Journal of Engineering Physics and Thermophysics, Vol. 65, No. 4, 1993

SOME KINETIC LAWS AND THE MECHANISM OF CARBONIZATION IN THE HIGH-TEMPERATURE SYNTHESIS OF CARBIDES OF TRANSITION METALS

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UDC 541.127-546.261-883.26

Results of investigations of the kinetic laws and the mechanism of carbonizing Ti, Zr, Nb, Ta, Mo, and W over a wide temperature range and for different schemes of metal-carbon interaction (Me+carbon-containing gas, Me+graphite) are given. Much attention has also been given to establishing the interrelation between the microstructure of carbide phases and the kinetics and mechanism of their formation.

SHS of carbides of transition metals occurs over a wide temperature range, and therefore realization of different regimes and interaction schemes is possible. From this viewpoint it is of interest to study the kinetic laws and the mechanism of high-temperature carbonization of metals in different media.

The investigations were carried out on an electrothermographic setup [1] in the isothermal heating regime and for reaction times under 1 min. Model systems of metallic thread+carbon-containing gas (mainly methane and in a number of cases ethylene and acetylene) served as the object of investigation. Threads of the investigated metals 100-150 μm in diameter and 8.5 cm long were used. The specimens were heated by passing an electric current in the carbon-containing medium. The kinetics of the process was kept track of by the increase in the specimen weight and by the growth of the carbide layers. The microstructure of the zone of the interaction products and the morphology of the specimen surface were investigated using a scanning electron microscope (SEM).

The temperature range of the investigations was T = 1100-1500°C (Ti), 1000-1800°C (Zr), 1400-2200°C (Nb), 1400-2800°C (Ta), 1300-2700°C (W), 1400-2200°C (Mo). The gas pressure was varied from 2.0 to 600 torr.

The chosen scheme of organizing the experiment permitted the study of the macrokinetic laws of the process both with direct contact of the metal with the gaseous medium (usually low pressures) and with preliminary application of a compact carbon layer, i.e., pyrocarbon, on the metal surface. In the second case the process of metal carbonization proceeds by the solid + solid mechanism.

Tantalum and Niobium. In heating of tantalum and niobium threads in a hydrocarbon medium a diffusion zone forms, consisting of two carbide layers Me_2C and MeC practically from the outset of the process ($t \geq 0.05$ sec). The carbide layers formed are compact and macrocrystalline (Fig. 1a).

It is established that depending on the pressure (and to a lesser extent on the temperature) three different kinetic regimes of carbonizing Nb and Ta in methane are realized. At $P_{CH_4} < 15-30$ torr no release of free carbon on the surface of the threads occurs until they are completely carbonized: the interaction of tantalum and niobium with carbon proceeds by the solid + gas mechanism, the carbonization rate not depending on the methane pressure. The growth of the carbide layers (as well as the rate of methane pyrolysis on the TaC and NbC surface) is described by a kinetic equation of parabolic type, i.e., the diffusion regime of carbonization is realized.

In the region $P_{CH_4} \geq 200-300$ torr the thread surface is covered with a solid layer of pyrocarbon practically from the outset of the process, and direct access of methane molecules to the metal (carbide) surface ceases. Carbonization proceeeds by the solid + solid mechanism, in which the rate of the process depends on neither the composition nor the gaseous phase pressure. The carbonization rate substantially decreases (3-20 times) in this case as compared to the interaction by the solid + gas mechanism. This results in violation of the parabolic law of

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Institute of Chemical Physics, Academy of Sciences of the Republic of Armenia, Erevan. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 4, pp. 423-427, October, 1993.

