

Synthesis and characterization of aluminum titanium carbonitride TiAlCN via mechanical alloying

J A Avila^{1,3}, H E Jaramillo^{1,2,4*}, N A de Sanchez^{1,2,4} and H Sánchez Sthepa^{3,4}

¹Grupo Ciencia e Ingeniería de Materiales, ²Departamento de Energética y Mecánica, Universidad Autónoma de Occidente

³Escuela de Materiales, Universidad del Valle, ⁴Centro de Excelencia de Nuevos Materiales, Cali-Colombia

Received 21 April 2010; revised 29 July 2010; accepted 30 July 2010

This study presents synthesis of titanium aluminum carbonitrides alloy (TiAlCN) by mechanical alloying in Attritor ball mill from elemental powders of titanium, aluminum and graphite in nitrogen atmosphere. TiAlCN was characterized by SEM, XRD, DSC and FTIR techniques. XRD showed presence of titanium aluminum nitride, aluminum nitride, titanium carbide and titanium aluminum carbon nitride, while SEM showed existence of micro and nano particles with high agglomeration. Energy-dispersive spectroscopy (EDS) analysis shows a homogeneous distribution of elements, and mapping analysis from X-rays confirms distribution of elements.

Keywords: Carbides, Elemental powders, Mechanical alloying, Nitrides, Titanium aluminum carbonitrides alloy

Introduction

Development of Ti-Al-N ternary alloy gives an increase in hardness and oxidation resistance in comparison with binary alloy TiN¹. Quaternary alloys type, titanium aluminum carbonitride titanium (Ti-Al-N-C) has been produced by pulsed laser deposition technique²⁻³, magnetron sputtering technique⁶, and chemical depositions techniques⁴. Titanium aluminum carbonitrides alloy (TiAlCN) hard coating shows high wear and erosion resistance, under high cutting velocity and without lubrication⁶. This study presents synthesis by mechanical alloying and characterization of powder alloy TiAlCN as target to obtain hard coatings.

Experimental Section

TiAlCN powder (Ti, 55.1; Al, 31.0; and C, 13.9%) was obtained by mechanical alloying in a ball milling attritor of vertical impeller⁶. A stainless steel vial and various Cr steel balls (diam, 6-8 mm) were used. Elemental powder contained: pure Ti (particle size, 150 μm), 99.7 wt%; Al (particle size, < 200 μm), 99.95 wt%; and C (particle size, < 45 μm), 99.99 wt%. Mill container air was evacuated using a vacuum pump and then filled with nitrogen gas. Mass balls and powder ratio was 70:1, with 500 rpm constant rotational velocity for 140 h.

Compaction process was carried out for specimen 1 with 70 h milling, and specimen 2 with 140 h milling using a universal compression machine, which has a 2000 KN loud cell and a compacting matrix that allows obtaining targets (diam, 1.2 cm). Powder material was compacted (as specimens 1 and 2 of 1 g each), by applied pressure (800 MPa), and target did not present visible defects and was easily ejected from die.

Sintering was realized in Nabertherm furnace model LHT 02/1. Specimen 1 was sintered at 1000°C for 1 h with a heating rate of 5°C/min, and specimen 2 at 1400°C for 2 h with a heating rate of 10°C/min. Sintering at 1400°C target showed cracks in bulk in many pieces. Sintering at 1000°C target showed a light delamination, indicating phase transformation between 25-1000°C, after having used differential calorimetry scanning (DSC) to corroborate.

X-Ray diffraction analyses (XRD) was carried out in a Panalytical reference X'Pert PRO MPD with Cu ceramic and solid state detector reference PixCel. Microstructure of milled powder, Energy-dispersive spectroscopy (EDS) and mapping of elements was studied in a SEM JEOL JSM 6490LV Scanning Electron Microscope (SEM). Samples transition temperatures were measured by a TA Instruments SDT Q600 Differential Scanning Calorimetry (DSC) Analyzer. Powders were heated to 1000°C at a rate of 10°C/min, and Fourier Transform Infrared Spectroscopy

