

The Effect of Adding ZrO₂-Cu Coating on the Physical Properties of Aluminium Matrix Composites

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Abstract- In this study the powder metallurgy technique was used to prepare the composite materials using the aluminum powder as the basis metal, with the additions of the 2, 4 and 6%Wt. of ZrO₂-Cu coating and mixing it manually for 15 minutes at (30-32 oC). Then the mixture are compacted at pressure 320 MPa and sintering at 640oC in the atmosphere furnace with argon gas protection.

The physical properties include the green density, sintering density, porosity, and microstructure were examined for the prepared samples. X-ray analyzer was used to identify the phases changes in order to find the chemical reaction which it can be excepted occurred in the sintering samples. The result of X-Ray diffraction shows that there is new phase exist after sintering for all weight percentage.

I. Introduction

The solid state process which is known as powder metallurgy technique are used for production of the composite materials, this technique in the synthesis of metal matrix composites found initial use because of the difficulty in wetting ceramic particles with molten metals, and this critical factor still generates problems in solidified composites [1].

The advantages of powder metallurgy over solidification processing in the fabrication of composites are ; minimum destructive interfacial reactions between the molten metal and the second phase, no use of melting facilities for melting matrix alloy, good distribution of the second phase and no limitation on the volume fraction of the second phase [2]. Also, this method improved compositional, microstructural control, homogeneity; refined grain size, supersaturated solid solution, less costly routine maintenance and tremendous improvements in mechanical properties of interest.

The principal of powder metallurgy route steps involved:

1-pre-treatment of the particulate materials, 2- elemental blending and mixing of the matrix powders and the reinforcements, then pressing into near-net shape green compacts, and 3-delubrication (or presintering), and reaction sintering of the compacts [3,4].

Composites are classified according to their matrix phase, which can be a metal, a ceramic and a polymer [5].

Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase [6].

Ceramic Matrix Composites are composed of a ceramic matrix and embedded fibers of other ceramic material (dispersed phase) [6].

Polymer Matrix Composites are composed of a matrix from thermoset (Unsaturated Polyester, Epoxy), thermoplastic (Polycarbonate, Polyvinylchloride, Nylon, Polysterene) and embedded glass, carbon, steel or Kevlar fibers (dispersed phase) [6]

II. Materials

-Basis metal:

Aluminum powder (minimum assay 93%) was used as a basis metal in this work.

-Reinforcement material:

ZrO₂ Zirconium oxide (assay 99%) was used after coated with Cu as a reinforcement material.

-Material for electroless coating ZrO₂:

ZnCl₂, PdCl₂, CuSO₄-0.5H₂O, NaOH, NaKC₄H₄O₆, HCHO, HCl, and deionized water, the detail of these materials explained as below:

a-ZnCl₂ Zinc chloride powder purified 97%.

b-PdCl₂ Palladium chloride 99.9%.

c-CuSO₄-0.5H₂O Copper (II) sulfate -5-hydrate.

d-NaOH Sodium hydroxide pellets assay 98%.

e-NaKC₄H₄O₆ Potassium sodium (+)_tartrate purified.

f-HCHO Formaldehyde solution 37-41%.

h-HCl minimum assay 35-38%.

III. Experimental Work

Preparation of aluminum matrix composites (AMCs) was manufactured by using Al powder of chemical composition shown in Table (1) below.

A. Classifications of powders grain size

The size distribution of aluminum powder particles was determined by conventional mechanical sieving (screening) techniques, where, the particle size distribution measured by tapped the powder through a set of sieves with increasing mesh size, according to B214-ASTM standard [7], as shown in Table (2) below, the amount of powder in each sieve is weighing, and the percents of each weight were determined as show in table below:

Table II Particles size distribution of a 100g Al powder with

Powder type	Particle size distribution μm , %								
	<300	300<106	106<90	90<63	63<53	53<45	45<38	38<25	25<
Al	0.21	0.62	0.53	2.67	15.25	10.28	70.41	0.03	0

B. Blending and mixing materials

After sieving all the powders, the materials used are blended, then each of the materials additives are mixed manually for 15 min, to get good mixture of the different material powders with respect to their compositions.

