Synthesis and Characterization of Spark Plasma Sintered Al - 4.5wt. % Cu Alloy Powder

Santosh K V [1],
[1] Trainee FEA Engineer,
COPES TECH India Private Ltd.
Bengaluru, Karnataka, India.

Robinson P [2],
[2]Assistant Professor,
School of Mechanical Engineering,
REVA University, Bengaluru,
Karnataka, India.

Syed Sameer[3],
[3]Assistant Professor,
School of Mechanical Engineering,
REVA University, Bengaluru,
Karnataka, India.

Madhu B P[4]
[4]Assistant Professor,
School of Mechanical Engineering,
REVA University, Bengaluru,
Karnataka, India.

Abstract - Al-4.5wt. % alloy is high strength, light weight, age-hardenable and structural materials potentially relevant for automotive and aerospace industries. The mechanical properties of alloy produced through casting and ingot metallurgy are generally inferior due to slow cooling rates encountered during the process. To overcome this problem Spark Plasma Sintering (SPS) method is a comparatively new sintering process it is a solid consolidation sintering process that has the key advantage of a very high degree of densification obtained at low sintering temperature and within a short time, compared with the conventional sintering methods. The main objective of the work is to investigate its Microstructures, Physical & Mechanical properties. Micrographs of the compacts reveals the uniform and homogenous microstructure and also confirms second phase particles are well dispersed in the interior of the grains results in good compact and porosity-free materials, it indicates that full densification is achieved at higher sintering pressures. The EDAX reports confirm the presence of Aluminum, Copper and Al_2Cu phase in the compact. The macro hardness of spark plasma sintered samples increases with the increase of compaction pressure from 30 to 50 MPa and reaches the values from 42.92 ± 0.31 to 45.34 ± 0.43 HV it confirms the increased higher sintering pressure not much influence on hardness. Compressive strength of spark plasma sintered samples increases with the increase of compaction pressure from 30 to 50 MPa and reaches the values from 278± 0.90 to 368± 0.31 MPa

Keywords: SPS; Pulse DC Current; cooling rate; Microstructure; Vickers hardness; Grain growth

1. INTRODUCTION

Al-4.5wt. % alloy is high strength, light weight, age-hardenable and structural materials potentially relevant for automotive and aerospace industries [1, 2]. An alloy is material made up of two or more metals. Alloys are designed and produced to have certain specific, desirable, characteristics, including strength, formability, and corrosion resistance. To The mechanical properties of alloy produced through casting and ingot metallurgy are generally inferior due to slow cooling rates encountered during the process [3].overcome this problem Spark Plasma Sintering (SPS) method is a comparatively new sintering process it is a solid consolidation sintering process that has the key

advantage of a very high degree of densification obtained at low sintering temperature and within a short time, compared with the conventional sintering methods.

Spark plasma sintering (SPS) system is a comparatively new sintering process with pulse current generation [4, 5]. As one of the novel sintering techniques, SPS has a great advantage over conventional sintering techniques [6, 7], such as hot pressing (HP) and hot isostatic pressing (HIP). Although the mechanisms for densification and grain growth have not been well explored yet, the fully dense compacts of ceramics and powdered metals can be prepared at low temperature with a short sintering time by SPS [8, 9]. For most materials, the high sintering speed and the low sintering temperature can effectively restrain the grain growth and allow the preparation of materials with high-density and fine crystalline structure [10, 11]. Hence, SPS technology pulsed DC current can be used to produce materials with improvements in microstructure, physical and mechanical properties and other special properties [12].

During the SPS process a strong heat flux is generated between the powder particles by applying high pulsed DC electric current under the suitable pressure leads to the limited grain growth. The field involved in the in the process, enhance the sintering kinetics and promotes full densification at lower temperature in a short time producing invariant microstructure [14, 15].The properties of SPS compacts were compared with the hot extruded material. The results shows that hot extruded material exhibited superior tensile properties than the SPS processed compact. This was due to the residual porosity present in SPS compacts at peripheral region. In the SPS process large pulsated DC current and high mechanical pressure promotes the increase in temperature and high densification [16]. Padmavathi et al. [17] showed that the density and mechanical properties of the aluminum alloys significantly increased with increase in sintering temperature and subsequent aging.

