Influence of carbon on energetics, electronic structure, and mechanical properties of TiAl alloys

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Abstract
We present first-principles calculations of carbon-doped TiAl alloys. The effect of carbon on the structural, electronic, and elastic behavior of the γ phase (L10 structure) of TiAl is investigated. The calculated enthalpy of formation at zero temperature indicates that carbon atoms favor to occupy rather interstitial than substitutional positions. The computed solubility of carbon in the stoichiometric γ phase is very low, in agreement with experimental findings. However, it is significantly enhanced for the Ti-rich alloy and when located inside Ti6 octahedra. Mechanical properties such as Cauchy pressure, elastic anisotropy, Young’s modulus, as well as Pugh and Poisson ratios of stoichiometric and off-stoichiometric compositions are analyzed as a function of carbon concentration and its location. As a general trend, we obtain that below a concentration of 3 at.%, carbon plays a minor role in changing the ductile behavior of γ-TiAl. A slight increase in ductility is found in the Ti-rich γα phase if either located in the Ti-plane (Ti4Al2 octahedral site) or in a Ti6 octahedra.

1. Introduction

TiAl alloys have been used in the last decades as structural materials at elevated temperatures, particularly for applications in gas turbines or in aerospace and automotive industries [1, 2]. They were intended to substitute conventional steels and Ni superalloys due to their attractive properties, such as very low density as well as high specific strength, stiffness, creep resistance, and oxidation resistance [1, 2]. The two main phases of TiAl are the tetragonal γ phase (labeled L10) and the hexagonal α2 phase (labeled D019). Like many other intermetallic phases, γ-TiAl alloys suffer from poor ductility as well as creep and oxidation resistance at temperatures above 1000 K. These shortcomings are even more pronounced for single-phase alloys based on the α2 phase. Alloying this phase by Nb, Mo, and other transition elements, leads to increased ductility and strength. However, alloying by elements like Si—which is needed for increasing oxidation resistance—deteriorates many of the advantageous properties of TiAl alloys [3].

Two-phase α2/γ-TiAl alloys exhibit much better mechanical properties than single-phase systems. The room-temperature ductility is sufficient, the toughness is increased, and the creep resistance is superior [4]. Unlike single-phase γ alloys, two-phase α2/γ ones do not suffer from the anomalous temperature dependence of yield stress which is characteristic for intermetallic alloys [5]. The increase of ductility in two-phase systems could be related both to α2/γ interfaces [1, 6] and to alloying elements, whose solubility can be much enhanced due to the lamellar structure of the α2/γ phases [1].

Even though the industrial utilization of TiAl alloys relies on the lamellar α2/γ structure, many theoretical and experimental investigations are dealing with single-phase γ or α2 TiAl for better understanding their behavior. Among these studies, we quote the investigation of solutes partitioning into γ and α2 phases [7], changes of c/a ratio and elastic properties with alloying by transitional elements (e.g. Mo,
W, Zr) [8, 67, 68], elasticity under pressure [9], as well as oxidation resistance and protective coatings hardening [10–12]. Concerning the mechanical properties of single phases, theoretical studies addressed the effect of alloying on cleavage strength [13] and to the stress–strain behavior [14, 15]. All above studies were related to the pure single phases or single phases alloyed by transition elements, their stability summarized in reference [74] and references therein.

It is commonly believed that alloying by substitutional elements may decrease the anisotropy of the electron distribution and, hence, increase the ductility of the alloy at room temperature [3]. A similar effect might be achieved by alloying the single phases ($\gamma$ or $\alpha_2$) with interstitials like B, C, O, and N. Several studies show a beneficial role of carbon additions in TiAl for mechanical properties at room and elevated temperatures [20, 71–73]. Available experiments give no clear answer to how large the solubility of C in the single phases is. Indeed, some experimental studies report an extremely low solubility of C and O, amounting to 150 and 260 ppm, respectively [16–18]. On the other hand, results of other investigations showed a C content in $\gamma$-TiAl up to 1 at.% [19], and even a carbon concentration as high as 2 at.% [20].

Recently in off-stoichiometric Ti–Al–Ta, a solubility of N up to 0.45 at.% was detected, while further increase of the N-concentration (up to 2 at.% led to formation of Ti$_3$AlN [69].

In carbon-doped TiAl alloys, a crucial role seems to be played by the appearance of the hexagonal Ti$_2$AlC structure (often referred to as H-phase), which acts as a limiting factor for the solubility. Nevertheless, it is still unclear why the solubility of interstitials is higher in $\alpha_2$ TiAl than in the $\gamma$ phase [18]. A possible explanation is provided by the occupation of octahedral cavities by interstitial elements. Indeed, in carbides and nitrides, C and N atoms are surrounded by six Ti atoms [21]. Similar situations can be found in the D0$_{19}$ structure of the $\alpha_2$ phase, where octahedral sites with a Ti$_6$-like and Al$_2$Ti$_4$-like configurations of the nearest neighbors are present. However, in the $\gamma$ phase, where the coordination of Ti atoms is lower, only the Al$_2$Ti$_4$-like and Ti$_2$Al$_1$-like octahedral sites are formed.

There is a number of ab initio investigations dealing with carbon-doped TiAl systems, i.e., electronic-structure calculations of TiAl with substitutional and interstitial C [22]. However, neither the energetics of carbon in different octahedral configurations nor the effect of C on elastic properties has been quantitatively determined. A number of studies deal with carbon as a main constituent of P- and H-perovskite precipitate phases, investigating structure, electronic structure, bulk moduli, elastic constants, and cohesive energies [24–27].

In this work, we address several questions dealing with the role of carbon in $\gamma$-TiAl: why is the solubility of carbon so low? What is the preferred location of C? Can carbon in concentrations as low as the real ones still affect elastic properties? What is the role of local disorder on heat of formation and the elastic behavior?

The paper is organized as follows. In section 2 we describe the used methodology. Section 3.1 is devoted to the study of structural changes of $\gamma$-TiAl with interstitial C, and the effect of these changes on its electronic structure, elastic behavior, and mechanical properties. Section 3.2 deals with the structural and elastic properties of substitutional carbon, while section 3.3 presents results for a variant of the $\gamma$ phase containing Ti$_6$ octahedra. Section 3.4 deals with the energetics of all considered structures, and concluding remarks are drawn in section 4.

