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Structure and Properties of Nanocomposites Prepared from Ball Milled 7475 Aluminum Alloy with ZrO_2 powders

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Nanocomposites were prepared from 40 hours ball milled 7475 alloy powder with addition of 0.5% Zr and 10 or 20 wt. % of ZrO_2, Y_2O_3 stabilized powders. Two types of ZrO_2 powder additions were used; one of size near 25 nm and the other in the range 0.3-0.5 μm to compare the strengthening effect. TEM studies confirmed grain size refinement after milling, down to about 50 nm of aluminum solid solution within powder's particles. The milled powder was consolidated in vacuum using uniaxial hot pressing at 380°C and pressure of 600 MPa. The hardness of consolidated samples was higher for nanocrystalline ceramic powder addition near 320 HV for 20 % of ZrO_2 addition in comparison to 280 HV for 20 % of coarser powder addition. Scanning electron microscopy of consolidated samples did not indicate agglomeration of nanoparticles. TEM studies allowed to determine the grain size of aluminum solid solution near 100 nm after hot pressing and homogeneous distribution of ZrO_2 fine particles. The fraction of monoclinic ZrO_2 was similar in the milled powder and in the hot pressed samples. It appeared that ZrO_2 nanoparticles did not retard grain boundaries movement, however addition of 0.5 % of Zr has a more pronounced effect in the prevention of grain growth. The compression tests showed 1000 MPa of ultimate compression strength of samples with ZrO_2 nanoparticles. This composite indicated also a higher plastic strain than that with ZrO_2 with a few μm size particles addition. SEM studies of deformed samples have shown initiation of cracks at the larger particles interfaces.

Keywords: *7475 aluminium alloy and ZrO_2 nanocomposite, mechanical alloying, hot pressing in vacuum, TEM*

1. Introduction

Aluminium alloys-matrix composites combine the metallic properties of ductility, toughness and environmental resistance with the ceramic properties of high strength and high modulus [1-12]. As a matrix of composites are often applied 7XXX series alloys due to the advantages of high strength, low density and a good plasticity [1-9]. The composites possess superior wear resistance [1,4,6] and high temperature properties [1,8] , however the room temperature strength is usually lower than that of common 7XXX alloys. Therefore attempts have been made to increase strength of composites by application of ceramic nanoparticles [10], nanotube reinforcement of aluminum [11], spray forming of the matrix [2] what allowed to improve the strength in comparison a base alloy. Application of mechanical alloying to a mixture of 2014 aluminium alloy and VC carbides allowed to obtain powder with uniformly distributed ceramic particles leading to a significant hardening [12]. Ball milling was used also to introduce Al_2O_3 nanoparticles into 6061 alloy, to produce a final composite by hot pressing what increased wear resistance by 145% in comparison to a conventional aluminum alloy. High strength approaching 1000 MPa and some ductility was obtained in a composite consisting of 6061 aluminium alloy and 20 % of ZrO_2 prepared from mechanically alloyed powder mixture. The

contribution to a high strength was not only due to addition of nanoparticles, but also due to grain refinement of aluminum solid solution during ball milling.

Considering the growing interest in the depelopment od nanocrystalline composites [11-13] in the present work a high strength 7475 aluminium alloy was ball milled with ZrO_2 nanoparticles to obtain hard nanocrystalline powders, which were subsequently hot pressed at such temperature not to increase substantially grain size, but to obtain nanocomposites, hardened not only by added ceramic nanopowders, but also by the aluminum alloy nanograin matrix material.

2. Experimental procedure

The powder from 7475 aluminum alloy enriched in zirconium of composition 5.7 % Zn, 2.2% Mg, 0.7% Fe, 1.6 % Cu, 0.1% Mn, 0.5% Zr- rest Al, was obtained from Norwegian Company. The powders were mixed with nanosize ZrO_2 yttrium stabilized powder of spherical shape of average diameter near 15 nm supplied by TOSOH Company. Then, powders were subjected to a high energy ball milling in the planetary Fritsch mill Pulverisette 5 at 200 rpm for 40 hours in tool steel containers filled with argon. The powders were compacted in VEB 40 hydraulic uniaxial press in the mould placed in vacuum, heated using high frequency generator. The temperature was controlled by a thermocouple. The powders were encapsulated in copper containers before placing in a mould. Discs 5mm thick of diameter 20 mm were obtained after hot pressing in vacuum of 10^{-2} bar, at pressure of 600 MPa and temperature of 380^{o}C.