The equivalent quantities of the reinforcement (ZrO₂-Cu coated) and metal matrix powders (Al) are taken by weight. The materials weighing are done in a balance with accuracy± 0.01g. The quantities of Al metal matrix powder with the additions were 25g for each samples compactions in order to ensure the same quantities exposed to 320MPa pressures compact and 640°C of sintering temperatures, as follow:

For the electro less technique of ZrO₂ -Cu coating, 10g of original ZrO₂ powder of less than 63 μm size, was first stirred in sensitizer bath composition of 500 ml aqueous solution containing 20 g of ZnCl₂ and 20 ml of HCl for 2 hr. This suspension was filtered out using filter paper and dried at room temperature for enough time to permit it to ensure dryness completed nearly 3 hr.

The ZrO₂ -Cu coating was prepared in laboratory according to the procedure found in reference [8].

After the completion of the electroless coating process, the white color of ZrO₂ particles changed to brown color, indicating Cu deposition, in order to get the best possible results more than 4 runs were carried out with for electroless coating.

Then the ZrO₂ - Cu coating were added in the form of particulates with an average size of about less than 63 μm after milled manually and sieving it.

The ZrO₂ - Cu coating particles in the samples were added by varying weight fraction of ZrO₂-Cu coating (2%, 4%, and 6 %), using mold lubricant with oil, without using binders/lubricants, the weighing was done in a very accurate weighing balance 0.01g, as shown in Table (3) below:

Table III Weight of Al/ZrO₂-Cu coated.

Al (g)	ZrO ₂ -Cu coated (g)
24.5	0.5
24	1
23.5	1.5

The correct proportional of each powders above II have been mixed manually by shaking it in a plastic bag for 15 min.

The shape of a particle is very important and must be considered together with the size distribution, a view of its determined using a digital camera and a transmitted polarized microscope., as shown in Fig. 1. The Al powder and the white powder of ZrO₂ before electroless coating.

Fig.(2) shows the powder of ZrO₂-Cu coating succeeded in filter and volumetric, and it show the brown/white powder of ZrO₂-Cu coating failed in filter and volumetric.

Fig.(3) shows the brown powder of ZrO₂-Cu coating after milled it manually by alumina crucible with the sieved below 63 μm, and it shows the brown/white powder of ZrO₂-Cu coating failed.

Fig.(4) shows the ZrO₂ before and after Cu coating after milled it manually by alumina crucible , then sieved it below 63 μm showing, it can be seen that rounded and

mostly spherical ZrO₂ after electroless coating but irregular ZrO₂ before electroless coating.



Fig. 1 The photographs of (a) the Al fine powder, and (b) ZrO₂ .



Fig. 2 The photographs of the (a) ZrO₂-Cu coating powder succeeded on stirrer plate and filter, (b) ZrO₂-Cu coating powder failure on stirrer plate and filter.



Fig. 3 The photographs of the (a) ZrO₂-Cu coating powder succeeded after extraction from filter and milling ,sieved it below 63μm (b) ZrO₂-Cu coating powder failed.

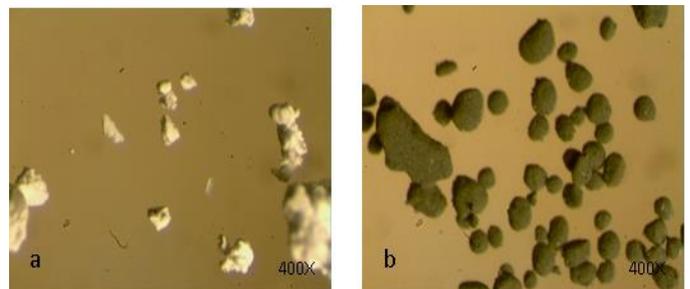


Fig. 4 The morphologies of the (a) ZrO₂ powder ,(b) ZrO₂-Cu coating powder after milling and sieved below 63μm.

