

Carbon diffusion in α -Ti and α_2 -Ti₃Al

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ABSTRACT The interstitial defect formation energies of carbon in various interstices, crystal orbital Hamilton populations, electron localization function, Voronoi volumes, and other characteristics in α -Ti and α_2 -Ti₃Al were calculated by the projector augmented wave method. The climbing image nudged elastic band method was used to estimate migration barriers along paths between stable interstitials. The temperature-dependent diffusion coefficients of carbon were evaluated along two nonequivalent crystallographic directions (*a* and *c*) in α -Ti and, for the first time, in α_2 -Ti₃Al. The energetically preferred site in both α -Ti and α_2 -Ti₃Al is an octahedral one, whose local environment contains only Ti atoms. This preference depends on material and is primarily due to low mechanical contribution to the defect formation energy in α -Ti and chemical one in the case of the alloy. The presence of Al leads to an increase in the defect formation energy in the alloy. In the case of α -Ti, the obtained diffusion coefficients are in good agreement with experiment. Aluminum in the alloy leads to a slowdown in carbon diffusion due to higher both defect formation and migration energies.

KEYWORDS titanium, titanium aluminide, carbon diffusion, ab-initio calculations

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1. Introduction

Titanium aluminides are attractive structural materials for use in the aerospace industry due to their low density, high melting point, high specific strength, creep resistance at high temperatures, and other good mechanical properties. For example, the α_2 -Ti₃Al alloy has an elastic modulus and tensile strength comparable to those of nickel superalloys; however, a complete lack of ductility at room temperature is a major problem in its use [1]. The addition of alloying elements and some heat treatment can significantly improve the mechanical properties of Ti₃Al [2, 3]. It is known that atomic diffusion determines a number of mechanical properties of materials [4, 5]. For example, the thermal stability of coatings and creep resistance depend on the diffusion, interdiffusion, and self-diffusion rate. Interstitial impurities can affect the mechanical properties of alloys, phase stability, and resistance to environmental degradation. Experimental measurement of the diffusion coefficient is quite difficult, and its experimental evaluation is accompanied by a number of problems related to purity of samples, availability of radioactive tracers, etc. As a result, the spread in the values of diffusion coefficients and activation energies is significant. Moreover, experimental methods allow one to estimate the diffusion rate, but not to determine its microscopic mechanisms. The results of an experimental study of the diffusion of Fe, Ni, Nb, Al, Ga, Si, and O in α_2 -Ti₃Al are presented in [6–10]. For example, it was shown that O diffusion in both *a* and *c* directions occurs faster than self-diffusion of Ti and Al [10] or diffusion of impurities such as Nb, Si, and Ga, but slower than Fe and Ni. It should be emphasized that both groups of elements are substitutional impurities, while O is an interstitial one. From the reviews given in [10, 11], it is clear that a similar phenomenon also occurs in α -Ti. In the latter case, the formation energies of interstitial and substitutional defects, their migration energies, and the exponential part of the diffusion coefficient at 1000 K were calculated for a number of impurities in paper [12]. The authors concluded that a small difference in the formation energies of interstitial and substitutional defects in the case of fast diffusers may be the main reason for the anomalously high diffusion rate via the interstitial mechanism. In our previous studies [13, 14], the temperature-dependent diffusion coefficient of a number of metal impurities within vacancy and interstitial mechanisms in α -Ti was calculated. It was shown that fast impurities prefer to diffuse via interstices, but the preferred site differs from that for non-metallic interstitial impurities. The diffusion coefficients of *d*-metals (Co and Fe) obtained within the interstitial mechanism are in good agreement with the available experimental values. At the

same time, normal diffusers migrate via interstitial sites more slowly than via vacancies. Similar calculations in the α_2 -Ti₃Al alloy [15, 16] demonstrated that Al in the local environment of the impurity leads to an increase in the interstitial defect formation energy compared to α -Ti and, as a consequence, to an increase in the diffusion coefficients. Despite the significant scattering in the diffusion coefficients of carbon in different experimental studies [17–20], carbon, which is a classic interstitial impurity, has a diffusion coefficient several orders of magnitude lower than that of some *d*-metals (Fe, Co, etc.).

The diffusion of C along with O and N in α -Ti was studied using an analytical model, the multi-state diffusion method as well as kinetic Monte Carlo simulations in the paper [21]. The obtained results showed the reliability of these two methods with respect to the experimental data [20]. It was demonstrated that C is the faster diffuser in comparison with O and N. However, the comparison diffusion coefficient of C within one theoretical approach in α -Ti and α_2 -Ti₃Al and with that for metallic impurities was not carried out. The aim of this work is a comparative study of C diffusion coefficients in both α -Ti and α_2 -Ti₃Al materials.

2. Computational details

The atomic and electronic structure of α -Ti and α_2 -Ti₃Al was calculated using the projector augmented wave (PAW) method [22, 23] in the plane-wave basis set with the generalized gradient approximation (GGA-PBE) [24] for the exchange-correlation functional. In the case of α -Ti with an HCP structure, a $4 \times 4 \times 3$ supercell containing 96 Ti atoms was used. The atomic structure of the α_2 -Ti₃Al alloy with the same crystal structure was modeled by a $2 \times 2 \times 3$ supercell also containing 96 atoms (72 Ti and 24 Al atoms). A full optimization scheme including relaxation of both atomic positions and supercell volume was used. The energy cutoff for the plane-wave basis set was 400 eV. Integration over the Brillouin zone was performed using a $3 \times 3 \times 3$ Γ -centered mesh of *k*-points. Convergence was considered achieved if the difference in the total energies of two consecutive iterations did not exceed 10^{-6} eV. Relaxation of atomic positions was carried out until the forces on the atoms reached approximately 10^{-4} eV/Å.

The defect formation energy (E^f) in α -Ti and α_2 -Ti₃Al was calculated using the following formula:

$$E^f = E^{def} - E^{id} - E(C) + nE(\text{Ti}/\text{Al}), \quad (1)$$

where E^{def} and E^{id} are the total energies of the defect and ideal supercells; $E(C)$ and $E(\text{Ti}/\text{Al})$ are the total energies of C and Ti or Al in the ground state per atom; the parameter *n* is equal to 0 or 1 in the case of interstitial or substitutional defect, respectively. With this definition, the smaller E^f , the easier it is for the defect to form.

To explain the preference for defect formation, the mechanical (*MC*) and chemical (*CC*) contributions to E^f [25], the crystal orbital Hamilton population (COHP) curves [26–28] and the integral from these curves to the Fermi level (ICOHP), as well as the electron localization function (ELF) [29] were calculated. Since on the COHP curve the negative values correspond to the bonding states, while historically these states are depicted as positive, the $-\text{COHP}$ curves and $-\text{ICOHP}$ values will be shown and discussed in the figures. The charge transfer and overlap population were estimated by DDEC6 method that is a refinement of the Density Derived Electrostatic and Chemical (DDEC) approach [30, 31].

