# PYROLYTIC CARBON COATING OF ZIRCALOY-4 CLADS AT RELATIVELY LOW TEMPERATURES

ABDELRAZEK, I.D., SHARKAWY, S.W., and El-SAYED, H.A.

Department of Metallurgy, Atomic Energy Authority, Cairo, 13759,Egypt.

## ABSTRACT

A new technique has been developed to apply pyrolytic carbon coating to the inner surface of Zircaloy-4 cladding tubes at relatively low temperatures. The coating gas was a mixture of commercial butane, as a source for carbon, and argon as a carrier gas.

The rate of the coating process was found to depend on the coating temperature and the concentration of butane in the coating gas mixture. The average deposition rate of pyrolytic carbon coating increased from 0.385 to 4.315 x $10^{-3}$ mg/($cm^2$.min) over the temperature range 250-450 $^{\circ}C$ and butane flow rate 50-90 $cm^3$/min. The reported coating efficiency ranged from 1.16 to 11.11 % over the temperature and the butane flow ranges of the study, whereas the activation energy of the coating process was estimated to be 8.9 kcal/mol. Tensile tests and microhardness measurements performed on samples prepared from the coated tubes indicated that the coating process has insiginificant effect on the mechanical properties of the sheath.

## INTRODUCTION

Fuel bundles of the CANDU-37 elements type have been used, with an excellent performance, to fuel CANDU power reactors, with burnups of 7-9 MW.d/kg U. The performance of the CANLUB coated elements, has been discussed in details (1,2), including the optimization of the coating thickness (3). It has been reported that the existing fuel element design, with the CANLUB sheath , is capable of reliable operation to a burnup of 17 MWd/t U under steady power conditions. Enhanced fission gas release, producing potentially fuel life-limiting effects, may occur at burnups higher than 22

MW.d/kg U, or at power ramping (4,5). New fuel designs which could allow for substantially higher burnups would call for improved coatings for the fuel clad.

In this investigation, a new technique has been carried out to coat the inner surface of Zry-4 tubes with pyrolytic carbon at relatively low temperature range (200 - 450° C). The coating gas was a mixture of commercial butane and argon. Also, the possible changes in some of the mechanical properties of the coated tubes were investigated at room temperature.

## EXPERIMENTAL WORK

### 1. Materials

Zircaloy-4 tubes (of 15 mm outside diameter, 0.5 mm wall thickness and average grain size of 12 um) have been used in this study. The coating gas mixture was composed of commercial butane (93 % butane and 7 % propane, by volume) and argon. Butane was used as source for carbon, whereas the argon served as the carrier gas.

### 2. Equipment

A tubular reactor (115 cm long and 6 cm inside diameter) was used in this investigation. The reactor was housed inside a 3.3 kw tubular furnace which was provided with a Ni-Ni Cr thermocouple, a temperature controller and a rotary vacuum pump. A schematic diagram of the experimental set up is shown in Fig. 1.

### 3. Coating Procedure

The samples of Zircaloy-4 tubes, having a length of about 7 cm, were cleaned by distilled water followed by acetone and were then dried with warm air. The weight of each sample and its inner surface area were determined. The sample was placed and secured in the reactor. The system was evacuated by the rotary pump then flushed five times with argon, to minimize the oxygen content. Heating started and continued until the pre-decided coating temperature was achieved (heating rate of 200 °C/h). Argon and buatne gases were introduced and their flow rates were adjusted according to the pre-decided rates. The experimental procedure included the systemic variation of the coating temperature (250-450 °C), coating time (30-90 min.), and the hydrocarbon flow rate (50-90 $cm^3$/min.) at a pressure slightly above the atmospheric pressure (about 1.2 bars). In all

experiments the argon flow rate was kept nearly constant (60 $cm^3$/min.). At the end of each run, the hydrocarbon gas flow was shut off and the electric power was disconnected. The argon gas flow was continued to cool the sample for several minutes.
It was possible to overcome the oxidation problems by using pyrogallol as an oxygen scavanger and calcium chloride to minimize moisture content in the flowing gases.

## 4. Testing Procedures

The rates of carbon deposition (coating) at the inner surface of the tube samples have been evaluated by measuring the weight gain of the samples using a sensitive balance (accuracy 0.1 mg). This technique is only suitable for coated samples having substantial weight gain .

A photo-cell reflection setup has been used to determine the low coating weight gain (to minimize errors in weighing in case of using ordinary balance). A schematic diagram of the photo-cell reflection system is shown in Fig. 2. In that system, the coated Zry-4 tube sample was placed between the light source and the photo- cell detector. A digital multimeter is connected with the photo-cell detector to measure the induced voltage. Tube samples having known coating densities and a blank sample were used to calibrate the system.

A correlation between the measured voltage (which is a function of the reflected light intensity) and the coating density was obtained. The correlation between the logarithmic of the measured voltage (by using the photo cell system) and the coating density of the deposited carbon on the inner surface of Zry-4 tubes is plotted in Fig 3. It is possible to put that correlation in the form:

$$V = V_0 e^{-\mu w} \qquad (1)$$

where:

V : is the induced measured voltage of coated tube due to the reflected light

$V_0$: is a constant (depending on the geometry, surface condition of the tube, and position of the light source), which was found to be 2.225 mV, for the setup under consideration.

$\mu$ : the absorption coefficient of carbon, which was estimated to be 3.6

w : is the coating density, mg/cm$^2$.

This equation helped in the estimating the non measurable coating weight gains. Also, it was possible to estimate the weight gain of the deposited carbon of the CANLUB cladding. For example, the measured voltage due to placing the CANLUB cladding in the photo-cell system was 0.7 mV. Therefore, a coating weight gain of approximately 0.30 mg/cm$^2$ could be predicted, as shown in Fig. 3.

In order to evaluate the effect of the coating process on the mechanical properties of the coated tubes, a tensile specimens has been prepared from the coated tubes. Tensile testing machine of type MP-0.5-1 was used at a strain rate of $2.22 \times 10^{-3}$ s$^{-1}$. All tests were carried out at room temperature ( 27 $^{\circ}$C). The microhardness across the tube wall of the coated and bare samples were measured using microhardness tester (Shimatzu-V type) with a load of 100 g, applied for a time of 10 sec. The tested tube had been mounted and polished carefully before testing. The microhardness identation was done in different directions and the average of three measurements was taken. Micrographs of the pyrolytic carbon coating and the blank tube surfaces were obtained using a scanning electron microscope (Shimatzu-V type).

