Chemical Engineering Journal 267 (2015) 297–305

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Toughening of complete solid solution cermets by graphite addition

E. Chicardi [a,*], Y. Torres [b], M.J. Sayagués [a], V. Medri [c], C. Melandri [c], J.M. Córdoba [a], F.J. Gotor [a]

[a] Instituto de Ciencia de Materiales de Sevilla (US-CSIC), Av. Américo Vespucio, 49, 41092 Sevilla, Spain
[b] Departamento de Ingeniería Mecánica y de los Materiales, E.T.S. de Ingeniería, Universidad de Sevilla, Avda. Camino de los Descubrimientos, s/n, 41092 Sevilla, Spain
[c] Institute of Science and Technology for Ceramics (CNR-ISTEC), Via Granarolo 64, 48018 Faenza, Italy

HIGHLIGHTS

- Complete solid solution (Ti,Ta)(C,N)-Co cermets were developed by MSR.
- The graphite addition reduces the dissolution of carbonitride ceramic particles.
- The graphite addition avoids the formation of undesirable intermetallic compounds.
- The graphite addition produces important changes in the nature of the binder.
- The graphite addition leads to an outstanding improvement in toughness.

ARTICLE INFO

Article history:
Received 3 October 2014
Received in revised form 30 December 2014
Accepted 7 January 2015
Available online 14 January 2015

Keywords:
Titanium carbonitride
Cermet
Toughness
Nanoindentation
Graphite
Intermetallics

ABSTRACT

$(Ti_{0.95}Ta_{0.05})(C_{0.5}N_{0.5})$-Co complete solid solution cermets (CSCs) were developed by a mechanochemical synthesis process and a pressureless sintering method. The effect of different percentages of graphite used as a sintering additive on the nature of the binder phase and the mechanical properties of the cermets was investigated. Microstructural and mechanical characterisations were carried out by X-ray diffraction, optical microscopy, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, Vickers hardness, indentation fracture toughness and nanoindentation. The addition of graphite modified the carbon activity during sintering, reducing the dissolution of carbonitride ceramic particles into the molten binder. The amount of Ti and Ta remaining in the binder after sintering gradually decreased as the amount of graphite added increased, which induced a change in the nature of the binder phase. When no graphite was added, the binder consisted of the brittle $Ti_xTa_{1-x}Co_2$ intermetallic phase. With the increase in the amount of graphite added, the formation of more ductile phases, such as $Ti_xTa_{1-x}Co_3$ and α-Co, was observed, causing a significant improvement in the toughness of the cermets.

1. Introduction

Cermets are ceramic–metal composites currently used in the production of tungsten-free cemented carbides for cutting tools [1]. Typically, cermets consist of titanium carbide (TiC) or titanium carbonitride (Ti(C,N)) ceramic particles embedded in a Co/Ni metal alloy that acts as a binder [2–5]. Cermets combine the advantages of ceramics and metals [3]; the ceramic phase must mainly provide hardness and wear resistance, whereas the binder phase provides fracture strength and impact resistance [6]. For the hard component, other binary carbides, such as TaC, NbC, Mo_2C, WC, HfC, VC and ZrC, are added to improve specific properties, for example, thermal shock resistance, hot hardness, chemical stability at high temperature, oxidation resistance and high-temperature creep resistance [7–11]. The binder phase can also contain other minor metallic components (Al, Cr, Mo, Fe, Mn, V or Ce) to support microstructure refinement, particulate dispersion, hardening of the binder and improvement of corrosion resistance [12,13].

Some of those good chemical, physics and mechanical properties makes cermets positively compared with conventional bulk and coated hard metals (WC–Co). They possess a superior cutting performance such as high cutting speeds at moderate chip cross-sections, performance reliability, surface quality of the machined piece, etc [7]. Particularly, the typical applications for cermets based on titanium carbonitride include high performance cutting and forming tools, high-speed milling, semi-finishing and finishing works of carbon steel and stainless steel, high-corrosion resistance coatings for molten metal containers, thermal barriers in fusion

* Corresponding author. Tel.: +34 954489217.
E-mail address: ernesto.chicardi@icmse.csic.es (E. Chicardi).

http://dx.doi.org/10.1016/j.cej.2015.01.022
1385-8947/

and chemical reactors and diffusion barriers in semiconductor technologies [14,15].

For fabricating cermets, the different starting materials are generally mixed by wet milling, and the resulting powder mixture, after being dried, is compacted and sintered in an inert atmosphere (Ar, He, N_2) or in vacuum at a temperature of 1400–1500 °C for a period of 1–3 h [1,16,17]. It is well known that during liquid-phase sintering ceramic particles in cermets develop a characteristic core-rim microstructure via a dissolution–reprecipitation process. The core corresponds to the undissolved original Ti(C,N) particles, and the rim is a newly formed carbonitride solid solution phase, (Ti, Mt1, Mt2,...)(C,N), which contains Ti and the other transition metals added as binary carbides [18]. The core-rim microstructure has a strong influence on the mechanical properties of cermets, and it is believed that the rim phase is the most responsible for the good mechanical behaviour of the final material. For this reason, the use of these carbonitride solid solution phases as raw ceramic materials in the manufacture of cermets has been proposed [19]. Furthermore, the development of so-called complete solid solution cermets (CSCs), in which the ceramic particles are composed only of a homogeneous solid solution single phase (without the core-rim microstructure), has been anticipated as the only way to approach the toughness values characteristic of hard metals because the strain developed at the interface between the core and rim phases, which facilitates crack propagation during machining, can be avoided [20].