Devaraj et al. [18] showed that the atomized powders comprises of spherical, elongated and irregular shape of the powder particles. The spherical powder particles exhibited cellular morphology, and other particles shows dendritic structure due to difference in the cooling rates of droplets. The SPS compact sintered at 500ºC revealed denser and uniform distribution of secondary phase with free of dendrites and high hardness and compression strength. In the recent study, Al-4.5wt% alloy powder with varied particle size range has been subjected to SPS at three different pressures keeping temperature, holding time and heating rates are constant.

2. EXPERIMENTAL DETAILS

2.1 SPS process
Al-4.5wt. % alloy powder with varied particle size range was used in SPS processing. The SPS machine Dr. sinter 1050(Japan) was employed to prepare sintered compacts and the equipment consists mainly of a pulsed direct current generator, a hydraulic press system, a vacuum and water-cooling chamber, upper and lower punch electrodes, upper and lower punches, a sintering die, and a controller system including positioning, operating environment, etc. The powders are loaded onto a graphite die. As the sintering process starts, a pulsed direct current and an external pressure are applied to the upper and lower punches. Subsequently, the sintering process is controlled by a computer program with the designed parameters such as the sintering temperature, heating rate, and holding time as the input. A graphite die with the dimensions of 30 mm in inner diameter and 60 mm in height and two graphite punches having dimensions 30 mm in diameter and 30 mm height were used for the compaction. The die and punches acts as heating elements for the powder particles and expected to be spread heat uniformly and the temperature was measured by a thermocouple inserted in the hole located in the middle wall of the graphite die.

2.2 Sintering parameters
In order to investigate the microstructure of the compacts and the sintering parameters in the SPS process, the following parameters involved.

(1) Sintering temperature T = 500ºC, holding time (t) = 5 min, heating rate (h) = 50ºC/min, and varying pressures P_1 = 30 MPa, P_2 = 40 MPa and P_3= 50 MPa.

2.3 Characteristic test
The relations between displacements and different sintering parameters were obtained by the SPS output system. After sintering runs, the each sample was cut by using EDM wire cut and the densities measured by the water displacement method (Archimedes principle). Digital scales whose precision were of ±0.0001 g and associated density kit were used for all density measurements. Each sample was measured first in air and then suspended in water so the both values can be recorded for calculating density of the test specimen. The samples were dried off with paper towels between suspension measurements. For microstructure investigation the compacted sintered samples are polished

using different grades of emery papers, alumina and diamond polishing and etched with Keller's (H_2O 190ml, HNO_3 5ml, HCL 3ml and HF 2ml) reagent for 10 seconds. The microstructure of the compact was observed by using optical microscopy (Leitz laborex 12 ME, Germany) and scanning electron microscopy (FEI Quanta 200, USA). Mechanical property of compression test by using UTM at ambient temperature for SPS compact alloys. The specimens were machined from the EDM wire cut process. The shape and dimension of the compression specimens conforming to ASTM specification. At least three compression specimens of 9.0 mm width and 14 mm length, machined out from EDM wire cutting process, were tested under uniaxial compression in a Universal testing machine (Model: KIC-2-1000-C, Capacity-100 KN. Supplier: Kalpak Tech services, Pune India) with a strain rate of 1.47×10^{-2} S^{-1} and the average of compression strength and percentage elongation is reported as the compression property of the material. Hardness was measured using WOLPERT 102 MVD Vickers tester (USA).Test samples are obtained as per the ASTM standard as aspect ratio of 1.5. In Vickers hardness test, a steel ball of diameter (D) is forced under a load (F) on to a surface of test specimen. Mean diameter (D) of indentation is measured after the removal of the load (F) using Bulk Vickers hardness machine.

3. RESULTS AND DISCUSSION

3.1 Micro structural characterization
The size and morphology of the gas atomized powder particles of range (150-210μm) used for the sintering are shown in Fig. 2. It can be clearly seen that both powders consists of particles with various shapes, including the spherical, elongated, and irregular. Also, the powders have a wide particle size range. During gas atomization disintegration of molten metal in to fine spray of different size of droplets by transferring high speed gas to molten metal. When these powder particles are used for compaction spherical powder particles experiences very high cooling rates during the atomization in contrast to elongated and irregularly shaped particles. From the evidence of literature, the variation of the microstructures within the droplets of different sizes and observed dendritic and cellular morphology. Further they showed that the lowest droplet diameter exhibited microcellular morphology since the smaller droplets undergo higher undercooling. Hence the variation in the microstructure observed in different powder particles can be attributed to the nucleation and growth of atomized droplets.