## RESULTS AND DISCUSSION

### 1. Coating Density

The variations of the coating density of pyrolytic carbon coated Zircaloy-4 tubes with time are plotted in Fig. 4 and generally indicate that the weight gain increased by increasing the coating temperature and by also increasing the butane concentration in the coating gas mixture. The same type of dependence has also been reported by Ogawa (6), for coatings deposited from the pyrolysis of n-Hexane at a the temperature range 800-900$^{\circ}$C and by Je (7) for the case of pyrolytic carbons deposited from propane.

### 2. Coating Rates

The estimated coating rates are plotted versus the coating temperature in Fig. 5 showing that the coating rate, although very slow, has increased about ten folds over the temperature range 250-450 $^{\circ}$C for the two tested hydrocarbon concentrations. The very slow nature of the carbon deposition by the pyrolysis of hydrocarbons, especially at low temperatures, has been reported by Savage (8), who suggested temperatures higher than

550 °C for measurable deposition rates for the pyrolysis of methane. The same conclusion was reported by Abdelhalim (9 ) for pyrolytic carbon coatings, from commercial butane, applied to $UO_2$ microspheres at 800-1200 °C and butane concentration 3-10%.

The activation energy was determined experimentally by plotting the logarithm of the coating rate ,w , versus the reciprocal of the absolute temperature ,1/T , as shown in Fig. 6. From the slope ( -Q/R), the activation energy , Q , was found to be equal ~ 8.9 kcal/mol. It was also reported (9) that the activation energy of the pyrolysis of commercial butane was 1.2 kcal/mole at the temperatures higher than 900 ° C However, the activation energy for temperatures below 900 °C was 10.4 kcal/mole. This fact, would indicate two deposition mechanisms, each correspond to a different reaction rate. Murphy (10) deduced that the activation energy of the pyrolytic carbon deposition for methane gas was found to be 12.95 kcal/mole at temperatures higher than 1500 °C. However, the activation energy for temperatures below 1500 °C, is about 63 kcal/mole. High values of activation energy of methane are attributed to that the mass transfer controls the deposition process at least down to 1500 °C, below this temperature kinetics would control the process.

3. Coating Efficiency

The coating efficiency was determined from the following equation:

$$\text{coating efficiency} = w_d/w_i \qquad (2)$$

where:

$w_d$ : is the weight of carbon deposited on the total bed surface area , and can be calculated as =deposition rate x coating time x total bed surface area,

$w_i$ : is the weight of carbon which enter to the system in the form of butane gas , and can be calculated from the flow rate of butane at coating time .

The effects of coating temperature and flow rate of butane on the coating efficiency are shown in Fig. 7. It was found that the coating efficiency dependents on the coating temperature, and the flow rate of butane. The coating efficiency increased from 1.16 % at 25 °C to 11.11 % at 450 °C at a butane flow rate of 50 $cm^3$/min ., whereas, it increased from 0.8 % at 250 °C to 7.25 % at 450 °C at a butane flow rate of 90 $cm^3$/min. It could also be noticed from Fig.8 that the increase in the concentration of butane in the coating

gas mixture resulted in decreasing the coating efficiency at the same coating temperature. The same trend was reported by Abdelhalim (9).

Bokros (11) found no variation of the coating efficiency with bed surface area, whereas Ford (12) reported that coating efficiency increase with the increase of bed surface area. At lower temperatures, they separately observed a decrease in the coating efficiency when methane was used. Also, Beatty (13) indicated that for propane as a hydrocarbon source, the coating efficiency decreases with increasing the concentration of hydrocarbon gas at low temperatures.

4. Mechanical Properties

The variation of the tensile strength (UTS) of the Zry-4 coated samples with the coating temperatures, for the cases of two hydrocarbon concentrations, are shown in Fig. 8. The UTS values varied between 605 MPa, for samples coated for 30 min . at 250°C, and 550 MPa for samples coated for 60 min. at 400 °C for . Above this temperature, the UTS started to drop remarkably.

The variation of the percent elongation of the same tested samples, with the coating temperatures are indicated in Fig. 9, showing also no remarkable change up to 400 °C. Coating for long periods at temperature above 400 °C would result in a noticeable increase in the percent elongation of the samples.

This variation in the mechanical properties of Zircaloy-4 has been reported by Abdelazim (14), where the UTS decreased from 500 MPa at 500 °C to 416 MPa at 600 °C. The elongation increased from 17 to 25% over that temperature range.

The results of the microhardness test for the blank and coated Zry-4 tubes at 400 and 450 °C are shown in Fig. 10. The Vickers Hardness Number (VHN) has slightly changed over the temperature range of the study after the coating process. Generally, the VHN is highest relatively near the surface of the tube than mid of the tube, however, due to the annealing effect of the coating process, the VHN profile became more uniform across the tube thickness. The minimum of VHN was 210 and the maximum was 245 for the blank tube. For tubes coated at 400 °C, for 45 min. at a butane flow rate of 50 $cm^3$/min., the minimum VHN was 200 and the maximum was 220, whereas tube samples coated at 450

°C, for the same conditions of coating time and hydrocarbon concentration, the minimum and the maximum VHN were 190 and 208, respectively.

It appears from the results of the UTS, percent elongation and microhardness measurements on the coated and blank tubes, that the coating process has not significantly changes of the hardness of Zry-4 tubes. In fact these results indicated that no hydride formation for the Zry-4 tubes during the coating process, which otherwise, could have led to higher microhardness (15 ).

5. Microstructure of Pyrolytic Carbon Coating

The scanning electron microscope examination was used to investigate the micro-structure of pyrolytic carbon coating. Fig. 11 shows the micrograph of the deposited carbon at coating temperature of 450 °C for coating time of 60 min. and a butane flow of 90 $cm^3$ /min., compared to the blank tube surface.

The extremely slow carbon deposition rates are characterized by a laminar, isotropic or granular microstructures, depending on the deposition temperature and the hydrocarbon used (9,11,16). The evaluation of the microstructure of the extremely thin coatings was beyond the scope of this study.

## CONCLUSIONS

1- Coating of Zircaloy-4 tubes by pyrolytic carbon through the thermal cracking of the commercial butane in the low temperature range (250 - 450 °C) is a practical and economical technique.
2- The coating process rate depends on the temperature and the hydrocarbon concentration in the coating gas mixture.
3- It is possible to determine very small coating densities by using a photo-cell reflection system
4- The average deposition rate of the carbon coating is very small at the temperature range of the study, which suggests coating of high thermal qualities and adhere to the sheath relatively better, compared to the CANLUB coatings which peal out during loading of the fuel pellets during the fabrication of fuel rods.
5- The coating process has not significantly affected the mechanical properties of Zry-4 tubes.
6- It is recommenced to perform the coating process at the temperature range (400-

450 °C) and at a butane flow rate of about 90 $cm^3$/min., for coating times longer than 90 min. to obtain reasonable coating densities higher than 0.3 mg/$cm^2$.