*Autor for correspondence
E-mail: hjsuarez@uao.edu.co

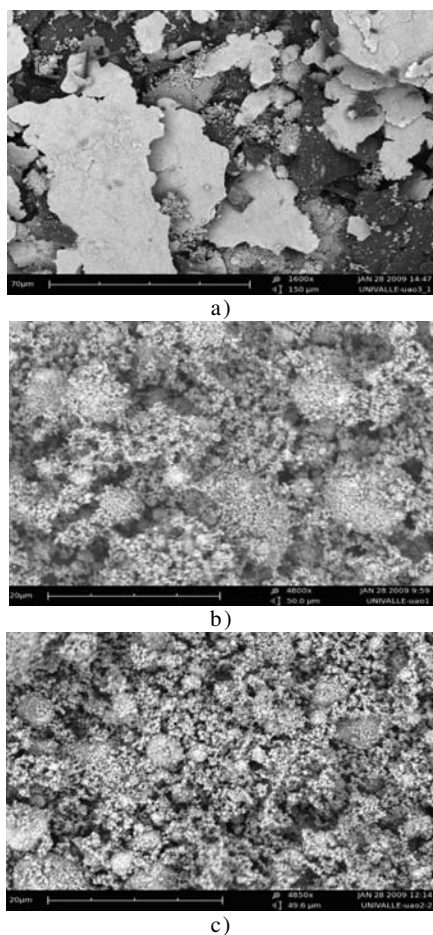


Fig. 1—SEM images; a) Powder without milling process, 4800X; b) Specimen 1 with 70 h of milling, 4850X; and c) Specimen 2 with 140 h of milling, 4850X

(FTIR) analysis was done in Thermo Electron Corporation IR 200 Spectrometer.

Results and Discussion

Al, Ti and C powders were manually mixed for better homogenization of elements. Laminar, flakes, and porous particles of Ti, Al and C were displayed with maximum size of 35 μm (Fig. 1). Specimen 2 with 140 h of milling (Fig. 1c) showed more homogeneity than specimen 1 with 70 h of milling. Clusters and porous particles, showed a particle size of 1-5 μm . EDS micro-analysis was located on 3 different places in each specimen, with 70 h and 140 h milling time respectively (Fig. 2). Under X-ray maps realized with SEM, for specimens 1 and 2 (Fig. 3), Ti Al, C and nitrogen elements were found homogeneously distributed in surface tested; Ti showed more homogeneity. XRD patterns milled powders showed (Fig. 4) presence of titanium aluminum nitride, aluminum nitride,

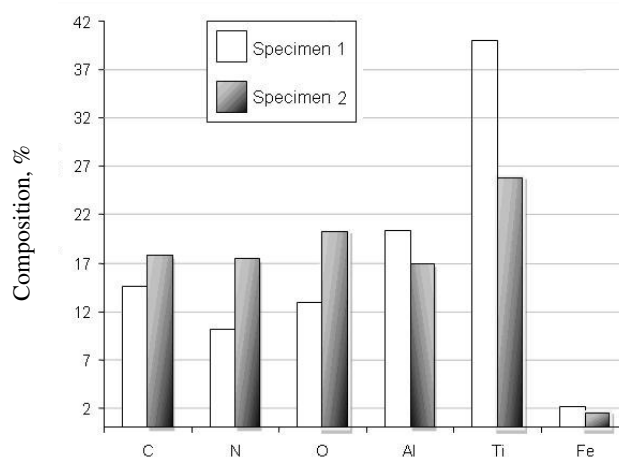


Fig. 2—Bar diagram of average quantitative analysis of specimens 1 and 2

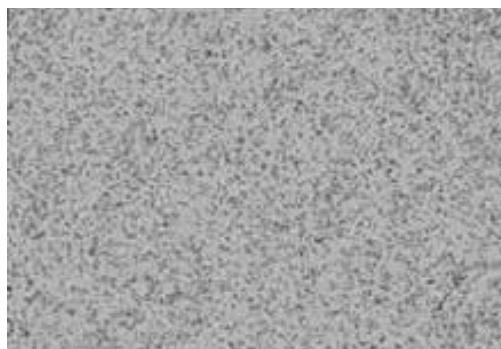


Fig. 3—X-ray map SEM of Ti in specimen 1

titanium carbide, aluminum titanium and carbon nitride. Refined XRD results indicated that in case of specimen 1 with 70 h of milling time, carbon nitride has highest content of total elements (54.5%); other elements present were aluminum titanium (15.2%), titanium aluminum nitride (12.1%), aluminum nitride (10.1%) and titanium carbide (8.1%). In case of specimen 2, with 140 h of milling, refining of XRD patterns showed presence of carbon nitride (57.6%), aluminum titanium (16.2%), titanium aluminum nitride (14.1%), titanium carbide (9.1%) and aluminum titanium nitride (3.0%).