The migration energies (E^m) were calculated using the nudged elastic band method with a climbing image [32]. For each migration path, five images were used, in which the positions of the diffusing atom along the migration path were determined by linear interpolation between its initial and final positions. By simultaneously relaxing all five images, each atom was assumed to be elastically bound to the same atom in adjacent images. This approach allows one to determine the minimum energy path, as well as the saddle point. Note that the difference in the total energies of system with diffusing atoms in the saddle point and in the initial position is equal to the height of the migration barrier.

The following positions of carbon in α -Ti were considered (Fig. 1a): octahedral (*O*); tetrahedral (*T*); hexahedral, located between *O*-sites (H_O) and *T*-sites (H_T); crowdions, in which the impurity atom is located between the nearest Ti atoms in a basal plane (*Cb*) and in adjacent planes (*C*). The substitution position is designated as *S*. Since the atomic structure of α_2 -Ti₃Al and α -Ti are similar, the same interstitial sites were considered in the alloy, but due to the presence of Al there are two sites of each type, differing in the Ti content in the local environment. Sites with a higher Ti content are designated as 1, and those with a lower Ti content as 2. Figure 1b shows all considered interstitial sites in the α_2 -Ti₃Al alloy: octahedral (*O1* and *O2*, in the centers of octahedra of the Ti₆ and Ti₄Al₂ compositions); tetrahedral (*T1* and *T2*, in the center of tetrahedrons of the Ti₃Al₁ composition, the difference between which lies in the position of the Al atom); hexahedral, located between the *O*-sites (H_{O1} and H_{O2}) and *T*-sites (H_{T1} and H_{T2}); crowdions, in which the impurity atom is located between the nearest Ti atoms in the same basal plane (*Cb1* and *Cb2*) and in adjacent planes (*C1* and *C2*). Positions *S1* and *S2* correspond to the substitution of Al and Ti atoms, since in the first case the nearest ones are 12 Ti atoms, and in the second case 8 Ti atoms and 4 Al atoms.

3. Results and discussion

3.1. Carbon diffusion in α -Ti

The calculated values of the carbon defect formation energies in α -Ti are given in Table 1. The most preferred position is the *O*-interstice. It is characterized by a negative value of E^f , which is due to the lowest value of *MC* contribution.

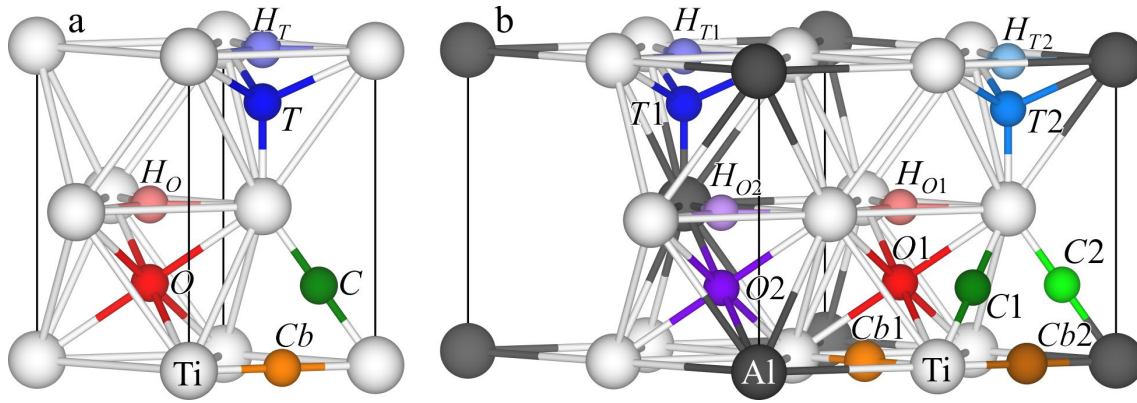
FIG. 1. Unit cell of α -Ti (a) and α_2 -Ti₃Al (b) with considered interstitial sites

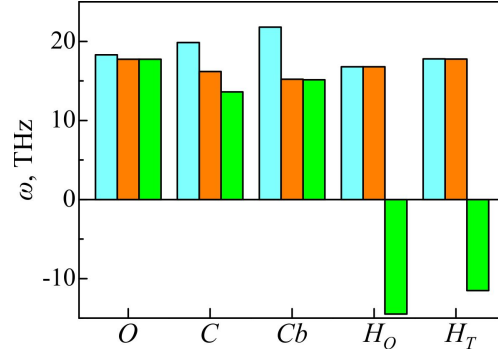
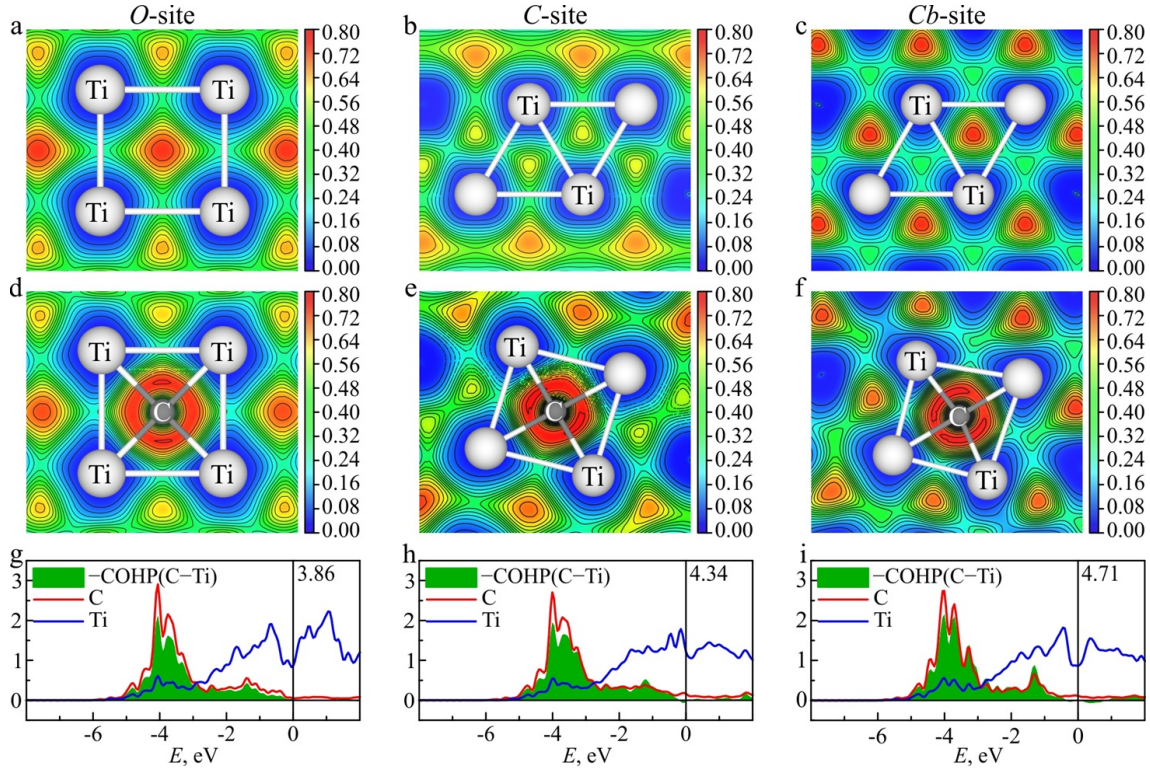
TABLE 1. The defect formation energy (E^f), the mechanical (MC) and chemical (CC) contributions to this energy, the changes in the Voronoi volume (ΔV_V) of the interstices due to carbon atom incorporation, interatomic distance between carbon and nearest titanium atoms (d), overlap population of these bonds (θ), charge state of carbon atom (q), integrated crystal orbital Hamilton population ($-ICOHP$). In the case of substitutional defect subscripts “in” and “out” indicate position of C and Ti atoms in the same (0001) plane and adjacent planes

