

High-Throughput Reaction Engineering to Assess the Oxidation Stability of MAX phases

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Abstract

The resistance to oxidizing environments exhibited by some MAX phases stems from the formation of stable and protective oxide phases at high operating temperatures. However, previous attempts to model and assess oxide phase stability in these systems has been limited in scope due to the high computational cost associated with this type of analysis. To address the issue, we have developed a machine learning driven high-throughput framework for the fast assessment of phase stability and oxygen reactivity with 211 chemistry MAX phase, M_2AX [2 (M):1(A):1(X)], where M=Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Co, Ni, and Cu, A=(Al, Si), and X=C. The proposed scheme combines a sure independence screening sparsifying operator (SISSO)-based machine learning model in combination with grand canonical linear programming to assess temperature dependent Gibbs free-energies, reaction-products, and chemical activity of reaction products during the oxidation. We perform high-throughput calculations of temperature-dependent free energy stability for 30 MAX phases with different compositions. The thermodynamic-stability, and chemical activity of constituent elements of Ti_2AlC with respect to oxygen is fully assessed to understand their oxidation behavior from 300-2000 K. The predictions are in good agreement with oxidation experiments performed on Ti_2AlC . We were also able to explain the metastability of Ti_2SiC MAX phase, which could not be synthesized experimentally due to higher stability of competing phases. For generality of the proposed approach, we discuss the oxidation mechanism of Cr_2AlC MAX phase. The insights of oxide phase stability will enable more efficient design and accelerated discovery of MAX phases with maintained performance at high temperatures in oxidizing environments.

Keywords: Machine learning, MAX phase, DFT, SEM, Oxidation.

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Introduction

$M_{n+1}AX_n$ (MAX) phases belong to the group of ternary carbides and nitrides in which M is early transition metal, A is group 13-16 element and X is C and/or N [1-3]. Unlike conventional ceramics, MAX phases are machinable [4] and have unique combination of properties such as low density, high strength [5], excellent thermal shock resistance, and damage tolerance [6]. MAX phases are particularly useful due to their high-temperature stability, making them suitable for structural applications—under extreme (or at least elevated) ambient temperature conditions—in a number of industries, including nuclear power and aerospace propulsion systems [4]. Tailoring the composition within the MAX crystal system can provide further control of the chemical, mechanical, magnetic and thermal properties of these compounds [2]. Unfortunately, at elevated temperatures and under oxidizing conditions, most MAX phases undergo detrimental self-sustaining oxidation reactions that result in catastrophic loss of mechanical integrity [4,7-11].

The oxidation behavior of ceramic materials such as MAX phases has often been used as a primary materials selection criterion for high temperature applications. The potential oxidation resistance of a candidate MAX phase depends on its ability to form a stable passivating oxide layer as weakly bonded elements that typically reside in the A-sites react with oxygen in the environment. The Al, Cr, or Si-containing MAX phases have been shown to provide varying degrees of protection from further oxidation by forming primarily Al_2O_3 , Cr_2O_3 , or SiO_2 protective coatings at high temperatures [9,12]. Ti_2AlC , Ti_3AlC_2 , Cr_2AlC , or Ti_3SiC_2 are few such examples of Al, Cr or Si-containing MAX phases, where the weakly bonded A-element (Al, Si) is capable of leaving the layered lattice to form protective predominately Al_2O_3 and SiO_2 oxide scales during high temperature oxidation [9,10,13]. The facile formation of a protective Al-/Si-based oxide layer is likely the result of a higher Al/Si diffusivity and chemical activity when compared to M element, that makes them readily available for oxidation at the surface of the MAX phase compound in contact with an oxidizing environment [14-17].

Despite the fact that the assessment of oxidation behavior in MAX phases is of critical importance for their further development as a high-temperature structural or coating material, to date there is no current computational approach capable of quickly assessing the oxide phase stability of arbitrary MAX phase compositions. Such an approach could in turn be used to guide the experimental discovery and optimization of MAX phases with superior high-temperature

performance under oxidizing conditions. Unfortunately, the oxidation process is very complex and expensive to model computationally, and to characterize experimentally. It requires detailed and definitive studies of oxide thickness, stresses, diffusion coefficients, equilibrium parameters, and volume change as functions of oxidation temperature and time [18-20]. On the computational front, assessment of the phase stability of a materials system under oxidation requires full knowledge of the finite-temperature thermodynamics of all phases likely to take part in equilibrium at particular conditions (temperature and composition of the system). This information may not be readily available in conventional thermodynamic databases and is exceedingly expensive to acquire from *first principles* methods [21].

To address the computational bottleneck, we present an automated machine learning-based scheme to predict favorable thermodynamic reactions and oxidation behavior of MAX phases at elevated temperatures at different oxygen partial pressures (p_{O_2}). Our workflow combines sure independence screening and sparsifying operator (SISSO) [22-24] with grand canonical linear programming (GCLP) [25,26] into a single framework to predict the phase stability of product phases of the general $[M_{n+1}AX_n + O_2]$ reaction at elevated temperatures. Here, we mainly focused on $n=1$ MAX phase, i.e., M_2AX , where early transition elements (M), group-13/14 ($A=Al, Si$), and group-14 (C, N) elements are mixed in 2:1:1 ratio. Experimental enthalpy and total energy database of transition metal oxides and other (binary, ternary) phases, required to predict finite temperature Gibbs' free energies (ΔG_{form}) by SISSO, are taken from the NIST-JANAF thermochemical tables [27,28], Open Quantum Materials Database (OQMD) [29], and first-principles density functional calculations. GCLP uses temperature dependent ΔG_{form} from SISSO to predict $[M_2AX+O_2]$ reaction products, fractions of the product states, and their chemical activities for given temperature and oxygen content. Among the alumina-forming MAX phases, we choose Ti_2AlC for detailed comparative theoretical and experimental study because of its practical applications [30,31]. Our high-throughput predictions compare well with experiments. We also present a detailed discussion on our predictions on oxidation behavior of Cr_2AlC in order to show the generality of our scheme.

Methods

High-throughput framework: We develop an in-house machine-learning based high-throughput scheme (see schematic in Fig. 1), which is capable of predicting ΔG_{form} using SISSO [23] and phase-prediction as well as chemical activity of constituent elements using GCLP model [25,26]

in inorganic stoichiometric phases. The SISSO model [23] uses NIST-JANAF [27,28], and OQMD (DFT) [29] database to predict ΔG_{form} across the temperature range.

NIST-JANAF and OQMD (DFT) database: The experimental formation energy (E_{form}) data for transition metal oxides was extracted from the NIST-JANAF thermochemical database [27,28]. We also calculated E_{form} from DFT using structure files from DFT based Open Quantum Materials Database (OQMD) [29] for each oxide phase.

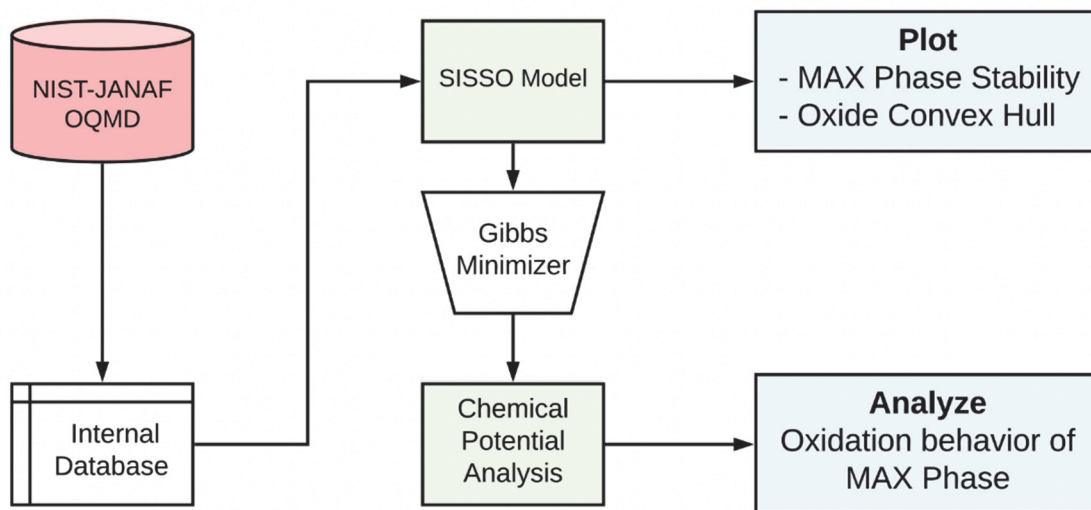


Figure 1. Schematic representation of the workflow. The SISSO and GCLP based machine learning workflow to predict oxide phase selection and stability of MAX phases.

Sure Independence Screening and Sparsifying Operator: Much of the research into developing models for predicting MAX phase stability has utilized computationally intensive methods [32,33], such as DFT calculations carried out using the Vienna Ab initio Simulation Package (VASP) [34,35]. Expensive DFT estimates of the entropic (ΔS) contributions in the calculation of ΔG_{form} limits their use in accelerated material design [36]. Fortunately, it has been demonstrated that DFT calculations augmented with machine learning and experimentally acquired information provides the means for predicting material properties quickly and accurately [23]. The SISSO framework, for example, is an emerging machine learning algorithm capable of arriving at accurate predictions of material properties through models that employ physically meaningful features [19-21]. Here,

we utilize the descriptor-based model from Bartel for the finite-temperature Gibbs energy of an arbitrary inorganic stoichiometric phase [23]:

$$G^{SISSO} (eV/atom) = (-2.48 \cdot 10^{-4} \cdot \ln(V) - 8.94 \cdot 10^{-5} \cdot mV^{-1})T + 0.181 \cdot \ln(T) - 0.882$$

Eq. (1)

for the fast assessment of $\Delta G_{form} = \Delta H_{form} + \Delta G^{SISSO}(T) - \sum_i x_i \Delta G_i(T)$, and validate the approach for binary oxides (Ti-O and Al-O) with respect to temperature and oxygen concentration. We test the predicted ΔG_{form} of transition metal oxides in 300 K – 2000 K temperature range [19-21]. The predicted ΔG_{form} were compared to experimental data from the NIST-JANAF thermochemical tables to determine the model accuracy across a wide temperature range. Additionally, a convex hull was generated for the titanium-oxygen chemical system using the model predictions as a validation test. The SISSO model was then used to assess the thermodynamic stability of M_2AC MAX phases to identify the effect of transition metal-elements (M), where M=Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Co, Ni, and Cu) in MAX phases with A=Al, and Si.

Grand Canonical Linear Programming: The linear nature of the Gibbs energy minimization problem allows the use of linear programming-based algorithms to identify the equilibrium configuration of chemical systems under arbitrary thermodynamic conditions. The GCLP method is one such approach [25,26], and we use it in this study to predict thermodynamically favorable phases from $Ti_2AlC + O_2$ reactions by breaking down the system into a series of linear equations for the different chemical reactions that can take place at given temperature and given oxygen content. The GCLP minimizes the Gibbs energy of the mixture of the elements at a given Ti, M, C, and O composition (for example):

$$\Delta G = \sum_{phase} f_{phase} \cdot \Delta G_{phase}$$

where, ΔG_{phase} is the Gibbs free-energy of each competing phase “*phase*” and f_{phase} is the phase-fraction. We minimize ΔG to determine the molar fraction of each phase. The predicted phase stability is used to estimate chemical potential of each element against given oxygen molar composition. These results are then compared with experimental data to assess the accuracy of the predictions. We note that the oxidation reaction at the interface of MAX phase is a phase selection process and the most favorable product phases tend to be those possessing the lowest combined

energy relative to the reactants, i.e., this yields highest possible oxidation reactivity. The reliability of GCLP approach depends on the accuracy of free energy database. We use free-energy database constructed from NIST-JANAF (experiments) [27,28], OQMD [29], and DFT [37,38].

Vacancy calculation: Our experiments indicate the importance of Al deficiency (vacancy formation) in the selective oxidation and oxidation stability of Ti_2AlC MAX phase (see supplemental **Fig. S6**). The input structures of $\text{Ti}_2(\text{Al}_{1-x}\text{V}_x)\text{C}$ for $x = 3.125$, $x = 6.25$, and $x = 9.375$ for the DFT calculations were modeled using 128-atom special quasi-random structures [39,40]. The stability of Al-depleted Ti_2AlC , $\text{Ti}_2(\text{Al}_{1-x}\text{V}_x)\text{C}$, relative to the competing intermetallic phases was investigated using GCLP. DFT-VASP [34,35] was used for structural minimization, total energy and formation enthalpy calculation of vacancy structures. Forces and total energies are converged to $-0.001 \text{ eV/\AA}$ and 10^{-5} eV/cell , respectively. Both for relaxation and energy calculation, we used Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation with a planewave cut-off energy of 533 eV [41]. The geometry-optimization and charge self-consistency of each MAX phase is done using gamma-centered Monkhorst-Pack [42] k-mesh a $3 \times 3 \times 3$ and $5 \times 5 \times 5$, respectively. The formation enthalpies of with and without vacancy MAX phases are calculated using the information of element energies.

Material preparation: Ti, Al, and TiC powders are mixed in 1.05:1.05:0.95 atomic ratio in a glass jar. The (Ti, Al, TiC) powder is ball milled for mixed for 24h. The ZrO_2 balls are used to grind the mixture to make the powder finer at the rotation speed of 300 rpm. The powder mixture is poured into an alumina crucible (AdValue Technology, US) and heated up to 1400°C at a 10°C/min heating rate in Ar atmosphere for 4h in a tube furnace (MTI Corporation, CA). The low-density Ti_2AlC is drilled and meshed into powder with particle size smaller than $90 \mu\text{m}$. The fine Ti_2AlC powder is poured into a graphite die (20 mm in diameter) loaded with 100 MPa pressure heated by Pulsed Electric Current Sintering (PECS, GT Advanced Technologies, CA) to 1400°C in the Ar-atmosphere and densified for 15 min. The full-dense Ti_2AlC cylinders are cut into discs of 19.6 mm diameter and 2 mm thickness using wire electrical discharge machining (EDM). The EDM layers are then removed followed by mechanical polishing to $0.1 \mu\text{m}$ prior and diamond paste finish before joining the pieces.

Fabrication of wedge-shaped samples and oxidation testing: An Al coupon is placed on a hot plate (Thermo Scientific) and heated up to 80°C. Then, the crystalbond (Ted Pella) is used to join the Ti₂AlC discs with Al coupon. After cooling down, the bonded couples are carefully polished on the Ti₂AlC side to a wedge shape with a $3.5 \pm 0.2^\circ$ taper and the thickness from 30 to 500 μm . Oxidation tests are carried out in a box furnace (Carbolite, UK). The couples are placed in acetone (Macron Fine Chemicals) to debond and the wedge-shaped Ti₂AlC samples are kept on the alumina crucibles in the hot chamber and oxidized in static air.

Characterization: The cross sections of the oxidized wedge-shaped Ti₂AlC samples are mechanically polished to 0.1 μm diamond paste finish. Scanning Electron Microscopies (FE-SEM, Quanta 600 FEG, FEI, Oregon, USA) equipped with Energy Dispersive Spectroscopy (EDS) are used to analyze the microstructure and composition of phases along the wedge. The average critical thickness is measured from SEM images. Electron microprobe analysis (EPMA) is used for a quantitative phase evaluation in the breakaway oxidation region in Ti₂AlC. We use electron backscattered diffraction (EBSD) in the same region to identify exact phases. The sample is polished using a 0.05 μm colloidal silica solution prior to the EBSD characterization. A Zeiss Ultra Plus FEGSEM equipped with an Oxford Instrument Aztec EBSD system and a Nordlys nano EBSD detector was used for the characterization.

