CVD-KINETICS OF PYROlYTIC CARBON FROM METHANE ON THE ST AINLESS STEEL 316L AT 600°C

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Introduction

Among the stainless steel 316L means low carbon content, >0.03%, contains 2 -3 % Mo and applies especially to the biomedical articles, e.g. endo- and cardiovascular stents But it has a shortage of Ni-and Cr-ion releases in the endo- and cardiovascular tissues and no good biocompatiblity in the muscular system[1]. Therefore it must be remedied in few years. In order to prevent this shortage it should be coated with carbon or with half-conductor ceramics such as SiC[2]. It is recognized that pyrolytic carbon is the most implantable material. So In this study on the CVD-kinetics of pyrolytic carbon from methane with stainless steel (STS) 316L at 600°C, which was canied out at the Institut fur Chernische Technik[3], Universitaet Karlsruhe, a rate law could be deduced from a model concept of catalytic deposition mechanism and curve fitted by easy plot program. It found optimal ratio of methane and hydrogen of 5:1 at 90 kPa and the highest deposition rate of 73 nrn/sec. at 1.5 sec. residence time of reactant gas. But the same kind of STS 304 which contains also similar contents of Ni, Cr but none of Mo would not be coated with pyrolytic carbon and SiC. That means Mo-catalysis in the stainless steel 316L. So STS 304 could be used as the sample holder in the reactor.

Experimental

One of the most important strategy is to carry out first experiments at the extremes (Max. and Min. setting) of the range of the controlled variables. After this theory the minimum number of runs in order to determination of rate law were selected as follows: Three different reactors were used which have volume ratio to the sample stent of $V_I : V_{II} : V_{III}$ = 1 : 2 : 20.(see Fig. 1). The partial pressure fraction of methane, hydrogenn and argon gas should be kept to unity, e.g. $F_{CH4} : F_{H2} : F_{Ar}$ = 0.4 : 0.08 : 0.52, while the partial pressure ratios of methane to hydrogen (P_{CH4}/P_{H2}) were changed from 1:1 to 5:1. The feed rate should be kept to 1-3 sec. The temperature was fixed to 600°C, because of metal property damage at higher temperature and total pressure was fixed from 90 to 101 kPa., because of slow deposition rate. After film growth rule the deposition rate was expressed in Ångstoms per second or nm/s and it was easily converted to a molar rate (moles/$m^2 \cdot s$) or (g-mol/g · cat · h) by multiplying by the molar density of carbon(=150 g-mol/m^3).

Results and Discussion

Modelling of catalytic CVD of methane on the metal with addition of H_2:

$$2CH_4 \underset{catalysis}{\overset{metallic}{\rightleftharpoons}} 2CH_3 + H_2$$

$$2CH_3 + 2s \overset{k_M, k_{-M}}{\rightleftharpoons} 2CH_3 \cdot s$$

$$H_2 + 2s \overset{k_M, k_{-M}}{\rightleftharpoons} 2H \cdot s$$

$$2CH_3 \cdot s + 2H \cdot s \overset{k_s}{\longrightarrow} 2C_s(s) + 2s$$

$$r_{dep} \cong \frac{k_s K_H K_M P_H (P_{CH3})^2}{[1 + 2\sqrt{K_M} P_{CH3} + K_M (P_{CH3})^2]^2}$$

$$= \frac{aX^2}{(1 + bX + cX^2)^2} \qquad (A)$$

Fig. 2 shows exact agreement with plot of deposition rate vs. feed rate, residence time and curve fitting by easy plot program. From this plot ks KM a:nd KH could be evaluated as follows:

$a = k_s(K_H K_M P_{H2} = 6098$, $b = 2\sqrt{K_M} = 4.172$;

$c = \sqrt{K_M} = 7.8$

and rate law;

$$r_{dep} = \frac{6098\,(P_{CH4})^2}{[1 + 19.2 P_{CH4} + 7.8 (P_{CH4})^2]^2} \qquad (A')$$

Fig.3 shows a plot with deposition rate of pyrolytic carbon against partial pressure of hydrogen and against the partial pressure ratio of methane to hydrogen(s. Fig. 4). The highest deposition rate was occurred at the partial pressure ratio of methane to hydrogen of 5:1. Fig. 5 shows stents coated pyrolytic carbon at 600°C for 1Oh and 2Oh, respectively. For the uniform coating it needs 15h. Fig. 6 shows SEM with LFM (latera1 force microscopy) and FMM (force modulation microscopy) of the stent coated by CVD of pyrolytic carbon from methane at 600°C. With this SEM we can identify a uniformlity of 300-400nm scale.

