Formation of Ti2AlC Nanocrystals via Vapor-Condensation through the Thermal Plasma Vaporization of TiC and Al

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Abstract

Ternary phase Ti2AlC was observed in vapor-condensed products obtained through the Ar–H2 or Ar–He thermal plasma in-flight heating of TiC micron powders containing aluminum and the subsequent rapid cooling of plasma. The Ti2AlC phase was well crystallized, appeared as facetted particles of hexagonal morphology with sizes of 40–80 nm that coexisted with TiC, in the vapor-condensed products. The fraction of the Ti2AlC phase increased significantly with an increasing hydrogen concentration in the Ar–H2 plasma. This work demonstrates that the ternary Ti2AlC phase can be produced via a high temperature vapor-condensation process.

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1. Introduction

Titanium-based ternary phases with a general formula of TiBx or Ti3Bx2, where B is a group B element (e.g., Al or Si) and x is C or N, have attracted considerable attention because of their unique electronic and thermal properties and their combined mechanical properties such as oxidation resistance, thermal shock resistance, moderate hardness, and low temperature ductility.1–10 The Ti2BX phase has the Cr2–AlC-type hexagonal structure with the space group of P63/mmc, which is traditionally denoted as the ‘H-phase’,11,12 and the Ti3BX2 phase has a filled Li2O-type or perovskite-type structure with the same space group as Ti2B2C.13 The synthetic materials of these ternary phases are microscopically characterized by a layered structure—towards which their ductility at low temperature (even at room temperature) is ascribed—that allows the materials to be machined with common cutting tools, a distinct property of this family of ceramics.

H-phase Ti2AlC in the Ti–Al–C system was first identified in the early 1960s.11,12 This phase has also been observed in refined-grain Al-alloys to which Ti and C were added4 and in melt-infiltrated Al–TiC composites,15 and has been formed by hot-pressing and in combustion synthesized Ti–Al–C composites,16 and has been formed by hot-pressing and in combustion synthesized Ti–Al–C composites from the reaction of elemental Ti, Al, and C powders.16,17 Barsoum et al. recently prepared single-phase Ti2AlC materials by hot-pressing, and these materials showed high electrical conductivity (2×106 Ω−1·m−1), low thermal expansion (8.2×10−6 K−1), moderate hardness (5.5 GPa), and excellent machinability.1,3,7

The growth of Ti-based ternary phases by vapor-phase condensation is of great interest for the fabrication of coatings/films and functional nano-particles for application as electrical and/or thermal conductivity coatings or as functional phases or reinforcing components. However, although Racault et al.18 and Pickering et al.19 have reported the formation of the Ti3Bx-type phase in the Ti–Si–C system (Ti3SiC2) through the chemical vapor reaction of TiCl4–SiCl4–CCl4–H2 gas mixtures, we know of no published report on the synthesis of this important H-phase in the Ti–Al–C system. In this paper, we describe formation of the Ti2AlC phase through the thermal plasma vaporization of TiC micron powders containing Al. We then characterize the Ti2AlC crystals formed regarding their morphology and phase structure.

2. Experimental

Commercial TiC micron powders (TiC–M, Japan New Metals Co., Ltd.) which contained a small amount of aluminum were heated in-flight by Ar–H2 and Ar–He thermal plasmas in an aerosol reactor. Chemical analysis showed the powders contained 19.63 mass% of carbon, suggesting the carbide was slightly carbon deficient (TiC0.98). The oxygen impurity in the powders was 0.25 mass%. Inductively coupled plasma (ICP) atomic spectrometric analysis showed that the powders contained 0.3 mass% of aluminum. X-ray diffraction detected a very weak but discernible diffraction line at 2θ = 38° that could be assigned to the strongest line of (100) for cubic aluminum, indicating that the aluminum existed in a free state in the TiC powders. Energy dispersive X-ray spectroscopy (EDX) showed that the aluminum was uniformly distributed in the TiC particles. The starting TiC powders, because of containing the small amount of Al, are denoted as TiC–Al hereafter. The mean diameter of the particles in the TiC–Al powders was 28.5 μm as measured by the laser diffraction method.