Site	E^f , eV	MC , eV	CC , eV	ΔV_V , Å ³	d , Å	θ , el.	q , el.	$-ICOHP$, eV
O	-1.56	0.13	-1.69	+1.61	2.10	0.55	-1.18	3.86
C	-0.13	1.46	-1.59	+2.47	2.05	0.60	-1.17	4.34
Cb	-0.13	1.27	-1.40	+0.34	2.00	0.63	-1.15	4.71
H_O	1.72	1.07	0.66	+2.69	2.00	0.64	-0.94	5.21
H_T	0.59	0.54	0.05	+1.39	1.97	0.65	-1.06	5.17
S	2.36	0.72	1.64	-3.75	2.81 _{in} , 2.64 _{out}	0.16 _{in} , 0.22 _{out}	-0.78	1.15 _{in} , 1.74 _{out}

Another stable insertion positions are crowdion C and basal crowdion Cb (Table 1). These defects are characterized by the same values of the formation energy because of close MC and CC contribution. It should be noted that structure relaxation results in the movement of carbon atom from T -site into H_T . For hexahedral positions H_O and H_T the defect formation energies equal to 1.72 and 0.52 eV, respectively. Table 1 also presents the results of some electronic and structural characteristics of carbon in α -Ti. The high value of the MC contribution among interstitial positions in the case of the C -site (1.46 eV) is manifested by a pronounced structural distortion and is a consequence of the smaller volume of the C -interstice compared to other positions. The O , C and Cb positions are characterized by a negative and high absolute value of the chemical contribution as well as almost the same charge state of the carbon atom. Calculation of the phonon frequencies of carbon revealed the presence of only one imaginary frequency in H_O and H_T sites (Fig. 2). It means that these hexahedral positions can be considered as the first-order transition states. Thus, in α -Ti the O , C and Cb sites have to be considered as interstitial positions for carbon diffusion. Note that, unlike metallic impurities, carbon has difficulty substituting for Ti, and the defect formation energy reaches 2.36 eV (Table 1).

The introduction of carbon into the O -position only slightly, up to 0.79, increases the value of electron localization function in the interstitial site (Fig. 3a,d), and the localization region has a spherical shape that is typical for ionic-covalent interaction. Calculations have shown that a charge of ~ 1.2 electrons is transferred to carbon, and the $-ICOHP$ value reaches 3.86 eV (Table 1). Although both crowdions in pure α -Ti are characterized by a low ELF (Fig. 3b,c), the C atom induces charge transfer and the formation of an electron localization region (Fig. 3e,f). The COHP curves for these positions (Fig. 3g-i) show a virtually complete absence of antibonding states as well as a low density of states at the Fermi level that indicates strong C-Ti interactions at these sites, consistent with the values of the chemical contributions (Table 1).

Table 2 presents the migration barriers for all considered jumps of carbon between stable interstices. It is seen that there are four paths oriented along the basal plane ($\parallel a$): $O \rightarrow C$ (and reverse jump $C \rightarrow O$), $C \rightarrow C$ and two variants of $Cb \rightarrow Cb$ which differ by saddle point given in brackets. Carbon diffusion along $[0001]$ direction can occur via only two paths: $C \rightarrow C$ and $O \rightarrow (H_O) \rightarrow O$. Other four jumps allow carbon to move simultaneously along both a and c axes. Due to

FIG. 2. Phonon frequencies of C atom in interstitial sites in α -TiFIG. 3. Distribution of ELF in ideal α -Ti (a–c) and near the C interstitial atom (d–f), as well as the local DOS of the C and nearest Ti atoms and the corresponding COHP curves (g–i)

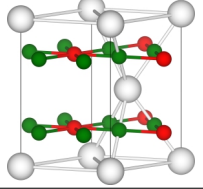
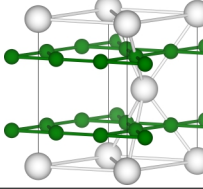
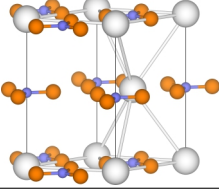
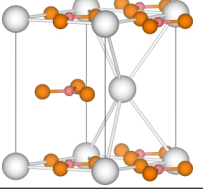
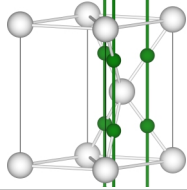
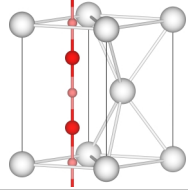
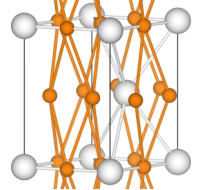
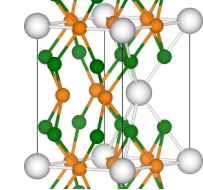
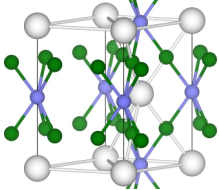
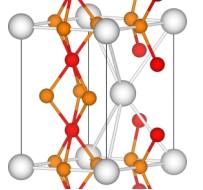
the highest preference for absorption in the O -site, E^m along the a -axis for the $O \rightarrow C$ path is 1.54 eV, while for the reverse path, $C \rightarrow O$, it is only 0.11 eV. The $C \rightarrow C$ jump along the a -axis requires 1.42 eV that is 0.3 eV more than this jump along the c -axis. The migration energy for the $Cb \rightarrow (H_T) \rightarrow Cb$ path (0.72 eV) is minimal, while for the $Cb \rightarrow (H_O) \rightarrow Cb$ path (1.85 eV) is maximal among atomic jumps oriented along basal plane (Table 2). The migration energy for the $C \rightarrow C$ and $O \rightarrow (H_O) \rightarrow O$ paths along c -axis are 1.12 and 3.28 eV, respectively. It should be noted that the high value of E^m for the $O \rightarrow (H_O) \rightarrow O$ jump allows us to exclude it from further consideration as the slowest but not the only diffusion channel along c -axis. The jumps between both crowdions, when carbon displacement occurs in both directions simultaneously, require 0.37–0.72 eV. Taking into account difference in E^f for $C(Cb)$ and O sites (1.43 eV), it is possible to conclude that $O \rightarrow Cb$ jump can make main contribution to diffusion among mixed paths.

