Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2017, **27**, 59–60

Mendeleev
Communications

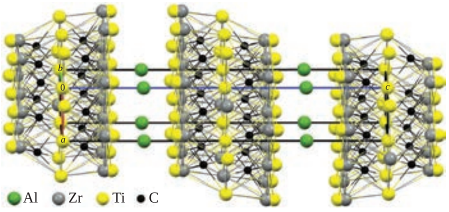
Synthesis of a new MAX phase in the Ti–Zr–Al–C system

**Dmitry Yu. Kovalev,* Marina A. Luginina, Sergei G. Vadchenko,
Sergei V. Konovalikhin, Aleksandr E. Sychev and Aleksandr S. Shchukin**

*Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 524 6222;
e-mail: kovalev@ism.ac.ru*

DOI: 10.1016/j.mencom.2017.01.018

The new MAX phase $(Zr_{0.5}Ti_{0.5})_3AlC_2$ was prepared using self-propagating high-temperature synthesis, and its crystal structure was determined by X-ray diffraction analysis.



Self-propagating high-temperature synthesis (SHS) is an important method for the preparation of new multicomponent materials. The synthesis of refractory materials of the general formula $M_{n+1}AX_n$, where M is a transition metal, A is a IIIA or IVA Group element, and X is carbon or nitrogen (MAX phases), is of considerable interest. Due to their laminated structure, the MAX phases have the combined properties of metals and ceramics: a low density, a high strength, a low thermal expansion coefficient and oxidation and thermal shock resistances. More than 60 compounds of similar structures have been synthesized.[1] The MAX phases can be doped with related elements; for example, solid solutions with the formulas $(Ti_{0.5}Nb_{0.5})_2AlC$,[2] $(Ti_{0.5}V_{0.5})AlC$,[3] and $(Ti_{0.5}Zr_{0.5})_2InC$[4] were prepared. The partial substitution of an element for another changes the mechanical and thermal characteristics of the material. It is interesting to synthesize MAX phases in the Ti–Zr–Al–C system with the total or partial replacement of Zr with Ti. Since Zr atoms have a small thermal neutron capture cross section, the MAX phase containing Zr would be promising as structural material for nuclear power engineering.[5]

Here, we describe the SHS of the new MAX phase $(Zr_{0.5}Ti_{0.5})_3AlC_2$. The Zr (M41), Ti (PTM), Al (PAD-1) and C (P804-T) powders were used as initial components. The reagents were mixed in the molar ratio Ti : Zr : Al : C = 1 : 1 : 1 : 1 in a ball mill in air to obtain a new phase. Cylindrical specimens 12 mm in diameter and 8 mm in height were pressed from the mixture. The synthesis was carried out in a reactor in argon at atmospheric pressure. The SHS process was initiated with a tungsten coil in a combustion regime. The combustion wave temperature was higher than 1200 °C.

The synthesis product was studied on a DRON-3M diffractometer equipped with a graphite monochromator on a secondary beam using CuKα radiation at 293 K. Diffraction patterns were recorded using a stepwise scanning mode within the angle range 2θ = 8–76° with a scan step of 0.02° and accumulation time of 2 s. The atomic structure of a polyphase specimen was refined from the diffraction experimental data using the PDW software (version 4.00) from Burevestnik Research and Production Enterprise. The crystal cell parameters were determined using an internal standard (silicon SRM640D as a reference material). The microstructure of the material was studied on a Zeiss Ultra plus field emission scanning microscope with ultra-high resolution using the Ultra 55 basis.

Figure 1 displays the X-ray diffraction pattern of the powder obtained by SHS. The pattern shows that the reaction products have no less than two phases, one of which is a cubic crystal system, whereas the second system is a hexagonal one. The cubic phase is the solid solution $(Zr_{1-y}Ti_y)C$. The diffraction lines of this phase are between the appropriate lines of TiC and ZrC phases. These carbides form a continuous series of solid solutions with the linear dependence of unit cell parameters on composition. The composition of the carbide phase $Zr_{0.25}Ti_{0.75}C$ was determined from the known cell parameters of TiC and ZrC