The Ar–H2 and Ar–He plasma was generated by an induction-plasma torch (Model PL–50, TEKNA Plasma Systems Inc., Sherbrooke, Quebec, Canada) in connection with a radio frequency (rf) power-supply system (YKN–70–20, Nihon Koshuha Co., Ltd.). Argon was injected as the central plasma gas, while a mixture of Ar and H2 (or He) was provided as a sheath gas. The TiC–Al particles were injected vertically from the top of the plasma torch into the center of the induction coils through a powder feeding probe. Argon gas was used as a powder-carrier gas. As the powders were injected into the plasma’s high temperature region, the particles were heated rapidly in-flight and vaporized totally or partially which led to condensation of fine particles through reactions among the vapor species, nucleation, and condensation. Experimental conditions were a plasma plate power of 40 kW, chamber pressure of 67 kPa, central plasma gas (Ar) flow rate of 30 l·min−1, powder feeding rate of 1.8 g·min−1, and carrier flow rate (Ar) of 5 l·min−1. The sheath gases were an Ar and H2 mixture in the Ar–H2 plas-
ma and an Ar–He mixture in the Ar–He plasma; the mixtures were varied while the total gas flow rate was maintained at 90 l·min⁻¹. A detailed experimental description of the plasma synthesis has been given elsewhere.²⁰

The plasma-heated products were a mixture of vapor-condensed fine powders and melt-solidified micron particles.²⁰ The fine particles were separated from the products by sedimentation treatment in ethanol. The fine powders were analyzed by X-ray diffraction, scanning electronic microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectrometry (EDX), and chemical analysis. The TEM was done with a transmission electron microscope equipped with an EDX attachment (Model HF–3000S, Hitachi) operated at 300 kV. The SEM was done with a Model S–5000, Hitachi. Lattice parameters of the TiC were determined by X-ray diffraction (XRD) (Cu Ka) according to the d value of the TiC (422) line. The carbon content in the powders was determined with a carbon analyzer (Model EMA–511, Horiba Ltd.).

3. Results and discussion

XRD patterns from the vapor-condensed products obtained at different hydrogen inputs in the sheath gases in the Ar–H₂ plasma are shown in Fig. 1. The stronger diffraction lines are from the cubic titanium carbide which was the major product in the vapor-condensed products. A set of weaker diffraction lines that are not due to the cubic TiC can be assigned unambiguously to the ternary Ti₂AlC according to the standard data in the JCPDS card (29–0095). Careful examination of the XRD results did not show any evidence of the formation of ternary phase AlTi₃C in the Ti–Al–C system or any other Ti–Al or Al–C phases. The hexagonal unit cell sizes determined by XRD were a = 0.3063 nm and c = 1.3621 nm, which are equal to the reported values for the single-phase Ti₂AlC.²¹,²² This suggests the Ti₂AlC crystals formed by the plasma vaporization have an ideal H-phase hexagonal structure without carbon deficiencies; Ti₂AlC cell dimensions are highly sensitive to processing conditions and to interaction with other coexisting phases or carbon deficiencies.²²

Figure 1 shows that the intensity of the diffraction lines for Ti₂AlC increased distinctly with the hydrogen input in the plasma sheath gases (PH₂) in Ar–H₂. This indicates that formation of the ternary phase is enhanced at a higher hydrogen concentration. At PH₂ < 2.5 l·min⁻¹, no diffraction lines for the ternary phase were detected by XRD, indicating that this phase was not formed when the hydrogen concentration was low. However, the formation of this ternary phase was not intrinsically related to the presence of hydrogen in the reaction system. We also detected formation of the ternary phase in the Ar–He plasma at PH₂ > 5 l·min⁻¹. A high temperature seems to be essential for the growth of this ternary phase, and the enhanced formation of the ternary phase with an increasing hydrogen concentration was probably due to enhanced heat transfer between the plasma gas and the vaporizing particles because hydrogen has higher thermal conductivity than Ar.²₀

