Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 1765–1774
www.elsevier.com/locate/jeurceramsoc

Microstructural characterization of ceramic–intermetallic composites using TEM related techniques

M.J. Sayagués *, M.A. Avilés, J.M. Córdoba, M.D. Alcalá, F.J. Gotor

Instituto de Ciencia de Materiales de Sevilla, Centro mixto CSIC-US, Av. Américo Vespucio 49, 41092 Sevilla, Spain

Received 5 October 2009; received in revised form 12 January 2010; accepted 27 January 2010
Available online 2 March 2010

Abstract

TiC_xN_y/Ti–Ni and TiC_xN_y/Ti–Co composites formed by ceramic and intermetallic binder phases were produced by pressureless sintering at 1400 °C from powders synthesized by a mechanically induced self-sustaining reaction (MSR) process. Four different composites were characterized using high-resolution electron microscopic techniques, in both scanning (SEM, HRSEM) and transmission (TEM, HRTEM, ED, EDS and EELS) modes and using an energy filtered technique (EFTEM) associated with electron energy loss spectroscopy (EELS). The microcharacterization showed that the ceramic phase with an *fcc*-cubic structure displayed a short-range order in many crystals detected by diffuse scattering in the ED patterns. This was possibly due to a sequence of C, N, and vacancies of both atoms along certain directions in the structure. On the other hand, even though the binder phase was introduced as metal in the reaction process, it was formed by Ni–Ti or Co–Ti known intermetallic compounds ($NiTi_2$, Ni_3Ti, and Co_3Ti). An unknown Ni–Ti intermetallic structure with a Ni:Ti ratio close to 2:1 was only found in one of the synthesized composites and displayed a cubic structure with a lattice parameter, *a*, of about 8.7 Å.

Keywords: A. Milling; B. Microstructure-final; D. Carbides and nitrides; E. Structural applications

1. Introduction

TiC_xN_y-based cermets (ceramic–metal composites) are materials of great interest in both fundamental investigation and practical applications, and they have been considered as substitutes for the conventional WC-based hard metals in the metal cutting industry due to their excellent combination of mechanical properties.[1,2] Hardness, toughness, wear resistance of TiC_xN_y-based cermets, and their resulting performance are influenced by both ceramic and metal (or binder) phases and can be improved by optimizing the microstructure and the material composition.[3] On the other hand, the chemical and physical properties (e.g., microhardness, electrical and heat conductivity, shear modulus[4,5]) of the TiC_xN_y ceramic phase, which is a solid solution between titanium carbide (TiC) and titanium nitride (TiN), rely on their C and N stoichiometry. Additionally, it has been shown that, in these composites, the shape and size of the ceramic particles after the liquid phase sintering are dependent on the C/N ratio.[6,7]

Several studies[8,9] have revealed that the best way to improve the properties of TiC_xN_y-based cermets is to reduce the grain size of the hard phase and to increase the homogeneity of the structural elements. Both features depend dramatically on the method of preparation. We have shown that the mechanochemical process known as mechanically induced self-sustaining reaction (MSR) allows the synthesis of TiC_xN_y-based powdered composites with nanometric character and excellent dispersion of the tough binder around the hard particles.[10] This method also permits the production of nanocrystalline carbonitride powders with homogeneous and controlled chemical composition (tailored C/N ratio) by adequately adjusting the milling parameters and the metal-to-carbon atomic ratio in the starting mixture.[11,12]

We have previously suggested that the optimal combination of properties found in TiC_xN_y-based cermets obtained by MSR and sintered by a pressureless method was due to the homogeneous chemical composition and microstructure developed during processing.[13] The present work focused on the detailed analysis of these two features (key factors to

* Corresponding author.
E-mail address: sayagues@cica.es (M.J. Sayagués).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.01.039

