Journal of the European Ceramic Society 37 (2017) 15–21

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Structure and thermal expansion of $(Cr_x,V_{1-x})_{n+1}AlC_n$ phases measured by X-ray diffraction

Joseph Halim [a,b], Patrick Chartier [c], Tatyana Basyuk [d], Tatyana Prikhna [d], El'ad N. Caspi [e], Michel W. Barsoum [a], Thierry Cabioc'h [c,*]

[a] Department of Materials Science & Engineering, Drexel University, Philadelphia, PA 19104, USA
[b] Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-583 31 Linköping, Sweden
[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] Bakul Institute for Superhard Materials, National Academy of Sciences of Ukrain, Avtozavods'ka 2, Kiev 040474, Ukraine
[e] Physics Department, Nuclear Research Centre – Negev, PO Box 9001, 84190 Beer-Sheva, Israel

ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form 18 July 2016
Accepted 19 July 2016
Available online 27 July 2016

Keywords:
MAX phases
Thermal expansion
Carbides
Solid solutions
XRD

ABSTRACT

MAX phases in the $(Cr_x,V_{1-x})_{n+1}AlC_n$ system were synthesized by reactive sintering or hot isostatic pressing of elemental powders at temperatures between 1400 °C and 1600 °C. For $n = 1$, a complete range ($0 \leq x \leq 1$) of solid solutions was found; for $n = 2$ and 3 the solubility ranges were $0.25 \leq x \leq 0.75$ and $0 \leq x \leq 0.5$, respectively. Powder X-ray diffraction revealed that the lattice parameters of all $(Cr_x,V_{1-x})_{n+1}AlC_n$ solid solutions followed Vegard's law. The thermal expansion coefficients of the various compounds were determined from Rietveld refinements of X-Ray patterns obtained at temperatures between ambient and 800 °C. For the $n = 1$ and 3 phases the thermal expansion coefficients were almost isotropic; those for the $n = 2$, however, were quite anisotropic with the expansion along the a-axis being significantly larger than along the c-axis. As a general trend, vanadium rich compounds have smaller thermal expansion coefficients than their Cr-rich counterparts.

1. Introduction

The $M_{n+1}AX_n$ (MAX) phases ($n = 1–3$) are nanolaminated layered carbides and nitrides, where M is an early transition metal, A is a group A element, mainly from groups 13 and 14, and X is C and/or N [1]. They have a hexagonal crystal structure (space group $P6_3/mmc$), where the M atoms are in a near-closed packed arrangement and are interleaved with pure A-group element layers, with the X-atoms occupying the octahedral sites between the M layers [2]. There are about 70 MAX phases reported to date, that are classified by their n values as M_2AX "211" ($n = 1$), M_3AX_2 "312" ($n = 2$), and M_4AX_3 "413" ($n = 3$) [3]. By this time, it is fairly well established that these materials have a unique combination of metal and ceramic properties. For example, they are thermally and electrically conductive, thermal shock resistant, machinable and damage tolerant like metals. In addition, some of them have low densities, high elastic stiffnesses and are oxidation and creep resistant like ceramics [4–7].

The structures and the properties of MAX phases can be modified, and even tuned, by introducing a fourth, or more, element into their structures. This is especially true here since, isostructural solid solutions can be obtained on the M, A and/or X sites. This compositional degree of freedom has been exploited by some to tailor the MAX phases' properties. For example the oxidation resistance of Ti_3SiC_2 improves upon the introduction of Al on the A-sites or when Ti atoms are introduced on the M site to create $Ti_3(Si_{1-x},Al_x)C_2$ and $(Nb_{1-x},Ti_x)_2AlC$ solid solutions, respectively [8,9]. Solid solution hardening effects were also reported for $(V_x,Ti_{1-x})_2AlC$ [10] and $Ti_2AlC_xN_y$ [11] whereas a solid solution softening effect was noticed for $Ti_3(Al_{1-x},Sn_x)C_2$ [12].