In a recent study [21], CSCs based on (Ti,Ta)(C,N) single phase were developed by exploiting the ability of the mechanochemical process referred to as mechanically induced self-sustaining reaction (MSR) [22] to yield homogeneous carbonitride solid solution powders [23–25]. This method uses the strong exothermic character of carbonitride formation from the starting materials to promote self-propagating reactions by the mechanical energy supplied by high-energy ball mills.

Planetary mills are the typical devices used at laboratory scale to carry out these combustion reactions [23,26]. However, there are now some industrial planetary mills [27,28], with a really high capacity, where it would be possible to implement those reactions by a simply and efficiently way at industrial scale.

After sintering, the resulting binder in these CSCs was observed to be a $Ti_xTa_{1-x}Co_2$ intermetallic phase instead of the initial elemental Co. The presence of intermetallics in cermets, which precipitate during cooling, is not a new phenomenon [2,29,30] and has been associated with the excessive dissolution of the ceramic particles in the molten binder, causing Ti enrichment. Although some authors have shown that ductile intermetallic alloys, especially aluminides, are good candidates for binders because the mechanical properties of cermets can be retained at high temperature [31,32], the formation of brittle intermetallics during sintering, such as $Ti_xTa_{1-x}Co_2$, can be extremely harmful for cermets, greatly damaging the fracture strength and toughness [8].

The effect of carbon activity on the coarsening of WC grains during liquid phase sintering has been extensively studied in hard metals [33,34]. Moreover, it has been observed in Ti(C,N)-based cermets that the grain growth rate of ceramic particles depends on the particles' solubility in the binder, which in turn depends on the C/N ratio, decreasing with a decrease in carbon content [35]. In this respect, it has been reported that the use of carbon as an additive can modify the microstructure and mechanical properties of cermets, as the dissolution of ceramic particles is affected [36,37]. Some authors have indicated that the presence of intermetallic phases observed in cermets is the consequence of the considerable dissolution of Ti in the molten binder promoted by denitridation processes, especially when sintering is performed under low nitrogen partial pressure [38].

In this context, the aim of this study was to develop (Ti,Ta)(C,N)-Co CSCs with high fracture toughness using the MSR mechanochemical process and carbon as a sintering additive. This goal was achieved, preventing the formation of brittle intermetallics via the reduction of the driving force (carbon activity) of ceramic dissolution during liquid phase sintering. In this study, different amounts of graphite were added to a cermet powder mixture, and after sintering, the chemical composition, microstructure and mechanical properties were characterised to relate the nature of the binder to the mechanical behaviour of the cermets.

2. Experimental

2.1. Development of cermets

Ti (99% purity, <325 mesh, Strem Chemicals), Ta (99.6% purity, <325 mesh, Alfa-Aesar), graphite (<270 mesh, Fe ⩽0.4%, Merck) and Co powders (99.8% purity, <100 mesh, Strem Chemicals), together with N_2 (H_2O and O_2 ⩽3 ppm, Air Liquide), were used as raw materials to develop the (Ti,Ta)(C,N)-Co CSCs. First, the ceramic phase, i.e., the Ti–Ta carbonitride solid solution with nominal composition $Ti_{0.95}Ta_{0.05}C_{0.5}N_{0.5}$, was synthesised from the starting materials by the mechanochemical MSR process using a planetary mill (Pulverisette 4, Fritsch) that allowed for operation at a constant gas pressure and for the detection of self-propagating reactions during milling [39]. This composition was chosen according to a previous study that showed that the presence of Ta significantly improves the oxidation resistance of cermets [40], which is of crucial importance for high-temperature applications.

Concretely, 46.5 g of an elemental Ti, Ta, and graphite powder mixture with an atomic Ti:Ta:C ratio of 0.95:0.05:0.5 were placed together with thirteen tempered steel balls (d = 20 mm, m = 32.6 g) in a 300 ml tempered steel vial (67Rc) and ball milled under 6 atm of N_2 at a spinning rate of 400 rpm, for both the rotation of the supporting disc and the superimposed rotation in the direction opposite to the vial. After detecting ignition, milling was prolonged for 5 min to ensure full conversion [21].

Subsequently, the carbonitride solid solution phase was mixed by dry milling (Pulverisette 7 planetary mill, Fritsch) with 20 wt.% or 30 wt.% of Co and different small amounts of C in the form of graphite from 0 wt.% to 2.2 wt.% to obtain the powdered cermets. They were introduced together with seven tempered steel balls (d = 15 mm, m = 13.7 g) in a 45 ml tempered steel vial (67Rc) and ball milled under 6 atm of high-purity helium gas (H_2O <3 ppm, O_2 <2 ppm and C_nH_m <0.5 ppm, Air Liquide) at a spinning rate of 600 rpm. The mixture was milled for 30 min, which was the minimum time necessary to produce the optimal homogenisation of the powdered cermets, as required to achieve an optimal densification after sintering [21].

The nominal compositions of the different cermets studied in this work are presented in Table 1. Cermets were labelled as xCoyG,

Table 1
Nominal composition of cermets.

Cermet	wt.% $Ti_{0.95}Ta_{0.05}C_{0.5}N_{0.5}$	wt.% Co	wt.% G
20Co0G	80	20	0
20Co0.5G			0.5
20Co1G			1.0
20Co1.4G			1.4
20Co1.8G			1.8
20Co2.2G			2.2
30Co0G	70	30	0
30Co1.4G			1.4
30Co1.8G			1.8
30Co2.2G			2.2