The morphology of milled powders and hot compacted composites was studied using Leica DM IRM optical microscope. The polished specimens were etched with 0.5 % HF solution. The structure of powders was studied using X-Ray Philips PW1840 diffractometer using Co Kα radiation after various milling times. The microstructure was observed using Philips CM 20 and Technai G^2 transmission electron microscopes (TEM) equipped with EDAX energy dispersive X-ray (EDX) detectors. Thin foils were cut out from powders immersed in epoxy using Leica microtome, while that from composites by mechanical thinning down to 0.1 mm and further electrolytic thinning using „double-jet" technique in Tenupol-5 device using an electrolyte containing 30 % solution of HNO_3 in methyl alcohol. The thinning was carried out at temperature -30 °C and voltage 15 V. Microhardness Vickers measurements were performed using CSM-Instruments tester.

3. Results and discussion

3.1 Ball milled powders

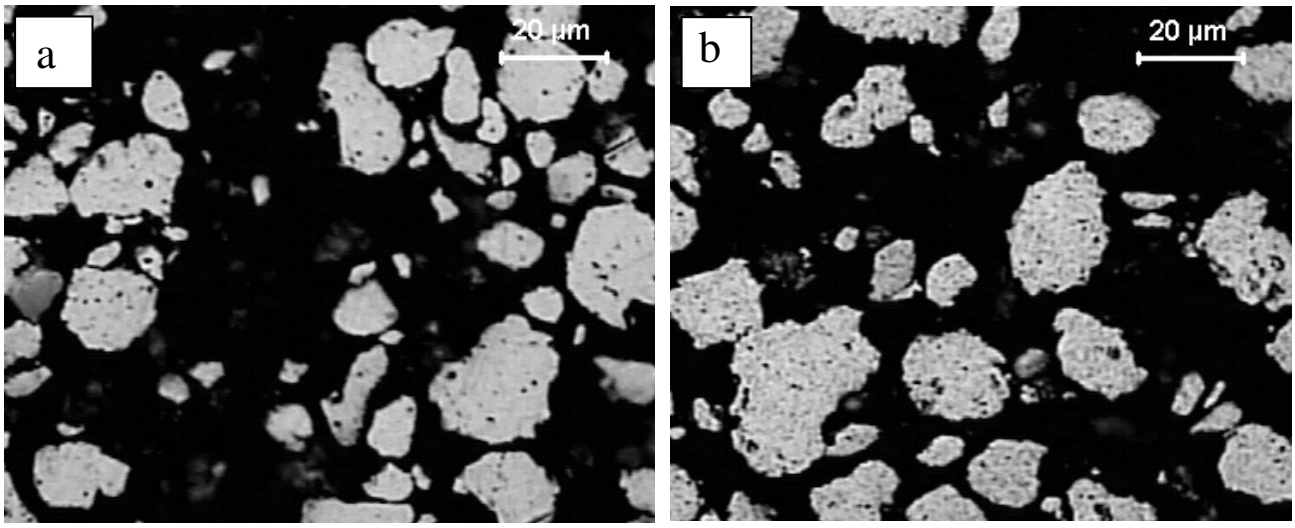

Fig.1 Optical microstructures of 40 hours ball milled powders of 7475 alloy with (a) 10 % nano ZrO_2 and (b) 10 % micro ZrO_2

Fig.1 shows optical microstructures taken from 40 hours ball milled powders containing 10% of ZrO_2, of average size 25 nm in (a) and near 0.3- 0.5 μm in (b) In both micrographs some darker dots can be seen within powders particles. In case of nanometric ZrO_2 additions they indicate most probably agglomerates of ceramic particles while in (b) they are most probably particle, however their size cannot be estimated. The average size of powders particles is similar in both cases below 20 μm. After milling the powders particles grow during first few hours, then break into smaller pieces and finally become smaller than initial elemental powders. Similar microstructures were obtained from milled powders with 20% of ZrO_2.