DSC curves present phase transformation at 417°C and 423°C for 70 h (Fig. 5a) and 140 h (Fig. 5b) respectively, confirming that cracking in sintering process is due to heating rate, 10°C/min, from 25°C to 1400°C, in comparison to heating rate 5°C/min, from 25°C to 1000°C whose specimen do not show fracture, only light delamination. FTIR spectrum (Fig. 6) demonstrates presence of compounds containing Al, C, N, O-H in both specimens, corresponding to 70 h and 140 h of milling time. Bands at 3800 and 2900 cm^{-1} corresponds to O, N and H atoms⁷⁻⁸, while peak between

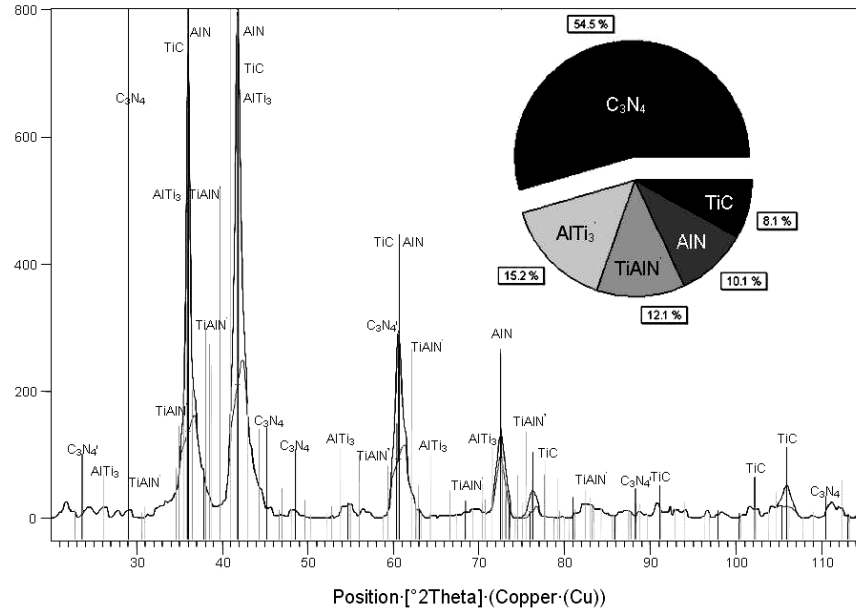
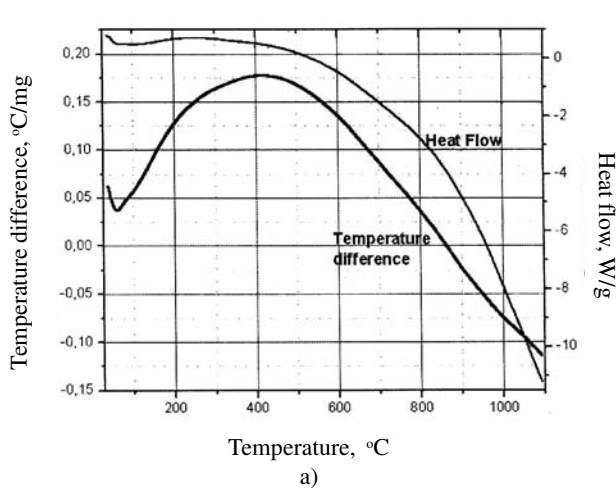
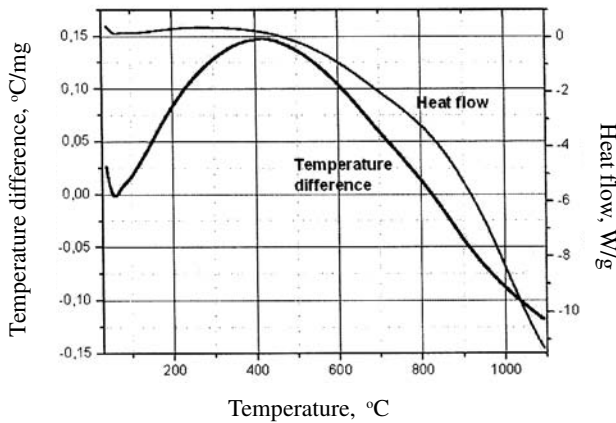


Fig. 4— XRD spectrum of elements present in alloy, 70 h of milling



a)



b)

Fig. 5—DSC curve; a) Specimen 1 whit 70 h of milling; b) Specimen 2 with 140 h of milling

