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High temperature activation energy for plastic deformation of titanium carbide single crystals as a function of the C : Ti atom ratio

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By applying the theoretical model of Mohamed and Langdon [1] the activation energy for high temperature plastic deformation of TiC_x single crystals as a function of C : Ti atom ratios is obtained. It is found that the values for the activation energy at the critical resolved shear stress are lower than the lattice self-diffusion data for carbon, except for $x = 0.75$. At this concentration a peak in the activation energy, 560 KJ, mol^{-1}, which is about 75% of that for lattice self-diffusion of Ti in TiC, appears. This situation is due to an ordering hardening caused by a contraction of the "window", formed by titanium atoms, through which the carbon atom diffuses. It is concluded that the x-dependence of the activation energy can be understood by considering that during deformation the diffusion processes of carbon and titanium atoms are coupled.

1. Introduction

Titanium carbide, TiC_x, which belongs to group IVa of the transition monocarbides, has an extremely high melting point (3340 K). This material is expected to have a large specific strength because it has a high temperature strength combined with the lowest density amongst the transition metal carbides ($4.9\ g\,cm^{-3}$) [2, 3]. In addition several properties of single crystal titanium carbide make its use as a substrate for nucleation and growth of β-SiC epitaxial layers potentially advantageous [4, 5]. These advantages are due to its crystal structure, lattice parameter, thermal expansion coefficient, and chemical stability [6–8]. In both cases improvements in the knowledge about the mechanical properties of TiC_x single crystals creates the possibility of producing better materials for structural or substrate applications.

Titanium carbide has a rock salt crystal structure which can exist as a single phase, over an extraordinarily wide range of C : Ti atom ratios, x, ranging from 0.5 to 1.0 [9]. Dislocations in the NaCl-structured transition-metal carbides have been compared to dislocations in f.c.c. metals because the major slip systems in both structures at high temperature is along $\{1\,1\,1\}$ planes in the $\langle 1\,\bar{1}\,0\rangle$ direction [10]. This situation is reasonable if the structure is considered as two interpenetrating f.c.c. lattices of titanium and carbon, with the octahedral interstice in the f.c.c. Ti lattice just large enough to accommodate a carbon atom and the Ti lattice being only about 2% from being close-packed, whereas the carbon atoms are widely separated [9]. According to Allison *et al.* [11] the presence of interstitial carbon atoms in the octahedral sites of the f.c.c. sublattice of the transition metal in the case of the carbides complicates the analysis of dislocation behaviour.

A considerable number of investigations on the high temperature mechanical behaviour of titanium carbide have been reported [2, 3, 9, 12–15]. However the high temperature activation energy for the yield or the critical resolved shear stress as a function of the whole allowed range of C : Ti atom ratios has not been previously determined.

In the present study, extensive experimental data on the mechanical properties of TiC_x are analysed using theoretical considerations due to Mohamed and Langdon [1] in order to obtain the x-dependence of the activation energy for the high temperature deformation of TiC_x, at the yielding point or the critical resolved shear stress.

2. The activation energy for plastic deformation

Before we start our detailed analysis, we wish to briefly discuss the technique of Kurishita *et al.* [2] that was used to determine the activation energy at the yield point of $TiC_{0.95}$, and also discuss how to determine the activation energy of plastically deformed samples using a general method developed by Mohamed and Langdon [1].

Kurishita *et al.* [2] investigated the deformation behaviour of single crystals of $TiC_{0.95}$ under compression in a vacuum of 0.3 mPa at temperatures from 1280–2273 K and at constant strain rates between 3.9×10^{-5}–$6.3 \times 10^{-5}\ s^{-1}$. The experimental data obtained from the constant strain rate test, suggest to Kurishita *et al.* a mechanical equation of state at yielding for $TiC_{0.95}$ single crystals which can be approximately expressed as:

$$\dot{\gamma} = A\left(\frac{\tau_c}{G}\right)^n \exp\left(\frac{-Q}{RT}\right) \tag{1}$$

where $\dot{\gamma}$ is the plastic shear strain rate, τ_c is the resolved shear stress, R is the gas constant, T the absolute temperature, A a constant, G is the shear modulus, n is the stress exponent and Q is the apparent activation energy of plastic deformation. For the high temperature range ($1840 \leq T \leq 2273$ K) the values for Q and n were respectively 471 $\pm$ 27 KJ mol^{-1} and $n = 5.3 \pm 0.4$. For the low temperature range ($1280 \leq T \leq 1510$ K) the obtained values were 240 ± 10 KJ mol^{-1} and 10.1 ± 0.4 (see Kurishita *et al.* [2]).