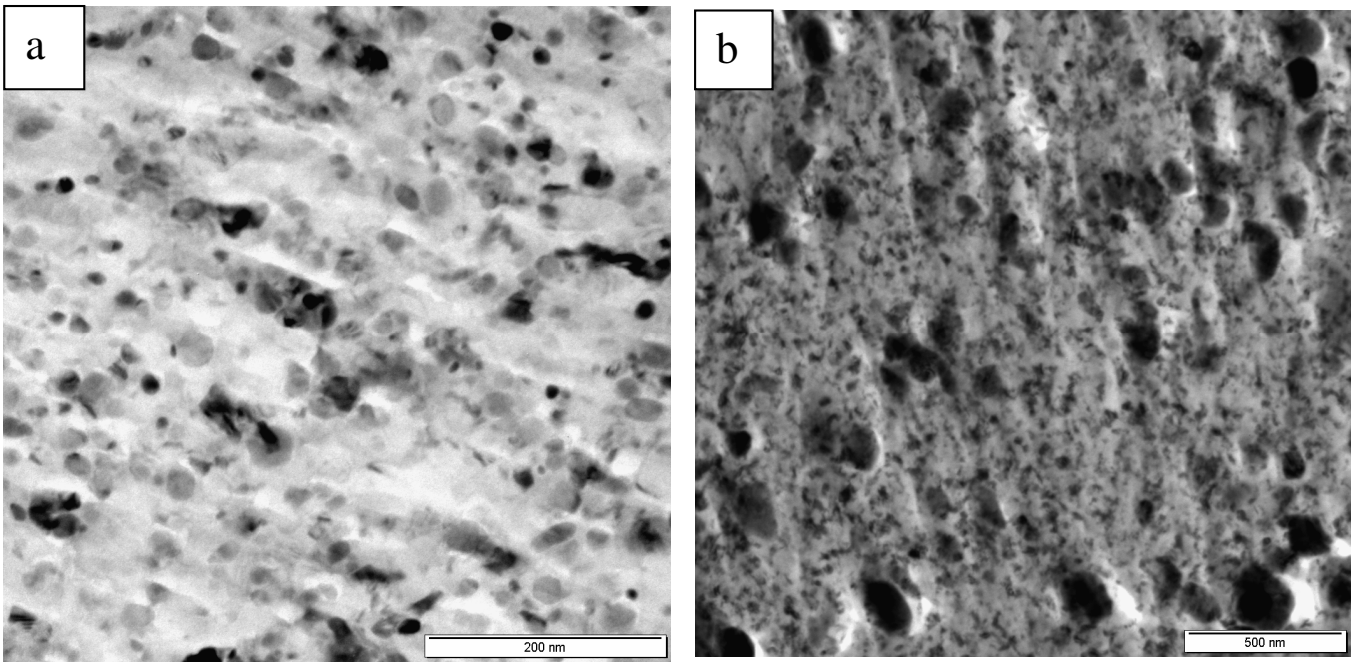

Fig.2 TEM micrgraph in the bright field from a thin section of the ball milled 7475 alloy powders milled 40 hours with 20 % of nano ZrO_2 (a) and 20% of micro ZrO_2 (b).

Fig. 2 shows a TEM micrographs taken from 7475 alloy powder particle milled 40 hours with 20 % of nano ZrO_2 (a) and micro ZrO_2 powder particles additions (b). One can see stripes within aluminum solid solution resulting from the multiple joining of particles during ball milling. Within bands grains of aluminum solid solution and that of ZrO_2, both of size of several nanometers can be seen. In fact it is difficult to distinguish between aluminum solid solution grains and that of ZrO_2 particles can be seen, both giving diffraction contrast, orientation dependant. In the case of composite with larger particles additions presented in (b) one can see that ZrO_2 particles are clearly larger than that of aluminum solid solution grains, both giving a similar dark contrast. The size of ZrO_2 particles can be estimated in the range of 0.2 μm.

Fig.3a shows a High Angle Annular Dark Field HAADF micrograph taken from a thin section of milled 7475 alloy powder particle with 20 % of micro ZrO_2 addition. EDS X-ray energy spectra from the alloy and particle area, presented in Figs 3b and 3c respectively, show a significant differences in aluminium, oxygen and zirconium additions confirming presence of particles in the brighter areas. Due to a different contrast under these imaging conditions, when „Z“ contrast is dominating, ZrO_2 particles are visible as brighter than the solid solution and can be easily distinguished in this micrograph within aluminium solid solution grains, contrary to that in a conventional TEM microstructure in Fig.2. Microhardness measurements of ball milled powders have shown some scattering and did not indicate significant differences between powders containing 10% and 20 % of ZrO_2. The microhardness results were in the range of 230- 260 HV and the Young modulus between 140 – 150 GPa increasing with ZrO_2 content.