Results & Discussion

Since model evaluation is a very important criteria in machine learning approaches, we use composition dependent Ti_xO_{1-x} (also see Fig. S1 for Al_xO_{1-x}) as a test set to validate the SISSO [22-24] predictions by calculating temperature dependent convex hull as shown in in Fig. 2a (also see Table S1). Our predictions and error in predictions of ΔG_{form} for Ti_xO_{1-x} are validated against the experimental dataset from NIST-JANAF thermochemical tables [27]. Model predicts TiO₂, Ti₃O₅, TiO₃, TiO, Ti₂O, Ti₃O, and Ti₆O as seven stable phases at 300 K, whereas Ti₂O and Ti₆O phases disappear from the convex hull at 1800 K. The convex hull at any given temperature suggests thermodynamic stability of that phase or composition, whereas any phase above the convex hull is thermodynamically metastable. The error (RMSE) in the predictions of ΔG_{form} of Ti_xO_{1-x} increases with temperature with outliers emerging at higher temperatures in Fig. 2b-d, which possibly originates from the use of 0 K cell volumes of the involved phases as a feature used

to compute the finite-temperature Gibbs free energy of formation. The increase in prediction error (R^2) at elevated temperatures, in part, may also stem from possible phase changes at higher temperatures. Regardless of these limitations, the close agreement between predicted and experimental ΔG_{form} at higher temperatures in **Fig. 2** indicates that the prediction error in ΔG_{form} can be minimized by proper assessment of formation enthalpies. The phases of Ti-O compounds that underwent gas phase transitions were omitted at higher temperatures [23].

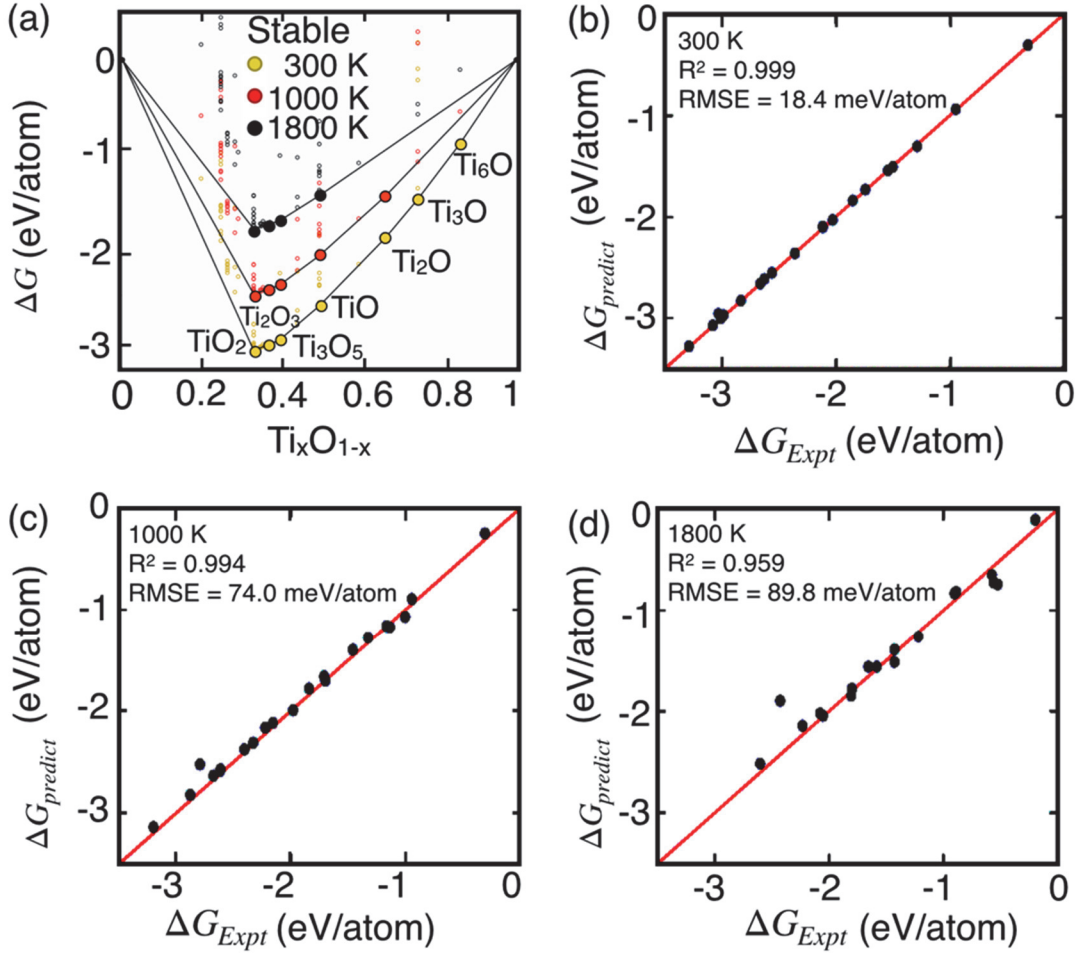


Figure 2: (a) Convex hull of $Ti_{1-x}O_x$ generated using SISSO model, and (b-d) corresponding error in prediction compared to experimental (NIST-JANAF) dataset at 300 K, 1000 K, and 1800 K. The error in prediction increases with temperature due to use of 0 K unit cell volumes.

The SISSO framework predicts the ΔG_{form} using the ΔH_{form} as input as accessed from OQMD [29], which is defined conventionally as the difference of total energies between a

compound and its constituent elements as $\Delta H_{\text{form}} = E_{\text{total}}^{\text{compound}} - \sum_i n_i E_i$, where $E_{\text{total}}^{\text{compound}}$ is the total energy of the alloy, (n_i, E_i) is the number of atoms and elemental energy of type 'i'. The SISSO predicted ΔG_{form} correspond to a single phase, not to the entire convex hull. A set of ΔG_{form} are used to compute the convex hull (as a function of temperature), see **Fig. 2** (Ti-O) and **Fig. S2** (Al-O).

SISSO predicted ΔG_{form} of MAX phases: The ΔG_{form} is the relevant thermodynamic potential to assess thermodynamic equilibrium under isobaric/isothermal conditions for closed systems. Its minimization naturally leads to the determination of the most stable equilibrium state and can thus be used to assess the resulting reaction products for a given set of reactants. Therefore, the knowledge of the temperature-dependent ΔG_{form} of reaction products during oxidation can greatly help the screening of MAX phases capable of withstanding high temperature oxidizing conditions. We use the proposed high-throughput scheme to calculate temperature dependent ΔG_{form} of 30 MAX phases with 211 stacking. The model uses the 0 K formation enthalpies ΔH_{form} [0 K; see **Table S2 & S3**] of M_2AC (M=Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, Fe, Co, Ni, and Cu; A=Al, and Si) MAX phases and elemental ΔG_i from experiments to estimate $\Delta G_{\text{form}} [= \Delta H_{\text{form}} + \Delta G^{\text{SISSO}}(T) - \sum_i x_i \Delta G_i(T)]$ at elevated temperatures; here x is the stoichiometric weight of each element in the compound, ΔH_{form} is the formation enthalpy; and ΔG^{SISSO} is SISSO predicted entropic contribution to the ΔG_{form} [23]. We note that the calculation of the finite-temperature phase stability of just one system *may take millions of supercomputing CPU-hours, and months of actual calculation time*, as demonstrated in work by a subset of these authors in the investigation of the phase stability in the Ti_2AlC - Cr_2AlC quaternary system [21].

The ΔG_{form} for aluminum- and silicon-based MAX phases is shown as a heat map in **Fig. 3a** and **Fig. 3b**, respectively for 300 K – 2000 K temperature range. The ΔG_{form} for $M_2\text{AlC}$ and $M_2\text{SiC}$ is arranged as increasing valence electron count (VEC) across the period in the periodic table for M from group III to XI with VEC of 3-11 [(III=Sc, Y), 4 (IV=Ti, Zr, Hf), 5 (V=V, Nb, Ta), 6 (VI=Cr, Mo), 7 (VII=Mn), 8 (VIII=Fe), 9 (IX=Co), 10 (X=Ni), and 11 (XI=Cu)]. The ΔG_{form} shows decreasing trend in stability with increase in valence electron counts. The Fe_2AlC , Co_2AlC , Ni_2AlC , Cu_2AlC MAX phases with higher VEC do not exist as they decompose to competing phases [2], which further confirms our results. In addition to highlighting a relationship between

the thermodynamic stability of MAX phases with VEC, we show the temperature dependent ΔG_{form} of Ti_2AC ($\text{A}=\text{Al}, \text{Si}$) and other possible binary phases in **Table S4** and **Table S5**. The jump in ΔG_{form} at Ta-to-Cr and Ni-to-Cu is clearly visible with increasing VEC in **Fig. 3a&3b**. This arises from near half-filling of d -states in Cr, and complete filling of non-bonding d -states in Cu. The ΔG_{form} also shows weakly separated stability regions with respect to temperature at 600 K, i.e., below 600 K and over 600 K (see **Fig. S2**). The change in the ΔG_{form} at higher temperatures implies an interplay of temperature dependent enthalpy and entropic contributions. The accuracy of the SISSO model in predicting ΔG_{form} of binary oxides and MAX phases shows good agreement between predicted and experimentally known Ti-O phases as shown in **Fig. 2**. Similarly, we show the heat map of M_2SiC ΔG_{form} , where $\text{M} = \text{Sc}, \text{Y}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu , for the temperature range 300 K – 2000 K. The fast assessment of ΔG_{form} using SISSO will allow us to quickly scan the thermodynamic stability of MAX phases in particular, and a wider range of materials in general.

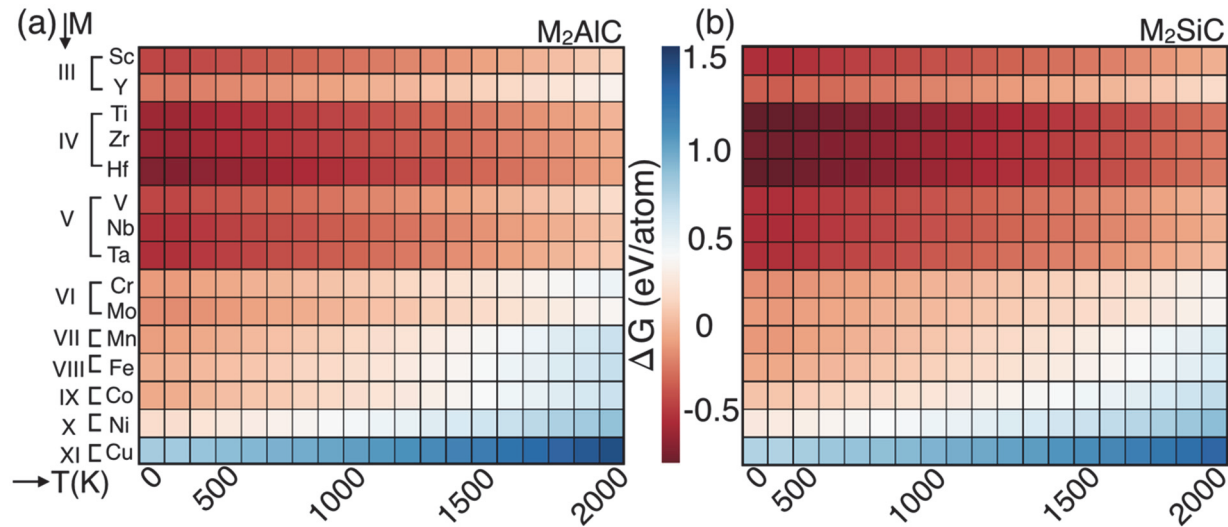


Figure 3. Stability heat map for (a) M_2AlC , and (b) M_2SiC MAX phases. M elements organized by periodic group, arranged by increasing valence electron count. Also see SISSO predicted ΔG_{form} in **Table S3** of other binary and ternary phases.

The ΔG_{form} for the different MAX phases in **Fig. 3** is a thermodynamically defined quantity that indicates the *intrinsic* stability of different MAX phases—relative to constituent elements—as a function of temperature. This just verifies whether the MAX phases are stable with regards to their constituent elements. We have discussed in the later part of the manuscript that analysis purely based on Gibb’s stability could be misleading. Therefore, results in **Fig. 3** should be seen

as the part of story. Moreover, the ΔG_{form} analysis of 211 MAX phases allows us to set up two-fold hypothesis to test the proposed high-throughput framework- (1) Can the predicted energies be used to assess oxidation behavior (reaction products and relative stability of competing phases) at higher temperatures, and (2) are we able to reproduce correct trends as experiments for the selected MAX phases.

Keeping this in mind, we choose systems with opposite characteristics- (a) stable M_2AlC , e.g., $\text{Ti}_2\text{AlC}/\text{Cr}_2\text{AlC}$, and *metastable* M_2SiC , e.g., Ti_2SiC —we note that the latter is thermodynamically stable against decomposition into its constituent elements but should not belong, as per (lack of) experimental evidence, to the convex hull at any temperature and under any oxidation condition. We show that for both the cases, we could correctly characterize the thermodynamic stability of competing phases and chemical activity of elements at higher temperatures. All possible (thermodynamically stable) binary/ternary phases are included in this work, which is based on convex-hull algorithm used both by OQMD [29] and AFLOW [43].

Oxidation in MAX phases: The oxidation reaction at the interface of any alloy and oxide layer is the result of a phase selection process, in which the most favorable products of this process tend to be those close to the lowest (free) energy hyper-surface (or convex hull). The 0K DFT derived free energies and enthalpies of MAX phases as well as other competing phases *are* corrected for entropic contributions using our machine learning based high-throughput framework.

GCLP analysis of Ti_2SiC —In this section, we analyze the oxidation behavior of Ti_2SiC . The reaction products of $\text{Ti}_2\text{SiC}+\text{O}_2$ oxidation process are shown in the heat map in **Fig. 4**. The color bar from 0-1 shows the molar fraction of each phase. We also found that the hypothetical Ti_2SiC MAX phase is intrinsically stable [44-47] but experimentally not yet been realized due to higher stability of other thermodynamically competing phases in the complex Ti-Si-C phase diagram [48]. At the onset of oxidation process, $\alpha\text{-SiO}_2$ forms, which is the most stable oxide that appears at all temperatures and all oxygen molar-concentrations. Other phases to form are Ti_2O_3 , Ti_3SiC_2 , Ti_4SiC_3 , and TiSi . At higher oxygen concentration, Ti_3SiC_2 and Ti_4SiC_3 further transforms into TiC to maintain Si supply required for $\alpha\text{-SiO}_2$ formation and completely disintegrates into $\alpha\text{-SiO}_2/\text{TiC}/\text{C}/\text{Ti}_2\text{O}_3$ as shown in Table 1. This can be seen by reduced amount of another MAX phase with smaller Si content, namely Ti_3SiC_2 and Ti_4SiC_3 phases in **Fig. 4**. Ti_2O_3 further

transforms into TiO_2 at high oxygen-concentrations. We can also see in **Fig. 4** and **Table S4** that Ti_3O_5 and Ti_2O_3 have competing ΔG_{form} , therefore, depending on phase-fraction size Ti_2O_3 disappears at some temperatures for low oxygen content. However, at high oxygen contents, Ti_3SiC_2 , Ti_4SiC_3 , Ti_3O_5 and Ti_2O_3 disintegrate to pave the way to the formation of more stable rutile phase, i.e., TiO_2 .