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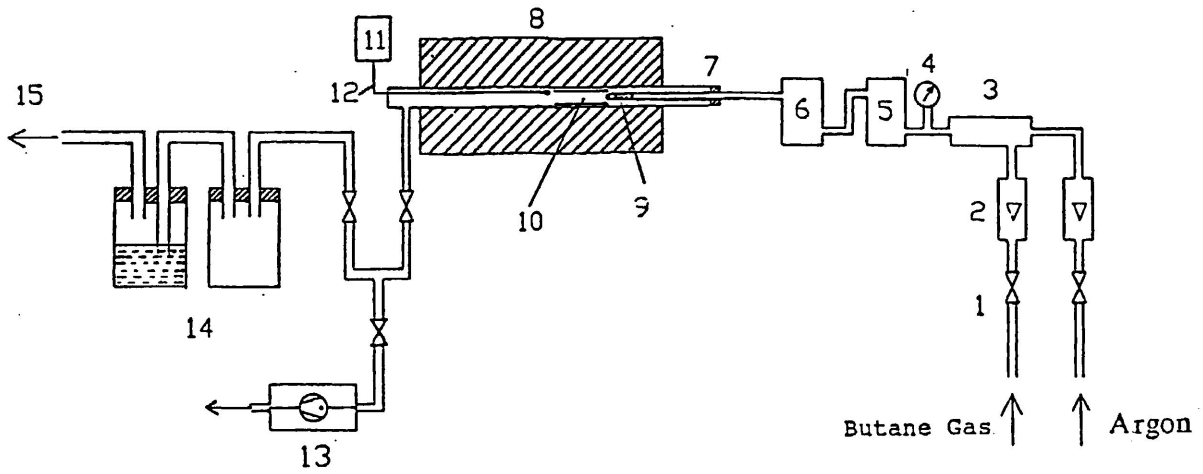
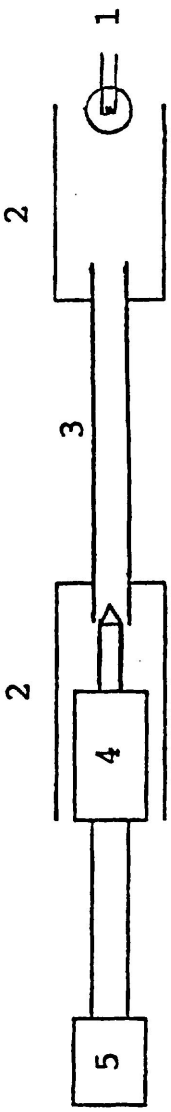



1- regulating valve
2- flow meter
3- gases mixing chamber
4- pressure gauge
5- pyrogallol
6- calcium chloride
7- stainless steel reactor
8- electrical furnace
9- gas nozzle
10- Zry-4 tube
11- temperature controller
12- Ni-NiCr thermo-couple
13- rotary vacuum pump
14- trap gas bottles
15- to vent

FIG. 1 A SCHEMATIC DIAGRAM FOR THE EXPERIMENTAL PYROLYTIC CARBON COATING SYSTEM OF ZRY-4 TUBES.




1- light source
2- shield
3- Zry-4 tube
4- photo cell detector
5- digital multimeter

Fig. 2 A SCHEMATIC DIAGRAM OF THE PHOTO-CELL REFLECTION SYSTEM.