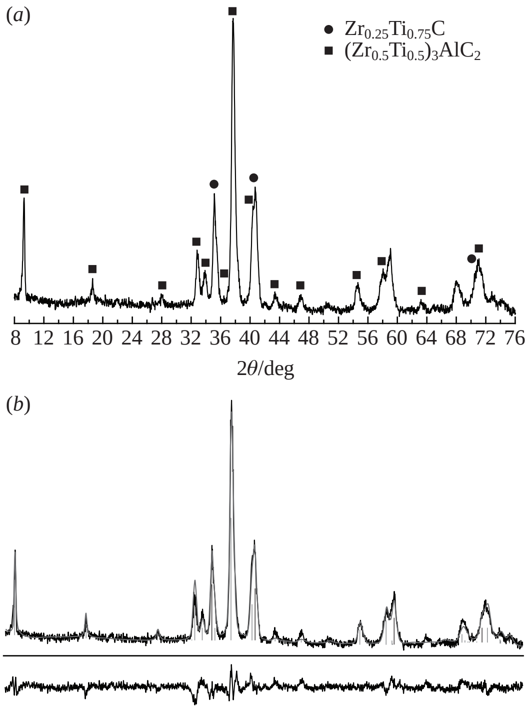


Figure 1 (*a*) Diffraction pattern of synthesis product in Ti–Zr–Al–C system. (*b*) Calculation results according to the Rietveld method and difference pattern.

Table 1 Crystallographic parameters of the MAX phases 312 in the Ti–Zr–Al–C system.

Structure	a/Å	c/Å	V/Å^3	d/g cm^{-3}	r(Zr^1–C)/Å	r(Zr^2–C)/Å	r(Zr^1–Zr^1)/Å	r(Zr^2–Zr^2)/Å	r(Zr^2–Zr^1)/Å	r(Zr^2–Al)/Å
Ti_3AlC_2[a,7]	3.075(1)	18.578(1)	152.2(1)	4.25	2.200	2.110	3.075	3.075	3.018	2.830
Zr_3AlC_2[8]	3.3331(1)	19.951(1)	191.94(4)	5.62	2.377	2.263	3.333	3.333	3.225	3.076
$(Zr_{0.5}Ti_{0.5})_3AlC_2$[b]	3.178(2)	19.099(9)	167.06(2)	5.16	2.270	2.178 (2.247)	3.178	3.178 (3.180)	3.109 (3.184)	2.915 (2.820)

[a] For Ti_3AlC_2, row shows the lengths of Ti atom bonds. [b] For $(Zr_{0.5}Ti_{0.5})_3AlC_2$ row, values in parentheses are the lengths of the Ti^2–Al bond.

phases based on the linear dependence of cell metrics on the amounts of elements in the $Zr_{1-x}Ti_xC$ solid solution series.

The Ti- and Zr-containing MAX phases 211 and 312 with a hexagonal structure (space group $P6_3/mmc$) can be obtained in the synthesis. The phases 211 have the formulas Ti_2AlC and Zr_2AlC,[6] whereas the phases 312 have the formulas Ti_3AlC_2[7] and Zr_3AlC_2.[8] The most characteristic line associated with the cell parameter c of a hexagonal structure is the line (002). The angle position of the first diffraction line in the experimental pattern $2\theta = 9.3°$ (Figure 1) is an intermediate position between the reflections (002) of the ternary phases 312 Ti_3AlC_2 and Zr_3AlC_2. The phases 211 have the characteristic diffraction line (002) within the angle range $2\theta = 12–13°$ when CuKα radiation is used. Unidentified diffraction lines may belong to the solid solution phase $(Zr_xTi_{1-x})_3AlC_2$. Assuming that the cell metric linearly depends on the fraction x of Zr atoms and the elementary cell volumes of Ti_3AlC_2 and Zr_3AlC_2 crystals are known, the ratio between Zr and Ti atoms in the solid solution phase $(Zr_xTi_{1-x})_3AlC_2$ can be evaluated. The value of x is ~0.4. The best compliance of the experimental diffraction pattern with a theoretically calculated one based on model structures was attained at $x = 0.5$ and a convergence factor of 6.7%.

When $(Zr_xTi_{1-x})_3AlC_2$ crystals were analyzed, an uncertainty in the positions of Ti and Zr atoms appeared. In the unit cell, the Ti and Zr atoms occupy 2*a* (0.0; 0.0; 0.0) and 4*f* (0.0; 0.0; *z*) positions. Three variants are possible in the disposition of atoms. In the first variant, the Ti atom exhaustively occupies the 2*a* position, whereas Zr occupies the 4*f* position. In the second variant, Zr atoms are placed at the 2*a* position, whereas Ti atoms, at 4*f*. In the third variant, Ti and Zr atoms partially occupy both positions. The Rietveld method was used to calculate these variants. The profile factors were 7.8, 8.2 and 6.7% for the first, second and third variants, respectively. The refinement of position populations with Ti and Zr atoms showed that the best coincidence of the experimental pattern with the theoretical one was attained in each position at the ratio Zr : Ti = 1 : 1. Therefore, the structures with Ti and Zr atoms disorderly disposed within a metal–carbon layer and occupied 2*a* and 4*f* positions in equal fractions are the most probable. The calculated R factors are $R_{wp} = 8.54\%$, $R_p = 6.69\%$, $R_e = 27.26\%$ and GOF = 0.31.