2. Methodology

All ab initio calculations presented in this work have been performed within density-functional theory (DFT) using the projected augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [28]. The gradient corrected exchange–correlation functional parametrized by Perdew–Burke–Ernzerhof [29] was employed. A plane wave cutoff of 480 eV was used for most properties including geometry optimization, whereas for the calculation of the stress tensor the cutoff needed to be increased up to 1200 eV. Atoms were represented by PAW pseudopotentials provided by VASP with the 3p$^4$4s$^2$3d$^3$, 3s$^2$2p$^1$, and 2s$^2$2p$^2$ valence electronic configuration for Ti, Al, and C atoms, respectively.

The Brillouin zone was sampled using Γ-centered Monkhorst–Pack grids of the following (almost) equivalent points of different supercell sizes: a $20 \times 20 \times 20$ k-point mesh for the tetragonal TiAl unit cell with 4 atoms, a $30 \times 30 \times 6$ mesh for the hexagonal phase of Ti$_2$AlC with 8 atoms in the unit cell, and a $28 \times 28 \times 13$ mesh for the rhombohedral Al$_4$C$_3$ supercell with 21 atoms (in hexagonal settings). The partial occupancies were determined using the Methfessel–Paxton method [30] using a smearing width of 0.1 eV. A combination of conjugate-gradient energy minimization and a quasi-Newton force minimization was employed to optimize the geometry and atomic positions of the supercells. Atomic positions were relaxed until the forces were smaller than $10^{-4}$ eV Å$^{-1}$; total energies were converged within $10^{-6}$ eV.

In order to test the reliability of the chosen parameters, calculations were performed for pure $\gamma$-TiAl using supercells of different sizes. Deviations in the total energy for the optimized configurations were less than 0.4 meV atom$^{-1}$; fitting the third-order Birch–Murnaghan equation of state [41] to the
energy–volume curves for a four-atom-basis $\gamma$-TiAl with optimized $c/a$ ratio, we obtained the lattice constants $a = 3.993$ Å and $c/a = 1.020$. Very similar values were calculated by fully optimizing supercells containing 16, 32, 54, 108, 128, and 256 atoms. The maximum deviation in the total energy was less than 0.75 meV per formula unit (f.u.) for the largest supercell (256 atoms). We note that at the investigated concentrations, the C–C distances in the Cartesian directions are unequal. However, this does not affect our results, as the valence charge density at the unit-cell boundary differs by less than $10^{-4}$ from its counterpart in the pristine material. Overall, the calculated values of $a$ and $c$ are in very good agreement with both experiments ($a = 3.976$ to 4.00 Å and $c/a = 1.016$ to 1.023) [32–34] and previous first-principles studies ($a = 3.901$ to 3.96 Å and $c/a = 1.01$ to 1.037), calculated by pseudopotential [35, 36] and all-electron [37] methods, respectively.

3. Results and discussion

3.1. Interstitial carbon in the $\gamma$ phase

3.1.1. Structural effects

The two possible octahedral positions of interstitial carbon in $\gamma$-TiAl are depicted in figure 1. In the first case (left panel), the C atom is located in the Al plane. The surrounding octahedron is formed by 4 Al and 2 Ti atoms. This configuration will be denoted in the following as $\gamma + C_{Al}$. In the second case (right panel), the C atom is situated in the Ti plane ($\gamma + C_{Ti}$), and the octahedron is formed by 4 Ti and 2 Al atoms.

The influence of C on the lattice was studied by fully relaxing the unit cell for different C concentrations and C located on both possible interstitial sites. It turned out that the tetragonal symmetry of the unit cell is preserved upon addition of carbon, and no distortion of the lattice vectors occurred. As shown in figure 2, the volume change as a function of the carbon concentration exhibits a linear behavior (Retger’s law) [75] if the concentration is less than 6 at. %.
Figure 3. Lattice constant $a$, in units of Å, of $\gamma$-TiAl as a function of carbon concentration, for C located in the Al plane (solid line) and Ti plane (dashed line), respectively. The green crosses indicate experimental values from reference [20]. Note the logarithmic scale of the $x$-axis.

Figure 4. $c/a$ ratio of $\gamma$-TiAl as a function of carbon concentration, for C located in the Al plane (solid line) and Ti plane (dashed line), respectively. The green crosses indicate experimental values from reference [20]. Note the logarithmic scale of the $x$-axis.

Trends of the lattice parameters $a$ and $c/a$ as a function of carbon concentration are shown in figures 3 and 4, respectively. Obviously, at both interstitial positions, the lattice constant $a$ of the pure $\gamma$ phase is approached with decreasing concentration of C. However, different behavior is found for the two kinds of octahedral sites. As seen in figure 3, for carbon within the Al plane ($\gamma + C_{\text{Al}}$), the lattice constant $a$ is very similar to that of the pure $\gamma$ phase for a range of concentrations up to about 6 at.%. In contrast, the presence of a C impurity in the Ti plane ($\gamma + C_{\text{Ti}}$) expands the lattice constant $a$ to a significant extent starting from 2 at.%. The variation of $c/a$ as a function of carbon concentration is shown in figure 4. For the $\gamma + C_{\text{Ti}}$ case, the expansion of $a$ is accompanied by a reduction of $c/a$. In contrast in the case of C in the Al plane, the $c/a$ increases considerable in the range from 2–6 at.% of C, while getting slightly smaller for 20 at.%. A corresponding experimental study of carbon-doped TiAl has been reported in reference [20]. This work, however, refers to the non-stoichiometric alloy Ti_{0.52}Al_{0.48} with a lamellar structure of both $\gamma$ and $\alpha_2$ phases. For the sake of comparison, these results (indicated by crosses) are also depicted in figures 3 and 4. Apparently, the experimental data are closer to our results for C in the Al plane (solid line) than to the ones for C in the Ti plane (dashed line).

3.1.2. Electronic properties
In order to characterize the electronic structure of $\gamma$-TiAl with C in both interstitial positions, we analyze the total densities of states (DOS) as well as the charge-density distribution in the crystal planes containing carbon atoms. In figure 5, the total DOS is plotted for C concentrations of 20 at.% (upper panel) and 0.9
Figure 5. Total density of states of $\gamma$-TiAl for two C concentrations, with the interstitial carbon in the Al plane (solid line) and the Ti plane (dashed line), respectively. For comparison, the DOS of the pure $\gamma$ phase is shown (dash-dotted line). The Fermi level is set to zero and denoted by a vertical line. The DOS in both panels is normalized to 2 formula units.