More recently, there has been a growing interest in MAX phase solid solutions as a way to achieve new properties. Most notably, it was demonstrated that a promising method to create magnetic MAX phases is to introduce Mn in the structure of MAX phases that do not contain Mn [13–17]. In addition, new ordered MAX phase solid solutions have been recently synthesized [18–21] and predicted [22]. Indeed, it is more accurate to refer to the ordered $n = 2$ and $n = 3$ solid solutions as $M'_2M''AX_2$ and $M'_2M''_2AX_3$, respectively, to emphasize the existence of two inequivalent crystallographic sites for the M atoms in these structures (M′ being closer to the

---

* Corresponding author.
E-mail address: thierry.cabioch@univ-poitiers.fr (T. Cabioc'h).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.07.022
0955-2219/© 2016 Elsevier Ltd. All rights reserved.

A atoms). Liu et al. [18] thus obtained the $(Cr_{2/3}Ti_{1/3})_3AlC_2$ compound in which the Ti and Cr atoms are on the M′ and M″ sites, respectively. In the same way, Caspi et al. [19] confirmed the strong tendency for the Cr atoms to occupy the M′ sites in $(Cr_{0.5}V_{0.5})_3AlC_2$ and $(Cr_{0.5}V_{0.5})_4AlC_3$ solid solutions. Similar behavior was obtained for Mo atoms in Mo_2TiAlC_2 and $Mo_2Ti_2AlC_3$ [20,21].

Most germane to this work is the fact that the thermal expansions of $Cr_2(Al_{1-x},Ge_x)C$ solid solutions can be tailored by varying x. For $x \approx 0.75$, the thermal expansion coefficients, TECs, of the a-lattice parameters, a-LPs, and c-lattice parameters, c-LPs, were nearly equal [23]. The present contribution builds on these results and deals with solid solutions in the Cr-V-Al-C system, *viz.* $(Cr_x,V_{1-x})_{n+1}AlC_n$ (n = 1, 2, 3) for x = 0; 0.25; 0.5; 0.75; 1.0. This system is of special interest since it is the only system, other than the Ta-Al-C system [24], where phases exist for n = 1, 2 and 3. In most other MAX phase systems, only a subset is stable. Previously, Schuster et al. [25] revealed that $(Cr_x,V_{1-x})_2AlC$ phases can be obtained for $0 \leq x \leq 1$. However, for the “312”, and “413” phases, only the x = 0.5 solid solutions have to date been synthesized [19,26].

It is of special interest to study the evolution of the TEC's of these $(Cr_x,V_{1-x})_{n+1}AlC_n$ solid solutions. In addition to the fundamental scientific interest that knowledge of this property garners, the TEC values can have an important influence on the oxidation resistance of these compounds, and therefore on possible applications. As mentioned above, some MAX phases are resistant to high temperature oxidation. For example Ti_3AlC_2 and Ti_2AlC resist high temperature oxidation up to 1400 °C due to the formation of a well adhered, protective Al_2O_3 scale [27]. However, Cr_2AlC shows cubic rate oxidation and good hot corrosion resistance against molten Na_2SO_4 up to 1000 °C only. Above that temperature spallation of the Al_2O_3 layer takes place [27,28]. This spallation occurs due to the TEC mismatch between Cr_2AlC (13 μK^{-1}) and Al_2O_3 (8 μK^{-1}) [29,30]. In this context, incorporation of V could improve the oxidation resistance of Cr_2AlC by decreasing its TEC. The rationale behind this proposition is that V_2AlC has a lower TEC (8 μK^{-1}) than Cr_2AlC. As noted above, we already showed that to be the case in the $Cr_2(Al_x,Ge_{1-x})C$ system [23].

Here, we use high temperature X-ray diffraction to report on the thermal expansions of $(Cr_xV_{1-x})_{n+1}AlC_n$ solid solutions as a function of both x and n.

2. Experimental details

Samples were synthesized by using powder metallurgy techniques. Chromium (−200 mesh, 99.95%, Alfa Aesar GmbH & Co KG Karlsruhe Germany), vanadium (−325 mesh, 99.8%, Alfa Aesar GmbH & Co KG Karlsruhe Germany), aluminum (40–325 mesh 99.8%, Alfa Aesar GmbH & Co KG Karlsruhe Germany) and graphite (<40 μm, Chemwatch) powders were first weighed to obtain the requisite molar compositions. In all cases, an excess of 10 at.% Al was used to compensate for its loss by evaporation during the sintering process. These powders were then mixed for 3 h in a Turbula™ mixer. Cylindrical compacts 3–4 g in weight, 12 mm in diameter, were obtained by cold pressing the mixed powders in a uniaxial press at a load corresponding to a pressure of 200 MPa.