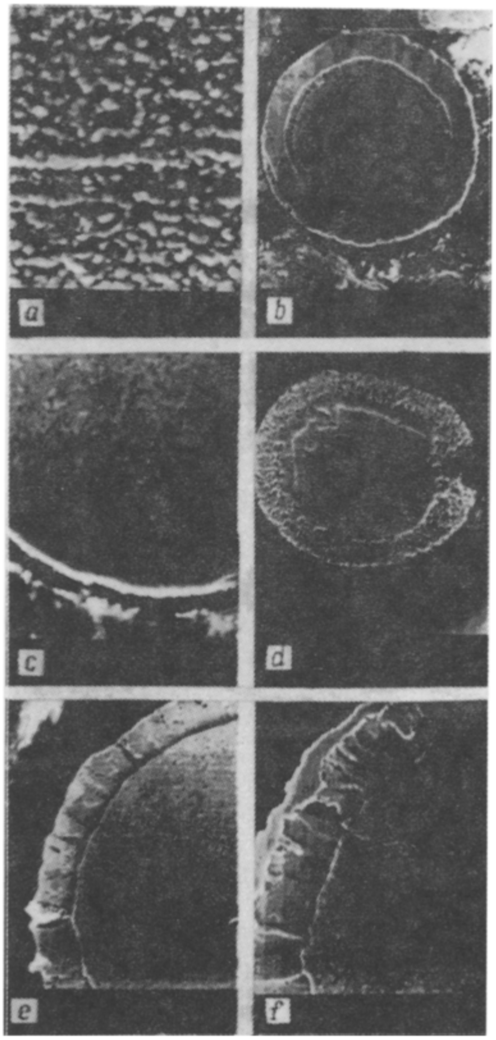

Fig. 1. SEM-microphotographs of the carbide microstructures in the interaction of metal threads with methane (a - surface, b, c, d, e, f - cross section of the threads): a) Ti+CH_4 , T = 1460°C, P_{CH_4} = 100 torr, t = 1.2 sec, ×5000; b) Ta+CH_4 = 10 torr, t = 5.0 min, x12)); c) Ti+CH_4, T = 1460°C, P_{CH_4} = 10 torr, t = 1.0 min, x300; d) Zr+CH_4, T = 1600 °C, P_{CH_4} = 100 torrm t = 2.0 min, ×800; e) W+CH_4, T = 2050°C, P_{CH_4} = 10 torr, t = 7.0 sec, ×3000; f) W+CH_4, T = 2050°C, P_{CH_4} = 10 torr, t = 20 sec, ×4000.

carbonization and the kinetics of the process is described by a nearly linear equation. With increasing temperature the gap in the rates of carbonization by the two mechanisms indicated decreases.

In the region P_{CH_4} = 30–200 torr the interaction proceeds in two stages.

Titanium and Zirconium. A characteristic feature of the interaction of titanium and zirconium with light hydrocarbons is the fact that, depending on the conditions of the process, realization of two different mechanisms of carbonization and, correspondingly, formation of two types of carbide layer microstructure are possible: a compact macrocrystalline microstructure or a porous finely dispersed one. Furthermore, in the titanium-methane interaction unlike the process of carbonization of zirconium (as well as Ta, Nb, and W under the identical conditions) there is no release of free carbon on the specimen surface until the threads are completely carbonized and the methane pressure is 600 torr.

As a result in the P-T region of the zirconium-methane interaction three characteristic regions and correspondingly three carbonization regimes are distinguished, and in the titanium-methane interaction - two regimes.

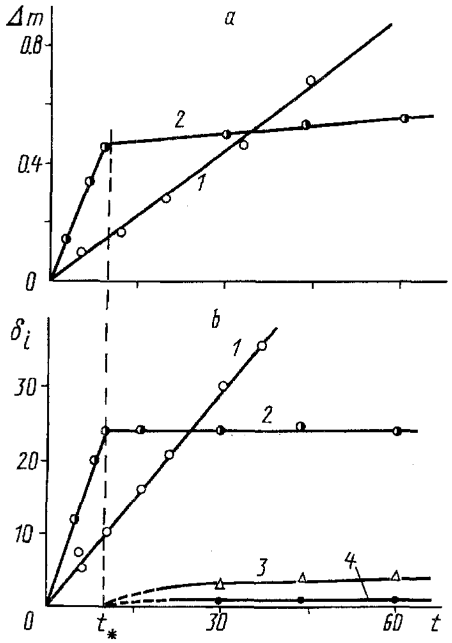

Fig. 2. Kinetic curves of the increase in weight (a) and the growth of carbide (porous and compact) layers and pyrographite (b) in carbonization of Zn in methane. T = 1600°C, $P_{CH_4} = 10$ (curves 1) and 100 torr (curves 2, 3, 4); b) 1, 2) thickness of the porous Zr carbide layer, 3) of the compact layer, 4) of the pyrographite. Δm, mg; δi, μm; t, sec.

In the titanium-methane interaction in the pressure region $P_{CH_4} < 20-30$ torr a compact macrocrystalline layer of titanium carbide forms (Fig. 1b) and at $P_{CH_4} > 20-30$ torr a porous layer with a finely dispersed structure forms (Fig. 1c). The interaction in both cases proceeds in one stage with a constant rate, in the second case much (by 1-2 orders) more rapidly than in the first one.

In the case of the zirconium-methane interaction in the pressure region $P_{CH_4} < 20-30$ torr a porous layer of zirconium carbide with a finely dispersed structure forms; the mechanism and laws of the process are similar to those of the titanium-methane interaction at $P_{CH_4} > 20-30$ torr.

With increase in pressure above 20-30 torr the zirconium-methane interaction proceeds in two stages, the first stage being similar to the process at low methane pressures and resulting in the formation of a finely dispersed carbide structure. However, at a certain stage of the process the surface of the porous carbide skeleton is blocked by a deposited layer of pyrocarbon and the direct access of methane to the metal surface ceases. The subsequent interaction proceeds by the solid + solid mechanism. The carbide zone becomes two-layer - a second compact carbide layer appears between the porous layer and the metal core (Fig. 1d). It is worth noting that the growth rate for the compact carbide layer is greatly exceeded by the growth rate for the porous carbide layer in the first stage of the process, the porous layer growth practically ceasing as the compact component appears.