Figure 6. Total DOS at the Fermi level (in states per eV, normalized to two formula units; upper panel) and valence-band width (in eV; lower panel) as a function of C concentration, with the interstitial carbon in the Ti plane (solid line) and Al plane (dashed line), respectively. Note the logarithmic scale of the x-axis. The dash-dotted line corresponds to pure $\gamma$-TiAl and serves as a reference.

at.% (lower panel). For comparison, the total DOS of pure $\gamma$-TiAl is indicated by a dot-dashed line in both panels. The total DOS of the $\gamma$ phase with 20 at.% C resembles the results of Matarand co-workers [22], which were obtained by the linear muffin-tin orbital method. For the higher carbon concentration, the DOS in the vicinity of the Fermi level is more affected, i.e. stronger hybridization occurs between C and Ti/Al atoms.

In figure 6, the DOS at the Fermi level (upper panel) and the valence-band width are shown as a function of carbon content (lower panel). Below 1%, both quantities are practically the same as those of the pure $\gamma$ phase (see also lower panel of figure 5). The DOS at $E_F$ oscillates around that of the pure $\gamma$ phase, approaching it at low C concentrations. For high carbon content, the width of the top occupied band is less affected when carbon is in the Al-plane. This supports previous results that the more directional and stronger bonding occurs among carbon and Ti-atoms ($T_4A_2$ octahedra) and is manifested by narrowing the top valence band.

To analyze the influence of carbon further, the difference in charge density between the cells with $(\rho_{TiAl+C})$ and without carbon $(\rho_{TiAl})$, $\Delta \rho = \rho_{TiAl+C} - \rho_{TiAl}$, is depicted in figure 7 for 20 at.% carbon being either located in the Al plane or Ti plane. Let us first consider the (100) plane (figure 7, left side): In the case of of C in the Al plane (upper panel), a filling of the the $d_2^*$ orbitals (not shown) of the Ti atoms in the corner, pointing along $z$, is encountered, together with a pronounced charge accumulation between the Ti atoms along $z$ (left and right edges of the plot). Both features clearly indicate a strengthening of the bonds.
in $z$ direction. Considering the region between Ti atoms along $y$ (top and bottom edge), only a small increase is seen. Interestingly, the Al atom in the center, which is the nearest neighbor of carbon, is not affected at all by its presence. The picture is completely different for C in the Ti plane (lower panel): a kidney-shaped charge accumulation around the Ti atom in the center is found, indicating that its $d_{x^2-y^2}$ orbitals (not shown) are getting filled. This goes along with a general increase in charge density above and below the Ti atom along the $z$ direction. No increase in charge density is found between the Al atoms along $z$ (left and right edge of the left figure). In contrast, the charge density between Al atoms along $y$ increases (top and bottom edge), indicating a stiffening of the bonds in this direction.

Let us now turn to the (002) plane, i.e., the one where the C atom is located (figure 7, right side). First of all, in contrast to the case where C is in the Al plane (upper panel), for C in the Ti plane (lower panel) the change in charge distribution is rather asymmetric. In fact, it shows a spike pointing from C to the Ti atoms, manifesting the formation of Ti–C bonds. Second, for C in the Ti plane, a dumbbell shaped increase of charge density along the edges of the plot is seen, which indicates a filling of the $d_{x^2-y^2}$ orbitals. Conversely, the region around the Al atoms (upper panel), does not show any increase in charge density. This means, that the bonding in $x$ direction is enhanced by C in the Ti plane, but is hardly affected by carbon in the Al plane.

3.1.3. Elastic behavior
In this section, the influence of interstitial carbon on the elastic constants is analyzed and discussed. The elastic constants are derived from stress–strain relations using the methodology by Yu et al [39] In order to get reliable results, both negative and positive distortions are considered. For high carbon concentrations in the pure gamma phase, we compare the elastic constants obtained from stress–strain relations to the ones derived from the second derivative of the total energy [48–50]. Both approaches lead to very similar results, differing by less than 2% for the single elastic constants.
The insertion of interstitial elements typically affects lattice parameters and chemical bonds in the host material, and, as a consequence, also the mechanical properties. The elastic constants as a function of C concentration, together with experimental results [40] for pure γ-TiAl, are summarized in Table 1.

The pure γ phase of TiAl is overall well described by our calculations. Significant deviations from experiment are only found for $C_{12}$ and $C_{66}$, amounting to about 20%. Similar differences were encountered in another theoretical work [9]. The bulk modulus can either be obtained as a function of total energy vs volume or using the elastic constants according to $B = (2C_{11} + 2C_{12} + 4C_{13} + C_{33})/9$ [48]. The values obtained with the two approaches differ by about 1 GPa only. The bulk modulus increases with C content for the phases with an interstitial C atom, suggesting an increase of the bonding strength. This effect is more pronounced for carbon positioned within the Ti plane, since here the C–Ti atoms can more easily hybridize with Ti 3$d$ states.

In the following, we examine in more detail Table 1. If not mentioned explicitly, we always refer to the case of the optimized structure. Let us first consider the results for 20 at.% C, where a few observations can be made:

(a) $C_{11}$ is strongly increased by carbon in the Ti plane, while $C_{12}$ is slightly decreased.
(b) The presence of C in the Al plane does not affect $C_{11}$. We assign this behavior to the strong Ti–Al bonding (Al$_7$Ti$_2$ octahedra) that is not altered by C lying in the Al plane.
(c) $C_{12}$ gets much stiffer upon adding carbon, where it has stronger impact in the Al plane than in the Ti plane. In the former case, C interstitials interact with the Ti atoms in adjacent layers above and below, forming a Ti–C bond along the z direction, as already shown in figure 7.
(d) $C_{44}$ and $C_{66}$ are clearly lower than in the pure γ phase, and they are twice as large in the case of C positioned in the Ti plane compared to the case of C in the Al plane. This behavior corresponds to the directional bonding between Ti and C, as it was already proposed in a number of publications [9, 14, 15, 23, 42].

Let us focus now on the results for lower carbon concentrations. There are two major trends (the same ones as in the γ phase):

(a) Carbon concentrations below 3% do not alter significantly the elastic constants of the γ-phase. At 3 at.% C, the only increased values are found for the shear resistance, i.e., $C_{12}$ for γ + C$_{Ti}$ and $C_{13}$ for γ + C$_{Al}$.
(b) $C_{66}$ is high along the direction of C–Ti atoms, i.e., $C_{11}$ for γ + C$_{Ti}$ and $C_{13}$ for γ + C$_{Al}$, respectively. These values naturally decrease with lower carbon concentration. So, the decisive bonding here is the hybridization between carbon and titanium atoms which, at higher C concentrations, alters the bond strength and hence mechanical properties.