3.2 Relative density
The Relative density is more easily and perhaps more accurately measured without measuring volume. Using a spring scale, the sample is weighed first in air and then in water. Relative density (with respect to water) can then be calculated using the following formula: ρ (Density) = $Weight_{water}$ / ($Weight_{air}$- $Weight_{water}$) Where W_{air} is the weight of the sample in air and W_{water} is the weight of the sample in water. The specimens were polished and analyzed for density by the Archimedes principle with water is a displacement fluid. The specimens consolidated at 30 MPa and 40 MPa are found to have densities of 2.80 and 2.81g/cm^{3}respectively.

The density of the specimens increased monotonically in density up to the stress of 50 MPa where the density was found to be 2.83g/cm^3. Fig.1 shows a plot of density vs. sintering pressure for the three specimens and indicates that the density appears to be reaching a peak around 2.83 g/cm^3; the obtained results are greater than base alloy of aluminum with a dense in nature. The specimen density increases with increase in sintering pressure which leads to the elimination of pores and voids and dense compact with better metallurgical bonding. As increase in sintering pressure the density values are increasing very slowly and even considered to be constant.

Table 1   Weight of the samples in grams.

Weight ╲ Samples	30Mpa	40Mpa	50MPa
Weight in air(g)	3.3395	3.5317	3.4050
Weight in water(g)	2.1505	2.2754	2.2024
Density(g/cm^3)	2.80	2.81	2.83
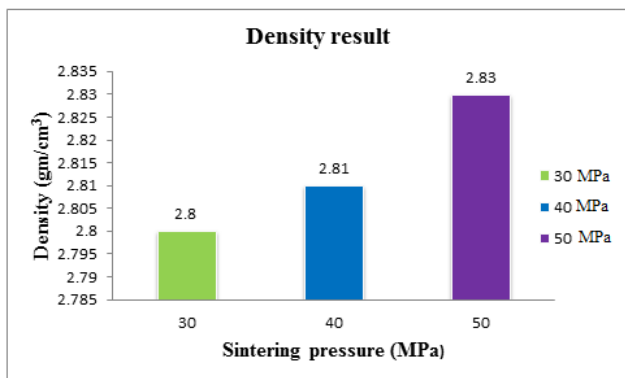
Fig. 1 Density V/S sintering pressure.

3.3 Micro structure of SPS compacts

Figures 3 to 5 shows the Optical micrographs of Al-4.5 wt. % Cu alloy powder particles (180-210μm) was subjected to SPS process for 5 min at 30,40 and 50 MPa keeping sintering temperature 500ºC as constant. In Figures. 3 (a) and (b) Some portions of SPS compacts shows cellular morphology, grains and grain boundaries, while other portion by dendritic structure. Figs. 4 (a) and (b) indicating grain, grain boundaries and pores can be seen clearly in Fig. 4 (b), the optical microscopy confirms the microstructure is bulk of grains, dendrites and cellular morphology with grain boundaries distributed unevenly due to change in particle size. It results in less dense, pores and voids can be eradicated by increasing sintering pressure. As increasing in sintering pressure change in reduced pores, voids and disintegration of dendritic structure leads to the fine microstructure. Finally
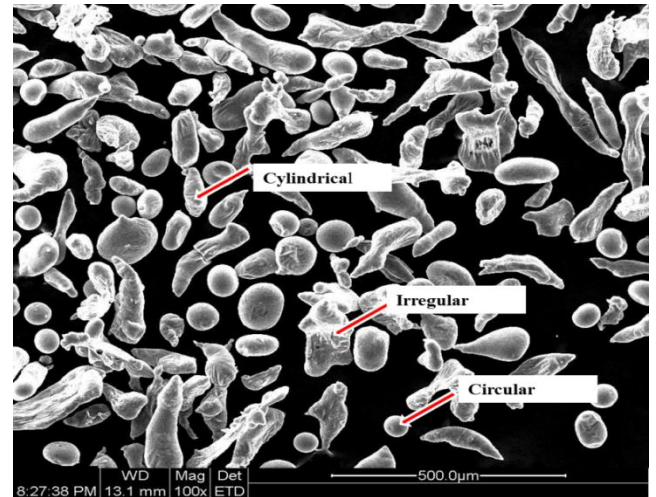