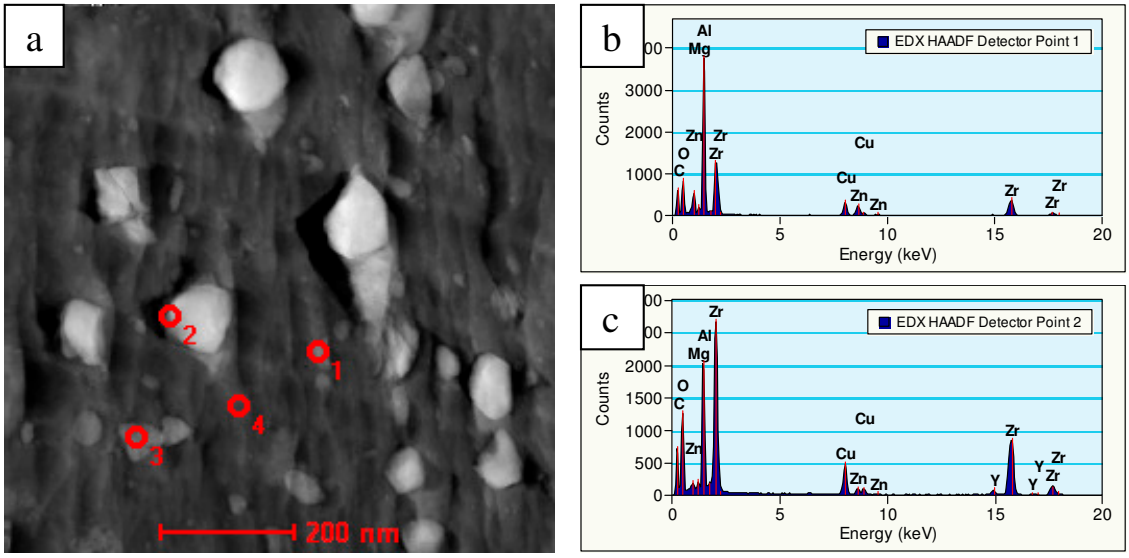

Fig.3 (a) HAADF micrograph of the milled powder 7475 + 20 % micro ZrO_2 (b) EDS X-ray energy spectra from point marked O_1 in the micrograph (c) EDS spectrum at point marked O_2, ZrO_2 particle area

3.2 Vacuum hot pressed composites

Next micrograph (Fig.4) shows a TEM micrograph taken from the hot pressed composite in vacuum, prepared from milled powders composed of 7475 alloy with 10 % of nano ZrO_2 powder. One can see a homogeneous microstructure containing uniformly distributed nanoparticles in a solid solution matrix. There are also precipitates formed during hot pressing from supersaturated after ball milling solid solution, however it is difficult at this magnification to distinguish them from nanoparticles of ZrO_2. In the central part of the micrograph one can see the area of lower density of precipitates. It is most probably caused by recrystallization process occurring during hot pressing, pushing nanoparticles ahead the recrystallization front, as also observed in [14] in composites based on 6XXX alloy. The addition of zirconium, increasing recrystallization temperature was expected to decrease this phenomenon, and indeed it is smaller than observed in [14], however still existing.