Additionally, Table 2 includes the values of the migration energy and the attempt frequency (ν) obtained in paper [21]. It is seen that almost all present E^m values agree well with earlier data. Exception is $C \rightarrow Cb$ jump for which the migration energy is found to be about twice less than that from [21]. Difference in the attempt frequencies is connected with different approach for their estimation. In the present paper, the classical expression [4] was applied:

$$\nu = \sqrt{\frac{E^m}{2md^2}}, \quad (2)$$

where m is mass of C atom, d is jump distance; whereas in [21] Vineyard's definition [33] was used.

TABLE 2. Migration energies (E^m), jump length (d) and attempt frequency (ν) for all considered jumps of carbon in α -Ti. The values in parentheses are given for the reverse jump. Results from paper [21] are marked by *

Path	$O \rightarrow C \parallel a$	$C \rightarrow C \parallel a$	$Cb \rightarrow (H_T) \rightarrow Cb \parallel a$	$Cb \rightarrow (H_O) \rightarrow Cb \parallel a$
E^m , eV	1.54 (0.11), 1.42* (0.12*)	1.42	0.72	1.85
d , Å	1.460	1.460	1.685	1.685
ν , 10^{12} s^{-1}	17.03 (4.55), 94.57* (3.21*)	16.36	10.09	16.18
Network				
Path	$C \rightarrow C \parallel c$		$O \rightarrow (H_O) \rightarrow O \parallel c$	
E^m , eV	1.12		3.28, 3.40*	
d , Å	2.319		2.319	
ν , 10^{12} s^{-1}	9.15		15.65, 16.70*	
Network				
Path	$Cb \rightarrow Cb$	$C \rightarrow Cb$	$C \rightarrow (H_T) \rightarrow C$	$O \rightarrow Cb$
E^m , eV	0.38	0.38 (0.38), 0.85* (0.84*)	0.72	1.77 (0.35), 1.69* (0.38*)
d , Å	2.467	1.433	2.867	1.433
ν , 10^{12} s^{-1}	5.01	8.62 (8.62), 10.85* (33.68*)	5.93	18.60 (8.27), 70.87* (17.60*)
Network				

The diffusion coefficients within the interstitial mechanism were calculated using the Landman method [34,35]. Since O , C and Cb sites in α -Ti correspond to $2a$, $6g$ and $6h$ Wyckoff positions, the Fourier transform matrix of displacement, $\tilde{p}(\mathbf{k})$, and the Laplace transform matrix of waiting-time function, $\tilde{\psi}(u)$, in the considered jump network have a dimension of 14×14 . We do not present these matrices in the present paper because they are very cumbersome. The propagator matrix is calculated using the following expression:

$$R(\mathbf{k}, u) = E - \tilde{\psi}(u) \circ \tilde{p}(\mathbf{k}), \quad (3)$$

where E is the identity matrix; the symbol " $\circ$ " denotes the Hadamard (element-wise) product of matrices.

The root-mean-square displacement of a diffusing atom in the $\mathbf{r}$ direction over time t is estimated as

$$\langle \sigma_{\mathbf{r}}^2(t) \rangle = \lim_{\mathbf{k} \rightarrow 0} \left(t \frac{1}{\Delta_0} \frac{\delta^2 \det R(\mathbf{k}, u)}{\delta \mathbf{k}_{\mathbf{r}}^2} \right), \quad (4)$$

where

$$\Delta_0 = \lim_{\mathbf{k} \rightarrow 0} \left(\frac{\partial \det R(\mathbf{k}, u)}{\partial u} \right). \quad (5)$$

According to the Einstein–Smoluchowski relation, the root-mean-square displacement over time t is:

$$\langle \sigma^2(t) \rangle = 2ntD, \quad (6)$$

where n is the dimension of the system and D is the diffusion coefficient.

The attempt frequencies (eq. (2)) are included in the formula for the jump rate Γ :

$$\Gamma = \nu \exp\left(-\frac{E^m}{k_B T}\right), \quad (7)$$

where k_B is the Boltzmann constant and T is the temperature. So, each jump are characterized by own rate determined by the values of E^m and ν (Fig. 4a). The ratio of polynomials composed of different Γ 's gives the diffusion coefficient.

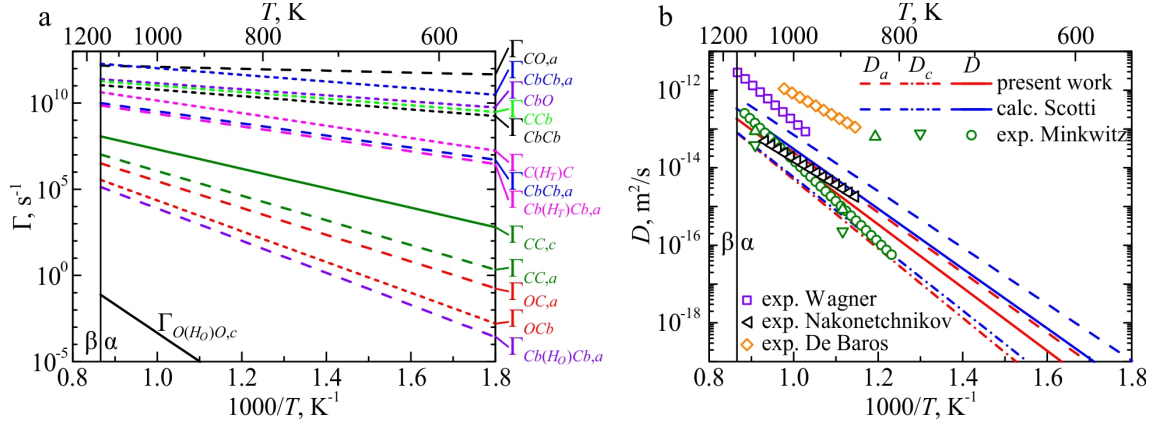


FIG. 4. Temperature-dependent jump rate (a) and diffusion coefficient (b) of carbon in α -Ti in comparison with earlier calculations of Scotti [21] and experimental data of Wagner [17], Nekonetchnikov [18], Minkwitz [19] and De Baros [20]

From Fig. 4a it is seen that, as expected, jumps from the O -site are slower than from both crowdions and the $O \rightarrow H_O \rightarrow O$ jump is the slowest. For convenient we use following designation: $\Gamma_{ij,k}$ is the rate of the $i \rightarrow j$ jump oriented along k -direction, the notation $\Gamma_{i(h)j,k}$ denotes a jump with a saddle point in position h . To apply obtained expressions for diffusion coefficients along a - and c -axis (D_a and D_c), they should be simplified. Since O -site is the preferable one and $\Gamma_{OC,a}$ and $\Gamma_{OCb,a}$ are the lowest one excepting $\Gamma_{O(H_O)O,c}$ and $\Gamma_{Cb(H_O)Cb}$, the expressions for D_a and D_c were expanded in a Taylor series for these rates:

$$D_a = a_0^2 \Gamma_{OC}, \quad (8)$$

and

$$D_c = c_0^2 \Gamma_{OCb}, \quad (9)$$

where a_0 and c_0 are the Ti lattice parameters.

