Ab Initio Study of the Influence of Alloying Elements on Stability and Mechanical Properties of Selected Ti_xAl_y Intermetallic Compounds and Their $\text{Ti}_x\text{Al}_y/\text{Al}$, $\text{Ti}_x\text{Al}_y/\text{Ti}$ Interfaces in Explosively Welded Metal–Metal Composites

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The overall performance of joints fabricated using the explosive welding method depends directly on the brittleness of created intermetallic phases and their cohesion with metallic substrates. In this article, we used first principles calculations to show that Sn, V, Cu, and Mg alloying elements present in Ti- and Al-based alloys have a significant influence on the elastic properties and plastic deformation ability of $\gamma\text{-TiAl}$ and Ti_3Al . Selected solutes exhibit diversified preferential site occupancy in bulk phases and ordered phase/metallic substrate interface regions. The largest positive effect on ductility and cleavage energy was found for Cu addition (25 pct increase in the B/G ratio), while Sn largely deteriorates cleavage resistance (up to 8 pct). The presented results reveal that further development in the explosive welding field can be reached through the design/application of new alloys composed of elements that improve the properties of the ordered phases present in the joints.

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I. INTRODUCTION

METAL–METAL laminate composites enable the attractive functional properties and high strength of two different materials to be combined. Such complex solutions offer unique properties that are often unachievable in single metals.^[1] The most widely used industrial method of production of layered metal composites is explosive welding, where the single-step process forms bimetallic joints.^[2,3] However, the typical conditions of the method, *i.e.*, extremely high strain rates (collision point velocity up to 4500 m/s^[4]) and local heating (in the range of 2500 K^[5]) promote a sophisticated structure of the welded zone with an extensively deformed region and brittle phases.^[2] This type of interface microstructure was observed in numerous laminates composed of pure Ti and Al,^[6–10] as well as those formed from Ti, Al, Fe, and Ni alloys.^[11–13] According to available reports, the crucial structural aspect of interface strength is related to the type and

number of ordered phases acting as the crack nucleation and propagation region. Moreover, recent studies of Ti–Al and Ti–Fe explosive joints indicate that intermetallic inclusions form a thin, continuous layer at the interface with a non-homogeneous shape and chemical stoichiometry.^[7,13] To date, considerable effort has been made to minimize the negative effect (brittleness) of these intermetallic systems, through annealing or hot rolling.^[7,14–16]

Another way to improve the properties of joints is to alloy the existing intermetallic phases to enhance their ductility and the cohesion of their phase boundaries. Improving the room temperature ductility of the ordered structures through alloying has been extensively explored over recent decades, leading to marked achievements arising from three separate mechanisms^[17,18]: (i) the activation of new, or the facilitation of, the original dislocation slip modes; (ii) the segregation of solutes at grain boundaries, increasing their cohesion and limiting intergranular fracture; and (iii) the reconfiguration of the base, brittle crystal lattice to achieve higher symmetry and more ductile structures. These strategies were adopted for various intermetallic systems, *e.g.*, NiAl alloyed with Fe or Mn exhibits large ductility improvement caused by lattice expansion induced by the magnetic coupling between solute and host atoms reducing the shear modulus and generalized stacking fault energy of 111{110} slip mode,^[19–21] Nb

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addition to Ti_3Al phase activates $11\bar{2}0(0001)$ basal slip, which is absent in unalloyed material,^[22] segregation of interstitial boron in Ni_3Al grain boundaries increase their cohesion and minimize intergranular cleavage,^[17,23,24] although, alloying with some substitutional elements (Zr, Hf, V, Nb, Mo, W, Co, Pd, Cu, Cr, Mn, and Fe) increases overall ductility of this phase as well.^[24]

As can be seen from the reviewed literature, the addition of the ternary element to the binary intermetallic phase can significantly improve its deformation ability. This behavior can be potentially utilized in the explosive welding method to reduce the detrimental effect of ordered structures formed at the interface area. However, to this end, a careful selection of alloying elements has to be made. As explosive welding is already a commercial technology, it is worth first investigating the effect of solutes present in commercial alloys. Such an approach is highly desirable from an industrial point of view, in order to identify materials whose joints may be less brittle. In this article, we follow the above idea and adopt *ab initio* modeling to explore the influence of solutes present in Ti and Al alloys on the mechanical properties (elastic constants, B/G Pugh plasticity criterion^[25]) of Ti_3Al and $\gamma\text{-TiAl}$, as well as the cleavage energy of selected interfaces between these phases and both metallic substrates at 0 K temperature. We consider four substitutional solutes, *i.e.*, Sn, V, Cu, and Mg, prevalent in a number of Ti (Ti-6Al-4V, Ti-3Al-2.5V, Ti-10V-2Fe-3Al, Ti-15V-3Cr-3Sn-3Al, Ti-11Sn-5Zr-2.25Al-1Mo-0.2Si, Ti-6Al-2Sn-4Zr-2Mo-0.08Si^[26]) or Al (Aluminum series 2XXX and 5XXX^[27]) commercial alloys.

