Ta-based 413 and 211 MAX phase solid solutions with Hf and Nb

Matteo Griseri^{*,a,b}, Benu Tunca^{a,b}, Shuigen Huang^b, Martin Dahlqvist^c, Johanna Rosén^c, Jun Lu^c, Per O.Å. Persson^c, Lucia Popescu^a, Jozef Vleugels^b and Konstantina Lambrinou^{a,d}

^a SCK•CEN, Boeretang 200, 2400 Mol, Belgium

^b KU Leuven, Dept. of Materials Engineering, Kasteelpark Arenberg 44, 3001 Leuven, Belgium

^c Dept. of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

^d School of Computing and Engineering, University of Huddersfield, Huddersfield HD1 3DH, UK

* Corresponding author: matteo.griseri@kuleuven.be

Abstract

New bulk MAX phase-based ceramics were synthesized in the Ta–Hf–Al–C and Ta–Nb–Al–C systems. Specifically, $(\text{Ta}_{1-x}\text{Hf}_x)_4\text{AlC}_3$ and $(\text{Ta}_{1-x}\text{Nb}_x)_4\text{AlC}_3$ stoichiometries with $x = 0.05, 0.1, 0.15, 0.2, 0.25$ were targeted by reactive hot pressing of Ta_2H , HfH_2 , $\text{NbH}_{0.89}$, Al and C powder mixtures at 1550°C in vacuum. The produced ceramics were characterized in terms of phase composition and microstructure by X-ray diffraction, scanning electron microscopy, electron probe microanalysis and scanning transmission electron microscopy. The investigation confirmed the existence of such M-site solid solutions with low solute concentrations, as predicted by first-principles calculations. These calculations also predicted a linear trend in lattice parameter evolution with increasing Hf concentration, in agreement with the experimental results. In order to increase the low phase purity of the produced ceramics, Sn was added to form $(\text{Ta}_{1-x}\text{Hf}_x)_4(\text{Al}_{0.5}\text{Sn}_{0.5})\text{C}_3$ and $(\text{Ta}_{1-x}\text{Nb}_x)_4(\text{Al}_{0.5}\text{Sn}_{0.5})\text{C}_3$ double solid solutions, thus resulting in a higher content of the 413 MAX phase compounds in the produced ceramics.

Keywords: MAX Phases, Tantalum, Hafnium, Niobium, Ta_4AlC_3

1. Introduction

The ternary carbides/nitrides known as the MAX ($\text{M}_{n+1}\text{AX}_n$) phases have been attracting a lot of attention, due to their unique properties and wide range of potential applications. In the $\text{M}_{n+1}\text{AX}_n$ phases, M is an early transition metal, A is a semimetal or metalloid, X is carbon or nitrogen, while the exact stoichiometry is defined by $n = 1, 2$ or 3 [1,2]. Solid solutions of two or more elements are possible on the M, A and X sites, generating an impressively large number of possible compositions, several of which have already been experimentally synthesized [1,2]. A two-element solid solution on the M-site could be described by the $(\text{M}_{1-x}\text{M}'_x)_{n+1}(\text{A})(\text{X})_n$ general stoichiometry, where x is the mole fraction of the M' secondary solute element. The present work focuses on the Ta–Hf–Al–C and Ta–Nb–Al–C systems, where the secondary M' solute elements are Hf and Nb, respectively.

The interest in Hf-containing solid solutions was motivated by the request for new metallurgical processes capable of synthesizing bulk, phase-pure ceramics with tunable stoichiometries in the Ta–Hf–C system; such compounds have been identified by ab-initio studies as candidate ultra-high temperature ceramics (UHTCs) with melting

points exceeding 3800°C [3,4]. From an application point of view, new highly refractory Ta-based carbides may be employed as advanced target materials in isotope separation on-line (ISOL) facilities. ISOL is a technique for the production of exotic radioactive ion beams (RIBs) by a process of on-line evaporation and extraction of radioisotopes from a target material, such as TaC_x, which has been irradiated by an accelerated particle beam [5,6]. ISOL target materials are typically porous, so as to facilitate radioisotope evaporation and their transport to the detecting devices. Therefore, high melting point target materials are desirable, as a high melting point typically implies the delayed material densification at high temperatures (i.e., 2000°C and above) and pore closure over time, assuring a more release-efficient operation over longer service periods [7].

In previous studies, (Ta_{1-x}Hf_x)C pseudo-binary carbide solid solutions were produced by spark plasma sintering (SPS) of TaC-HfC powder mixtures at temperatures above 2000°C, with x ranging from 0 to 1 [8]. However, due to a miscibility gap below 888°C [9], the solute Hf atoms cannot be homogeneously dispersed in the cubic TaC host lattice. Taking this into account, it was decided to investigate the miscibility of Hf with a ternary carbide, such as Ta₄AlC₃. The first aim of this study is to explore whether it would be possible to produce bulk MAX phase-based ceramics with the (Ta_{1-x}Hf_x)₄AlC₃ overall stoichiometry. These ceramics would then serve as precursors for the synthesis of pseudo-binary (Ta_{1-x}Hf_x)₄C₃ solid solutions, based on the known tendency of Ta-based MAX phase compounds to decompose at high temperatures in vacuum due to the evaporation of Al, as reported in recent work [10]. This study was also motivated by the fact that ternary Ta- and Hf-based MAX phase compounds (i.e., Ta₂AlC, Hf₂AlC, Hf₃AlC₂, and Ta₄AlC₃) have been produced as highly pure bulk ceramics by reactive uniaxial hot pressing (HP) of Ta₂H–Al–C and HfH₂–Al–C powder mixtures [10–13].

