Synthesis of the new MAX phase Zr₂AlC

T. Lapauw, K. Lambrinou, T. Cabioch, Joseph Halim, Jun Lu, A. Pesach, O. Rivin, O. Ozeri, E. N. Caspi, Lars Hultman, Per Eklund, Johanna Rosén, Michel Barsoum and J. Vleugels

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

T. Lapauw, K. Lambrinou, T. Cabioch, Joseph Halim, Jun Lu, A. Pesach, O. Rivin, O. Ozeri, E. N. Caspi, Lars Hultman, Per Eklund, Johanna Rosén, Michel Barsoum and J. Vleugels, Synthesis of the new MAX phase Zr₂AlC, 2016, Journal of the European Ceramic Society, (36), 8, 1847-1853.

<http://dx.doi.org/10.1016/j.jeurceramsoc.2016.02.044>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-127738>

Title

Synthesis of the new MAX phase Zr_2AlC

T. Lapauw^{a,b,*}, K. Lambrinou^b, T. Cabioc'h^c, J. Halim^{d,e}, J. Lu^d, A. Pesach^f, O. Rivin^f, O. Ozeri^g,
E. N. Caspi^f, L. Hultman^d, P. Eklund^d, J. Rosén^d, M. W. Barsoum^{d,e} and J. Vleugels^a

^a KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium

^b SCK•CEN, Boeretang 200, B-2400 Mol, Belgium

^c Institut PPRIME, Département de Physique et Mécanique des Matériaux, CNRS, Université de Poitiers, ENSMA UPR 3346, SP2MI, Téléport 2, Boulevard Marie et Pierre Curie, BP30179 86962 Futuroscope Chasseneuil Cedex, France

^d Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

^e Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, USA

^f Nuclear Research Centre-Negev, P.O. Box 9001, 84190 Beer-Sheva, Israel

^g Reactor Department, Nuclear Research Center – Soreq, Yvne 81800, Israel

* Corresponding author. Address: KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium. Tel.: + 32 16 37 36 05; fax: + 32 16 32 19 90

E-mail address: thomas.lapauw@mtm.kuleuven.be (T. Lapauw)

Keywords

MAX phase ceramics; Diffraction analysis; Reactive hot pressing;

Abstract

This study reports on the first experimental evidence of the existence of the Zr_2AlC MAX phase, synthesised by means of reactive hot pressing of a ZrH_2 , Al and C powder mixture. The crystal structure of this compound was investigated by X-ray and neutron diffraction. The lattice parameters were determined and confirmed by high-resolution transmission electron microscopy. The effect of varying the synthesis temperature was investigated, indicating a relatively narrow temperature window

for the synthesis of Zr_2AlC . ZrC was always present as a secondary phase by hot pressing in the 1475-1575°C range.

Introduction

Layered ternary carbides with a M_2AC stoichiometry, where M is a transition metal and A is a metatmetal, were discovered in the 1960's. These phases, at the time called H-phases, had a Cr_2AlC -type crystal structure with an ordered close-packed hexagonal lattice [1, 2]. Later on, due to the synthesis and characterization of Ti_4AlN_3 [3] and the existence of a number of 312 phases, the family expanded and became known as the $\text{M}_{n+1}\text{AX}_n$ (MAX) phases with M an early transition metal, A an A-group element (mainly groups 13-16 in the periodic table), X corresponding to C or N, and n an integer, commonly equal to 1, 2 or 3 [4-6]. The respective stoichiometries are commonly referred to as 211, 312, and 413-type MAX phases. The regained interest in these thermodynamically stable layered carbides and nitrides in the late 1990s and early 2000s [6], and the fact that they form an established research field today [7-10], can be attributed to the fact that some of them have attractive properties combining the merits of metals and ceramics, i.e., good mechanical properties (flexural strength, fracture toughness), stability at elevated temperatures, high thermal and electrical conductivity, and remarkable machinability. Most of these properties result from their characteristic nanolaminated crystal structure, where the A-planes act as metallic atomic layers between the MX ceramic layers [7].

New MAX phases are still being discovered. The n-value is not limited to 3 and can take higher values of 4 or 5 [11, 12]. Hu *et al.* recently provided a partial list of the new MAX phases discovered in the period 2004-2013 [13], bringing the total count to well above 70. Other important additions are the new 211 phases Nb_2GeC [14] and Mn_2GaC [15]. There is also plenty of work on solid solutions where existing phases are mixed, as reported in a recent overview by Naguib *et al.* [16]. In some cases, this yields new phases (where neither end member exists) [11, 17] and/or ordered quaternary phases [18-21]. Furthermore, the recently synthesised $\text{Mo}_2\text{Ga}_2\text{C}$ (with double "A" layers) "may be the first of a distinct family of MAX-related phases" [22]. More recently, we reported on the synthesis of Zr_3AlC_2 , the first experimentally-produced MAX phase in the Zr-Al-C system [23].

Zr-based materials are of great interest for the nuclear industry because Zr atoms have a small cross-section for thermal neutrons. Apart from this economical argument, the fuel cladding materials of next generation (Gen-III+) light water reactors (LWRs) must withstand severe operating conditions where mechanical and thermal loads are combined with high neutron irradiation doses and strongly oxidative or corrosive environments [24]. Based on their superior properties, MAX phases are considered as candidate materials for fuel cladding applications, either in bulk form or as coatings.