II. METHODOLOGY

The *ab initio* calculations were performed with a Vienna *ab initio* Simulation Package (VASP) code,^[28,29] using the projector augmented wave (PAW) technique^[30] and a Perdew–Burke–Ernzerhof generalized gradient functional.^[31] The 0.2 eV smearing of electronic occupancy was approximated with a Methfessel–Paxton method and a plane wave cut-off energy of 600 eV was used. The valence configuration for the PAW pseudopotentials adopted in this study is as follows: Ti ($3p^6, 3d^2, 4s^2$), Al ($3s^2, 3p^1$), Sn ($5s^2, 5p^2$), V ($3p^6, 3d^3, 4s^2$), Mg ($2p^6, 3s^2$), and Cu ($3p^6, 3d^{10}, 4s^1$). The simulation boxes utilized for elastic constants calculations were constructed by the multiplication of TiAl and Ti_3Al primitive cells, as shown in Figure 1. While the Ti_3Al exhibits DO_{19} symmetry, $\gamma\text{-TiAl}$ has an ordered L1_0 configuration that can be represented by face-centered tetragonal (FCT) or body-centered tetragonal (BCT) structures (the BCT primitive cell is achieved by a 45 deg rotation of the FCT unit cell around the $[001]$ axis^[32,33]). In this study, we used a BCT representation for $\gamma\text{-TiAl}$, allowing it to reach the same number of atoms (16 atoms) per simulation box in both the considered phases. It is worth noting that, although, C_{ij} elements of $\gamma\text{-TiAl}$ determined for FCT and BCT representations

are different, the polycrystalline B , G , E moduli remain equivalent. The atomic models of the alloyed systems were created using the supercell approach, *i.e.*, one of the Al or Ti ions was substituted by Mg, Sn, Cu, or V solutes, leading to their 6.25 at. pct concentration in both the studied phases. The chosen number of solutes corresponds to the upper boundary of their content in the commercial Ti and Al alloys.^[26,27] In addition to the elastic constants calculations, the solute segregation to seven selected Ti_3Al (0001) || Al {111}, Ti_3Al (0001) || Ti (0001), Ti_3Al {1010} || Ti {1010}, $\gamma\text{-TiAl}$ {001} || Al {001}, $\gamma\text{-TiAl}$ {100} || Al {100}, $\gamma\text{-TiAl}$ {111} || Al {111}, $\gamma\text{-TiAl}$ {111} || Ti (0001) interfaces was investigated. To this end, additional, 12 atomic layers models (96 atoms in total) were created, and are presented in Figure 1. The Brillouin zones of all models were sampled in accordance with the Monkhorst–Pack scheme,^[34] using the $24 \times 28 \times 18$ and $24 \times 24 \times 18$ gamma centered k-points mesh per primitive cells of Ti_3Al and $\gamma\text{-TiAl}$, respectively. The electronic and ionic relaxation loops were stopped when reaching the 0.2 meV energy and 0.5 meV/Å Hellman–Feynman force convergence criteria. All energies were calculated with the additional, single-step electronic relaxation utilizing tetrahedron method with Blöchl corrections.^[35]

The elastic constants C_{ij} of particular systems were determined using the energy–strain relationship of distorted crystal in a Taylor expansion form^[36–38]:

$$E(V, \varepsilon) = E_0 + V_0 \left(\sum_{i=1}^6 \sigma_i \varepsilon_i + \frac{1}{2} \sum_{i,j=1}^6 C_{ij} \varepsilon_i \varepsilon_j \right), \quad [1]$$

where E is the total energy (including all electrostatic interactions, exchange correlation and kinetic energy of the electrons, as well as energy of the ions in the PAW approach) of the elastically distorted crystal, E_0 and V_0 are the total energy and volume of the system in its ground state, and σ_i, ε_j are the stress and strain tensors, respectively, written in Voigt notation. In the approach above, the elastic constants are extracted by fitting the total energies derived under different strains to quadratic function close to the energy minimum. The six and five independent elastic constants of tetragonal $\gamma\text{-TiAl}$ and hexagonal Ti_3Al , respectively, were determined with the distortions D_x given in Table I ($C_{66} = (C_{11} - C_{12})/2$ for Ti_3Al).^[39,40] Having C_{ij} it is possible to calculate the polycrystalline shear G , bulk B , and Young E moduli of the studied phases with Reuss–Hill approximation^[41–43]:

$$B = \frac{B_V + B_R}{2} \quad [2]$$

$$G = \frac{G_V + G_R}{2} \quad [3]$$

$$E = \frac{9BG}{3B + G}, \quad [4]$$

where B_V, G_V, B_R , and G_R are Voigt and Reuss bulk and shear moduli obtained by

