RSC Advances



View Article Online

View Journal | View Issue

PAPER

Check for updates

Cite this: RSC Adv., 2017, 7, 37852

First principles DFT study of interstitial hydrogen and oxygen atoms in the MAX phase Ti₂AlN

Francesco Colonna^{(Dab} and Christian Elsässer^{ba}

MAX phases are ternary metal carbides and nitrides with multi-layered crystal structures and mixed metalliccovalent bonding. They have very good thermal, chemical, and mechanical properties which make them potentially suitable as corrosion protection coatings for high-temperature energy-conversion devices such as solid oxide fuel cells. To assess the capability of MAX phases as diffusion barriers for hydrogen and oxygen, we investigate absorption and migration of interstitial H and O atoms in the MAX phase Ti₂AlN by means of first-principles calculations based on density functional theory. The resulting calculated formation and migration energies indicate that a Ti₂AlN coating can act as a protective diffusion barrier for both oxygen and hydrogen, but according to two different mechanisms.

Received 4th May 2017 Accepted 19th July 2017

DOI: 10.1039/c7ra05045c

rsc.li/rsc-advances

Introduction 1

MAX phases are a class of ternary nano-multi-layered crystalline compounds which exhibit an outstanding combination of high mechanical stiffness, electrical and thermal conductivity, corrosion resistance, and tolerance to thermomechanical shocks.1,2 All these properties make MAX phases an interesting class of materials for a wide spectrum of technological applications.

Recently, the proposed applicability of MAX as protective surface coatings of irradiated bulk metallic materials in nuclear fission or fusion reactors has stimulated several simulation studies of properties of atomic defects in MAX phases.³⁻⁵ The investigation of atomic defects, namely their formation and migration properties, is of great interest also for corrosionprotection applications in other thermo-chemo-mechanically aggressive environments. Solid Oxide Fuel Cells (SOFCs) operated at intermediate temperatures are an interesting case for the potential use of MAX phases as protective coatings. The SOFC technology offers an environment-friendly and costeffective way of efficient energy conversion. However, the success of SOFC stack devices is impeded by the fast corrosive degradation of the stainless-steel interconnect plates between the individual oxydic cells and the concomitant cathode poisoning of the cells.^{6,7} Indeed, to prevent the degradation in oxidizing and reducing environments at the operating temperatures of 600-800 °C, interconnect plates made of chromiumalloyed steel6-8 are used. This material, in turn, is prone to the formation of chromium hydroxides at the surface of the

interconnect plate, their subsequent evaporation, and their deposition on the surface of the oxydic cell cathode.

This chromium-poisoning mechanism is often responsible for a rapid decrease in the efficiency of energy conversion in SOFCs.7-10 Since MAX phases are known to be electrically conducting and stable in both hot and corrosive environments, they offer a good potential to be deployed as a protective surface coating for the steel interconnect plates in SOFCs stacks, and they may also enable the use of steels containing a lower concentration of chromium and thus leading to chromium poisoning at a reduced rate. In order to achieve the goal of longterm stable and efficient SOFC stack devices, it is essential to evaluate the capability of MAX phases as a protective barrier against the diffusion of both hydrogen and oxygen atoms.

Important pre-requisites for MAX phases to be usable in SOFC applications are a good thermal stability at the operation temperature and a coefficient of thermal expansion (CTE) close to those of the ceramic oxide cathodes and electrolytes, which typically range between 10.5 and $12.5 \times 10^{-6} \text{ K}^{-1}$.^{7,8}

In this work, employing a computational first-principles method based on density functional theory (DFT), we investigate the solution of interstitial hydrogen and oxygen atoms and the pathways and barriers for their migration in the crystal structure of the prominent MAX phase Ti₂AlN. The elucidation of the migration mechanisms for interstitial atoms in Ti₂AlN allows to assess the potential of such a MAX phase as a protective coating material. In Section 2 we describe the computational DFT method and the atomistic structure models used for the investigation. In Section 3.1 we report our results on the solution of interstitial H and O atoms in Ti₂AlN. In Section 3.2 we illustrate the migration paths, report the calculated energy barriers, and describe the distinct migration mechanisms for H and O. In Section 4 we discuss the results. Finally in Section 5 we make a summary and give some conclusions.