On the other hand, according to Mohamed and Langdon [1], when the plastic deformation of a material is dictated by a thermally activated process, then the strain rate, $\dot{\varepsilon}$, may be expressed in terms of rate reaction theory as

$$\dot{\varepsilon} = A'(S, \sigma, \mathrm{T}) \exp\left[-\frac{\Delta H(S, \sigma, \mathrm{T})}{\mathrm{RT}}\right] \tag{2}$$

where A' is the frequency factor, S a structural parameter related to lattice imperfections, σ is the applied stress, and ΔH is the activation enthalpy. If $S = S(\sigma)$, Equation 2 simplifies and the activation enthalpy ΔH, which is an important element in the strain rate equation is uniquely defined by the expression:

$$\Delta H = R\left[\frac{\partial \ln\dot{\varepsilon}}{\partial(-1/T)}\right]_\sigma \tag{3}$$

Mohamed *et al.* note that any attempt to identify the microscopic rate controlling mechanism requires that ΔH be determined from experimental data.

Although the activation enthalpy defined by Equation 3 can be termed an activation enthalpy at constant stress, it is not immediately apparent from Equation 2 whether it is also possible to define a different activation enthalpy at a constant strain rate. This uncertainty arises because the functional dependence of σ on T is not explicitly included in Equation 2, and it is not known whether it follows an Arrhenius type expression.

Equation 2 can be rewritten in the form:

$$\ln\dot{\varepsilon} = f\left(\ln\sigma, \left(\frac{-1}{T}\right)\right) \tag{4}$$

and it can be mathematically shown that the three partial derivatives

$$(\partial\ln\dot{\varepsilon}/\partial\ln\sigma)_T, \quad (\partial\ln\sigma/\partial(-1/T))_{\dot{\varepsilon}}$$
$$(\partial(-1/T)/\partial\ln\dot{\varepsilon})_\sigma$$

are interrelated by the following expression,

$$\left[\frac{\partial\ln\dot{\varepsilon}}{\partial\ln\sigma}\right]_T \left[\frac{\partial\ln\sigma}{\partial(1/T)}\right]_{\dot{\varepsilon}} \left[\frac{\partial(1/T)}{\partial\ln\dot{\varepsilon}}\right] = -1 \tag{5}$$

Therefore, Equation 5 may be expressed in a more explicit form as:

$$\Delta H = R\left[\frac{\partial\ln\dot{\varepsilon}}{\partial(-1/T)}\right]_\sigma = \left[\frac{\partial\ln\dot{\varepsilon}}{\partial\ln\sigma}\right]_T R\left[\frac{\partial\ln\sigma}{\partial(1/T)}\right]_{\dot{\varepsilon}} \tag{6}$$

For simple materials (including pure metals, many alloys, and many non-metallics) deformed at temperatures above $\approx 0.5\ T_m$, where T_m is the melting point temperature of the material in Kelvin, two experimental results have been reasonably established. Firstly, the flow process is diffussion-controlled with an activation enthalpy which is insensitive to stress and equal to the apparent activation energy, Q_a. Secondly, the stress is related to the strain rate through a power law at low and intermediate stress levels, thereby implying that stress and temperature are related exponentially. Under these conditions, Equation 2 may be written as

$$\dot{\varepsilon} = A''\sigma^n \exp\left(\frac{-Q_a}{RT}\right) \tag{7}$$

where A'' is a constant.

By defining the apparent activation energy at a constant strain rate, $(Q_a)_{\dot{\varepsilon}}$ as:

$$(Q_a)_{\dot{\varepsilon}} \equiv R\left(\frac{\partial\ln\sigma}{\partial(1/T)}\right)_{\dot{\varepsilon}} \tag{8}$$

Equation 6 reduces to:

$$Q_a = (Q_a)_\sigma = n(Q_a)_{\dot{\varepsilon}} \tag{9}$$

where $(Q_a)_\sigma$ is the apparent activation energy for the constant stress condition. It must be emphasized, that, although it is possible to mathematically define two apparent activation energies, $(Q_a)_\sigma$ and $(Q_a)_{\dot{\varepsilon}}$, the deformation process has a unique activation energy Q_a, which is independent of the method of determination (whether through Equation 3 or Equation 6).