As is evident from Fig. 2, both methane pyrolysis and carbide layer growth are described by a kinetic equation of linear type within each stage.

In the region $P_{CH_4} > 300$ torr the zirconium-methane interaction is accompanied by accumulation of free carbon on the specimen surface practically from the outset of the process and only a compact layer of zirconium carbide forms. Carbonization proceeds by the solid + solid mechanism and the laws of the process are similar to those of carbonizing Ta and Nb in the same range of methane pressures.

Tungsten and Molybdenum. The interaction of W and Mo with light hydrocarbons is characterized, depending on the saturation conditions (pressure and type of the gas, temperature), by successive or simultaneous formation of a diffusion zone consisting of two compact macrocrystalline carbide layers of Me_2C and MeC. For example, in the pressure range $P_{CH_4} = 5-50$ torr there is successive formation of the carbide phases W_2C and WC (Fig. 1e and f). At lower pressures only the W_2C phase forms, and at $P_{CH_4} \geq 50$ torr, on the one hand, practically simultaneous appearance of W_2C and WC carbide layers is observed and, on the other hand, on the thread surface a pyrocarbon layer forms, which is the basic product of methane pyrolysis at $P_{CH_4} \geq 600$ torr.

A change in the methane pressure affects the methane pyrolysis rate on W_2C and WC in different ways. For example, whereas an increase in the methane pressure from 2 to 50 torr leads to a considerable increase (5-25 times) in its pyrolysis rate on W_2C, it is by no means dependent on pressure at all (at $P = 5\text{-}100$ torr) on the WC phase surface. As a result of this the average rate of carbonization as a function of the methane pressure has a maximum whose position depends on temperature and lies in the range $P_{CH_4} = 5-15$ torr.

In the interaction of tungsten threads with pyrocarbon, carbonization, similarly to the case of Ta and Nb carbonization, proceeds at a rate 1-2 orders of magnitude smaller than with carbon supply from the gaseous phase.

The molybdenum-methane interaction, being some analog of the process of tungsten-methane interaction, is more diverse from the viewpoint of realization of different kinetic laws of interaction. An important feature of the interaction of Mo with light hydrocarbons is the absence of free carbon release on the thread surface until the methane, ethylene, and acetylene pressure is 100-300 torr. Only at $P_{CH_4} \geq 300$ torr or $P_{C_2H_4}$ and $P_{C_2H_2} \geq 100$ torr is the release of separate islands of pyrocarbon observed on the thread surface basically at places of fracture formation. As a result of this, a parabolic law is realized for carbide layer growth and pyrolysis in a number of cases. Along with this, according to the phase diagram for Mo-C, at $T < 1650^\circ C$ formation of just one carbide phase Mo_2C is possible in this system, and at $T > 1650^\circ C$ Mo_2C and MoC_{1-x} are formed, which is actually realized in the experiments.

In summary we can note the following:

1. In carbonization of transition metals under the conditions of a limited rate of carbon supply to the contact surface a variety of carbonization mechanisms and, correspondingly, different kinetic laws can be realized. Along with this the formation of different types of carbide layer microstructures is found and their interrelation with the laws and mechanism of carbonization is established.

2. Carbonization of the indicated metals from the gaseous phase proceeds much (by 1-2 orders) more rapidly than from the solid phase (soot, graphite). In formation of porous carbide layers of titanium and zirconium carbidization proceeds with abnormally high rates.

3. Thermodynamic equilibrium on the metal-gaseous medium interface and more so on the metal-graphite interface is not always and not at once established. Therefore, parabolic laws of carbide phase growth are realized only in some cases, and the phases often appear successively and grow according to a linear law.

On the basis of direct kinetic measurements of the carbonization rate and investigations of the combustion regimes it may be concluded that impurity gases play a significant part in realizing one or another mechanism of carbonization of Ta, Nb, Ti, and Zr, which in turn has an effect both on the carbide phase microstructure and the combustion limits and on the basic characteristics of combustion. For example, in carbonization of titanium in the regime of combustion and realization of the Me+solid carbon mechanism the lower limit of the combustion temperature is $1900^\circ C$ (min.C/Me = 0.4), and when the Me+gas mechanism is realized it is $900^\circ C$ (min.C/Me = 0.1).

On the other hand, comparison of the obtained data on growth rates for tantalum and niobium carbide layers with the temperature-time characteristics of the combustion process for powders of tantalum with soot and niobium with soot and the real dimensions ($\mu < 15\ \mu m$) and shape of the particles used in the combustion of the tantalum and niobium powders permit the assumption that the mechanism of reaction diffusion may ensure the transformation rates that occur in the SHS wave of tantalum and niobium carbide.

NOTATION

P_{CH_4}, methane pressure; T, temperature; t, time; μ, particle dimension.

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