C. Compactions

The compacting of powders mixture was conducted using universal testing machine(SANS,WAW-1000, Shenzhen, China, capacity 100 ton, as shown in Fig.(5)) at (30-32°C). The mixing powder was poured into the die cavity, care was taken to make sure that the powder was dispersed properly within the die cavity. Rectangular specimens with

the size of 12×12×70 mm obtained by uniaxially cold pressed at pressures 320 MPa for the mixed powders.

D. Sintering

In this work sintering of green compacts was carried out in a high temperature vacuum tube furnace (MTI, GSL1100X, Richmond, USA, as shown in Fig.(6) at constant heating rate of 10°C/min.. The thermal cycle profiles for sintering of material used in this work at 640°C was shown in Fig.(7), the green compact samples were sintered in five steps within Argon atmosphere trapped inside furnace, the heating rate are 10°C /min. The samples were held at sintering temperature for 1hr, in order to reduce the microstructural inhomogeneity .



Fig. 5 Computer controlling versatile electronic testing machine and the compaction tools.



Fig. 6 Vacuum tube furnace.

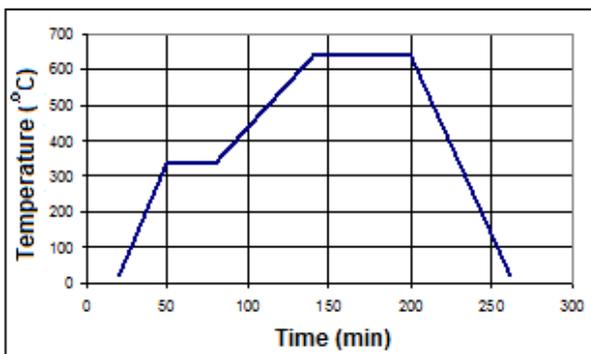


Fig. 7 Schematic of temperature versus time in setting up the sintering process showing the various stages of sintering temperatures 640 °C.

E. microstructures examination

The microstructures of the compacted samples at 320MPa and 640°C sintering temperature were examining by using scanning electron microscope SEM, this examination was

carried out, without any grinding and polishing processes in order to avoid entire the impurities in the pore, which, can be results when the using emery paper [9].

Identification of the phases of the composites after sintering and the phases of the prepared powder were evaluated by using X-ray diffraction analyzer (XRD)(X’Pert Pro MPD, Germany).

F. Density and porosity measurements

The green and sintering densities of the base Al compact and different composites were determined using Archimedes’ principle accordance to according to B328-96 ASTM standard [10], in this method densities are determined by measuring the difference between the specimen’s weight in air and when it was suspended in distilled water at room temperature by using the electronic balance (Shimadzu BX4200H) to an accuracy of 0.0001 g, the following equation was used [10]:

$$\rho_{MMC} = \frac{W_a}{W_a - W_w} \times \rho_{H_2O} \dots\dots\dots(1)$$

For determining the relative densities which is define by the ratio between actual and theoretical densities (compact density/theoretical density) is measured for the green and or/sintering samples.

G. Porosity measurements

Theoretical density of powder mixtures $\rho_{mixture}$ which it is represent the maximum density of material attained in the final stage, which it can be used for determine the apparatus porosity where, in the ideally cases the porosity is zero, it is calculated by the rule of mixtures, as the following relationship [10]:

$$\rho_{mixture} = \frac{100}{\sum_{i=1}^n \frac{x_i}{\rho_i}} \dots\dots\dots(2)$$

The measured porosity (the pore volume fraction) P of compacted sintered parts was made by the following equation [10]:

$$P = \left[1 - \frac{\rho_u}{\rho_{mixture}} \right] \times 100\% \dots\dots\dots(3)$$

V. Results and discussions

A-Microstructures examination

Scanning electron micrograph of a matrix material (Al particles), is shown in Fig.(8). As seen from the Fig., the particle shape of the Al powder (in light gray) provided by the manufacturer is not spherical but rather irregular.