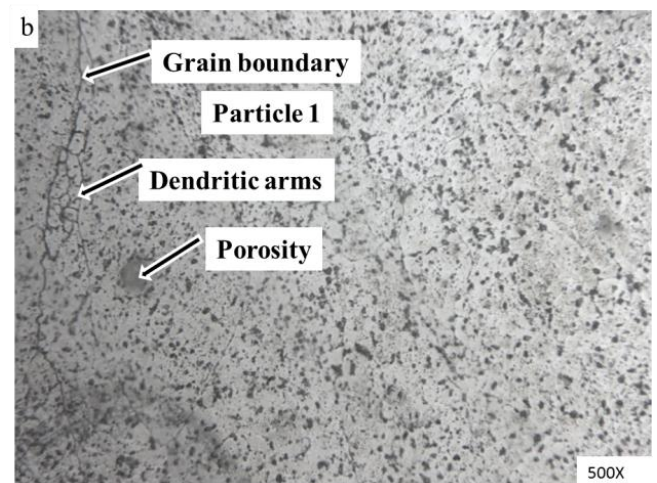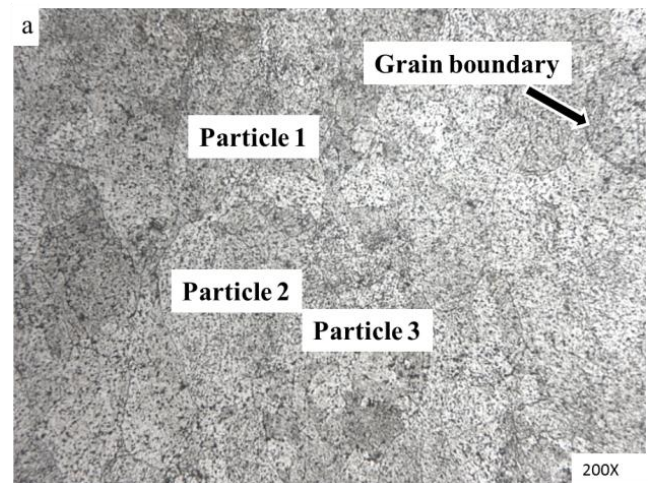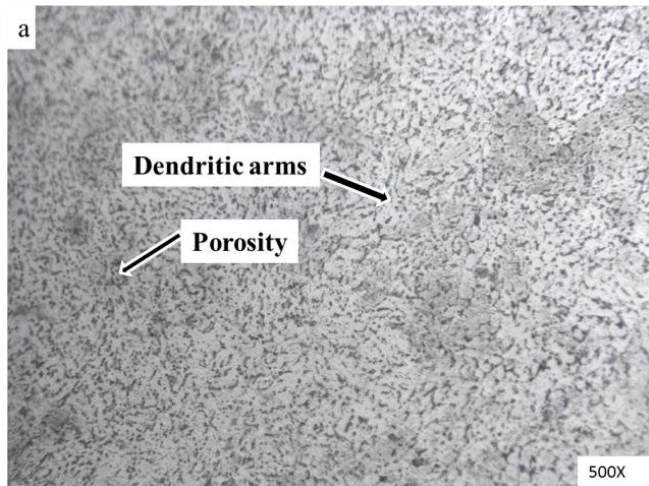Fig. 2 SEM micrograph of Al-4.5wt% Cu alloy powder.

Fig. 3 Optical micrographs of SPS Al-4.5 wt. % Cu alloy at 30 MPa sintered at 500^{0}C. a) at resolution of 200x, b) at resolution of 500x

