Ti₃AlC₂ coatings deposited by liquid plasma spraying

Haicheng Yu, Xinkun Suo, Yongfeng Gong, Yuejin Zhu, Jie Zhou, Hua Li, Per Eklund and Qjng Huang

Linköping University Post Print

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

Original Publication:

Haicheng Yu, Xinkun Suo, Yongfeng Gong, Yuejin Zhu, Jie Zhou, Hua Li, Per Eklund and Qjng Huang, Ti₃AlC₂ coatings deposited by liquid plasma spraying, 2016, Surface & Coatings Technology, (299), , 123-128.

<http://dx.doi.org/10.1016/j.surfcoat.2016.04.076>

Copyright: Elsevier

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

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-130257>

Accepted Manuscript

Ti₃AlC₂ coatings deposited by liquid plasma spraying

Haicheng Yu, Xinkun Suo, Yongfeng Gong, Yuejin Zhu, Jie Zhou, Hua Li, Per Eklund, Qing Huang

PII: S0257-8972(16)30359-0
DOI: doi: [10.1016/j.surfcoat.2016.04.076](https://doi.org/10.1016/j.surfcoat.2016.04.076)
Reference: SCT 21151

To appear in: *Surface & Coatings Technology*

Received date: 11 January 2016
Revised date: 16 March 2016
Accepted date: 30 April 2016

Please cite this article as: Haicheng Yu, Xinkun Suo, Yongfeng Gong, Yuejin Zhu, Jie Zhou, Hua Li, Per Eklund, Qing Huang, Ti₃AlC₂ coatings deposited by liquid plasma spraying, *Surface & Coatings Technology* (2016), doi: [10.1016/j.surfcoat.2016.04.076](https://doi.org/10.1016/j.surfcoat.2016.04.076)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Ti₃AlC₂ coatings deposited by liquid plasma spraying

Haicheng Yu^{a,b}, Xinkun Suo^a, Yongfeng Gong^a, Yuejin Zhu^b, Jie Zhou^a, Hua Li^a, Per

Eklund^c, Qing Huang^{a,*}

^aEngineering Laboratory of Specialty Fibers and Nuclear Energy Materials, Ningbo Institute of Materials Engineering and Technology, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, China

^bDepartment of Physics, Ningbo University, Ningbo 315211, Zhejiang, China

^cThin Film Physics Division, Linköping University, IFM, 581 83 Linköping, Sweden

*Corresponding author:

Tel: +86-574-86686062

E-mail: huangqing@nimte.ac.cn

Abstract

Ti_3AlC_2 tends to partially decompose into TiC phase during deposition by traditional thermal spray techniques, preventing their use in surface anti-corrosion applications. Here, Ti_3AlC_2 coatings were synthesized using liquid plasma spraying (LPS). Although the average temperature of particles measured in LPS was higher than 2200 K, enough to decompose Ti_3AlC_2 phase, the resulting sprayed Ti_3AlC_2 particles were intact. This is probably due to formation of a protective oxide on the surface in the high-temperature steam. The phase purity of Ti_3AlC_2 coating was high when using water as solvent, but low with a solvent of a mixture of water and alcohol. Different pH values of the solutions influence the phase purity of Ti_3AlC_2 coatings. The alkaline solutions show detrimental effect on the conservation of Ti_3AlC_2 phase. The mechanism of improved structural integrity of Ti_3AlC_2 phase at high temperature through LPS was revealed by microstructural and compositional analysis.

Key words: liquid plasma spraying, Ti_3AlC_2 , decomposition

1. Introduction

MAX phases, with a general formula $M_{n+1}AX_n$ (M, early transition metal; A, an A-group element; X, carbon or nitrogen; n, 1-3) [1] have attracted attention because of their unique advantage of combined metallic and ceramic merits [2, 3]. On one hand, MAX phases exhibit metallic properties, such as good electrical and thermal conductivity, good machinability, and excellent thermal shock resistance. On the other hand, they exhibit ceramic properties, such as good high temperature mechanical properties [4], and good oxidation resistance and corrosion resistance. Barsoum [5] listed potential applications as substitutes for machinable ceramics, wear and corrosion protection, heat exchangers, components where rotating parts are used, low friction applications based on basal plane lubricity [6] and ohmic contacts to SiC [7-9]. The archetypical MAX phase material, Ti_3AlC_2 , is composed of hexagonal layers of Al separated by the layers of edge-sharing Ti-C. It is considered as a candidate for cladding tube coating materials in nuclear application owing to its good irradiation resistance [10] and good oxidation resistance [11-13].