Zr-based MAX phases have been reported mainly in the 211-stoichiometry with In, Pb, S, Sn or Tl as A element [2, 6, 25-28]. In the Zr-Al-C system, a series of hexagonal phases have been reported based

on the chemical formula $(\text{ZrC})_n\text{Al}_3\text{C}_2$ or $(\text{ZrC})_n\text{Al}_4\text{C}_3$ (where $n = 1, 2, 3 \dots$). These phases show crystallographic similarities with the typical MAX phases but have a higher hardness that makes them less machinable by means of conventional tools [29-32]. Similar to the chemically-related Ti-Al-C system, where both Ti_3AlC_2 and Ti_2AlC phases exist, Zr_2AlC is predicted. Although this phase has not been previously synthesized experimentally, the structure of Zr_2AlC was proposed by Reiffenstein *et al.* in 1966 [33] and more recently predicted by *ab initio* calculations [34-36].

Regarding solid solutions related to Zr_2AlC , the partial substitution of Nb with Zr, resulting in $(\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}$, has been experimentally reported as well as some systematic studies by Horlait *et al.* [16, 37, 38]. Considering theoretical predictions, Shang *et al.* calculated the energy of mixing for $(\text{Cr}_{1-x}, \text{Zr}_x)_2\text{AlC}$ with varying x . $(\text{Cr}_{0.5}, \text{Zr}_{0.5})_2\text{AlC}$ was found to be metastable, whereas solid solutions with x equal to 0.25 and 0.75 were predicted to be unstable [36].

Considering the oxidation resistance, Tallman *et al.* reviewed the behaviour of Ti_2AlC , Ti_3AlC_2 , and Cr_2AlC in air. One of the conclusions is that the 211-stoichiometry exhibits a better resistance against oxidation due to its higher Al-content that enables the formation of a protective Al_2O_3 oxide layer [39]. Due to the volume expansion related with the oxidation, Al_2O_3 is able to ‘heal’ cracks and recover the strength of the material [40, 41]. This self-healing of Cr_2AlC could be improved by adding 0.2 at% Y metal [42]. A theoretical study on the self-healing capacity of MAX phases suggested that Zr_2AlC could fulfil the requirements for crack healing by high-temperature selective oxidation [43]. Furthermore, apart from Al_2O_3 , ZrO_2 can form as an oxidation product, where the presence of Al can help to further improve the hydrothermal stability of the ZrO_2 scale [44]. For the high-temperature steam environment in Gen-III+ LWRs during a loss of coolant (LOCA) accident, Zr_2AlC is one of the MAX phases of interest that could potentially surpass the performance of the commercial zircaloy clads. In this study, the experimental synthesis of Zr_2AlC is reported for the first time.

Experimental procedure

ZrH_2 (grain size $< 6 \mu\text{m}$, $> 99\%$ purity, Chemetall, Germany), Al ($< 5 \mu\text{m}$, $> 99\%$ purity, AEE, US) and C ($< 5 \mu\text{m}$, $> 99\%$ purity, Asbury Graphite Mills, US) powders were used as starting materials for the synthesis of the MAX phases. The powders were mixed in a Zr:Al:C molar ratio of 50:20:30 (corresponding to a 2:0.8:1.2 stoichiometry) in a Turbula multidirectional mixer. The original intent was to synthesize Zr_3AlC_2 , with this starting stoichiometry (equivalent to 3:1.2:1.8). ZrO_2 (Tosoh 3Y-TZP, 5 mm Ø) milling balls and isopropanol were added in order to homogenize the mixing and break-up soft agglomerates. After drying, the powder mixture was poured into a 30 mm inner-diameter graphite die and cold-compacted at 20 MPa. Subsequently, the die/punch/powder set-up was hot pressed (W100/150-2200-50 LAX, FCT Systeme, Frankenblick, Germany) in a vacuum environment at a heating rate of $25^\circ\text{C}/\text{min}$ up to 1475, 1525 or 1575°C . Once the processing temperature was

reached, the samples were held at temperature for 0.5 h. The initially-applied load of 7 MPa was increased to 20 MPa upon reaching the dwell temperature.

The outer 1 mm-thick layer was ground off from the hot pressed disc prior to mechanical polishing for X-ray diffraction (XRD) characterization and microstructural analysis. XRD data were obtained from the polished top and cross-sectional surfaces using Cu K_α radiation in a Bruker D8 advance diffractometer operated at 40 kV and 40 mA in the Bragg-Brentano geometry with a divergence slit of 0.4° . For room temperature characterization, 2θ step intervals of 0.005° were applied from 8 to 158° with a counting time of 3 s per step. The lattice parameters of the top and cross-section of the disk-shaped sample were determined. No statistically-significant difference between those two surfaces was found and the reported value is the average of both. Rietveld refinements of the diffraction patterns were performed using the Materials Analysis Using Diffraction (MAUD) software [45].

Electron probe microanalysis (EPMA, JXA-8530F, JEOL Ltd., Japan) was used for microstructural and chemical analysis. The Zr:Al ratio in the MAX phase grains was determined by quantitative energy dispersive X-ray spectrometry (EDS, EDAX, US). Furthermore, the elemental distribution of Zr, Al, and C in the sintered ceramics was mapped. The beam current and accelerating voltage were fixed at 15 nA and 15 kV.

High-resolution transmission electron microscopy (HRTEM), EDS and selected area diffraction (SAED) were performed using a FEI Tecnai G2 TF20 UT equipped with a field emission gun operating at 200 kV with a point resolution of 0.19 nm. The TEM sample was prepared by embedding manually crushed powder obtained from the hot pressed samples in a Ti grid with a carbon-based glue. The sample was then mechanically polished down to 50 μm followed by ion milling to reach electron transparency.

Neutron powder diffraction (NPD) experiments were done on the KARL double axis diffractometer [46], mounted on the Israeli Research Reactor 1. The measurements were performed at room temperature (RT) with an incident neutron wavelength of $0.982(2)$ Å. This low incident wavelength, combined with an angular step of 0.05° , generated sufficient angular range and angular resolution for this structural study. A powder sample of ~ 5 g, taken from the sample hot pressed at 1525°C , was loaded into a cylindrical vanadium sample holder, which was used to significantly reduce coherent scattering from the holder. The results were analysed using the Rietveld refinement method with the FullProf software package [47].