The Ta–Hf–Al–C quaternary system has only been discussed in literature in terms of defining the equilibrium phase diagrams below 1000°C and considering the formation of complex carbides in that temperature domain, reporting only M₂AlX phases with no solid solutions on the M-site [14].

The second aim of the study is to compare, in terms of achieved purity and solubility limits, Ta–Hf–Al–C MAX phase solid solutions with similar compositions in the Ta–Nb–Al–C system. Unlike Hf and Ta, Nb and Ta have identical atomic radii, with NbC and TaC binary carbides exhibiting a solid solubility over the full compositional range and forming mixed (Ta_{1-x}Nb_x)C pseudo-binary carbides [9]. Similar to the Hf-containing MAX phases, Nb-containing MAX phase compounds have been reported in literature, such as the ternary compounds Nb₂AlC and Nb₄AlC₃ [1], as well as M-site solid solutions, such as (Nb_{1-x}Zr_x)₄AlC₃ with x = 0.05, 0.1, 0.15, 0.2 and 0.25 [15], (Nb_{0.5}Sc_{0.5})₂AlC [16] and (Nb_{1-x}Ti_x)₄AlC₃ with x = 0.2 [17] and 0.3 [18].

Moreover, the synthesis of (Ta_{1-x}Hf_x)₄(Al_{0.5}Sn_{0.5})C₃ and (Ta_{1-x}Nb_x)₄(Al_{0.5}Sn_{0.5})C₃ double solid solutions was explored in an attempt to produce MAX phase-based bulk ceramics with higher phase purity. This approach has already been successfully implemented in the synthesis of double solid solution (Zr,Nb)₂(Al,Sn)C and (Zr,Ti)₂(Al,Sn)C MAX phase ceramics [19,20].

In order to assess the formation of 413 MAX phase compounds in the Ta–Hf–Al–C and Ta–Nb–Al–C systems, Ta₂H, HfH₂, NbH, Al and C (graphite) powders were mixed with varying relative amounts of Hf and Nb. The powder mixtures were compacted and reaction hot pressed. The obtained materials were characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM) combined with energy & wavelength

dispersive X-ray spectroscopy (EDS & WDS). Ultimately, select specimens were analyzed by scanning transmission electron microscopy (STEM) combined with EDS to obtain elemental maps from the areas of interest.

2. Experimental procedure

Tantalum hydride (Ta_2H) powder was obtained by the hydrogenation of metallic Ta (particle size $<44\ \mu\text{m}$, purity 99.95%, H.C. Starck) in pure H_2 at 800°C for 2 h. The brittle Ta_2H powder was milled in a planetary ball mill (Retsch PM4-MA, Germany) for 30 min at 250 rpm, in isopropanol and in an air atmosphere, using zirconia milling balls ($\varnothing\ 5\ \text{mm}$ and $10\ \text{mm}$) in a 3Y-TZP ZrO_2 container. The maximum particle size was reduced from $50\ \mu\text{m}$ to $10\ \mu\text{m}$, in order to improve the mixing with the other constituents. The milled Ta_2H was dried in a rotating evaporator (Heidolph 4010) and was sieved using a $32\text{-}\mu\text{m}$ fabric sieve.

The refined Ta_2H powder was mixed with HfH_2 (particle size $<10\ \mu\text{m}$, purity $>98\%$, Rockwood Lithium, grade PS, Germany), $\text{NbH}_{0.89}$ (particle size $<40\ \mu\text{m}$, CBMM, Brazil), Al (particle size $<5\ \mu\text{m}$, purity $>99\%$, Atlantic Equipment Engineers, USA), and graphite (particle size $<5\ \mu\text{m}$, purity $>99\%$, Asbury Graphite Mills, USA) to obtain the various $(\text{Ta}_x, \text{Hf}_{1-x})_4\text{AlC}_3$ and $(\text{Ta}_x, \text{Nb}_{1-x})_4\text{AlC}_3$ starting powder compositions. A 25% molar excess of Al and a 13% substoichiometric C content were chosen to inhibit the formation of TaC_y , HfC_y and $(\text{Ta}_x, \text{Hf}_{1-x})\text{C}_y$ carbides, as suggested previously [10,15]. For the synthesis of Sn-containing double solid solutions, metallic Sn powder (particle size $<5\ \mu\text{m}$, purity $>99\%$, Atlantic Equipment Engineers, USA) was used.

As this work targeted the synthesis of Ta-rich $(\text{Ta}_{1-x}, \text{M}'_x)_4\text{AlC}_3$ MAX phase solid solutions, the Hf and Nb secondary solute concentrations x were set at 0.05, 0.1, 0.15, 0.2 and 0.25. The different $(\text{Ta}_{1-x}, \text{Hf}_x)_4\text{AlC}_3$ starting powder grades are herein referred to as “TH05” ($x = 0.05$), “TH10” ($x = 0.1$), “TH15” ($x = 0.15$), “TH20” ($x = 0.2$), and “TH25” ($x = 0.25$). Similarly, the $(\text{Ta}_{1-x}, \text{Nb}_x)_4\text{AlC}_3$ mixtures are referred to as “TN05” ($x = 0.05$), “TN10” ($x = 0.1$), “TN15” ($x = 0.15$), “TN20” ($x = 0.2$), and “TN25” ($x = 0.25$).

The powder mixtures were cold-pressed into green pellets ($\varnothing\ 30\ \text{mm}$, 5–6 mm in thickness), under a load of 30 MPa, in a graphite die. Reaction sintering was performed in a hot press (W100/150-2200-50 LAX, FCT Systeme, Frankenblick, Germany) at 1550°C in vacuum (0.4 mbar) for 30 min dwell time, after a heating ramp of $20^\circ\text{C}/\text{min}$. The uniaxial pressure of 30 MPa was applied exclusively during the dwell time. Afterwards, the sintered compacts were allowed to cool naturally by switching off the power supply.