At a carbon content of 5.88%, $C_{66}$ — the elastic constant associated with the shear between carbon-containing and carbon-free planes—shows a strong decrease for carbon located at both positions. At a content of 3.03 at.% C, $C_{11}$, $C_{12}$, and $C_{66}$ show almost negligible differences to the corresponding values of the pure γ phase. Also $C_{11}$ and $C_{13}$ are unaffected when C is located in the Ti plane.

Let us finally also compare our bulk moduli of the γ phase with C interstitials with those where carbon atoms form a carbide or a stable precipitate in the Ti–Al system. Going from the highest to the lowest value for $B$ one finds: 270 GPa for TiC [27], 185 GPa for Ti$_3$AlC [24], 169 GPa for Ti$_2$AlC [27], and 130 GPa for Al$_4$C$_3$ [43]. It appears that a high bulk modulus is related to a high content of Ti atoms within the structure.

| at.% C | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ | $B$ |
|--------|---------|---------|---------|---------|---------|---------|-----|
| 0.0    | 183 74  | 178 105 | 78 113  |         |         |         |     |
| Theory, C$_{Al}$-plane | 0.0 | 174 90  | 174 111 | 69 113  |         |         |     |
| 3.0    | 176 85  | 187 105 | 69 114  |         |         |         |     |
| 5.9    | 172 81  | 205 97  | 45 114  |         |         |         |     |
| 20.0   | 171 124 | 309 44  | 129     |         |         |         |     |
| Theory, C$_{Ti}$-plane | 0.0 | 174 90  | 174 111 | 69 113  |         |         |     |
| 3.0    | 172 91  | 172 106 | 64 116  |         |         |         |     |
| 5.9    | 172 81  | 186 105 | 34 118  |         |         |         |     |
| 20.0   | 294 68  | 265 87  | 63 143  |         |         |         |     |
as already found in reference [27]. From our results, we find a simple relation: the bulk modulus of phases where carbon is located at interstitial positions is lower than in the case where carbon leads to the formation of intermetallic compounds where it is more strongly bound.

### 3.1.4. Mechanical stability and ductility

Based on the calculated elastic constants and the analysis of the charge-density, we predict a change of the mechanical stability and ductility (brittleness) of γ-TiAl upon carbon doping. In order to be stable against any homogeneous elastic deformation, a crystalline material has to fulfill stability conditions with respect to its symmetry [51]. Considering tetragonal systems, the elastic constants $C_{11}$, $C_{33}$, $C_{44}$, and $C_{66}$ must be positive, and $C_{11} > C_{12}$. Such criteria are satisfied by both the pure and C-alloyed γ-TiAl phases as is evident from table 1. More restrictive conditions suggested by Beckstein and co-workers [49] are the following:

$$S_1 = C_{11} + C_{33} - 2C_{13} > 0$$

$$S_2 = 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0$$

$$S_3 = (2C_{11} + C_{33})/3 > B$$

As can be seen in table 2, all three stability conditions are fulfilled for both interstitial sites of C, for any concentration considered here (20 at.%, 5.88 at.%, and 3.03 at.% C). Indeed, the corresponding values are in most cases even higher than those for pure γ-TiAl, and they increase with carbon concentration.

The elastic anisotropy [52] tells us about the system’s shear resistance, i.e., the energy change in a crystal associated with the shear modes along different slip directions. There are three elastic anisotropy ratios in tetragonal systems, defined as:

$$A_1 = 2C_{66}/(C_{11} - C_{12})$$

$$A_2 = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$$

$$A_3 = C_{44}/C_{66}.$$
and the degree of covalency, i.e., directionality of bonding. Similarly, the ductile behavior was proposed to be related to the so-called Cauchy pressures \[58\]. Even though the Cauchy relations were questioned \[56\], they are still widely used a material’s ductility. For tetragonal systems, the Cauchy pressures are defined as:

\[
\text{Positive or negative values of } C_1 \text{ and } C_2 \text{ indicate ductile or brittle behavior, respectively. Measured elastic constants suggest brittle behavior of the } \gamma \text{ phase at room temperature (see table 3). In contrast to this, but in agreement with other calculations } [9, 37], \text{ we find } C_1 \text{ positive (} T = 0 \text{ K results). Note that experimentally reported values for } C_{66} \text{ and } C_{44} \text{ show a significant spread, see reference } [34] \text{ and references therein. For } C \text{ concentrations lower than 6 at.} \% \text{ } C_1 \text{ is always positive, whereas } C_2 \text{ is always negative, but less than in the pristine } \gamma \text{ phase (see table 3). For the } C \text{-alloyed } \gamma \text{ phases the values of } C_2 \text{ are less negative than those of pure } \gamma \text{-TiAl. Suprisingly, carbon contributes to a higher DOS in the vicinity of the Fermi level, thus increasing metallicity. In other words, the presence of carbon increases the ductility (see table 3).}

As an empirical rule found by Pugh \[59\], a } B/G \text{ ratio of 1.75 separates ductile } (B/G > 1.75) \text{ from brittle } (B/G < 1.75) \text{ materials. The inverse ratio } (G/B) \text{ indicates the relative degree of directional bonding, supposing that the bulk modulus corresponds to the average bond strength and the shear modulus to the resistance against changing the bond angles as discussed in reference } [38]. \text{ For macroscopic samples, one should use average values of the different single crystal shear moduli, as the polycrystalline specimen, composed of differently oriented grains, is more isotropic. To mimic such polycrystalline materials, minimum and maximum values of the elastic constants are obtained by either imposing uniform strain (Voigt notation) or uniform stress (Reuss notation), see reference } [52] \text{ and references therein. Therefore, we calculate the Voigt and Reuss bounds for shear } (G_\nu, G_R) \text{ and bulk } (B_\nu, B_R) \text{ moduli and obtain their averages } (G_{11}, B_{11}) \text{ as proposed by Hill } [60]. \text{ In the following, we always refer to the Reuss–Voigt–Hill averaged values of } B_{11}, G_{11}, E_{11}, \text{ and } A_{11}, \text{ and we define the elastic anisotropy ratio as}

\[
A_{11} = \frac{G_{11} - B_{11}}{G_{11} + B_{11}}.
\]

For the averaged quantities we also drop the indices, e.g. } A_{11} \rightarrow A, B_{11} \rightarrow B.

