COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 25 ANNÉE 1979

Carburizing of Type 1.4988 Steel with Uranium Carbide

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Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Carburizing of Type 1.4988 Steel with Uranium Carbide*

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(Received 22 January 1979, accepted 15 February 1979)

ABSTRACT

In this study, carburizing of the austenitic steel of type 1.4988 by using uranium carbide has been investigated. For the annealing process, uranium carbide containing 5 % C brought in contact with the steel specimens by sodium in argon atmosphere. The anneling temperatures were 773, 873, 973 and 1073 K. The annealing period was 1000 h. Diffusion of carbon in the steel has been investigated kinetically and thermodynamically during the carburizing based on only the measurements of the hardness gradients in the steel. The diffusion distance and the diffusion coefficient vere determined. It was assumed that the diffusion process takes place on the activated complex and the diffusion coefficient is equal to the rate constant of the reaction. Equilibrium constant, free enthalpy, enthalpy and entropy changes for the chemical equilibria between the reactants and the activated complex were calculated. The temperature dependencies of thermodynamic quantities, given above, were obtained.

INTRODUCTION

The mixture of uranium carbide and plutonium carbide was proposed to become a nuclear fuel in the future by some research workers[1,2,3]. The corrosion of the steel, used as cladding material, with uranium carbide has been investigated in order to prove the validity of this idea. The steel with uranium carbide was shrinked, because of the carburizing at the working temperature of the reactor. The changes of mechanical properties of the steel such as 0.2 % yield strength, tensile strenght, percent elongation and hardness due to carburizing, were determined experimentally[4,5,6]. The kinetics of the carburizing of the stainless steel was usually investigated by using ^{14}C isotope[7,8]. In this study, based only on the microhardness measu-

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* The experiments in this research have been made in Karlsruhe Nuclear Research Center in West Germany.

rements, diffusion of carbon in 1.4988 type steel has been investigated kinetically and thermodynamically.

THEORETICAL

If there are concentration gradients of impurity atoms in a solid, there will be a flux of these through the solid. This flux of atoms in a solid is called diffusion. For this one-dimensional problem, the concentration C is given as number of atoms per unit length. The concentration of atoms at any time t is a function of only diffusion distance x. When diffusion occurs in the x-direction only, first and second Fick's Law of Diffusion[9] may be defined respectivey as follows:

$$J = -D\left(\frac{\partial C}{\partial x}\right)_t \tag{1}$$

$$\left(\frac{\partial C}{\partial t}\right)_x = D\left(\frac{\partial^2 C}{\partial x^2}\right)_t \tag{2}$$

Here J is the diffusion flux across unit area normal to the x-direction, $(\partial C/\partial x)$, is the concentration gradient at a fixed time t, D is the diffusion coefficient, and $(\partial C/\partial t)_x$ is the rate of change of concentration with time at a fixed distance x. The minus sign in the first Fick's Law means that diffusion occurs away from regions of high concentration.

The partial differential equation (2) is the second-order, linear, and homogenous. It is of the parabolic type and the solution is done by using boundary and initial conditions. It can be shown that the appropriate solution[10] of the equation (2) is

$$\frac{C - C_0}{C_s - C} = \frac{1}{2\pi(Dt)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{3}$$

where C is the concentration at a distance x below the surface after diffusion, occurred at any time t; C_s is the surface concentration, and C_0 is the initial concentration in the solid.

The mean square distance $\overline{x^2}$, that represents the average sum of the square of the individual jumps at time t, has been obtained from the definition of mean value theorem as follows

$$\overline{x^2} = 2Dt.$$

Let us assume that, the diffusion in a solid proceeds in the same way as a chemical reaction which is occurred according to the activated-complex theory. The reaction rate is assumed to be equal to the time independent diffusion coefficient at constant temperature. Therefore, the diffusion related to the absolute temperature is given by

$$D = D_o \exp\left(-\frac{E_a}{RT}\right), \quad (5)$$

where D_o is called the frequency factor; E_a is the activation energy, and R is the gas constant.