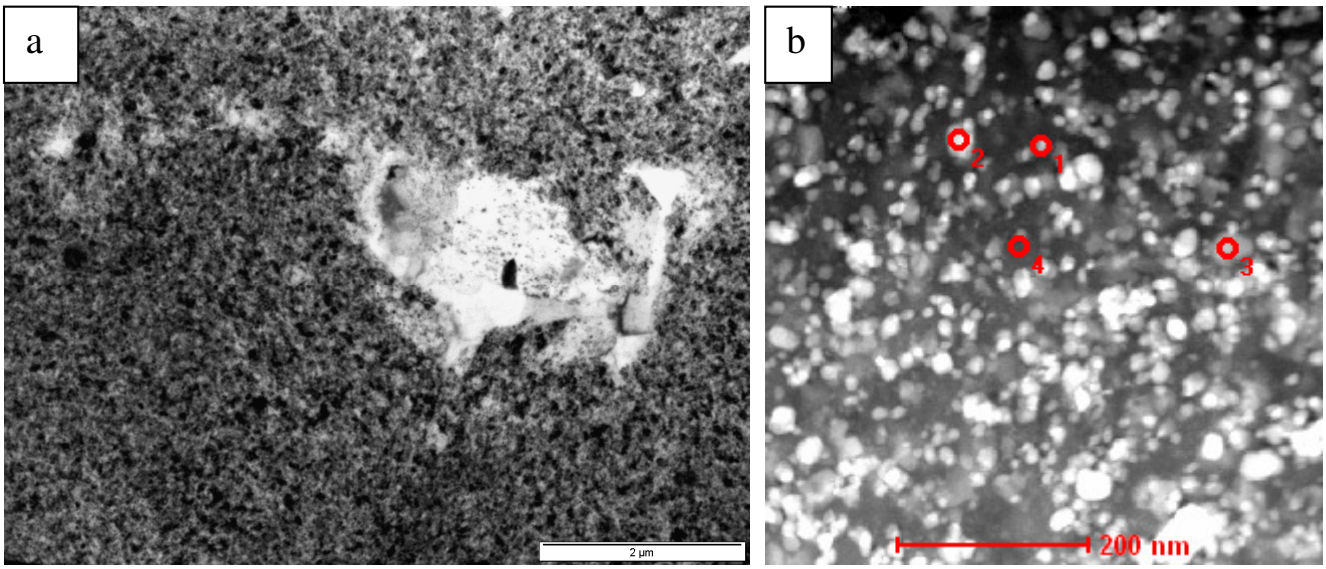

Fig.4 Vacuum hot pressed composite prepared from milled powders composed of 7475 alloy and 10 % nano size addition ZrO_2 (a) TEM micrograph (b) HAADF micrograph

HAADF micrograph in Fig.4b shows ZrO_2 nanoparticles in much better contrast as in this techique it is „Z“ number dependant. Fairly uniform distribution of ZrO_2 and $MgZn_2$ particles can be seen. Weak

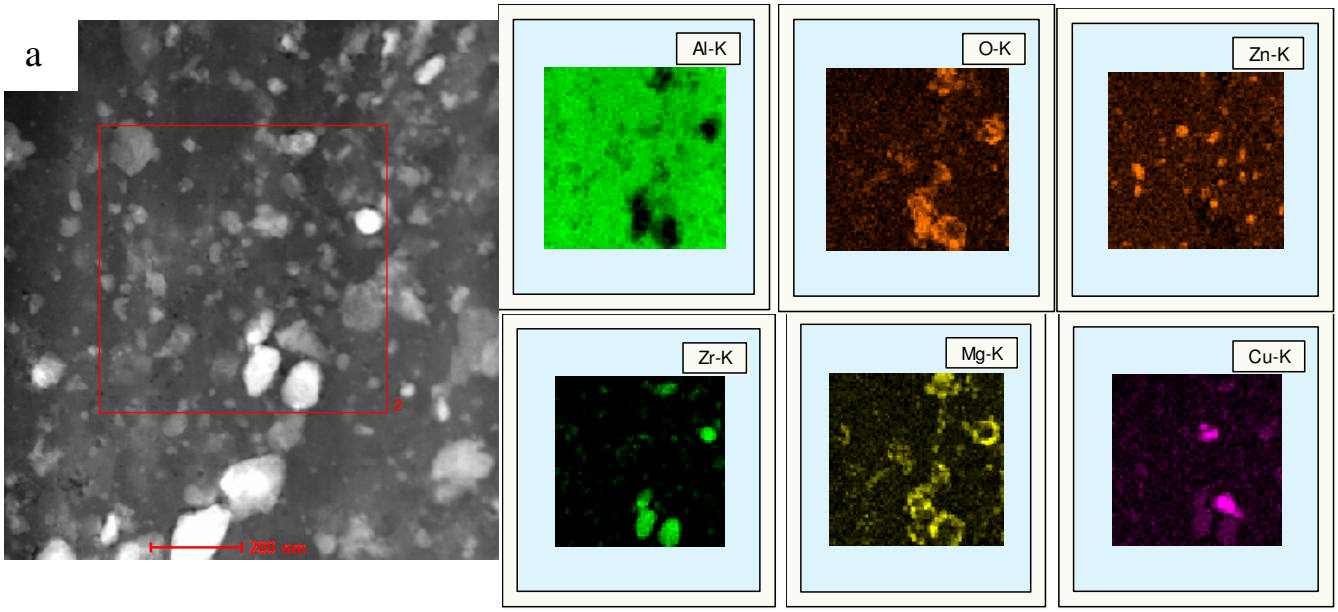

Fig.5 Vacuum hot pressed composite prepared from milled powders composed of 7475 alloy and 10 % of micro size addition ZrO_2 (a) HAADF micrograph and to the right elemental mapping of Al-Kα, O - Kα,Zn - Kα,Zr - Kα,Mg - Kα and Cu - Kα.