^aUniversity of Freiburg, Freiburg Materials Research Center (FMF), Stefan-Meier-Straße 21, 79108 Freiburg, Germany. E-mail: francesco.colonna@fmf. uni-freiburg.de

^bFraunhofer Institute for Mechanics of Materials IWM, Wöhlerstraße 11, 79108 Freiburg, Germany. E-mail: christian.elsaesser@iwm.fraunhofer.de

2 Structural models and computational method

2.1 Composition and structure of the MAX phase Ti_2AIN

MAX phases are defined by the composition formula $M_{n+1}A_1X_n$ (n = 1, 2 or 3), where M is a transition-metal element, A is a main-group element, and X is either carbon or nitrogen. Atoms are arranged in a hexagonal crystal structure, space group P_{63}/mmc (193), with $M_{n+1}X_n$ layers interleaved by an A monolayer.

2.2 Methodological details of the DFT calculations

To model formation energies and migration barriers of interstitial atoms, a hexagonal $2 \times 2 \times 1$ supercell of the Ti₂AlN crystal was used. The supercell was structurally relaxed by firstprinciples DFT calculations of total energies, forces, and stresses, using the GGA-PBE functional for exchange-correlation.11 All DFT calculations were done with the PWscf code of the Quantum Espresso software package12 and run with an ASE interface.13 The wave-functions of the valence electrons are represented by a plane-waves basis set with a cutoff energy of 544 eV, and the electron density and effective Kohn-Sham potential by discrete Fourier series with a cutoff energy of 2721 eV. The interactions of valence electrons with the atomic nuclei and core electrons are described by Vanderbilt's ultrasoft pseudopotentials as provided in the open-source pseudopotential library 'GRBV'.14 Brillouin-zone integrals are evaluated on a Monkhorst-Pack mesh of $6 \times 6 \times 4$ k-points with a Gaussian smearing of 0.02 eV. The convergence criteria was set to 1.36×10^{-6} eV for the total energy and to 2.57 imes 10⁻⁴ eV Å⁻¹ for the forces on atoms.

All thermodynamic quantities were calculated following the *ab initio* thermodynamics formalism¹⁵ at zero pressure and temperature. The solution energy $E^{f}[X, i]$ of an atom X (X = H or O) at an interstitial site i in the supercell of the Ti₂AlN crystal is calculated as

$$E^{f}[X, i] = E_{tot}[X, i] - E_{tot}[bulk] + \mu_{X}$$
(1)

where $E_{tot}[X, i]$ is the total energy of the supercell of the pure crystal with the interstitial atom X, $E_{tot}[bulk]$ is the total energy of the reference supercell of the perfect crystal, and μ_X is the chemical potential of either hydrogen or oxygen. The lattice constants were kept fixed during total energy calculations of point-defects. The chemical potentials with respect to the H₂ and O₂ gas phases were calculated as half of the binding energies of the H₂ and O₂ molecules. Our computed values for the binding energies of H₂ and O₂ are respectively -4.12 eV and -5.93 eV, in line with data from previous calculations.¹⁷ It is known for oxygen that LDA or GGA functionals result in an overbinding with respect the experimental value of -5.22 eV. For a discussion of this issue and possible empirical corrections we refer to, *e.g.*, ref. 17.

To validate the computational methodology, the lattice parameters of Ti_2AIN and formation energies of the three intrinsic point defects, namely the monovacancies v_{Ti} , v_{Al} and v_N were calculated and compared to literature benchmarks. Both the

resulting lattice-parameter values (a = 2.995 and c = 13.65) and the formation energies for v_{Ti} , v_{Al} and v_{N} (3.48 eV, 3.03 eV, and 4.58 eV respectively) are in agreement with data from previous experimental measurements¹⁸ and DFT simulations.⁴ In Fig. 1 we compare our results for the vacancy formation energies (top) and the chemical potentials (bottom) to literature data.