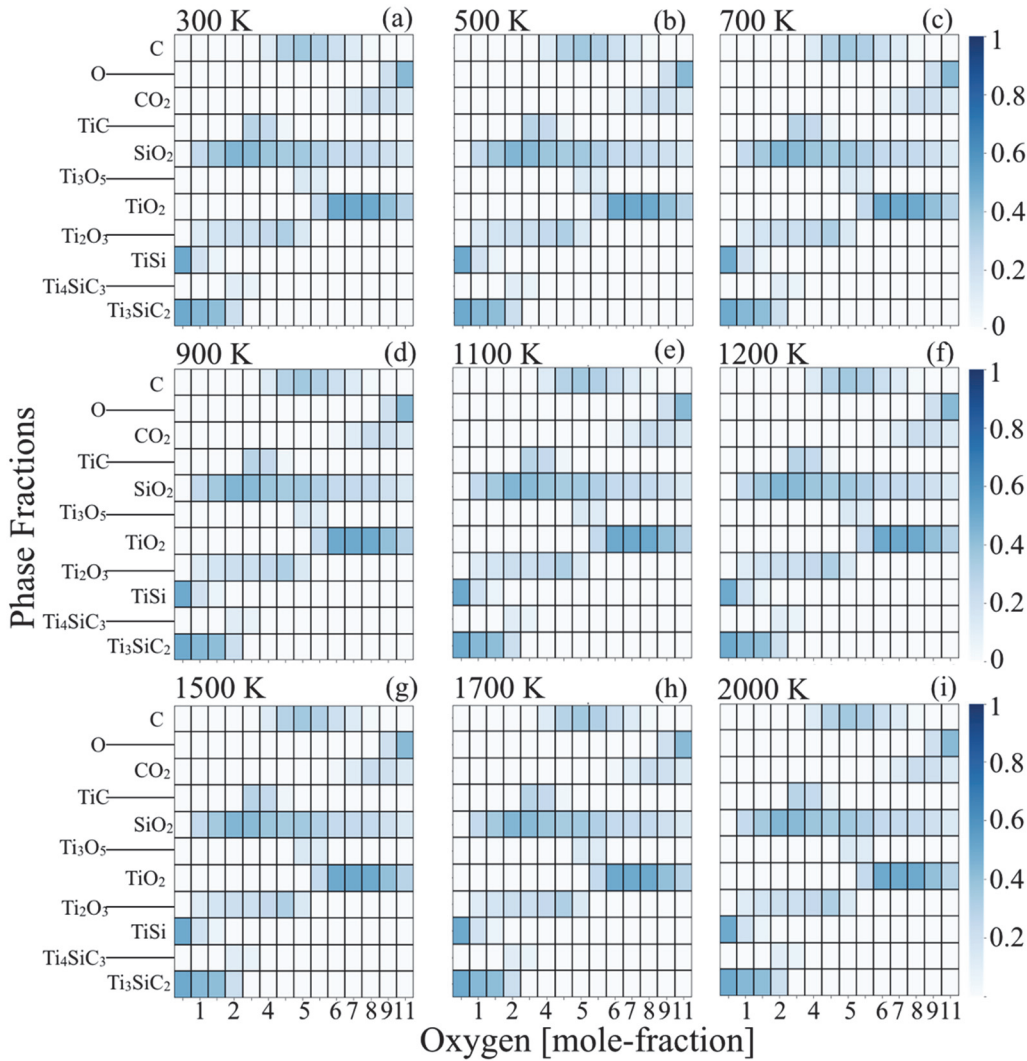
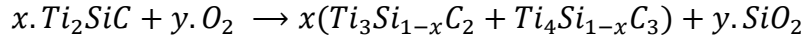


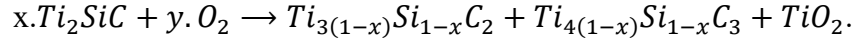
Figure 4. (a-i) Phase fractions of $[\text{Ti}_2\text{SiC} + \text{O}_2]$ reaction products at different temperatures with changing molar percent oxygen (0-11 moles). The color gradient (shades of blue) shows molar phase fractions. Blank spot [white (0)] suggests no phases. Note that Ti_2SiC never belongs to the convex hull.

Thermodynamically feasible oxidation reaction products predicted using GCLP analysis at 1500 K for $x.\text{Ti}_2\text{SiC} + y.\text{O}_2$ at varying oxygen-concentrations are shown in **Table. 1**. The reaction

product of x moles of Ti_2SiC and y moles of O_2 can qualitatively be written for selective oxidation of Ti or Si as:



or



At high enough oxygen content, TiC further breaks away and C diffuses through rutile layer (TiO_2) and oxidizes into CO_2 , i.e.,

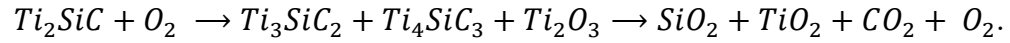


Table 1. Predicted set of thermodynamically favored reaction products in $Ti_2SiC + O_2$ at reaction temperature of 1500 K. The GCLP minimizes SISO predicted grand-canonical ΔG_{form} (see **Table S4**) to estimate possible phase-fractions.

Stages	Mole Oxygen	Reaction products and Phases-Fractions [$Ti_2SiC + O_2$]	
		1500 K	
		Phase	Phase-fraction
I.	1	$SiO_2 + Ti_2O_3 + Ti_3SiC_2 + TiSi$	(0.25, 0.125, 0.437, 0.188)
			(0.44, 0.22, 0.22, 0.11)
II.	2	$SiO_2 + Ti_2O_3 + Ti_3SiC_2 + Ti_4SiC_3$	(0.44, 0.22, 0.22, 0.11)
	3	$SiO_2 + Ti_2O_3 + TiC + Ti_4SiC_3$	(0.429, 0.214, 0.285, 0.07)
III.	4	$C + SiO_2 + Ti_2O_3 + TiC$	(0.125, 0.37, 0.245, 0.25)
	4.75		(0.295, 0.340, 0.318, 0.045)
IV.	6.3	$C + CO_2 + SiO_2 + TiO_2$	(0.213, 0.038, 0.25, 0.50)
	7		(0.125, 0.125, 0.25, 0.50)
	7.75		(0.025, 0.225, 0.25, 0.50)
V.	9	$SiO_2 + CO_2 + O_2 + TiO_2$	(0.20, 0.20, 0.20, 0.040)
	11		(0.143, 0.143, 0.429, 0.286)

Chemical activity analysis of Ti_2SiC : We plot the chemical activity of constituent elements of the Ti_2SiC+O_2 oxidation process at 1500 K in **Fig. 5**. The (partial) chemical potential of (Ti, Al, C, O) is calculated for an open system using unknown molar concentration of reaction products by

mixing of grand-canonical ΔG_{form} at 1500 K. The reaction chain is associated with the reductions in the partial chemical potentials of Ti, Si, and C, but increase in the chemical potential of O with increasing oxygen content. The higher Ti/Si/C activity at the early oxidation stage is directly related to their partial chemical potentials. Two chemical potentials zones in **Fig. 5** with increasing oxygen content are identified - (a) slowly varying (I-III); and (b) sharp changing (IV-V). The sharp change in chemical potential occurs in the region IV-V as $\text{Ti}_3\text{SiC}_2/\text{Ti}_4\text{SiC}_3/\text{TiC}$ completely disintegrates by then, moreover, C oxidizes to form gaseous CO_2 . The occurrence of C and CO_2 at higher temperature suggests loss of carbon. The predicted trend in chemical potential suggests increased oxygen activity at higher oxygen content.

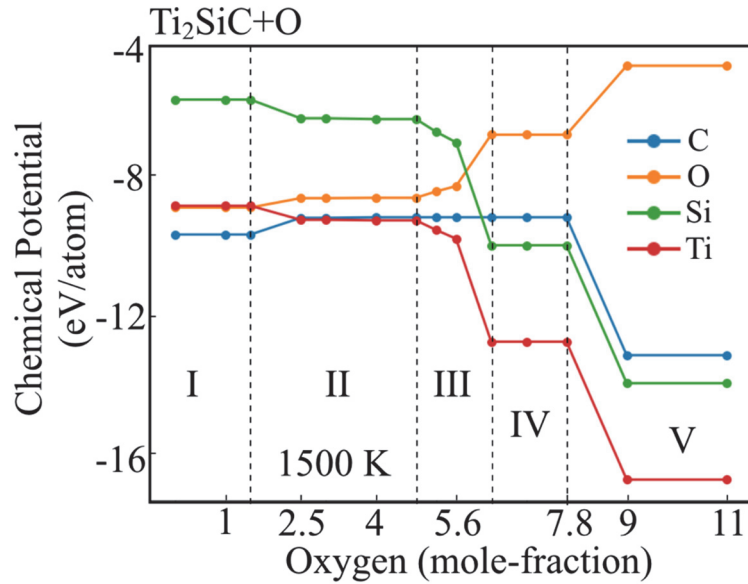


Figure 5: Oxidation reaction chain showing change in chemical potential of Ti_2SiC as a function of changing molar percent oxygen at 1500 K. On oxidation, the partial chemical potentials of Ti/Si/C reduce while the chemical potential of invading O_2 increases.

GCLP analysis of Ti_2AlC — In this section, we analyze the oxidation behavior of Ti_2AlC and show the heat map of the molar phase-fractions of $\text{Ti}_2\text{AlC}+\text{O}_2$ reaction product in **Fig. 6** (the color bar on right represents the molar percent, or phase fraction, of each phase). The heat map shows the presence of Al_2O_3 at all oxygen mole-fractions and for 300 K - 2000 K, whereas, different Ti-O phases are observed at low (TiO), intermediate (TiO, Ti_2O_3 , Ti_3O_5), and high (TiO_2) oxygen contents. At the onset of oxidation process Al_2O_3 , Ti_3AlC_2 , and TiO forms first, which is followed by the reaction of oxygen with Ti_3AlC_2 that gradually transforms to TiC. At high oxygen contents,

the MAX phase eventually disintegrates completely into solid Al_2O_3 and TiO_2 , and gaseous CO_2 phase.

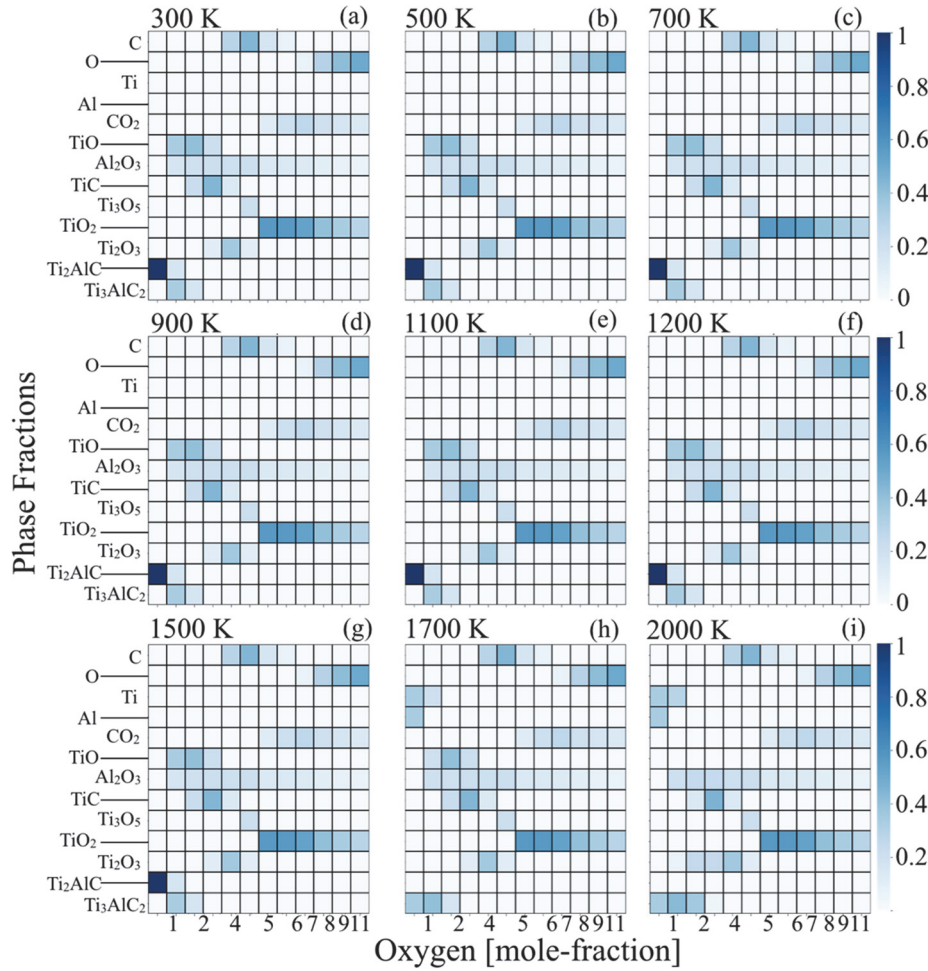
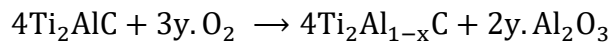
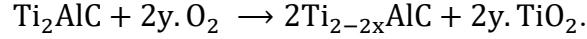


Figure 6. (a-i) Phase fractions of $[\text{Ti}_2\text{AlC}+\text{O}_2]$ reaction product at different temperature with changing molar percent oxygen (1-11 moles). The color gradient (shades of blue) shows molar phase fractions. Blank spot [white (0)] suggests no phases present.

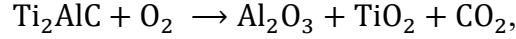
The predicted oxidation reaction chain for Ti_2AlC at 1500 K is shown in **Table. 2**. The reaction table shows thermodynamically stable oxidation reaction products at varying oxygen mole-fractions. The molar-oxygen content is varied to show its effect on reaction products, which represents the exposure time of the alloy to static air in experimental conditions. The reaction products of the chemical process during the selective oxidation of Al or Ti in Ti_2AlC can be written as:



and



Considering longer exposure time to static air, C diffuses through TiO_2 and oxidizes into CO_2 –



i.e., C from Ti-C diffuses through the mixed Ti-oxides layer and oxidize. The diffusion of Ti to the surface and O into the MAX phase or oxidation product during the oxidation process works as the rate-limiting condition.

More importantly, Al_2O_3 is seen at all temperatures and all oxygen-concentrations due to the high chemical activity of Al, see **Fig. 6**, as well as the very exothermic nature of the Al_2O_3 phase itself. The weak metallic bonding between Ti-Al can also contribute to the increased Al diffusivity [49]. The formation of Al_2O_3 results into Al depletion in Ti_2AlC substrate at the early stage oxidation. This in turn leads to the decomposition of the MAX phases into TiO , Al_2O_3 , and Ti_3AlC_2 [50] at low oxygen concentration. This indicates that Ti and Al are the first oxidizing elements when Ti_2AlC is exposed to ambient air at elevated temperatures. On further increasing the oxygen concentrations, the Al_2O_3 oxide scale remains stable compared to other oxides as partial pressure to form Al_2O_3 is much lower than of TiO_2 [48]. The weaker binding of Al with C or Ti in Ti_2AlC [52,53] and better Al diffusion [49] eases the Al_2O_3 growth [54]. Al diffusion becomes easier at higher temperature that helps Al_2O_3 to grow further. The better thermodynamic stability of Al_2O_3 compared to other phases (see **Table S2**) during oxidation of Ti_2AlC also helps in stabilizing Al_2O_3 at elevated temperatures. The C and CO_2 appear as the reaction products at higher temperature, which suggests C loss and the evaporation of CO_2 from the oxide scale. The reaction product of Ti_2AlC oxidation reaction correctly reproduces experimentally observed phase-fractions [8].

Table 2. Predicted set of thermodynamically favored reaction products in $\text{Ti}_2\text{AlC} + \text{O}_2$ at reaction temperature of 1500 K. The GCLP minimizes SISSO predicted ΔG_{form} (see **Table S4**) to estimate possible phase-fractions.

Stages	Mole-Oxygen	Reaction products and Phases-Fractions [$\text{Ti}_2\text{AlC} + \text{O}_2$]	
		1500 K	
		Phase	Phase-fraction
	1	$\text{Al}_2\text{O}_3 + \text{Ti}_2\text{AlC} + \text{Ti}_3\text{AlC}_2 + \text{TiO}$	(0.167, 0.167, 0.33, 0.33)

I.	1.75	$\text{Al}_2\text{O}_3 + \text{Ti}_3\text{AlC}_2 + \text{TiC} + \text{TiO}$	(0.20, 0.17, 0.23, 0.40)
II.	2.75	$\text{Al}_2\text{O}_3 + \text{Ti}_2\text{O}_3 + \text{TiC} + \text{TiO}$	(0.22, 0.11, 0.44, 0.22)
III.	4	$\text{Al}_2\text{O}_3 + \text{C} + \text{TiC} + \text{Ti}_2\text{O}_3$	(0.214, 0.285, 0.143, 0.357)
	4.75	$\text{Al}_2\text{O}_3 + \text{C} + \text{Ti}_3\text{O}_5 + \text{Ti}_2\text{O}_3$	(0.22, 0.44, 0.22, 0.11)
IV.	6.3	$\text{Al}_2\text{O}_3 + \text{C} + \text{CO}_2 + \text{TiO}_2$	(0.143, 0.17, 0.11, 0.571)
	7		(0.143, 0.07, 0.21, 0.571)
V.	7.75	$\text{Al}_2\text{O}_3 + \text{CO}_2 + \text{O}_2 + \text{TiO}_2$	(0.133, 0.266, 0.07, 0.53)
	9		(0.10, 0.20, 0.30, 0.40)
	11		(0.071, 0.14, 0.50, 0.286)

We show that using proposed high-throughput scheme that combines Gibbs free energies useful to predict high-temperature reaction paths *without doing expensive DFT calculations*. The approach is general, and can be used to assess the oxidation stability of arbitrary inorganic crystalline solids. Among the alumina-forming MAX phases, Ti_2AlC is one of the most widely studied, and it is, by far, the most attractive for practical applications because it forms protective oxide layer that is resistant to thermal cycling [30]. The chemical activity of Al in Ti_2AlC are large enough to result in preferential oxidation of Al into protective a $\alpha\text{-Al}_2\text{O}_3$ passivating layer [30]. Therefore, we choose to test the oxidation behavior of Ti_2AlC MAX phase to establish the applicability of proposed ML based high-throughput scheme.