In order to enable applications in the above fields, several synthesis techniques for MAX phase films have been reported such as chemical vapor deposition (CVD) [14-16], solid state reaction [8, 17,18], physical vapor deposition (PVD) by cathodic arc [19-21] and magnetron sputtering [22, 23]. All these methods present many advantages in fabricating MAX phases, such as ohesion, good compactness, controllable element ratio, and the possibility to synthesize multilayer coatings [1]. However, these processes also have some limitations. For example, a high process

temperature (900°C) is necessary to activate the chemical reactions in CVD [19]. Sputter-deposition allows for synthesis of MAX phases at lower temperature than CVD, but typically still requires a deposition temperature of 700°C or more [1]. In some circumstances, the preparation temperature should be kept low so as not to damage the substrates, especially during the deposition of coatings on steel or other temperature-sensitive substrates [24]. Cold spraying can maintain the integrity of Ti_3AlC_2 phase because of its moderate operation temperature [25-27]. Rech et al. [25] and Gutzmann et al. [26] have fabricated MAX phase coatings using cold spraying. However, because of the poor plasticity of Ti_3AlC_2 , broken particles and cracks were found in the coatings. Recently, thermal spraying has been utilized to fabricate MAX phase coatings [28-30]. The obvious advantage of thermal spraying process over other deposition techniques lies in the fact that the spray facility has no strict requirement on the atmosphere (vacuum or gas-protection) and industrial scale synthesis is readily achievable. However, current popular thermal spraying techniques, such as atmospheric plasma spraying (APS), high velocity oxy-fuel spraying (HVOF), are not much applied to synthesize Ti_3AlC_2 phase coatings because of the high flame temperature which tends to cause severe phase decomposition and/or oxidation of MAX phases [31]. Ti_2AlC , rather than Ti_3AlC_2 , coatings have been fabricated by HVOF [29]. For bulk materials, at high temperature (1550°C), Ti_3AlC_2 phase tends to decompose while Ti_2AlC experienced decomposition to a more limited extent [36]. Because of the lower thermal stability than Ti_2AlC , high-purity Ti_3AlC_2 coatings have not been synthesized by HVOF. It can be concluded that the remaining amount of the

Ti₃AlC₂ phase is low for APS and HVOF.

Another new thermal spraying technology is liquid plasma spraying (LPS). Unlike traditional air plasma spraying, LPS employs a liquid flow to feed powder into heat source instead of the carrier gas. This change bypasses the heating step for the powder by the plasma torch, thus enabling the deposition of thermally-sensitive coatings [32]. Many researchers have used this method to fabricate thermal barrier coatings [33]. However, no liquid plasma sprayed MAX coatings have been reported until now.

Therefore, the aim of this work is to investigate the feasibility of fabricating Ti₃AlC₂ coating from aqueous media using liquid plasma spraying. In order to obtain high purity coatings, a stable aqueous suspension containing Ti₃AlC₂ was prepared by adjusting the pH values. The deposition mechanism of MAX phase deposited using LPS was also discussed.

2. Experimental details

(1) Materials

According to the procedure in reference [34], Ti₃AlC₂ powders were synthesized by spark plasma sintering in our laboratory, and then grinded to break up the agglomerated materials. The particles with a size distribution from 1 to 100 μm (30% of particles are smaller than 8.8 μm, and 80% of particles are smaller than 39.9 μm) were used as raw materials for atmospheric plasma spraying and liquid plasma spraying. 304 stainless steel plates with a dimension of 20×15×2 mm³ were used as substrate. The substrates were sand-blasted to remove the oxides and cleaned with ethanol before deposition.

(2) Ti_3AlC_2 suspension preparation and liquid spraying parameters

The suspensions were prepared by adding 10 wt % Ti_3AlC_2 particles in deionized water.

The mixture of deionized water and alcohol with the ratio of 1:1 was also used at the same content of Ti_3AlC_2 particles. The pH was adjusted by nitric acid (HNO_3) and sodium hydroxide (NaOH).

A plasma spray system (APS-2000, Sulzer Metco) was used to fabricate Ti_3AlC_2 coatings. The spraying distance from the outlet to the substrate was set as 100 mm and the power was 15 ± 0.5 kW. For APS coatings, an F4 torch was utilized using an Ar/ H_2 plasma gas mixture. The F4 torch is a commonly used torch in plasma spraying. Details of the F4 torch can be found in reference [35]. The gun velocity was 0.25 m/s. The same plasma spray system was used to produce both type of the coatings.

A system which detects the velocity and temperature of sprayed particles (DPV) was used to monitor the temperatures of the particles passing through the monitored surface. The distance from outlet to the temperature monitoring instrument was set to 100 mm.