According to the theory of absolute reaction rates, the reactants are in equilibrium with the activated complex. The equilibrium constant for the formation of complex is shown by $K^{\neq}$. The diffusion coefficient and the relation with the equilibrium constant can be given as follows. [11,12,13]

$$D = \frac{k_B T}{h} \frac{Q^{\neq}}{\prod_r Q_r} \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

$$D = \frac{k_B T}{h} K^{\neq}. \quad (7)$$

Here k_B is Boltzmann constant, h is Planck constant, T is the absolute temparature, $Q^{\neq}$ and Q_r are the partition functions of activated complex and the reactants respectively. According to the chemical thermodynamics, free enthalpy of activation $\Delta G^{\neq}$ can be defined by the following equation,

$$\Delta G^{\neq} = -RT \ln K^{\neq}. \quad (8)$$

After taking logarithms and differentiating of the equation (7) and then by using Arrhenius and van't Hoff equations, the relation between the activation energy E_a and the enthalpy of activation $\Delta H^{\neq}$ can be expressed as follows,

$$\frac{d \ln D}{dT} = \frac{1}{T} + \frac{d \ln K^{\neq}}{dT}$$

$$\frac{E_a}{RT^2} = \frac{1}{T} + \frac{\Delta H^{\neq}}{RT^2}$$

$$E_a = \Delta H^{\neq} + RT.$$

The entropy of activation $\Delta S^{\neq}$ can be calculated by the following equation

$$\Delta S^{\neq} = (\Delta H^{\neq} - \Delta G^{\neq}) / T. \qquad (10)$$

EXPERIMENTAL

The austenitic steel of type 1.4988 is chosen as a sample for carburizing and analyzed chemically and found as 65. 9 % Fe, 16.1 % Cr, 13. 6 % Ni, 1. 28 Mo, 1.1 % Mn, 0.8 87 % (Ta+Nb), 0.7%V, 0.27 % Si, 0.08%C, traces P, S and N. Uranium carbide powder contained 4% C is chosen as a carburizing material.

The steel was obtained commercially in sheet-form with nominal thickness of 1 mm and carburizing test specimens with a gauge length of 20 mm and width of 5 mm, were die-pressed from this steel. These specimens have been annealed for homogenization in vacuum c.a. 10^{-4} mm Hg for 30 min at 1323 K. During the homogenization, the concentration gradients present in steel were dissappeared. For annealing experiment four specimens were placed into each capsule at the same distance.[5] The uranium carbide powder was then vibrated into the steel capsules until the specimens were covered under argon atmosphere in a glove-box. The final density of the uranium carbide powder was found in the capsules only 65 % of the theretical density. A liquid sodium was added in the capsules to obtain a uniform heat transfer. The capsules were tightly closed then taken out from the glove-box into a desiccator. The capsules were then placed in quartz tubes and evacuated to 10^{-4} mm Hg, then sealed off. The quartz tubes were annealed in the muffle furnaces at 773, 873, 973 and 1073 K respectively for 1000 h.

After completion of the annealing treatments in uranium carbide the capsules were cooled and opened at an argon atmosphere. By dissolving sodium with methanol the carburized steel specimens were taken out and washed with water, aceton and methanol in a shaking container.

The specimens were covered with plastic at high pressure and temperature to handle it easily. The surface of the steel must be cleaned carefully in order to see the structure under microscope and measure the microhardness. A mirror polish was produced on one face perpendicular to the carburized surface of the specimen by grinding on an abrasive wheel, polishing on successively finer emery papers, and lapping on revolving cloth-covered wheels with fine abrasives. To dissolve thin oxide layer and reveal the structural details this polished surface was etched with electrolysis.

On the perpendicular direction of carburized surface the Vickers microhardness was measured at certain distances by using Leitz Durimet machine.

RESULTS and DISSUSSION

In Fig. 1 the 250 times enlarged traces of diamond pyramid of Leitz Durimet machine were shown. Depending on the intensity of carburizing and annealing temperature microhardness decrease from the surface to the inside of the specimens are given after 1000 h in contact with uranium carbide at four different temperatures.