The produced materials were characterized by XRD in the 0° to $75^\circ\ 2\theta$ range, in steps of 0.01° , and at 0.2 s/step detection time, using a $\text{Cu } K_\alpha$ source operated at 40 kV and 30 mA (Bruker D2 Phaser, Germany) on both polished bulk and milled powder samples. The carbide-rich surface reaction layer was removed by grinding the as-sintered discs prior to polishing and XRD analysis. Calculations of the predicted patterns and Rietveld refinement were performed using the MAUD software, obtaining R_{wp} values ranging from 6% to 12% [21]. The XRD patterns used to calculate lattice parameters were measured from powders obtained by crushing the bulk specimens in a vibratory ring mill (Retsch RS 200, Germany).

The microstructure was examined on mirror-polished ceramics by SEM/EDS (XL30-FEG, FEI). Since the Hf and Ta characteristic X-ray signals cannot be differentiated by EDS, due to the similar energy of both M ($65\ \text{eV}$ difference) and L_α ($247\ \text{eV}$ difference) transitions, the Hf-containing grades were also examined by WDS using an electron

probe microanalyser (EPMA; JEOL Ltd, JXA-8530F, Japan) with a wavelength resolution of 0.155×10^{-3} nm (as compared to the 5×10^{-3} nm difference in L_{α} characteristic X-rays). Select specimens were used for the extraction of thin foils using focused ion beam (FIB); the thin foils were investigated by transmission electron microscopy (STEM) and EDS, using the Linköping double-corrected FEI Titan³ 60-300, equipped with high-brightness gun (XFEG), monochromator, Super-X EDS detector and Quantum ERS-GIF.

All first-principles calculated energies were obtained based on the Vienna Ab initio Simulation Package (VASP 5.4.4) [22] implementation of density functional theory (DFT), using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [23] description of the exchange-correlation energy. The plane wave energy cutoff was set to 400 eV, using k -point grids with a spacing of $0.05 \text{ \AA}^{-1}$ according to the Monkhorst-Pack method [24]. The electronic energy convergence threshold was set to 10^{-6} eV/atom for energy and 10^{-2} eV/Å for force.

The Special Quasi-random Structures (SQS) method [25], as implemented in the Alloy Theoretic Automated Toolkit (ATAT) package [26], was used to generate representative supercell structures that approximated a fully random alloy of Ta and M', with M' = Nb and Hf on the M-sites of the $(\text{Ta}_{1-x}\text{M}'_x)_2\text{AlC}$, $(\text{Ta}_{1-x}\text{M}'_x)_4\text{AlC}_3$, and $(\text{Ta}_{1-x}\text{M}'_x)\text{C}$ stoichiometries. The SQS supercell, thus, represented the best possible periodic supercell that mimics the local pair and multisite correlation functions of a random alloy, under the constraint of a given supercell size N.

The thermodynamic stability of $(\text{Ta}_{1-x}\text{M}'_x)_2\text{AlC}$ and $(\text{Ta}_{1-x}\text{M}'_x)_4\text{AlC}_3$ MAX phase solid solutions was investigated at 0 K with respect to their decomposition into any combination of competing phases. To identify the set of most competing phases, known as the equilibrium simplex, a linear optimization procedure based on the simplex method was used under the constraint of a fixed MAX stoichiometry [27,28]. The stability of a MAX phase was quantified in terms of its formation enthalpy, ΔH , by comparing its energy to the energy of the equilibrium simplex:

$$\Delta H = E(\text{compound}) - E(\text{equilibrium simplex}), \quad (1)$$

where $\Delta H < 0$ indicates a stable phase, while $\Delta H > 0$ indicates either an unstable or, at best, metastable phase. The selection of competing phases includes all known elemental, binary, ternary, and quaternary phases within the herein considered quaternary systems. Hypothetical phases, based on compounds existing in similar systems and/or with neighboring elements in the periodic table, were also included as competing phases.

Other temperature-dependent effects on the formation enthalpy, such as lattice vibrations and electronic entropy, were deemed negligible, as their contributions to a phase, significant or not, tend to be cancelled out in the Gibbs free energy of formation term [29]. This approach has been proven to work exceptionally well for previous theoretical studies of both ternary and quaternary MAX phases [28,30–36]. However, since solid solutions were investigated and approximated through modelled disorder (SQS), the contribution of configurational entropy to the Gibbs free energy of formation, ΔG , at elevated temperature was approximated using:

$$\Delta G = \Delta H - T\Delta S, \quad (2)$$

where T is the temperature and ΔS the configurational entropic contribution per M-site, assuming an ideal solution of Ta and M' on the M-sites; ΔS is given by:

$$\Delta S = -wk_B[x\ln(x) + (1-x)\ln(1-x)], \quad (3)$$

where x is the concentration of the M' solute, $w = 0.5$, and k_B is the Boltzmann constant.