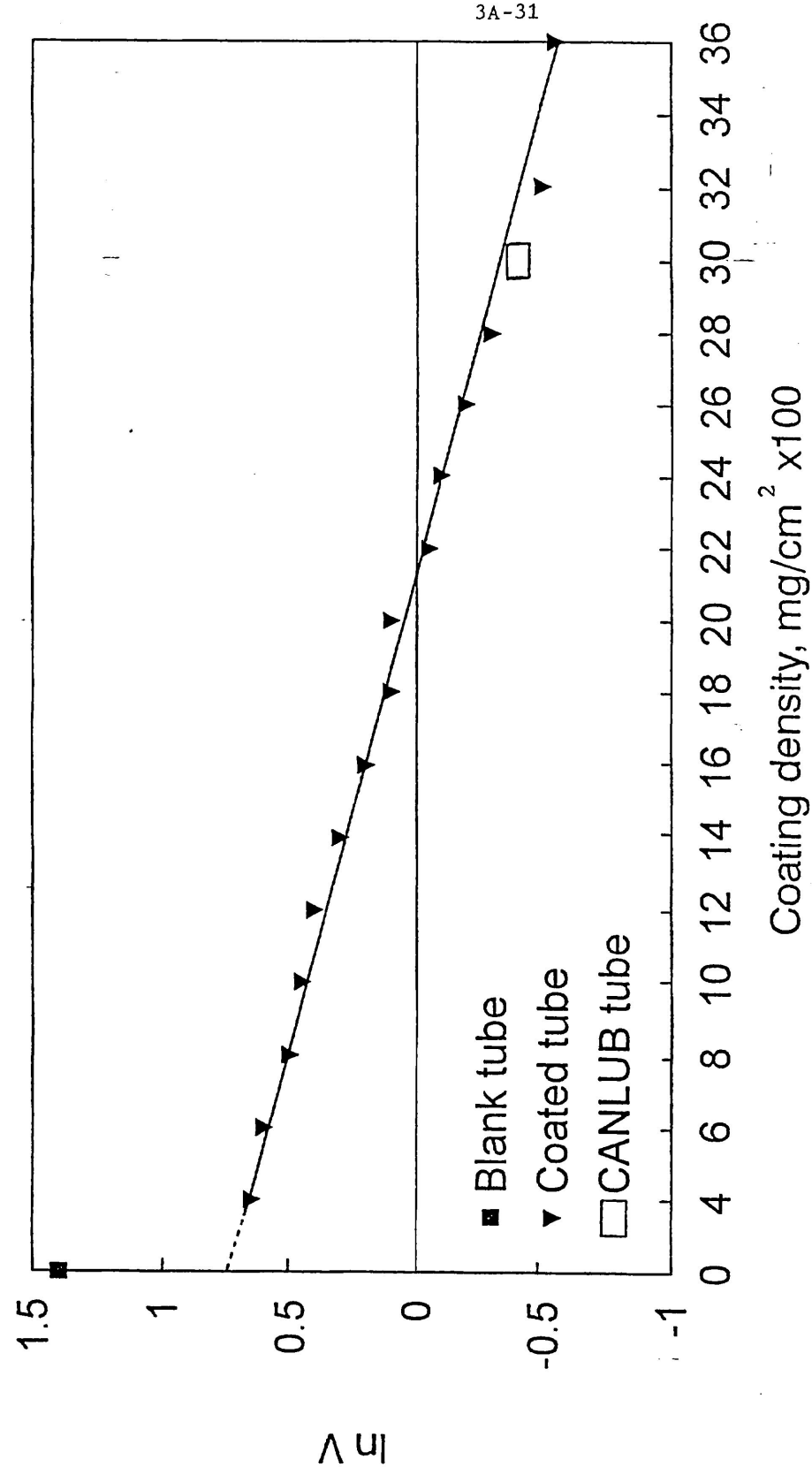



FIG. 3 THE CORRELATION BETWEEN THE LOGARITHMIC OF THE MEASURED VOLTAGE AND THE COATING DENSITY

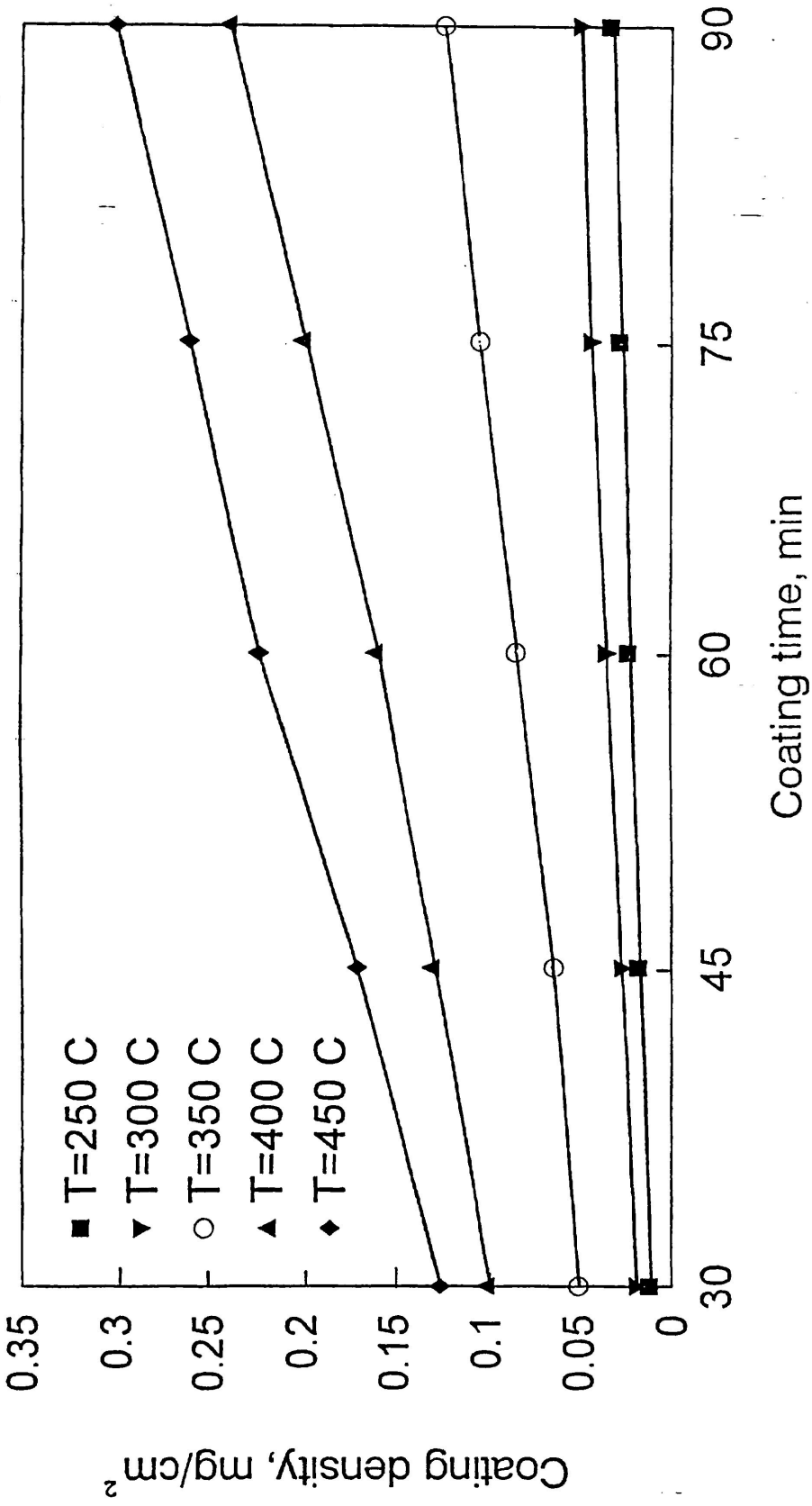



FIG. 4(a) VARIATION OF COATING DENSITY WITH TIME AT BUTANE FLOW RATE OF 50 $cm^3$/min.