3. Experimental method of determining the activation energy for high temperature plastic deformation of $TiC_{0.95}$

In the following paragraphs, using the Mohamed and Langdon ideas discussed previously, the Kurishita *et al.* technique is applied in order to determine the activation energy for plastic deformation in $TiC_{0.95}$.

Stress–strain curves for $TiC_{0.95}$ single crystals deformed by compression at various temperatures between 1280–2273 K at different strain rates ranging from 10^{-5}–$10^{-2} s^{-1}$, have been obtained by Kurishita *et al.* [2]. Starting from this type of test, in a straightforward manner graphs of $\ln\sigma$ versus $(1/T)$, can be constructed and $(Q_a)_{\dot{\varepsilon}}$ determinations can finally be obtained. However from these experimental data an activation energy at a constant stress level $(Q_a)_\sigma$ has been obtained by Kurishita *et al.* In order to obtain such results Kurishita *et al.* assume in an implicit way the existence of a functional relation which involves σ, $\dot{\varepsilon}$ and T; that is $\sigma = F_1(\dot{\varepsilon}, (+1/T))$ which then allows the proposal of a functional relation $\dot{\varepsilon} = F_2(\sigma_1(-1/T))$ in the explicit form given by Equation 1. This equation, allows one to obtain the activation energy for deformation at constant stress level as dictated by the theoretical analysis due to Mohamed and Langdon.

Therefore, with the use of the theoretical considerations due to Mohamed and Langdon, in principle it is easy to make determinations on the activation energy for plastic deformation of TiC$_x$, as a function of the carbon concentration, by starting from the analysis of constant strain rate experimental data.

4. Determination of the activation energy for TiC$_x$ by using the variation of stress at constant strain rate

Under the conditions of a constant strain rate test, it follows from Equations 6 and 7 that Q_a is given by the relationship

$$Q_a = nR\left[\frac{\partial \ln\sigma}{\partial(1/T)}\right]_{\dot{\varepsilon}} \qquad (10)$$

In order to apply this equation, the values of the stress exponent, *n*, the strain rate, and also the temperature dependence of the critical resolved shear stress as a function of the C:Ti atom ratio, are required.

Fig. 1 shows the temperature dependence of the stress exponent of the strain rate for TiC$_{0.95}$, as given by Kurishita *et al.* [2]. Because the values of *n* for other C:Ti atom ratios have not been determined until now, we have taken the temperature dependence of the stress exponent of the strain rate to be given by Fig. 1 for all the C:Ti atom ratios.

Fig. 2 shows the *x*-dependence of the critical resolved shear stress as reported by Tsurekawa *et al.* [3].

In Fig. 3 we show the *x*-dependence of the *Q* value in the high temperature range ($1500 \leq T \leq 2270$ K) for titanium carbide single crystals as determined from Equation 10 together with data from Figs 1 and 2. Also, in Fig. 4 we show the *x* dependence of the activation energy in the low temperature range ($1180 \leq T \leq 1450$ K) for single crystals (dot points), as determined by using data from Figs 1 and 2 together with Equation 10. In Fig. 4, the values of *Q* for polycrystalline TiC$_x$ (triangular points) as calculated from the experimental data due to Miracle and Lipsitt [14] (see Fig. 5), also appear. And finally in Figs 3 and 4 one data point for $x = 0.95$ due to Kurishita *et al.* [2] appears as a square symbol.

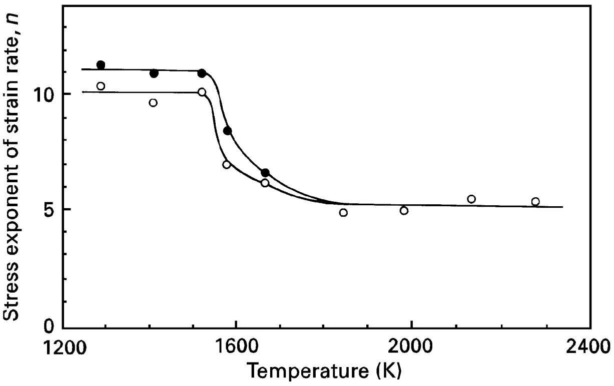

Figure 1 Stress exponent *n* of strain rate as a function of temperature for TiC$_{0.95}$: (○) upper yield stress; (●), lower yield stress. After Kurishita *et al.* [2].