The hardness gradients due to concentration gradients of carbon in carburized steel are shown in Fig. 1. The curves in Fig. 2 were analyzed to fit the equation (3) by using hardness instead of concentration. Let us assume that H is the hardness at a distance x below the surface after diffusion has occurred for the time t, H_s is the surface hardness, and H_0 is the initial hardness in the steel. If $(H-H_0) / (H_s-H_0)$ is taken instead of $(C-C_0) / (C_s-C_0)$ in equation (3); $\log (H-H_0) = f(x^2)$ were plotted at four different temperatures and the straight lines were obtained as shown in Fig. 3. This result shows that the curves in Fig. 2 and equation (3) are in good agreement.

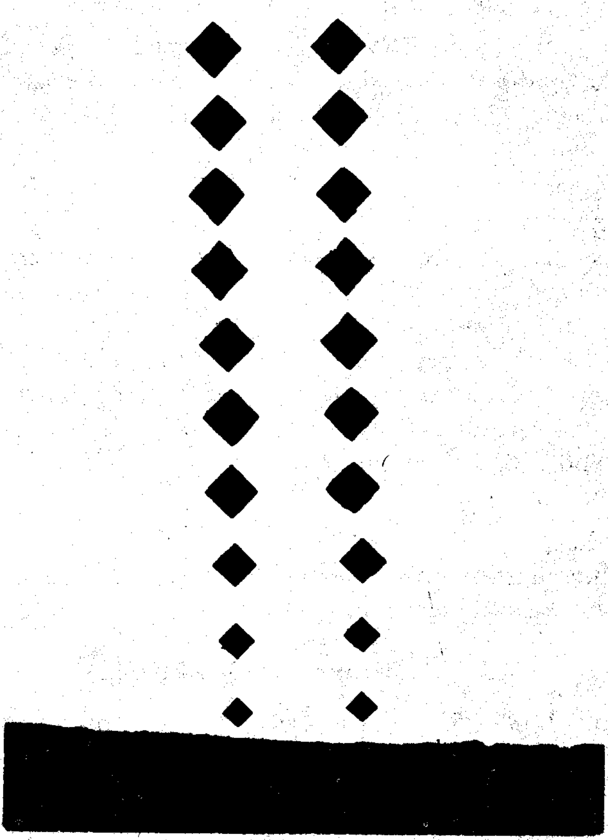

Fig. 1. Traces of diamond pyramid on polished steel face

The diffusion time is taken constant as 1000 h and the slope of the straight lines equal to -1 /4Dt, the diffusion coefficients have been calculated. Using these diffusion coefficients, the mean square distances $\overline{x^2}$, in time 1000 h, have been calculated with the equation (4) at four different temperatures. In addition, maximum diffusion distances x can be obtained from Fig. 2 when the hardness gradients was zero. These results were shown in Table 1.

The values in Table 1 were plotted in Fig. 4 and Fig. 5. Applying the method of reduction to a straight line, the equations of the curves which is parabolic as shown in Fig. 4 and can be expressed as follows