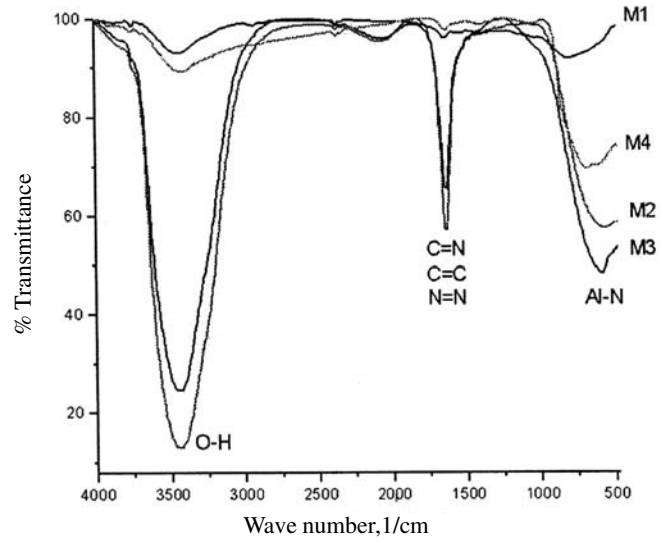


Fig. 6—FTIR spectrum of powder specimen analyzed at different temperatures of sintering (M1, alloyed material with 70 h of milling; M2, alloy material with 140 h of milling; M3, alloyed powder with 70 h and sintering at 1000°C; and M4, alloyed powder with 70 h and sintering at 1400°C)

1630 and 1645 cm^{-1} corresponds to double bonds of C=N, C=C and N=N. A band located at 600, 950 and 980 cm^{-1} is associated with Al-N phases⁹; a wide band located between 1300 and 1700 cm^{-1} is correlated with graphite¹⁰.

Conclusions

Powders processed by mechanical alloying with 70 h and 140 h of milling, were analyzed with FTIR and

XRD characterization techniques. Presence of carbon nitride, titanium aluminum, titanium aluminum nitride, aluminum nitride and titanium carbide compounds was found. SEM images showed evolution of particle size in initial state, 70 h and 140 h of milling time, confirming size reduction from 35 μm to 1 μm in final state of milling. EDS and mapping analyses present a successful elements homogenous distribution of TiAlCN alloys. EDS showed a phase transition close to 420°C; therefore it is suggested that sintering process is to be made with a heating rate over 10°C/min in order to avoid phase transition.

Acknowledgments

Authors thanks support of Colciencias, Universidad Autónoma de Occidente and its Languages Institute, Material School of Universidad del Valle for DSC and SEM characterization; Universidad Nacional de Medellin for obtaining and analyzing XRD patterns by Alejandro Toro and Adrian Gomez; FTIR test was realized in Cauca University. This study was partially sponsored by CENM under grant no. RC-043-2005.

References

- Lai C, Cheng K, Lin S & Yeh J, Mechanical and tribological properties of multi-element (AlCrTaTiZr)N coatings, *Surface Coatings Technol*, **202** (2008) 3732-3738.
- Lackner J M, Waldhauser W, Ebner R, Bakker R J, Schöberl T & Major B, Room temperature pulsed laser deposited (Ti, Al) C_xN_{1-x} coatings chemical, structural, mechanical and tribological properties, *Thin Solid Films*, **468** (2004) 125-133.
- Lackner J M, Waldhauser W, Ebner R, Keckes J & Schöberl T, Room temperature deposition of (Ti,Al)N and (Ti,Al)(C,N) coatings by pulsed laser deposition for tribological applications, *Surface Coatings Technol*, **177-178** (2004) 447-452.
- Shieh J & Hon M H, Observation of plastic deformation in TiAlCN/a-C ceramic nanocomposite coating, *Appl Phys*, **A80** (2005) 131-134.
- Zhang X, Jiang J, Yuqiao Z, Lin J, Wang F & Moore J J, Effect of carbon on TiAlCN coatings deposited by reactive magnetron sputtering, *Surface Coatings Technol*, **203** (2008) 594-597.
- Torres A F, Torres J G, Jaramillo H E, de Sánchez N A & Sánchez H, Obtención de blancos de carburo de titanio TiC mediante aleamiento mecánico, *Suplemento de la Revista Latinoamericana de Metalurgia y Materiales*, **S1** (2009) 851-855.
- Castañeda J P & Martínez P, *Evaluación de la tensión, elongación y temperatura de transición vítrea en los termoplásticos obtenidos a partir de almidones nativos de achira y cidra papa mediante el método "casting"*, Undergraduate Thesis, Universidad del Cauca, Facultad de Ciencias Agropecuarias, Popayán, Colombia, 2009.
- Rosliza R, WanNik W B, Izman S & Prawoto Y, Anti-corrosive properties of natural honey on Al-Mg-Si alloy in sea water, *Curr Appl Phys* **10** (2010) 923-929.
- Yate L, Aperador W, Caicedo J C, Espinoza F J, Zambrano G & Muñoz J, Efecto del Voltaje Bias D.C. en las propiedades electroquímicas de películas delgadas de AlN obtenidas por Medio de la técnica Magnetron Sputtering RF, *Revista Colombiana de Física* **41** (2009) 40-42.
- Alba N C, *Producción, caracterización y optimización de recubrimientos de nitruro de carbono CN_x* , Ph D Thesis, Universidad del Valle, Departamento de Física, Cali, Colombia, 2002.