3. Results and discussion

3.1. Phase assembly

The effect of the Hf content in the produced $(Ta_{1-x},Hf_x)_4AlC_3$ ceramics was assessed by XRD in terms of the relative abundance of the 413 and 211 MAX phases. Fig. 1a shows the XRD patterns of the $(Ta_{1-x},Hf_x)_4AlC_3$ compositions as function of the Hf amount, x , including the reference compound Ta_4AlC_3 ($x = 0$), while Fig. 2a shows the relative phase amounts, as determined by Rietveld refinement of the XRD patterns. The reported phase assemblies are averages deduced from XRD measurements performed on 2-3 samples per ceramic grade. Increasing the Hf concentration decreased linearly the amount of the 413 MAX phase, while the amount of both the 211 MAX phase and the $(Ta_{1-x},Hf_x)C_y$ pseudo-binary carbides (denoted as “TaC” in Fig. 1) increased at the expense of the 413 phase, which eventually disappeared above $x = 0.2$, as shown in Fig. 2a. Since no XRD peaks could be attributed to Ta–Al or Hf–Al intermetallic phases, $(Ta_{1-x},Hf_x)C_y$ mixed carbides were the only detectable non-MAX phase compounds in these bulk ceramics. As the starting powder ratios targeted a 413 stoichiometry, the formation of 211 MAX phases and pseudo-binary $(Ta_{1-x},Hf_x)C_y$ carbides implies that these phases compete thermodynamically with the 413 MAX phases when Hf is added as a secondary solute M' element; this finding agrees with the fact that the 413 phase is predominant in the Ta_4AlC_3 ceramic, i.e., in the absence of Hf. These results indicate that Hf destabilizes the 413 crystal structure configuration in favor of a 211 solid solution, and this effect becomes progressively more severe as the Hf concentration increases. At $x = 0.2$, the resulting phase assembly showed only a minor amount of the 413 MAX phase. At $x = 0.25$, no 413 phase could be detected. The 211 Ta_2AlC phase, which is known to form at temperatures below $1500^\circ C$ in the ternary Ta–Al–C system [10], was observed in all Hf-containing grades, especially at higher Hf concentrations. While Hf_2AlC is a well-documented ternary MAX compound [13], no 413 stoichiometry was ever reported in the Hf–Al–C system, which agrees with the observed instability of the 413 MAX phase with increasing Hf content.

Hot pressed ceramics with the $(Ta_{1-x},Nb_x)_4AlC_3$ starting powder composition and $x = 0.05, 0.10, 0.15, 0.20$, and 0.25 were also characterized by XRD, in order to quantify the produced phases as function of the Nb concentration, x . The peak-indexed XRD patterns of these ceramics are presented in Fig. 1b, including the XRD pattern of Ta_4AlC_3 ($x = 0$), while the results of phase quantification by Rietveld refinement are shown in Fig. 2b. Peaks of the 211 phase are clearly detected for $x = 0.05$, while the major MAX phase is the 413. The lack of lattice distortion due to the same atomic radius of Ta and Nb was reflected in the absence of any shift in the diffraction peaks. Similar to the Hf-containing grades, a substantial amount of the cubic $(Ta_{1-x},Nb_x)C$ pseudo-binary carbides was observed with increasing Nb content, while the presence of sharp (111) and (200) peaks reveals that this phase formed as random solid solution.

In this system, the 211 MAX phase accounted for less than 20 wt% at low Nb concentrations, and it was almost absent at $x = 0.25$. This shows that the stability of both 413 and 211 MAX phases decreases with increasing Nb content, favouring the formation of the $(Ta_{1-x},Nb_x)C$ pseudo-binary carbides. In contrast to the Hf-containing grades (Fig. 2a), the $(Ta_{1-x},Nb_x)_4AlC_3$ phase was converted into $(Ta_{1-x},Nb_x)C$ carbides

with increasing Nb content (Fig. 2b). This implies that the excess Al can only form Nb–Al intermetallic phases, which were, however, not unequivocally detected by XRD, whereas Al in the Hf-containing grades contributed to the formation of a 211 phase at high x. In all cases, no evidence of a β -413 polymorph was found, as expected from a previous study that showed that no polymorphism occurs upon hot pressing Ta_4AlC_3 below 1600°C [10]. Al_2O_3 could not be unequivocally identified, although its presence was revealed locally by EDS/WDS analysis, as explained in section 3.3.

For the evaluation of the thermodynamic stability of the $(\text{Ta}_{1-x},\text{Hf}_x)_2\text{AlC}$, $(\text{Ta}_{1-x},\text{Hf}_x)_4\text{AlC}_3$ and $(\text{Ta}_{1-x},\text{Hf}_x)\text{C}$ phases by first-principle calculations, the energy of each phase was compared to an identified set of most competing phases (equilibrium simplex) in terms of the formation enthalpy, ΔH , using Eq. 1. Fig. 3a shows the calculated phase stability at 0 K for $M' = \text{Hf}$, where only $(\text{Ta}_{1-x},\text{Hf}_x)_4\text{AlC}_3$ is found to be thermodynamically stable with a negative formation enthalpy, ΔH , while $(\text{Ta}_{1-x},\text{Hf}_x)_2\text{AlC}$ is the only phase with a slightly positive ΔH . The contribution of the configurational entropy at 1873 K (1600°C) to the Gibbs free energy was considered for all quaternary MAX phases and competing phases that have been modelled with disorder. The Gibbs free energy of formation, ΔG , of the MAX phases (calculated using Eq. 2), as compared to an identified set of the most competing phases (equilibrium simplex), is also shown in Fig. 2a. All solid solution MAX phases were found to be thermodynamically stable with $\Delta G < 0$, becoming increasingly more stable with increasing Hf content, except for the 413 phase that shows a slight increase in ΔG at $x = 0.25$. This particular result relates to the experimental evidence and the observed absence of the Hf_4AlC_3 phase. Given the small deviation in ΔG between 211 and 413 phases, no direct correlation could be established between these equilibrium approximations and the experimental findings in terms of 413 vs. 211 phase abundance; however, the ΔG of the pseudo-binary carbide phases decreases significantly with increasing x, thus gaining stability over the MAX phases, in agreement with experimental observations.