X-ray photoelectron spectroscopy (XPS) employing monochromatic Al K_α radiation ($h\nu = 1486.6$ eV) was used to determine compositions in the surface region of a powder sample. Prior to the analysis, samples were sputter-cleaned *in-situ* with 4 keV Ar^+ ions incident at an angle of 70° with respect to the surface normal for 10 minutes. Sputtering was performed until a steady-state (i.e., minimizing

surface oxygen contaminations in the powder) was observed for the core levels. Deconvolution and quantification was performed using the CasaXPS software with elemental sensitivity factors supplied by Kratos Analytical Ltd.

The hardness was measured using a Vickers indenter (FV-700, Future-Tech Corp., Tokyo, Japan) and an indentation load of 30 N was applied for 10 s on a polished surface. The reported value is the average of 5 indents.

Results and discussion

The XRD patterns of the top surface of the samples that were reaction hot pressed in the 1475-1575°C range with a Zr:Al:C starting powder molar ratio of 50:20:30 are compared in Figure 1. At 1475°C, the main compound was the binary carbide ZrC_x . The stoichiometry of the binary carbide can vary between $ZrC_{0.99}$ and $ZrC_{0.55}$ [48]. Additionally, Zr_2AlC was detected as a secondary phase together with the intermetallic Zr_2Al_3 . When the synthesis temperature increased to 1525°C, the amount of Zr_2AlC increased significantly, the intermetallic phase disappeared and the ZrC_x content decreased. Based on this observation, the following formation reaction may be proposed:

Figure 2 shows the refined XRD pattern of the sample synthesized at 1525°C. The quantified phase analysis indicates 67 wt% Zr_2AlC and 33 wt% ZrC_x , corresponding to 48.9 mol% Zr_2AlC and 51.1 mol% ZrC_x . This phase assembly is expected since, as noted above, the starting powder was mixed in a near '312' stoichiometry. The reason why an off-stoichiometric composition of the starting powder results in the formation of Zr_2AlC is unclear at this time. A further increase in synthesis temperature up to 1575°C resulted in formation of Zr_3AlC_2 according to:

Based on the initial composition, pure Zr_3AlC_2 should have been ideally obtained after reaction (2). However, ZrC_x was present at all investigated temperatures and the intermetallic Zr_2Al compound appeared at 1575°C, which is an indication for a competing decomposition of the Zr_3AlC_2 phase:

The existence of two phases in the sample processed at 1525°C is further supported by microstructural analysis and elemental maps shown in Figure 3. The microstructure shows a homogeneous distribution of the Zr_2AlC and ZrC phases. The Zr:Al:C atomic ratios of the sample synthesized at 1525°C was 52.1 : 23.1 : 24.8, as measured by XPS. This result is consistent with the presence of the Zr_2AlC phase in the XRD patterns and indirectly confirms its 211 chemistry.

Rietveld refinement was performed on the XRD pattern in Figure 2. The obtained a and c lattice parameters are summarised in Table 1 together with the z -coordinate of the Zr atoms z_{Zr} . The values predicted in literature are listed for comparison. The experimental data are in good agreement with most of the predicted values [35, 36]. The largest difference is observed with the results of Yakoubi *et al.* Their exchange-correlation potentials were determined by the Perdew-Wang implementation of the local density approximation (LDA) [34]. This approximation generally overestimates the bond strengths and thus underestimates the lattice parameters [49, 50]. There is a good correspondence with the values given by Reiffenstein *et al.* for what was referred to as “der Fiktiven H-Phase “Zr₂AlC”...” (i.e., “the fictive H-phase “Zr₂AlC”...”) [33].

Table 1. Comparison of experimentally-measured and predicted (literature) lattice parameters and z_{Zr} values for Zr₂AlC.

Zr ₂ AlC	a (Å)	c (Å)	z_{Zr}
Experimental XRD	3.3237(2)	14.5705(4)	0.0871(1)
Experimental SAED	3.3	14.6	/
Experimental NPD	3.3239(4)	14.556(2)	0.0898(7)
Calculated [33]	3.25	14.5	/
Calculated [34]	3.2104	14.2460	0.0869
Calculated [35]	3.3174	14.6304	0.0861
Calculated [36]	3.334	14.600	/

The layered atomic stacking in the Zr₂AlC phase was confirmed by HRTEM, as shown in Figure 4, presenting the structure with the beam aligned along the $[11\bar{2}0]$ zone axis and the corresponding SAED pattern. The derived lattice parameters – listed in Table 1 – are in line with the values obtained by XRD.

The full-profile Rietveld analysis of a sample hot pressed at 1525°C (Figure 5, line) of the NPD data (Figure 5, symbols) was carried out assuming a $P6_3/mmc$ space group for the major phase, Zr₂AlC, with the Zr, Al, and C atoms occupying the ‘4f’, ‘2c’ and ‘2a’ sites, respectively. The refined lattice parameters and the z_{Zr} atomic position of the Zr atom are listed in Table 1 and are in good agreement with the XRD results. As an example, the c lattice parameter obtained by NPD differs by less than 0.1% from the one obtained by XRD. The refined weight percent of this phase is 65(3) wt%, again in excellent agreement with the XRD results. The presence of a large amount (30(1) wt%) of ZrC was also deduced. The refined cell parameters of the cubic ZrC phase (4.6796(3) Å) deviates by ~0.2% from previous reports (see, e.g. [51]). Due to the large coherent scattering length of thermal neutrons

by C, neutron diffraction is readily used for C occupancy determination. Refinement of this parameter in both Zr_2AlC and ZrC phases resulted in full C occupancy in both compounds. A small amount (~5 wt%) of Zr_3AlC_{2-x} was identified as a third phase. This phase was not detected by XRD and might be the consequence of the early stage of the transition from '211' to '312' according to reaction (2).