Fig. 1—Primitive unit cells of γ -TiAl (a) hexagonal Ti_3Al (b), corresponding supercells (the same orientation) for elastic constants calculations (c, d) and examples of simulation boxes with Ti_3Al $\{1010\} \parallel \text{Ti}$ $\{1010\}$ (e) and γ -TiAl $\{111\} \parallel \text{Al}$ $\{111\}$ (f) interfaces. The positions of the Ti and Al atoms are denoted by blue and gray, respectively (Color figure online).

$$B_V = \frac{2C_{11} + C_{33} + 2C_{12} + 4C_{13}}{9} \quad [5]$$

$$G_V = \frac{2C_{11} + C_{33} + 6C_{44} + 3C_{66} - C_{12} - 2C_{13}}{15} \quad [6]$$

$$B_R = \frac{C_2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} \quad [7]$$

$$G_R = \frac{15}{18B_V/C_2 + 6/(C_{11} - C_{12}) + 6/C_{44} + 3/C_{66}} \quad [8]$$

$$C_2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2. \quad [9]$$

The final evaluation of the brittle/ductile nature of investigated phases is quantified based on the B/G Pugh plasticity criterion, originally proposed for pure metals^[25] and later used for a wide group of compounds with complex structures and diversified stoichiometry.^[44] The considered intermetallic phases exhibit a metallic nature (no band gap,^[45] good electrical conductivity^[46,47]). As the constituent elements are simple (Al) and transition (Ti) metals, the bond character is mixed, metallic (s and p-type electrons), and covalent (d-type electrons). For such systems, the transition from brittle cleavage to ductile failure of the material occurs at $B/G = 1.75$. This critical value should not be viewed as a definitive transition point, as the criterion fails to capture the entire complexity of such a transition. Nevertheless, the higher the B/G the larger the expected ability of the material to undergo plastic deformation.

III. RESULTS AND DISCUSSION

A. Solute Site Occupancy and Mechanical Properties

To determine the preferential site of solutes (Ti- or Al-sublattice) in γ -TiAl and Ti_3Al phases, the average formation energy E_f has been calculated according to

$$E_f = \frac{E_{\text{tot}} - n_{\text{Ti}}E_{\text{solid}}^{\text{Ti}} - n_{\text{Al}}E_{\text{solid}}^{\text{Al}} - E_{\text{solid}}^{\text{X}}}{N}, \quad [10]$$

where E_{tot} is the total energy of alloyed γ -TiAl or Ti_3Al structures composed of n_{Ti} and n_{Al} numbers of Ti and Al atoms; $E_{\text{solid}}^{\text{Ti}}$, $E_{\text{solid}}^{\text{Al}}$, and $E_{\text{solid}}^{\text{X}}$ are energy per atom of Ti, Al, and solute element in their reference, stable states, respectively. The total number of atoms in the simulation box is denoted as N (in this study, $N = 16$). Negative formation energy indicates that the solute prefers to dissolve in the intermetallic phase rather than forming separate pure structures. The lower the E_f the larger the structural stability of the given configuration at 0 K. The calculated E_f are presented in Table II, which shows that Cu and Sn occupy the Al site in γ -TiAl, while Mg and V are located at the Ti sublattice. On the other hand, in the case of Ti_3Al for all of the investigated solutes except Sn, the Ti site is the lower energy one. The preferential occupancy of the Al site by Sn in Ti_3Al can be clarified by the presence of Ti_3Sn compound with an analogous configuration to Ti_3Al .^[50] The available experiments confirm the determined site occupancies for V and Sn in γ -TiAl and Ti_3Al also at room temperature,^[51] and indicate good solubility of transition and simple metals in these structures, at least up to 5 at. pct.^[52]

Knowing the preferential site occupancy of substitutional solutions, the elastic constants of both pure and alloyed γ -TiAl and Ti_3Al were calculated and are listed in Table III. It can be found that B and G values

determined in this work predict the properties of materials at 0 K temperature. The highest error relative to low temperature experiments reaches 4 and 8 GPa for B and G , respectively. It is worth noting that, according to experimental data, these moduli are relatively constant between 0 K and 298 K, with the largest change equal to 5.1 pct (G of Ti_3Al). The B/G plasticity criterion agrees reasonably well with the available experiments and other theoretical data. Some discrepancy between calculated elastic constants results from different pseudopotential approaches and computational parameters used by different authors. Considering the alloyed systems, it can be found that elements of the C_{ij} matrix change significantly for both phases, leading to noticeable variations of B/G . The addition of Mg or Sn enhances the brittleness, while V merely affects the plasticity $\gamma\text{-TiAl}$. The most pronounced variations of Pugh plasticity criterion have been observed for $\gamma\text{-TiAl} + \text{Cu}$ alloy, which shows a great increase in ductility in comparison to the pure system. The same positive effect of Cu is also visible in Ti_3Al , making Cu a potentially universal solute in terms of the ductility improvement of the investigated intermetallic compounds. The positive influence of Cu on the ductility of $\gamma\text{-TiAl}$ has already been reported by Shu *et al.*, who linked the modification of these mechanical properties with the weakening of the directionality of Ti–Ti bonds in the vicinity of the Cu in $\gamma\text{-TiAl}$ host structure.^[59] Moreover, it is worth mentioning that other studied solutes, *i.e.*, Mg, Sn, V, also tend to slightly reduce the brittleness of Ti_3Al .