The Fig.(9) and Fig.(10) represent scanning electron micrograph taken from a section of AMCs sintered at 640°C, and compacted at 320MP.

In Fig.(9) , it can be shown that there are many pores in the matrix as compared with Fig.(10), it can be shown the interface between the matrix and material addition and there are little pores in this composites.

The use of coating of ZrO_2 provide adequate wettability for ZrO_2 to sinter with aluminum, this it can be show more effective and interface between matrix and particles added in 6%percent as in Fig.9c. and in Fig. 10 a, and b., can be observed irregular pore.

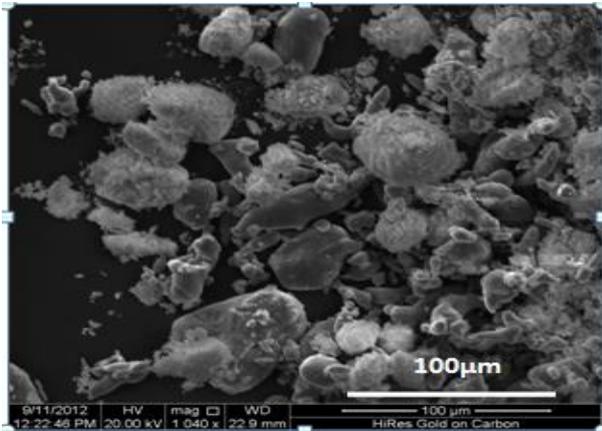


Fig. 8 SEM images of Al powder.