(3) Characterization

The X-ray diffraction (XRD) patterns of powders and coatings were acquired in a diffractometer (D8 Advance, Bruker AXS, Germany) with $\text{Cu K}\alpha$ radiation. The 2θ range, collection time per step and step size were set to $5^\circ - 90^\circ$, 0.2 s and 0.02° , respectively. The surface and cross section were observed using scanning electron microscopy equipped with an energy-dispersive X-ray spectrometer (SEM-EDS, Quanta FEG 250). The voltage and spot size in SEM were 15 kV and 3.5, respectively. Quantitative phase analysis was conducted by means of the Rietveld analysis (TOPAS

software). The peak shape parameters are FPA (Fundamental Parameters Approach). The 2θ range is $5^\circ - 90^\circ$ during Rietveld analysis. Raman (Renishaw inVia Reflex) spectroscopy was used to detect the type of bonding, in the wavenumber range from 50 cm^{-1} to 1800 cm^{-1} . The Nd:YAG laser was focused to a spot size of $\sim 1\text{ }\mu\text{m}$ with an incident power of 6 mW. DPV was used to test temperature and velocity of particles in APS and LPS process. Surface profiler (Alpha-step, KCA Tencor) was used to determine the roughness of Ti_3AlC_2 coating. The scan length and time was $500\text{ }\mu\text{m}$ and 10 s, respectively.

3.1 Phase composition and morphologies of the sprayed powders

XRD analysis was performed in order to investigate the phase transformation of the feedstock powder during deposition. Fig. 1a shows the XRD patterns of feedstock powder and as-sprayed powders using APS and LPS approaches, respectively. The feedstock powders (bottom in Fig. 1a) contained the Ti_3AlC_2 phase in majority (93.2%) and also a small amount of TiC phase (6.8%). After deposition by traditional APS (second from bottom in Fig. 1a), TiC phase became predominant in the coating, and most of the Ti_3AlC_2 phase had been depleted, which suggests that the Ti_3AlC_2 phase decomposed heavily due to the high temperature of the plasma torch. Only 20% of feedstock powders remained in the original phase, while others decomposed and oxidized into Ti_2AlC , TiC, Al_2O_3 and TiO_2 . This result is in agreement with others [31]. The average temperature of particles in APS was higher than 2500 K as determined by the DPV temperature monitoring instrument. This temperature is much higher than

Ti_3AlC_2 decomposition temperature (1300°C) [36].

According to the XRD pattern of LPS coatings deposited with a mixture of water and alcohol (with the ratio of 1:1), most of the Ti_3AlC_2 decomposed (second from top in Fig. 1a). During this spraying process, a flame on the substrate could be observed optically. The flame should be caused by the burning of alcohol, which implies high temperature under these circumstances. However, in aqueous LPS, no flame could be observed. Compared with aqueous LPS, the flame would impart additional heat to cause the decomposition of Ti_3AlC_2 rather than protect Ti_3AlC_2 from decomposition. However, in the coating sprayed by aqueous LPS (with only deionized water as solvent) technique, the Ti_3AlC_2 phase was preserved (top in Fig. 1a). There is no obvious difference in the XRD patterns when compared with the raw powder. The number of peaks and the intensities of peaks are similar. As indicated by the vertical lines (Fig. 1a), the main characteristic peaks of Ti_3AlC_2 ($2\theta=9.517$ and 39.037) are strong for coatings synthesized by aqueous LPS. The phase-purity of Ti_3AlC_2 in the LPS coating was calculated, and the result shows that the percentage of Ti_3AlC_2 phase in aqueous LPS coatings was 84.5%, which is considerably higher than what has been achieved by traditional thermal spraying [31]. The average velocity of the particles in LPS is 90 m/s. Another interesting observation is that no TiO_2 phase was found in the XRD pattern of aqueous LPS coatings. This is in good agreement with previous work [37, 38], where the early stages of oxidation of Ti_3AlC_2 were investigated at 1373 K and 773 K. In our experiment, the spraying time was extremely short ($\sim 10^{-3}\text{s}$) and the temperature was much higher than 1373 K. In addition, the lack of observed TiO_2 may be attributed to

the different nucleation and growth rate of Al_2O_3 and TiO_2 as a function of the temperature [12, 13]. Low temperature facilitates the preferential nucleation of TiO_2 , while at high temperature, the nucleation of Al_2O_3 is preferred over TiO_2 . In LPS process, the temperature is higher than 2200 K which facilitates the nucleation of alumina. No TiO_2 could be found in the XRD patterns.

In order to see whether TiO_2 formed in the aqueous LPS coatings, Raman spectroscopy was used, as shown in figure 1b. A Raman mode at 400 cm^{-1} is seen in the spectra, which is identified as rutile [39]. The rutile is presumably not observed in XRD because it is too fine-grained and/or has low phase content. Apart from TiO_2 (vary from 100 cm^{-1} to 1000 cm^{-1}), two vibrational modes at 270 cm^{-1} and 610 cm^{-1} which are identified as intrinsic vibrational modes of Ti_3AlC_2 [40] were detected. Some vibrational modes of Ti_3AlC_2 (there are six in total [40]) are not observed in our Raman spectroscopy results. The reason may be that the structure of Ti_3AlC_2 experienced some disorder, and that some of the Raman peaks are quite weak [41].

