Alumina/tungsten nano-composites obtained by Spark Plasma Sintering

T. Rodriguez-Suarez¹, L.A. Díaz¹, R. Torrecillas¹, S. Lopez-Esteban¹, W.-H. Tuan²,

M. Nygren³ and J.S. Moya^{*4}

¹ Centro de Investigación en Nanomateriales y Nanotecnología (CINN). Principado de Asturias, Consejo Superior de Investigaciones Científicas (CSIC), Universidad de Oviedo (UO). Parque Tecnológico de Asturias, 33428 Llanera, (Asturias) Spain.

² Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

³ Inorganic Chem., Arrh. Lab. Stockholm University, 10691 Stockholm, Sweden

⁴ Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), C/ Sor Juana Inés de la Cruz, 3, 28049, Cantoblanco, Madrid, Spain

*Author to whom all correspondence should be addressed:

e-mail: jsmoya@icmm.csic.es

Tel/Fax: + 34 913349083/+ 34 913720623

Abstract

In the present work, the parameters controlling the Alumina/W nano-powders Spark Plasma Sintering (SPS) process are studied. The important and crucial role of C diffusion from the SPS die in the microstructure, fraction of porosity and new phases formation (W_2C) is discussed. It is also pointed out the importance of the processing parameters of the starting powder on the density and mechanical properties of the final compacts. In this regard, dense Alumina/nW compacts containing 4 vol. % W with a hardness value as high as 24.6 ± 0.9 GPa were obtained.

Keywords: A. Ceramic-matrix composites (CMCs), A. Nano composites, D. Hardness testing, E. Sintering, Spark Plasma Sintering

1. Introduction

Nowadays, ceramic/metal nano-composites are considered of great interest in materials science due to the singular properties they can present [1]. New materials synthesis and devices require a deep knowledge and a controlled microstructure handling, on atomic levels.

This particular case of alumina/W nano-composites have been chosen because of the commercial availability of alumina nano-powder and because tungsten thermal expansion coefficient is lower than the one of alumina ($4.5 \cdot 10^{-6} \text{ K}^{-1}$ and $8.5 \cdot 10^{-6} \text{ K}^{-1}$, respectively). The latter is a very important factor to take into account in order to minimize residual stresses at ceramic/metal interfaces. Then, metal nano-particles will be subjected to the more stable compressive stresses in the final compact.

It is well known that nano-metric metal particles present a less ductile behaviour compared to micrometric levelled ones [2]. In the particular case of tungsten, it possesses an extremely high G module value (161 GPa), and due to the linear dependence that can be found between this property and hardness, the expected H_V value would be as high as 30 GPa [1].

Studies of the alumina/W system can be found in the scientific literature, at the micrometric scale in part due to those compounds, in this system, exhibit useful properties for various applications in different industrial and technological fields [3]. In this work, a new processing route is proposed comprising a controlled synthesis of tungsten nano-particles over alumina nano-grains and employing the Spark Plasma Sintering technique for retaining nano-particles sizes and distribution in the final compact. In the present study, we report the important effect of powder processing, sintering procedure and carbon impurities on the final microstructures and mechanical properties of the obtained nano-composites.

2. Nano-composites Processing and Characterization

2.1. Powder processing

2.1.1. Starting materials

The following commercially available powders were used: (1) WCl_6 (Tungsten (VI) chloride 99.9 %, Aldrich, Germany) and (2) α -alumina powder (99.99 %, Taimei Chemical Co., Ltd., Japan) with an average particle size of $d_{50} = 300 \pm 50$ nm.

2.1.2. Synthesis of nano-powders

In order to study the influences of C and aggregates presence on the nano-powders Spark Plasma Sintering behaviour, before the deposition of tungsten nano-particles onto the alumina grains, the alumina commercial powder was treated as follows:

- (1) Not processed labelled as “as received” below
- (2) Calcined at 750 °C for 2 h in order to remove any organic additive present in the commercial powder and subsequently passed through a 63 μm sieve (alumina aggregates were formed), and
- (3) Calcined at 750 °C for 2 hours, sieved down to 63 μm and attrition milled during 30 minutes in alcoholic media (anhydrous 99.97 % ethanol) in order to break aggregates.