Fig. 3b shows the calculated phase stability of the Nb-containing phases as ΔH at 0 K and ΔG at 1873 K. Nb-containing phases show a steady increase in ΔH as function of x and less fluctuation when compared to Hf-containing phases. This can be associated with the similar atomic sizes of Nb and Ta, even though the ΔH variation for Hf-containing MAX phases is still within the 5 meV/atom range (Fig. 3a). Also in this case, all examined phases appear stable ($\Delta G < 0$) at equilibrium with decreasing ΔG as x increases, especially for the pseudo-binary carbides that are indeed more abundant in the higher-Nb grades. Even though Nb–Al intermetallics were considered competing phases, their stability was not checked individually against the other phases; hence, it is possible that their stability competes with that of the MAX phases, especially the 211 phase, with increasing Nb concentration, as observed during the microstructural analysis of the produced ceramics.

3.2. Lattice parameters of $(\text{Ta}_{1-x},\text{Hf}_x)_4\text{AlC}_3$ and $(\text{Ta}_{1-x},\text{Hf}_x)_2\text{AlC}$ MAX phases

Rietveld refinement allowed the determination of the lattice parameters a and c of the 413 and 211 Hf-containing MAX phases. These are shown in Figs. 4a and 4b, respectively, as function of the Hf content in the starting powder composition, and are compared to those of the ternary Ta_4AlC_3 MAX phase compound. Both the a and c lattice parameters increased with increasing the Hf content, x, in the $(\text{Ta}_{1-x},\text{Hf}_x)_2\text{AlC}$ and $(\text{Ta}_{1-x},\text{Hf}_x)_4\text{AlC}_3$ phases, due to the larger atomic radius of Hf as compared to Ta. Due to the low amount of $(\text{Ta}_{0.95},\text{Hf}_{0.05})_2\text{AlC}$ and $(\text{Ta}_{0.80},\text{Hf}_{0.20})_4\text{AlC}_3$ in the produced

ceramics, the estimated lattice parameters of these phases resulted in a rather high error margin. The measured lattice parameter values are compared to those obtained by computation in Figs. 4a and 4b, showing a difference of 1-2% between computed and experimental values. Even though the measured lattice parameters are slightly smaller compared to the calculated ones, they both show comparable trends. In general, the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) systematically overestimates lattice parameters, while the local-density approximation (LDA) underestimates them. Such behavior has been previously well established [37].

Despite the uncertainty ranges, the lattice parameters increased linearly with the Hf content (Fig. 4), following Vegard's law [38]. The observed trend seems to indicate, however, that the lattice parameters of the 211 phase deviate from linearity at higher Hf concentration ($x = 0.25$), after having reached a maximum at $x = 0.2$. A similar trend is observed for the 413 phase, despite the large error stemming from the low phase content at $x = 0.25$. Such deviation from linearity can most likely be associated with a Hf solubility limit in these MAX phases at around $x = 0.2$.

3.3. Microstructure

In agreement with the XRD phase quantification results, SEM analysis of metallographic cross-sections of the bulk ceramics revealed the presence of MAX phase grains and binary carbide regions, as shown in Fig. 5a for TH10 and Fig. 5b for TH25, respectively. In the low-Hf TH10 grade, MAX phase lamellae are visible in the backscattered electron (BSE) mode (Fig. 5a). The lamellar crystal habit assumed by the faceted MAX phase grains reflects the high aspect ratio (c/a) of the lattice parameters, and results from the much faster crystal growth parallel to the basal planes than perpendicular to them [39]. The 413 MAX phase grains appear brighter than the 211 ones in the BSE mode, due to a higher average atomic number. The 413 grains have an average length of $\sim 10\ \mu\text{m}$ and a strongly varying thickness. In particular, a fraction of very thin 413 grains are present within the 211 phase-rich areas. The 211 phase grains are generally shorter, with lengths not exceeding $5\ \mu\text{m}$ and typical aspect ratios of about 3:1. The observed difference in the grain size of the two MAX phases could be attributed to differences in the driving force for crystal growth, which is in turn associated with the relative undercooling below the solidification temperature of each one of the 2 phases; typically, higher undercooling means higher driving force for nucleation and growth [38]. Since the 413 crystal structure is stable at higher temperatures than the 211, the growth of 413 grains is expected to be faster than the growth of 211 grains at the sintering temperature (1550°C), forming 413 grains with higher aspect ratios when compared to the 211 grains.

In the higher Hf TH25 grade, only 211 grains are observed along finer-grained binary carbide phases (Fig. 5b), in accordance with the XRD results. In both grades, Al_2O_3 grains were detected (Figs. 5a and 5b), as it is often observed in Al-containing MAX phases. The formation of alumina is generally caused by a slight oxidation of the starting powder, in combination with an imperfect vacuum during reaction sintering, both of which supply oxygen to the powder mixture. The study of the fracture surface of the TH25 grade revealed a mixture of MAX phase lamellae and fine-grained binary carbides (Fig. 5c).

Figs. 5d and 5e show the microstructure of the TN10 and TN25 grade, respectively, indicating that the 413 grains in TN10 exhibit variation in the Nb distribution, as reflected in the non-uniform compositional contrast and confirmed by EDS point

analyses. The TN25 grade contained minor amounts of $(\text{Ta}_{0.75}, \text{Nb}_{0.25})\text{Al}_2$ intermetallics between the MAX phase grains. In all Nb-containing materials, equiaxed Nb–Al intermetallic grains (10–100 μm in diameter) were detected, as may be seen on the fracture surface of grade TN25 (Fig. 5f), as well as in Fig. 6a, which depicts a Nb–Al intermetallic grain enveloped by a MAX phase grain in the TN10 grade. EDS point analysis estimated the composition of this intermetallic as $\text{Al}_{0.8}\text{Nb}_{0.2}$, which is close to the Al_3Nb phase in the Nb–Al phase diagram [40]. As shown in Figs. 6e and 6f, the fraction of Nb–Al intermetallics is lower in TN10 than in TN25. The presence of Al-rich Nb–Al intermetallics in the Nb-containing ceramics indicates that the stabilization of the 413 and 211 MAX phases at the specific processing conditions becomes progressively more difficult as the Nb content increases. Al_2O_3 grains formed also in the Nb-containing ceramics, as shown in Figs. 5d, 5e, 5f, 6a, and 6b.