Figs. 5 (a) and (b) indicates disappear of pores and dendritic arms to fully dense in compact and uniformly distribution of alloy particles are observed.
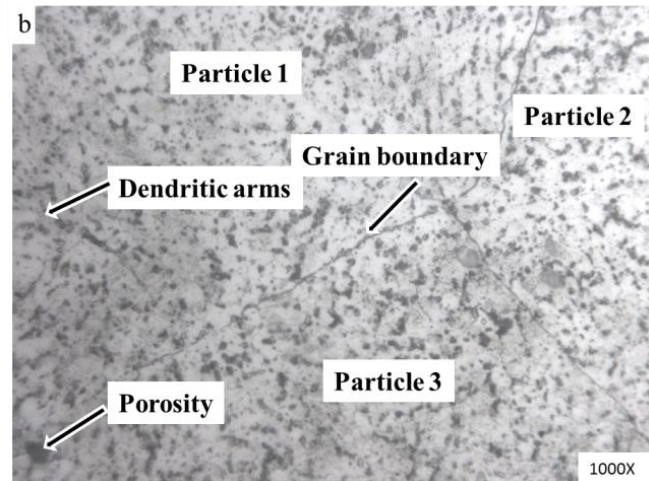

Fig. 4 Optical micrographs of SPS Al-4.5 wt. % Cu alloy at 40 MPa sintered at 500^{0}C. a) at resolution of 500x, b) at resolution of 1000x

Fig. 5 Optical micrographs of SPS Al-4.5 wt. % Cu alloy at 50 MPa sintered at 500^{0}C. a) at resolution of 500x, b) at resolution of 1000x

It seems that at lower sintering pressure leads to the less dense and insufficient metallurgical bonding between the grains. The samples were sintered at a higher pressure and temperature of 500ºC; however, there was no further improvement of densification with increase in pressure.

Figures 6 to 8 show the SEM micrographs of Al-4.5wt. % Cu alloy powder was subjected to SPS process for 5 min at 30, 40 and 50 MPa keeping sintering temperature 500ºC as constant. Figs. 6 (a) and (b) shows not many pores after spark plasma sintering at 30 MPa, and only very small pores are present; and in Figs. 7(a) and (b) indicate less presence of pores and increasing the dense of the compact. While Figs. 8 (a) and (b) do not reveal the presence of any pore. The figure show a uniform and homogenous microstructure and confirms second phase particles are well dispersed in the interior of the grains and even rarely presence of secondary phase along the grain boundaries which means that full
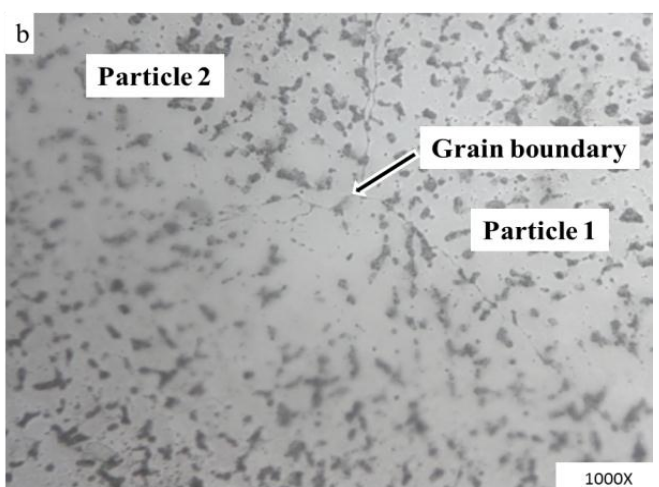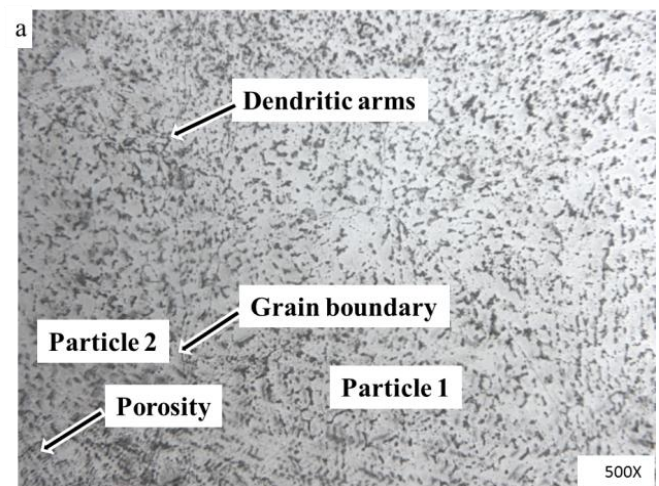
densification is achieved at these pressures, and it can be confirmed from the density values presented in Table 1. The samples were sintered at a higher temperature of 550ºC; however, there was no further improvement of densification. The complete densification, i.e., total elimination of pores, (99%) has been achieved in SPS sintered alloys. It was clear that, at the constant sintering time (5 min), the sintering temperature had an important influence on the densification of samples, because the sintering was a thermally activated process controlled mainly by diffusion. Therefore, the higher the sintering temperature and pressures, the higher the diffusion rate, and the less the pores remained.

