Nanostructured Al-ZrAl₃ materials consolidated via spark plasma sintering: Evaluation of their mechanical properties.

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Abstract

Aluminium based nanostructured materials with additions of 0.5, 1 and 1.5 weight% of zirconium have been produced and sintered using the spark plasma sintering technique in order to promote the nucleation of ZrAl₃ platelets. The mechanical behaviour of all these nanocomposites was determined by means of the Small Punch Test. Zirconium additions significantly decrease the mechanical properties of these products when sintering time at the sintering temperature (650°C) is short (3 minutes). Nevertheless, when the sintering time increases to 1 hour (intermetallic crystallization), the zirconium additions show the expected effect: the stiffness and the yield strength increase while ductility and toughness decrease. The maximum load increases until a 0.5 weight% Zr is attained and suddenly drops when the Zr content surpasses 1 weight%.

1. Introduction

Modern composite materials, nanocomposites, are reinforced with nanometric particles in order to obtain properties much higher than those of conventional composites. Aluminium is a metallic material which easily combines with many different chemical elements, like Mg, Si, Cu, Zn, etc., giving place to numerous aluminium alloys [1]. In this context, zirconium, which presents very low solubility in solid aluminium, forms the ZrAl₃ intermetallic compound, effectively contributing to an increase in strength, moreover controlling grain coarsening and inhibiting recrystallization [2]. The presence of this intermetallic compound can also be interesting due to its high melting point (1853 K), low density and even its excellent oxidation resistance [3, 4].

Among the different methods that exist for the manufacture of metal matrix nanocomposites (MMNCs), the consolidation and sintering of powders is one of the most effective. However, in many occasions the heterogeneous agglomeration of the nanoparticles is difficult to avoid, leading to a significant

deterioration of the material mechanical properties. In order to prevent this problem, a surface modification of the aluminium powders was used in this work, through a colloidal process using a zirconium alcoxide. Afterwards, the powders were consolidated via spark plasma sintering (SPS), which is a sintering, process assisted by a pulsed electric field. The mechanical properties of the sintered products were measured and compared by means of the Small Punch Test (SPT), which is a very useful characterization methodology when material is scarce.

1.1. Spark plasma sintering

Spark plasma sintering (SPS) also known as field assisted-sintering technique (FAST) or pulsed electric current sintering (PECS) is a newly developed process -a synthesis and processing technique- that involve a pulsed DC current to assist densification [5]. With this technique the powder is uniaxially pressed between two graphite punches in a graphite die and heated up in defined atmospheres (vacuum or inert gases), and an electrical current is applied through the graphite die and punches, so that the pressing tool acts as a heating element by means of the Joule effect. In our case, the electrical conductivity of aluminum being high enough, contribute to the direct heating of the sintering powder.

1.2. Small punch test

The Small Punch Test is a miniature mechanical testing procedure that uses small samples, typically with a section of 10x10 mm and a thickness of 0.5 mm or a disc with a diameter of 3 mm and a thickness of 0.25 mm [6-9]. In the first case, the square sample is firmly clamped between two circular dies and it is deformed until failure into a 4 mm diameter cavity using a 2.5 mm hemispherical punch, as shown in Figure 1.

The applied load, P , and the specimens central point displacement, d , are measured with the aid of a COD (Crack Opening Displacement) type extensometer, and are simultaneously recorded during the test. Figure 2 shows a typical load-displacement curve obtained from a ductile metallic alloy. This curve has different regions, which correspond to different states of deformation of the specimen during the test.

Zones I and II correspond to different states of deformation under bending. Zone I, the linear portion of the curve, corresponds to elastic bending, while Zone II corresponds to plastic bending. The shape of these two parts of the curve depends on the elastic-plastic material properties, i.e., elastic modulus, E , yield strength, σ_{ys} , and hardening coefficient. From a certain point onwards, bending leads to a membrane regime, which predominates throughout most of the curve and corresponds to Zone III. This phase ends with the initiation and propagation of damage, the formation of a neck similar to that developed in tensile tests of ductile materials and the ultimate failure of the sample. All these events correspond to Zone IV, which also includes the point of maximum load registered during the test [10].