Powder mixtures with different metallic contents (1 – 10 vol. %) were prepared. Alumina powders, pretreated in one of the two ways described above or “as received”, were weighed and dispersed in anhydrous 99.97 % ethanol and a solution of tungsten (VI) chloride (WCl_6) in ethanol (with the corresponding concentration needed for obtaining the desired final metallic content) was added drop wise [4]. When alumina was calcined first and then attrition milled in ethanolic media, the powder was not dried

but was directly composed with the corresponding WCl_6 solution. The slurries were first heated under magnetic stirring at 70 °C and subsequently in air at 60 °C for 24 h in order to start nucleation and eliminate any traces of alcohol. The dried powders were crushed and thermally treated in air at 600 °C for 1 h to eliminate organic compounds and promote the formation of tungsten (VI) oxide (WO_3) particles onto the alumina grains. X-Ray analysis was performed to control the decomposition of the tungsten precursor into the most stable oxide (WO_3). The powders were then sieved down to 63 μm before being reduced. Reduction of WO_3 to tungsten was carried out at 900 °C for 2 h in a pure H_2 atmosphere.

2.2. Spark Plasma Sintering (SPS)

The spark plasma sintering was chosen as it is a relatively novel technique that makes it possible to obtain dense nano-composites having the nano-structured feature of the ceramic/metal mixed powder previously processed. Moreover, it provides many advantages since very rapid sintering slopes can be achieved, giving uniform densities in the final compact with the addition of less additives and quite easy handling and low processing costs [5]. For comparison, monolithic alumina specimens were also SPSed.

The compaction of the obtained powders was performed in different spark plasma sintering furnaces (Dr Sinter 2050, SPS Syntex Inc., Japan, and FCT Systeme GMBH, HPD 25, Germany) for comparing the slight differences in operating conditions for both kind of commercial SPS equipments today available in the market, essentially temperature measurement and vacuum reached (pyrometer measuring temperature in a vertical way (on top of the compact) in the case of FCT furnace and horizontal temperature measurement for the Dr Sinter furnace, vacuum level reached around 10^{-2} mbar in the FCT furnace and 10^{-5} mbar in the case of the Dr Sinter furnace). Cylindrical

samples with a diameter ranging from 12 to 30 mm and height of 2-4 mm were prepared as follows; i) the samples were heated from room temperature to 600 °C at a rate of 600 °C/min, using a pressure of ~ 10 MPa; ii) From 600 °C to 1100 °C a heating rate of 200 °C/min and a pressure of ~ 10 MPa was applied; iii) From 1100 °C to 1350 °C or 1400 °C a heating rate of 50 °C/min and pressure of 60 or 100 MPa, respectively, was used; iv) Finally the samples were heat treated at final temperature for 3 min. It is worth noting that when pressure of 60 MPa was used a temperature of 1400 °C was required for obtaining dense samples, that is 50 °C higher than the temperature needed for obtaining dense compacts when a pressure of 100 MPa was applied.

2.3. Compacts characterization

2.3.1. Microstructural characterization

The microstructural features of the obtained nano-sized powder as well as the SPSed samples were studied in a transmission electron microscopy TEM (Jeol microscope, model FXII, JEM 2000, operating at 200 kV). Reflected light optical microscopy was performed with a Leica DMRM microscope.

Fracture surfaces for the different compacts were studied in a SEM model DSM 960, Zeiss Thornwood, NY.

2.3.2. X-Ray Characterization

X-Ray diffraction analysis (XRD) of the starting and processed powders and the final compacts obtained was performed using Cu $K\alpha$ radiation (Bruker D8 diffractometer). In the final compacts case, cross-sections or the external dense surfaces were analyzed by this technique.

2.3.3. Mechanical Properties evaluation

The Vickers hardness, H_V , of the SPSed samples was determined by microindentation (Buehler model Micromet 5103) on sample surfaces polished down to 1 micron, applying a 1.96 N load with an indentation time of 10 s. For each sample, 30 indentations were made and 60 diagonals length were measured in order to have a representative mean value of the hardness. The magnitude of the Vickers hardness was determined according to,

$$H_V = 1.853 \frac{P}{d^2} \quad (1)$$

where P is the applied load (in N) and d is the diagonal length (in m)

The toughness, K_{IC} , was also determined by microindentation (diamond indenter Leco 100-A, St. Joseph, MI), but, for this specific property, the applied load was 98 N with an indentation time of 10 s. The fracture toughness was calculated using the formula given by Miranzo and Moya [6],

$$K_{IC} = \frac{0.047 \cdot P}{(d^{0.42} \cdot c^{1.08}) \cdot \left[f\left(\frac{E}{H_V}\right) \right]} ; \quad c/d > 2.8 \quad (2)$$

$$K_{IC} = \frac{0.0232 \cdot P}{(d \cdot c^{1/2}) \cdot \left[f\left(\frac{E}{H_V}\right) \right]} ; \quad c/d < 2.8 \quad (3)$$

$$\text{Where } \left[f\left(\frac{E}{H_V}\right) \right] = \frac{0.768 \cdot \left(\frac{E}{H_V}\right)}{0.05 + 0.612 \cdot \ln\left(\frac{E}{H_V}\right)} - 2 \quad (4)$$

and H_V is the hardness (given by Eq. 1), P the applied load, E the elastic modulus and d and c are the indentation diagonal and crack length, respectively.