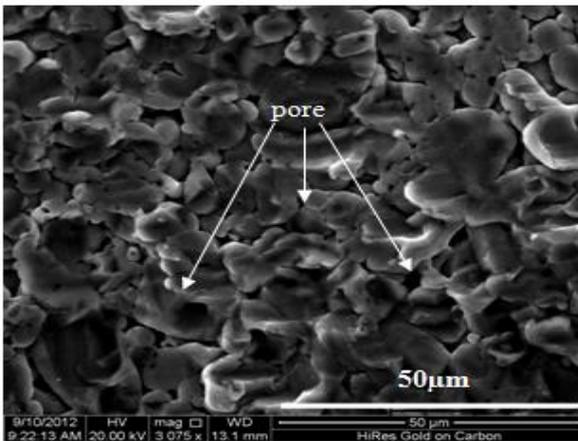


Fig. 9 SEM images of Al matrix

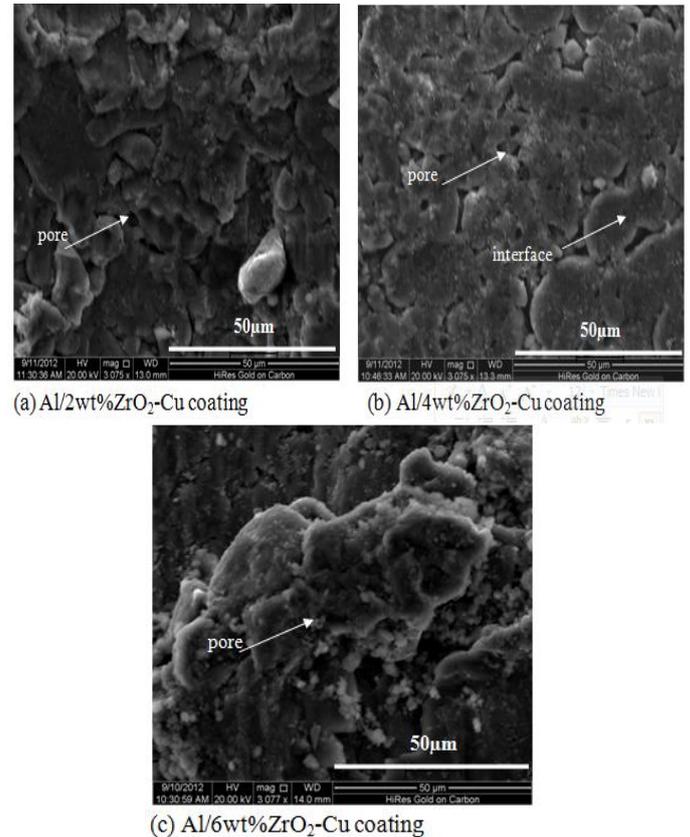


Fig. 10 SEM images of AMCs with different ZrO_2 -Cu coating percents

B. Result of phase's identification

All XRD patterns are shown in the Fig.s from 11 to 14; an examination of the match of the all materials with the peak list extracted from the experimental data now reveals that there are several unidentified peaks still remaining to be identified, which are identified by a reliable PCPDFWIN software program of typical XRD patterns.

XRD patterns of the uncoated ZrO_2 particles and ZrO_2 -Cu coated particles are presented in Fig.(12), which refers to disappear some peak and present of a new peak after coated processes related to different additive.

New phases may be presented with addition of ZrO_2 -Cu coated to the Al matrix as shown in the Fig.(14). It can be noted from this Fig. that there is different phase ($AlZr_2$, Al_3Zr_5 , $ZrAl$, Cu_8Zr_3 , $AlCu_9$, ZAl , Cu_4Zr , $CuAlO_2$, $AlCu_3$, $CuZr_2$, and $AlCu_4$) which is referred to the interactions between the matrix and the material added.

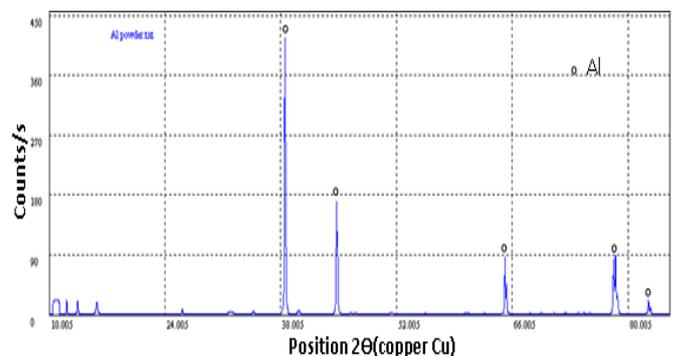


Fig. 11 XRD powder patterns of Al particles.

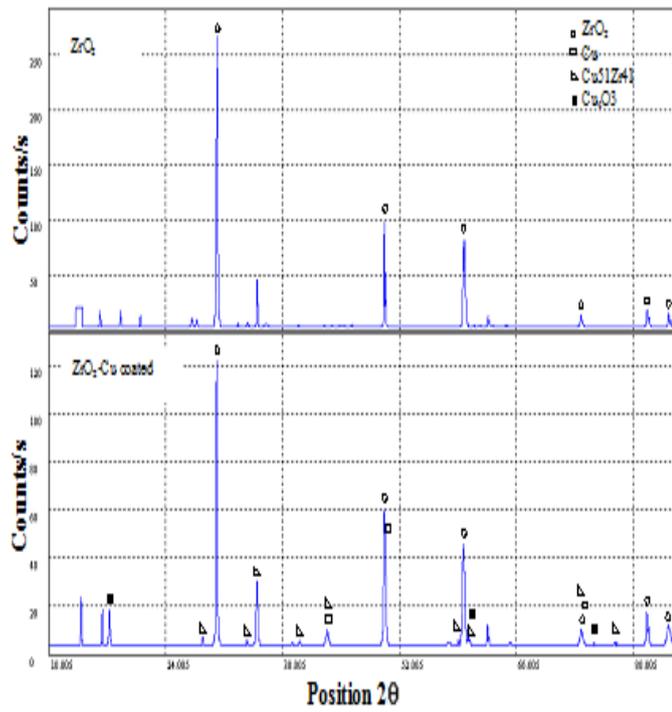


Fig. 12 XRD of different phases present before and after coating of ZrO_2 .

