Thermochimica Acta, 92 (1985) 137-140
Elsevier Science Publishers B.V., Amsterdam

ELECTROTHERMOGRAPHICAL STUDIES ON KINETICS OF HIGH TEMPERATURE INTERACTION BETWEEN TRANSITION METALS AND SIMPLE HYDROCARBONS

Souren L.Kharatian, Yuri S.Sardarian, Larisa S.Abovian, Hakob A.Chatilian, Institute of Chemical Physics, Armenian Academy of Sciences, Yerevan, USSR
Alexander G.Merzhanov, Institute of Chemical Physics (Branch) Academy of Sciences USSR, Chernogolovka, USSR

ABSTRACT

The kinetics of the interaction of transition metals of subgroups Ti, V and Cr with simple hydrocarbons has been studied at an interval T=1200-3000°C and P=10-100 torr. Constants of pyrolysis of methane, ethylene and acetylene on surfaces of corresponding carbide phases and on pyrographite have been measured.

INTRODUCTION

The heating of metallic samples in a medium of carbon containing gaseous compounds is an effective method for the thermochemical treatment of surfaces, at the same time, being a very convenient technic for the study of the kinetics of carbide formation at high temperatures. During this process the stage of immediate interaction of carbon with the metal is preceded by the decomposition of gas on the surface and regularities of pyrolysis, in certain cases, may determine, in general, the process of carbide formation.

Interaction of simple carbon containing gases and mixtures (CH_4, C_2H_4, C_2H_2, $CO+H_2$, CO_2+H_2 and others) with metallic surfaces is also fundamental in the process of carbide formation in carbon containing solid materials.

So far only a few works have been performed dealing with transformations of hydrocarbons on the surfaces of carbide-forming metals. Existing data deal with processes carried out at low temperatures ($T \leq 1200°C$) and are related to the stage of graphite growth on the metallic sublayer, or at very low pressures ($P \leq 10^{-2}$ torr) when the only product is the solid solution of carbon in the metal.

In this work we describe the results obtained for the kinetics of the interaction of methane, ethylene and acetylene with surfaces of hot filaments of transition metals of subgroups Ti, V and

---

Proceedings of ICTA 85, Bratislava

Cr (Ti, Zr, Nb, Ta, W, Mo) at high temperatures (T=1200-3000°C) and pressures P=10-100 torr, which are interesting from the point of view of metallic carbide formation.

MEASURING METHODS

Experiments were carried out on electrothermographic apparatus /1/ under static conditions. The thin filament (d=100 μm, l=8.4 cm) of metal was heated in a medium of hydrocarbon gas by passing a constant electrical current until the desired temperature was reached and kept constant by low-inertial optical thermoregulator.

During the experiments, electrical resistance of the filament R(t), its electrical power W(t) and increase in weight $\Delta m_c(t)$ were registered. The gas phase products were analysed chromotographically while the solid samples were analysed by means of metallographic and X-ray analysis.

RESULTS AND DISCUSSION

Fig.1 presents three typical curves showing the change in increase in weight of the metal depending on the interaction time with the hydrocarbon.

a) $Ta+CH_4$, P=100 torr: Two stages are due to methane decomposition on the carbide TaC (I stage) and pyrographite (II stage) surfaces. Increase of the pressure sharply shortens the length of stage I. When the pressure is reduced to 10 torr, pyrographite is no longer formed while the filament is completely transformed to carbide. Similar results are obtained in the following systems $Ta+C_2H_4$, $Ta+C_2H_2$, $Nb+C_2H_4$, $Nb+C_2H_2$, $Zr+C_2H_4$, $Zr+C_2H_2$, $W+C_2H_4$, $Mo+C_2H_4$ (all at pressures P=10-100 torr).

b) $Ti+C_2H_2$, P=10 torr: Due to the fact that a loose, high dispersive layer of titanium carbide is formed, the process proceeds very quickly. Increase of acetylene pressure leads to an increase of pyrolysis rate: free carbon is not formed till the filament is completely transformed to carbide (P=10-100 torr). Similar results are obtained in the following systems $Ti+CH_4$, $Ti+C_2H_4$, $Zr+CH_4$ (P=10-100 torr) and $Nb+CH_4$ (P=10 torr).

c) $W+CH_4$, P=10 torr: The 2-stage process is related to the stepwise formation of tungsten carbide W_2C (I stage) and WC (II stage). At $P \gg 50$ torr the length of stage I sharply decrease and a