Chemical activity analysis of Ti_2AlC : We plot the chemical activity of constituent elements of $\text{Ti}_2\text{AlC} + \text{O}_2$ oxidation process at 1500 K in **Fig. 7**. The (partial) chemical potential of (Ti, Al, C, O) is calculated for an open system using unknown molar concentration of reaction products by mixing of grand-canonical ΔG_{form} for 300 K – 2000 K (see **Fig. S5**). The reaction chain is associated with the reductions in the partial chemical potentials of Ti, Al, and C but increase in the chemical potential of O_2 with increasing oxygen content. Expectedly, the Ti/Al/C activity at the early oxidation stage comes out higher, which is directly related to the partial chemical potentials. Similar as in the case of Ti_2SiC , we could see two different zones of chemical potentials in **Fig. 7**, (a) slowly varying region I-III; and (b) sharply changing region IV-V with increasing oxygen content. The sharp change in chemical potential in region IV-V occurs as C oxidizes into gaseous

CO₂. The occurrence of C and CO₂ at higher temperature suggests loss of carbon. The calculated trend in chemical potential in **Fig. 7** suggests increased oxygen activity at higher oxygen content (see **Fig S5**).

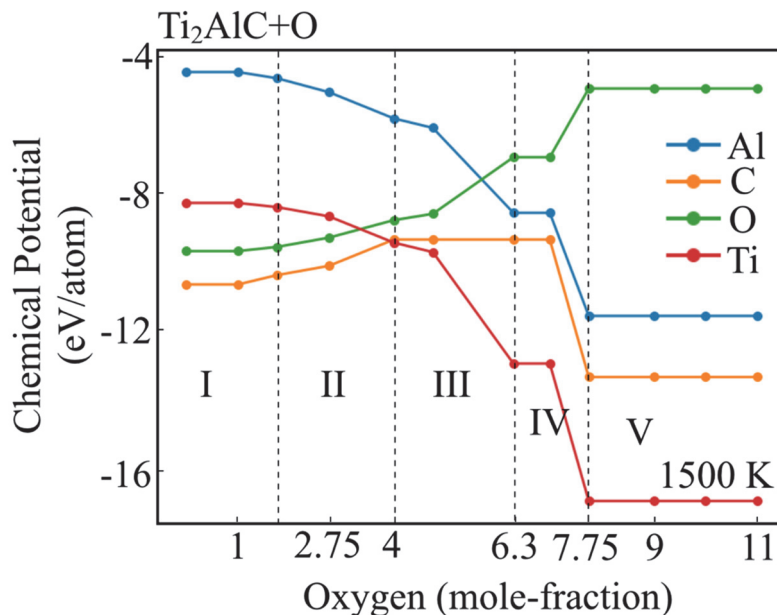


Figure 7: Oxidation reaction chain showing change in chemical potential of Ti₂AlC as a function of changing molar percent oxygen at 1500 K. On oxidation, the partial chemical potentials of Ti/Al/C reduce while the chemical potential of invading O₂ increases (see Fig. S3).

The low oxygen content regime, i.e., region I-II, replicates the shorter exposure time to oxygen. This region occurs below a critical thickness level of Ti₂AlC substrate, also shown by schematic of wedge experiment in **Fig. S4b** [8]. In the oxygen rich region (IV-V; see **Fig. S3j**), the Ti₂AlC substrate has large surface to volume ratio, i.e., larger exposure to air/oxygen. The chemical activity of the oxygen significantly changes compared to low oxygen region I-III. As oxygen content increases, the Ti₂AlC MAX phase decomposes into stable TiO₂, Al₂O₃ and CO₂ phases. In **Fig. 7**, the oxidation of Ti₂AlC lowers the chemical potential Al and Ti, which results into increased outward diffusion of Al and Ti. The lowered chemical potential with increasing oxygen content and weak Ti-Al bonding keep the constant supply of Al at all temperatures for the Al-O reaction. The chemical activity of Al, as shown in **Fig. 7**, is much higher than that of Ti and C, suggesting that the formation of Al₂O₃ is a much faster process. Therefore, protective Al₂O₃ layers are formed quickly on Ti₂AlC substrate and stops further degrading due to oxygen attack. Al₂O₃ formation is also preferred because of lower vapor pressure of Al with respect to O when compared

to Ti with respect to O. At low oxygen content (region I-III), the oxidized surface of the film is a mixture of the Al_2O_3 as well as TiO (I), TiC (I), Ti_2O_3 (I), and/or Ti_3O_5 (II) depending on exposure time or oxygen content to O_2 .

When compared to alumina-forming alloys [55-57], MAX phases do experience different breakaway oxidation mechanisms after long-term exposure [58] to static air. As soon as the Al-containing reservoir exceeds a certain Al loss level, the reservoir decomposes into competing phases rather than remaining in an Al-deficient form, which can not form anymore Al_2O_3 .

To test our predictions of oxidation reaction mechanism for Ti_2AlC under controlled oxygen exposure as predicted by our GCLP analysis in Table 2, we prepared wedge-shaped samples and performed breakaway oxidation at 1500 K temperature in the presence of static air. The oxidation tests are carried out in a box furnace (Carbolite, UK) (more detailed discussion about material preparation and characterization will appear in a companion paper [8]). The use of wedge-shaped samples to study breakaway oxidation have been applied successfully to FeCrAl based alloys [59]. We used scanning electron microscopies (FE-SEM, Quanta 600 FEG, FEI, Oregon, USA) equipped with energy dispersive spectroscopy (EDS) to identify the microstructure and phases along the wedge. Electron microprobe analysis (EPMA) is used for a quantitative phase evaluation in the breakaway oxidation region in Ti_2AlC . The SEM shows five distinct regions as also shown in **Fig. 8** based on oxidation activity as marked:

- I. Very thin protective Al_2O_3 oxide layer forms on the surface,
- II. Small $\text{Al}_2\text{O}_3+\text{TiO}_2$ nodules in this region, with no other phases except Ti_2AlC substrate in the middle,
- III. Mixed $\text{Al}_2\text{O}_3+\text{TiO}_2$ oxides on the surface. Part of the Ti_2AlC substrate survived with Ti_3AlC_2 phase according to EPMA,
- IV. Mixed $\text{Al}_2\text{O}_3+\text{TiO}_2$ oxide layer on the surface with pure TiO_2 replacing the pure Ti_2AlC ,
- V. Ti_2AlC at thin end is completely oxidized to $\text{TiO}_2+\text{Al}_2\text{O}_3$, which is in agreement with our predictions in **Fig. 7**.

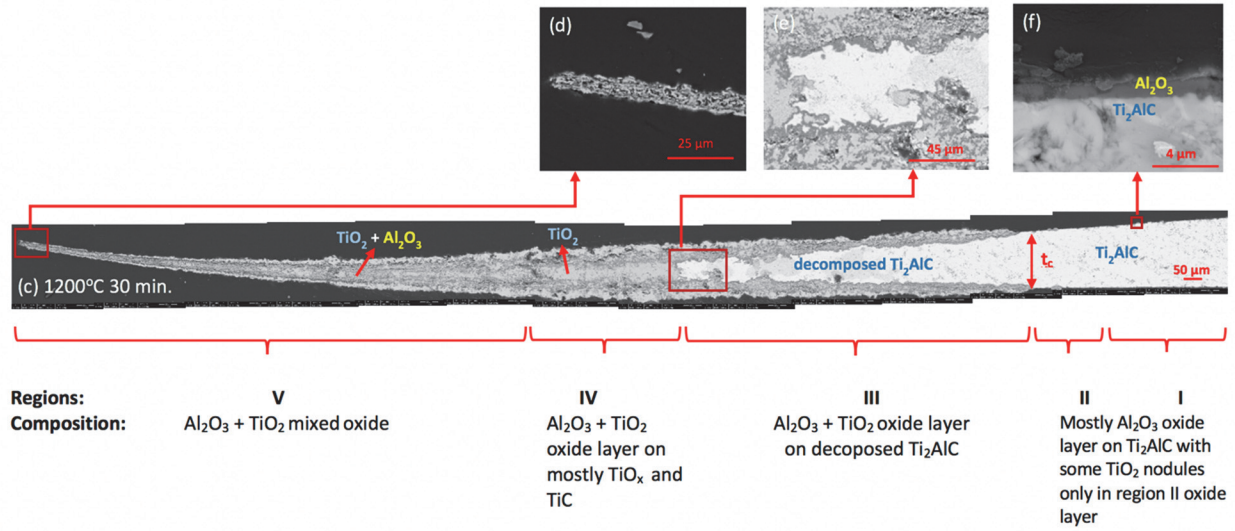


Figure 8. Backscattered Electron SEM images of selected wedge-shaped Ti_2AlC oxidized at 1200 °C for 30 min. Insert (d), (e) and (f) shows magnified tip, middle and end, respectively, of the wedge-shaped sample oxidized at 1200°C for 30 min.

The five regions in **Fig. 8** can further be categorized as low (I-III), intermediate (IV), and high (V) oxygen activity zones, which compares well with the highlighted regions in the chemical activity plot **Fig. 7** (see **Fig. S3j**) calculated at 1500 K. The mixed oxide ($\text{Al}_2\text{O}_3 + \text{TiO}_2$) in region III and IV is quite similar to the small nodules observed in region II. This indicates the start of nucleation that grows into large and continuous regions (also see **Fig. 8 inset-b**). We believe that the intermediate phase (III) plays a key role in the decomposition path from Ti_2AlC to TiO_2 and Al_2O_3 . Therefore, the oxygen content is important at the onset of phase III to evaluate oxidation stability of different MAX phases because if onset is at higher O concentrations, the MAX phase is more stable. This is in agreement with the theoretically proposed reaction path in **Table. 2**. Notably, our EPMA analysis in **Fig. 8 (inset-a)** on the wedge-shaped Ti_2AlC sample, which oxidized at 1200 °C for 30 minutes, shows that Ti_2AlC decomposes into Ti_3AlC_2 and TiC (also marked in **inset-a**) [8]. For Ti_3AlC_2 , the reported critical Al loss is 5.99% [57], whereas Ti-C binary is believed to form due to the depletion of Al in the substrate [60]. A recent study also suggest the increase in volume fraction of Ti_3AlC_2 and TiC phases in the substrate in Region III [8]. The thick oxide layer (mixed) in region III conforms with the breakaway mechanism. The formation of Al-deficient Ti_3AlC_2 and TiC phases are leading factors for the mixed oxide layer formation. Our high-throughput study suggests the presence of mixed $\text{Al}_2\text{O}_3 + \text{TiO}_2$ oxide layer in region IV and region

V as shown in Table I. The experiments on region IV and region V shows the presence of thick mixed oxide layer in **Fig. 8**. This is similar to the mixed oxide phase observed in region III. In region V (at the tip of the wedge sample), the fast Al depletion from Ti_2AlC allows only mixed oxide layers, e.g., even very short exposure to static air at ~ 1500 K, the very tip of the wedge-shaped sample oxidizes to the mixed Al_2O_3 and TiO_2 phase. Similar to the high-throughput predictions at higher oxygen content, experiments suggest that on longer exposure to oxygen, O_2 will penetrate and react with Ti_2AlC , which will lead to gradual decomposition of Ti_2AlC to Ti_3AlC and TiC along with the formation of Al_2O_3 and TiO_x phases. The formation of Al_2O_3 (7.9×10^{-6} - $8.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) have outstanding match of thermal expansion with Ti_2AlC (9 - $9.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) compared to other MAX phases [61], which makes Ti_2AlC better candidate for high-temperature application.

Experiments indicates that the breakaway oxidation is possibly caused by gradual decomposition of Al deficient $\text{Ti}_2\text{Al}_{1-x}\text{C}$, to Ti_3AlC_2 and further to TiC and subsequent oxidation of those phases to form mixed oxide. To understand this, we perform direct calculations considering (3.125; 6.25; 9.375)-%vacancy concentration in Ti_2AlC .

$\text{Ti}_2[\text{Al}_{1-x}\text{Va}_x]\text{C}$ vacancy stability: Given that oxygen diffuses into the bulk material via the Al_2O_3 grain-boundary channels, sub-interface oxidation would result into the formation and distributions of various phases according to the predicted reaction chain. This is however the less likely case as the diffusion of Al from within the Ti_2AlC towards its interface is a faster process. As the latter happens, depletion of Al in Ti_2AlC can result in decomposition of the MAX phase into energetically more favorable competing reaction products. We assess this possibility of $\text{Ti}_2[\text{Al}_{1-x}\text{Va}_x]\text{C}$ stability relative to the other competing phases.

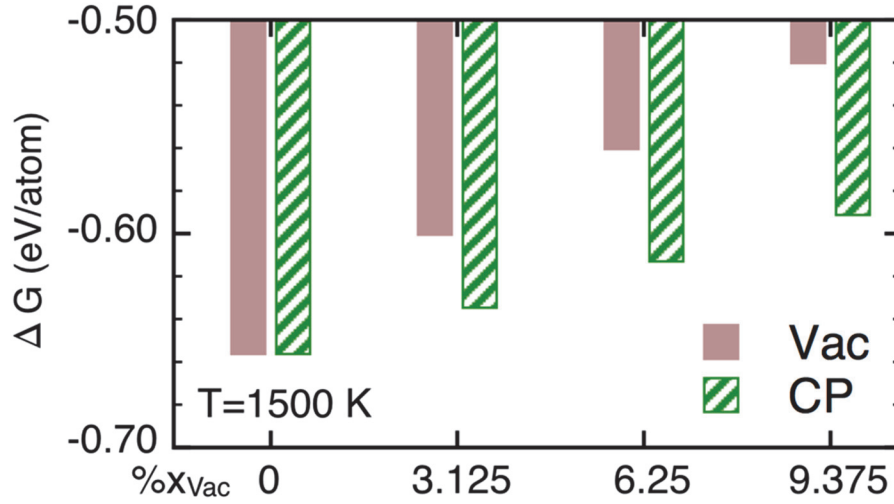


Figure 9. Calculated ΔG_{form} of Al-depleted $\text{Ti}_2[\text{Al}_{1-x}\text{Va}_x]\text{C}$, i.e., with vacancy, relative to the competing phases (CP) (Ti_2AlC , Ti_3AlC , and Ti_3AlC_2) at 1500 K shows that $\text{Ti}_2(\text{Al}_{1-x}\text{Va}_x)\text{C}$ is energetically less stable. The configurational entropy term is included for vacancy cases using $\Delta S_{\text{config}} = -[(x_{\text{vac}} \ln x_{\text{vac}} + (1 - x_{\text{vac}}) \ln(1 - x_{\text{vac}}))]$, here $x_{\text{vac}} = (0.03125; 0.0625; 0.09375)$.