By approximating the temperature dependence of D_a and D_c according to the Arrhenius equation using the least squares method over points with a step of 50 K, we obtain the final expressions for the diffusion coefficients of carbon within the framework of the interstitial mechanism:

$$\begin{aligned} D_a &= 1.45 \cdot 10^{-6} \exp\left(-\frac{1.54}{k_B T}\right) \text{ m}^2/\text{s}, \\ D_c &= 4.16 \cdot 10^{-6} \exp\left(-\frac{1.77}{k_B T}\right) \text{ m}^2/\text{s}. \end{aligned} \quad (10)$$

Figure 4b shows the calculated results of the carbon diffusion coefficients in α -Ti. It is evident that C diffusion is faster along the a -axis than along c -axis that is in agreement with calculations from [21] and experimental data for single crystal diffusion from [19]. The diffusion anisotropy (D_c/D_a) is 0.27–0.29 for the temperatures of 896–1100 K (0.27–0.43 for the same temperature range [19]). The values for polycrystalline D (solid line in Fig. 4b) estimated as geometric mean of D_a and D_c are in good agreement with the experiments [18, 19] and 1–2 orders of magnitude lower than in the experimental works [17, 20].

Figure 5 demonstrates the polycrystalline diffusion coefficient of C in comparison with those for other impurities obtained previously by the same method in [13, 14, 36] and with the self-diffusion coefficient of Ti from the paper [37]. It is seen that the diffusion rate of C is 4–6 and 4–8 orders of magnitude higher than the self-diffusion of Ti and diffusion of normal metal impurities (Al and Ga) at the temperature of 600–1155 K, respectively. Compared to oxygen, carbon diffuses 2–3 orders of magnitude faster that is in agreement with experiment [10]. At the same time, the C diffusion coefficient is found to be somewhat lower than that of the anomalously fast d -metal impurities (Fe and Co).

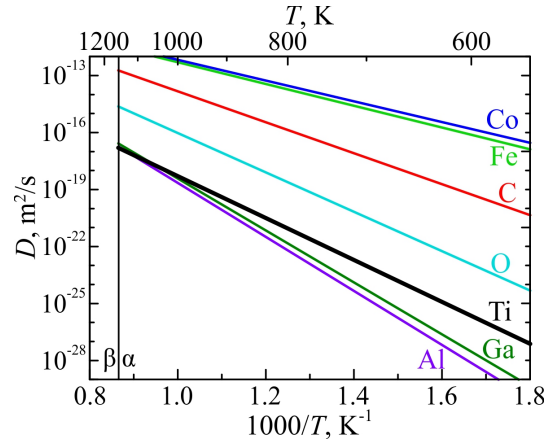


FIG. 5. Temperature-dependent diffusion coefficients of C in α -Ti and their comparison with the diffusion coefficients of Fe, Co, Ga, Al, O [13, 14, 36] and the Ti self-diffusion coefficient [37]

3.2. Carbon diffusion in α_2 -Ti₃Al

Similar calculations of the C diffusion coefficient were performed in the α_2 -Ti₃Al alloy as well. It should be noted that the same interstitial sites were considered in this alloy as in α -Ti, but due to the presence of Al, there are two sites of each type, differing in the Ti content in the local environment. Sites with a higher Ti content are designated 1, and those with a lower Ti content are designated 2 (Fig. 1b). As in α -Ti, in the alloy during structural optimization carbon atom moves from $T1$ and $T2$ sites into H_{T1} and $Cb1$ ones. Similarly, both H_{O1} and H_{O2} sites are dynamically unstable with respect to vibrations along the $[0001]$ direction, whereas unlike α -Ti the H_{T1} and H_{T2} sites are stable (Fig. 6a). The $C1$ crowdion is unstable and, during structural optimization, the carbon atom shifted to the $O1$ -site. Thus, in α_2 -Ti₃Al the stable interstices are the $O1$, $O2$, $C2$, $Cb1$, $Cb2$, H_{T1} and H_{T2} .

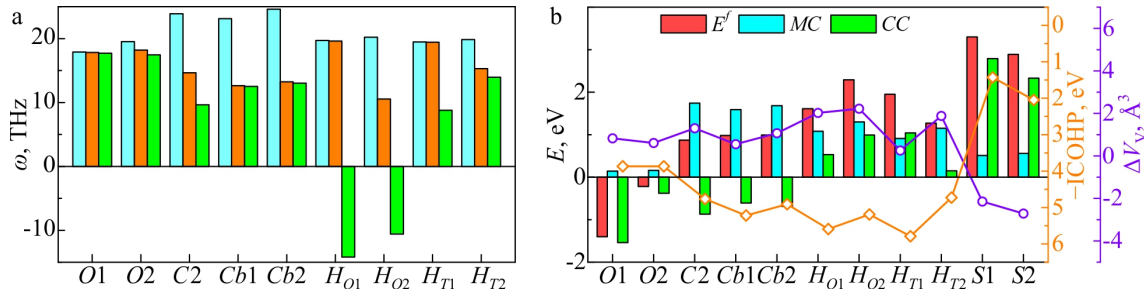


FIG. 6. Phonon frequencies of carbon atom (a) as well as defect formation energies, mechanical and chemical contributions in comparison with the change in the Voronoi volume and the average population of the Hamiltonian crystal orbitals (b) in interstitial sites in the α_2 -Ti₃Al alloy

The calculated defect formation energies and several additional data for these sites are given in Table 3. It is evident that the $O1$ -site is the most preferred for carbon due to the high absolute negative value of the CC contribution. Despite low MC in E^f in both $O1$ and $O2$ sites (almost the same as in α -Ti), the difference in CC contribution is quite large. The insertion of carbon into the $O1$ -site induces a large charge transfer to it (Fig. 7), with the charge accumulation region consistent with the electron pair localization region, indicating the covalent polar nature of the C–Ti bond. It should be noted that, as in the case of α -Ti, carbon induced enough high charge transfer (Table 3), and a correlation between the MC contribution to E^f and the increase in interstitial volume (ΔV_V) also occurs (Fig. 6b). In general, the covalency of bonds in α_2 -Ti₃Al is higher than in α -Ti due to the presence of Al, which leads to higher E^f values in the alloy. The mechanical contribution to the defect formation energy for C as well as Fe, Co, Al, Ga [15] correlates with the change in the volume of the Voronoi polyhedron in both studied materials, but for the same $|\Delta V_V|$ the MC contribution in the alloy is higher (Fig. 8). It can be seen that the slope of the trend line for the α_2 -Ti₃Al alloy ($0.65 \text{ eV}/\text{\AA}^3$) is almost twice as large as that for α -Ti ($0.36 \text{ eV}/\text{\AA}^3$), indicating higher rigidity of the alloy. The latter is consistent with the higher Young's modulus of the alloy (185 GPa [38]) compared to the metal (113 GPa [39]). The correlation coefficients for titanium and the alloy are 0.92 and 0.90, respectively.

