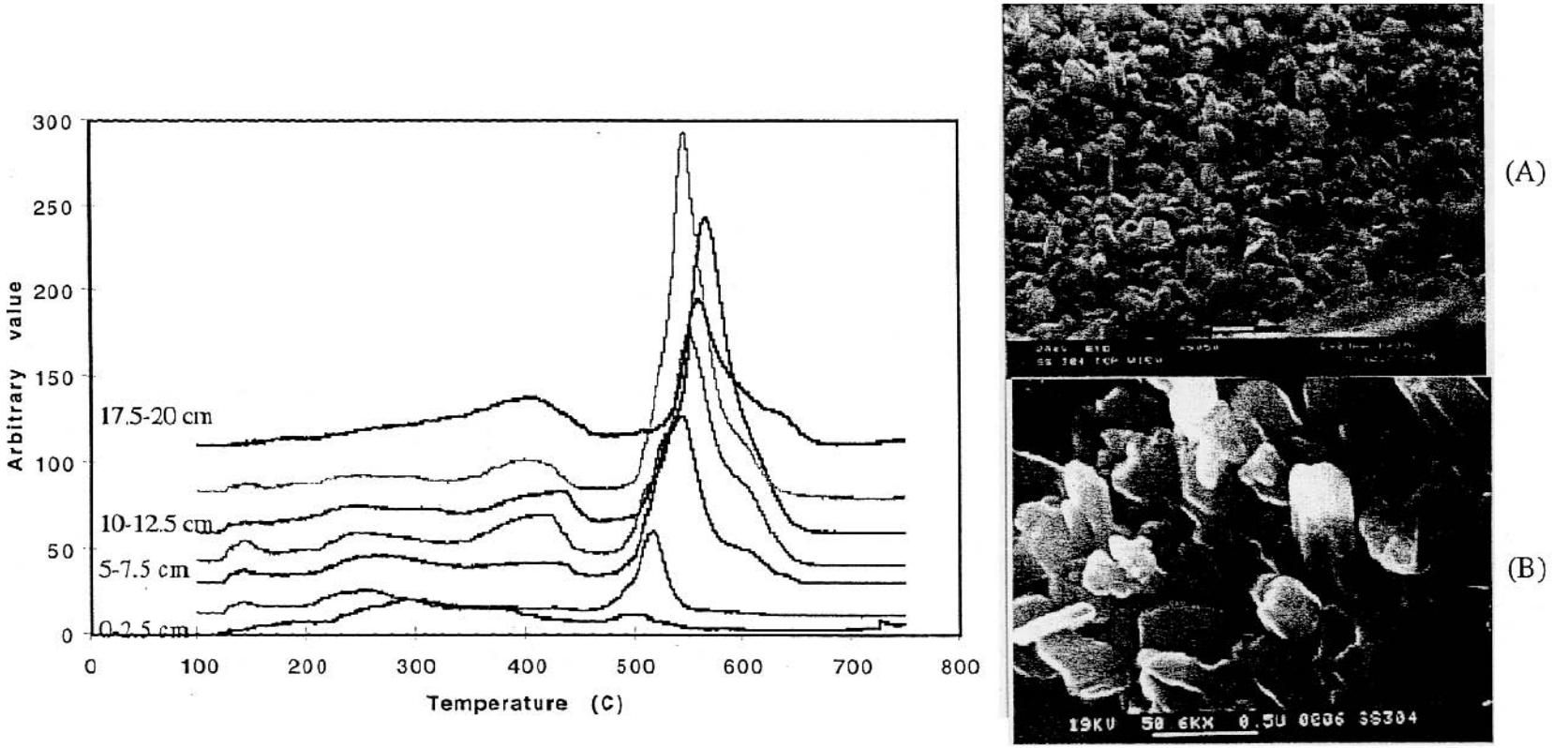

Figure 4. Carbon burn-off profiles for 2.5 cm segments of a stressed ss304 tube and SEM micrographs for the 0-2.5 cm (A), and 17.5-20 cm (B) segments .