Even though the ΔG_{form} for $\text{Ti}_2[\text{Al}_{1-x}\text{Va}_x]\text{C}$ in **Fig. 9** suggests the intrinsic stability (i.e. negative heats of formation), it remains less stable when compared to competing phases, i.e., Ti_2AlC (90.625; 81.25; 71.875), Ti_3AlC (3.125; 6.25; 9.375), and Ti_3AlC_2 (3.125; 6.25; 9.375) for all considered vacancy cases - x_{vac} (3.125; 6.25; 9.375). This indicates that Al deficient Ti_2AlC is not energetically favored and tends to decompose into Ti_3AlC_2 . The predicted decomposition, however, depends on the energy barrier required to nucleate the precipitates of those phases, which is not easily accessible due computational complexity of the Ti_2AlC supercells with vacancy. In spite of this, similar to the experiments, not only do we predict the formation of Al_2O_3 and TiO_y with increasing O_2 but also the gradual decomposition of Al-deficient Ti_2AlC into Ti_3AlC and TiC . Our experiments found Al deficiency of ~5% in Ti_2AlC (see supplement **Fig. S6**) that leads to the breakaway oxidation, i.e. formation of alumina and titania, instead of a protective predominately Al_2O_3 oxide layer.

The Al deficiency further leads to the decomposition of Ti_2AlC and the formation of Ti_3AlC_2 , however, the traces of Ti_3AlC and Ti_3AlC_2 precipitates are not discernable in Regions I and II. This could be either due to a high energy barrier for nucleation of Ti_3AlC_2 that arrests the decomposition of the metastable $\text{Ti}_2[\text{Al}_{1-x}\text{Va}_x]\text{C}$, or Ti_3AlC and Ti_3AlC_2 precipitates are formed

below oxide/substrate interface in relatively smaller fractions and the phase-fraction remains well below the experimental detection limit.

In spite of some degree of disagreement between phase stability in vacancy-containing Ti_2AlC with experiments, the relative shift in stability with respect to competing phases could be used as a metric for selection and/or screening of potentially promising Al-forming MAX compounds or alloys. In previous work [49], for example, we have discovered that alloying in the A sublattice creates energetically favorable environment for the formation of vacancies, while at the same time benefitting from the configurational entropic contributions. This would necessarily result in a delay to the onset of decomposition into competing phases once vacancies start to form in the A sublattice of Al-containing MAX phases, for example. *The search for alloys with reduced vacancy formation energy and fast vacancy mobility could guide the development of more oxidation resistant MAX alloys and compounds.*

Prediction of oxidation behavior in Cr_2AlC MAX phase:

GCLP analysis of Cr_2AlC — Higher stiffness, smaller Vickers hardness, and machinable [62], similar to Ti_2AlC [63], makes Cr_2AlC an outstanding candidate for the high-temperature application. Lin *et al.* [64] reported excellent oxidation resistance, which is probably due to the formation of protective Al_2O_3 and Cr_2O_3 layers as oxides. The oxidation is an important factor [65], however, we found no detailed discussion on Cr_2AlC . Therefore, we analyze the oxidation behavior of Cr_2AlC .

The heat map of the molar phase-fractions of $\text{Cr}_2\text{AlC}+\text{O}_2$ reaction product in **Fig. 10** (the color bar on right represents the molar percent, or phase fraction) at 300 K, 500 K, 700 K, 900 K, 1200 K, 1500 K, 1700 K, and 2000 K for 0-11 moles of oxygen content. We considered 13 thermodynamically most stable phases based on Gibbs formation energy, see **Fig. S7**. Different Cr based phases were observed: at low/intermediate (Cr_7C_3 , Cr_2O_3 , Cr, Cr_3C_2), intermediate (Cr_7C_3 , Cr_2O_3 , Cr_3C_2), and high (Cr_2O_3) oxygen content. At the onset of oxidation process, at low oxygen content, Cr_7C_3 , Cr, and Cr_3C_2 forms first, which is followed by the reaction of oxygen with Cr_2AlC that gradually transforms from Cr_7C_3 to Cr_3C_2 and disappears at oxygen higher exposure, i.e., the Cr_2AlC MAX phase eventually disintegrates into Al_2O_3 and Cr_2O_3 , and gaseous CO_2 .

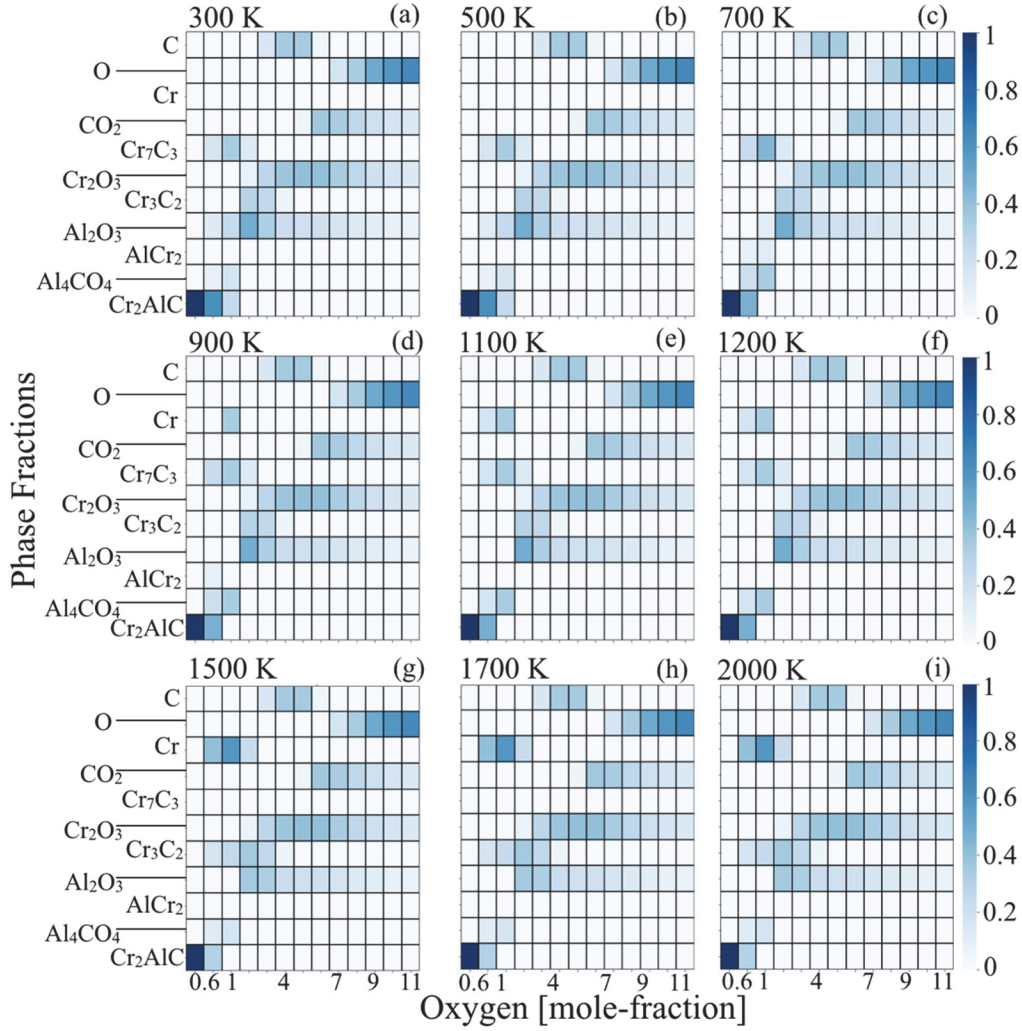


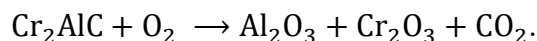
Figure 10. (a-i) Phase fractions of $[\text{Cr}_2\text{AlC}+\text{O}_2]$ reaction product at different temperature with changing molar percent oxygen. Each block refers to specific oxygen molar content from 1-11 moles. The color gradient (shades of blue) shows molar phase fractions. Blank spot [white (0)] suggests no phases present.

The predicted oxidation reaction chain for Cr_2AlC at 1200 K is shown in **Table. 3**. The reaction table shows thermodynamically stable oxidation reaction products at varying oxygen mole-fractions. The molar-oxygen content is varied to show its effect on reaction products, which represents the exposure time of the alloy to static air in experimental conditions. The reaction products of the chemical process during the selective oxidation of Al or Cr in Cr_2AlC for low/intermediate oxygen exposure can be written as:



i.e., the Cr_2AlC oxidation shows Al_2O_3 and Cr_7C_3 as the reaction product. The Cr_7C_3 forms just below the surface layer of Al_2O_3 due to Al consumption [65].

For longer exposure time to static air, Cr_7C_3 further decomposes and allows the formation of Cr_2O_3 while excess C diffuses through Cr_2O_3 and oxidizes into CO_2 –



Here, the diffusion of Cr to the surface and O into the MAX phase or oxidation product during the oxidation process works as the rate-limiting condition. The C and Al_2O_3 were formed at intermediate/higher mole oxygen in region III/IV, see **Table 3**, while no Cr was found. Also, the presence of Cr_2O_3 along with Al_2O_3 [67] agrees with our prediction, which is known to help the formation of Al_2O_3 [68].

Importantly, Al_2O_3 starts appearing from intermediate (region II-III) to higher (IV-V) at all temperatures due to the high chemical activity of Al compared to Cr/C, see **Fig. 11**. The strong ionic/covalent bonding of Cr with C in Cr_2AlC [69, 70] decreases the oxygen affinity of Cr. The presence of Al_2O_3 can also be understood in terms of weaker bonding of Cr with Al, where weak metallic bonding between Cr-Al [49] can contribute to the increased Al diffusivity at higher temperature and oxygen content. This makes the reaction Al with O more favorable, which leads to the formation of Al_2O_3 surface layer. The formation of the Al_2O_3 layer at the surface will slow down the oxidation of Cr_2AlC , i.e., protects the MAX phase.

Table 2. Predicted set of thermodynamically favored reaction products in $\text{Cr}_2\text{AlC} + \text{O}_2$ at reaction temperature of 1200 K. The GCLP minimizes SISSO predicted ΔG_{form} (see **Table S4**) to estimate possible phase-fractions.

Stages	Mole-Oxygen	Reaction products and Phases-Fractions [$\text{Ti}_2\text{AlC} + \text{O}_2$]	
		1200 K	
		Phase	Phase-fraction
I.	0.6	$\text{Cr}_2\text{AlC} + \text{Cr}_7\text{C}_3 + \text{Cr} + \text{Al}_4\text{CO}_4$	(0.47, 0.18, 0.18, 0.18)
	1	$\text{Cr}_2\text{AlC} + \text{Cr}_7\text{C}_3 + \text{Cr} + \text{Al}_4\text{CO}_4$	(0.00, 0.33, 0.33, 0.33)
II.	1.75	$\text{Cr}_7\text{C}_3 + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{Cr}_3\text{C}_2$	(0.13, 0.49, 0.29, 0.08)
III.	2.75	$\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{Cr}_3\text{C}_2 + \text{C}$	(0.32, 0.27, 0.25, 0.15)
	4		(0.23, 0.38, 0.05, 0.35)

IV.	4.75	$\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C} + \text{CO}_2$	(0.20, 0.40, 0.35, 0.05)
	6.3		(0.20, 0.40, 0.04, 0.36)
V.	7	$\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{CO}_2 + \text{O}$	(0.17, 0.33, 0.33, 0.17)
	9		(0.09, 0.20, 0.50, 0.19)
VI.	11		(0.07, 0.14, 0.64, 0.14)

In spite of good oxidation behavior, Cr_2AlC also has some drawbacks, e.g., the thermal-expansion coefficients of three major phases Cr_2AlC , Al_2O_3 , and Cr_7C_3 were $13.3 \times 10^{-6} (\text{K}^{-1})$, [62] $10.6 \times 10^{-6} (\text{K}^{-1})$, [71] and $(7.2 \times 8.6) \times 10^{-6} (\text{K}^{-1})$, respectively. Large difference in thermal expansion coefficient of Al_2O_3 and Cr_7C_3 with respect to Cr_2AlC that forms immediately below the Al_2O_3 surface layer can generate excessive thermal and compressive stress in Al_2O_3 , which may lead to spalling and cracking.

Chemical activity analysis of Cr_2AlC : The chemical activity of constituent elements in $\text{Cr}_2\text{AlC} + \text{O}_2$ oxidation process at 1200 K is shown in **Fig. 11**. Four zones in chemical potentials plot can be classified as (region I-II) quick change in Al/ O_2 activity for Al/O; (region III-IV) slow activity region, and (region V) sharply varying region at higher increasing oxygen content. The sharp change in chemical potential in region V occurs as C oxidizes into gaseous CO_2 . The occurrence of C and CO_2 at higher temperature suggests loss of carbon. The calculated trend in chemical potential in **Fig. 11** suggests increased oxygen activity at higher oxygen content.

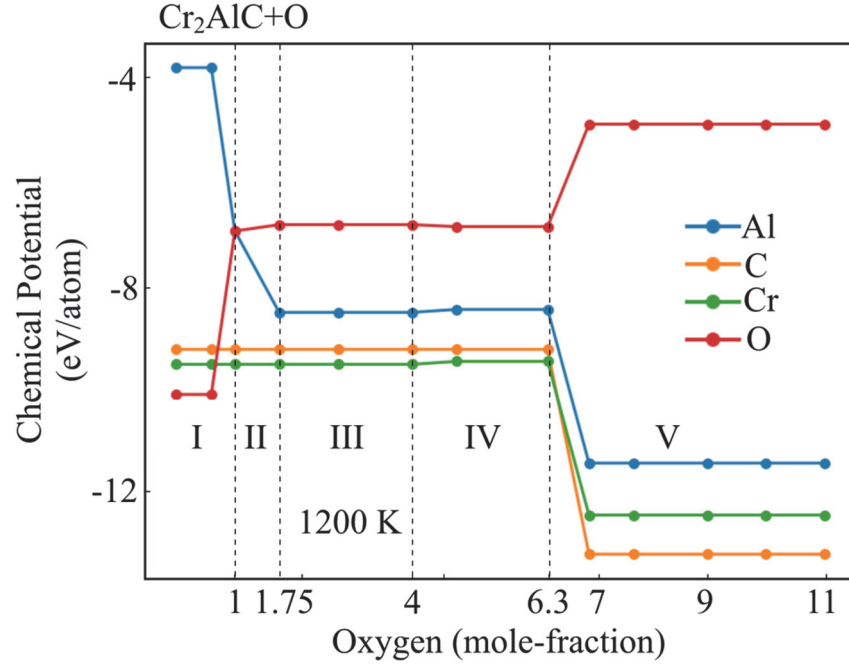


Figure 11: Oxidation reaction chain showing change in chemical potential of Cr_2AlC as a function of changing molar percent oxygen at 1200 K. On oxidation, the partial chemical potentials of Cr/Al/C reduce while the chemical potential of invading O_2 increases (see Fig. S3).

At higher oxygen content in region V, the Cr_2AlC MAX phase decomposes into stable Cr_2O_3 , and Al_2O_3 phases, which lowers the chemical potential Cr/Al/C compared to O_2 . This suggests an increased outward diffusion of Al and Cr and leads to formation protective oxide layers. The lowered chemical potential with increasing oxygen content and weak Cr-Al bonding [49] keep the constant supply of Al at all temperatures for the Al-O reaction. The chemical activity of Al, as shown in **Fig. 11**, is slightly higher than that of Cr and C, suggesting that the formation of Al_2O_3 is relatively faster process. Therefore, protective Al_2O_3 layers are formed quickly on Cr_2AlC substrate and stops further degrading due to oxygen attack. Al_2O_3 formation is also preferred because of lower vapor pressure of Al with respect to O when compared to Cr with respect to O. At low oxygen content (region I-III), the oxidized surface of the film is a mixture of the Al_2O_3 and Cr_2O_3 depending on exposure time or oxygen content to O_2 .