3. Results and Discussion

Two different sintering cycles were selected as they give more dense materials:
(i) 1350°C/3min/100MPa and (ii) 1400°C/3min/60MPa. Compacts obtained were characterized and tested.

3.1. Microstructural characterization

3.1.1 SPSed at 1350°C/3min/100MPa

Cross-sections of SPSed disks were polished and microscopically studied. In Fig. 1 optical micrographs corresponding to the polished sections of compacts processed by one of the three different ways described in section 2.1.2 can be observed. It is shown that just dense materials were obtained when the alumina powder was processed according to route (2) described above. When alumina processed according to routes (1) or (3) were used, compacts having a dense surface section were obtained while the inner part of the sample always contained porosity (open porosity $\geq 20\%$). This was observed independently of the SPS furnace used or the sintering cycle chosen.

A more extended microstructure study was performed using the SEM. In the case of dense materials processed according to route (2), peculiar microstructures were observed containing large alumina aggregates ($<63\ \mu\text{m}$ and medium agglomeration size of $28 \pm 14\ \mu\text{m}$) present in the 50% of the microstructure surrounded by W nano- ($<150\ \text{nm}$) and sub-micron sized particles (coarsened particles between 300 - 600 nm in size, mainly aggregated by the presence of C in the system during sintering) attached to smaller alumina grains ($d_{50} \approx 320 \pm 50\ \text{nm}$). A fracture surface corresponding to a dense alumina/2 vol. % W SPSed compact at 1350°C/3min/100MPa is shown in Fig.2, where (a) is a general overview and (b)-(d) are (a) close-ups. The peculiar microstructure described above can be clearly observed in these figures.

It could be determined by EDS- analysis that tungsten was present, in a less significant amount, inside the alumina aggregates (Table 1). A more extended study of these large aggregates by TEM, showed that very small W nano-particles ($d_{50} = 16 \text{ nm}$) were mostly located at triple points but also at alumina grain boundaries providing a pinning effect and constraining alumina grains sizes to $<300 \text{ nm}$ ($d_{50} = 200 \pm 50 \text{ nm}$), as shown in Fig. 3. The W concentration inside the aggregates was 50 % the theoretical one. The presence of W nano-particles inside the aggregates is not so unexpected, due to the preparation procedure of tungsten nano-particles. When the alumina slurry is prepared, the aggregates present certain porosity allowing penetration of WCl_6 solution.

Fracture surfaces of compacts prepared according to routes (1) to (3) were also studied in the SEM (Fig. 4). In the case of composites processed according to route (1), the outer dense parts of the specimens did not present such aggregates, tungsten was well dispersed yielding homogeneous composites (Fig. 4a). On the other hand, in the porous inner parts of the specimens, abnormal alumina grain growth, also known as “dynamic ripening” was also observed as shown in Fig. 4b. This micrograph shows how alumina has grown in an exaggerated way embedding tungsten nano-particles during the sintering process. Thus well-faceted large alumina grains of sizes between 2 and 10 μm are present. On the contrary, in between these large grains, alumina grains of sizes between 300 nm and 1 μm are present.

This exaggerated grain growth phenomena has been previously observed in other materials like $(\text{Ba,Sr})\text{TiO}_3$ [7] and α -sialon [8].

Below a critical temperature, the grain growth progresses very slowly, while above it, the grain growth takes place dramatically fast. It is essential to define a temperature range, or kinetic window, where materials can be sintered without exceeding that critical temperature [8].

The presence of these well-faceted large alumina grains can be related to the high heating rates used in the SPS processor or to the electrical field the material is exposed during the sintering. To the extent vapour formation takes place, enhance grain growth is expected.

Monolithic alumina sintered differently. Dense compacts were obtained and no abnormal alumina grain growth was observed. A SEM micrograph of the fracture surface of monolithic alumina SPSed at 1350°C/3min/100MPa is shown in Fig. 4d. Intergranular fracture features are mainly observed. The measured mean SPSed alumina grain size was $2.5 \pm 1 \mu\text{m}$.