changes of contrast within the matrix is due to orienation changes. The microanalysis performed in places marked by points 1-4 confirms this observation showing lowest oxygen and zirconium content in the place number 4 from the matrix. In Fig.5 the HAADF microstructure of the composite based on 7475 alloy with 10 % of micro size addition ZrO_2, with elemental mapping (within the area marked by a square) of Al-Kα, O - Kα,Zn - Kα,Zr - Kα,Mg - Kα and Cu - Kα. One can see that the brightest contrast particles are that of ZrO_2 since in the mapping they are Zr and O rich, slightly less contrast show smaller $MgZn_2$ precipitates and Cu rich precipitates. One can see also magnesium enrichment around ZrO_2 particles most probably due to reaction between ZrO_2 and magnesium from the solid solution. This reaction cause formation of a different contrast observed around ZrO_2 particles at higher magnification.

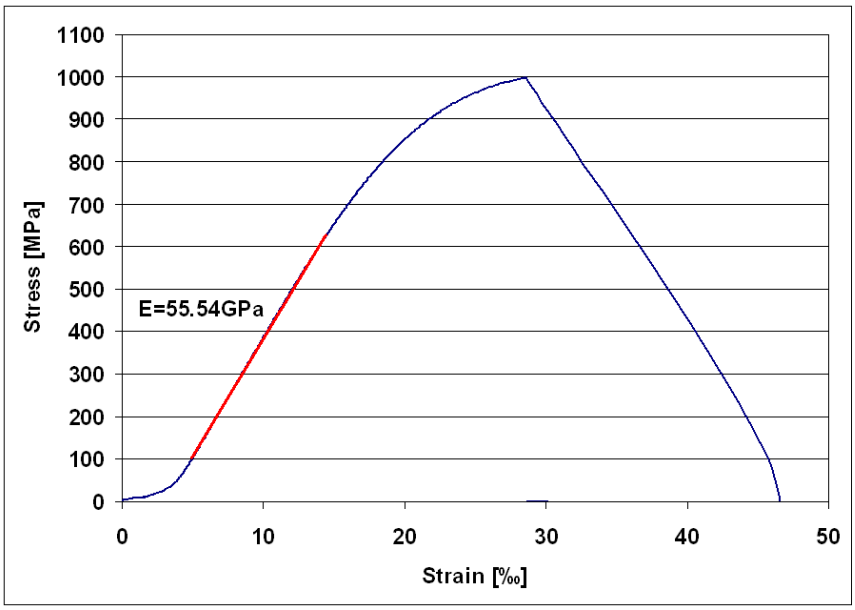

Fig.6 Stress strain curve of the composite based on 7475 with 10 % of ZrO_2 nano particles.

Fig.6 shows a stress-strain curve obtained from a compression test of the composite based on 7475 with 10 % of ZrO_2 nano particles. One can see that maximum strength is 1000 MPa at the deformation of 3 %. Measured Young modulus is smaller than that from the hardness measurements, however due to a small size of specimen of height of 5 mm the value obtained from the hardness test seems more reliable. The strength of the sample with larger size of ZrO_2 additions is slightly lower, near 920 MPa. The compression tests show high values of compression strength not only due to ceramic phase additions, but also due to grain refinement down to nano range.

4. Conclusions

1. 40 hours ball milled powders of 7475 alloy powder with additions of 10% or 20% of ZrO_2 of size near 25 nm or 0.2 μm allowed to obtain powders of uniform distribution of ceramic particles and nanometric size of aluminum solid solution. The hardness of powders was in the range of 240 HV and the Young modulus near 140 GPa.
2. After hot pressing in vacuum under pressure of 600 MPa and temperature 380^{o}C the low porosity composites of uniform distribution of ZrO_2 particles and precipitates $MgZn_2$ and copper rich of size below 100 nm was obtained. Only insignificant grain growth of aluminium solid solution was observed. ZrO_2 particles react with magnesium forming transition Mg rich layer around ceramic particles.
3. The compression strength of composites with nano ZrO_2 particles additions was near 1000 MPa, while those of larger particles additions was slightly lower. It means that contribution of nanosize grains of aluminum and $MgZn_2$ precipitates is also important. All composites show also good plastic deformation near 3 %.

5. Acknowledgements

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6. References

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