2.3 Interstitial sites for H and O atoms in the MAX phase Ti_2AlN

Following the work of Baben *et al.*¹⁹ on Ti₂AlC, Duan *et al.*⁴ investigated the solution of oxygen and hydrogen atoms at substitutional positions as well as at octahedral (Ti₃Al₃) and triangular (Al₃) interstitial sites of the Ti₂AlN crystal. Cui *et al.*²⁰ reported that the dynamics of oxidation of Ti₂AlN differs from that of Ti₂AlC. Therefore we extended the previous studies by considering the whole set of interstitial locations in the Ti₂Al (Ti–Al–Ti) double layer which are relevant for the solution and migration of H and O atoms (see Fig. 2): the Ti₃Al₃ octahedron, the Ti₃Al and TiAl₃ tetrahedrons, and the two non-equivalent triangular barrier locations Al₃^{II} and Al₃^{II} in the Al-plane. Moreover, Ti₄ tetrahedral sites in the Ti₂N (Ti–N–Ti) double layer are also considered.

The migration barriers were assumed to be located either at the interface of face-sharing polyhedrons (see Fig. 2), or at the



Fig. 1 Validation of the computational DFT setup. Top: Calculated formation energies (connected by lines) for the Ti, Al, and N vacancies in Ti₂AlN and for the H and O interstitials in the octahedral position Ti₃Al₃ compared to literature benchmarks⁴ (crosses). Bottom: Calculated chemical potentials (connected by lines) for H, N, and O compared to literature benchmarks¹⁶ (crosses).

RSC Advances





Fig. 2 Schematic representation of the Ti₂AlN supercell. Ti atoms are represented by red spheres, Al by blue ones, and N by grey ones. Polyhedra Ti₃Al₃, Ti₃Al, and TiAl₃ in the Ti₂Al (Ti–Al–Ti) layer are shown explicitly; grey arrows point to the triangular interfaces Ti₂Al, Al₂Ti, Al₃, and Al₄.

centre of N–N bonds of the Ti_2Al (Ti–Al–Ti) double layer for symmetry considerations. Migration barriers were obtained *via* a structural relaxation in which hydrogen atoms were constrained either on the planes spanned by triangles on the polyhedron's faces, or at the N–N bond centres.

3 Results

3.1 Solution of interstitial H and O atoms

Baben *et al.* reported that interstitial sites are the most stable sites for atomic species dissolved in Ti₂AlC and other MAXphase carbides.¹⁹



In contrast, oxygen exhibits a negative (exothermal) solution energy of several eV for all the interstitial sites. The results are displayed in Fig. 3 (bottom). The most stable positions for an O atom are the tetrahedral site Al_3Ti and the triangular barrier location Al_3 . Their very small energy difference is within the computational accuracy limit. Since the Al_3 triangle is the interface separating two mirror-imaged Al_3Ti tetrahedra, these two geometrical locations are effectively within one single site surrounded by a triangular bipyramidal Al_3Ti_2 cage. The solution energy for this site is -5.51 eV. The solution energies of the tetrahedral Ti_3Al and octahedral Ti_3Al_3 sites are higher by 0.24 and 0.91 eV, respectively. For the interstitial oxygen atom at the Ti_3Al_3 site our calculated solution-energy value -2.38 eV is 0.18 eV higher than the value reported by Duan *et al.*⁴



Fig. 3 Solution energies of interstitial hydrogen (top) and oxygen (bottom) in Ti_2AIN .



Fig. 4 (Top) Hydrogen lateral migration barriers (*i.e.* in a Ti–Al plane) between tetrahedral stable sites; (bottom) transversal migration barriers (*i.e.* between adjacent Ti–Al planes and through the Ti_2N double layer) between tetrahedral stable sites.