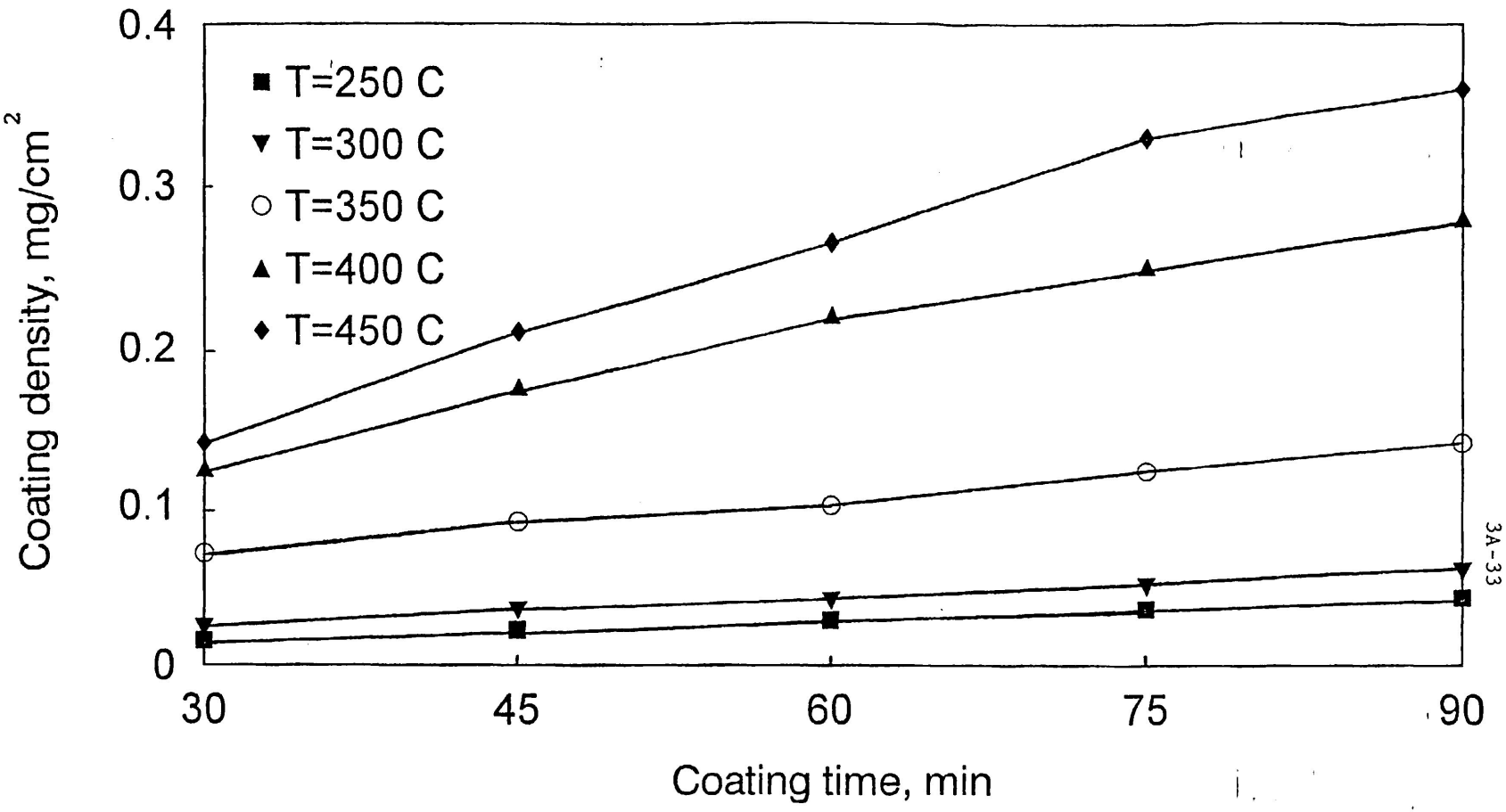



FIG. 4(b) VARIATION OF COATING DENSITY WITH TIME AT BUTANE FLOW RATE OF 90 $cm^3$/min.

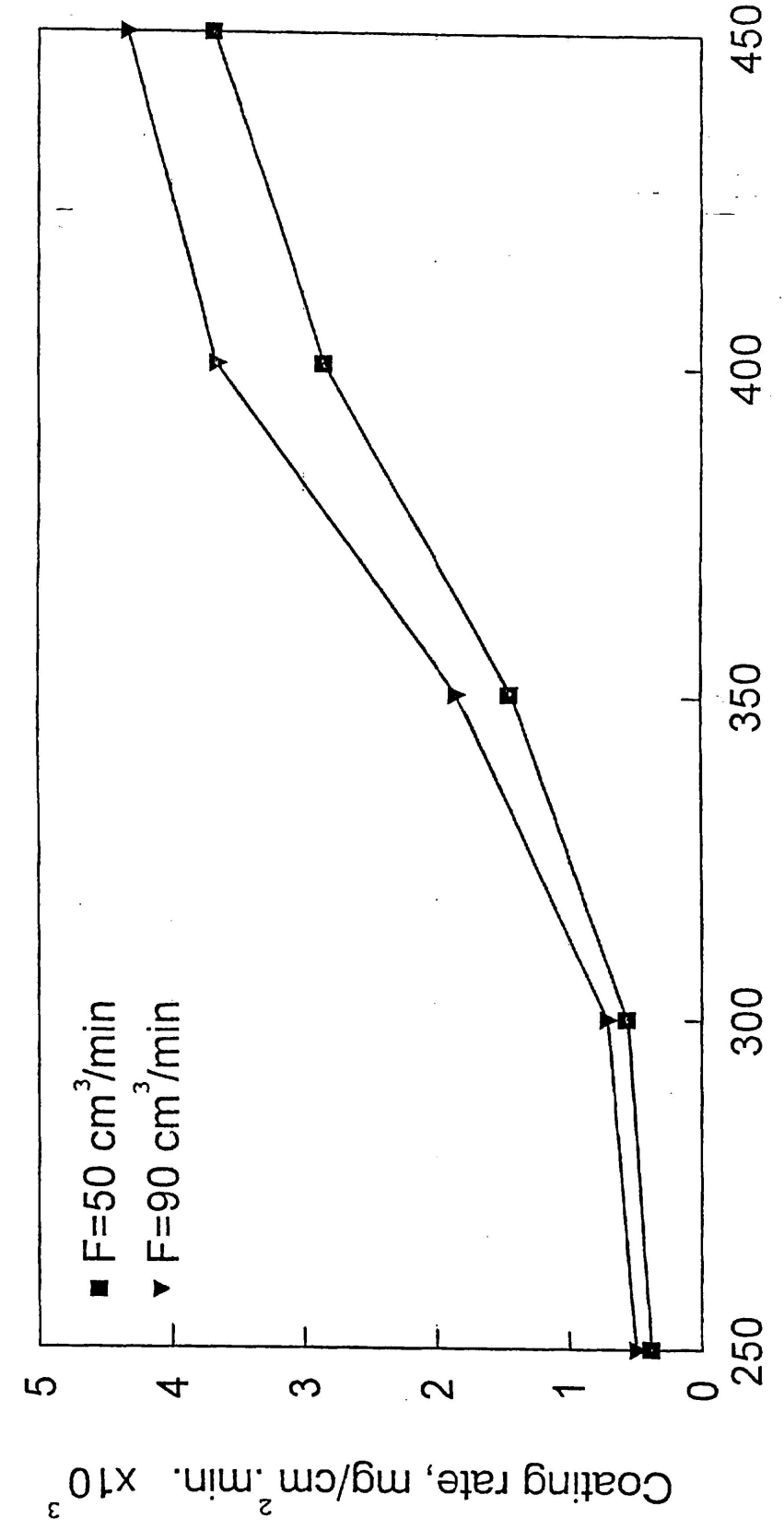



FIG. 5. VARIAION OF COATING RATE WITH TEMPERATURE AT BUTANE FLOW RATES OF 50 AND 90 $cm^3$/min.