Ten different starting nominal compositions – all listed in first column in Table 1 – were prepared. These compositions were then either pressureless sintered, PS, in a tube furnace under flowing Ar, in the 1400 °C to 1600 °C temperature range or hot-isostatically pressed, HIPed at 1450 °C. Twenty eight different runs – listed in columns 2 and 3 – of varying durations were carried out.

As noted above, several samples were also HIPed. Those are designated by HIP in column 2 in Table 1. In this case, the cold pressed cylindrical samples were sealed under a mechanical vacuum inside borosilicate glass (Pyrex) tubes. The HIP was then heated to 1450 °C and pressurized, using Ar gas, to a pressure of 80 MPa and held at temperature for 4 h, before furnace cooling. The dense compacts were then further annealed for 1 h at 700 °C under Ar flow to relax any internal stresses that may have accrued during the HIPing process.

After a mechanical polishing, all samples were characterized at room temperature, RT, by XRD in a Bragg-Brentano configuration using a diffractometer (B8 Bruker) operating at 40 kV, 40 mA with Cu-Kα radiations with a LynxEye™ rapid detector and a fixed divergence slit of 0.4°. Steps scan of $\Delta\, 2\theta = 0.01–0.02°$ for 2–3 s per step were typically used for obtaining the RT XRD patterns.

In situ HT-XRD patterns were also obtained for select samples using an Anton-Paar device (Domed Hot Stage for Four-Circle Goniometers (DHS 1100)) with a graphite dome mounted in line in the same X-Ray diffractometer. To accurately determine the temperature of the samples hexagonal boron nitride, h-BN, powder was evenly distributed on the MAX samples' surfaces. h-BN possess a relatively large and well known thermal expansion along its c-axis ($c\ (Å) = 6.6516\ Å + 2.74 \times 10^{-4}\ T\ Å\ °C^{-1}$) [31] allowing a precise determination of the samples' temperatures when the c-LP of h-BN were deduced from Rietveld refinement of the X-Ray diffractograms.

A XRD pattern of a chromia standard powder (NIST 674b) was collected at the same geometrical conditions to generate an instrumental resolution function to account for experimental broadening, and to estimate the systematic uncertainty in the determination of the lattice parameters (LP). Rietveld refinements of all diffractograms were performed using the Materials Analysis Using Diffraction (MAUD) software [32]. At RT, the uncertainty in the LPs is lower than 0.013% and 0.03% for the *a* and *c* LPs, respectively; at higher temperatures the uncertainly is lower than 0.03% and 0.07% for the *a* and *c* LPs, respectively.

Using the Rietveld refined LPs in the 200–800 °C temperature range, the linear TECs of the phases in this study were calculated by fitting $\Delta L/L_o$, where L is either the *a*- or *c-LPs*, and L_o is their value at RT, with a linear fit. This method, however, underestimates the uncertainty in the calculated values, as it ignores the variations on the TECs with temperature. Thus, an average linear method was also used to calculate the TECs using discreet derivatives of the measured data. For more details see Refs. [33,34].

3. Results and discussion

Columns 5–10 in Table 1 summarize the weight percentages of the different phases – obtained from Rietveld analysis – for all 28 runs carried out in this study. The RT XRD for the HIPed samples are plotted in Fig. 1 whereas a typical result of a Rietveld refinement of a XRD diagram is given in Fig. 2. Before proceeding, it is worth noting that the weight percentages, listed in Table 1, are not necessarily fully representative of the average composition of each sample. Said otherwise, they need to be taken with a grain of salt because Al loss from the powdered bed samples is not uniform. For example, Al loss was found to be highest near the surfaces exposed to the Ar gas for the pressureless sintered samples. It follows that the exact fraction of each phase obtained will depend on where exactly the XRD were obtained. Fortunately, this does not affect any of the conclusions reached herein since the TEC results are obtained from the peaks belonging to each phase.

A perusal of the results listed in columns 5–10 in Table 1 indicate that for the PS samples of the 211 composition, the 211 phase is predominantly obtained when the reactive sintering temperature was 1400 °C. Nevertheless, even at this temperature, the lowest used in this study, in some cases and especially for the V-rich compounds, Al-loss resulted in the formation of 413 phases for x = 0 composition, and 312 phases for the x = 0.25 and 0.5 compositions.