B. Influence of Solutes on Cleavage Energy

Solute atoms, apart from the effects provoked in bulk crystal structures, influence the mechanical properties of materials through the segregation on grain boundaries and/or interfaces. Such segregation can both increase and reduce the cohesion of above 2D lattice defects, leading to typical for metals dislocation/twinning mediated plasticity or intergranular cleavage fracture frequently observed in the intermetallic phases.^[17,23,24] This aspect is especially important for welded joints or multiphase materials, where a variety of interfaces between metal and ordered structures can occur. To determine the structural stability (at 0 K temperature) of solutes at $\text{Al}(\text{Ti})/\gamma\text{-TiAl}(\text{Ti}_3\text{Al})$ interfaces, the E_s segregation energy was calculated using the following formula:

$$E_s = E_{\text{tot}+\text{X}} - E_{\text{tot}} - E_{\text{X}} - u_{\text{Ti}(\text{Al})}, \quad [11]$$

where $E_{\text{tot}+\text{X}}$ and E_{tot} are the total energies of interface with and without solute, respectively, E_{X} is the energy per atom of the substitutional solute in the reference ground state and $u_{\text{Ti}(\text{Al})}$ is the chemical potential of Ti or Al atom and depends on the position of the solute. If the alloying element is located on the metallic site of interface, $u_{\text{Ti}(\text{Al})}$ is equal to the energy per the Ti or Al atom in the hcp or fcc structure, respectively. For solutes placed in the intermetallic compounds $u_{\text{Ti}(\text{Al})}$ is obtained by

$$E_{\text{TiAl}} = u_{\text{Ti}} + u_{\text{Al}} \quad [12]$$

and

$$E_{\text{Ti}_3\text{Al}} = 3u_{\text{Ti}} + u_{\text{Al}}, \quad [13]$$

where E_{TiAl} and $E_{\text{Ti}_3\text{Al}}$ are the total energies of $\gamma\text{-TiAl}$ and Ti_3Al unit cells. Such obtained chemical potentials ($u_{\text{Ti}} = -8.05$ eV and $u_{\text{Al}} = -4.40$ eV agree well with the available theoretical data: $u_{\text{Ti}} = -7.89$ eV and $u_{\text{Al}} = -4.46$ eV calculated at 0 K temperature in Reference 60) correspond to the two-phase field of Ti and Al phase diagram, which is typically obtained in the welded Ti/Al joints, *i.e.*, $\gamma\text{-TiAl}$, Ti_3Al as well as non-stoichiometric compositions of intermetallic phases occur in the direct mutual vicinity.^[7] Investigated E_s has a similar physical meaning to E_f from Eq. [10], *i.e.*, E_s describes the formation energies of solutes located close to the interface at 0 K, thus, negative E_s indicates the (meta-)stable position of a given element. Lattice vibrations existing at finite temperatures may also influence the most favorable location of particular alloying elements, when E_s is similar for different configurations. In this study, we selected seven interfaces, Ti_3Al (0001) || Al (111), Ti_3Al (0001) || Ti (0001), Ti_3Al (1010) || Ti (1010), $\gamma\text{-TiAl}$ (001) || Al (001), $\gamma\text{-TiAl}$ (100) || Al (100), $\gamma\text{-TiAl}$ (111) || Al (111), $\gamma\text{-TiAl}$ (111) || Ti (0001), which include different types of crystallographic planes between Ti–Al compounds and Ti- or Al-substrates, and various distributions of constituent elements. The selected interfaces are coherent with the maximum misfit strains up to 4 pct, as listed in Table IV. According to recent reports, the interaction of alloying elements with 2D defects depends non-linearly on their relative distance.^[61] This effect arises from the local relaxation of atomic positions, lattice misfit strains, and 3D perturbation of electronic structure present in the thin region above and below the planar imperfections of the crystal structure. In view of the above phenomenon, the E_s was calculated for six positions of solutes, *i.e.*, the three closest to the interface atomic planes from both intermetallic and substrate sites, as shown in Figure 2. Furthermore, depending on the interface type, alloying elements can also occupy Ti or Al position in the same atomic plane.