In table 3, we show } B/G \text{ values for different carbon concentrations. Despite the fact that the experimental } B/G \text{ value of the } \gamma \text{ phase is slightly above 1.75, TiAl is known to be brittle at ambient conditions } [1]. \text{ Our calculated results show that the } \gamma \text{ phase with } C \text{ located in the Ti-plane has a } B/G \text{ ratio above the one of the pure } \gamma \text{ phase, while for the material with } C \text{ located in the Al-plane it is converse. For 3.03 at.} \% \text{ carbon content, the } G/B \text{ ratios are similar to pure } \gamma \text{-TiAl if } C \text{ is located in the Al-plane, but higher if } C \text{ is in the Ti-plane, reflecting the higher degree of hybridization with the four neighboring Ti atoms and an increase of ductility } [34]. \text{ The elastic anisotropy ratio } A, \text{ with } G \text{ and } B \text{ as obtained by Hill’s approximation } [60], \text{ becomes lower as the } C \text{ concentration is decreased. At 3.03 at.} \%, \text{ } A \text{ is lower (higher) when } C \text{ is in the Al-plane (Ti-plane). The last columns of table 3 summarize the results for the Poisson ratio, } \nu, \text{ and the Young modulus, } E. \text{ The trends for the lowest } C \text{ concentration are clearly independent of the carbon location. Lower values of } E \text{ and } G \text{ and higher } \nu \text{ correlate with weaker and less directional interatomic bonding, and hence with an increase of ductile behavior } [62]. \text{ This is the case for interstitial } C \text{ located in the Ti-plane.}

The effect of carbon on the elastic constants can be compared to alloying by transition elements. In the work of Music and Schneider [8], it is shown that the bulk modulus and } C_{44} \text{ are only slightly increased.

Table 3. Cauchy pressures } (C_1 \text{ and } C_2), \text{ Hill’s averaged ratio } (B/G), \text{ elastic anisotropy } (A), \text{ Poisson ratio } (\nu), \text{ and Young modulus } (E) \text{ for polycrystalline carbon-alloyed } \gamma \text{-TiAl. } C_1, C_2, \text{ and } E \text{ are given in GPa.}

| at.% \text{ C} | C_1 | C_2 | B/G | A | \nu | E |
|---|---|---|---|---|---|---|
| Experiment | 0.0 | 3.9 | -31 | 1.84 | 0.325 | 0.270 | 156 |
| Theory, C_{Al-plane} | 0.0 | 21 | -30 | 2.07 | 0.387 | 0.292 | 141 |
| | 3.0 | 16 | -25 | 2.06 | 0.358 | 0.291 | 132 |
| | 5.9 | 26 | -24 | 2.00 | 0.276 | 0.286 | 149 |
| | 20.0 | 5 | -22 | 3.7 | 0.439 | 0.376 | 96 |
| Theory, C_{Ti-plane} | 0.0 | 21 | -30 | 2.07 | 0.387 | 0.292 | 141 |
| | 3.0 | 28 | -20 | 2.23 | 0.385 | 0.305 | 136 |
| | 5.9 | 19 | -25 | 1.96 | 0.282 | 0.282 | 154 |
| | 20.0 | 90 | 26 | 1.84 | 0.208 | 0.270 | 19 |
Figure 8. Change of lattice parameter $a$ and $c/a$ ratio as a function of carbon concentration for substitutional carbon. Solid red and dashed black line correspond to substitution of Al and Ti, respectively. The dash-dotted green line denotes the case of a Ti$_6$ octahedron surrounding the interstitial C. Note the logarithmic scale of the $x$-axis.

Table 4. Elastic constants of $\gamma$-TiAl with substitutional carbon (3.12 at.%) in the Al-plane ($\gamma + C_{sub}^{Al}$) and Ti-plane ($\gamma + C_{sub}^{Ti}$), respectively.

|       | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ | $B_C$ |
|-------|----------|----------|----------|----------|----------|----------|-------|
| Pure $\gamma$ | 183     | 74       | 74       | 178      | 105      | 78       | 113   |
| $\gamma + C_{sub}^{Al}$ | 112     | 143      | 88       | 176      | 102      | 68       | 115   |
| $\gamma + C_{sub}^{Ti}$ | 170     | 74       | 74       | 167      | 90       | 82       | 105   |

upon alloying TiAl with 6.25 at.% of 3$d$, 4$d$, and 5$d$ metals, $C_{44}$ going from 126 to 128 GPa. However, in this work, $C_{44}$ of 126 GPa for the pure $\gamma$ phase is rather high, i.e. about 20% higher than the experimental value of Tanaka et al. [34] as well as our and other DFT results [9, 37]. Overall, we conclude that interstitial carbon has higher impact by significantly lowering $C_{44}$ (see table 1) than alloying by transition metals.

Recently, Kanchana [24] reported results for $B/G$, $E$, and $\nu$ for perovskite Ti$_3$AlC [24], with values of 1.70, 272 GPa, and 0.255, respectively. Again, the conclusion can be drawn, that if the carbon atoms are constituents of the structure the material is more brittle than the $\gamma$ phase with up to the 20 at.% of carbon atoms just located at any of the interstitial positions.

3.2. Substitutional C

There is a finite probability of C to occupy an Al or Ti site. The work of Matar and Etourneau [22] suggests that carbon prefers the Al site and stabilizes the TiAl-phase. In figure 8, we show how the calculated lattice constant $a$ and the $c/a$ ratio change upon C substitution on both sites. Again, it clearly illustrates the trend that C on an Al site does not interact strongly with the Ti and Al atoms. It slightly expands the lattice constant $a$ and makes the structure almost cubic ($c/a \approx 1$). The much stronger influence is found for Ti substitution. Here, the lattice constant is smaller (the $c/a$ ratio higher) than for the pristine phase as the carbon $sp$ states strongly hybridize with neighboring Ti atoms. Therefore, the carbon concentration has to be far below 1 at.% to have no influence.

The effect of substitutional C on the elastic properties of TiAl are summarized in table 4. The values for Al-substitution do not seem to be reasonable at first glance as, for a system with almost cubic symmetry, it is expected that $C_{11} \approx C_{33}$, $C_{12} \approx C_{13}$, and $C_{44} \approx C_{66}$. The first two relations are, on the contrary, fulfilled for C at the Ti site. So, why is this so? The reason for the surprising elastic behavior of C at the Al-site is that the Ti atoms surrounding carbon in the first two adjacent layers are unevenly shifted from their original $x$ ($y$) or $z$ positions by 1.3% and 2.7% respectively. Already in the next layer these displacements are only 0.4% and 0.7%, respectively. In contrast to this, having carbon at the Ti-site, four Ti atoms in the first coordination shell are shifted in $x$ and $y$ direction simultaneously, preserving the tetragonal symmetry. Therefore, carbon at the Ti-site (3.12 at.%) leads to an almost cubic phase (lower $a$ and $c/a \approx 1$) demonstrated by the elastic constants resembling the ones of a cubic system, except for the values of $C_{44}$ and $C_{66}$.