The obtained load-deflection curve can be used to calculate different material properties. Due to the complexity of the stress distribution that develops during the test, the work performed so far has been focused on establishing empirical relationships between different mechanical properties and certain characteristic parameters calculated from the points of the curve shown in Figure 2 [11-14]:

- $(P/d)_{ini}/t$, where $(P/d)_{ini}$ is the initial slope measured in the elastic region (Zone I), and t is the initial thickness of the specimen. This parameter is closely related to the Young's modulus, E .
- P_y/t^2 , where P_y is the load at which plastic strain starts. It is obtained by drawing a straight line parallel to the initial slope of the graph, but displaced by $t/10$ (Fig. 2, [12]). This parameter is directly related to the material's yield strength, σ_{ys} .
- P_{max}/t^2 , where P_{max} is the maximum load registered during the test. This parameter is directly related to the ultimate tensile strength, σ_u .
- d_{max} , is the deflexion at the point of maximum load and it is directly related to the tensile elongation, e .
- W_{max}/t^2 and W_f/t^2 , being W_{max} the energy absorbed up to the point of maximum load and W_f the energy absorbed up to the point of failure load (area under the SPT curve). These parameters are related to the toughness of the material.

2. Experimental procedure

The aluminium nanocomposites reinforced with intermetallic compounds were prepared using two raw materials: aluminium powders (99.5%Al from William Rowland®), having an average particle size of 6 μm , and a zirconium alcoxide (Zirconium IV-propoxide from Sigma-Aldrich®). Suspensions with different percents of zirconium were prepared, Al-0%Zr, Al-0.5%Zr, Al-1%Zr and Al-1.5%Zr (weight per cent), using a colloidal method developed by Schehl et al [15] and Díaz, et al. [16]. Sintering was performed in an SPS machine (HPD-25, FCT System GmbH, Germany), using an initial heating rate of 45°C/min up to 420°C, followed by a rate of 70°C/min up to a final temperature of 625°C. Two different dwell times were used: 3 minutes (under vacuum and also under 30 mbar dynamic nitrogen flow) and 1 hour (under vacuum). A uniaxial pressure of 80 MPa was applied onto 20 mm diameter cylindrical graphite moulds. The structure of the samples was analysed by X-ray diffraction (Siemens D 5000) using the $\text{CuK}\alpha$ radiation line under 40kV and 30 mA, and the sample microstructures were studied in a field emission scanning electron microscope (ZEIS Ultra Plus) equipped with a Link EDX spectrometer. Vickers microhardness (Buehler-Micromet 5103) measurements were performed applying a load of 10 g during 10 s and the average of 30 determinations was calculated for each sample.

The 10x10 mm² SPT specimens were cut directly from the sintered pieces using a laboratory cutting device and, afterwards, they were precisely machined until a uniform thickness of 0.5 mm was attained. All the SPT tests were carried out at room temperature in a device composed of a hemispherical punch with a diameter of 2.5 mm and a 4 mm diameter cavity, under a displacement rate of 0.2 mm/min. The CEN code of practice procedure was applied in this work [17]. A minimum of four tests were performed under each condition.

3. Results and discussion

Figure 3 shows the SEM microstructure corresponding to the Al-1.5%Zr alloy. The time consumed at the sintering temperature (3 minutes or 1 hour) has a large influence on the final microstructure of the product. When a short time is used (under vacuum or under a nitrogen atmosphere) intermetallic compounds do not have enough time to crystallize (fig. 3a), but after one hour (fig. 3b) a random precipitation was already observed. The nature of these precipitates has been determined by X-ray diffraction, being the ZrAl_3 intermetallic. These ZrAl_3 platelets have lengths shorter than 1.5 μm and widths smaller than 230 nm. The intermetallic precipitation takes place by a mechanism of reactive synthesis [9] as a result of the interdiffusion between the aluminium powders and their colloidal coating and is of course very dependent on the sintering time.

Figure 4 shows the average microhardness results corresponding to all the analysed materials. Zirconium reinforcement always leads to an increase in hardness which is independent of the sintering process. However, this tendency is more consistent and the zirconium effect on the composite hardness is more effective when longer sintering times are employed.