Based on the experimental XRD data, a list of calculated d-spacings, 2θ angles and relative intensities is generated using generated using Powder Cell (see Table 2). The experimentally-obtained 2θ angles are included for a comparison.

Table 2. The d-spacings, corresponding 2θ angles and relative intensities of the (hkl) reflections starting with the lattice parameters obtained by the XRD Rietveld refinement listed in Table 1, together with the observed 2θ angles and relative intensities. The (008) peak was not observed due to its low intensity (*). The (202) and (109) peak were hidden by the ZrC_x (311) diffraction peak (**).

h k l	d (Å)	2θ (°) Calculated	I/I_{max} (%) Calculated	2θ (°) Observed
0 0 2	7.2851	12.14	34.32	12.17
0 0 4	3.6426	24.42	3.34	24.44
1 0 0	2.8783	31.04	20.40	31.07
1 0 1	2.8237	31.66	15.36	31.68
1 0 2	2.6769	33.45	1.20	33.46
1 0 3	2.4761	36.25	100.00	36.28
0 0 6	2.4284	36.99	18.74	37.02
1 0 4	2.2583	39.89	5.73	39.90
1 0 5	2.0478	44.19	2.70	44.20
1 0 6	1.8560	49.04	16.18	49.06
0 0 8	1.8213	50.04	0.12	*
1 0 7	1.6867	54.35	5.63	54.38
1 1 0	1.6618	55.23	21.04	55.26
1 1 2	1.6202	56.77	3.51	56.79
1 0 8	1.5391	60.06	0.42	60.07
1 1 4	1.5119	61.26	3.29	61.28
0 0 10	1.4570	63.83	1.09	63.85
2 0 0	1.4392	64.72	2.55	64.73
2 0 1	1.4322	65.07	1.90	65.08
2 0 2	1.4119	66.13	0.22	**
1 0 9	1.4110	66.17	16.09	**
2 0 3	1.3798	67.87	15.46	67.89
1 1 6	1.3714	68.34	18.46	68.37
2 0 4	1.3385	70.27	0.96	70.30
1 0 10	1.3000	72.67	0.69	72.71
2 0 5	1.2904	73.30	0.6	73.27

The Vickers hardness of the Zr_2AlC - ZrC composite material produced by hot pressing at 1525°C, was measured to be 6.4 ± 0.1 GPa under a load of 30 N. This value is rather low considering the high

hardness of ZrC and indirectly confirms the deformability and machinability of this MAX-phase material. A secondary electron (SE) image of an indent is shown in Figure 6. As with most MAX phases, no cracks were found to originate from the corners of the Vickers indent, despite the high load. The typical block-shaped cross-section of the laminated MAX phase grains is visible in the area around the indent.

Two MAX phases have been discovered in the Zr-Al-C system. The recent report on Zr_3AlC_2 [23] together with the present study on Zr_2AlC reveals the existence of a ‘211’ and ‘312’ type in this system. The similarity with the Ti-Al-C MAX phase system is conspicuous, especially taking into account that Ti is chemically related to Zr as they belong to the same group in the periodic table. Comparing the synthesis routes of Ti_2AlC and Zr_2AlC , a similarity between the antecedent intermetallic phases is observed. Starting from elemental powders, TiAl and Ti_3Al are the intermetallic phases that have been reported during the synthesis of Ti_2AlC [52]. Ti_3Al is only stable up to $\sim 1150^\circ\text{C}$ according to the Ti-Al phase diagram, [48] while the synthesis of Ti_2AlC during pressure-assisted sintering takes place around $1300\text{--}1400^\circ\text{C}$ [53–56]. In this temperature range, TiAl is the only stable intermetallic phase. The suggested in [56] formation reaction is:

Considering the stoichiometry window in which the TiAl phase can exist, this reaction is similar to reaction (2). No quantitative results on the Ti:Al ratio of the MAX phase forming intermetallic have been found in literature, but a Ti:Al ratio of 2:3 is possible around the synthesis temperature. The stoichiometry of the Zr-Al intermetallics, however, is not a solid solution range but fixed [48]. This rigidity in chemical composition combined with the narrow synthesis temperature window might explain why Zr_2AlC had not been synthesised before. Moreover, the fact that the initial chemical composition of the starting powder results in the MAX phases discovered is counterintuitive. In general, a larger Al-content and a smaller C-content than those indicated by the chemical formula, help to improve the phase purity of M-Al-C compounds, as for example done for the synthesis of Nb_4AlC_3 [57]. In the case of Zr-Al-C, lower amounts of Al and a higher amounts of C resulted in the first synthesis of Zr_3AlC_2 [23] and Zr_2AlC . Said otherwise, to synthesize the Zr_2AlC phase we started with a 5:2:3 chemistry and to synthesize the 312 phase we started with a 4:1.25:2.6 chemistry [23]. No clear reason for this behaviour was found, as the XPS results indicate an excellent agreement with the stoichiometric ratio of the elements and the C-occupancy determined by NPD was found to be close to 1. A possible explanation of this trend is that the initial chemistry determines the reaction paths. In particular the formation of ZrC is a competing reaction, which should be compensated for in the starting powder composition. Several reaction steps might occur before reaction (1) takes place. These steps can be influenced by the dehydrogenation reaction, as well as by the initial C and Al contents. In

order to verify this explanation, a more in-depth investigation combining experimental evidence with a first-principle study is required and is currently ongoing.