Conclusions

The thermodynamic stability, outstanding mechanical behavior, and superior oxidation resistance make MAX phases a promising material for high temperature applications, such as,

nuclear, aerospace, and/or turbines. We present a ML based high-throughput scheme to assess oxidation behavior of crystalline MAX phases. The workflow combines the *Bartel* (SISSO) model (based on SISSO approach) with grand canonical linear programming (GCLP) method into a single framework. The scheme predicts temperature dependent ΔG_{form} , possible reaction products, and chemical activity of alloying elements. The validation test performed on binary oxides, e.g., Ti-O and Al-O, which shows good agreement with existing experiments. We performed phase stability of analysis of 30 MAX phases of 211 chemistry. To exemplify our approach, we choose Ti_2AlC MAX phase due to its superior oxidation resistance. The theoretically predicted reaction path with increasing oxygen content at high operating temperatures confirmed by our breakaway oxidation experiments. We believe that the prediction of improved high temperature behavior due to ever-growing demand of new structural materials for high-temperature application makes our scheme useful, and timely. The application of the proposed method for Cr_2AlC establishes the generality of the scheme, which will further guide experimentalists in understanding the relative phase stability of any inorganic alloy system and its reaction path during oxidation. We successfully explain the metastable Ti_2SiC MAX phase, which further establishes the strength of our framework.

Our proposed high-throughput scheme enables the quick assessment of the oxidation stability of a large alloy space and reduce the time and cost for alloy selection for design—this approach is many orders of magnitude faster than when using conventional DFT-only approaches and is applicable even when no suitable CALPHAD databases are available. This will help to filter specific elements during alloy design to minimize material degradation due to formation unstable oxides. We also note some minor disagreement between prediction and the experiment. The most plausible reason for disagreement may arise from not including all possible non-stoichiometric compounds, ternary-oxides/oxycarbides, and/or contributions from kinetics, i.e. sluggish diffusion and/or significant barriers to nucleation and growth of phases. However, keeping the complexity of the problem in mind, the proposed scheme provides good quantitative agreement with experiments.

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Data Availability

The authors declare that the data supporting the plots and findings of this study are available within the paper/supplement, and also with the corresponding author upon reasonable request.

Competing interests

The authors declare no competing interests.

Author Contributions

R.A. proposed and supervised the entire project. D.S., A.R.F., and P.S. worked on the development and testing of the model. G.V. assisted at the final stage of model development. P.S. and T.D. performed DFT simulations. D.S., P.S., and R.A. analyzed and discussed theory results. Y.C. prepared the wedge samples and performed oxidation experiments. M.R. supervised the experimental work. P.S. and R.A. prepared the final draft of the manuscript with input from all the authors.

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Supplemental material

High-throughput reaction engineering to assess oxidation stability of MAX phases

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Table S1. Seven stable phases of Ti-O along with energies of end points Ti, O. The SISSO is been used to assess temperature dependent energy stability of Ti-O in Fig. 2a. The 298 K dataset is chosen from the NIST-JANAF thermochemical tables [20,21]. The Al-O energies used in Formation energies from DFT (at 0K) are also listed for comparison. The training data and training approach of SISSO based model is based on work of Bartel *et al.* in **Ref 23** of the main text.

#	System	E _{form} [Expt.]	E _{form} [0 K]	E _{total}
		[eV/atom]		
1	O	0.000	0.000	-4.844
2	Ti	0.000	0.000	-7.776
3	Al	0.000	0.000	-3.745
4	TiO ₂	-3.264	-3.351	-8.824
5	Ti ₃ O ₅	-3.186	-3.420	-9.888
6	Ti ₂ O ₃	-3.153	-3.275	-8.915
7	TiO	-2.812	-2.933	-8.853
8	Ti ₂ O	-1.986	-2.088	-8.626
9	Ti ₃ O	-1.550	-1.635	-8.454
10	Ti ₆ O	-0.933	-0.987	-8.178
11	Al ₂ O ₃	-3.077	-3.265	-7.4814

Al_xO_{1-x} oxide phase stability: We also assess the phase stability of composition dependent Al_xO_{1-x}. We plot temperature (300 K, 1000 K, 1800 K) dependent convex hull calculated using our machine-learning framework in **Fig. S1**.

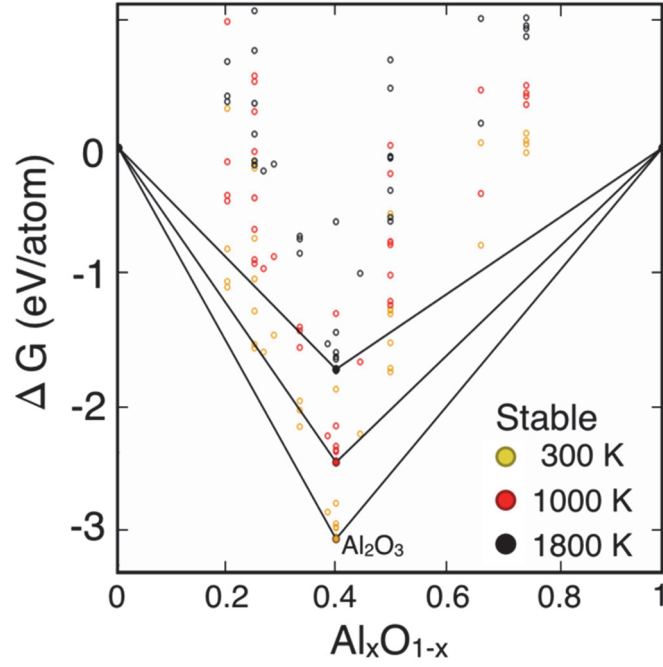


Figure S1: SISSO predicted $\text{Al}_x\text{O}_{1-x}$ convex hull showing thermodynamic stability of various phases at 300 K, 1000 K, and 1800 K.

Table S2. We identify 25 possible reaction products of $\text{Ti}_2\text{AlC} + \text{O}_2$ oxidation reaction. SISSO uses 0 K enthalpies as input to assess temperature dependent ΔG_{form} . The 0 K energies and enthalpy database was extracted from the Open Quantum Materials Database (OQMD) [22].

#	System	Ti	Al	C	O	E_{form} [eV/atom]	E_{total} [eV/atom]
1	Ti	1	0	0	0	0	-7.776
2	Al	0	1	0	0	0	-3.745
3	C	0	0	1	0	0	-9.213
4	O	0	0	0	1	0	-4.844
5	Al_2O_3	0	2	0	3	-3.265	-7.536
6	Al_3C	0	3	1	0	1.135	-3.978
7	Al_4C_3	0	4	3	0	-0.319	-6.188
8	AlC	0	1	1	0	1.313	-5.169
9	AlC_3	0	1	3	0	2.849	-5.001
10	CO_2	0	0	1	2	-1.359	-7.628

11	TiC	1	0	1	0	-0.954	-9.262
12	Ti ₂ C	2	0	1	0	-0.655	-8.859
13	Ti ₈ C ₅	8	0	5	0	-0.729	-9.012
14	Ti ₂ AlC	2	1	1	0	-0.71	-7.8
15	Ti ₃ AlC	3	1	1	0	-0.608	-7.82
16	Ti ₃ AlC ₂	3	1	2	0	-0.766	-8.312
17	Ti ₂ O	2	0	0	1	-1.986	-8.626
18	Ti ₂ O ₃	2	0	0	3	-3.153	-8.915
19	TiO	1	0	0	1	-2.812	-8.853
20	TiO ₂	1	0	0	2	-3.264	-8.824
21	Ti ₃ O	3	0	0	1	-1.55	-8.454
22	Ti ₃ O ₅	3	0	0	5	-3.186	-9.888
23	Ti ₆ O	6	0	0	1	-0.933	-8.178
24	TiAl	1	1	0	0	-0.436	-6.158
25	TiAl ₂	0	2	0	0	-0.45	-5.513
26	TiAl ₃	0	3	0	0	-0.412	-5.699
27	Ti ₂ Al	2	1	0	0	-0.317	-6.698
28	Ti ₃ Al	3	1	0	0	-0.328	-7.038
29	Ti ₄ Al ₃	4	3	0	0	0.365	-6.369

Table S3. We identify 25 possible reaction products of Ti₂SiC+O₂ oxidation reaction. SISSO uses 0 K enthalpies as input to assess temperature dependent ΔG_{form} . The 0 K energies and enthalpy database was extracted from the Open Quantum Materials Database (OQMD) [22].

#	System	Ti	Al	C	O	E _{form} [eV/atom]	E _{total} [eV/atom]
1	Ti	0	0	0	1	0	-7.776
2	O	0	1	0	0	0	-4.844
3	C	1	0	0	0	0	-9.213
4	Si	0	0	1	0	0	-5.4254
5	CO ₂	1	2	0	0	-1.359	-7.628
6	SiO ₂	0	2	1	0	-3.147	-7.897
7	TiC	1	0	0	1	-0.954	-9.262
8	TiO	0	1	0	1	-2.812	-8.853
9	TiO ₂	0	2	0	1	-3.264	-8.824

10	Ti ₂ C	1	0	0	2	-0.655	-8.859
11	Ti ₂ O	0	1	0	2	-1.986	-8.626
12	Ti ₂ O ₃	0	3	0	2	-3.153	-8.915
13	Ti ₃ O	0	1	0	3	-1.55	-8.454
14	Ti ₃ O ₅	0	5	0	3	-3.186	-9.888
15	Ti ₆ O	0	1	0	6	-0.933	-8.178
16	Ti ₈ C ₅	5	0	0	8	-0.729	-9.012
17	TiSi ₂	0	0	2	1	-0.591	-6.76321
18	Ti ₂ SiC	1	0	1	2	-0.86	-8.401
19	Ti ₃ SiC ₂	2	0	1	3	-0.825	-8.65028
20	Ti ₅ Si ₃ C	1	0	3	5	-0.82	-8.0407
21	SiC	1	0	1	0	-0.379	-7.52989
22	Ti ₅ Si ₄	0	0	4	5	-0.814	-7.50077
23	Ti ₅ Si ₃	0	0	3	5	-0.765	-7.64415
24	TiSi	0	0	1	1	-0.752	-7.35231
25	Ti ₃ Si	0	0	1	3	-0.535	-7.66447
26	Ti ₄ SiC ₃	3	0	1	4	-0.820	-8.902401

Table S4. The SISSO predicted ΔG_{form} of possible stable binary-ternary reaction products of Ti₂AlC+O₂ oxidation process. The 0 K enthalpies were used as input by SISSO as starting point.

	ΔG_{form} (eV/atom)									
T(K)	TiO ₂	TiO	TiC	Ti ₃ O ₅	Ti ₃ AlC ₂	Ti ₂ O ₃	Ti ₂ O	Ti ₂ AlC	CO ₂	Al ₂ O ₃
0	-3.2426	-2.7428	-0.8041	-3.1736	-0.7662	-3.1219	-1.9864	-0.7098	-1.5403	-3.2649
300	-3.0641	-2.5981	-0.8016	-3.0016	-0.7683	-2.9537	-1.8845	-0.7113	-1.3795	-3.0860
400	-2.9692	-2.5143	-0.7655	-2.9088	-0.7334	-2.8622	-1.8145	-0.6760	-1.2914	-2.9909
500	-2.8810	-2.4366	-0.7361	-2.8227	-0.7045	-2.7772	-1.7503	-0.6463	-1.2113	-2.9025
600	-2.7961	-2.3618	-0.7096	-2.7397	-0.6781	-2.6952	-1.6885	-0.6190	-1.1355	-2.8172
700	-2.7128	-2.2882	-0.6843	-2.6582	-0.6526	-2.6148	-1.6275	-0.5924	-1.0620	-2.7335
800	-2.6302	-2.2150	-0.6592	-2.5773	-0.6270	-2.5349	-1.5666	-0.5656	-0.9896	-2.6503
900	-2.5477	-2.1416	-0.6337	-2.4964	-0.6008	-2.4549	-1.5053	-0.5381	-0.9178	-2.5670
1000	-2.4649	-2.0677	-0.6076	-2.4152	-0.5724	-2.3747	-1.4432	-0.5076	-0.8461	-2.4802

1100	-2.3817	-1.9930	-0.5804	-2.3335	-0.5422	-2.2938	-1.3801	-0.4748	-0.7742	-2.3912
1200	-2.2973	-1.9168	-0.5515	-2.2506	-0.5100	-2.2116	-1.3149	-0.4401	-0.7021	-2.3014
1300	-2.2115	-1.8386	-0.5203	-2.1660	-0.4755	-2.1278	-1.2471	-0.4028	-0.6295	-2.2110
1400	-2.1250	-1.7594	-0.4881	-2.0807	-0.4397	-2.0432	-1.1783	-0.3644	-0.5564	-2.1197
1500	-2.0377	-1.6794	-0.4547	-1.9946	-0.4028	-1.9577	-1.1085	-0.3247	-0.4828	-2.0276
1600	-1.9497	-1.5985	-0.4203	-1.9077	-0.3646	-1.8715	-1.0375	-0.2837	-0.4086	-1.9347
1700	-1.8609	-1.5166	-0.3846	-1.8200	-0.3253	-1.7844	-0.9654	-0.2415	-0.3338	-1.8409
1800	-1.7712	-1.4337	-0.3479	-1.7314	-0.2846	-1.6964	-0.8922	-0.1979	-0.2583	-1.7463
1900	-1.6807	-1.3498	-0.3099	-1.6420	-0.2428	-1.6075	-0.8178	-0.1531	-0.1823	-1.6509
2000	-1.5878	-1.2625	-0.2684	-1.5498	-0.1973	-1.5157	-0.7391	-0.1047	-0.1056	-1.5547

Table S5. The SISSO predicted ΔG_{form} of possible stable binary-ternary reaction products of $\text{Ti}_2\text{SiC}+\text{O}_2$ oxidation process. The 0 K enthalpies were used as input by SISSO as starting point.

	ΔG_{form} (eV/atom)							
T(K)	TiSi	TiO₂	TiC	Ti₃SiC₂	Ti₃O₅	Ti₂O₃	SiO₂	CO₂
0	-0.7908	-3.2426	-0.8041	-0.8247	-3.1736	-3.1219	-3.0736	-1.5403
300	-0.8028	-3.0641	-0.8016	-0.8295	-3.0016	-2.9537	-2.9135	-1.3795
400	-0.7706	-2.9692	-0.7655	-0.7955	-2.9088	-2.8622	-2.8250	-1.2914
500	-0.7437	-2.8810	-0.7361	-0.7677	-2.8227	-2.7772	-2.7437	-1.2113
600	-0.7189	-2.7961	-0.7096	-0.7426	-2.7397	-2.6952	-2.6660	-1.1355
700	-0.6946	-2.7128	-0.6843	-0.7185	-2.6582	-2.6148	-2.5901	-1.0620
800	-0.6700	-2.6302	-0.6592	-0.6944	-2.5773	-2.5349	-2.5151	-0.9896
900	-0.6448	-2.5477	-0.6337	-0.6698	-2.4964	-2.4549	-2.4404	-0.9178
1000	-0.6185	-2.4649	-0.6076	-0.6444	-2.4152	-2.3747	-2.3656	-0.8461
1100	-0.5910	-2.3817	-0.5804	-0.6180	-2.3335	-2.2938	-2.2905	-0.7742

1200	-0.5615	-2.2973	-0.5515	-0.5897	-2.2506	-2.2116	-2.2150	-0.7021
1300	-0.5296	-2.2115	-0.5203	-0.5590	-2.1660	-2.1278	-2.1389	-0.6295
1400	-0.4964	-2.1250	-0.4881	-0.5273	-2.0807	-2.0432	-2.0622	-0.5564
1500	-0.4619	-2.0377	-0.4547	-0.4944	-1.9946	-1.9577	-1.9849	-0.4828
1600	-0.4262	-1.9497	-0.4203	-0.4603	-1.9077	-1.8715	-1.9069	-0.4086
1700	-0.3868	-1.8609	-0.3846	-0.4243	-1.8200	-1.7844	-1.8266	-0.3338
1800	-0.3331	-1.7712	-0.3479	-0.3826	-1.7314	-1.6964	-1.7368	-0.2583
1900	-0.2781	-1.6807	-0.3099	-0.3398	-1.6420	-1.6075	-1.6464	-0.1823
2000	-0.2195	-1.5878	-0.2684	-0.2934	-1.5498	-1.5157	-1.5553	-0.1056

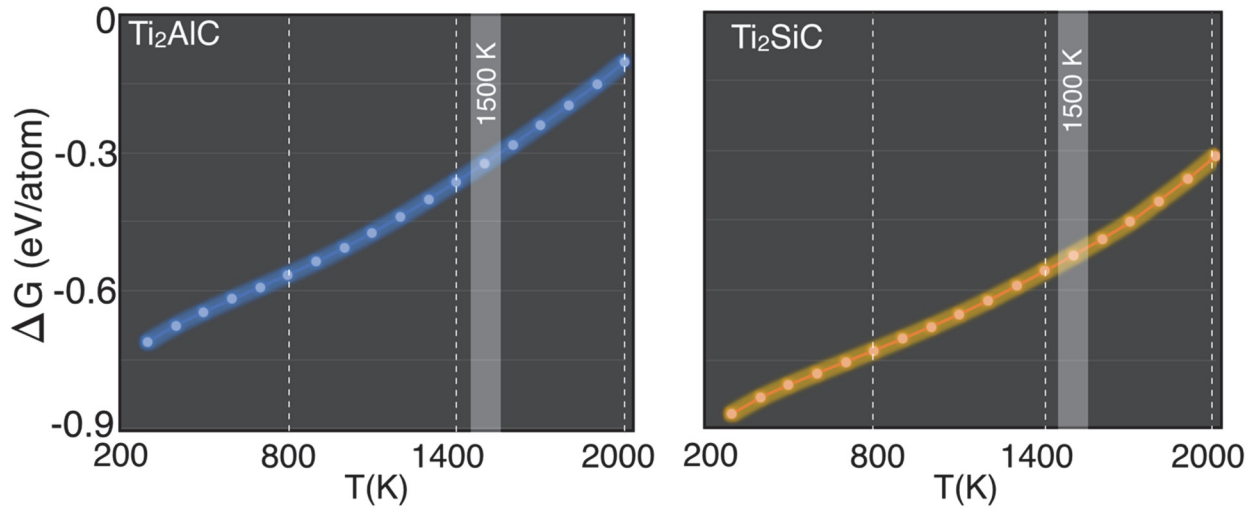


Figure S2. The SISSO predicted ΔG_{form} of (left-panel) Ti_2AlC , and (right-panel) Ti_2SiC shows monotonous behavior with temperature in the 300 K – 2000 K range.