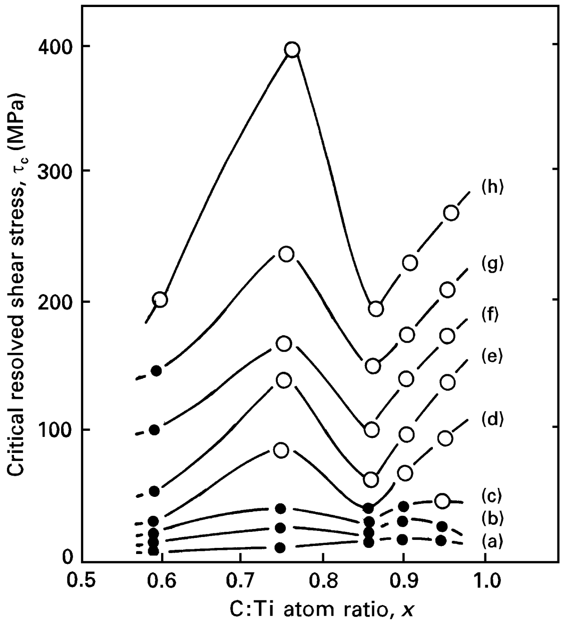

Figure 2 Dependence of the critical resolved shear stress, τ_c, on the C:Ti atom ratio, *x*, for TiC$_x$ single crystals compressed at temperatures of (a) 2270 K (b) 2070 K, (c) 1870 K, (d) 1670 K, (e) 1530 K, (f) 1400 K, (g) 1280 K and (h) 1180 K and at a strain rate of $6 \times 10^{-4}\,\mathrm{s}^{-1}$. Open and solid marks indicate the presence and the absence of yield drop, respectively. After Tsurekawa *et al.* [3]

5. Discussion

Before we proceed to analyse the activation energy for deformation of TiC$_x$ the values of the self-energy of carbon as a function of the C:Ti atom ratios are required. In Fig. 6 the self diffusion energy data as a function of composition are shown. The experimental data used to produce this curve were obtained by Sarian [16, 17] for the temperature range $1723 \leq T \leq 2553$ K.

The values of the activation energy for plastic deformation both at high and low temperatures ranges are smaller than the self-diffusion energy for carbon, except for $x = 0.75$. For this carbon concentration the value of the activation energy for plastic deformation at both temperature ranges is approximately $560 \pm 20\ \mathrm{KJ\,mol^{-1}}$, which presumably can be taken as the pipe diffusion activation energy for titanium atoms in TiC$_x$ crystals [3]. For the high temperature range a peak in the activation energy of plastic deformation appears with a value $Q_h = 568 \pm 32.0\ \mathrm{KJ\,mol^{-1}}$ and for the low temperature range

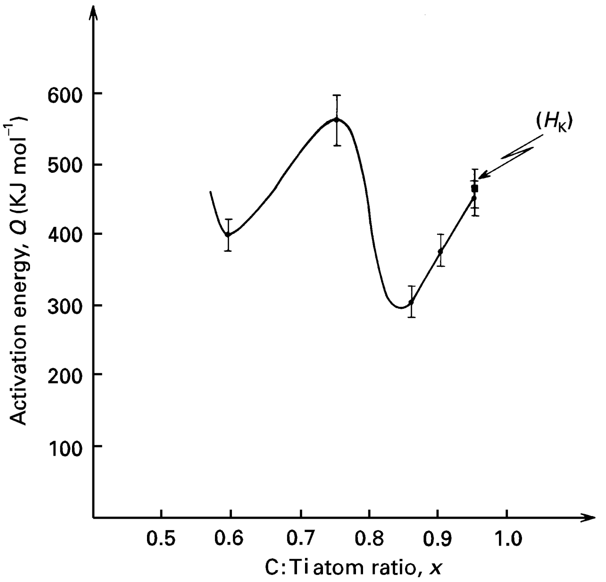

Figure 3 Dependence of the activation energy, Q, at the critical resolved shear stress on the C:Ti atom ratio for TiC$_x$ single crystals in the high temperature range ($1500 \leq T \leq 2270$ K). The point marked as H_K, (■) was determined by Kurishita *et al.* [2], all the other points were determined by using the currently described procedure.