Conclusions

The Zr_2AlC MAX phase was synthesized for the first time by the reactive hot pressing of a ZrH_2 , C, and Al starting powder mixture with a Zr:Al:C molar ratio of 50:20:30. The optimal synthesis temperature was found to be 1525°C . Experimental investigation revealed that ZrC is always present as secondary phase. At lower temperatures, Zr_2Al_3 is identified as the Zr_2AlC -forming intermetallic. Between 1525 and 1575°C , there is a transition towards the Zr_3AlC_2 phase, which appears to decompose into ZrAl_2 and ZrC starting at around 1575°C . The Zr_2AlC atomic structure was investigated by HRTEM, clearly revealing the 211-type atomic stacking. The a and c lattice parameters determined by X-ray and neutron diffraction (XRD/NPD) are $3.3237(2) \text{ \AA}$ / $3.3239(4) \text{ \AA}$ and $14.5705(4) \text{ \AA}$ / $14.556(2) \text{ \AA}$, respectively. The Vickers hardness of the Zr_2AlC ceramic with 28 vol% ZrC, measured under a load of 30 N, was $6.4 \pm 0.1 \text{ GPa}$. It is worthwhile mentioning that two new phases (i.e., Zr_2AlC and Zr_3AlC_2) could be identified in a rather well-known system as Zr-Al-C. These discoveries can be taken as an example to reconsider other established systems and start with a regained interest in search of new promising MAX phases.

Acknowledgements

The research leading to these results is partly funded by a PhD grant No. 131081 of the Agency for Innovation by Science and Technology (IWT), Flanders, Belgium, partly by the European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement No. 604862 (MatISSE project) and falls within the framework of the EERA (European Energy Research Alliance) Joint Programme on Nuclear Materials (JPNM). The authors thank the Hercules Foundation under project ZW09-09. LH, JL, and MWB also acknowledge the Swedish Research Council and the Swedish Government Strategic Research Area Grant in Materials Science (MAT-LiU). We also acknowledge the Swedish Foundation for Strategic Research for support through the Synergy Grant FUNCASE (JR, MWB, PE) and the Future Research Leaders 5 program (PE, JL). ENC, AP, OR, and OO thank Hanania Ettegui for his assistance in the NPD measurements. Grzegorz Greczynski is acknowledged for the XPS measurements.

References

- [1] W. Jeitschko, H. Nowotny, and F. Benesovsky, "Kohlenstoffhaltige ternäre Phasen (H-Phase)," *Monatshefte für Chemie*, vol. 94, pp. 672 - 676, 1963
- [2] W. Jeitschko, H. Nowotny, and F. Benesovsky, "Carbides of formula T_2MC ," *Journal of the Less Common Metals*, vol. 7, pp. 133-138, 1964.

- [3] M. W. Barsoum, T. El-Raghy, and A. Procopio, "Characterization of Ti_4AlN_3 ," *Metallurgical and Materials Transactions A*, vol. 31, pp. 333-337, 2000.
- [4] M. W. Barsoum and T. El-Raghy, "Synthesis and Characterization of a Remarkable Ceramic: Ti_3SiC_2 ," *Journal of the American Ceramic Society*, vol. 79, pp. 1953-1956, 1996.
- [5] M. W. Barsoum and T. El-Raghy, "The MAX phases: Unique new carbide and nitride materials - Ternary ceramics turn out to be surprisingly soft and machinable, yet also heat-tolerant, strong and lightweight," *American Scientist*, vol. 89, pp. 334-343, 2001.
- [6] M. W. Barsoum, "The $\text{M}_{n+1}\text{AX}_n$ phases: A new class of solids: Thermodynamically stable nanolaminates," *Progress in Solid State Chemistry*, vol. 28, pp. 201-281, 2000.
- [7] M. W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*: Wiley-VCH Verlag GmbH & Co., 2013.
- [8] P. Eklund, M. Beckers, U. Jansson, H. Högborg, and L. Hultman, "The $\text{M}_{n+1}\text{AX}_n$ phases: Materials science and thin-film processing," *Thin Solid Films*, vol. 518, pp. 1851-1878, 2010.
- [9] J. Wang and Y. Zhou, "Recent Progress in Theoretical Prediction, Preparation, and Characterization of Layered Ternary Transition-Metal Carbides," *Annual Review of Materials Research*, vol. 39, pp. 415-443, 2009.
- [10] Z. M. Sun, "Progress in research and development on MAX phases: a family of layered ternary compounds," *International Materials Reviews*, vol. 56, pp. 143-166, 2011.
- [11] L. Zheng, J. Wang, X. Lu, F. Li, J. Wang, and Y. Zhou, " $(\text{Ti}_{0.5}\text{Nb}_{0.5})_5\text{AlC}_4$: A New-Layered Compound Belonging to MAX Phases," *Journal of the American Ceramic Society*, vol. 93, pp. 3068-3071, 2010.
- [12] Z. Lin, M. Zhuo, Y. Zhou, M. Li, and J. Wang, "Microstructures and Theoretical Bulk Modulus of Layered Ternary Tantalum Aluminum Carbides," *Journal of the American Ceramic Society*, vol. 89, pp. 3765-3769, 2006.
- [13] C. Hu, H. Zhang, F. Li, Q. Huang, and Y. Bao, "New phases' discovery in MAX family," *International Journal of Refractory Metals and Hard Materials*, vol. 36, pp. 300-312, 2013.
- [14] P. Eklund, M. Dahlqvist, O. Tengstrand, L. Hultman, J. Lu, N. Nedfors, U. Jansson, and J. Rosén, "Discovery of the Ternary Nanolaminated Compound Nb_2GeC by a Systematic Theoretical-Experimental Approach," *Physical Review Letters*, vol. 109, pp. 035502, 2012.
- [15] A. S. Ingason, A. Petruhins, M. Dahlqvist, F. Magnus, A. Mockute, B. Alling, L. Hultman, I. A. Abrikosov, P. O. Å. Persson, and J. Rosen, "A Nanolaminated Magnetic Phase: Mn_2GaC ," *Materials Research Letters*, vol. 2, pp. 89-93, 2014.
- [16] M. Naguib, G. W. Bentzel, J. Shah, J. Halim, E. N. Caspi, J. Lu, L. Hultman, and M. W. Barsoum, "New Solid Solution MAX Phases: $(\text{Ti}_{0.5}, \text{V}_{0.5})_3\text{AlC}_2$, $(\text{Nb}_{0.5}, \text{V}_{0.5})_2\text{AlC}$, $(\text{Nb}_{0.5}, \text{V}_{0.5})_4\text{AlC}_3$ and $(\text{Nb}_{0.8}, \text{Zr}_{0.2})_2\text{AlC}$," *Materials Research Letters*, vol. 2, pp. 233-240, 2014.
- [17] Y. Zhou, F. Meng, and J. Zhang, "New MAX-Phase Compounds in the V-Cr-Al-C System," *Journal of the American Ceramic Society*, vol. 91, pp. 1357-1360, 2008.
- [18] B. Anasori, J. Halim, J. Lu, C. A. Voigt, L. Hultman, and M. W. Barsoum, " $\text{Mo}_2\text{TiAlC}_2$: A new ordered layered ternary carbide," *Scripta Materialia*, vol. 101, pp. 5-7, 2015.
- [19] E. N. Caspi, P. Chartier, F. Porcher, F. Damay, and T. Cabioc'h, "Ordering of (Cr,V) Layers in Nanolamellar $(\text{Cr}_{0.5}\text{V}_{0.5})_{n+1}\text{AlC}_n$ Compounds," *Materials Research Letters*, vol. 3, pp. 100-106, 2015.
- [20] Z. Liu, E. Wu, J. Wang, Y. Qian, H. Xiang, X. Li, Q. Jin, G. Sun, X. Chen, J. Wang, and M. Li, "Crystal structure and formation mechanism of $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ MAX phase," *Acta Materialia*, vol. 73, pp. 186-193, 2014.
- [21] B. Anasori, M. Dahlqvist, J. Halim, E. J. Moon, J. Lu, B. C. Hosler, E. Caspi, a. N., S. J. May, L. Hultman, P. Eklund, J. Rosén, and M. W. Barsoum, "Experimental and theoretical characterization of ordered MAX phases $\text{Mo}_2\text{TiAlC}_2$ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$," *Journal of Applied Physics*, vol. 118, pp. 094304, 2015.
- [22] C. Hu, C. C. Lai, Q. Tao, J. Lu, J. Halim, L. Sun, J. Zhang, J. Yang, B. Anasori, J. Wang, Y. Sakka, L. Hultman, P. Eklund, J. Rosen, and M. W. Barsoum, " $\text{Mo}_2\text{Ga}_2\text{C}$: a new ternary nanolaminated carbide," *Chemical Communications*, vol. 51, pp. 6560-6563, 2015.