WDS elemental mapping was performed on metallographic cross-sections of the TH10 and TH25 grades as shown in Figs. 7 and 8, respectively. In agreement with XRD results, the main phases identified in TH10 were the 413 and 211 MAX phases (Fig. 7). The 413 phase appears brighter than the 211 phase, due to its lower Al and higher C contents. Within the 211 MAX phase regions, the growth of isolated, thin 413 laths (similar to TH10, see Fig. 5a) with lower relative Hf concentration was observed. In the TH25 grade (Fig. 8), a wide region of $(\text{Ta}_{1-x}, \text{Hf}_x)\text{C}_y$ pseudo-binary carbides was observed, as indicated by the complete absence of Al. Hf was non-uniformly dispersed in the $(\text{Ta}_{1-x}, \text{Hf}_x)\text{C}_y$ regions, in agreement with the fact that the TaC–HfC system has a miscibility gap [9].

Additionally, elemental mapping showed the prevalence of the 211 MAX phase, where the central area contained comparatively less Hf and more Ta than the rest of the phase. Point analysis in this area indicated the following composition: $(\text{Ta}_{0.86}, \text{Hf}_{0.14})_4\text{AlC}_3$. The distribution of Hf was not entirely homogeneous, as shown from the elemental analysis at select points. However, in both TH10 and TH25 grades, the Hf concentration averaged at the initially targeted x . Intermetallic phases, normally found between the MAX phase laths, could not be observed, in agreement with XRD. This is most likely due to the comparatively more favorable formation of Al_2O_3 from the excess Al. Al, Ta and Nb EDS elemental maps of an area in TN10 (Fig. 6a) are shown in Figs. 6b, 6c, and 6d, respectively.

STEM imaging was performed on FIB thin foils extracted from 413 and 211 MAX phase grains in both TH10 and TH25 grades. The 211 phase is shown in Fig. 9a for $x = 0.1$ and in Fig. 9b for $x = 0.25$, whereas the 413 phase is shown in Fig. 9c for $x = 0.1$, while a hybrid structure is shown in Fig. 9d for $x = 0.25$. All structures were observed along the $\langle 11\bar{2}0 \rangle$ zone axis. The contrast allows to clearly distinguish the single rows of dark Al atoms arranged along the single-atom-thick A-layers of the MAX phase lattice and between the bright layers of Ta and Hf atoms. As result of the increased average c parameter caused by the presence of Hf atoms in the M sub-lattice, the mismatch in interplanar spacing can be directly seen by comparing a small sequence of parallel A-layers at identical magnifications. This is shown in Figs. 9a and 9b for the 211 phase in the TH10 and TH25 grade, respectively.

Further proof of the solubility of Hf in the MAX phase lattice was provided by TEM/EDS elemental maps showing the distribution of solute elements in the MX sheets, as may be seen in Figs. 9e and 9f for $x = 0.1$ and 0.25, respectively. Fig. 9f shows an ABAB sequence of mixed 413 and 615 structures as well, similar to what was observed in Ta–Al–C MAX phases [11]. The maps show a superimposed EDS signal of homogeneously

mixed Ta and Hf within the MX sheets, indicating the uniform distribution of these two elements in the MX layers.

STEM images of 413 MAX phase atomic stacks in the TN10 and TN25 grades are shown in Figs. 9g and 9h, respectively. Similar to the TH25 grade, defects in the 413 structure were found in TN25 with occasional alternating 413–211 stacking sequences (Fig. 9h), however, the 413 MAX phase conserves a regular ABCD stacking. This points out the non-uniformity in the number of atomic layers introduced in the MX sheets by higher Nb concentrations. TEM/EDS elemental mapping revealed a homogeneous distribution of Ta and Nb in the MX sheets, alternated by Al layers, as shown in Figs. 9i and 9j for TN10 and TN25, respectively. Quite interestingly, TEM analysis did not reveal the presence of the β -413 polymorph.

3.4. Effects of Sn addition

The $(\text{Ta}_{0.75}\text{Hf}_{0.25})_4\text{AlC}_3$ starting composition, hot pressed at 1550°C, contained 63 wt% of the 211 MAX phase, 37 wt% of the $(\text{Ta}_{1-x}\text{Hf}_x)\text{C}_y$ pseudo-binary phase, and only a very small amount (below the XRD detection limit) of the 413 MAX phase (Fig. 1). In order to increase the amount of the 413 MAX phase, 50% of the Al content was substituted for Sn, in analogy with prior studies on the synthesis of phase-pure $(\text{Zr,Nb})_2(\text{Al,Sn})\text{C}$ [41] and $(\text{Zr,Ti})_2(\text{Al,Sn})\text{C}$ [20] MAX phase ceramics. In those studies, the enhanced stability of the 211 MAX phases over the competing binary phases (carbides, intermetallics) was associated with the trigonal prism distortion parameter and the relative size of the M and A atoms in the M_6A prism [42]. These studies demonstrated experimentally that highly phase-pure bulk MAX phase ceramics can be produced by forming solid solutions on both M and A sites [42]. Apart from giving a comprehensive review of the importance of steric effects in MAX phase lattice distortions, one of these studies demonstrated that a reduced prismatic distortion in the crystal lattice due to smaller differences in the M and A atomic sizes could ensure the synthesis of phase-pure $(\text{Zr}_{0.8}\text{Nb}_{0.2})_2(\text{Al}_{0.5}\text{Sn}_{0.5})\text{C}$ MAX phase ceramics [41].