Constructing a similar graph for the CC contribution is significantly more difficult, since it is determined by several factors, including charge transfer, which explained well the observed trends in the case of non-metallic impurities (O, H, B, C) [40, 41]. In addition, the appearance of aluminum near the defect leads to an increase in its formation energy along with an increase in the strength of the bonds, which should lead to a decrease in the diffusion coefficient.

TABLE 3. The defect formation energy (E^f), the mechanical (MC) and chemical (CC) contributions to this energy, the changes in the Voronoi volume (ΔV_V) of the interstices due to carbon atom incorporation, charge state of carbon atom (q), interatomic distance between carbon and nearest titanium/aluminum atoms (d), overlap population of these bonds (θ), integrated crystal orbital Hamilton population ($-\text{ICOHP}$). In the case of substitutional defect subscripts “*in*” and “*out*” indicate position of C and Ti/Al atoms in the same (0001) plane and adjacent planes

Site	E^f , eV	MC , eV	CC , eV	ΔV_V , Å ³	q , el.	d , Å		θ , el.		$-\text{ICOHP}$, eV	
						C–Ti	C–Al	C–Ti	C–Al	C–Ti	C–Al
$O1$	−1.40	0.14	−1.54	+0.83	−1.35	2.10	–	0.26	–	3.87	–
$O2$	−0.22	0.16	−0.38	+0.61	−1.08	2.07	2.04	0.55	0.51	4.10	3.40
$C2$	0.87	1.74	−0.87	+1.30	−1.09	1.97	1.92	0.66	0.62	5.20	4.33
$Cb1$	0.98	1.59	−0.61	+0.55	−1.15	1.91	–	0.66	–	5.22	–
$Cb2$	0.99	1.68	−0.69	+1.07	−1.12	1.94	1.92	0.69	0.61	5.49	4.33
H_{O1}	1.61	1.08	0.53	+2.02	−1.10	1.96	–	0.67	–	5.59	–
H_{O2}	2.29	1.30	0.99	+2.22	−0.92	2.00	1.91	0.62	0.63	5.39	4.80
H_{T1}	1.95	0.91	1.04	+0.25	−0.87	1.93	–	0.65	–	5.79	–
H_{T2}	1.27	1.15	0.15	+1.88	−1.07	1.99	1.94	0.63	0.60	4.95	4.28
$S1$	3.30	0.51	2.79	−2.15	−0.87	2.76 _{in} , 2.72 _{out}	–	0.18 _{in} , 0.20 _{out}	–	1.36 _{in} , 1.49 _{out}	–
$S2$	2.89	0.56	2.33	−2.71	−0.97	2.26 _{in} , 2.42 _{out}	3.11 _{in} , 3.45 _{out}	0.42 _{in} , 0.33 _{out}	0.09 _{in} , 0.05 _{out}	3.33 _{in} , 2.63 _{out}	0.28 _{in} , 0.10 _{out}

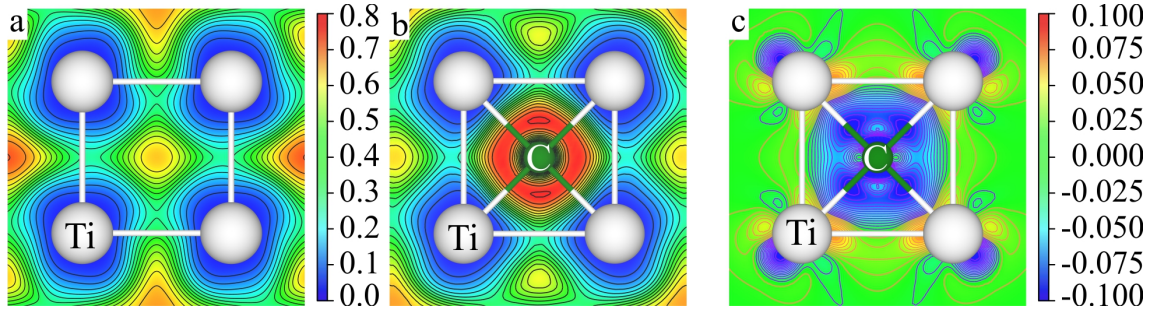


FIG. 7. ELF in ideal α_2 -Ti₃Al (a) and near the carbon interstitial atom (b) as well as $\Delta\rho$ (c) at the $O1$ -site

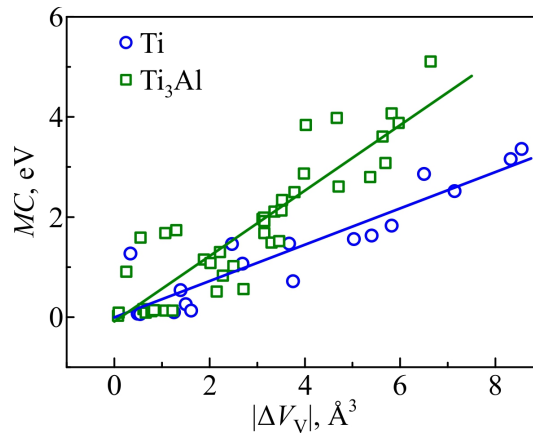


FIG. 8. Correlation between the mechanical contribution to the interstitial defect formation energy and the change in the modulus of the Voronoi volume of corresponding interstices in α -Ti and α_2 -Ti₃Al

The possible migration paths between stable positions are shown in Fig. 9, 10. It is seen that there are several migration paths along the $[0001]$ direction. There are the paths from preferable $O1$ and $O2$ sites: direct ones $O1 \rightarrow O1$ and $O2 \rightarrow O2$ with H_{O1} and H_{O2} saddle points, indirect ones $O1 \rightarrow Cb1 \rightarrow O1$, $O2 \rightarrow Cb1 \rightarrow O2$ and $O2 \rightarrow Cb2 \rightarrow O2$ (Fig. 9a). There are also path without any O sites, this is $C2 \rightarrow Cb1 \rightarrow C2 \rightarrow Cb2 \rightarrow C2$ (Fig. 9b). It should be noted that only such a long path satisfies translation invariance. Diffusion along basal plane (0001) can pass through $O1$ and $O2$ sites – $O1 \rightarrow O2 \rightarrow O1$, $O2 \rightarrow C2 \rightarrow O2$ and $O1 \rightarrow C2 \rightarrow C2 \rightarrow O1$ (Fig. 10a), as well as bypassing them – $Cb1 \rightarrow Cb1 \rightarrow Cb2 \rightarrow Cb2 \rightarrow Cb1$ (Fig. 10b). Migration through positions H_{T1} and H_{T2} only results in an increase in the number of jumps, so these positions should not be considered as intermediate ones. Nevertheless, H_{T2} -site can be considered as initial one for a diffusion path $H_{T2} \rightarrow Cb2 \rightarrow Cb2 \rightarrow H_{T2}$ (Fig. 10b). The migration energies and the attempt frequencies for all possible carbon atom jumps are given in Table 4.