3.2 Migration of interstitial H and O atoms

3.2.1 Hydrogen. By calculating the migration barriers between interstitial sites, the energetically most favourable migration paths were identified (Fig. 4). The migration barrier between polyhedral sites is assumed to be located on or at least very close to their shared face. The Ti₃Al₃ octahedra are connected to Ti₃Al and TiA₃l tetrahedra through Ti₂Al and TiAl₂ faces, respectively, as shown in Fig. 2. The Ti₃Al₃ octahedra and Ti₃Al tetrahedra are connected to mirror-images with respect to the plane of Al atoms by the triangles labelled Al_3^I and Al₃^{II}. Finally, the transition state for the migration of an interstitial atom through a Ti₂N double layer is assumed to be centred at a N-N bond. The reason for this choice is the following: the octahedral sites Al₃Ti₃ in the Ti₂N double layer are occupied by nitrogen atoms, while the tetrahedral sites Ti₃Al therein are free to host interstitial atoms. To migrate through the Ti₂N double layer, a hydrogen or oxygen atom needs therefore first to enter a Ti₃Al tetrahedron and next to migrate to a mirrorimaged one by crossing an edge of Al₃Ti₃ at the mid point of the edge, *i.e.* at the centre of a N-N bond.

The calculated lowest migration-barrier value for interstitial hydrogen resulted to be 0.32 eV for the path $TiAl_3 \rightarrow Ti_3Al_3$. The inverse path has a slightly lower barrier of 0.28 eV. The barrier for the path $Ti_3Al_3 \rightarrow Ti_3Al$ is about twice as high. These results indicate the presence of two parallel, mirror-imaged, diffusion networks in between neighbouring Ti and Al layers, as illustrated in Fig. 5 (right). Indeed, a hydrogen atom can get to the mirror-imaged Ti–Al layer via the path $Ti_3Al \rightarrow Ti_3Al_3 \rightarrow TiAl_3$ \rightarrow Ti₃Al₃ \rightarrow Ti₃Al₃^{mirror} \rightarrow Ti₃Al^{mirror}. This migration path has a barrier of 1.2 eV, which is associated with the $Ti_3Al_3 \rightarrow TiAl_3$ step and located in the Al₃^I triangle. A schematic representation of these diffusion channels is shown in Fig. 5 (left). An interstitial H atom migrating in the c-axis direction of the MAX crystal, with a transition state assumed in a N-N bond as motivated above, has to overcome a high barrier of more than 3 eV, which is one order of magnitude higher than the barriers in the *ab*-plane directions.



Fig. 5 (Left) Schematic representation of migration paths of interstitial hydrogen in Ti₂AlN highlighting the in-plane migration network in the Ti₂Al double layer. Green arrows indicate the path with the lowest migration barrier between Ti₃Al interstitials. Yellow circles indicate the metastable states from where a migration between mirror-imaged Ti–Al planes is possible. (Right) Hydrogen migration path in the transversal direction. Green arrows indicates the in-plane migration network in the Ti₂Al double layer, while yellow arrows indicates the transition between mirror-imaged Ti–Al planes.

Hence, the network of migration pathways for long-range diffusion of interstitial H atoms in Ti₂AlN can be described as follows: there are two mirror-imaged honey-comb networks between two neighbouring planes of Ti and Al atom with a migration barrier of 0.32 eV. These networks enable the long-range diffusion in the "lateral" directions, *i.e.* in the *ab*-plane spanned by the lattice vectors \vec{a} and \vec{b} of the hexagonal cell. The networks are further connected by a shifted hexagonal network with a barrier of 1.2 eV, which allows for a migration in the *c*-axis (transversal) direction at least between the adjacent Ti₂Al double layer. The migration to a more remote Ti₂Al double layer is hindered by the presence of the Ti₂N double layer in between, with a barrier that is one order of magnitude higher. This network of pathways is illustrated by the schematic sketches in Fig. 5.