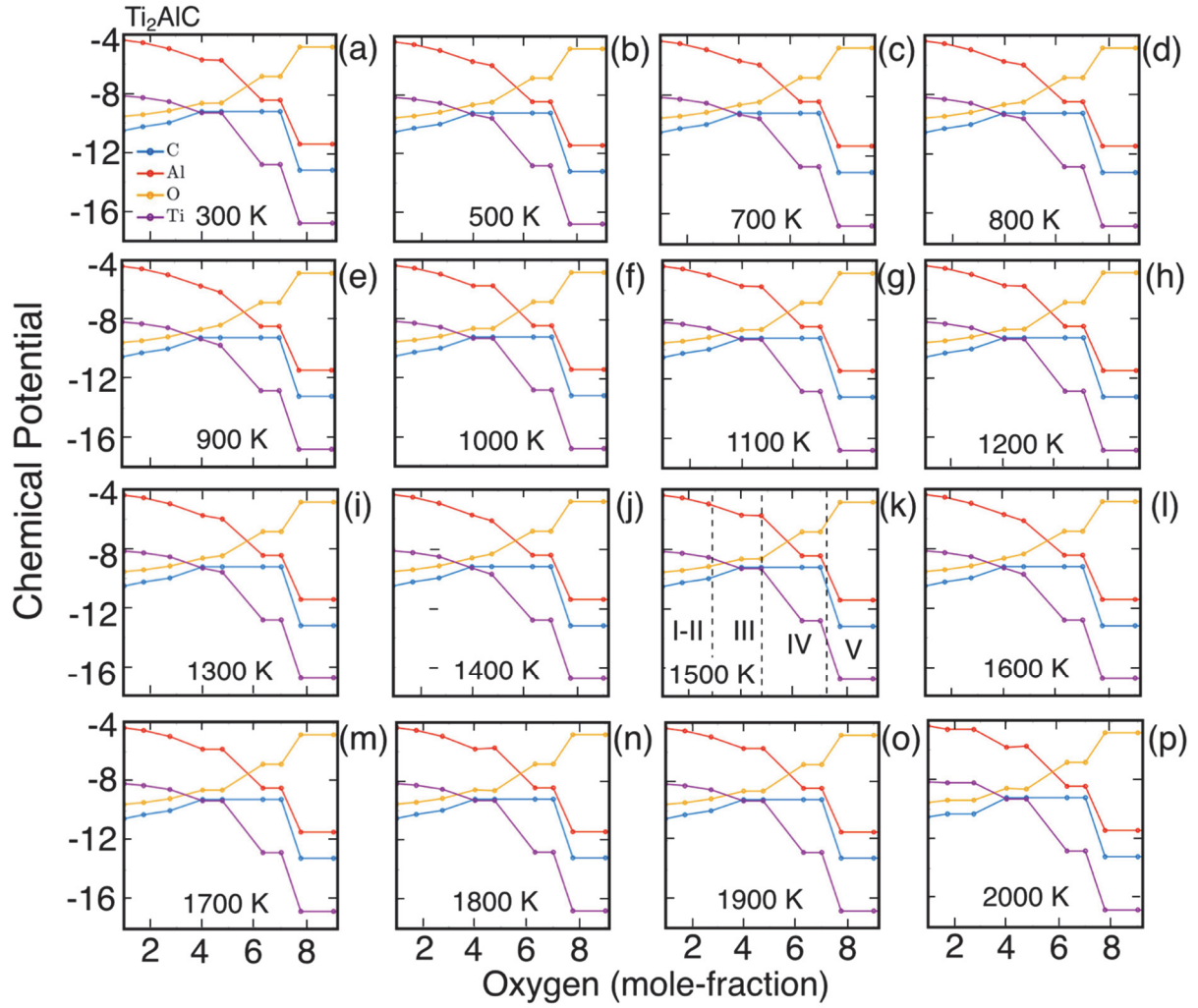


Figure S3: (a-p) Oxidation reaction chain showing change in chemical potential as a function of changing molar percent oxygen for the temperature range 300 K to 2000 K. On oxidation, the partial chemical potentials of Ti, Al, and C reduces while the chemical potential of invading O_2 increases.

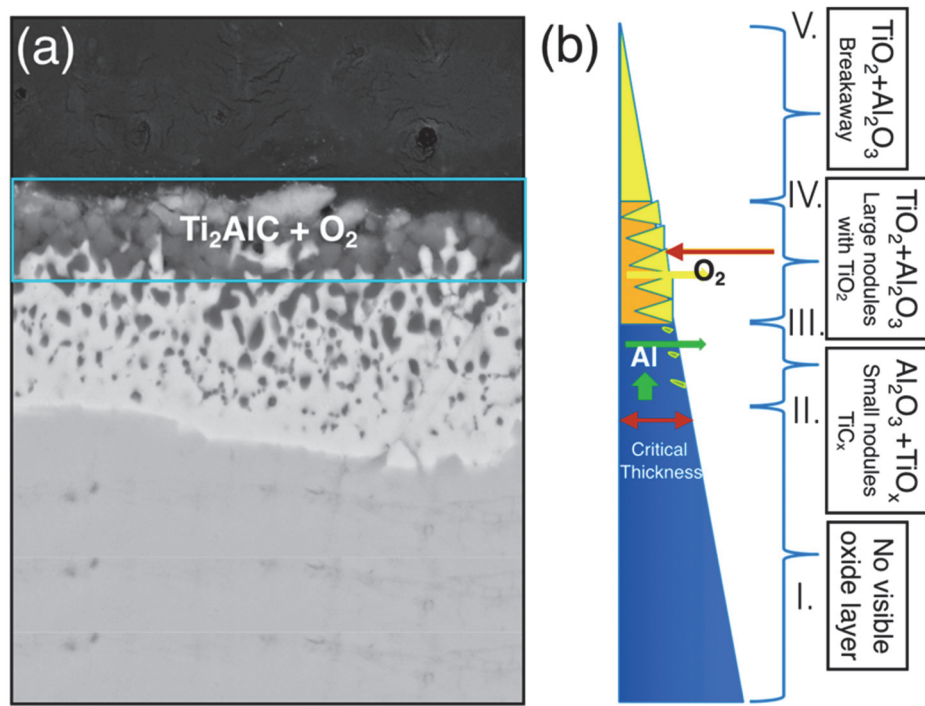


Figure S4. (a) SEM micrographs of cross-sectioned wedge-shaped Ti_2AlC (region v) oxidized at 1473 for 30 min. The schematic of reaction product distribution, i.e., TiO_2 , Al_2O_3 , O_2 , and Ti_2AlC , predicted from with GCLP minimizer.

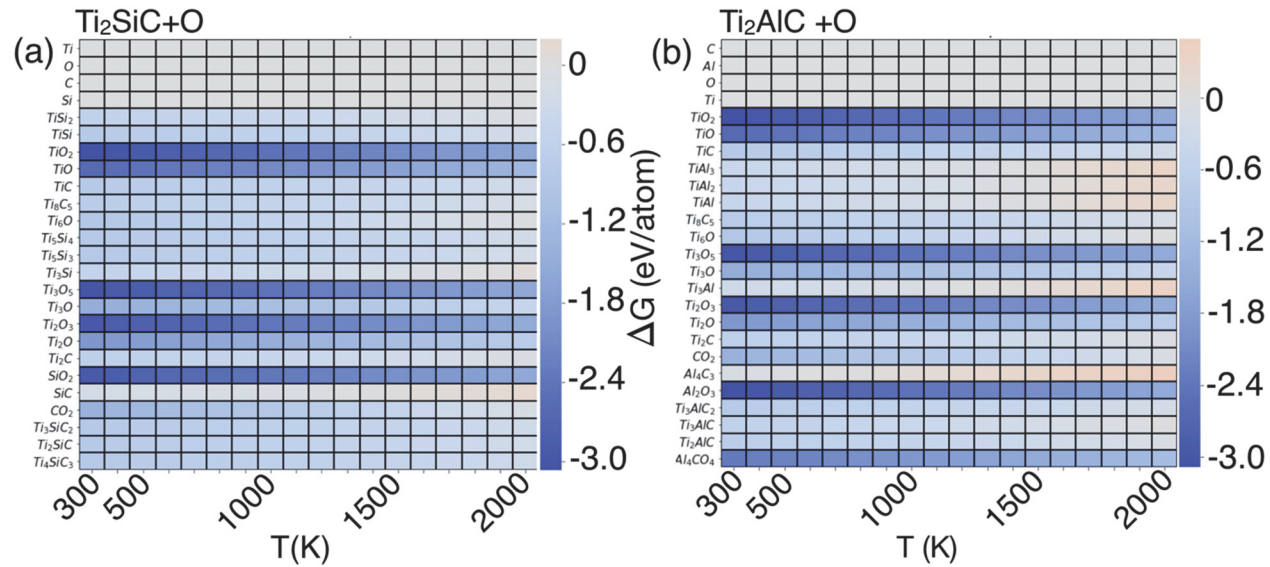


Figure S5. Heat map for possible reaction products from Ti-Si-C-O and Ti-Al-C-O MAX phases with respect to temperature 300 -2000 K. The data related to this plot is provided below in Table S6 and Table S7.

Determination of Al loss during the oxidation process: For the known critical thickness, t_c , and thickness of the alumina scale layer in *Regions I* and *II*, t_o , the critical Al deficiency, x , in $\text{Ti}_2\text{Al}_{1-x}\text{C}$ at which the oxidation mechanisms breaks away from that observed in bulk samples can be determined as:

$$x = \frac{\text{mols of Al in Al}_2\text{O}_3 \text{ layer}}{\text{mols of Al in Ti}_2\text{AlC substrate}} = \frac{2 \cdot \rho_{\text{Al}_2\text{O}_3} \cdot t_a / M_{\text{Al}_2\text{O}_3}}{\rho_{\text{Ti}_2\text{AlC}} \cdot t_c / M_{\text{Ti}_2\text{AlC}}} \quad (3)$$

where $\rho_{\text{Al}_2\text{O}_3}$ and $\rho_{\text{Ti}_2\text{AlC}}$ are densities of Al_2O_3 and Ti_2AlC , respectively and $M_{\text{Al}_2\text{O}_3}$ and $M_{\text{Ti}_2\text{AlC}}$ are molecular masses of Al_2O_3 and Ti_2AlC , respectively.

The critical Al deficiency that results in breakaway oxidation was found to be approximately 0.05 (or 5%), regardless of the oxidation temperature and time. Note here that standard deviations and scattering are much larger for results obtained at shorter oxidation times mostly due to larger variation in the thickness of the oxide layer in *Regions I* and *II*. With longer time, i.e. 10 hours, the critical Al converge to value between 0.045 and 0.055.

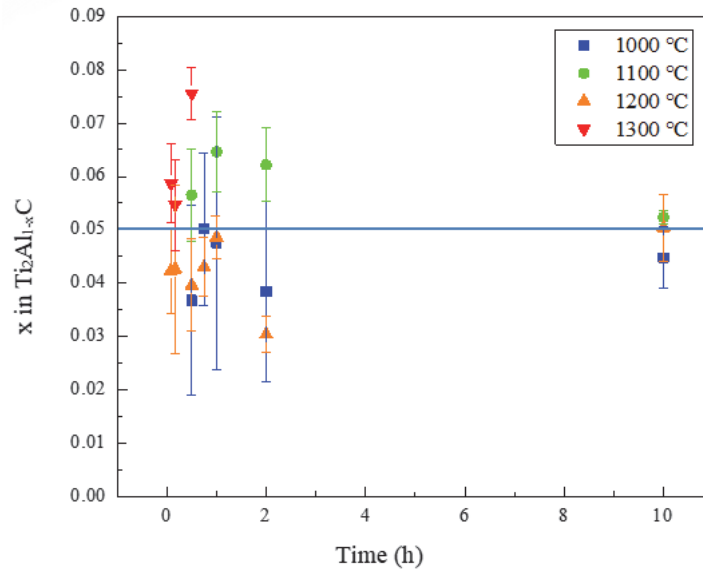


Figure S6: Critical Al loss, x , in $\text{Ti}_2\text{Al}_{1-x}\text{C}$ that leads to breakaway oxidation.

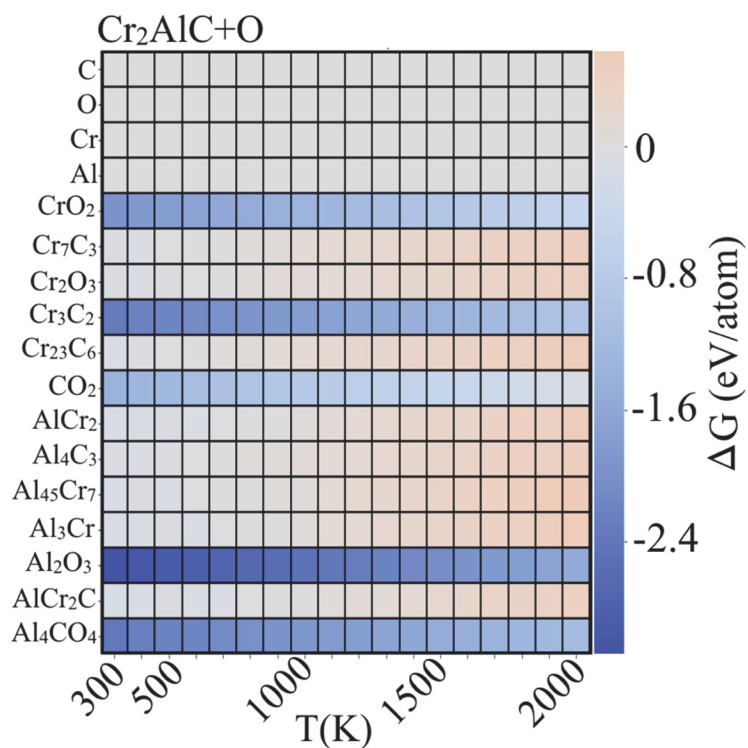


Figure S7. Heat map for possible reaction products from Cr-Al-C-O MAX phases with respect to temperature 300 - 2000 K. The data related to this plot is provided below in Table S8.