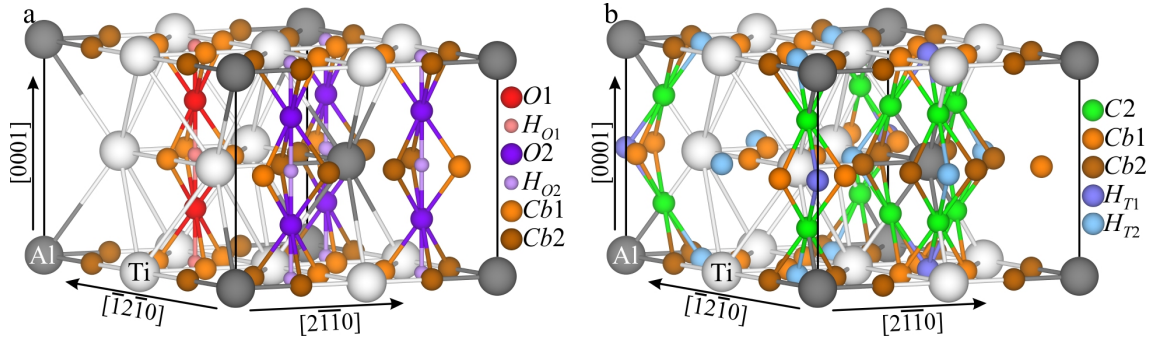


FIG. 9. Migration paths in the α_2 -Ti₃Al alloy oriented along the $[0001]$ direction and passing through octahedral sites (a) or bypassing them (b)

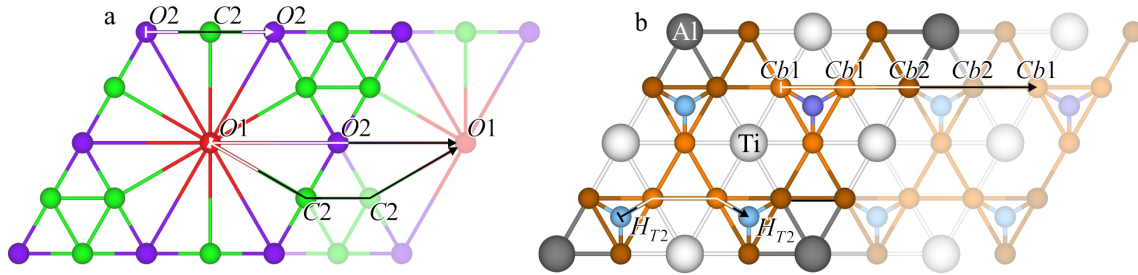


FIG. 10. Migration paths in the α_2 -Ti₃Al alloy oriented along the (0001) plane and passing through octahedral sites (a) or bypassing them (b)

According to the statistical approach, the partial diffusion coefficient for a particular path $i \rightarrow j$ has the following form:

$$D(i \rightarrow j) = F(i) \left(\frac{\mathbf{s} \cdot \mathbf{u}}{|\mathbf{u}|} \right)^2 \frac{P(i \rightarrow k_1)P(k_1 \rightarrow k_2) \dots P(k_n \rightarrow j)}{\tau(i \rightarrow k_1) + \tau(k_1 \rightarrow k_2) + \dots + \tau(k_n \rightarrow j)}, \quad (11)$$

where $F(i)$ is the probability that the initial position is occupied by an impurity atom, calculated using the formula:

$$F(i) = \frac{n(i) \exp(E^f(i))}{\sum_k n(k) \exp(E^f(k))}, \quad (12)$$

where $n(i)$ is the multiplicity of position i in the unit cell of the α_2 -Ti₃Al alloy, the summation is over all stable interstitial positions;

$\mathbf{s}$ is the displacement vector, $\mathbf{u}$ is an arbitrary vector along which the diffusion coefficient is calculated, $P(i \rightarrow j)$ is the probability of jumping $i \rightarrow j$ before all jumps from position i :

$$P(i \rightarrow j) = \frac{\Gamma(i \rightarrow j)}{\sum_k n(k) \Gamma(i \rightarrow k)}; \quad (13)$$

$\tau(i \rightarrow j)$ is the average time required for the jump $i \rightarrow j$, equal to

$$\tau(i \rightarrow j) = \frac{1}{\Gamma(i \rightarrow j)}. \quad (14)$$

The product and sum in the numerator and denominator of eq. (11) arise when diffusion is considered along a path consisting of several jumps. The resulting diffusion coefficient is the sum of all partial coefficients that contribute to

TABLE 4. Migration energies (E^m), jump length (d) and attempt frequency (ν) for all considered jumps of carbon in α_2 -Ti₃Al. The values in parentheses are given for the reverse jump

Path	$O1 \rightarrow O1 \parallel c$	$O2 \rightarrow O2 \parallel c$	$O1 \rightarrow Cb1 \parallel c$	$O2 \rightarrow Cb1 \parallel c$	$O2 \rightarrow Cb2 \parallel c$
E^m , eV	3.01	2.51	2.50 (0.12)	2.23 (1.03)	1.58 (0.37)
d , Å	2.320	2.320	1.425	1.425	1.425
ν , 10^{12} s^{-1}	14.98	13.69	22.26 (5.01)	20.99 (14.24)	17.69 (8.56)
Path	$C2 \rightarrow Cb1 \parallel c$	$C2 \rightarrow Cb2 \parallel c$	$C2 \rightarrow H_{T1} \parallel c$	$C2 \rightarrow H_{T2} \parallel c$	–
E^m , eV	0.95 (0.84)	0.31 (0.19)	1.21 (0.13)	0.95 (0.55)	–
d , Å	1.425	1.425	1.425	1.425	–
ν , 10^{12} s^{-1}	13.72 (12.89)	7.88 (6.16)	15.48 (5.07)	13.71 (10.44)	–
Path	$O1 \rightarrow O2 \parallel a$	$O1 \rightarrow C2 \parallel a$	$O2 \rightarrow C2 \parallel a$	$C2 \rightarrow C2 \parallel a$	$Cb1 \rightarrow Cb1 \parallel a$
E^m , eV	3.14 (1.96)	2.79 (0.52)	1.20 (0.11)	1.09	0.63
d , Å	2.868	2.484	1.434	1.434	1.434
ν , 10^{12} s^{-1}	12.38 (9.78)	13.48 (5.82)	15.31 (4.63)	14.59	11.08
Path	$Cb2 \rightarrow Cb2 \parallel a$	$Cb1 \rightarrow Cb2 \parallel a$	$H_{T1} \rightarrow Cb1 \parallel a$	$H_{T2} \rightarrow Cb1 \parallel a$	$H_{T2} \rightarrow Cb2 \parallel a$
E^m , eV	1.30	0.31 (0.30)	0.13 (1.10)	0.02 (0.31)	0.10 (0.38)
d , Å	1.434	1.434	0.828	0.828	0.828
ν , 10^{12} s^{-1}	15.92	7.77 (7.64)	8.66 (25.36)	3.49 (13.45)	7.67 (14.89)