3.2.2 Oxygen. The diffusion of interstitial oxygen was investigated on the same network of sites and paths as for interstitial hydrogen. However, as discussed above, in this case the two mirror-imaged tetrahedra Al_3Ti connected by the same A_3 interface do effectively form one single interstitial transition state in the center of the trigonal bipyramid $Al_3Ti_2^*$. Therefore in the case of oxygen the channels for long-range diffusion in the two mirror-imaged planes of the Ti_2Al double layer are separated by virtually no barrier. As a result, there is one single effective honey-comb network for the *ab*-plane diffusion that connects directly two stable interstitial sites along the migration path $Al_3Ti_2^* \rightarrow Al_3Ti_3^*$.



Fig. 6 (Top) Oxygen lateral migration barriers (*i.e.* in a Ti–Al plane) between tetrahedral stable sites; (bottom) oxygen transversal migration barriers (*i.e.* between adjacent Ti–Al planes and through the Ti₂N double layer) between tetrahedral stable sites.

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

RSC Advances



Fig. 7 Schematic representation of interstitial diffusion paths of oxygen in Ti₂AlN. (Left) In-plane migration network in the Ti₂Al double layer. Circles indicate the stable Al₃Ti₂^{*} interstitial connecting the two mirror-imaged TiAl planes. (Right) Oxygen migration path in the transversal direction.

The migration barrier for the path $Al_3Ti_2^* \rightarrow Al_3Ti_3$ is 1.37 eV and located at the triangular Al_2Ti face as shown in Fig. 6. The barrier for the inverse path $Al_3Ti_3 \rightarrow Al_3Ti_2^*$ is 0.42 eV. The interstitial diffusion through the Ti_2N double layers is hindered by a large barrier of over 8 eV (Fig. 6). The resulting diffusion network is depicted schematically in Fig. 7. As in the case of hydrogen the *ab*-plane migration for oxygen has a much lower barrier than the *c*-axis migration. In contrast to hydrogen, the *ab*-plane migration of oxygen has a simpler mechanism, namely $Al_3Ti^* \rightarrow Al_3Ti_3 \rightarrow Al_3Ti^*$, on a honey-comb network. But for oxygen there is a more than four times higher barrier as compared to that of hydrogen.

4 Discussion

There is only few discussion in literature about the absorption and diffusion of hydrogen in MAX phases. A MAX phases coating can protect a substrate from diffusing hydrogen in two ways: (1) by a high migration barrier, and (2) by a high solution energy, which hinders the absorption of the diffusing species in a first place. In the literature hydrogen absorption on interstitial sites is reported to be favoured by a slightly negative (exothermal) energy of solution, however depending on its chemical potential as function of the thermodynamic conditions.4 In the hydrogen-rich limit, instead, we get a close-to-zero but positive (endothermal) solution energy of 0.06 eV for a H atom at a Al₃Ti site. This value is lower than the solution energy of hydrogen in α-iron (DFT-GGA values: 0.19 eV,²¹ 0.16;²² experimental values: 0.296 eV,23 0.28 eV 24), which indicates that Ti₂AlN cannot act as a diffusion barrier for iron-based interconnects by hindering absorption.

The calculated migration barriers for both interstitial H and O atoms indicate strongly anisotropic diffusion in the MAX phase. Even in the absence of other atomic or microstructural defects, hydrogen is expected to be relatively mobile along the Ti–Al *ab*-planes because of its modest activation barrier of 0.32 eV for migration. This value can be compared to the *ab*-plane diffusion in the MAX phase Ti₃AlC₂, which was recently calculated by Yang *et al.*²⁵ Here two non-equivalent barriers of 0.21 eV and 0.67 eV along the [-1, 0, 0] and [0, 1, 0] directions were found, indicating as well a fast *ab*-plane diffusion of

interstitial hydrogen. Hence, the potential of Ti₂AlN as a diffusion barrier for hydrogen is apparently linked to the capability of depositing dense Ti₂AlN films with the *ab*-plane atomic layers of Ti, Al, and N growing parallel to the surface of the substrate. In this case the high migration barrier of the Ti₂N double layer in the *c*-axis direction can effectively impede the diffusion of hydrogen.