The determined E_s reveals that Mg is the only insoluble element in the investigated interfaces, while Sn and V can occupy numerous metastable (with negative but not the lowest segregation energy) positions on both the intermetallic and metallic parts of the crystals. Cu displays moderate E_s values, exhibiting a relatively low structural stability in most cases. Another important result is related to the preferential Ti or Al site of solutes in ordered phases. According to Table II, V occupies the position of Ti atoms in both bulk $\gamma\text{-TiAl}$ and Ti_3Al structures, while closer to the interfaces, a more stable configuration can be changed to an Al sublattice, as in $\gamma\text{-TiAl}$ (100) || Al (100), $\gamma\text{-TiAl}$ (111) || Al (111) systems (Figure 3).

To reveal the effect of solute atoms on the strength of $\gamma\text{-TiAl}(\text{Ti}_3\text{Al})/\text{Ti}(\text{Al})$ interfaces, the γ_c cleavage energy of

Table I. Crystal Distortions D_x Used to Calculate the Elastic Constants and Corresponding Coefficients of the Second Degree Variable of the Parabolic Fit of Energy Variations at the Applied Strain State

Structure	Distortion	$\frac{1}{V_0} \frac{\partial^2 E(V, \varepsilon)}{\partial \varepsilon^2} \Big _{\varepsilon=0}$
γ -TiAl (L1 ₀)	$D_1 = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$C_{11} + C_{12}$
	$D_2 = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & \frac{1}{(1+\varepsilon)^2} \end{pmatrix}$	$C_{11} + C_{12} + 2C_{33} - 4C_{13}$
	$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix}$	$\frac{C_{33}}{2}$
	$D_4 = \begin{pmatrix} \left(\frac{1+\varepsilon}{1-\varepsilon}\right)^{\frac{1}{2}} & 0 & 0 \\ 0 & \left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$C_{11} - C_{12}$
	$D_5 = \begin{pmatrix} 1 & 0 & \varepsilon \\ 0 & 1 & \varepsilon \\ \varepsilon & \varepsilon & 1+\varepsilon^2 \end{pmatrix}$	$4C_{44}$
	$D_6 = \begin{pmatrix} (1+\varepsilon^2)^{\frac{1}{2}} & \varepsilon & 0 \\ \varepsilon & (1+\varepsilon^2)^{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$2C_{66}$
Ti ₃ Al (DO ₁₉)	$D_1 = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$C_{11} + C_{12}$
	$D_2 = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$C_{11} - C_{12}$
	$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix}$	$\frac{C_{33}}{2}$
	$D_4 = \begin{pmatrix} 1 & 0 & \varepsilon \\ 0 & 1 & 0 \\ \varepsilon & 0 & 1 \end{pmatrix}$	$2C_{55}$
	$D_5 = \begin{pmatrix} 1+\varepsilon & 0 & 0 \\ 0 & 1+\varepsilon & 0 \\ 0 & 0 & 1+\varepsilon \end{pmatrix}$	$\frac{1}{2}(2C_{11} + 2C_{12} + 4C_{13} + C_{33})$

Table II. The Formation Energies (Eq. [10]) Calculated for Pure and Alloyed γ -TiAl and Ti₃Al (Solute Concentration 6.25 At. Pct)

Structure	E_f —Ti Site	E_f —Al Site	Solute Preferred Site
γ -TiAl + Cu	− 0.361	− 0.367	Al
γ -TiAl + Mg	− 0.353	− 0.326	Ti
γ -TiAl + Sn	− 0.341	− 0.393	Al
γ -TiAl + V	− 0.382	− 0.368	Ti
γ -TiAl	− 0.408, − 0.416 ^{E[48]} , − 0.449 ^{T[33]} , − 0.401 ^{T[49]}	—	—
Ti ₃ Al + Cu	− 0.248	− 0.198	Ti
Ti ₃ Al + Mg	− 0.227	− 0.173	Ti
Ti ₃ Al + Sn	− 0.279	− 0.284	Al
Ti ₃ Al + V	− 0.261	− 0.178	Ti
Ti ₃ Al	− 0.282, − 0.256 ^{E[48]} , − 0.279 ^{T[49]}	—	—

The “E” and “T” superscript symbols indicate the reference experimental and theoretical data, respectively. E_f given eV/atom.

Table III. The Single Crystal and Polycrystalline Elastic Constants of Pure and Alloyed γ -TiAl and Ti₃Al (Solute Concentration 6.25 At. Pct)