A systematic shift of the diffraction lines for the TiC phase with the increase of hydrogen is discernible in Fig. 1 (b). This shift was associated with the incongruent vaporization of TiC with the preferential vaporization of Ti which gave the highly carbon-deficient compounds TiCX, x = 0.38–0.58, and the degree of carbon-deficiency increased with higher hydrogen input.²² A systematic shift in the peak position did not occur for the Ti₂AlC phase. However, a small shift of the peak position is discernible for the Ti₂AlC phase formed at PH₂ = 7.5 l·min⁻¹, implying that the stoichiometry of the ternary compound also changed, within a small range, with the hydrogen concentration. Figure 2 shows SEM morphologies of the vapor-condensed TiC products formed under different hydrogen inputs (PH₂) in the Ar–H₂ plasma. The powders formed at PH₂ = 2.5 l·min⁻¹ consisted of uniform spherical particles that were 30–50 nm in diameter. Some larger faceted particles (40–80 nm in diameter) were formed at PH₂ = 7.5 and 10 l·min⁻¹. These faceted particles of hexagonal morphology were identified as Ti₂AlC grains through TEM and EDX analysis (Fig. 3). The fraction and sizes of the hexagonal particles increased as the hydrogen input rose, indicating enhanced formation of this ternary phase under such conditions, which agreed with the XRD results (Fig. 1). The morphologies of the condensed TiC and Ti₂AlC were different, which were determined by the nature of the crystallography of the two phases or the deficient structures. The condensation of the round TiC nano particles rather than faceted particles was probably due to the high degree of carbon deficiencies in the nanosize TiC particles.

Figure 3 shows the detailed structure and composition identification of the condensed particles in the Ar–H₂ plasma obtained through TEM, SAED, and EDX. EDS (Fig. 3 (b)) revealed the presence of Ti, Al, and C elements in the powders (the Cu signal was from the Cu grid). SAED (Fig. 3 (c)) recorded from the particles shown in Fig. 3(a) produced a set of polycrystalline diffraction rings which
arose mainly from the very fine sized cubic-TiC particles. We detected a set of single diffraction spots that were identified as arising from Ti$_2$AlC. The dark-field image (Fig. 3 (d)) obtained by filtering the (004) spot (Fig. 3(e)) revealed that the single-crystal diffraction originated from the larger faceted particles.

These results clearly demonstrate the efficient formation of the Ti$_2$AlC phase from TiC and Al at high plasma temperatures. Tomoshige and Matsushita$^{17}$ observed the formation of the Ti$_2$AlC phase through the reaction of elemental Ti, Al, and C in self-propagating high temperature synthesis (SHS), and discussed the formation of TiC as the first step in the formation of the Ti$_2$AlC phase. The reaction between Ti and C gave off sufficient heat to generate temperatures enough to melt Al and Ti (2173 K) and the grown TiC subsequently dissolved in the Al-Ti melt with precipitation of the Ti$_2$AlC phase through the liquid phase. In our process, this ternary phase seems to have formed by means of the reactions among elemental Ti, C, and Al in a vapor phase under plasma temperatures as high as 3000–10000 K. TiC vaporizes at $T>$ 4674 K at 1 atm, and decomposes into Ti and C gases (TiC molecules are unstable in the vapor phase$^{24}$). This temperature of $T>$ 4674 K is necessary to vaporize TiC, but a still higher temperature seems necessary for the nucleation of the Ti$_2$AlC phase. We deduced this from the experimental observation that no Ti$_2$AlC phase was formed at the lower reaction temperature when a lower hydrogen concentration was used. We did not observe the formation of this phase in the re-melted TiC particles, which precludes the possibility of any reaction having occurred between liquid TiC and Al. The distinct hexagonal morphology itself suggests that this phase nucleated and grew directly from the vapor phase.

## 4. Conclusion

This study demonstrated the possibility of synthesizing ternary phase Ti$_2$AlC via a vapor-condensation process through thermal plasma vaporization of TiC and Al. The Ti$_2$AlC phase formed by this process was well crystallized: it appears as nanosize (40–80 nm) hexagonal grains. The formation of this phase was enhanced by increasing hydrogen input to the system. It is assumed that the Ti$_2$AlC phase grew through the reaction between the elemental Ti, Al, and C vapors generated at the high plasma temperatures.

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Fig. 3. TEM morphology, selected area electronic diffraction (SAD), and energy dispersive X-ray spectrum (EDX) of the vapor-condensed phases formed in Ar–H₂ plasma: (a) TEM morphology; (b) EDX spectrum from the particles shown in (a); (c) SAD results for the particles shown in (a); and (d) the dark-field image obtained by filtrating the spot (004) for Ti₂AlC from the SAD results shown in (c), which reveals that the Ti₂AlC phase corresponded to the facet particles.