Substitution of Al makes $C_{12}$ and $C_{13}$ stiffer but $C_{11}$ and $C_{44}$ softer. Therefore the stability criterion $C_{11} > C_{12}$ does not hold any more, and the compound becomes inherently unstable. Substituting Ti by carbon makes $C_{33}$ and $C_{44}$ softer, while $C_{66}$ is getting much harder. Quantifying the most important changes
induced by the substituents, the elastic anisotropy ratio $A_3$ for C at the Al-site is about 40% higher than that for C at the Ti-site. We conclude this section by stating that if carbon enters the $\gamma$ phase substitutionally at the Ti site, it makes the material softer by lowering the bulk modulus and decreasing the shear modulus $C_{44}$. A substitution of carbon at the Al-site is very unlikely to be found, as the elastic constants point to an intrinsic instability of such solid.

### 3.3. Effect of Ti$_6$-octahedra formation

The first coordination shell of interstitial carbon in the regular $\gamma$ phase is composed of 4 Ti and 2 Al atoms or vice versa, see figure 1. However, in the $\alpha_2$-phase of Ti–Al alloys, the octahedral interstitial position is formed solely by 6 Ti atoms. Scheu and co-workers [31] suggested that also in the $\gamma$ phase carbon would prefer a location of complete Ti$_6$ octahedra, i.e., octahedra where the Ti atoms also occupy the two Al sites, similarly to the $\alpha_2$-phase. Moreover, they considered such arrangement to be responsible for a higher solubility of carbon in the $\alpha_2$-phase. Therefore, we investigate the influence of such a ‘local disorder’ by calculating the corresponding elastic behavior and heat of formation. Already for moderate Ti-rich concentrations, the $c/a$ ratio goes toward 1, without any effect from the carbon atom occupying an interstitial position in Ti$_6$ octahedra. This is in contrast to the situation where carbon substitutes the Ti- or Al-sites. The presence of carbon inside Ti$_6$ octahedra expands $a$ only slightly, but to a larger extent than carbon substitution of Al or Ti (see figure 8). For concentrations less than 3 at.% the compound becomes cubic (see figure 8). The elastic constants of the $\gamma$ phase containing Ti$_6$ octahedra are summarized in table 5. First, the $C_{ij}$ wrt. to the ones of pure $\gamma$ phase are softer, as the lattice expands (see lines 2 and 6 of table 1), second, by the presence of carbon (3.03 at.%) the initial elastic stiffness of the material is restored. In the precipitate compound Ti$_5$AlC the same Ti$_6$ octahedra surrounding carbon atoms exists. The elastic behavior of this phase was calculated by Kanchana [24], obtaining a $C_{44}$ of 89 GPa. This is very close to our values of $\gamma$-TiAl with 20 at.% C located in the Ti-plane (see table 1); but it is by ca. 20% lower than those of the pure $\gamma$ phase and the $\gamma$ phase with Ti$_6$ octahedra and/or very low carbon concentration. Concomitantly, Ti$_5$AlC has a bulk modulus more than 50 GPa higher ($B = 185$ GPa) than that of the $\gamma$ phase with 3.03 at.% of carbon or less (with or without Ti$_6$ octahedra). This indicates very interesting elastic behavior. The periodic occurrence of the carbon atoms in the structure increases the resistance against hydrostatic pressure (bulk modulus), but at the same time lowers the shear resistance with respect to the pure $\gamma$ phase.

The elastic constants as well as the bulk modulus of the $\gamma$ phase with incorporated Ti$_6$ octahedra indicate that this material is somewhat softer than the pristine phase (see tables 5 and 1). Occupying Ti$_6$ octahedra by carbon slightly expands $a$, where one could expect a softening of $C_{11}$ and $C_{33}$. However, our results show the opposite effect, i.e. a stiffer material with some values of $C_{ij}$ being higher by about 7–10 GPa. These values are comparable to or only slightly larger than those of the $\gamma$ phase with 3.03 at.% or less interstitial carbon, regardless of its location (see tables 5 and 1).

We conclude this section by stating that the formation of Ti$_6$ octahedra enhances the ductility of the $\gamma$ phase to the same extent as carbon alloying. No further effects by carbon located in (off-stoichiometric) Ti$_6$ or Ti$_5$Al$_2$ octahedra on the ductility are found.

### 3.4. Energetic considerations and C site-preference

#### 3.4.1. Substitutional and interstitial C in the regular $\gamma$ phase

For considerations on the energetics, we adopt the approach of chemical potentials as described in references [53] and [54]. We obtain the chemical potentials of Ti and Al from the total energies of the pure...
\( \gamma \) TiAl and \( \alpha_2 \) Ti\(_3\)Al phase, respectively, yielding \( \mu_{Ti} = -8.102 \) eV and \( \mu_{Al} = -4.399 \) eV, in accord with similar values as in reference [7]. The chemical potential of carbon, \( \mu_C \), will be treated as a variable. The stable carbides of pure Al and Ti are naturally \( Al_4C_3 \) and TiC. However, as indicated by many experiments [45, 64], aging and quenching of C-doped TiAl alloys at high temperatures (above 1000 K) yields a metastable cubic perovskite phase of Ti\(_3\)AlC and, after a longer time, a stable hexagonal phase of Ti\(_2\)AlC. Consequently, it would be these phases that are in equilibrium with the \( \gamma \)- and \( \alpha_2 \)-phases, and hence their chemical potentials should be the most relevant ones. Recently, electronic structure and mechanical properties of Ti\(_3\)AlC and Ti\(_2\)AlC were investigated from first-principles, and the phase stability of these precipitates was verified experimentally, see references [24–27].

Table 6 summarizes the experimental and calculated lattice parameters of TiC, \( Al_4C_3 \), Ti\(_3\)AlC, and Ti\(_2\)AlC, and the corresponding chemical potentials of carbon \( \mu_C \), derived from the total energies of these stable carbides using constant values for \( \mu_{Al} \) and \( \mu_{Ti} \). In order to facilitate the comparison of our results with literature data, using the chemical potentials of C derived from graphite or diamond [74], the corresponding data are also added.