- [23] T. Lapauw, J. Halim, J. Lu, T. Cabioch, L. Hultman, M. W. Barsoum, K. Lambrinou, and J. Vleugels, "Synthesis of the novel Zr_3AlC_2 MAX phase," *Journal of the European Ceramic Society*, vol. 36, pp. 943-947, 2016.
- [24] E. N. Hoffman, D. W. Vinson, R. L. Sindelar, D. J. Tallman, G. Kohse, and M. W. Barsoum, "MAX phase carbides and nitrides: Properties for future nuclear power plant in-core applications and neutron transmutation analysis," *Nuclear Engineering and Design*, vol. 244, pp. 17-24, 2012.
- [25] W. Jeitschko, H. Nowotny, and F. Benesovsky, "Die H-Phasen: Ti_2CdC , Ti_2GaC , Ti_2GaN , Ti_2InN , Zr_2InN und Nb_2GaC ," *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*, vol. 95, pp. 178-179, 1964.
- [26] H. Kudielka and H. Rohde, "Strukturuntersuchungen an Carbosulfiden von Titan und Zirkon," *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, vol. 114, pp. 144, 1960.
- [27] E. Hoffman, M. W. Barsoum, W. Wang, R. D. Doherty, and A. Zavaliangos, "On the Spontaneous Growth of Soft Metallic Whiskers " *Holm Conf. Proceedings (IEEE), Chicago, IL*, pp. 121-126, 2005.
- [28] T. El-Raghy, S. Chakraborty, and M. W. Barsoum, "Synthesis and characterization of Hf_2PbC , Zr_2PbC and M_2SnC ($\text{M}=\text{Ti}$, Hf , Nb or Zr)," *Journal of the European Ceramic Society*, vol. 20, pp. 2619-2625, 2000.
- [29] J. C. Schuster and H. Nowotny, "Investigations of the ternary systems (Zr , Hf , Nb , Ta)-Al-C and studies on complex carbides," *Zeitschrift fuer Metallkunde*, vol. 71, pp. 341-346, 1980.
- [30] P. Villars, K. Cenzual, J. Daams, R. Gladyshevskii, O. Shcherban, V. Dubenskyy, N. Melnichenko-Koblyuk, O. Pavlyuk, S. Stoiko, and L. Sysa, " $\text{ZrAlC}_{1.67}$," in *Structure Types. Part 3: Space Groups (194) $P6_3/mmc$ - (190) $P-62c$* , vol. 43A3, *Landolt-Börnstein - Group III Condensed Matter*, P. Villars and K. Cenzual, Eds.: Springer Berlin Heidelberg, 2006, pp. 1-1.
- [31] L. He, Z. Lin, J. Wang, Y. Bao, M. Li, and Y. Zhou, "Synthesis and Characterization of Bulk $\text{Zr}_2\text{Al}_3\text{C}_4$ Ceramic," *Journal of the American Ceramic Society*, vol. 90, pp. 3687-3689, 2007.
- [32] Y. Zhou, L. He, Z. Lin, and J. Wang, "Synthesis and structure-property relationships of a new family of layered carbides in $\text{Zr-Al}(\text{Si})\text{-C}$ and $\text{Hf-Al}(\text{Si})\text{-C}$ systems," *Journal of the European Ceramic Society*, vol. 33, pp. 2831-2865, 2013.
- [33] E. Reiffenstein, H. Nowotny, and F. Benesovsky, "Strukturchemische und magnetochemische Untersuchungen an Komplexcarbiden.," *Monatsh für Chem verw Teile anderer Wiss.*, vol. 97, pp. 1428-1436., 1966.
- [34] A. Yakoubi, L. Beldi, B. Bouhafs, M. Ferhat, and P. Ruterana, "Full-relativistic calculation of electronic structure of Zr_2AlC and Zr_2AlN ," *Solid State Communications*, vol. 139, pp. 485-489, 2006.
- [35] F. Luo, Z.-c. Guo, X.-L. Zhang, C.-Y. Yuan, and L.-C. Cai, "Ab initio Predictions of Structural and Thermodynamic Properties of Zr_2AlC Under High Pressure and High Temperature," *Chinese Journal of Chemical Physics*, vol. 28, pp. 263-268, 2015.
- [36] L. Shang, D. Music, M. Baben, and J. Schneider, M. , "Phase stability predictions of Cr_{1-x} , $\text{M}_x)_2(\text{Al}_{1-y}, \text{A}_y)(\text{C}_{1-z}, \text{X}_z)$ ($\text{M} = \text{Ti}$, Hf , Zr ; $\text{A} = \text{Si}$, $\text{X} = \text{B}$)," *Journal of Physics D: Applied Physics*, vol. 47, pp. 065308, 2014.
- [37] D. Horlait, S. C. Middleburgh, A. Chroneos, and W. E. Lee, "Synthesis and DFT investigation of new bismuth-containing MAX phases," *Scientific Reports*, vol. 6, pp. 18829, 2016.
- [38] D. Horlait, S. Grasso, A. Chroneos, and W. E. Lee, "Attempts to synthesise quaternary MAX phases $(\text{Zr}, \text{M})_2\text{AlC}$ and $\text{Zr}_2(\text{Al}, \text{A})\text{C}$ as a way to approach Zr_2AlC ," *Materials Research Letters*, pp. 1-8, 2016.
- [39] D. J. Tallman, E. N. Hoffman, E. N. Caspi, B. L. Garcia-Diaz, G. Kohse, R. L. Sindelar, and M. W. Barsoum, "Effect of neutron irradiation on select MAX phases," *Acta Materialia*, vol. 85, pp. 132-143, 2015.
- [40] H. J. Yang, Y. T. Pei, and J. T. M. De Hosson, "Oxide-scale growth on Cr_2AlC ceramic and its consequence for self-healing," *Scripta Materialia*, vol. 69, pp. 203-206, 2013.