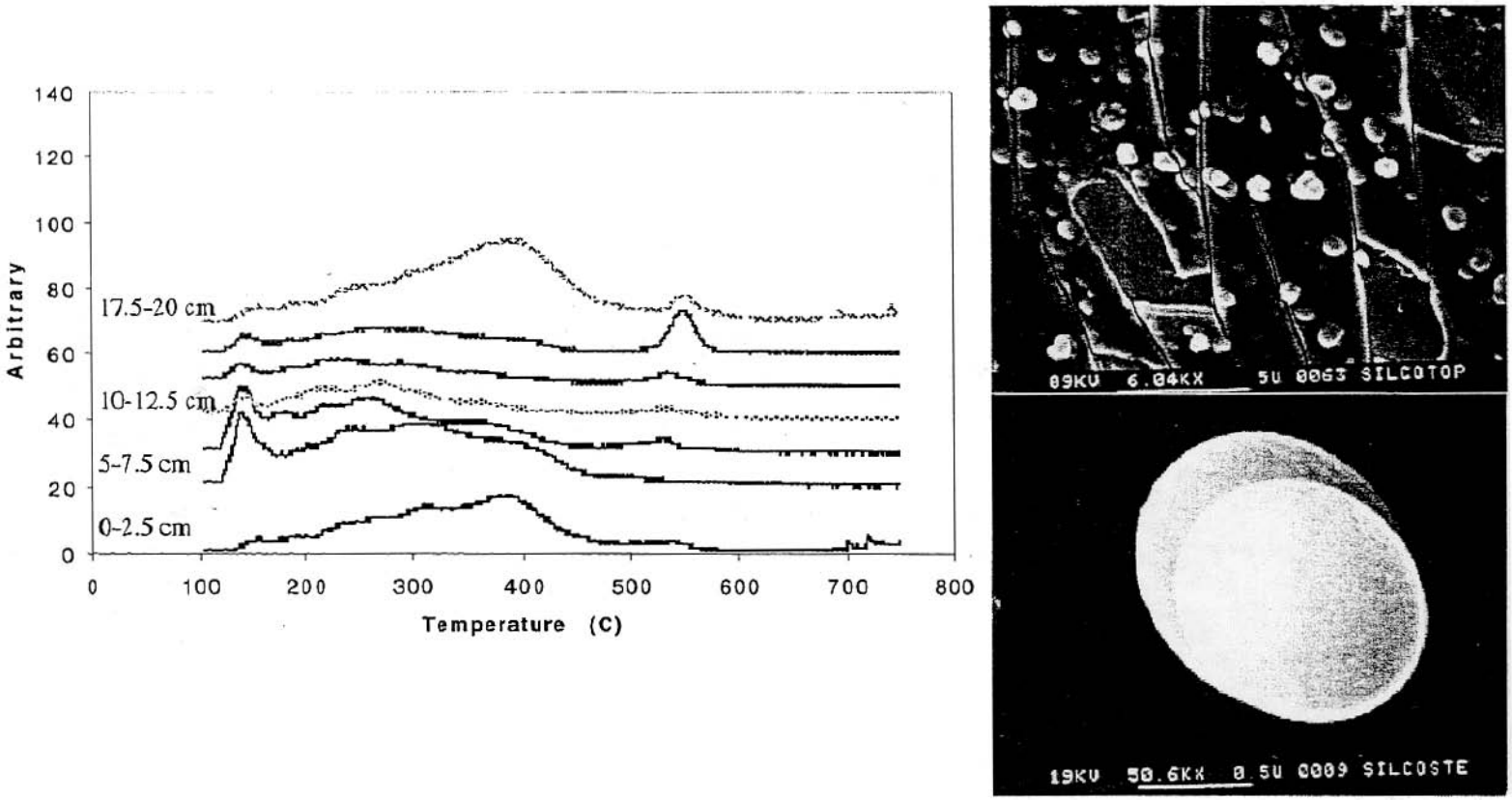

Figure 5. Carbon burn-off profiles for 2.5 cm segments of a stressed Silcosteel tube and SEM micrographs for the 17.5-20 cm segment .