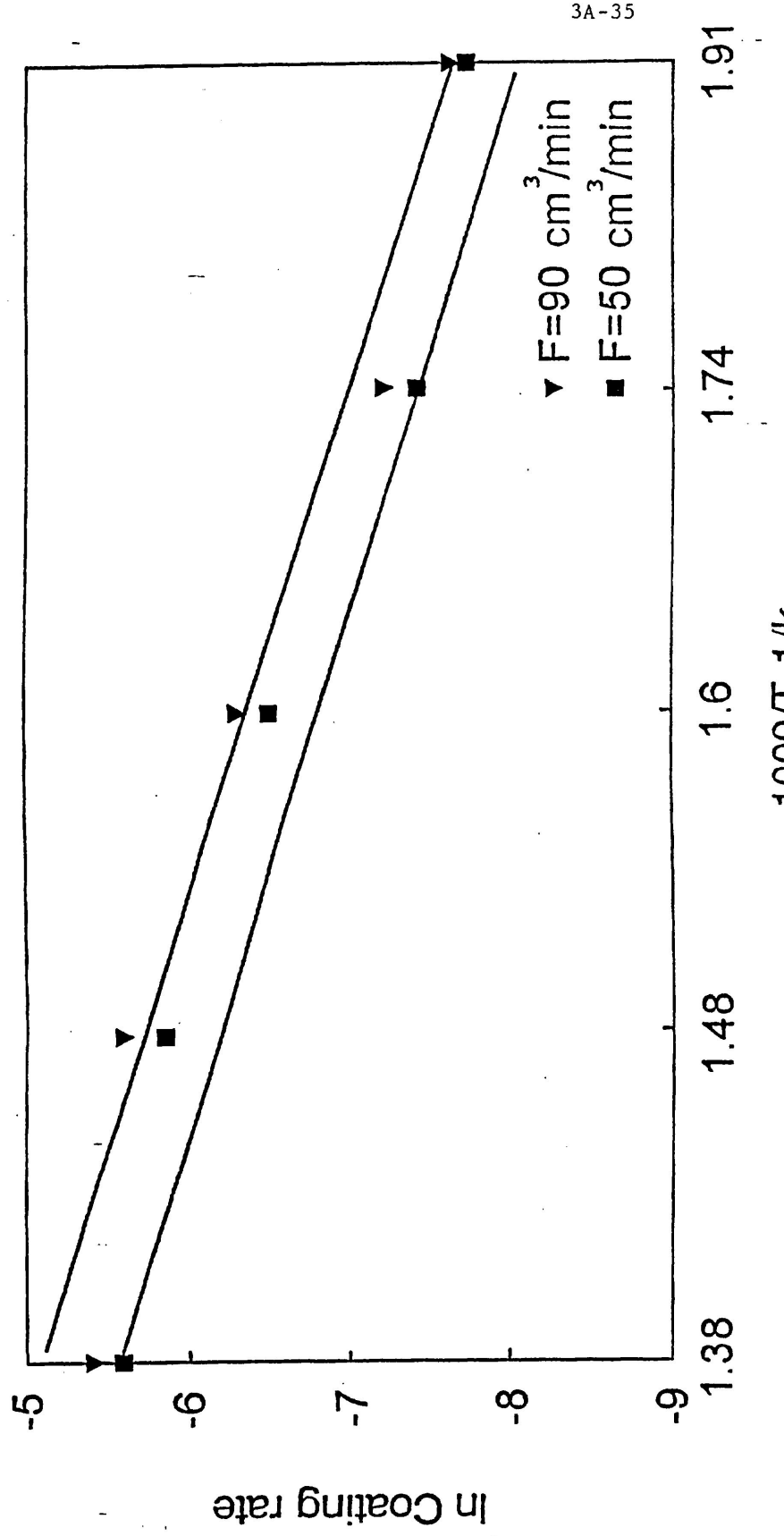



FIG. 6 VARIATION OF THE COATING RATE WITH TEMPERATURE.

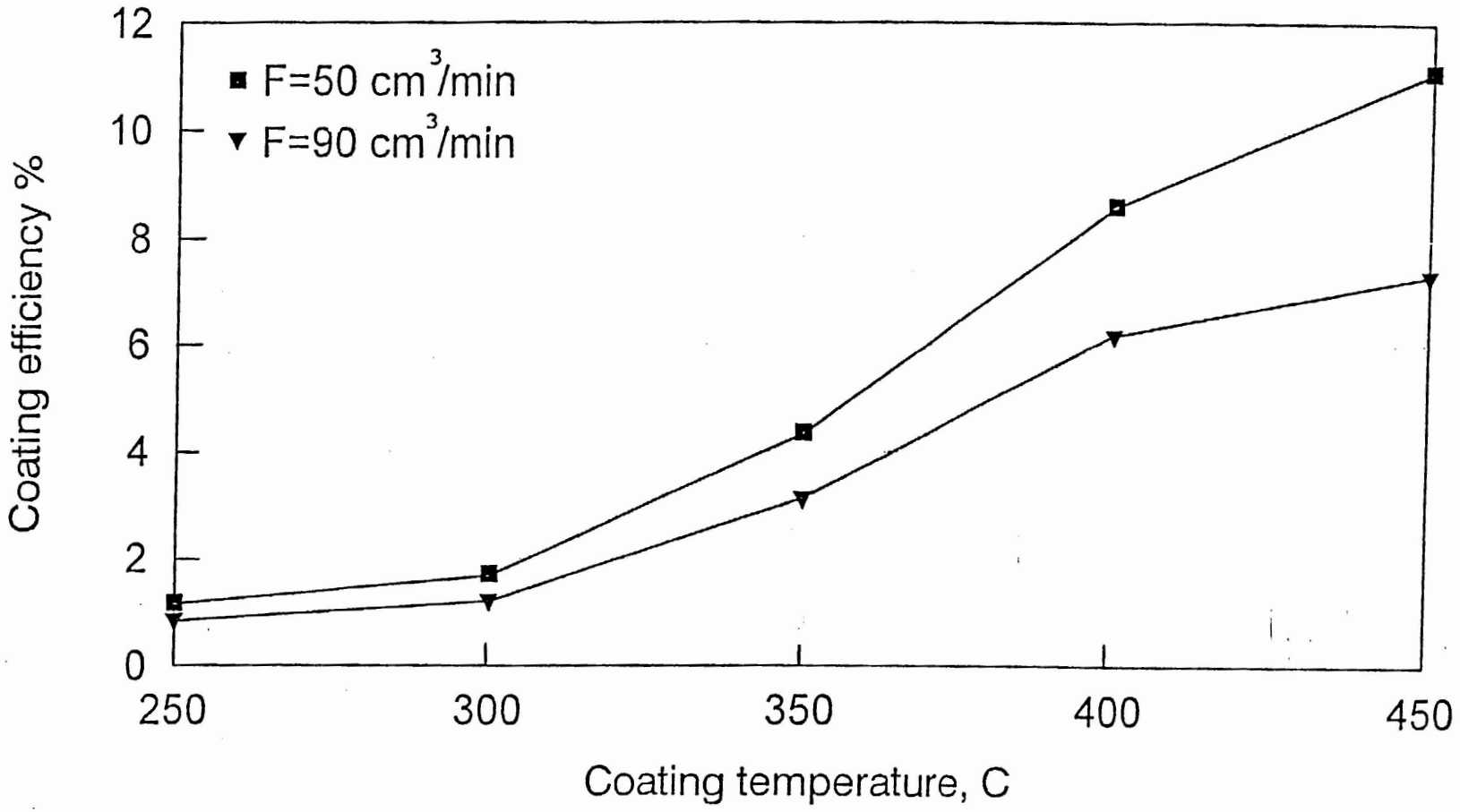



FIG. 7 VARIATION OF COATING EFFICIENCY WITH TEMPERATURE AT BUTANE FLOW RATES OF 50 AND 90 $cm^3$ /min.