Comparing microstructures depicted in Fig. 2 and 4 it can be stated that W nano-particles prevent alumina grain growth. This is known as “pinning effect”.

3.1.2. SPSed at 1400°C/3min/60 MPa

Fracture surfaces of samples SPSed at 1400°C/3min/60MPa and processed by route (2) were studied in the SEM. In this case, dense composites with the presence of large alumina aggregates were obtained.

The microstructure contained in this case larger alumina grains ($d_{50} \approx 5.75 \pm 1 \mu\text{m}$) and this is due to the use of a higher sintering temperature and a lower pressure.

Fracture surfaces of this composition and of monolithic alumina are shown in Fig. 5. Intergranular fracture features are mainly observed.

3.2. Compositional characterization

All SPSed compacts were X-rayed. The presence of a tungsten carbide, W_2C , was always noticed, independently of the processing route used or SPS furnace employed. The X-ray patterns of selected compacts are given in Fig. 6.

As the sintering of the compact is taking place in a graphite die, it is reasonable to think that carbon can diffuse into the sample from the die and this process is promoted by the applied pressure. The formation of tungsten carbide, W_2C , is thermodynamically feasible in the temperatures range where the sintering takes place. ΔG value varies between -21.736 kJ/mol at room temperature to -34.694 kJ/mol at 1350 °C. By quantitative XRD analysis, the fraction of W_2C formed ranged from 15 – 35 % of the initial W volumetric content.

The presence of W_2C does not favour the densification of the composites. Its density, 17.14 g/cm³ is lower than the one for W, 19.25 g/cm³, so a volume expansion is going to be induced inside the material during its formation. The molar volume change produced is around 16 vol.%. This expansive magnitude is quite large and, to a certain extent, can counteract the uni-axial load applied during SPS process, yielding a non homogeneous material densification. On the other hand, W_2C is a very rigid compound and, in this sense, it could also hinder grain boundary sliding during sintering.

3.3. Densification and powders packing

The different levels of densification achieved according to the processing ways can be rationalized considering (i) The starting green body density reached at the SPS die, and (ii) The presence of carbon:

(i) As it is stated by the principles of ceramics processing [9], continuous particle size distributions of the log-normal type used for ceramics have a maximum packing density of about 65 %. This packing density for a mono-size system can be increased above 75 % by adding a specific proportion of a finer size that packs efficiently in the interstices among the coarse grains. In this sense, compacts processed according to routes (1) or (3) may present a lower green body density than the ones

processed according to route (2). That is, when the starting powder was formed by large alumina aggregates and a fraction of smaller alumina grains that placed at the aggregates interstices during compaction, higher green body densities, when comparing to mono-size systems as in routes (1) and (3), were reached.

(ii) In this particular ceramic-metal system, carbon plays a crucial role during SPS and its presence comes from graphite die diffusion. Some authors have reported that where carbon is placed, special reducing conditions are created favouring interfacial diffusion and bonding [10] and, hence, densification. This happens when carbon acts as lubricant, but in our particular case, carbon does not favour densification since it reacts with W particles yielding W_2C .

For SPSed compacts processed according to route (2) W_2C is expected to be located at interstices between large alumina aggregates, as shown in Fig. 3, being these interstices preferential pores for C diffusion; while inside these aggregates, C diffusion would be hindered and W would be present as a metallic phase.

On the other hand, SPSed compacts processed according to routes (1) and (3) present open porosity and C can diffuse along the whole samples. In this regard, densifications are inhomogeneous, as seen in Fig. 4, since plastic phase is replaced by a rigid one as carbon diffusion front propagates hindering densification.

Sintering kinetics is not perfectly understood due to the amount of parameters involved in the process and, moreover, carbon diffusion that in this particular case takes part as a reactant, is an external and uncontrollable process.

3.4. Mechanical properties

Hardness and toughness have been evaluated. Due to the observed porosity in all the specimens processed by routes (1) and (3) (open porosity $\geq 20\%$ located at the inner

part of the specimens), toughness could only be determined for the fully dense samples prepared according to route (2). Dense areas obtained for compacts processed by routes (1) or (3) were not wide enough for toughness evaluation by indentation according to the method described before, cracks were not well developed and hence, the method could not be applied.