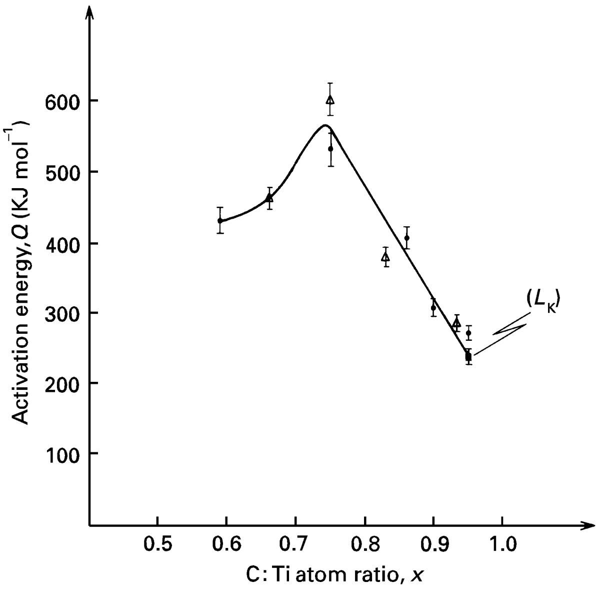

Figure 4 Dependence of the activation energy, Q, at the critical resolved shear stress on the C:Ti atom ratio for TiC$_x$ samples in the low temperature range ($1180 \leq T \leq 1450$ K). The point marked as L_K, (■) was determined by Kurishita *et al.* [2], all the other points have been determined by following the current procedure. The triangular points were calculated from polycrystalline data (see Fig. 5), and the solid points from single crystal data (see Fig. 2) respectively.

the peak appears at the following value $Q_l = 536 \pm 21.4\ \mathrm{KJ\,mol^{-1}}$. The occurrence of these peaks in the activation energy for plastic deformation at a specific value $x = 0.75$, is considered to be caused by an ordering in TiC$_x$ which is known to induce a volume contraction [3]. This volume contraction has been determined from the rigid lattice part of neutron diffuse scattering data on TiC$_{0.76}$($\cong$ 7 meV) which indicates that the atomic displacements

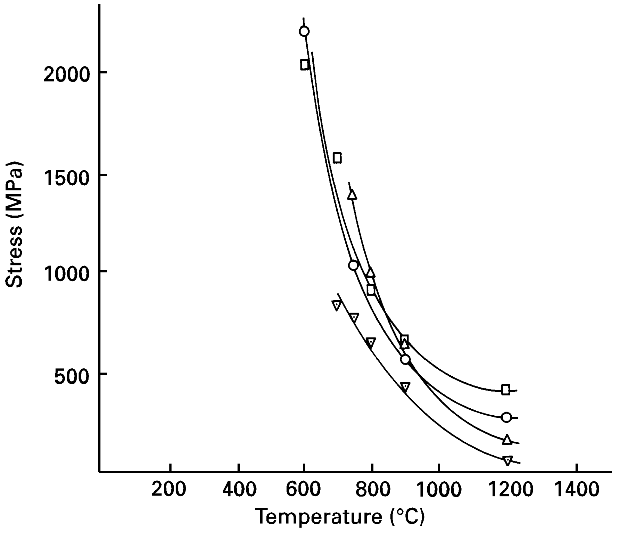

Figure 5 Variation of the 0.2% yield stress for TiC$_x$ polycrystalline (grain size ranged between 14–22 μm and increased monotonically with decreasing stoichiometry) as a function of temperature for C:Ti atom ratios of (□) 0.93, (○) 0.83, (△) 0.75 and (▽) 0.66. After Miracle and Lipsitt [14].