Conclusions

STS 316L which contains 3% Mo catalyze CVD of pyrolytic carbon at low temperature of 600°C. Also small amount of H_2 catalyze, but too much plays as inhibitor. The max.

deposition rate at the ratio of 5:1 $=P_{CH4}/P_{H2}$ and residence time 1.8 sec was 73 nm/s, or 12.6 x 10^{-5}g-mol/g-cat-h. With this deposition thickness of 15h it could prevent the Ni and Cr ion release and has the adapt flexibility for water balloon expander. The uniformity of nm scale was identified with LFM and FMM of SEM photo.

References

1. W. van Oeveren, et al., Prog. Biomed Res. 1999; 4, 17-23
2. A. Bolz, et al. Tex. Heart Inst J. 1999; 23, 162-172
3. K.]. HUttinger, et al. Chemirol Vapor Deposition. 2000; 6(2). 77-87

Acknowledgments

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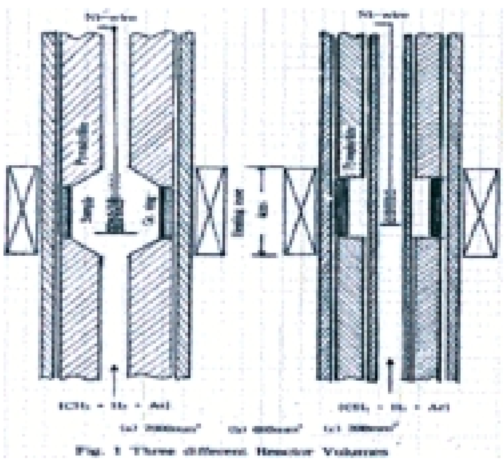