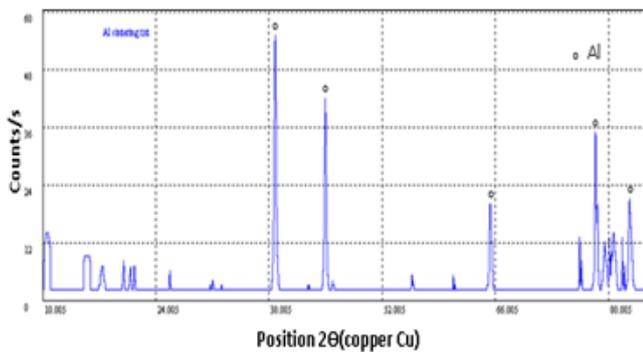


Fig. 13 XRD patterns of sintering aluminum 320MPa compact pressure, and 640°C sintering temperature.

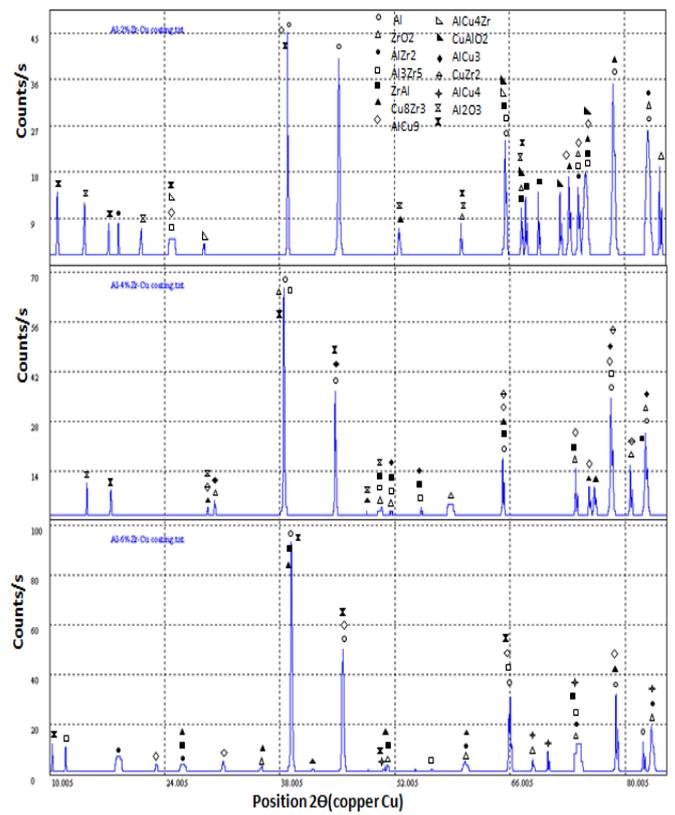


Fig. 14 XRD patterns of sintered different weight percent of ZrO_2 -Cu coating in AMCs at 320MPa compact pressure, and 640°C sintering temperature.

C. Results of Density and porosity measurements

In Fig.(15) can be shows the decreased of densities ; theoretical, green and sintering as the increased of ZrO_2 -Cu coating content from 2% wt to 6% wt in AMCs , at 320MPa Fig.(16) shows the convergence between the values of relative green and sintering densities; which are increases as the percent content of ZrO_2 -Cu coating increasing from 2wt% to 6wt% in AMCs, at 320MPa. The theoretical density of Al/ ZrO_2 -Cu coated composites increases with increasing the weight percent of ZrO_2 -Cu coated because of the decrease in porosity with increasing weight percent of ZrO_2 -Cu coated due to the effect of wettability which causes by the coating ZrO_2 [8].