Table S6. The SISSO predicted ΔG_{form} of all possible binary-ternary reaction products of Ti-Al-C+O₂ oxidation process. The 0 K enthalpies were used as input by SISSO as starting point.

Formula	Temperature																	
	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
TiO2	-3.06408	-2.96919	-2.88102	-2.79613	-2.71284	-2.63022	-2.5477	-2.46494	-2.38168	-2.29733	-2.2115	-2.12498	-2.03773	-1.94971	-1.86088	-1.77123	-1.68074	-1.58782
Ti1O1	-2.59814	-2.51426	-2.43659	-2.36178	-2.2882	-2.21497	-2.14159	-2.06769	-1.99305	-1.91684	-1.83857	-1.75944	-1.67942	-1.59847	-1.51656	-1.43366	-1.34976	-1.26248
Ti1C1	-0.80159	-0.76549	-0.73605	-0.70958	-0.68428	-0.65918	-0.63373	-0.60757	-0.58043	-0.55152	-0.52033	-0.48808	-0.45474	-0.42026	-0.38464	-0.34786	-0.30989	-0.26838
Ti1Al3	-0.4137	-0.37771	-0.34661	-0.31725	-0.28812	-0.2584	-0.2276	-0.18947	-0.14686	-0.10239	-0.05584	-0.00786	0.041528	0.092311	0.144465	0.19797	0.252801	0.310113
Ti1Al2	-0.45043	-0.41424	-0.38291	-0.3533	-0.32392	-0.29395	-0.2629	-0.22519	-0.18334	-0.1395	-0.09339	-0.04586	0.003074	0.053407	0.105119	0.158193	0.212613	0.269931
Ti1Al1	-0.43613	-0.39967	-0.36803	-0.33808	-0.30833	-0.27799	-0.24661	-0.2099	-0.16971	-0.1273	-0.08221	-0.03572	0.01216	0.061443	0.112119	0.164185	0.217634	0.274815
Ti8C5	-0.72817	-0.69219	-0.6624	-0.63525	-0.60904	-0.58286	-0.55617	-0.52865	-0.50002	-0.46935	-0.43603	-0.40159	-0.36599	-0.3292	-0.2912	-0.25195	-0.21146	-0.1668
Ti6O1	-0.88506	-0.83277	-0.7856	-0.74036	-0.69559	-0.6505	-0.60466	-0.55777	-0.50958	-0.45883	-0.40472	-0.34943	-0.2929	-0.2351	-0.17599	-0.11556	-0.05377	0.013442
Ti3O5	-3.0016	-2.90884	-2.82266	-2.73967	-2.65818	-2.57728	-2.49642	-2.41524	-2.33351	-2.25057	-2.166	-2.0807	-1.99463	-1.90775	-1.82002	-1.73144	-1.64196	-1.54983
Ti3O1	-1.472	-1.40992	-1.35328	-1.29885	-1.24512	-1.19128	-1.13686	-1.08154	-1.0251	-0.9664	-0.90473	-0.84197	-0.77807	-0.71301	-0.64675	-0.57926	-0.51052	-0.43697
Ti3Al1	-0.32774	-0.29097	-0.25894	-0.22854	-0.19832	-0.16752	-0.1357	-0.10058	-0.06296	-0.02275	0.020731	0.065574	0.111804	0.159436	0.208483	0.25896	0.310878	0.367777
Ti2O3	-2.95373	-2.86219	-2.77716	-2.69524	-2.61478	-2.53486	-2.45494	-2.37467	-2.29379	-2.21164	-2.12778	-2.04316	-1.95774	-1.87149	-1.78437	-1.69637	-1.60745	-1.51573
Ti2O1	-1.88445	-1.81451	-1.75027	-1.68845	-1.62751	-1.56661	-1.50527	-1.44317	-1.38007	-1.31494	-1.24714	-1.17833	-1.10846	-1.03751	-0.96544	-0.89222	-0.81783	-0.73911
Ti2C1	-0.65343	-0.61736	-0.58728	-0.5597	-0.53295	-0.50615	-0.47879	-0.45052	-0.4211	-0.38951	-0.35511	-0.31957	-0.28283	-0.24488	-0.20568	-0.16521	-0.12346	-0.07726
C1O2	-1.37949	-1.2914	-1.21135	-1.13552	-1.06197	-0.9896	-0.91777	-0.84606	-0.77422	-0.70208	-0.62951	-0.55644	-0.48281	-0.40861	-0.33379	-0.25835	-0.18228	-0.10557
Al4C3	-0.09786	-0.06249	-0.03366	-0.00772	0.017123	0.041882	0.06716	0.097848	0.131838	0.166937	0.203186	0.240604	0.279188	0.31893	0.35981	0.40181	0.444904	0.489068
Al2O3	-3.08599	-2.99092	-2.90247	-2.81723	-2.73349	-2.65028	-2.56702	-2.48018	-2.39116	-2.30145	-2.21097	-2.11969	-2.02759	-1.93466	-1.8409	-1.74632	-1.65092	-1.55471
Ti3Al1C2	-0.76835	-0.73339	-0.70448	-0.6781	-0.65257	-0.62699	-0.60082	-0.5724	-0.54217	-0.51002	-0.47545	-0.43972	-0.40278	-0.36463	-0.32525	-0.28463	-0.24276	-0.19728
Ti3Al1C1	-0.6083	-0.57229	-0.5418	-0.51348	-0.48574	-0.45774	-0.42898	-0.39754	-0.36403	-0.32832	-0.28986	-0.25015	-0.20916	-0.16689	-0.12331	-0.07841	-0.03219	0.018187
Ti2Al1C1	-0.71133	-0.67596	-0.64633	-0.61902	-0.59241	-0.5656	-0.53809	-0.50757	-0.47481	-0.44006	-0.40283	-0.36437	-0.32467	-0.2837	-0.24146	-0.19794	-0.15314	-0.1047
Al4C1O4	-2.35519	-2.27965	-2.2107	-2.14489	-2.08046	-2.01645	-1.95227	-1.88404	-1.81333	-1.74183	-1.66945	-1.59619	-1.52201	-1.44692	-1.37092	-1.29401	-1.21622	-1.13755

Table S7. The SISSO predicted ΔG_{form} of all possible binary-ternary reaction products of Ti-Si-C+O₂ oxidation process. The 0 K enthalpies were used as input by SISSO as starting point.

Formula	Temperature																	
	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Ti1Si2	-0.59712	-0.5666	-0.54159	-0.51878	-0.49664	-0.47433	-0.45141	-0.42757	-0.40261	-0.37599	-0.34735	-0.31752	-0.28646	-0.25415	-0.21751	-0.16216	-0.10564	-0.04639
Ti1Si1	-0.80279	-0.77061	-0.74374	-0.71891	-0.69461	-0.67005	-0.64478	-0.6185	-0.591	-0.56152	-0.52956	-0.49637	-0.46191	-0.42617	-0.38682	-0.33307	-0.27807	-0.21946
Ti1O2	-3.06408	-2.96919	-2.88102	-2.79613	-2.71284	-2.63022	-2.5477	-2.46494	-2.38168	-2.29733	-2.2115	-2.12498	-2.03773	-1.94971	-1.86088	-1.77123	-1.68074	-1.58782
Ti1O1	-2.59814	-2.51426	-2.43659	-2.36178	-2.2882	-2.21497	-2.14159	-2.06769	-1.99305	-1.91684	-1.83857	-1.75944	-1.67942	-1.59847	-1.51656	-1.43366	-1.34976	-1.26248
Ti1C1	-0.80159	-0.76549	-0.73605	-0.70958	-0.68428	-0.65918	-0.63373	-0.60757	-0.58043	-0.55152	-0.52033	-0.48808	-0.45474	-0.42026	-0.38464	-0.34786	-0.30989	-0.26838
Ti8C5	-0.72817	-0.69219	-0.6624	-0.63525	-0.60904	-0.58286	-0.55617	-0.52865	-0.50002	-0.46935	-0.43603	-0.40159	-0.36599	-0.3292	-0.2912	-0.25195	-0.21146	-0.1668
Ti6O1	-0.88506	-0.83277	-0.7856	-0.74036	-0.69559	-0.6505	-0.60466	-0.55777	-0.50958	-0.45883	-0.40472	-0.34943	-0.2929	-0.2351	-0.17599	-0.11556	-0.05377	0.013442
Ti5Si4	-0.82382	-0.79121	-0.76384	-0.73846	-0.71357	-0.68838	-0.66245	-0.63548	-0.60726	-0.57695	-0.54401	-0.50982	-0.47436	-0.4376	-0.39747	-0.34438	-0.29001	-0.23174
Ti5Si3	-0.80738	-0.77406	-0.74589	-0.71965	-0.69385	-0.66771	-0.64078	-0.61277	-0.58349	-0.55196	-0.51762	-0.48202	-0.44512	-0.40692	-0.36564	-0.3132	-0.25944	-0.20143
Ti3Si1	-0.54122	-0.50703	-0.47783	-0.45043	-0.42338	-0.39591	-0.36758	-0.33812	-0.30729	-0.27399	-0.23752	-0.19976	-0.16069	-0.12028	-0.07733	-0.02646	0.025792	0.082962
Ti3O5	-3.0016	-2.90884	-2.82266	-2.73967	-2.65818	-2.57728	-2.49642	-2.41524	-2.33351	-2.25057	-2.166	-2.0807	-1.99463	-1.90775	-1.82002	-1.73144	-1.64196	-1.54983
Ti3O1	-1.472	-1.40992	-1.35328	-1.29885	-1.24512	-1.19128	-1.13686	-1.08154	-1.0251	-0.9664	-0.90473	-0.84197	-0.77807	-0.71301	-0.64675	-0.57926	-0.51052	-0.43697
Ti2O3	-2.95373	-2.86219	-2.77716	-2.69524	-2.61478	-2.53486	-2.45494	-2.37467	-2.29379	-2.21164	-2.12778	-2.04316	-1.95774	-1.87149	-1.78437	-1.69637	-1.60745	-1.51573
Ti2O1	-1.88445	-1.81451	-1.75027	-1.68845	-1.62751	-1.56661	-1.50527	-1.44317	-1.38007	-1.31494	-1.24714	-1.17833	-1.10846	-1.03751	-0.96544	-0.89222	-0.81783	-0.73911
Ti2C1	-0.65343	-0.61736	-0.58728	-0.5597	-0.53295	-0.50615	-0.47879	-0.45052	-0.4211	-0.38951	-0.35511	-0.31957	-0.28283	-0.24488	-0.20568	-0.16521	-0.12346	-0.07726
Si1O2	-2.91348	-2.82501	-2.74368	-2.66595	-2.59008	-2.51508	-2.44038	-2.3656	-2.29053	-2.21501	-2.13894	-2.06225	-1.9849	-1.90685	-1.82656	-1.73682	-1.6464	-1.55531
Si1C1	-0.22316	-0.19307	-0.17025	-0.15087	-0.13306	-0.11576	-0.09838	-0.08056	-0.06207	-0.04277	-0.02258	-0.00143	0.020712	0.043854	0.070321	0.110881	0.152375	0.194789
C1O2	-1.37949	-1.2914	-1.21135	-1.13552	-1.06197	-0.9896	-0.91777	-0.84606	-0.77422	-0.70208	-0.62951	-0.55644	-0.48281	-0.40861	-0.33379	-0.25835	-0.18228	-0.10557
Ti3Si1C2	-0.82948	-0.79551	-0.76773	-0.74262	-0.71847	-0.69437	-0.66979	-0.6444	-0.61796	-0.58968	-0.55904	-0.52729	-0.49439	-0.46031	-0.42426	-0.38263	-0.3398	-0.29341
Ti2Si1C1	-0.79868	-0.76486	-0.73703	-0.7117	-0.68722	-0.66272	-0.63768	-0.61178	-0.58479	-0.55592	-0.52466	-0.49227	-0.45869	-0.42391	-0.38674	-0.3418	-0.29564	-0.2459
Ti4Si1C3	-0.82432	-0.79028	-0.76256	-0.73757	-0.7136	-0.68972	-0.66539	-0.64028	-0.61413	-0.58616	-0.55585	-0.52445	-0.4919	-0.45819	-0.42272	-0.38277	-0.34162	-0.29691

Table S8. The SISSO predicted ΔG_{form} of all possible binary-ternary reaction products of Cr-Al-C+O₂ oxidation process. The 0 K enthalpies were used as input by SISSO as starting point.

Formula	Temperature																	
	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Cr1O2	-1.92537	-1.85896	-1.79942	-1.7433	-1.68886	-1.63513	-1.58153	-1.52769	-1.47337	-1.4184	-1.36265	-1.30604	-1.2485	-1.18998	-1.13044	-1.06983	-1.00814	-0.94532
Cr7C3	-0.0938	-0.08442	-0.08121	-0.08067	-0.08108	-0.08149	-0.08132	-0.08024	-0.078	-0.07444	-0.06943	-0.06289	-0.05474	-0.04491	-0.03335	-0.02001	-0.00483	0.012222
Cr3C2	-0.09391	-0.08558	-0.08378	-0.08489	-0.08713	-0.0895	-0.09142	-0.09254	-0.0926	-0.09145	-0.08896	-0.08504	-0.07962	-0.07265	-0.06406	-0.05383	-0.0419	-0.02824
Cr2O3	-2.31474	-2.25412	-2.20021	-2.14955	-2.10045	-2.05195	-2.00348	-1.95467	-1.90527	-1.85512	-1.8041	-1.75211	-1.6991	-1.645	-1.58977	-1.53336	-1.47575	-1.4169
Cr23C6	-0.06893	-0.05876	-0.05443	-0.05256	-0.05146	-0.05023	-0.04831	-0.04537	-0.04118	-0.03557	-0.02842	-0.01963	-0.00913	0.003162	0.017301	0.033346	0.05135	0.071367
C1O2	-1.37279	-1.3129	-1.26105	-1.21342	-1.16807	-1.1239	-1.08027	-1.03676	-0.99312	-0.94918	-0.90481	-0.85994	-0.81451	-0.76851	-0.72189	-0.67465	-0.62678	-0.57827
Al1Cr2	-0.13453	-0.12783	-0.12621	-0.12648	-0.12711	-0.12726	-0.12641	-0.12162	-0.11402	-0.10483	-0.09398	-0.0814	-0.06705	-0.05088	-0.03285	-0.01294	0.008898	0.032686
Al4C3	-0.09116	-0.08399	-0.08336	-0.08562	-0.08898	-0.09242	-0.09534	-0.09285	-0.08706	-0.08016	-0.07211	-0.0629	-0.05251	-0.04097	-0.02829	-0.01449	0.000404	0.016368
Al45Cr7	-0.1162	-0.10975	-0.10827	-0.10861	-0.10923	-0.10928	-0.10824	-0.09894	-0.08471	-0.06897	-0.05171	-0.03294	-0.01266	0.009085	0.032284	0.05691	0.082936	0.11034
Al3Cr1	-0.13685	-0.12985	-0.12785	-0.12768	-0.12781	-0.1274	-0.12591	-0.11709	-0.10381	-0.089	-0.07264	-0.05471	-0.03523	-0.0142	0.008365	0.03246	0.058069	0.085179
Al2O3	-3.07929	-3.01242	-2.95217	-2.89513	-2.83959	-2.78458	-2.72952	-2.67088	-2.61006	-2.54855	-2.48627	-2.42319	-2.35929	-2.29456	-2.229	-2.16262	-2.09542	-2.02741
Al1Cr2C1	-0.15873	-0.15197	-0.15118	-0.15289	-0.15543	-0.15784	-0.15959	-0.15833	-0.15486	-0.15006	-0.14383	-0.13611	-0.12685	-0.11602	-0.10358	-0.08951	-0.07379	-0.05638
Al4C1O4	-2.34849	-2.30115	-2.2604	-2.22279	-2.18656	-2.15075	-2.11477	-2.07474	-2.03223	-1.98893	-1.94475	-1.89969	-1.85371	-1.80682	-1.75902	-1.71031	-1.66072	-1.61025