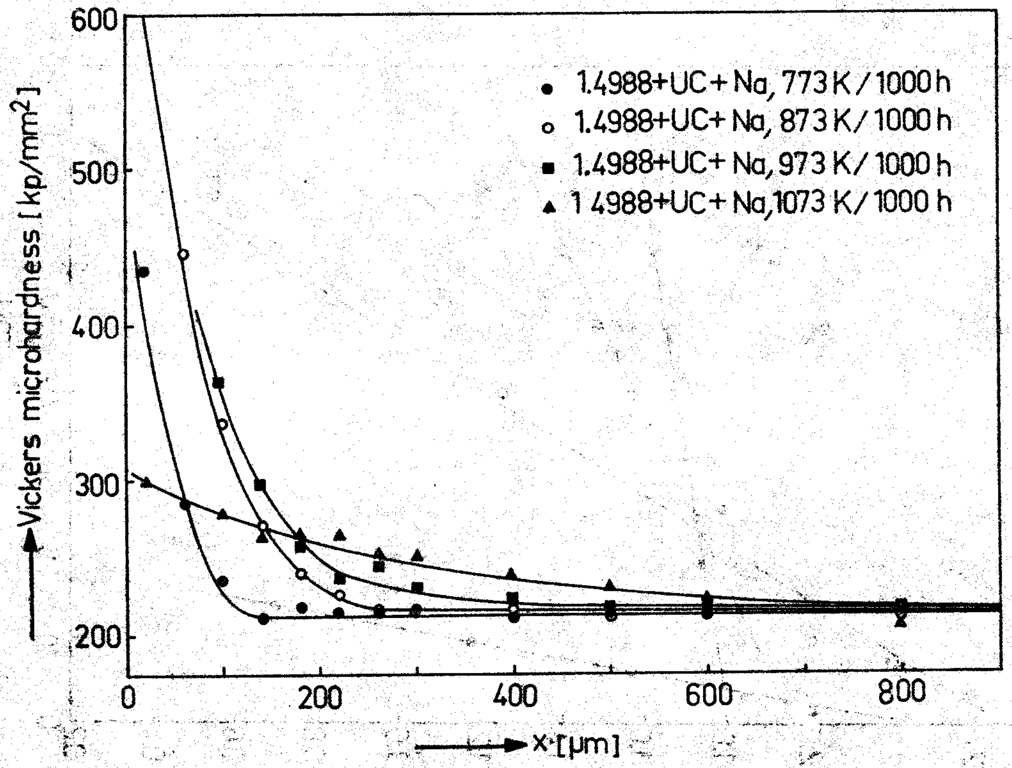

Fig. 2. Microhardness gradients in carburized steel 1.4988

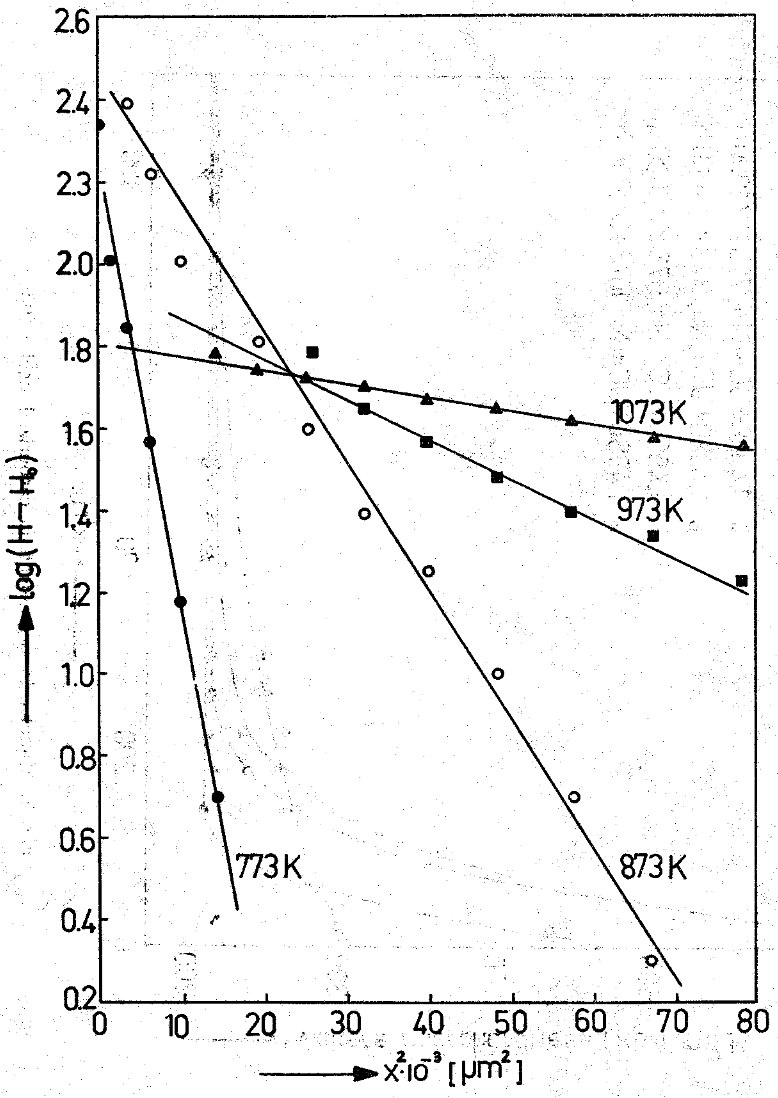

Fig. 3. log $(H\text{-}H_0) = f(x^2)$ straight lines.