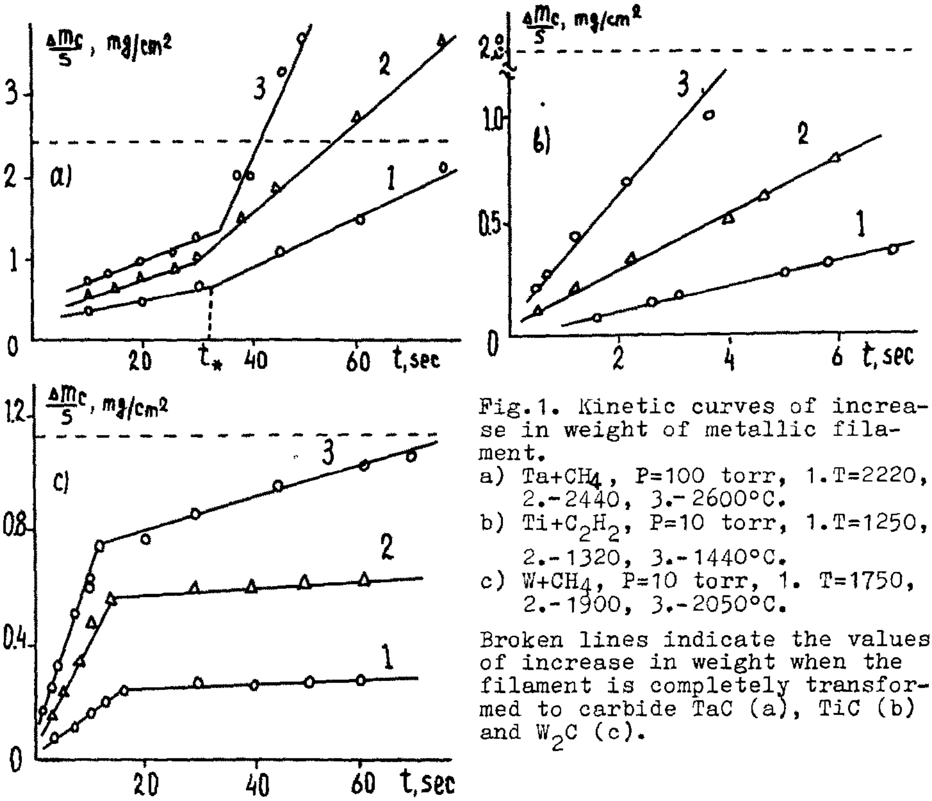

Fig.1. Kinetic curves of increase in weight of metallic filament.
a) $Ta+CH_4$, P=100 torr, 1.T=2220, 2.-2440, 3.-2600°C.
b) $Ti+C_2H_2$, P=10 torr, 1.T=1250, 2.-1320, 3.-1440°C.
c) $W+CH_4$, P=10 torr, 1. T=1750, 2.-1900, 3.-2050°C.

Broken lines indicate the values of increase in weight when the filament is completely transformed to carbide TaC (a), TiC (b) and W_2C (c).

new fast stage of free carbon formation takes place.

It follows from Fig.1 that the increase in weight of the filament on time for each stage may be expressed by the simple equation

$$\frac{\Delta m_c}{S} = Kt + b$$

where Δm_c - the increase in weight of the filament at time t, S - the lateral surface of the filament,.K - the constant of heterogeneous decomposition of gas on the surface, depending upon temperature and pressure.

In Table I the values of pyrolysis constants as a function of temperature for all systems studied are given at P=10 torr.

Experimental data for pyrolysis and also for carbide formation are explained by the theoretical results obtained /2/ for reactive diffusion under the boundary condition of II order. It has been shown that there are two limiting regimes of carbide formation: kinetic - when the rate of carbide formation is completely determined by the rate of pyrolysis of the gas on the given surface

TABLE I

Surface phases	Temperature interval, T°C	Gas	K, $g/cm^2 sec$	Characteristics of carbide layers
TiC	1130-1510	C_2H_4	$1 \cdot 10^{-3} \cdot \exp(-54000/RT)$	Porous, with longitudinal cracks
TiC	1020-1440	C_2H_2	$2.4 \cdot 10^{6} \cdot \exp(-76000/RT)$	
ZrC	1290-1650	CH_4	$2.4 \cdot 10^{-2} \cdot \exp(-60000/RT)$	
TiC	1130-1420	CH_4	$1 \cdot 10^{-3} \cdot \exp(-18200/RT)$	Compact, well coupled with base, large crystaline
ZrC	1520-1780	C_2H_4	$1.35 \cdot \exp(-40000/RT)$	
ZrC	1400-1600	C_2H_2	$3.9 \cdot 10^{-2} \cdot \exp(-32000/RT)$	
NbC	1400-2100	CH_4	$2.2 \cdot 10^{-2} \cdot \exp(-34200/RT)$	
NbC	1400-2200	C_2H_4	$7.8 \cdot 10^{-3} \cdot \exp(-26000/RT)$	
TaC	1700-3000	CH_4	$3.8 \cdot 10^{-2} \cdot \exp(-46500/RT)$	
TaC	2220-3000	C_2H_4	$7.03 \cdot \exp(-20000/RT)$	
W_2C	1400-2050	CH_4	$0.97 \cdot \exp(-45000/RT)$	Large crystaline, pores formed when thickness of carbide layer is $\geqslant 15 \mu m$
W_2C	2050-2700	CH_4	$6 \cdot 10^{3} \cdot \exp(-86000/RT)$	
WC	1300-1850	CH_4	$4.75 \cdot 10^{-4} \cdot \exp(27000/RT)$	
WC	1850-2700	CH_4	$1.5 \cdot 10^{5} \cdot \exp(-110000/RT)$	
WC	1300-1700	C_2H_4	$8.6 \cdot 10^{-2} \cdot \exp(-40000/RT)$	
MoC	1000-1600	C_2H_4	$2.5 \cdot 10^{-2} \cdot \exp(-27000/RT)$	

$(t \leqslant t_*)$; and diffusive - when on the exterior phase surface a constant concentration of carbon sets in $(t > t_*)$. At that point the heterogeneous processes occuring on the surface do not influence the rate of carbide formation.

On the basis of experimental data obtained and results of theoretical analysis /2/ we have suggested ways to intensify the process of carbide formation and determined the optimal regimes to obtain the desired carbide phase in pure form or carbide-graphite coatings with definite relationships of film thicknesses.

REFERENCES

1. A.G.Merzhanov, Yu.M.Grigorjev, S.L.Kharatian, L.B.Mashkinov, J.S.Vardanian, Fiz.Goreniya i Vzryva, No 4 (1975) 563.
2. S.L.Kharatian, A.B.Harutiunian, A.G.Merzhanov, Dokl.Akad.Nauk SSSR 266 (1982) 665.