In general, the thermodynamic free energy is temperature dependent. One contribution to this temperature dependence is the configurational entropy that lowers the enthalpy of formation (see equation (2) in reference [71]). Despite the fact that, at higher temperatures, the entropy term as well as the shift of chemical potentials play a role [7], for simplicity, both are omitted here. In figure 9, the enthalpy of formation is shown as a function of C concentration (as justified above the \( \mu_C \) from the Ti\(_3\)Al\(_2\)C is used here), for both interstitial positions (upper panel) and C substituting Al and Ti (lower panel). Two models are considered: solid lines correspond to a model with fully optimized geometry after insertion of or substitution by a carbon atom, while dashed lines denote the situation where the lattice constant \( a \) and the \( c/a \) ratio are fixed to the values of the pure \( \gamma \) phase, and only the atomic positions are relaxed. From figure 9 it is apparent that the C atom prefers to incorporate itself into the \( \gamma \) phase as an interstitial rather than to substitute Al or Ti atoms, as the energy scale for the former is much lower than the one for the latter. A study by Matar am co-workers [22], based on the DOS and analysis of the crystal-overlap-population, did not give a decisive answer which position C would prefer. In contrast, figure 9 clearly shows for a large concentration range that the interstitial position in the Ti-plane of the \( \gamma \) phase is preferred by about 1.5 eV compared to interstitial carbon located in the Al-plane (upper panel). However, the energy cost of incorporating the carbon atom is indeed higher than the calculated antisite energies of stoichiometric TiAl of 0.7 eV and 0.3 eV for Ti and Al sites, values being in accord with other studies [7, 37].

A work of Liu et al [70] indicates that interstitial oxygen within \( \gamma \)-TiAl increases the impurity-formation energy. Interestingly, if carbon substitutes Ti at a C concentration lower than 4 at.%, \( H_{Ti} \) is higher than in the case where Al is replaced by C, as evident from figure 9. Let us point out one more aspect here: the enthalpies of formation for the above described models, denoted by solid and dashed lines in the upper panel of figure 9, start to coincide below a concentration of 2 at.%. In the same concentration range, very small variations of \( a \) and \( c/a \) are observed as indicated in figures 3 and 4. It also coincides with the \( a \) and \( c/a \) values for the highest carbon concentration found in the \( \gamma \) phase experimentally. This indicates that, reaching higher carbon concentrations in the Ti–Al system would go hand-in-hand with an increase in energy, which is an unlikely scenario. It seems that carbon located at the Ti or Al sites of the \( \gamma \) phase introduces so-called Friedel oscillations [47], i.e. oscillations of the charge density, as indicated by a somewhat oscillating behavior of \( a \) and \( c/a \) as well as \( H_{Ti} \), see figures 8 and 9.

As evident from table 6, \( \mu_C \) can vary over a certain range (\(-8.576 \) to \(-11.075 \) eV atom\(^{-1}\)). However, the highest value, derived from \( Al_4C_3 \), can be disregarded since it leads to a negative enthalpy of formation for any interstitial positions of C in the \( \gamma \) phase. As stated above, in many experimental studies of TiAl alloys (see, e.g., reference [22]), carbon is introduced via TiC, and due to high temperature, aging, or other treatments, the carbides Ti\(_3\)AlC and Ti\(_2\)AlC are formed. Therefore, these precipitates are in equilibrium with the \( \gamma \)-phase as well as with \( \alpha_2 \)-TiAl. This fact justifies to reduce \( \mu_C \) to values bounded by TiC and

| Phase       | \( \mu_C \) (in eV atom\(^{-1}\)) | \( a_{exp} \) | \( a_{calc} \) | \( c_{exp} \) | \( c_{calc} \) |
|-------------|----------------------------------|---------------|---------------|--------------|--------------|
| TiC         | -10.695                          | 4.338         | 4.32 [44]     |              |              |
| TiAlC       | -11.074                          | 4.183         | 4.16 [45]     |              |              |
| Ti\(_3\)AlC| -11.075                          | 3.069         | 3.058 [26]    | 13.742       | 13.642 [26]  |
| Al\(_4\)C3 | -8.576                           | 3.354         | 3.333 [46]    | 25.118       | 24.997 [46]  |
| Diamond    | -9.090                           | 3.573         | 3.567 [76]    |              |              |
| Graphite   | -9.221                           | 2.455         | 2.464 [77]    | 7.831        | 6.711 [77]   |

\[ eq(2) \] in reference [7].
Figure 9. Enthalpy of formation ($H_f$) of $\gamma$-TiAl as a function of C concentration for the cases of interstitial carbon (upper panel) and substitutional carbon (lower panel). C located in the Al-plane (Ti-plane) is marked by a black (red) line. Solid lines denote full relaxation, dashed lines stand for relaxation of atomic positions only, with $a$ and $c/a$ fixed to the values of the pure $\gamma$ phase. Note that the x axis is in logarithmic scale.

Ti$_2$AlC, i.e., to the range of $-10.695$ to $-11.075$ eV/atom. Employing different values for $\mu_C$, one can lower or increase the enthalpy of formation and the corresponding equilibrium concentration of solute carbon, corresponding to different thermodynamic equilibria or experimental conditions of alloy formation. From table 6 it is apparent that the chemical potential of C obtained using Ti$_2$AlC and Ti$_3$AlC are very similar, in accord with previous calculations [7]. The processing temperature of TiAl alloys with TiC as a carbon reservoir is high, i.e., $T = 1623$ K [20], such that the configurational entropy—a negative term—would play a role and decrease the thermodynamic free energy [7].

The equilibrium solute concentration $c(i)$ is related to the enthalpy of formation (neglecting the configurational entropy term) by the exponential expression [7, 53, 54]:

$$c(i) = \exp\left(\frac{-H_f}{k_B T}\right),$$

where, for our situation, all quantities are already known. One reaches a converged enthalpy of formation by increasing the supercell or, equivalently, decreasing the concentration of atomic impurities. From figure 9 one can see that for both interstitial positions, $H_f$ exhibits a plateau for carbon concentrations lower than 6 at.%, oscillating around the mean value by not more than 0.1 eV atom$^{-1}$. The energy difference related to the two different interstitial positions occupied by carbon is nearly constant, i.e, about 1.5 eV atom$^{-1}$.