Table 1. The values of D, $\overline{(x^2)}^{1/2}$ and x at four different temperatures

T [K]	D [$\mu m^2 h^{-2}$]	$\overline{(x^2)}^{1/2}$ [μm]	x [μm]
773	0.99	44	120
873	3.46	83	250
973	11.38	151	420
1073	32.30	257	640

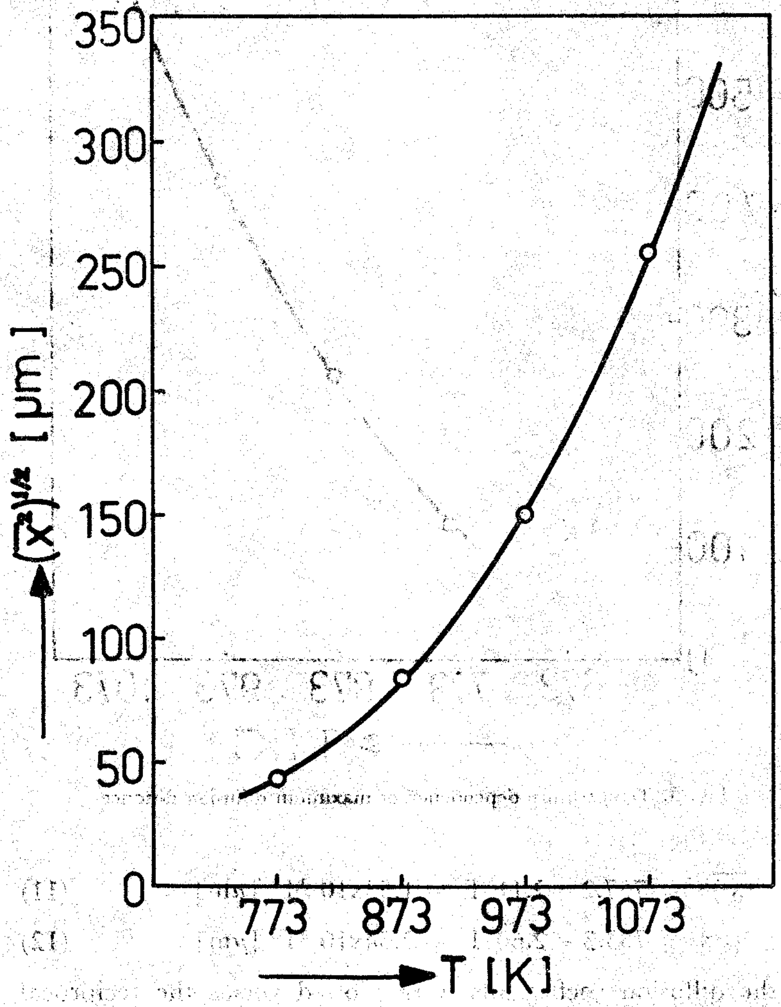

Fig. 4. Temperature dependency of the mean square distance

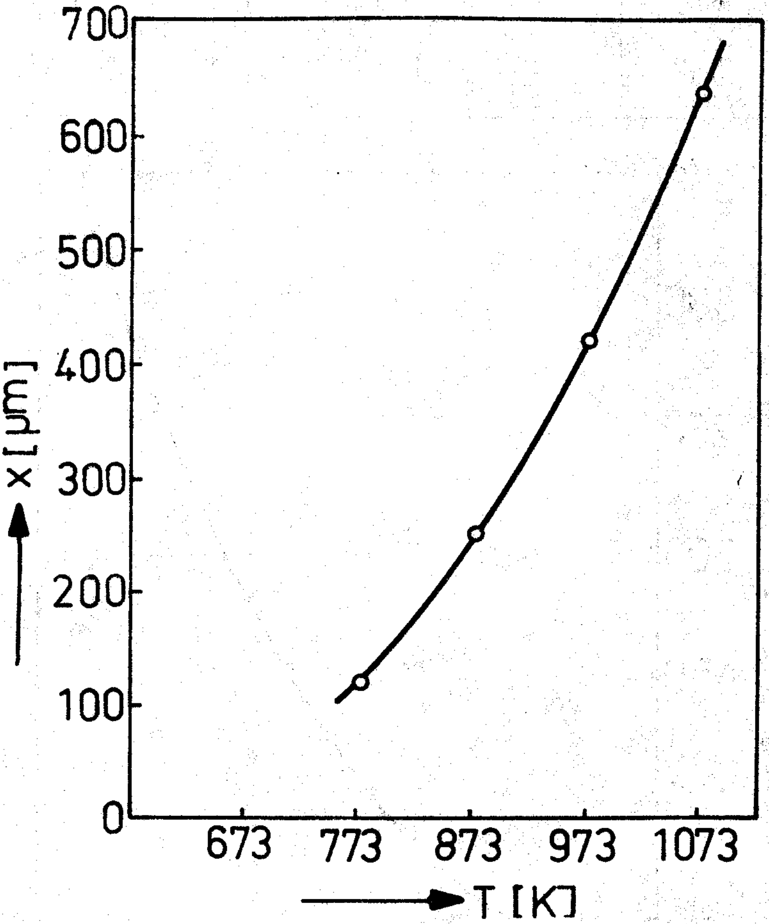

Fig. 5. Temperature dependency of maximum diffusion distance

$$(\overline{x^2})^{1/2} = 757.2 - 2.11\ T + 1.53 \times 10^{-3} T^2\ [\mu m] \qquad (11)$$

$$x = 753.3 - 2.60\ T + 2.34 \times 10^{-3} T^2\ [\mu m] \qquad (12)$$

If the diffusion coefficients were plotted versus the reciprocal of the temperatures; straight line with a negative slope was obtained as shown in Fig. 6. From the slope of this straight line