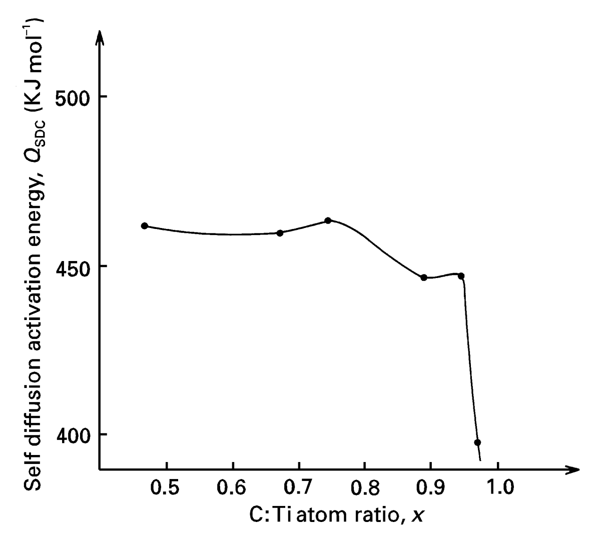

Figure 6 The self-diffusion energy data for TiC$_x$ as a function of composition. The experimental data were taken from the reported data by Sarian [16, 17] for the temperature range $1723 \leq T \leq 2553$ K.

($\cong$ 0.005 nm for titanium) play an important role in the energetics of the system [18]. These results are contrary to the notion that at the critical resolved shear stress the carbon diffuses many times faster than the metal atom [3].

The commonly accepted idea that carbon diffuses along its own sublattice is appealing because of its simplicity and the large number of vacant octahedral sites [16]. In our theoretical frame the peak appearing at $x = 0.75$ for the activation energy during plastic deformation can be attributed to a contraction of the window (formed by titanium atoms) for the carbon atom diffusion. In other words, for this concentration of carbon atoms both titanium and carbon diffusion processes (occurring during deformation) are coupled.

Consequently, these facts suggest the possibility of a coupled mechanism for carbon and titanium diffusion during plastic deformation for other C:Ti atom ratios. In order to prove such a hypothesis in the following paragraphs the experimental activation energy data at the critical resolved shear stress for TiC_x at the low temperature range (see Fig. 4) will be analysed.

In the concentration range $0.75 \leq x \leq 0.95$ it can be demonstrated that, the apparent activation energy at the critical resolved shear stress, $Q(x)$, as a function of the C:Ti atomic ratio can be described by the following expression:

$$Q(x) = Q_{PC} + 5(Q_{PTi} - Q_{PC})(0.95 - x) \qquad (11)$$

where Q_{PC} is the value of the activation energy for pipe diffusion of carbon taken as $240\ \mathrm{KJ\,mol^{-1}}$ [2] and Q_{PTi} is the value of activation energy for pipe diffusion of titanium atoms taken as $560\ \mathrm{KJ\,mol^{-1}}$ [3]. This equation describes the apparent activation energy for deformation with no more than $\pm 8\%$ of relative error. An interesting feature of this phenomenological equation is that the apparent activation energy for plastic deformation in the low temperature range is proportional to the product of the difference between the pipe diffusion activation energy for titanium and carbon atoms, as well as the apparent carbon deficiency, $(0.95 - x)$. Also it is clear that in the range of composition given by $0.75 \leq x \leq 0.95$, the activation energy for plastic deformation increases linearly with increasing number of carbon vacancies. This final piece of experimental evidence, is in qualitative agreement with experimental data for the self diffusion of carbon in TiC_x reported by Sarian [19].

6. Conclusions

By using a general theoretical consideration proposed by Mohamed and Langdon [1], and experimental data for the deformation of TiC_x single crystals at a constant strain rate, the following results were obtained.

1. The Ci:Ti atomic ratio x-dependence of the activation energy at the critical resolved shear stress ($1180 \leq T \leq 2270$ K) has been established.
2. The obtained activation energy values are lower, than the self diffusion data for carbon, except for $x = 0.75$.
3. For $x = 0.75$ there is a peak value for Q_a. This value corresponds to the activation energy for pipe diffusion of titanium atoms. This situation is due to an ordering hardening caused by a contraction of the "window" of titanium atoms through which the carbon atoms diffuse.
4. For the low temperature range ($1180 \leq T \leq 1500$ K) in the concentration range ($0.75 \leq x \leq 0.95$) the activation energy for deformation is proportional to the product of the apparent carbon deficiency and the difference between the pipe diffusion activation energies for titanium and carbon atoms.
5. During plastic deformation of TiC_x, the diffusion processes of carbon and titanium are coupled.

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