In this work, the same approach was adopted to increase the fraction of the 413 phase in the ceramic with the least 413 amount, i.e., the TH25 grade. More precisely, Sn (atomic radius: 145 pm) [42] was replaced 50% of Al (atomic radius: 125 pm) [42] to compensate for the increase in average M atomic size caused by the partial replacement of Ta by Hf (atomic radii: 145 pm and 155 pm, respectively) [42]. The $(\text{Ta}_{0.75}\text{Hf}_{0.25})_4(\text{Al}_{0.5}\text{Sn}_{0.5})\text{C}_3$ MAX phase double solid solution (“THS25” grade), processed under exactly the same conditions as the TH25 grade, contained 62.8 wt% of the 413 phase as compared to the negligible 413 amount in the TH25 grade. The same approach was also applied on the TN25 grade, where a higher 413 MAX phase content was targeted by synthesising the $(\text{Ta}_{0.75}\text{Nb}_{0.25})_4(\text{Al}_{0.5}\text{Sn}_{0.5})\text{C}_3$ double solid solution (“TNS25” ceramic).

The obtained XRD patterns are shown in Fig. 10a for the Hf-containing ceramics and Fig. 10b for the Nb-containing ceramics. Table 1 summarizes the phase compositions of these ceramic grades as determined by Rietveld refinement. In the THS25 grade, no 211 MAX phase was observed as a result of the Sn addition, in contrast with the TH25 grade, where its formation was favored over that of the 413 phase. At $x = 25\%$, the addition of Sn as lattice distortion modifier reduced both lattice parameters of the 413 MAX phase to $a = 3.11(6)$ Å and $c = 24.10(1)$ Å, respectively; these values coincide with those of the Ta_4AlC_3 ternary compound [10], confirming the reduction in lattice distortion. Therefore, the Sn addition promoted the formation of the 413 MAX phase as intended; however, 39.2 wt% of the $(\text{Ta}_{1-x}\text{Hf}_x)\text{C}_y$ pseudo-binary carbide was still

present in the produced ceramic. It is also worthwhile mentioning that the Sn addition to the $(\text{Ta}_{0.75}, \text{Hf}_{0.25})_4\text{AlC}_3$ system stabilized only the 413 phase, while completely suppressing the formation of the 211 MAX phase.

In the TNS25 grade, $(\text{Ta}_{0.75}, \text{Nb}_{0.25})_4(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}_3$ and $(\text{Ta}_{0.75}, \text{Nb}_{0.25})_2(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}$ MAX phase double solid solutions formed, substantially increasing the overall MAX phase content as compared to the TN25 grade. Due to the coinciding atomic radii of Nb and Ta (145 pm) [42], the incorporation of Nb in the MAX phase crystal lattice did not produce a measurable lattice distortion. For this reason, the loss of stability of the 413 MAX phase at higher Nb concentrations in the quaternary phases should not be explained in terms of lattice distortion, but rather in terms of a reduction in the thermodynamic stability of the MAX phases as compared to that of the binary carbide and intermetallic phases. Even though no first-principle studies were done for these double solid solutions, the results suggest that adding Sn increases the stability of both 413 and 211 phases at the cost of the $(\text{Ta}_{1-x}, \text{Nb}_x)\text{C}_y$ pseudo-binary carbide, the content of which was substantially decreased from 45.1 wt% in the TN25 grade to 5.8 wt% in the TNS25 grade.

Figs. 11a and 11b show the microstructure of the THS25 and TNS25 double solid solution grade, respectively: MAX phase lamellae and equiaxed pseudo-binary carbide grains were observed, similar to the respective grades without Sn and those with lower M' solute concentrations. TNS25 also contained an intergranular Ta–Nb–Al–Sn intermetallic phase, the formation of which was confirmed by EDS. However, the formation of large Al–Nb intermetallic grains could not be observed, as in the case of the TN25 grade.

In order to further increase the purity of MAX phase ceramics in the Ta–Hf–Nb–Al–C system by the addition of a second solute element on the A site, a systematic study must be performed to define the optimum stoichiometry and corresponding lattice distortion parameters, as was previously done for Zr-based 211 MAX phase solid solutions [41].

4. Conclusions

$(\text{Ta}_{1-x}, \text{Hf}_x)_4\text{AlC}_3$, $(\text{Ta}_{1-x}, \text{Nb}_x)_4\text{AlC}_3$, $(\text{Ta}_{1-x}, \text{Hf}_x)_2\text{AlC}$ and $(\text{Ta}_{1-x}, \text{Nb}_x)_2\text{AlC}$ MAX phase solid solutions with $x = 0.05, 0.1, 0.15, 0.2$ and 0.25 were synthesized by reactive hot pressing of Ta_2H , HfH_2 , $\text{NbH}_{0.89}$, Al and C powder mixtures.

The stability of the 413 compound $(\text{Ta}_{1-x}, \text{Hf}_x)_4\text{AlC}_3$ decreased with increasing Hf content, due to the crystal lattice distortion by the introduction of the larger Hf atom, and in favor of the 211 compound $(\text{Ta}_{1-x}, \text{Hf}_x)_2\text{AlC}$ and $(\text{Ta}_{1-x}, \text{Hf}_x)\text{C}_y$ pseudo-binary carbides. The estimated solubility limit for Hf in the 413 and 211 MAX phases was around $x = 0.2$. The 413 phase content exceeded 80 wt% only in ceramic grades with low amounts of solute ($x = 0.05$).