Additional peaks in the spectrum of coating appeared at 1320 and 1580 cm^{-1} . These peaks could be distinguished as graphite band (G band) and disordered/nanocrystalline carbon band (D band) [42, 43], which demonstrates the formation of carbon after LPS. This result is in agreement with references [44, 45]. The affinity of metals to oxygen is higher than that of carbon [44], resulting in the formation of metallic oxides and the survival of carbon from oxidation. Similarly, carbon is present after hydrothermal oxidation and air oxidation of transition metal carbides [45]. But in this Raman spectroscopy, the intensity of the D and G bands was low, which means low

free-carbon content in the coatings. Because of the reaction between water vapor and carbon, the content of remaining carbon should be in accordance with these Raman results. According to the reference [46,47], CO_2 possesses higher partial pressures than CO at any temperature. At high temperature (higher than 500°C), the partial pressure of H_2 is far higher than CH_4 . In the LPS process, the average temperature is higher than 2200 K and the water vapor is abundant which all facilitate the formation of CO_2 and H_2 .

Surface morphologies of powders which were sprayed into liquid nitrogen by APS and LPS are presented in Fig. 2a to 2d. As shown in Fig. 2a, the morphology of the feedstock powders is irregular. In addition, small submicron-scale chips can be found on the particle surface. Compared with feedstock powders, some spherical particles which indicated the decomposition of Ti_3AlC_2 occurred in the APS process (shown in Fig. 2b). Additionally, newly-occurring phases in XRD patterns of APS coating verified the decomposition behavior. The high temperature caused the decomposition of Ti_3AlC_2 and then remelted, forming spherical particles. EDS of the spherical particle surface and cross-section (as seen in Table 2) was applied to analyse the composition of these spherical particles. The result is that the constituent of this spherical particle is a mixture of titanium oxides and aluminium oxides.

Fig. 2c shows the morphologies of particles sprayed into liquid nitrogen by aqueous LPS. It presents a similar morphology to the feedstock particles which implies high content of retained Ti_3AlC_2 . According to the XRD pattern of aqueous LPS and SEM micrograph (Fig. 2c), the Ti_3AlC_2 content and morphology is consistent with feedstock

powders. Only tiny amounts of spherical particles could be found in aqueous LPS powders. As the solvent was a mixture of water and alcohol with the volume ratio of 1:1, the morphologies were significantly different from that of feedstock powders. In this spraying condition, some spherical particles occurred and the edges of particles became smooth and diffuse, indicating that the temperature was high enough to cause Ti_3AlC_2 decomposition. The difference between these methods is mainly the Ti_3AlC_2 particle temperature, which determines the decomposition of Ti_3AlC_2 . Considering all of this, deionized water was used as solvent in the following experiments.

3.2 Effect of solution characteristics on fabrication of Ti_3AlC_2 coatings

As is known, Ti_3AlC_2 is more stable in basic solution than in acidic solution [48]. However, in the LPS process, circumstances differ greatly from the situation in a static solution. For example, the processing temperature is high. Therefore, it is necessary to know the influence of pH value of aqueous solution using LPS. Accordingly, pH values of the liquid were adjusted by NaOH and HNO_3 , and the effect of solution characteristics on the microstructure of Ti_3AlC_2 coatings was investigated. XRD patterns of Ti_3AlC_2 coatings are shown in Fig. 3. The evolution of phase content in coatings as a function of pH values of liquid solutions was also studied, and the result is summarized in Table 1. The content of Ti_3AlC_2 shows little divergence in acidic solution and neutral solution, respectively. Ti_3AlC_2 is the predominately phase in these coatings.

However, it can be found that the content of Ti_3AlC_2 phase remaining in the coatings deposited using alkaline solution was lower than that in coatings deposited using acidic

and neutral solution. Besides water vapor, hydroxyl ion in alkaline solution can also react with Ti_3AlC_2 . As aluminium can be leached out from Ti_3AlC_2 , it can immediately react with OH^- which makes more Ti_3AlC_2 will be decomposed. This explanation may account for the influence of pH values.

3.3 Protective mechanism of Ti_3AlC_2 coatings in aqueous LPS

Apart from the evaporation of water which absorbed heat from the spraying, other factors might play a role in protecting Ti_3AlC_2 from heavy decomposition. The average temperature of particles in aqueous LPS measured by DPV2000 was 2261 K, which exceeded the decomposition temperature of Ti_3AlC_2 particles. The average temperature of particles in APS is 2615 K. These two temperatures exceeded the decomposition temperature, but the results exhibited significant divergence. The composition of in-flight Ti_3AlC_2 particles prior to impact to substrates was also investigated in order to reveal the deposition mechanism of aqueous LPS coatings. Ti-Al bonds in Ti_3AlC_2 phase are relatively weak and the Al element is highly active, which is characterized by low vacancy formation energy and vacancy migration energy [50, 51]. The layered structure is favorable for the fast diffusion of water vapor or/and oxygen in the grains, which facilitates the rapid reaction of aluminium.