3.4.1. Vickers Hardness

The samples prepared at 1350 and 1400 °C exhibit a similar trend in the plot of H_V versus vol. % W as seen in Fig. 7a. The SPSed samples prepared at 1350°C/3min/100MPa were the one with highest H_V -value. This fact is supported by the observation that the mean grain size for this composite ($2.5 \pm 1 \mu\text{m}$) is smaller than for the one prepared at 1400°C/3min/60MPa ($d_{50} \approx 5.7 \pm 1 \mu\text{m}$).

The observed trend in Fig. 7a is similar to the one obtained in the case of alumina-nNi [11]. An increase of the H_V -value with the nW content is observed. Even considering that the theoretical model proposed by Pecharromán et al.[11] can not be applied in this particular case, the obtained value for the apparent aggregation threshold $f_{ci} \approx 4 \text{ vol. \%}$ is not far away from the one expected if the nW particles would be homogeneously distributed (2.6 vol.%) as in the case of Al_2O_3 -nNi with a similar matrix grain size ($\sim 0.3 \mu\text{m}$). We have to take into account that in the alumina/nW (4 vol. %) a fraction of metal is clearly agglomerated and other fraction is presented as W_2C .

3.4.2. Toughness

Toughness was evaluated for SPSed compacts of monolithic alumina and its tungsten composites. The sample SPSed at 1400 °C exhibited higher toughness value than the one prepared at 1350 °C as seen in Fig. 7b, that in turn can be ascribed to

different alumina grain sizes in these compacts. Alumina presents R-curve behaviour [12] much more pronounced than alumina-based composites as the second phase exert a pinning effect to the grain growth.

4. Conclusions

- (i) Carbon diffusion plays a crucial role when SPS materials presenting carbon reactive phases, acting as a reactant and not as a lubricant. This issue is relevant and needs to be taken into account when spark plasma sintering carbon reactive metals or compounds (as for example, W, Ti, TiO, SiO₂, etc) especially when handling nano-particles where reactivity is enhanced.
- (ii) Fully dense SPSed alumina/4 vol. % W with high hardness values (≈ 25 GPa) were obtained when processing bi-modal grain size distribution favouring compaction and, hence, densification.

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FIGURE CAPTIONS

Fig. 1. Optical micrographs corresponding to the cross-sections of **(a)** Al_2O_3 /2.5 vol. % nW processed according to route (1), **(b)** 4 vol. % nW composite processed according to route (2) and **(c)** 4 vol. % nW processed according to route (3), SPSed at $1350^\circ\text{C}/3\text{min}/100\text{MPa}$.

Fig. 2. SEM micrographs corresponding to fracture surfaces of Al_2O_3 /W composites with a metallic content of 2 vol. % (processed according to route (2) and SPSed at $1350^\circ\text{C}/3\text{min}/100\text{MPa}$). **(b)**, **(c)** and **(d)** are close-ups from **(a)**.

Fig. 3. TEM images corresponding to alumina/2 vol. % W composite processed by route (2) and SPSed at $1350^\circ\text{C}/3\text{min}/100\text{MPa}$, where **(a)** corresponds to the inner part of the large alumina aggregates and **(b)** to the outer part. It could be determined that W concentration was 50 % theoretical (1 vol. %) and W nano-particles size was around 16 nm.

Fig. 4. SEM micrographs of the fracture surfaces corresponding to **(a)** the dense surface of alumina/2.5 vol. % W composite, **(b)** the porous core for the same probe obtained according to route (1) and **(c)** alumina/4 vol. % W processed by (3), SPSed 1350°C/3min/100MPa. For comparison, **(d)** corresponds to monolithic alumina SPSed at 1350°C/3min/100MPa.

Fig. 5. SEM fracture surfaces corresponding to **(a)** monolithic alumina and **(b)** alumina/4 vol. % W composite SPSed at 1400°C/3min/60MPa.

Fig. 6. X-Ray patterns corresponding to the cross-sections of **(a)** the dense surface of alumina/2.5 vol.% W processed according to route (1), **(b)** alumina/2 vol.% W dense composite processed according to route (2) and **(c)** alumina/4 vol. % W processed according to route (3), where W_2C formation during SPS at 1350°C/3min/100MPa is shown.

Fig. 7. **(a)** Hardness and **(b)** toughness values as a function of metal content for different alumina/W composites.

TABLE CAPTION

Table 1. EDS-analysis for two representative areas (inter- and intra-aggregate) of an alumina/2 vol. % W SPSed compact. Elements concentrations are displayed in net counts.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1

	<i>O-K</i>	<i>Al-K</i>	<i>W-L</i>
<i>Intra-aggregates area</i>	453	21631	530
<i>Inter-aggregates area</i>	327	17489	1808