Structure	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	E	B/G
γ -TiAl	202.9	58.3	87.7	174.4	112.7	43.2	116.4 110 ^{E[53]} (298 K) 110 ^{E[54]} (298 K) 112 ^{E[54]} (0 K) 114 ^{T[33]} 124 ^{T[55]} 113 ^{T[58]}	70.5 74 ^{E[53]} (298 K) 75.7 ^{E[54]} (298 K) 78.3 ^{E[54]} (0 K) 70.5 ^{T[33]} 72 ^{T[55]} 68 ^{T[58]}	176.0 181.5 ^{E[53]} (298 K) 185 ^{E[54]} (298 K) 190 ^{E[54]} (0 K) 175 ^{T[33]} 181 ^{T[55]} 170 ^{T[58]}	1.65 1.49 ^{E[53]} (298 K) 1.45 ^{E[54]} (298 K) 1.43 ^{E[54]} (0 K) 1.62 ^{T[33]} 1.72 ^{T[55]} 1.66 ^{T[58]}
γ -TiAl + Cu	178.6	75.1	102.9	157.3	108.8	37.6	119.6	57.6	149.0	2.07
γ -TiAl + Mg	194.9	42.9	78.6	158.3	101.8	44.0	105.4	67.4	166.7	1.56
γ -TiAl + Sn	212.8	59.1	75.8	192.4	104.7	43.7	115.5	73.7	182.2	1.57
γ -TiAl + V	216.2	52.9	88.9	182.2	115.3	36.8	119.5	71.4	178.7	1.67
Ti ₃ Al	199.7 183 ^{E[54]} (3.3K) 176 ^{E[54]} (270 K)	89.3 89 ^{E[54]} (3.3K) 88 ^{E[54]} (270K)	61.1 63 ^{E[54]} (3.3K) 61 ^{E[54]} (270K)	231.9 225 ^{E[54]} (3.3K) 219 ^{E[54]} (270K)	64.6 64 ^{E[54]} (3.3K) 62 ^{E[54]} (270K)	55.2 47 ^{E[54]} (3.3K) 44 ^{E[54]} (270K)	117.1 113 ^{E[54]} (3.3 K) 110 ^{E[54]} (270 K) 129 ^{T[56]} 114 ^{T[57]} 114 ^{T[58]}	64.0 59 ^{E[54]} (3.3 K) 56 ^{E[54]} (270 K) 72 ^{T[56]} 59 ^{T[57]} 63 ^{T[58]}	162.4 150.6 ^{E[54]} (3.3 K) 144 ^{E[54]} (270 K) 182 ^{T[56]} 152 ^{T[57]} 159 ^{T[58]}	1.83 1.91 ^{E[54]} (3.3 K) 1.96 ^{E[54]} (270 K) 1.79 ^{T[56]} 1.93 ^{T[57]} 1.81 ^{T[58]}
Ti ₃ Al + Cu	177.0	94.0	70.8	210.1	45.8	41.5	116.1	55.8	144.4	2.08
Ti ₃ Al + Mg	177.5	84.0	66.0	206.7	64.2	46.7	113.8	60.6	154.4	1.88
Ti ₃ Al + Sn	189.4	92.2	67.0	223.3	57.5	48.6	117.1	60.5	154.8	1.94
Ti ₃ Al + V	198.1	93.4	65.5	239.5	58.9	52.4	118.8	62.3	159.1	1.91

The “E” and “T” superscript symbols indicate the reference experimental and theoretical data, respectively. Please note that C_{ij} elements are determined for BCT representation of γ -TiAl.^[32,33] The theoretical data correspond to 0 K and all the results given in GPa.

Table IV. Misfit Strains Measured for the Directions Parallel to the Subsequent Interfaces

Interface	Phase and Direction	Dimension (Å)	Misfit Strain (pct)
γ -TiAl(001) Al(001)	γ -TiAl [010]	3.995	1.7
	Al [010]	4.061	− 1.6
γ -TiAl(100) Al(100)	γ -TiAl [010]	3.995	1.7
	Al [010]	4.061	− 1.6
	γ -TiAl [001]	4.070	− 0.2
	Al [001]	4.061	0.2
γ -TiAl(111) Al(111)	γ -TiAl [011]	5.703	− 0.1
	Al [011]	5.698	0.1
γ -TiAl(111) Ti(0001)	γ -TiAl 1/2[011]	2.852	2.9
	Ti [11 $\bar{2}$ 0]	2.936	− 2.9
Ti ₃ Al(0001) Al(111)	Ti ₃ Al [11 $\bar{2}$ 0]	2.824	0.9
	Al 1/2 [011]	2.849	− 0.9
Ti ₃ Al(0001) Ti(0001)	Ti ₃ Al [11 $\bar{2}$ 0]	2.824	4.0
	Ti [11 $\bar{2}$ 0]	2.936	− 3.8
Ti ₃ Al(1010) Ti(1010)	Ti ₃ Al [11 $\bar{2}$ 0]	2.824	4.0
	Ti [11 $\bar{2}$ 0]	2.936	− 3.8
	Ti ₃ Al [0001]	4.655	− 0.02
	Ti [0001]	4.648	0.02

Depending on the lattice symmetry, particular systems exhibit two independent misfit strains along two perpendicular crystallographic directions. The listed dimensions were calculated for defect-free structures.

pure and most stable alloyed systems (configurations with the lowest E_s from Figure 2) was calculated using the following equation:

$$\gamma_c = \frac{E_{\text{Ti(Al)}}^{\text{slab}} + E_{\text{TiAl(Ti}_3\text{Al)}}^{\text{slab}} - E_{\text{Ti(Al)/TiAl(Ti}_3\text{Al)}}^{\text{slab}}}{2A} \quad [14]$$

and

Fig. 2—Examples of the investigated γ -TiAl(Ti₃Al)/Ti(Al) interfaces. The analyzed positions of solutes lying on six (−3, −2, ..., 3) closest to the interface atomic planes are marked by black squares. The Ti and Al atoms are denoted by blue and gray, respectively (Color figure online).