Figure 9 shows the Elemental analysis of the Al-4.5 Wt. % alloy compacted at 30 MPa and temperature of 500ºC for 5min, which was carried out to investigate the chemical composition of the alloy powder. The EDAX confirms the presence of Al and Cu and some minor impurities. The EDAX analysis results of the Al-4.5 Wt. % alloy sintered at compaction pressure of 40 and 50 MPa are shown in Fig. 10 and Fig. 11 which confirms the presence of Aluminum, copper and Al_2Cu. Mapping of the distribution of the different chemical elements constituting the specimen can be obtained. X-ray data is processed to obtain the percentage of each measured element present in the

individual particles. The compositional and morphological data are then combined for exploratory data analysis. SEM-EDAX is many times routinely used to obtain morphological information of the stone surface and identification of chemical composition. During experimentation careful deep observation in to the matrix a whitish cellular phase is observed.

3.4 Mechanical Properties

3.4.1 Hardness

The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average is calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation. When the mean diagonal of the indentation has been determined the Vickers hardness may be calculated from the formula $HV= [2F \sin 136/2]/D^2$ Where, HV5 = Vickers hardness number for 5 kg F= Imposed load in kg, D_1 and D_2=Diameter of the spherical indenters in mm D=Diameter of the resulting indenter impression in mm. The Vickers' macro hardness of spark plasma sintered alloy at 500°C for 5 min is presented in Fig. 12. The hardness measured using Vickers hardness tester by applying 5 kg load at different location of the samples and its average is found to be 42.92 ± 0.31, 45.32 ± 0.50 and 45.34 ± 0.43 HV for 30, 40 and 50MPa respectively. For spark plasma sintering, increasing the sintering pressure from 30 to 50 MPa increases the macro hardness from 42.92 ± 0.31 to 45.34 ± 0.43 HV. A further increase of sintering pressure there is slightly increases the macro hardness for SPS and densification which results in elimination of porosity. Fig. 12 illustrates the variation in HV of SPS sintered test specimen at different sintering pressures. It can be observed that the addition of Cu powder particles has increased the hardness of the sintered compact compared to that of the base alloy. Test results also indicate the progressive increase in hardness of sintered compact.
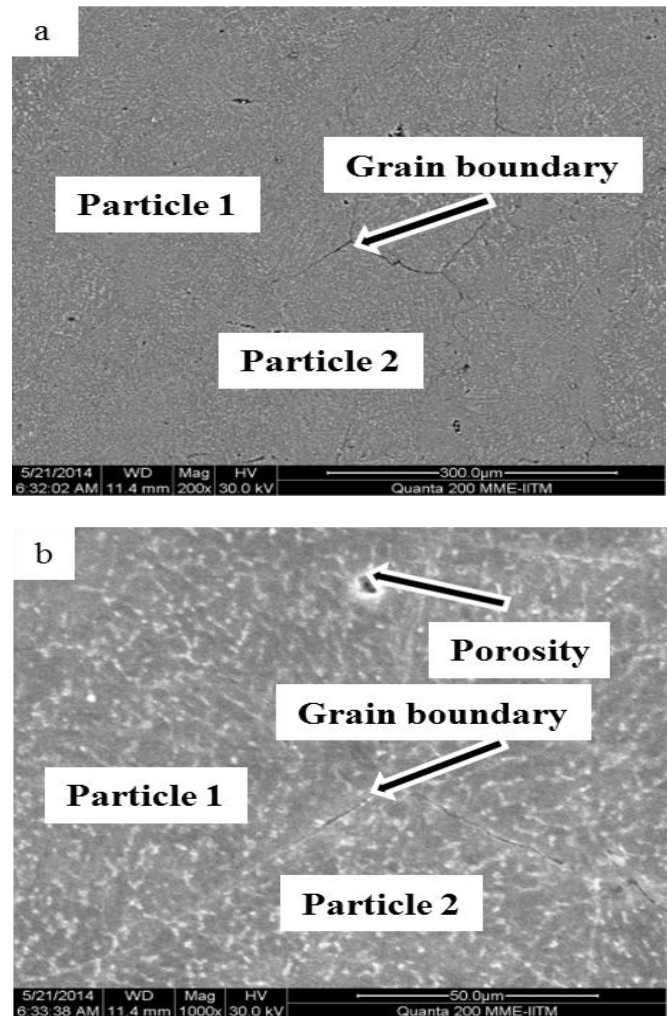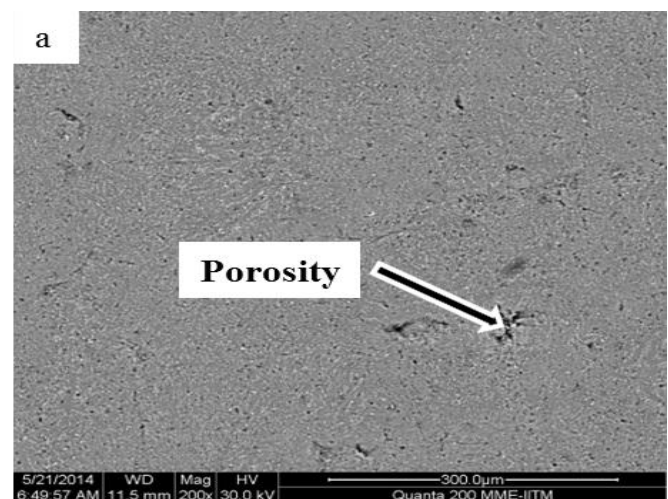
Fig. 6 SEM micrographs of SPS Al-4.5 wt. % Cu alloy at 30 MPa sintered at 500⁰C a) at resolution of 300.0μm b) at resolution of 50.0μm.
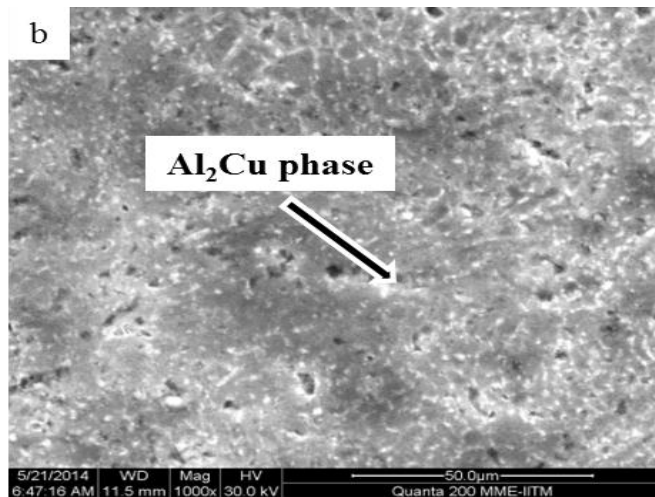
Fig. 7 SEM micrographs of SPS Al-4.5 wt. % Cu alloy at 40 MPa sintered at 500^0C . a) at resolution of 300.0μm b) at resolution of 50.0μm.
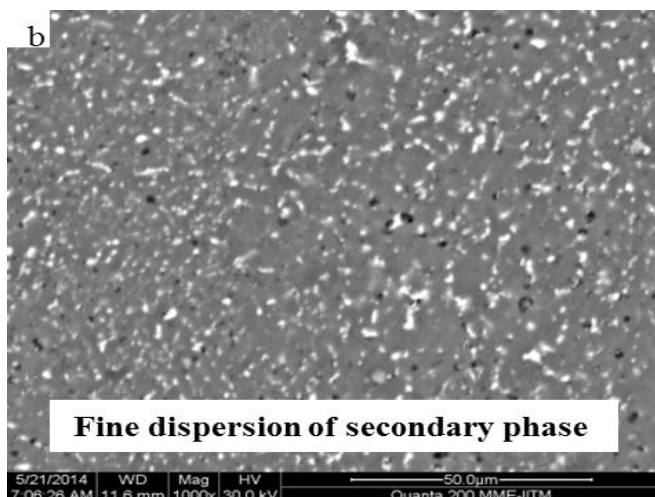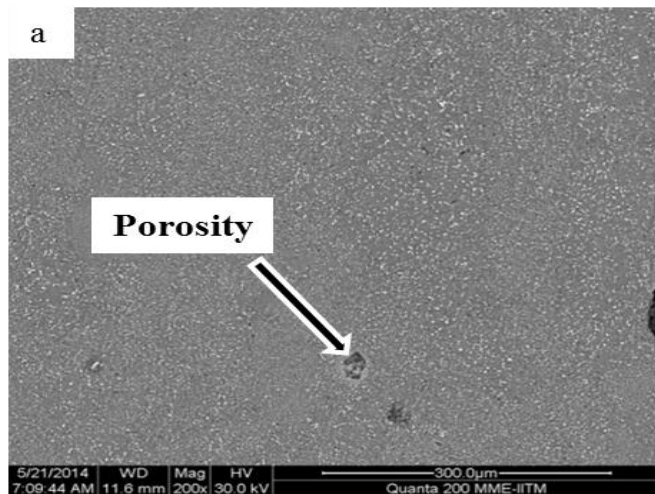