The reaction between Al and water vapor or/and oxygen may occur at the surface. The in-diffusion rate of water vapor and oxygen and out-diffusion rate of aluminium in alumina is slow. Besides the slow diffusion rate, the whole time of spraying process is extremely short. Therefore, the formed alumina attached to the surface plays an important role in protecting Ti_3AlC_2 from heavy decomposition. The absence of Raman

signal from the coatings is due to the screening effect of thin outer layer of titania phase. In order to support our discussion, cross sections of collected Ti_3AlC_2 particle were observed. The Ti_3AlC_2 powders were sprayed into liquid nitrogen, and then dried. As shown in Fig. 4, the contents of Al and O elements suddenly increased near the surface of the particles. Meanwhile, the Ti elemental content greatly decreased at the surface, which suggested that alumina formed outside particles in water vapor.

3.4 Microstructure of Ti_3AlC_2 coatings

The Ti_3AlC_2 coatings were prepared using aqueous LPS. The cross section microstructure and surface morphology of coatings are shown in Fig. 5a and 5b, respectively. In Fig. 5a, it can be seen that the thickness of the coatings ranged from 10 μm to 20 μm , and no cracks could be found in the coating. The crack observed in the cross section micrograph is at the interface between the coating and the epoxy resin. Some pores can be observed in the cross-section (Fig. 5a). Fig. 5b shows that the particles on surface of the coatings exhibit a similar morphology to the feedstock particles. Compared with the morphology of particles sprayed in liquid nitrogen (Fig. 2c), the morphology of particles in the corresponding coating (Fig. 5b) is similar. Their morphologies are all consistent with that of the raw powder.

From the observed surface morphology of coatings, it could also be found that the coatings exhibit a large roughness. Some cavities smaller than 4 μm was also found on the surface of coatings. The roughness of the Ti_3AlC_2 coating determined by a surface profiler varies from less than 1 μm to 8 μm . Because of the low densification, the adhesion could not be obtained by pull-out test.

As a concluding point, LPS is a feasible method to synthesize Ti_3AlC_2 coatings, but also leaves space for the further improvement (techniques to reduce the residual pores and roughness of the coatings). The drop of velocity of Ti_3AlC_2 particles due to the evaporation of solvent during LPS process is the key factor. In future work, the protection of Ti_3AlC_2 particles by steam and the minimization of kinetic-energy-loss due to solvent evaporation, should be balanced to achieve dense coating fabrication.

4. Conclusions

Liquid plasma spraying was used to fabricate Ti_3AlC_2 coatings, and the influences of pH value and acid property on microstructures of coatings were evaluated. The main result can be drawn:

- (1) The fabrication of Ti_3AlC_2 coatings with high Ti_3AlC_2 content using liquid plasma spraying is feasible.
- (2) The pH value of solutions plays an important role for the purity of Ti_3AlC_2 coatings. The content of Ti_3AlC_2 in coating is high when the solvent is acidic and neutral solution. The content of Ti_3AlC_2 phase remained in the coatings deposited using alkaline solution was lower than that in acidic and neutral solution.
- (3) The high content of Ti_3AlC_2 phase in coatings is attributed to the formation of alumina protective phase during the decomposition process of Ti_3AlC_2 phase, which impedes further decomposition.

5. Acknowledgements

The present work was supported by the National Natural Science Foundation of China (Grant No. 91226202 and 91426304), the “Strategic Priority Research Program” of the

Chinese Academy of Sciences (Grant No. XDA 02040105 and XDA03010305), and the Major Project of the Ministry of Science and Technology of China (Grant No.2015 ZX06004-001). P. E. also acknowledges support from the Swedish Foundation for Strategic Research (SSF) through the Future Research Leaders 5 program and the Synergy Grant FUNCASE.