Fig. 3—The calculated E_s segregation energy for all studied interfaces. The solute positions −3, −2, ..., 3 correspond to the distribution of alloying elements presented in Fig. 2. The lower the E_s value the higher the structural stability at 0 K of the given alloying element–interface configuration. The in-plane concentration of solutes is equal to 1/8 (12.5 at. pct).

$$\gamma_c = \frac{E_{\text{Ti(Al,TiAl,Ti}_3\text{Al)+X}}^{\text{slab}} + E_{\text{Ti(Al,TiAl,Ti}_3\text{Al)}}^{\text{slab}} - E_{\text{Ti(Al)/TiAl(Ti}_3\text{Al)+X}}^{\text{slab}}}{2A}, \quad [15]$$

where $E_{\text{Ti(Al)}}^{\text{slab}}$ and $E_{\text{TiAl(Ti}_3\text{Al)}}^{\text{slab}}$ are the total energies of the 6-layer, pure Ti (or Al) and TiAl (or Ti₃Al) crystals, $E_{\text{Ti(Al)/TiAl(Ti}_3\text{Al)}}^{\text{slab}}$ is the total energy of the 12-layer, interface-involved structures composed of the same Ti (or Al) and TiAl (or Ti₃Al) systems and A is the interface area. For alloyed configurations, $E_{\text{Ti(Al,TiAl,Ti}_3\text{Al)+X}}^{\text{slab}}$ and $E_{\text{Ti(Al,TiAl,Ti}_3\text{Al)}}^{\text{slab}}$ denote the total energies of the 6-layer Ti, Al, TiAl, or Ti₃Al enriched by one solute element and pure crystals, respectively. The final $E_{\text{Ti(Al)/TiAl(Ti}_3\text{Al)+X}}^{\text{slab}}$ term is the total energy of the alloyed, 12-layer γ -TiAl(Ti₃Al)/Ti(Al) structure. It should be noted that, due to periodic boundary conditions, the original interface-involved models (Figure 1) were transformed to slab structures by adding an 8 Å

vacuum region in each case (the size of the 6- and corresponding 12-layer simulation boxes was always equal, to ensure the same density of k-points). According to Eqs. [14] and [15], γ_c is the energy per unit area required to separate the solid into two semi-infinite blocks, creating two free surfaces.^[60,62] The calculated γ_c of pure and alloyed γ -TiAl(Ti₃Al)/Ti(Al) interfaces are presented in Table V, and the investigated systems are listed in terms of increasing cleavage energy: γ -TiAl(111) || Al(111) < γ -TiAl(100) || Al(100) < Ti₃Al(0001) || Al(111) < γ -TiAl(111) || Ti(0001) < γ -TiAl(001) || Al(001) < Ti₃Al(0001) || Ti(0001) < Ti₃Al(1010) || Ti(1010). The gathered data illustrate a pronounced difference in the strength of interfaces formed between the analyzed phases. The strongest (the highest γ_c) systems are those containing the largest fraction of Ti atoms, which, thanks to d-type electrons, form more directional, covalent bonds.^[38,63] The addition of solute atoms, overall, leads to relatively small changes of

Table V. Cleavage Energy Calculated for the Lowest Energy Configuration of Solutes from Fig. 3

Interface Type	Element	Preferential site	Sublattice	Solute position (lattice plane)	γ_c [mJ/m ²]
γ -TiAl (001) Al (001)	—	—	—	—	1957
	Sn	γ -TiAl	Al	— 2	1975
	V	Al	Al	2	2006
	Cu	Al	Al	2	1945
γ -TiAl (100) Al (100)	—	—	—	—	1349
	Sn	γ -TiAl	Al	— 3	1338
	V	Al	Al	2	1420
	Cu	γ -TiAl	Al	1	1402
γ -TiAl (111) Al (111)	—	—	—	—	1317
	Sn	γ -TiAl	Al	— 3	1322
	V	Al	Al	3	1323
	Cu	γ -TiAl	Al	— 1	1351
γ -TiAl (111) Ti (0001)	—	—	—	—	1820
	Sn	Ti	Ti	2	1859
Ti ₃ Al (0001) Al (111)	—	—	—	—	1553
	Sn	Ti ₃ Al	Al	— 3	1549
	V	Al	Al	3	1551
	Cu	Al	Al	3	1546
Ti ₃ Al (0001) Ti (0001)	—	—	—	—	3909
	Sn	Ti	Ti	1	3587
	Cu	Ti	Ti	1	3779
Ti ₃ Al (1010) Ti (1010)	—	—	—	—	3941
	Sn	Ti	Ti	1	3653
	Cu	Ti	Ti	1	3829