The stability of the $(\text{Ta}_{1-x}, \text{Nb}_x)_4\text{AlC}_3$ and $(\text{Ta}_{1-x}, \text{Nb}_x)_2\text{AlC}$ MAX phases decreased with increasing Nb content, presumably due to the thermodynamically more stable $(\text{Ta}_{1-x}, \text{Nb}_x)\text{C}_y$ pseudo-binary carbides and Nb–Al intermetallics at higher Nb contents. Substitution of 50% of the Al on the A site for Sn increased the stability of the $(\text{Ta}_{0.75}, \text{Hf}_{0.25})_4(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}_3$ MAX phase in equilibrium with $(\text{Ta}, \text{Hf})\text{C}$ pseudo-binary carbides, whereas no $(\text{Ta}_{0.75}, \text{Hf}_{0.25})_2(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}$ MAX phase was observed. Substitution of 50% of the Al for Sn in the $(\text{Ta}_{0.75}, \text{Hf}_{0.25})_4\text{AlC}_3$ system increased the stability of both $(\text{Ta}_{0.75}, \text{Nb}_{0.25})_4(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}_3$ and $(\text{Ta}_{0.75}, \text{Nb}_{0.25})_2(\text{Al}_{0.5}, \text{Sn}_{0.5})\text{C}$ MAX phases, limiting the content of the $(\text{Ta}, \text{Nb})\text{C}$ pseudo-binary carbides to ~6 wt%.

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Fig. 1. XRD patterns of reaction hot pressed ceramics with (a) $(\text{Ta}_{1-x}\text{Hf}_x)_4\text{AlC}_3$, and (b) $(\text{Ta}_{1-x}\text{Nb}_x)_4\text{AlC}_3$ starting powder compositions, for different x contents of Hf and Nb.

Fig. 2. (a) Relative abundance of the 413 and 211 MAX phases, and the $(\text{Ta}_{1-x}\text{M}'_x)\text{C}_y$ pseudo-binary carbides as function of x , in the produced $(\text{Ta}_{1-x}\text{Hf}_x)_4\text{AlC}_3$ and (b) $(\text{Ta}_{1-x}\text{Nb}_x)_4\text{AlC}_3$ ceramics.

Fig. 3. Calculated formation enthalpy, ΔH , at 0 K and Gibbs free energy of formation, ΔG , at 1873 K as function of x for (a) $(\text{Ta}_{1-x}\text{Hf}_x)_4\text{AlC}_3$, $(\text{Ta}_{1-x}\text{Hf}_x)_2\text{AlC}$, and $(\text{Ta}_{1-x}\text{Hf}_x)\text{C}$ phases, and (b) $(\text{Ta}_{1-x}\text{Nb}_x)_4\text{AlC}_3$, $(\text{Ta}_{1-x}\text{Nb}_x)_2\text{AlC}$, and $(\text{Ta}_{1-x}\text{Nb}_x)\text{C}$ phases.

Fig. 4. Measured and calculated lattice parameters a and c for the (a) $(\text{Ta}_{1-x}\text{Hf}_x)_4\text{AlC}_3$ and (b) $(\text{Ta}_{1-x}\text{Hf}_x)_2\text{AlC}$ MAX phase solid solutions.

Fig. 5. BSE images of the microstructure of (a) TH10, (b) TH25, (d) TN10 and (e) TN25; the latter two include several EDS point analyses. Fracture surfaces of (c) TH25 and (f) TN25; the latter shows the presence of Nb–Al intermetallics.

Fig. 6. (a) BSE image of the TN10 grade microstructure, showing a MAX phase region enveloping Nb-rich Nb-Al intermetallics. (b-d) EDS maps of Al, Ta, and Nb. BSE images of the relative abundance of Nb-Al intermetallics (dark spots) in TN10 (e) and TN25 (f).

Fig. 7. WDS elemental mapping of grade TH10. The distribution of Al, C, Hf and Ta is shown along with secondary electron (SE) and BSE images of the area of interest. The composition is quantified at given points (circles), Ta and Hf are given as at% of the M element.

Fig. 8. WDS elemental mapping of grade TH25. The distribution of Al, C, Hf and Ta is shown along with SE and BSE images of the area of interest. The composition is quantified at given points (circles), Ta and Hf are given as at% of the M element.

Fig. 9. STEM images of 211 atomic stacks in the (a) TH10 (a) and (b) TH25 grades; (c) 413 atomic stacks in the TH10 grade; and (d) 2nAB+Al stacks in the TH25 grade. The location of the darker Al planes is shown by red lines. TEM/EDS maps of Al, Ta and Hf in select areas of interest in the (e) TH10 and (f) TH25 grades. STEM images of (g) a 413 atomic stack in the TN10 grade, and (h) a mixed 413–211 stacking in the TN25 grade. TEM/EDS maps of Al, Ta and Nb in 413 areas in the (i) TN10 and (j) TN25 grades.

Fig. 10. XRD patterns of (a) the TH25 and THS25 grades, and (b) the TN25 and TNS25 grades.

Fig. 11. SEM images of the microstructure of the (a) THS25 and (b) TNS25 grades.

Table 1. Phase assembly of the THS25, TH25, TNS25, and TN25 grades, where M' is Hf or Nb.

Grade	THS25	TH25	TNS25	TN25
413 (wt%)	62.8	0.0	74.6	48.6
211 (wt%)	0.0	62.5	19.6	6.3
(Ta,M')C (wt%)	39.2	39.5	5.8	45.1