The situation is more complicated for the case of oxygen. Recently Cui et al.20 investigated spark plasma sintered Ti2AlN and its oxydic surface scales formed after high-temperature oxidation for 1 hour. Below 900 °C (i.e. at operation temperatures of SOFCs) a double-layer scale is formed: the first layer is composed of porous TiO2 scale in contact with the bulk Ti2AlN phase, the second layer is a dense mixture of TiO2 and α-Al2O3 with a nominal composition Al₂TiO₅. At higher temperatures (1000-1400 °C), a complex interplay of mixing and demixing of α-Al₂O₃ and Al₂TiO₅ phases is observed. Above 1100 °C the growth rate of the scale increases steeply and void-containing layers are formed, probably due to the formation of gaseous NO_x . These temperatures are above the stability limit of the MAX phase, as reported by Scabarozi et al.26 The emerged scenario is consistent with our finding that oxygen tends to be absorbed interstitially in Ti₂Al double layers and to diffuse along these. Only at very high temperatures there may be some incorporation of oxygen atoms into the Ti₂N double layers, which may be also facilitated by dislocations or cracks induced by the mismatch in the thermal expansions of the oxydic constituents of the scale and the bulk MAX phase. It is not clear whether complicated mixing and demixing of TiO₂, α-Al₂O₃, and Al₂TiO₅ should be expected for longer operation times of SOFCs also at temperatures below 900 °C. Zhang et al.27 showed that thin films of Ti₂AlN oxidized at 900 °C for 20 hours have an α -Al₂O₃ scale with a low content of TiO₂ second phase growing parabolically in time. This indicates a diffusion-limited growth mechanism, which can be associated to slow diffusion of oxygen through the surface scale and into the Ti₂AlN. Moreover, they find a low oxygen content in the interior of the Ti₂AlN layer, which also indicates a diffusion rate which is significantly lower than that of H atoms, in line with our results. The analysis of results of simulations and experiments, therefore, indicates that for the case of oxygen a two-fold protection mechanism is apparently present. First, due to the formation of an oxydic scale, solution of oxygen inside the MAX phase is hindered, except for an adsorption on the surface. Second, due to a high migration barrier for interstitial oxygen in all crystal directions of the MAX phase, the oxydic scale remains confined to the surface. In contrast to the case of hydrogen, the migration barrier for oxygen is therefore expected to be significantly high even for the diffusion in the ab-plane of the MAX-phase crystal.

5 Summary and conclusions

Solution and migration of interstitial hydrogen and oxygen atoms in the MAX-phase crystal Ti_2AIN were investigated in order to assess the potential capability of a MAX phase to act as a protective diffusion-barrier coating of steel components in SOFC stacks. There are further mechanisms for the solution

View Article Online RSC Advances

and migration of hydrogen and oxygen relevant in practice, namely substitutional solution and vacancy-mediated diffusion of foreign atomic species inside the crystal structure or at extended microstructural defects, namely dislocations and grain boundaries. The present study, however, focused on the evaluation of the protection potential of Ti₂AlN by assessing the case of the ideal crystalline limit, where no other defects than the interstitial H or O atoms are present. We obtained solution energies and migration barriers by means of first-principles DFT calculations. The results indicate that a Ti₂AlN coating layer can act as a barrier against diffusion of interstitial H atoms in the c-axis direction of the MAX phase but offers no significant protection against diffusion along *ab*-plane directions. For interstitial O atoms, in contrast, the migration barriers in all directions are of the order of several eV. Moreover, absorption calculations and experimental results reported in the literature suggest that, when the surface of a MAX phase is in contact with oxygen, alumina and titania scales are formed. Hence, we speculate that a Ti₂AlN coating on a steel interconnect plate has the potential to act as a protective diffusion barrier for hydrogen and oxygen in a SOFC stack, provided that the formation of a compact, coarse-grained, well c-axis oriented, and well abplane textured Ti₂AlN coating can be achieved on steel by a robust and efficient deposition process.