References

- [1] P. Eklund, M. Beckers, U. Jansson, H. Högberg and L. Hultman, The $Mn+1AX_n$ phases: materials science and thin film processing, *Thin Solid Films*, 518 (2010) 1851-1878.
- [2] M.W. Barsoum, N. Tzenov, A. Procopio, T. El-Raghy, M. Ali, Oxidation of $Ti_{n+1}AlX_n$ ($n=1-3$ and $X = C, N$) - II. Experimental results, *J Electrochem Soc*, 148 (2001) C551-C562.
- [3] M.W. Barsoum, Oxidation of $Ti_{n+1}AlX_n$ ($n=1-3$ and $X = C, N$) - I. Model, *J Electrochem Soc*, 148 (2001) C544-C550.
- [4] M. W. Barsoum, M. Radovic, Elastic and Mechanical Properties of the MAX Phases, *Annu. Rev. Mater. Res.*, 41 (2011) 195-227.
- [5] M.W. Barsoum, The $M(N+1)AX(N)$ phases: A new class of solids; Thermodynamically stable nanolaminates, *Prog Solid State Ch*, 28 (2000) 201-281.
- [6] Z.M. Sun, Progress in research and development on MAX phases: a family of layered ternary compounds, *International Materials Reviews*, 56 (2011) 143-166.
- [7] S. Tsukimoto, T. Sakai, M. Murakami, Electrical properties and microstructure of ternary Ge/Ti/Al ohmic contacts to p-type 4H-SiC, *J Appl Phys*, 96 (2004) 4976-4981.
- [8] H. Fashandi, M. Andersson, J. Eriksson, J. Lu, K. Smedfors, C.M. Zetterling, A.L. Spetz, P. Eklund, Single-step synthesis process of Ti_3SiC_2 ohmic contacts on 4H-SiC by sputter-deposition of Ti, *Scripta Mater*, 99 (2015) 53-56.
- [9] K. Buchholt, R. Ghandi, M. Domeij, C.M. Zetterling, J. Lu, P. Eklund, L. Hultman, A.L. Spetz, Ohmic contact properties of magnetron sputtered Ti_3SiC_2 on n- and p-type 4H-silicon carbide, *Appl Phys Lett*, 98 (2011) 042108
- [10] K.R. Whittle, M.G. Blackford, R.D. Aughterson, S. Moricca, G.R. Lumpkin, D.P. Riley, N.J. Zaluzec, Radiation tolerance of $Mn+1AX_n$ phases, Ti_3AlC_2 and Ti_3SiC_2 , *Acta Materialia*, 58 (2010) 4362-4368.
- [11] X.H. Wang, Y.C. Zhou, Oxidation behavior of Ti_3AlC_2 at 1000–1400 °C in air, *Corros Sci*, 45 (2003) 891-907.
- [12] D.J. Tallman, B. Anasori, M.W. Barsoum, A Critical Review of the Oxidation of Ti_2AlC , Ti_3AlC_2 and Cr_2AlC in Air, *Materials Research Letters*, 1 (2013) 115-125.
- [13] S. Basu, N. Obando, A. Gowdy, I. Karaman, M. Radovic, Long-Term Oxidation of

Ti₂AlC in Air and Water Vapor at 1000-1300 degrees C Temperature Range, J Electrochem Soc, 159 (2012) C90-C96.

[14] S. Jacques, H. Di-Murro, M.P. Berthet, H. Vincent, Pulsed reactive chemical vapor deposition in the C-Ti-Si system from H₂/TiCl₄/SiCl₄, Thin Solid Films, 478 (2005) 13-20.

[15] H. Fakhri, S. Jacques, M.P. Berthet, F. Bosselet, O. Dezellus, J.C. Viala, The growth of Ti₃SiC₂ coatings onto SiC by reactive chemical vapor deposition using H₂ and TiCl₄, Surface & Coatings Technology, 201 (2006) 3748-3755.

[16] H. Fakhri, S. Jacques, O. Dezellus, M.P. Berthet, F. Bosselet, M. Sacerdote-Peronnet, J.C. Viala, Phase equilibria and reactive chemical vapor deposition (RCVD) of Ti₃SiC₂, J Phase Equilib Diff, 29 (2008) 239-246.

[17] B. Veisz, B. Pecz, Polarity dependent Al-Ti contacts to 6H-SiC, Applied Surface Science, 233 (2004) 360-365.

[18] S. Tsukimoto, K. Nitta, T. Sakai, M. Moriyama, M. Murakami, Correlation between the electrical properties and the interfacial microstructures of TiAl-based ohmic contacts to p-type 4H-SiC, J Electron Mater, 33 (2004) 460-466.

[19] J. Rosen, L. Ryves, P. Persson, M. Bilek, Deposition of epitaxial Ti₂AlC thin films by pulsed cathodic arc, J Appl Phys, 101 (2007) 056101

[20] M.C. Guenette, M.D. Tucker, M. Ionescu, M.M.M. Bilek, D.R. McKenzie, Cathodic arc co-deposition of highly oriented hexagonal Ti and Ti₂AlC MAX phase thin films, Thin Solid Films, 519 (2010) 766-769.

[21] A. Mockute, P.O.A. Persson, F. Magnus, A.S. Ingason, S. Olafsson, L. Hultman, J. Rosen, Synthesis and characterization of arc deposited magnetic (Cr,Mn)₂AlC MAX phase films, Phys Status Solidi-R, 8 (2014) 420-423.