The unit cell parameters of $(Zr_{0.5}Ti_{0.5})_3AlC_2$ crystals were refined by an internal standard method and found to be close to those calculated according to the Rietveld method. Differences in the parameters a and c and the volume were < 0.004 Å, 0.016 Å and 0.5 Å^3, respectively. The crystallographic parameters of the phases 312 in the Ti–Zr–Al–C system are given in Table 1.

The X-ray diffraction data are confirmed by the scanning electron microscopy (Figure 2). The fracture surface microstructure showed the presence of two phases, one of which had a pronounced laminated structure, *i.e.*, pertains to the MAX phase family, whereas the second phase was characteristic of carbide phases with typical rounded grains. The quantitative X-ray phase analysis of the materials obtained in three syntheses showed that the $Zr_{1-x}Ti_xC$ content was ~30 wt%, and the $(Zr_{0.5}Ti_{0.5})_3AlC_2$ content was ~70 wt%. The crystal structure of the $(Zr_{0.5}Ti_{0.5})_3AlC_2$ phase is shown in Figure 3. The positions 4*f* occupied with Zr and Ti atoms are divided: the Zr^2 and Ti atoms have the crystallographic coordinates 0.0; 0.0; 0.1314(6) and 0.0; 0.0; 0.1379(3), respectively.

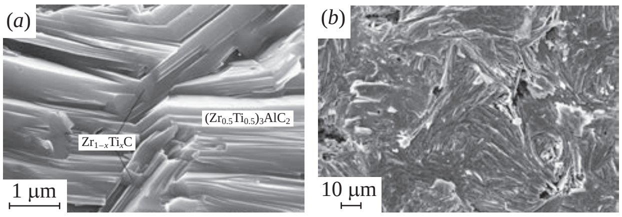


Figure 2 Structure of the synthesis product in the Ti–Zr–Al–C system.

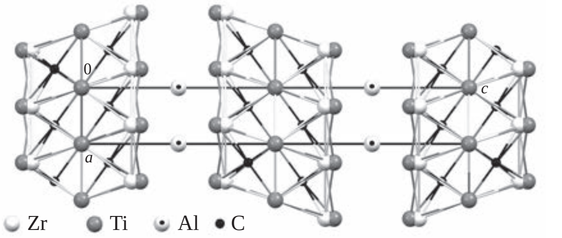


Figure 3 Crystal structure of the MAX phase $(Zr_{0.5}Ti_{0.5})_3AlC_2$.

In conclusion, the two-phase material containing a cubic phase of the binary carbide $Zr_{1-x}Ti_xC$ and the new MAX phase $(Zr_{0.5}Ti_{0.5})_3AlC_2$ was prepared using SHS. The crystallographic parameters of the MAX phase were revealed. $(Zr_{0.5}Ti_{0.5})_3AlC_2$ has a laminated structure where the carbide blocks $(Zr_{0.5}Ti_{0.5})_3C_2$ are divided by the layers of Al atoms. The Ti and Zr atoms are disorderly disposed within a metal–carbon layer and occupied the 2*a* and 4*f* positions in equal fractions.

This work was supported by the Presidium of the Russian Academy of Sciences (project no. 31).

References

1 M. W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*, Wiley-VCH, Weinheim, 2013.
2 I. Salama, T. El-Raghy and M. W. Barsoum, *J. Alloys Compd.*, 2002, **347**, 271.
3 S. Gupta and M. W. Barsoum, *J. Electrochem. Soc.*, 2004, **151**, D24.
4 S. Gupta, E. N. Hoffman and M. W. Barsoum, *J. Alloys Compd.*, 2006, **426**, 168.
5 B. F. Myasoedov and S. N. Kalmykov, *Mendeleev Commun.*, 2015, **25**, 319.
6 T. Lapauw, K. Lambrinou, T. Cabioc’h, J. Halim, J. Lu, A. Pesach, O. Rivin, O. Ozeri, E. N. Caspi, L. Hultman, P. Eklund, J. Rosén, M. W. Barsoum and J. Vleugels, *J. Eur. Ceram. Soc.*, 2016, **36**, 1847.
7 Y. C. Zhou, X. H. Wang, Z. M. Sun and S. Q. Chen, *J. Mater. Chem.*, 2001, **11**, 2335.
8 T. Lapauw, J. Halim, J. Lu, T. Cabioc’h, L. Hultman, M. W. Barsoum, K. Lambrinou and J. Vleugels, *J. Eur. Ceram. Soc.*, 2016, **36**, 943.

Received: 20th April 2016; Com. 16/4915