Figure 5 shows representative SPT load-displacement curves of un-reinforced and Zr-reinforced aluminium alloys, sintered during 3 minutes under nitrogen (similar curves were also obtained when the same dwell times were applied under vacuum). The mechanical behaviour of the zirconium reinforced aluminium alloys was worse than that of pure aluminium so it can be said that, on the contrary to what was expected, zirconium additions visibly deteriorate the mechanical response of these alloys, especially the maximum load and the maximum deflexion, which decrease significantly in the reinforced materials. As already mentioned, an SPS sintering time of only 3 minutes is not enough to give way to the reaction that produces the intermetallic ZrAl_3 . It is also interesting to remember that zirconium has a high melting point (1855°C), so its diffusion coefficient at the sintering temperature (625°C) is expected to be quite low.

Figure 6 shows the SPT load-displacement curves of the different Al-Zr alloys sintered under vacuum during one hour at 625°C. It can be seen that in this case the Zirconium additions have produced the expected effects, as the stiffness of the reinforced alloys (initial linear part of the curves) has increased significantly, and this effect is larger as the percentage of zirconium content increases. The maximum load also increases with the zirconium addition up to 0.5-1%Zr, and the maximum displacement of the curves only slightly decreases until 1%Zr. Nevertheless, the 1.5%Zr reinforced aluminium alloy has both a lower maximum load and displacement when compared to the 100% aluminium alloy. These results were also expected as the reinforcement with nanoparticles is effective in a first stage, but when a larger fraction content is attained the brittleness also induced finally predominates.

Table 1 shows the average values of the SPT parameters that describe the mechanical behaviour of the Al-Zr alloys sintered at 625°C during one hour under vacuum. The stiffness of the product is given by the initial slope of the SPT curve (it is related to the elastic modulus) and the P_y/t^2 parameter (directly related to the yield strength), both increase when the reinforcement content increases. While, on the other hand, the P_{max}/t^2 parameter (directly related to the ultimate tensile strength) initially increases up to a 0.5% Zr reinforcement content and clearly decreases for larger zirconium reinforcement contents. Finally, the parameters related to the ductility and toughness (d_{max} and W_{max}/t^2) always decrease as the zirconium

content increases. All these results compare satisfactorily with the mechanical behaviour measured on the same materials consolidated by hot press [16].

4. Conclusions

A surface modification of the aluminium powders was carried out by means of a colloidal process which involved the use of a zirconium alcoxide precursor in order to produce nanocomposite powders that were consolidated and sintered by spark plasma sintering.

Regarding the dwell time at the sintering temperature (625°C), during a short stay (3 minutes), the crystallization of the reinforcement intermetallic compound does not have enough time to take place and thus the addition of zirconium deteriorates the mechanical properties of the alloys. In this case, only a small microhardness increase was detected.

However, when a sintering time of one hour is used, the ZrAl_3 intermetallic crystallizes and distributes itself randomly producing the expected reinforcement effect. ZrAl_3 platelets with lengths shorter than 1.5 μm and widths smaller than 230 nm have been produced.

The Small Punch Test was employed to mechanically characterize these alloys. The analysis of the obtained SPT curves reflected that the expected elastic modulus and the yield strength of these nanocomposites increase as the percentage of zirconium content increases, but their ductility and toughness continuously decrease. On the other hand, it can be deduced that the ultimate tensile strength increases up to 0.5-1% of zirconium and then suddenly decreases when the zirconium content becomes larger than 1%.

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Figures

Figure 1. Small Punch Test device

Figure 2. SPT load-displacement curve, showing the most relevant SPT parameters.

Figure 3. FESEM microstructures of SPS vacuum sintered Al-1.5%Zr during (a) 3 minutes and (b) 1 hour.

Figure 4. Microhardness against zirconium content

Figure 5. Small Punch Test load-deflexion curves of Aluminium and Al-Zr alloys sintered at 625°C in nitrogen during 3 minutes

Figure 6. SPT load-deflexion curves of Aluminium and Al-Zr alloys sintered at 625°C during one hour under vacuum.

Tables

	$(P/d)_{ini}/t$ (MPa)	P_y/t^2 (MPa)	P_{max}/t^2 (MPa)	d_{max} (mm)	W_{max}/t^2 (kJ/mm ²)
Al	1150	319	1520	1.77	0.78
Al-0.5%Zr	1290	349	1701	1.41	0.68
Al-1%Zr	1500	358	1305	0.95	0.31
Al.-1.5%Zr	1535	408	1042	0.74	0.23

Table 1. SPT parameters. Al-Zr alloys sintered at 625°C during one hour under vacuum