Acknowledgements

This research is supported by the Baden-Württemberg Stiftung GmbH through the research programme "CleanTech" (project CT-6 "LamiMat"). We thank Dr D. Di Stefano, Mr L. Gröner, and Dr F. Burmeister for valuable discussions, and Dr B. Ziebarth for his interface of the PWScf code to the ASE software.

References

- 1 M. W. Barsoum, Prog. Solid State Chem., 2000, 28, 201-281.
- 2 P. Eklund, M. Beckers, U. Jansson, H. Högberg and L. Hultman, *Thin Solid Films*, 2010, **518**, 1851–1878.
- 3 S. C. Middleburgh, G. R. Lumpkin and D. Riley, *J. Am. Ceram. Soc.*, 2013, **96**, 3196–3201.
- 4 J. Z. Duan, J. R. Zhang, C. L. Wang, Y. Qiu, W. S. Duan and L. Yang, *RSC Adv.*, 2014, **4**, 42014–42021.
- 5 Z. Zhang, H. Jin, J. Pan, J. Chai, L. M. Wong, M. B. Sullivan and S. J. Wang, *J. Phys. Chem. C*, 2015, **119**, 16606–16613.
- 6 J. Wu and X. Liu, J. Mater. Sci. Technol., 2010, 26, 293-305.
- 7 N. Mahato, A. Banerjee, A. Gupta, S. Omar and K. Balani, *Prog. Mater. Sci.*, 2015, **72**, 141–337.

- 8 G. Jia and L. Yang, Phys. B, 2010, 405, 4561-4564.
- 9 J. Fergus, Int. J. Hydrogen Energy, 2007, 32, 3664-3671.
- 10 N. Shaigan, W. Qu, D. G. Ivey and W. Chen, *J. Power Sources*, 2010, **195**, 1529–1542.
- 11 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.
- 13 S. R. Bahn and K. W. Jacobsen, *Comput. Sci. Eng.*, 2002, **4**, 56–66.
- 14 K. F. Garrity, J. W. Bennett, K. M. Rabe and D. Vanderbilt, *Comput. Mater. Sci.*, 2014, **81**, 446–452.
- 15 C. G. V. de Walle and J. Neugebauer, J. Appl. Phys., 2004, 95, 3851–3879.
- 16 C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti and C. G. Van de Walle, *Rev. Mod. Phys.*, 2014, 86, 253–305.
- 17 L. Wang, T. Maxisch and G. Ceder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, 73, 5419–5423.
- 18 M. W. Barsoum, M. Ali and T. El-Raghy, *Metall. Mater. Trans.* A, 2000, **31**, 1857–1865.
- 19 M. Baben, L. Shang, J. Emmerlich and J. M. Schneider, *Acta Mater.*, 2012, **60**, 4810–4818.
- 20 B. Cui, D. D. Jayaseelan and W. E. Lee, *Acta Mater.*, 2011, **59**, 4116–4125.
- 21 D. E. Jiang and E. A. Carter, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 064102.
- 22 D. Di Stefano, R. Nazarov, T. Hickel, J. Neugebauer, M. Mrovec and C. Elsässer, *Phys. Rev. B*, 2016, 93, 184108.
- 23 J. P. Hirth, Metall. Trans. A, 1980, 11, 861-890.
- 24 H. Wipf, Phys. Scr., T, 2001, 94, 43-51.
- 25 S. Yang, N. Hu, X. Gou, C. Wang, X. Zhu, X. Duan, W. Duan and L. Yang, *RSC Adv.*, 2016, **6**, 59875–59881.
- 26 T. H. Scabarozi, S. Amini, O. Leaffer, A. Ganguly, S. Gupta,
 W. Tambussi, S. Clipper, J. E. Spanier, M. W. Barsoum,
 J. D. Hettinger and S. E. Lofland, *J. Appl. Phys.*, 2009, 105, 13543.
- 27 T. Zhang, H.-B. Myoung, D.-W. Shin and K. H. Kim, J. Ceram. Process. Res., 2012, 13, S149–S153.