- [41] S. Li, G. Song, K. Kwakernaak, S. van der Zwaag, and W. G. Sloof, "Multiple crack healing of a Ti_2AlC ceramic," *Journal of the European Ceramic Society*, vol. 32, pp. 1813-1820, 2012.
- [42] O. Berger, C. Leyens, S. Heinze, M. To Baben, and J. M. Schneider, "Self-healing of yttrium-doped Cr_2AlC MAX phase coatings deposited by hipims," in *ICSHM 2013: Proceedings of the 4th International Conference on Self-Healing Materials*. Ghent, Belgium, 2013.
- [43] A.-S. Farle, C. Kwakernaak, S. van der Zwaag, and W. G. Sloof, "A conceptual study into the potential of $\text{M}_{n+1}\text{AX}_n$ -phase ceramics for self-healing of crack damage," *Journal of the European Ceramic Society*, vol. 35, pp. 37-45, 2015.
- [44] F. Zhang, K. Vanmeensel, M. Inokoshi, M. Batuk, J. Hadermann, B. Van Meerbeek, I. Naert, and J. Vleugels, "3Y-TZP ceramics with improved hydrothermal degradation resistance and fracture toughness," *Journal of the European Ceramic Society*, vol. 34, pp. 2453-2463, 2014.
- [45] L. Lutterotti, S. Matthies, and H. Wenk, "MAUD: a friendly Java program for material analysis using diffraction," *Newsletter of the CPD*, vol. 21, pp. 14-15, 1999.
- [46] O. Rivin, E. N. Caspi, H. Etteedgui, H. Shaked, and A. Gukasov, "Magnetic structure determination of TbCo_2Ni_3 using polarized and nonpolarized neutron powder diffraction," *Physical Review B*, vol. 88, pp. 054430, 2013.
- [47] J. Rodríguez-Carvajal, "Recent advances in magnetic structure determination by neutron powder diffraction," *Physica B: Condensed Matter*, vol. 192, pp. 55-69, 1993.
- [48] T. B. Massalski, *Binary Alloy Phase Diagrams*, 2nd ed: Metals Park, OH, 1990.
- [49] A. Khein, D. J. Singh, and C. J. Umrigar, "All-electron study of gradient corrections to the local-density functional in metallic systems," *Physical Review B*, vol. 51, pp. 4105-4109, 1995.
- [50] I.-H. Lee and R. M. Martin, "Applications of the generalized-gradient approximation to atoms, clusters, and solids," *Physical Review B*, vol. 56, pp. 7197-7205, 1997.
- [51] K. Nakamura and M. Yashima, "Crystal structure of NaCl-type transition metal monocarbides MC (M = V, Ti, Nb, Ta, Hf, Zr), a neutron powder diffraction study," *Materials Science and Engineering: B*, vol. 148, pp. 69-72, 2008.
- [52] P. Wang, B. Mei, X. Hong, J. Zhu, and W. Zhou, "Fabrication of Ti_2AlC by spark plasma sintering from elemental powders and thermodynamics analysis of Ti-Al-C system," *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, vol. 22, pp. 325-328, 2007.
- [53] X. H. Wang and Y. C. Zhou, "Layered Machinable and Electrically Conductive Ti_2AlC and Ti_3AlC_2 Ceramics: a Review," *Journal of Materials Science & Technology*, vol. 26, pp. 385-416, 2010.
- [54] M. W. Barsoum, T. El-Raghy, and M. Ali, "Processing and characterization of Ti_2AlC , Ti_2AlN , and $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$," *Metallurgical and Materials Transactions A*, vol. 31, pp. 1857-1865, 2000.
- [55] X. Wang and Y. C. Zhou, "Solid-liquid reaction synthesis and simultaneous densification of polycrystalline Ti_2AlC ," *Zeitschrift für Metallkunde*, vol. 93, pp. 66-71, 2002.
- [56] P. Wang, B.-c. Mei, X.-l. Hong, and W.-b. Zhou, "Synthesis of Ti_2AlC by hot pressing and its mechanical and electrical properties," *Transactions of Nonferrous Metals Society of China*, vol. 17, pp. 1001-1004, 2007.
- [57] C. Hu, F. Li, J. Zhang, J. Wang, J. Wang, and Y. Zhou, " Nb_4AlC_3 : A new compound belonging to the MAX phases," *Scripta Materialia*, vol. 57, pp. 893-896, 2007.