The particular positions of alloying elements are indicated by preferential sites relative to the interface (γ -TiAl, Ti₃Al or Ti, Al), sublattice occupation, and distance to interface expressed in the next nearest lattice plane.

cleavage energy. However, the absolute values of γ_c variations are comparable to the influence of alloying elements on the energy of other types of 2D defects, the stacking faults.^[61,64]

To gain a better understanding of the influence of solute atoms on cleavage energy, the electronic structure of two alloyed interfaces with the largest variations of γ_c *i.e.*, γ -TiAl (100) || Al (100) + V, Sn and Ti₃Al (0001) || Ti (0001) + Sn, Cu is investigated using the electron localization function (ELF) describing the probability of finding two electrons with the same spin in space.^[65–68] ELF is normalized to the range of 0 to 1, where 0.5 indicates a homogeneous electron gas, whereas values close to 1 represent a highly localized covalent or ionic interactions. As shown in Figures 4(a) and (c), the vanadium atom located close to the γ -TiAl (100) || Al (100) interface significantly increases the ELF, forming a strong covalent bond with the neighboring Al atoms and increasing γ_c . On the other hand, the preferential position of Sn is more distant from this planar defect (Figures 4(b) and (d)) and its impact on γ_c is low. It should also be noted that the bonds formed by Sn exhibit a different character. Although the localization of electrons around Sn is pronounced, covalent bonds characterized by a local and directional increase in ELF surrounded by ELF depletion^[63,69] are not formed. Such a topology of ELF function (a closed shell around an ion) corresponds to electrostatic, ionic-like interactions with adjacent atoms. In the case of Ti₃Al (0001) || Ti (0001), the addition of Cu (Figures 4(e) and (g)) results in considerable, mixed metallic-covalent bonding visible as an extended, partially directional ELF distribution with moderate value.

For this composition, the γ_c is lower than in an unalloyed system, as the amount of original covalent bonds is reduced. The Sn forms again, mainly with electrostatic interaction (Figures 4(f) and (h)) leading to the lowest γ_c .

IV. CONCLUSIONS

In this article, systematic, first principles calculations were performed to investigate the effect of Sn, V, Cu, and Mg alloying elements on the mechanical properties and structural stability of γ -TiAl and Ti₃Al intermetallic phases present in Ti/Al laminates fabricated with the explosive welding method. Apart from the bulk structures, seven ordered phase/metallic substrate interfaces were analyzed in terms of solutes segregation and cleavage resistance. The gathered data include low temperature (0 K) single- and polycrystalline elastic constants, *B/G* plasticity criterion, as well as the formation and cleavage energies of the studied systems. It was found that the effect of selected alloying elements is pronounced, especially for the elastic moduli and brittle/ductile behavior of γ -TiAl and Ti₃Al. The presented results can be useful for the proper selection of alloys used in explosive welding techniques and in future simulations extended by temperature effects or detailed plasticity analysis, such as dislocation modeling. The main findings of this work are as follows:

1. Sn, V, Cu, and Mg at 6.25 at. pct concentration are able to dissolve in γ -TiAl and Ti₃Al with negative formation energy.

Fig. 4.—The electron localization function of the selected alloyed interface with the largest cleavage energy variation: γ -TiAl (100) $\parallel$ Al (100) + V on (a) and (c), γ -TiAl (100) $\parallel$ Al (100) + Sn on (b) and (d), Ti_3Al (0001) $\parallel$ Ti (0001) + Cu on (e) and (g), Ti_3Al (0001) $\parallel$ Ti (0001) + Sn on (f) and (h). Cross-section planes are given below each ELF map. Ti, Al, and solute atoms are denoted by blue, gray and red, respectively. The interface plane is denoted by a black dashed line (Color figure online).

2. V and Mg always occupy the Ti sublattice, while Sn tends to substitute Al atoms. Cu prefers the Al and Ti position in γ -TiAl and Ti_3Al , respectively.
3. All the analyzed alloying elements increase the ductility of Ti_3Al , while Mg and Sn enhance the brittle nature of γ -TiAl.
4. Cu increases the B/G Pugh ratio of γ -TiAl and Ti_3Al by 25 and 14 pct, respectively. The above changes make this element a potentially universal solute in terms of the ductility improvement of the studied intermetallic compounds.
5. The investigation of seven selected γ -TiAl(Ti_3Al)/Ti(Al) interfaces showed that Mg is always insoluble close to 2D defects and only Sn is energetically stable at all the interfaces.
6. Solute elements have a noticeable effect on the mechanical properties of the intermetallic phases formed in the joints. Accordingly, the overall strength of the welded systems can be improved by careful selection of the composition of the substrate materials.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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