In Fig.(17) the porosity increased to over 2.9460 when 4%wt of ZrO_2 -Cu content in 1.6714% AMC in 2% wt of ZrO_2 -Cu content, at 320MPa, and 640°C.

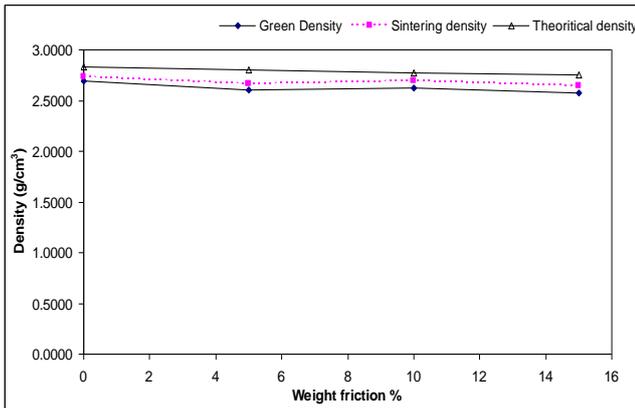


Fig. 15 Relationship between the ZrO_2 -Cu coating content and the density of AMCs, at 320MPa compact pressure, 640°C sintering temperature.

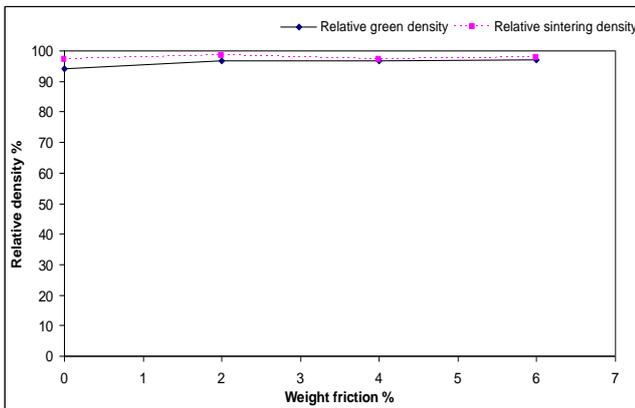


Fig. 16 Relationship between the ZrO_2 -Cu coating content and the relative density of AMCs, at 320MPa compact pressure, 640°C sintering temperature.

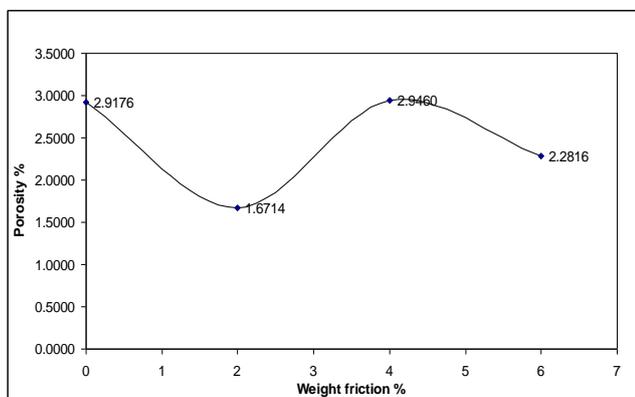


Fig. 17 Relationship between the ZrO_2 -Cu coating content and the porosity of AMCs at 320MPa compact pressure, 640°C sintering temperature.

IV. Conclusion

The main conclusions that can be produced from this study are the following:

I-The diffraction patterns of X-Ray diffraction reveal the influence of varying material percent of, ZrO_2 -Cu coating by appears some phase which is refer to that the Al powder reacts with these materials at 640°C .

II-The compatibility between Al matrix and ZrO_2 -Cu coated was indicated from the microstructure examination, the porosity reach an minimum value of 1.671% in 2wt% ZrO_2 -Cu, at 320MPa, and 640°C.