Table 1. Comparison of experimentally-measured and predicted (literature) lattice parameters and z_{Zr} values for Zr_2AlC .

Zr_2AlC	a (Å)	c (Å)	z_{Zr}
Experimental XRD	3.3237(2)	14.5705(4)	0.0871(1)
Experimental SAED	3.3	14.6	/
Experimental NPD	3.3239(4)	14.556(2)	0.0898(7)
Calculated [33]	3.25	14.5	/
Calculated [34]	3.2104	14.2460	0.0869
Calculated [35]	3.3174	14.6304	0.0861
Calculated [36]	3.334	14.600	/

Table 2. The d-spacings, corresponding 2θ angles and relative intensities of the (hkl) reflections starting with the lattice parameters obtained by the XRD Rietveld refinement listed in Table 1, together with the observed 2θ angles and relative intensities. The (008) peak was not observed due to its low intensity (*). The (202) and (109) peak were hidden by the ZrC_x (311) diffraction peak (**).

h k l	d (Å)	2θ (°) Calculated	I/I_{max} (%) Calculated	2θ (°) Observed
0 0 2	7.2851	12.14	34.32	12.17
0 0 4	3.6426	24.42	3.34	24.44
1 0 0	2.8783	31.04	20.40	31.07
1 0 1	2.8237	31.66	15.36	31.68
1 0 2	2.6769	33.45	1.20	33.46
1 0 3	2.4761	36.25	100.00	36.28
0 0 6	2.4284	36.99	18.74	37.02
1 0 4	2.2583	39.89	5.73	39.90
1 0 5	2.0478	44.19	2.70	44.20
1 0 6	1.8560	49.04	16.18	49.06
0 0 8	1.8213	50.04	0.12	*
1 0 7	1.6867	54.35	5.63	54.38
1 1 0	1.6618	55.23	21.04	55.26
1 1 2	1.6202	56.77	3.51	56.79
1 0 8	1.5391	60.06	0.42	60.07
1 1 4	1.5119	61.26	3.29	61.28
0 0 10	1.4570	63.83	1.09	63.85
2 0 0	1.4392	64.72	2.55	64.73
2 0 1	1.4322	65.07	1.90	65.08
2 0 2	1.4119	66.13	0.22	**
1 0 9	1.4110	66.17	16.09	**
2 0 3	1.3798	67.87	15.46	67.89
1 1 6	1.3714	68.34	18.46	68.37
2 0 4	1.3385	70.27	0.96	70.30
1 0 10	1.3000	72.67	0.69	72.71
2 0 5	1.2904	73.30	0.6	73.27

[Click here to download high resolution image](#)

Figure

[Click here to download high resolution image](#)

Figure
[Click here to download high resolution image](#)

Figure
[Click here to download high resolution image](#)

Figure

[Click here to download high resolution image](#)

Figure 1. XRD patterns of the samples reactively hot pressed at 1475, 1525 and 1575°C.

Figure 2. XRD pattern (blue) and the refinement (black) of the sample hot pressed at 1525°C.

Figure 3. Scanning electron micrograph and corresponding elemental maps of the sample hot pressed at 1525°C, showing the presence of two phases: Zr_2AlC and ZrC (67 wt% and 33 wt%, respectively).

Figure 4. (a) HRTEM image and (b) SAED of Zr_2AlC with the beam aligned along the $[11\bar{2}0]$ zone axis.

Figure 5. NPD profiles of a sample hot pressed at 1525°C, observed at room temperature (symbols) as a function of scattering angle, 2θ . Rietveld-refined profiles (black lines) fit the observed results. The differences between the observed and refined patterns are shown in the lower part of each figure (blue lines). The three rows of tags represent the expected peak positions of Zr_2AlC , Zr_3AlC_2 and ZrC , respectively.

Figure 6. Secondary electron image of a 30 N Vickers indentation on the Zr_2AlC ceramic synthesised at 1525°C. The characteristic rectangular, laminated grains can clearly be distinguished. Note the absence of cracks from the corners of the indents.