Fig 1. Three different CVD-reactor

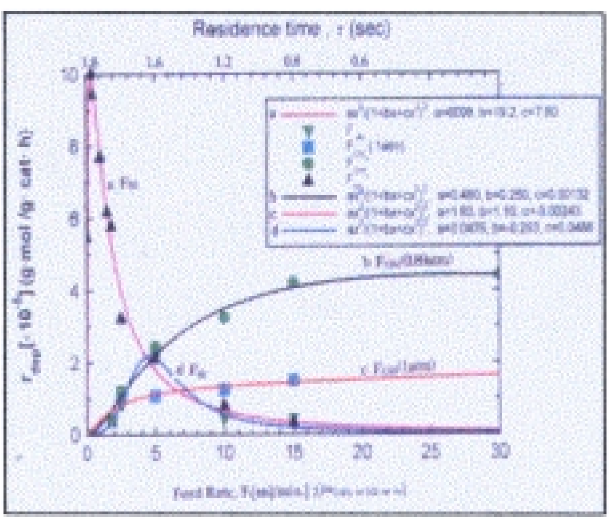

Fig 2. Deposition rate vs. feed rate of CH_4, H_2 and Ar

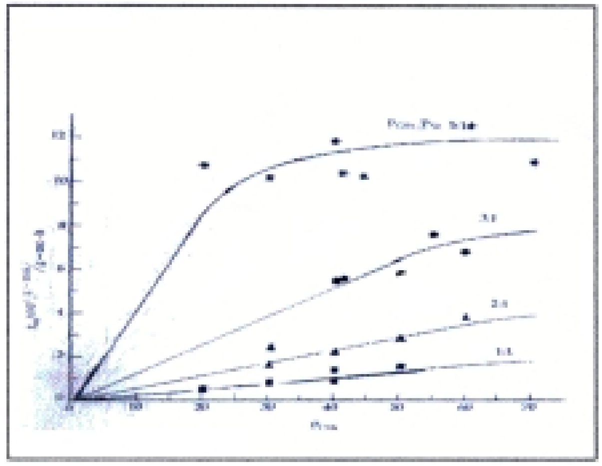

Fig 3. Deposition rate vs. partial pressure of hydrogen

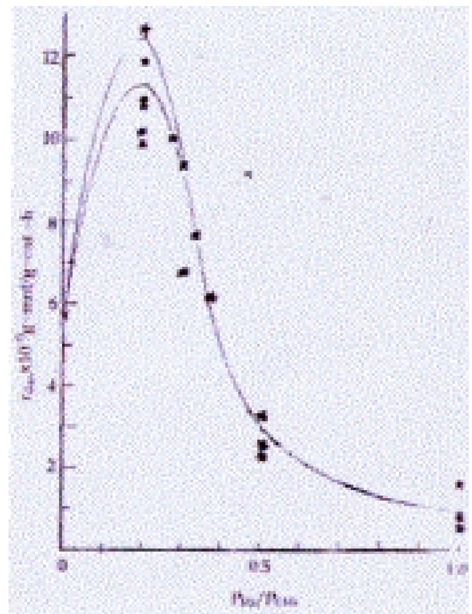

Fig 4. Deposition rate vs. P_{CH4}/P_{H2}

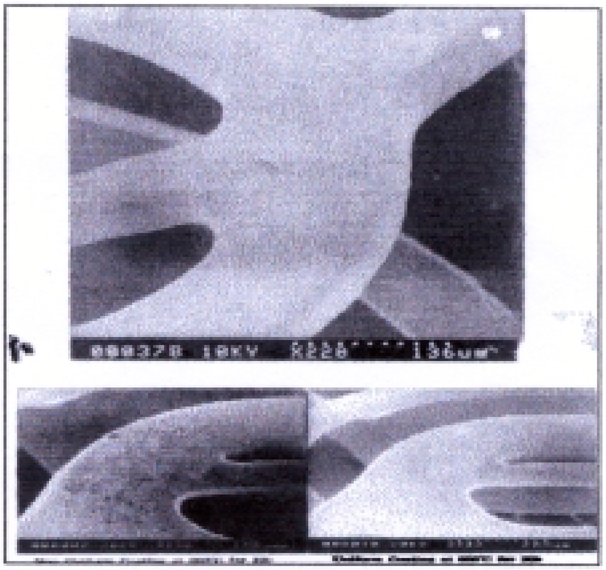

Fig 5. Stents coated with pyrolytic carbon

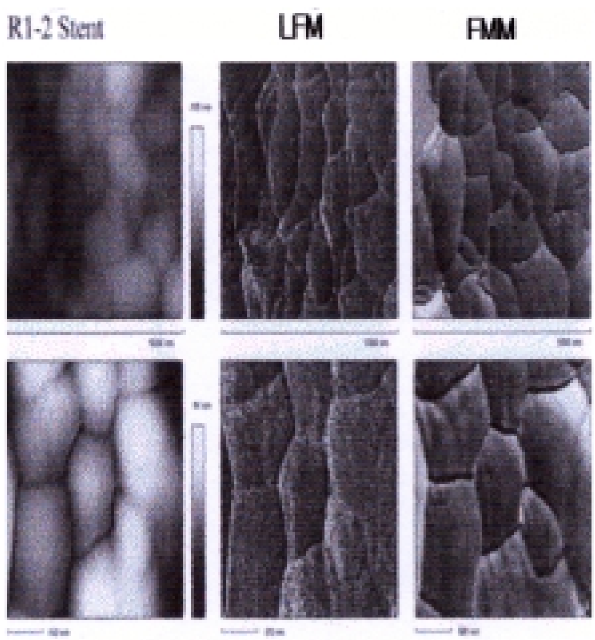

Fig 6. SEM with LFM and FMM of pyrolytic carbon coated on stents