[22] O. Wilhelmsson, J.P. Palmquist, E. Lewin, J. Emmerlich, P. Eklund, P.O.A. Persson, H. Hogberg, S. Li, R. Ahuja, O. Eriksson, L. Hultman, U. Jansson, Deposition and characterization of ternary thin films within the Ti-Al-C system by DC magnetron sputtering, J Cryst Growth, 291 (2006) 290-300.

[23] D.P. Sigumonrong, J. Zhang, Y.C. Zhou, D. Music, J.M. Schneider, Synthesis and elastic properties of V₂AlC thin films by magnetron sputtering from elemental targets, J Phys D Appl Phys, 42 (2009) 185408

[24] Y. Liang, Z.Q. Sun, J.X. Chen, X.X. Liu, Y.C. Zhou, Electrophoretic Deposition of Ti₃Si(Al)C₂ from Aqueous Suspension, J Am Ceram Soc, 93 (2010) 1916-1921.

- [25] S. Rech, A. Surpi, S. Vezzu, A. Patelli, A. Trentin, J. Glor, J. Frodelius, L. Hultman, P. Eklund, Cold-spray deposition of Ti₂AlC coatings, *Vacuum*, 94 (2013) 69-73.
- [26] H. Gutzmann, F. Gärtner, D. Höche, C. Blawert, T. Klassen, Cold spraying of Ti₂AlC MAX-phase coatings, *Journal of thermal spray technology*, 22 (2013) 406-412.
- [27] H. Assadi, F. Gartner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Materialia*, 51 (2003) 4379-4394.
- [28] V. Pasumarthi, Y. Chen, S.R. Bakshi, A. Agarwal, Reaction synthesis of Ti₃SiC₂ phase in plasma sprayed coating, *J Alloy Compd*, 484 (2009) 113-117.
- [29] J. Frodelius, M. Sonestedt, S. Bjorklund, J.P. Palmquist, K. Stiller, H. Hogberg, L. Hultman, Ti(2)AlC coatings deposited by High Velocity Oxy-Fuel spraying, *Surface & Coatings Technology*, 202 (2008) 5976-5981.
- [30] J. Frodelius, E.M. Johansson, J.M. Cordoba, M. Oden, P. Eklund, L. Hultman, Annealing of Thermally Sprayed Ti₂AlC Coatings, *Int J Appl Ceram Tec*, 8 (2011) 74-84.
- [31] R. Trache, R. Puschmann, C. Leyens, L. Berger, B. Matthey, M. Herrmann, Thermally sprayed Ti₃SiC₂ and Ti₂AlC MAX-phase coatings, *Conference proceedings: Int. Thermal Spray Conf.* (2013) 74-78
- [32] H. Kassner, R. Siegert, D. Hathiramani, R. Vassen, D. Stoeber, Application of suspension plasma spraying (SPS) for manufacture of ceramic coatings, *Journal of Thermal Spray Technology*, 17 (2008) 115-123.
- [33] N. Schlegel, S. Ebert, G. Mauer, R. Vassen, Columnar-Structured Mg-Al-Spinel Thermal Barrier Coatings (TBCs) by Suspension Plasma Spraying (SPS), *Journal of Thermal Spray Technology*, 24 (2015) 144-151.
- [34] W.B. Zhou, B.C. Mei, J.Q. Zhu, Fabrication of high-purity ternary carbide Ti₃AlC₂ by spark plasma sintering (SPS) technique, *Ceram Int*, 33 (2007) 1399-1402.
- [35] J.F. Coudert, V. Rat, Influence of configuration and operating conditions on the electric arc instabilities of a plasma spray torch: role of acoustic resonance, *Journal of Physics D: Applied Physics*, 41 (2008) 205208.
- [36] W.K. Pang, I.M. Low, B.H.O. Connor, A.J. Studer, V.K. Peterson, Z.M. Sun, J.P. Palmquist, Comparison of thermal stability in MAX 211 and 312 phases, *Journal of Physics: Conference Series*, 251 (2010) 012025-012029.