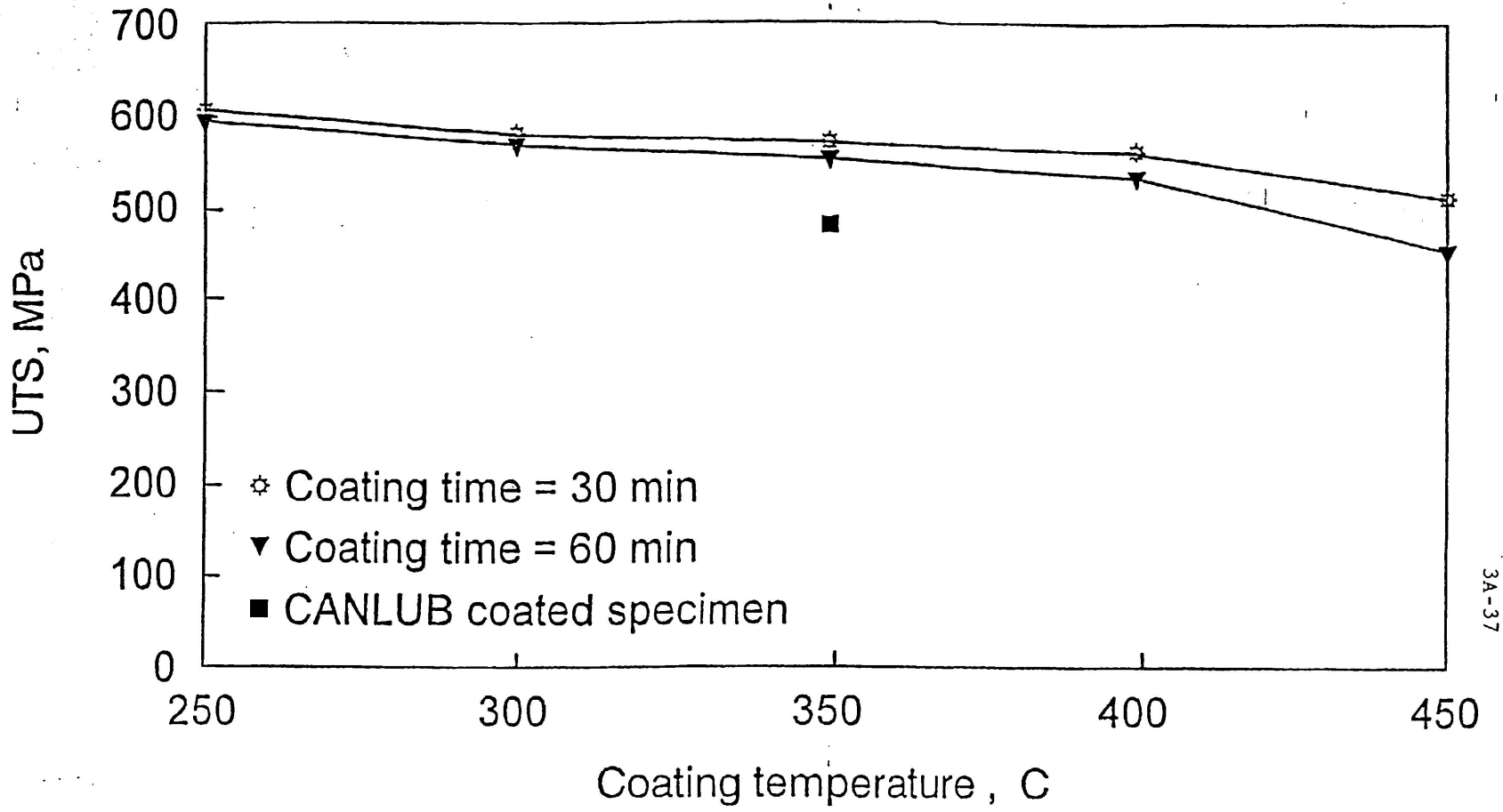



FIG. 8 THE VARIATION OF THE ULTIMATE TENSILE STRENGTH OF THE COATED ZRY-4 TUBES WITH COATING TEMPERATURE

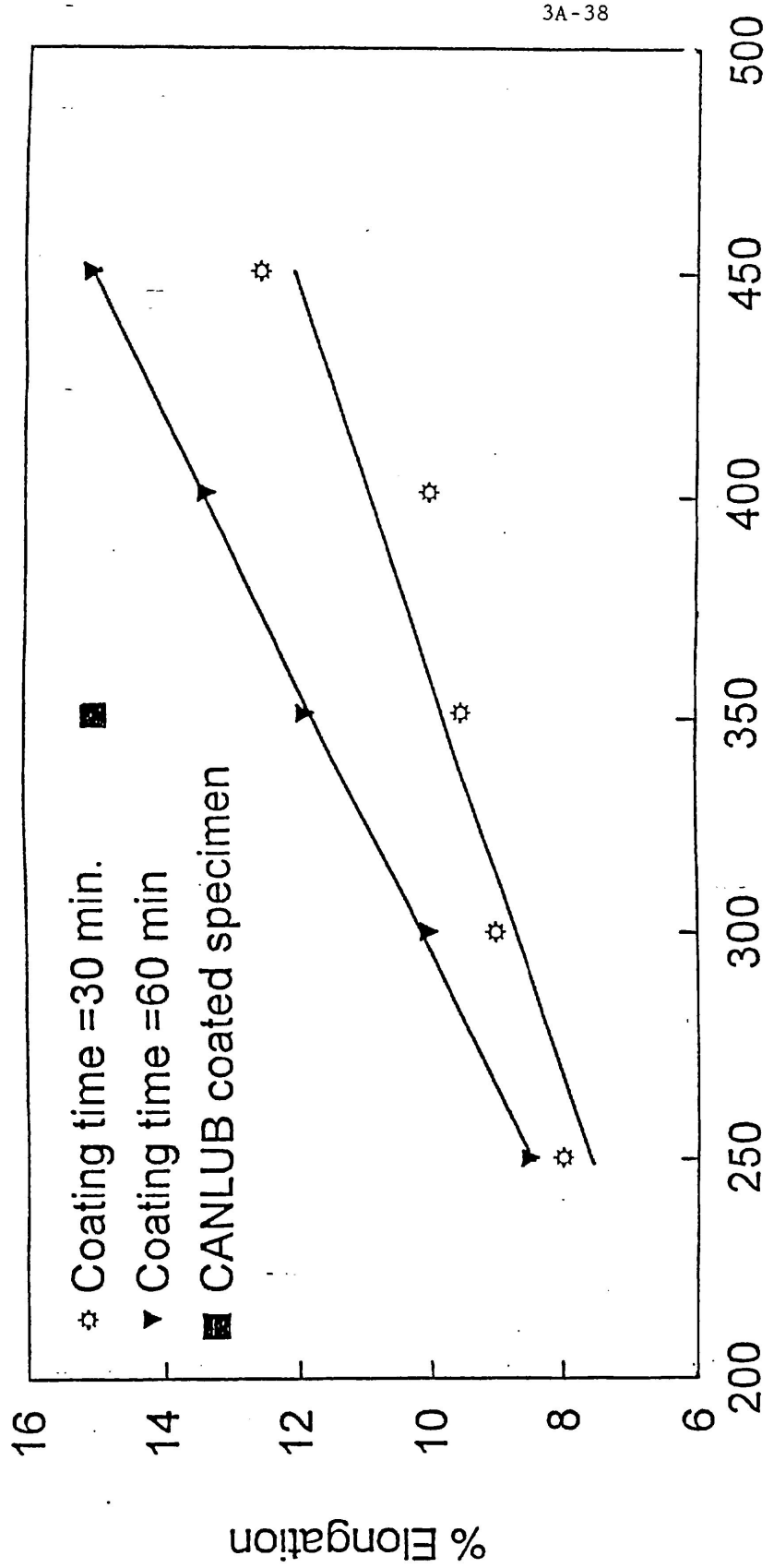



FIG. 9 THE VARIATION OF THE TOTAL ELONGATION OF ZRY-4 TUBES WITH COATING TEMPERATURE.