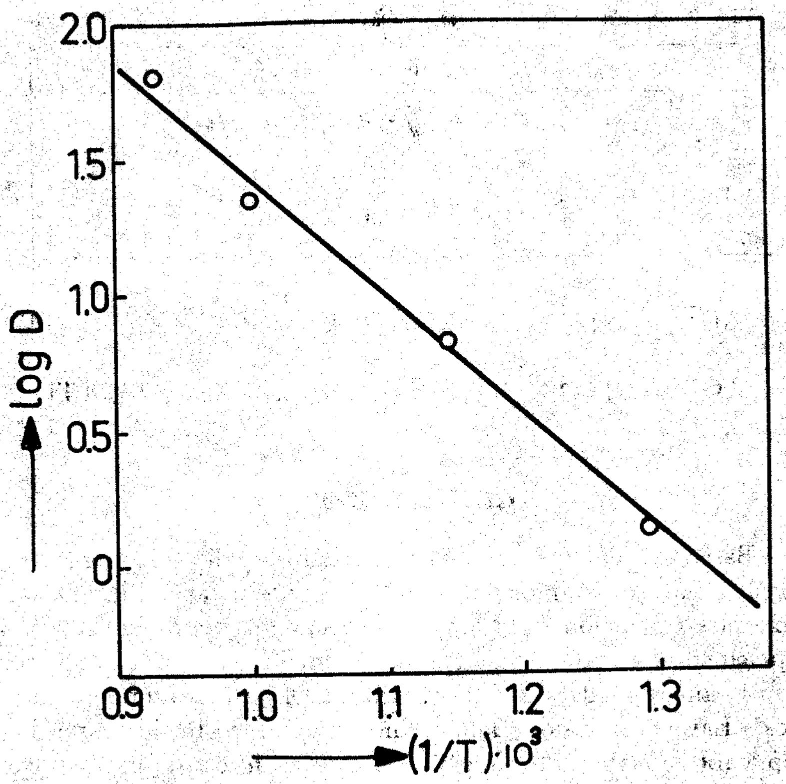

Fig. 6. Temperatura dependency of diffusion coefficient.

activation energy of diffusion was found as $E_a = 82400$ J mol^{-1}. Using the same figure the frequency factor was calculated as $D_0 = 5.47 \times 10^3$ μm^{2}h^{-1}= 1.52×10^{-11}cm^{2}s^{-1}. If these values were inserted in to equation (5) the temperature dependency of the diffusion coefficient was found as equation below

$$D = 1.52 \times 10^{11} \exp\left(-\frac{82400}{RT}\right) [\mathrm{cm^2 s^{-1}}] \tag{13}$$

Using the diffusion coefficients and the equations (6), (7), (8) and (9) thermodynamical properties were calculated at four different temperatures as shown in Table 2.