V. References

- [1] Ejiiofor, J.U. and Reddy, R.G., " Developments in the Processing and Properties of Particulate Al-Si composites ", Journal of Materials Engineering and Performance, Vol.6, No.3, pp. 326-334, 1997.
- [2] Parvina, N. and et al., "Preparation and mechanical properties of SiC-reinforced Al6061 composite by mechanical alloying", Journal of Materials Science and Engineering, A 492, pp.134–140, 2008.
- [3] Froyen, L. and Verlinden, B., "Aluminum Matrix Composites Materials", EAA - European Aluminum Association, 1994.
- [4] ASM Metal Hand book, "Powder Metal Technologies and Applications", Vol.7, ASM International, 1999.
- [5] Chen, D. L. , "Composites material", second edition, Springer, New York, USA, 2010.
- [6] Lehman, R.L and et al., "Materials", Mechanical Engineering Handbook, Ed. Frank Kreith, Boca Raton: CRC Press LLC, USA, pp.13, 1999.
- [7] ASTM-Designation, " Standard Test Method for Sieve Analysis of Metal Powders", Annul book of ASTM standard ASTM B214-99, 1999.
- [8] Shukla, S. and Seal, S., "Electroless Copper Coating of Zirconia Utilizing Palladium Catalyst", Journal of the American Ceramic Society, Vol.86, No.2, pp. 279–85, 2003.
- [9] Arik, H., and Bağci, C., "Investigation of Influences of Pressing Pressure and Sintering Temperature on the Mechanical Properties of Al- Al_4C_3 Composite Materials", Turkish, J. Eng. Env. Sci., Vol.27, pp.53-58, 2003.
- [10] ASTM-Designation, " Standard Test Method for Density, Oil Content, and Interconnected Porosity of Sintered Metal Structural Parts and Oil-Impregnated Bearings ", Annul book of ASTM standard ASTM B328-96, 1996.

Table I Chemical composition of the matrix

No.	Si	Fe	Cu	Mn	Mg	Zn	Ni	Cr	Pb	Sn	Ti	Ag	B
1	0.12	0.72	0.032	0.011	0.0033	0.012	1.19	0.019	0.053	0.039	0.11	0.0052	0.0019
2	0.14	0.5	0.0088	0.0044	0.01	<0.008	0.67	0.0067	0.025	0.075	0.11	0.0036	<0.001
3	0.18	0.52	0.058	0.019	0.014	0.082	2.94	0.057	0.14	0.17	0.16	0.012	0.0056
4	0.15	0.46	0.021	0.015	0.0088	0.089	3.22	0.046	0.16	0.2	0.18	0.012	0.0056
5	0.13	0.25	0.0066	0.0066	0.0057	0.039	1.94	0.023	0.09	0.073	0.12	0.0077	0.0028
mean	0.144	0.49	0.02528	0.011	0.00836	0.046	1.992	0.03014	0.0936	0.1114	0.136	0.0081	0.00338
No.	Be	Bi	Ca	Cd	Na	Sr	Li	Zr	Co	V	Ga	In	Al
1	<0.0001	<0.006	0.0032	0.014	0.0018	0.0038	0.0001	0.0091	0.0081	0.012	0.017	0.013	97.6
2	0.0005	<0.006	0.035	0.014	0.018	0.0027	0.0001	0.021	0.002	0.018	0.012	0.0083	98.3
3	0.0005	0.021	>0.06	0.012	0.0048	0.012	0.0002	0.046	0.058	0.026	0.03	0.019	95.3
4	0.0008	0.019	0.021	0.012	0.005	0.014	0.0002	0.035	0.056	0.026	0.031	>0.019	95.1
5	0.0001	0.006	0.022	0.013	0.014	0.0075	0.0002	0.013	0.027	0.015	0.022	>0.019	97.1
mean	<0.0004	<0.0116	0.02824	0.013	0.00872	0.008	0.00016	0.02462	0.03022	0.0194	0.0224	>0.01566	96.68