- [37] G.M. Song, Y.T. Pei, W.G. Sloof, S.B. Li, J.T.M. De Hosson, S. van der Zwaag, Early stages of oxidation of Ti_3AlC_2 ceramics, *Mater Chem Phys*, 112 (2008) 762-768.
- [38] J. Frodelius, J. Lu, J. Jensen, D. Paul, L. Hultman, P. Eklund, Phase stability and initial low-temperature oxidation mechanism of Ti_2AlC thin films, *Journal of the European Ceramic Society*, 33 (2013) 375-382.
- [39] V. Swamy, Size-dependent modifications of the first-order Raman spectra of nanostructured rutile TiO_2 , *Phys Rev B*, 77 (2008) 195414.
- [40] V. Presser, M. Naguib, L. Chaput, A. Togo, G. Hug, M.W. Barsoum, First-order Raman scattering of the MAX phases: Ti_2AlN , $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$, Ti_2AlC , $(\text{Ti}_{0.5}\text{V}_{0.5})_2\text{AlC}$, V_2AlC , Ti_3AlC_2 , and Ti_3GeC_2 , *J Raman Spectrosc*, 43 (2012) 168-172.
- [41] D.D. Sun, A.G. Zhou, Z.Y. Li, L.B. Wang, Corrosion behavior of Ti_3AlC_2 in molten KOH at 700 degrees C, *J Adv Ceram*, 2 (2013) 313-317.
- [42] N.S. Jacobson, Y.G. Gogotsi, M. Yoshimura, Thermodynamic and experimental study of carbon formation on carbides under hydrothermal conditions, *J. Mater. Chem.*, 5 (1995) 595-601.
- [43] E. Barringer, Z. Faiztompkins, H. Feinroth, T. Allen, M. Lance, H. Meyer, L. Walker, E. Lara - Curzio, Corrosion of CVD silicon carbide in 500 C supercritical water, *J Am Ceram Soc*, 90 (2007) 315-318.
- [44] S. Shimada, Oxidation and mechanism of single crystal carbides with formation of carbon, *J Ceram Soc Jpn*, 109 (2001) S33-S42.
- [45] S. Shimada, Interfacial reaction on oxidation of carbides with formation of carbon, *Solid State Ionics*, 141 (2001) 99-104.
- [46] H.B. Zhang, V. Presser, K.G. Nickel, C. Berthold, Y.C. Zhou, Hydrothermal Oxidation Behavior of Bulk Titanium Aluminum Carbide, *J Am Ceram Soc*, 94 (2011) 3460-3466.
- [47] H.B. Zhang, X. Wang, K.G. Nickel, Y.C. Zhou, Experimental and thermodynamic study of the hydrothermal oxidation behavior of Ti_3SiC_2 powders, *Scripta Mater*, 59 (2008) 746-749.
- [48] D. Li, Y. Liang, X.X. Liu, Y.C. Zhou, Corrosion behavior of Ti_3AlC_2 in NaOH and H_2SO_4 , *Journal of the European Ceramic Society*, 30 (2010) 3227-3234.

-
- [49] L. He, Y. Zhou, Y. Bao, Z. Lin, J. Wang, Synthesis, physical, and mechanical properties of bulk $\text{Zr}_3\text{Al}_3\text{C}_5$ ceramic, *J Am Ceram Soc*, 90 (2007) 1164-1170
- [50] T. Liao, J.Y. Wang, Y.C. Zhou, First-principles investigation of intrinsic defects and (N, O) impurity atom stimulated Al vacancy in Ti_2AlC , *Appl Phys Lett*, 93 (2008) 261911
- [51] X.H. Wang, F.Z. Li, J.X. Chen, Y.C. Zhou, Insights into high temperature oxidation of Al_2O_3 -forming Ti_3AlC_2 , *Corros Sci*, 58 (2012) 95-103.

Figure captions:

Fig. 1a XRD patterns of feedstock powder, APS coating, LPS coating (the solvent is a mixture of water and alcohol), aqueous LPS coating (the solvent is water). Fig.1b Raman spectra of Ti_3AlC_2 coatings synthesized by aqueous LPS.

Fig. 2 SEM micrographs (secondary electron images) of (a) feedstock powders, (b) APS powders, (c) LPS powders (the solvent is water), (d) LPS powders (the solvent is a mixture of water and alcohol)

Fig. 3 X-ray diffractogram from as-sprayed Ti_3AlC_2 coating with different pH values

Fig. 4 Line scanning analysis of particle cross-section by LPS

Fig. 5 SEM micrographs (secondary electron images) of (a) cross section and (b) surface morphology of the Ti_3AlC_2 coating

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1 The percentage of phases in coatings by aqueous LPS

pH	Phase Content				Rwp[49]	χ^2
	Ti ₃ AlC ₂	Ti ₂ AlC	Al ₂ O ₃	TiC	(wt%)	
1	82.56	0.87	10.9	5.68	7.678	1.57
3	80.09	1.25	12.51	6.15	5.897	1.39
7	84.48	0.02	5.85	9.65	8.897	1.44
12	77.34	1.26	11.49	9.91	9.054	1.68
14	74.32	1.22	13.27	11.19	8.750	1.70

 χ^2 : the goodness –of-fit

Rwp: R-weighted pattern

Table 2 The element content of surface and cross section of spherical particle
Estimated error (± 1 at%)

Element	surface	Cross section
C	14	6
O	61	67
Al	4	5
Ti	21	22

Highlights

- (1) High purity of Ti_3AlC_2 coatings were fabricated using liquid plasma spraying
- (2) The effects of solution properties on coating microstructures were evaluated
- (3) The deposition mechanism of liquid plasma sprayed Ti_3AlC_2 coatings was discussed