Temperature dependency of the enthalpy and the free enthalpy of activation have been drived by using the values in Table 2,

Table 2. Some thermodynamical properties for carburizing of steel 1.4988

<table>
<tr><td colspan="6">E_a=82400 J mol^{-1}, k_B = $1.38x10^{-23}JK^{-1}molekül^{-1}$, h=$6.62x10^{-34}Js$</td></tr>
<tr><th>T [K]</th><th>D[cm^2s^{-1}] $x10^{12}$</th><th>$K^{\neq}x10^{25}$</th><th>$\Delta G^{\neq}$ [kJ]</th><th>$\Delta H^{\neq}$ [kJ]</th><th>$\Delta S^{\neq}$ [JK^{-1}]</th></tr>
<tr><td>773</td><td>2.7</td><td>1.7</td><td>357.2</td><td>76.3</td><td>— 365</td></tr>
<tr><td>873</td><td>9.6</td><td>5.3</td><td>405.4</td><td>75.1</td><td>— 378</td></tr>
<tr><td>973</td><td>31.6</td><td>15.6</td><td>443.1</td><td>74.3</td><td>— 379</td></tr>
<tr><td>1073</td><td>89.6</td><td>40.1</td><td>480.2</td><td>73.5</td><td>— 379</td></tr>
</table>

$$\Delta H^{\neq} = 91442 - 27.25\,T + 9.86x10^{-3}T^2[J] \qquad (14)$$

$$\Delta G^{\neq} = 91442 + 27.25\,T\ln T - 9.86x10^{-3}T^2 + 148.8\,T[J] \qquad (15)$$

CONCLUSION

Based on the measurement of hardness, this investigation reveals that some information about kinetics and thermodydynamics of carbon diffusion in steel can be obtained. It was experimentally shown that the hardness of steel due to carbon atoms can be used as the concentration of carbon atoms in the Fick's Laws of diffusion. The method mentioned in this paper is applicable to the diffusion processes which cause hardening of metals.

It was assumed that the carbon diffusion in steel proceeds via an activated complex and the diffusion coefficient is equal to the reaction rate constant. In accordance with these assumptions, the thermodynamical properties of the equilibrium between reactants and activated complex can be predicted and the activation energy of diffusion can possibly be calculated.

The positive value for the free enthalpy of activation suggests that the activated complex can not be formed spontaneously at working temperatures. The high negative value for the entropy of activation implies that the activated complex formed contains great number of atoms. Because of the bonding among these atoms in the activated complex the total degrees of freedom decreases. Since the entropy of activation does not change notable with temperature, the degree of freedom for the vibration of activated complex is considered as independent of temperature.

ÖZET

Bu çalışmada 1. 4988 tipinde paslanmaz çeliğin uranyum karbür ile karbürleşmesi incelenmiştir. Kızdırma için % 5 C içeren uranyum karbür sodyum yanında ve argon atmosferinde çelik örneklerle temasa getirilmiştir. Kızdırma sıcaklıkları 773, 873, 973 ve 1073 K'dir. Kızdırma süresi 1000 saat'tir. Yalnızca karbürleşmeden doğan sertlik grantyentleri ölçülerek karbonun çelik içindeki yayılması kinetik ve termodinamik olarak incelenmiştir. Yayılmanın bir etkinleşmiş kompleks üzerinden yürüdüğü ve yayılma katsayısının tepkime hız sabitine eşit olduğu varsayılmıştır. Tepkimeye giren maddelerle etkinleşmiş kompleks arasındaki kimyasal dengenin; denge sabiti ile serbest entalpi, entalpi ve entropi değişimleri hesaplanmıştır. Yukarıda adı geçen termodinamik büyüklüklerin sıcaklığa bağlılığı belirlenmiştir.

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Prix de l'abonnement annuel

Turquie : 15 TL; Étranger: 30 TL.

Prix de ce numéro : 5 TL (pour la vente en Turquie).

Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi, Ankara - 1979