diffusion along the considered direction. It should be noted that the diffusion coefficient values were calculated for temperatures of 900–1500 K, after that these values were approximated using the Arrhenius law.

Calculations of partial diffusion coefficients for the above-mentioned paths showed that the main diffusion channels are $O2 \rightarrow C2 \rightarrow O2$ along a -axis and $O1 \rightarrow Cb1 \rightarrow O1$ along c -axis. As a result, the activation energies for the diffusion along a and c axes are approximately equal to the sum of the relative formation energy and the migration energy, i.e. $E^f(O2) - E^f(O1) + E^m(O2 \rightarrow C2)$ and $0 + E^m(O1 \rightarrow Cb1)$, respectively, and the diffusion coefficient D_a and D_c can be written as follows:

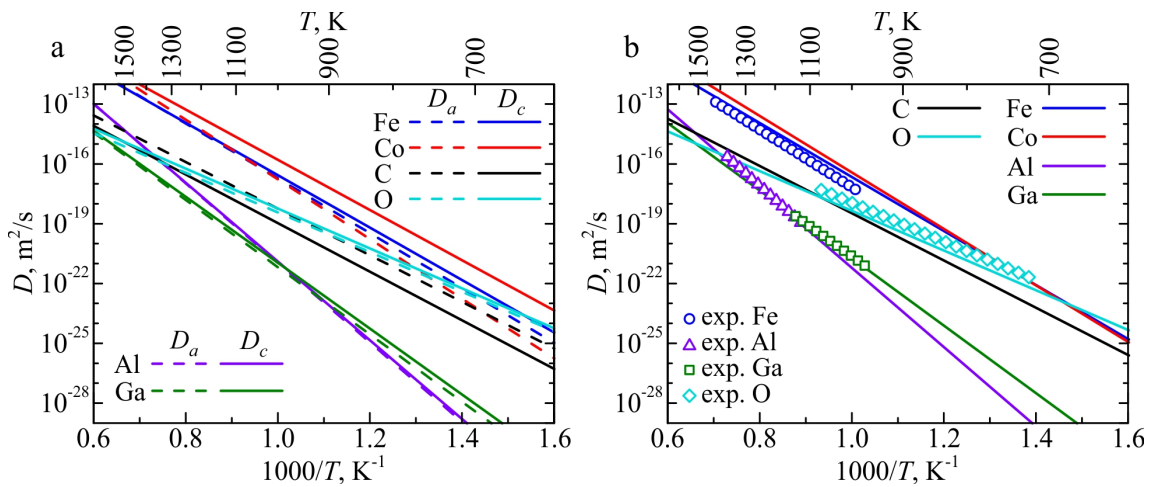


FIG. 11. Single-crystal (a) and polycrystalline (b) diffusion coefficients of carbon in α_2 -Ti₃Al in comparison with our earlier calculations for Fe, Co, Al, Ga [16] and O [36] as well as experimental data for Fe [6], Al [7], Ga [8] and O [10]

$$\begin{aligned}
 D_a &= 2.79 \cdot 10^{-7} \exp\left(-\frac{2.32}{k_B T}\right) \text{ m}^2/\text{s}, \\
 D_c &= 1.68 \cdot 10^{-7} \exp\left(-\frac{2.42}{k_B T}\right) \text{ m}^2/\text{s}.
 \end{aligned}
 \tag{15}$$

The Arrhenius plot for the single-crystal diffusion coefficients of carbon in the α_2 -Ti₃Al alloy in comparison with those for other impurities obtained previously in [16, 36] are shown in Fig. 11a. It is seen that carbon, like oxygen, is characterized by lower activation energies than that of metal impurities. At temperatures 700 to 1300 K both nonmetals diffuse faster than normal diffusers (Al, Ga) and slower than anomalous ones (Fe, Co). The carbon diffusion anisotropy (D_c/D_a) is 0.17–0.27 for the temperatures of 900–1500 K. It is interesting that the ratio $D_c/D_a < 1$ is valid only for carbon among the impurities shown in Fig. 11a and the same diffusion anisotropy was found for carbon in α -Ti (Fig. 4b). To the best of our knowledge, there are no experimental or theoretical data on carbon diffusion in the α_2 -Ti₃Al alloy; however, the polycrystalline diffusion coefficients of Fe, Al, Ga and O that we calculated earlier [16, 36] are in good agreement with the experimental data (Fig. 11b), which allows us to hope that the results obtained for carbon are correct. Finally, it should be noted that although the general trend in the diffusion coefficients of the above-mentioned elements in α_2 -Ti₃Al is the same as in α -Ti, the values are several orders of magnitude lower. This is consistent with experimental data and is explained by higher values of both the defect formation energy in the alloy and the migration barriers.

4. Conclusion

In this work, a comparative *ab-initio* study of carbon diffusion in α -Ti and α_2 -Ti₃Al was performed using the combination of density functional theory and transition state theory. Octahedral interstitials were found to be the most energetically favored positions in both materials, mainly due to the mechanical (in α -Ti) and chemical (in α_2 -Ti₃Al) contributions to defect formation energy. Moreover, in the alloy carbon prefers the Ti local environment. The presence of Al significantly increases the interstitial defect formation energy, which is directly attributed to the higher rigidity of the alloy compared to pure titanium. This also induces higher migration barriers, slowing down the carbon diffusion in the alloy by several orders of magnitude. At the same time, in both materials carbon diffuses faster than normal diffusers (Al and Ga) and slower than anomalously fast *d*-metal impurities (Fe and Co) and $D_c/D_a < 1$. In the case of α -Ti the calculated temperature-dependent diffusion coefficients demonstrate good agreement with available experimental and theoretical data. In general, the obtained results provide insight into the atomic diffusion of interstitial impurities, offering a theoretical basis for predicting the improvement of thermal stability of coatings and creep resistance of titanium aluminide-based aerospace materials.

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