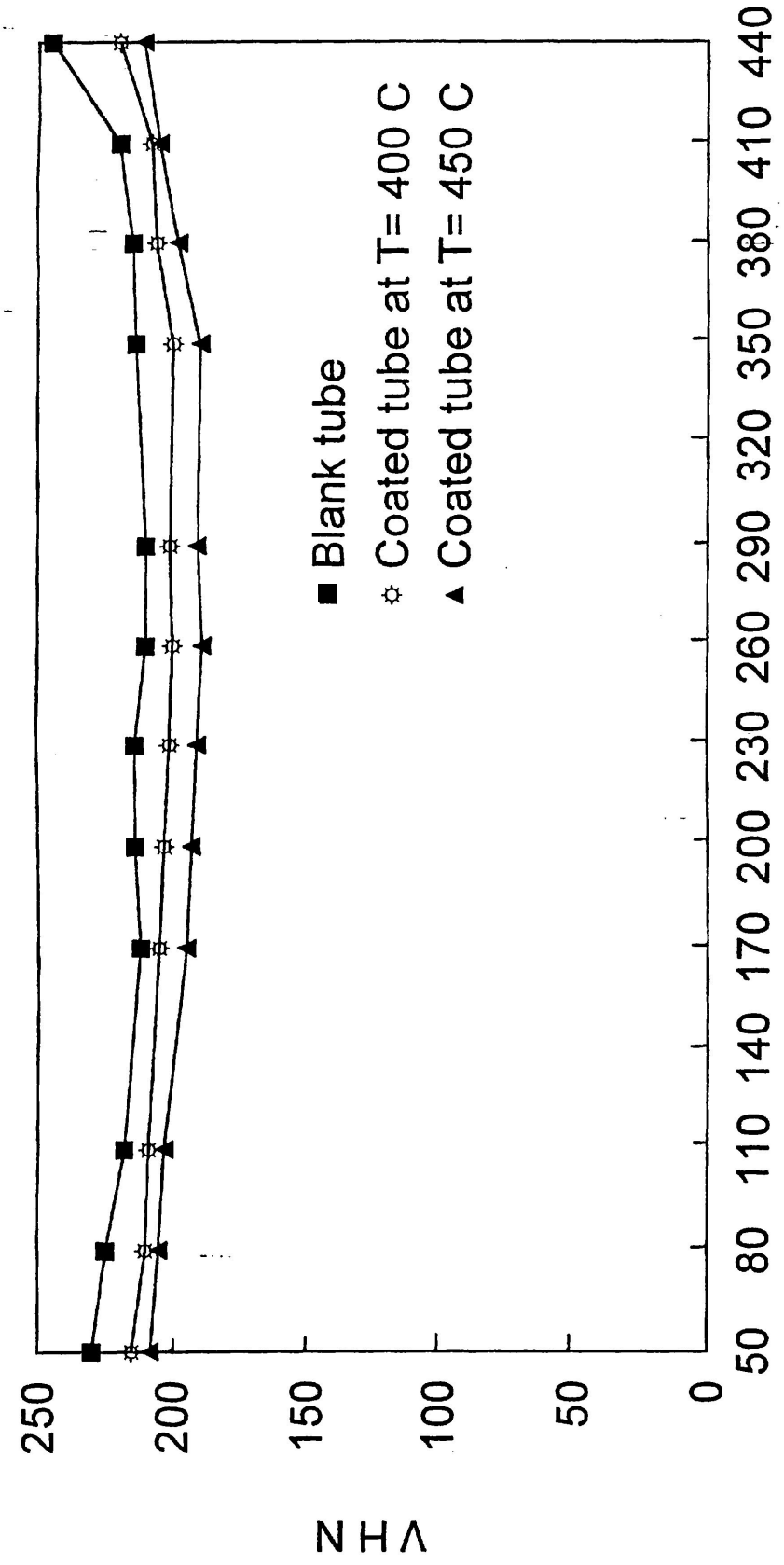



Fig. 10 THE VARIATION OF MICROHARDNESS ALONG THE TUBE THICKNESS


FIG. 11 SEM SURFACE MICROGRAPHS
(A) BLANK ZRY-4 TUBE, (B) ZRY-4 TUBE COATED AT 450 °C for 60 min.
AND 90 $cm^3$/min. BUTANE FLOW