Employing the chemical potential of TiC as upper bound and the one of Ti$_2$AlC as lower bound, then, for a temperature of $T = 1623$ K [20], the resulting concentration of interstitial carbon located in the Ti-plane is of the order of 180–2720 ppm, whereas it is negligible for the one in the Al-plane (0.005–0.07 ppm). These results are in good agreement with values found by atomic-probe analysis of single-as well as two-phase TiAl alloys [16, 18].

3.4.2. Effect of Ti$_6$ octahedra on the enthalpy of formation

The formation of a Ti$_6$ octahedron where the C atom is located in the Ti-plane involves substitution of two Al atoms by Ti (2 antisites). This leads to a non-stoichiometric (Ti-rich) alloy, which impacts the chemical potentials of Ti and Al. We follow the work of Woodward et al [37] to obtain the chemical potentials, $\mu_{\text{Ti}}$ and $\mu_{\text{Al}}$, for the non-stoichiometric (Ti-rich, Al-rich) $\gamma$ phase, which are related to the antisite energies depending on the defect concentration. From references [37] and [65] it follows that formation of a second antisite is at zero energy cost. The contributions to the enthalpy of formation concern (i) the formation of Ti$_6$ octahedra; (ii) C entering into $\gamma$-TiAl already containing Ti$_6$ octahedra; (iii) the combination of both. The chemical potential for carbon is here again the one taken from TiAl$_2$C.

Figure 10 shows $H_f$, including all three contributions, as a function of C or Ti concentration, using equation (1) and $T = 1623$ K as in figure 9. The result for forming Ti$_6$ octahedra is indicated by a dash-dotted green line, showing a decrease of energy as the system goes toward more Ti-rich concentrations, i.e., higher Ti$_6$ content (top x axis). Eventually, $\mu_{\text{Ti}}$ adopts the same value as for pure hcp Ti, i.e., lower in energy than the one for Ti in the $\gamma$ phase. The opposite trend is visible for C entering $\gamma$-TiAl (red dashed line) as well as the overall trend, i.e., the probability of inserting Ti$_6$ octahedra occupied by carbon into the pure stoichiometric $\gamma$ phase (black solid line). We conclude that the energy cost for low carbon concentrations entering Ti$_6$ octahedra is about two times lower than for carbon to be soluted into

$$\text{Figure 10.}$$

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Figure 10. Enthalpy of formation ($H_f$) for creating Ti$_6$ octahedra occupied by carbon in stoichiometric $\gamma$-TiAl (solid black line), C in $\gamma$-TiAl already containing Ti$_6$ octahedra, i.e., Ti-rich (dashed red line), and Ti$_6$ octahedra with respect to stoichiometric $\gamma$-TiAl (dash-dotted green line, upper axis).

stoichiometric $\gamma$-TiAl, i.e., inside of Ti$_4$Al$_2$ or Ti$_2$Al$_4$ octahedra (compare black solid lines of figures 10 and 9 (upper panel)). If one uses $\mu_C(Ti_2AlC)$, then the corresponding solubility of carbon is about 0.2–0.5 at.%, i.e., definitively higher than for the stoichiometric $\gamma$ phase, which is in very good agreement with experimental studies [19, 20].

4. Conclusions

Total-energy calculations have revealed that in the $\gamma$ phase of TiAl, carbon atoms rather occupy interstitial than substitutional positions. An interstitial position in the Ti-plane is preferred over the Al-plane by $\approx 1.5$ eV for any carbon concentration lower than 6 at.%. But even for C in the Ti-plane, the energy of formation (enthalpy of formation at $T = 0$ K) is about 1.2 eV, which is comparable to the one of a vacancy [7, 11, 37, 65]. As a consequence, the expected concentration of interstitial carbon is very low, i.e., in the range of 180–2720 ppm, in accord with experiment [16, 18]. Indeed, the energy cost to solute carbon within the $\gamma$ phase is higher than the energy of formation of Ti and Al antisites in stoichiometric TiAl, which is $\approx 0.7$ eV and 0.3 eV, respectively, in accord with literature [7, 37]. For off-stoichiometric Ti-rich $\gamma$-TiAl, however, where Ti$_6$ octahedral positions are occupied, the solubility of carbon is much higher (by at least a factor two), and the probability of carbon to sit on an interstitial position inside such an octahedron is higher than on corresponding interstitial sites in stoichiometric TiAl. Since in experiment, an expansion of both $a$ and $c/a$ is observed, we suggest that a mixture of both interstitial sites is present in C-alloyed $\gamma$-TiAl, with a higher probability of carbon to be found in the Ti-plane.

The bonding properties and electronic structure of $\gamma$-TiAl are not significantly affected by carbon concentrations lower than about 1 at.%. At such a concentrations, the Fermi level and the DOS at the Fermi energy are similar for $\gamma$-TiAl with or without C interstitial. An analysis of the change in charge density due to carbon addition for the largest C concentration reveals that C partially fills the Ti $d$ orbitals, but affects the bonding of Al rather little. For the case of C in the Ti plane, the bonds in the $(x, y)$ plane are strengthened. For C in the Al plane, a very pronounced enhancement of the Ti–Ti bonds along $z$ is found.

If carbon occupies one of the interstitial octahedral or substitutional sites, it affects the lattice constants and also the mechanical properties, depending on the concentration. We predict the elastic behavior of $\gamma$-TiAl including substitutional or interstitial C as well as of the Ti-rich material. Elastic anisotropy, Cauchy pressures, Pugh ratio, Poisson ratio, and Young modulus have been computed to quantify the effect of C on the ductility of $\gamma$-TiAl as a function of C concentration. These criteria reveal, for example, that C alloying at a concentration of about 3 at.% increases the ductility only very slightly, owing mainly to the position of C in the Ti-plane. At a similar concentration, substitutional C affects the elastic properties to a larger extent. In contrast, for the case of C located at the Al-site, the elastic constants indicate that such a solid is intrinsically unstable.

For C concentrations lower than 3 at.%, which correspond to the concentrations of the experimentally characterized samples reported in literature, we conclude that the mechanism of ductilization is not related to the presence of interstitial C within the bulk $\gamma$ phase. It will be interesting to shed further light on
whether a possible mechanism of ductilization is promoted by segregated carbon at grain boundaries or \(\alpha_2/\gamma\) interfaces in the lamellar structure of the material. We anticipate that the role of interstitial carbon (and possibly other interstitials) must be more pronounced at grain boundaries, interfaces, and extended defects than within bulk \(\gamma\)-TiAl.

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**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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