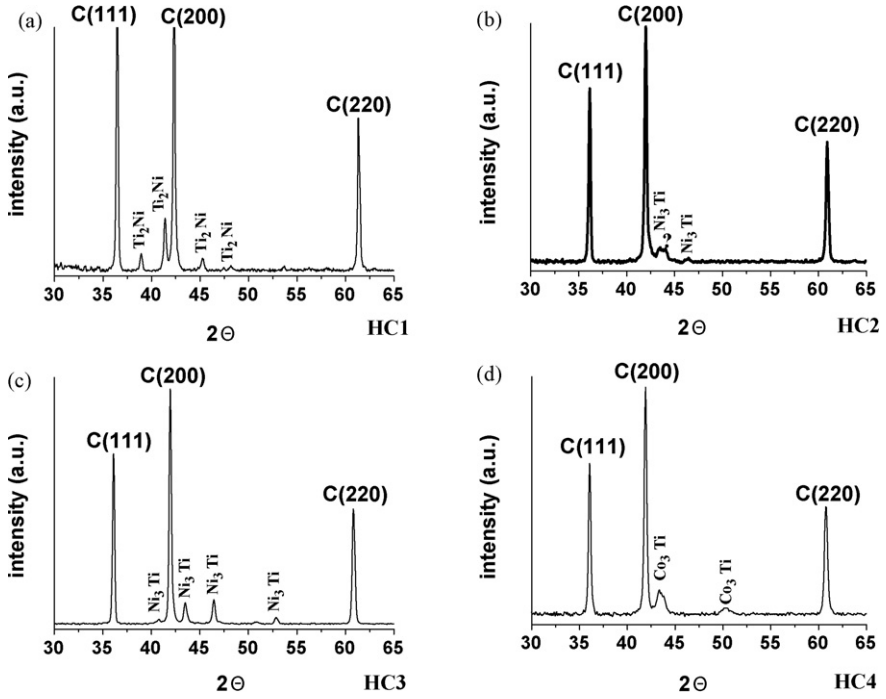

Fig. 1. X-ray diffraction patterns corresponding to the four composites: (a) HC1; (b) HC2; (c) HC3 and (d) HC4. The ceramic phase peaks (C) with the corresponding (*h k l*) index are marked and the intermetallic phases are identified. The peak marked with a "?" in the HC2 sample could not be assigned.

obtain improved properties) at a microscopic level by means of electron microscopy-related techniques: scanning electron microscopy and high-resolution scanning electron microscopy (SEM and HRSEM), transmission electron microscopy and high-resolution transmission electron microscopy (TEM and HRTEM), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), and energy filtered transmission electron microscopy (EFTEM).

2. Experimental

Titanium powder (99% in purity, <325 mesh, Strem Chemicals), graphite powder (<270 mesh, Fe ≤ 0.4%, Merck), nickel powder (puriss., Fluka), and cobalt powder (99.9% in purity, <100 mesh, Sigma) were used in this work. Powdered composites were obtained in one step by MSR from elemental powder mixtures under a nitrogen atmosphere (H_2O and $O_2 \leq 3$ ppm) using a modified planetary ball mill (model Micro Mill Puverisette 7, Fritsch, Idaroberstein, Germany).

The metal binder, Ni or Co, was added to the titanium/graphite mixture that is necessary to form the TiC_xN_y hard phase before the MSR process was performed. More details of the preparation method can be found elsewhere.[10] Four different composites were synthesized using the following Ti:C atomic ratios and weight percentages of metal: Ti:C = 1:0.25, 15 wt% Ni (HC1); Ti:C = 1:0.50, 15 wt% Ni (HC2); Ti:C = 1:0.75, 15 wt% Ni (HC3); and Ti:C = 1:0.50, 15 wt% Co (HC4).

Powdered composites were isostatically cold-pressed at 200 MPa during 5 min to give cylinders of 12 mm in diameter and 45 mm in height. The green bodies were sintered without pressure at 1400 °C for 60 min (heating rate 10 °C/min, free cooling) under inert atmosphere (helium gas, $H_2O \leq 3$ ppm, $O_2 \leq 2$ ppm and $C_nH_m \leq 0.5$ ppm, Air Liquid) in a horizontal furnace (Thermolyne Type 59300 model no. F-59340-CM, Thermolyne).

X-ray diffraction patterns of the polished surfaces of the consolidated composites were obtained with a Philips X'Pert Pro instrument equipped with a Θ/Θ goniometer using Cu Kα radiation (40 kV, 40 mA), a secondary K_β filter, and an X'Celerator detector. The diffraction patterns were scanned from 30° to 130° (2Θ) at a scanning rate of 0.42° min^{-1}. Silicon powder (NIST) was used to correct XRD shift peaks.

Thin disks (3 mm Ø) of the consolidated composites were subsequently prepared by cutting, polishing, dimpling, and ion milling (DuoMill, Gatan Inc.). Microcharacterization was performed using the following techniques and equipments:

- Scanning electron microscopy (SEM) with a ***PHILIPS XL-30*** (resolution 3.5 nm) and high-resolution scanning electron microscopy (HRSEM) with a ***HITACHI S5200*** with a field emission gun (FEG) (resolutions of 0.4 nm at 30 kV and 1.6 nm at 1 kV) (Seville University, CITIUS Centre).

Table 1
Lattice parameter, ***a***, and the estimated stoichiometry for the TiC_xN_y ceramic phase, and binder phases present in each consolidated composite observed by XRD.

Composites	*a* (Å)	TiC_xN_y composition by XRD (Vegard's law)	Binder phase
HC1	4.2705	$TiC_{0.36}N_{0.64}$	Ti_2Ni
HC2	4.3037	$TiC_{0.75}N_{0.25}$	Ni_3Ti
HC3	4.3071	$TiC_{0.79}N_{0.21}$	Ni_3Ti
HC4	4.3125	$TiC_{0.85}N_{0.15}$	Co_3Ti