Fig. 9 EDAX Results of SPS Al-4.5 wt. % Cu alloy sintered at 500^0C at 30 MPa

Element	Wt.%
AlK	93.74
CuK	06.26
Matrix	Correction

Element	Wt. %
AlK	93.89
CuK	06.11
Matrix	Correction

Fig. 10 EDAX Results of SPS Al-4.5 wt. % Cu alloy sintered at 500^0C at **40 MPa**

Fig. 8 SEM micrographs of SPS Al-4.5 wt. % Cu alloy at 50 MPa sintered at 500^0C a) at resolution of 300.0μm b) at resolution of 50.0μm.
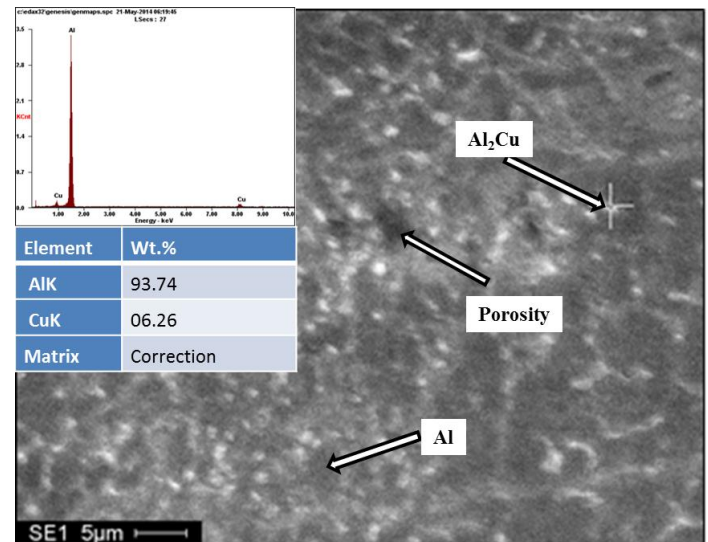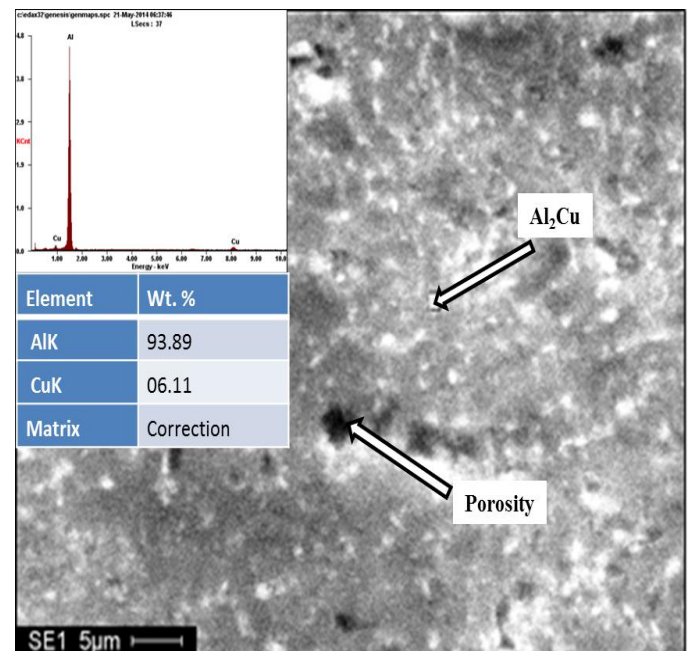
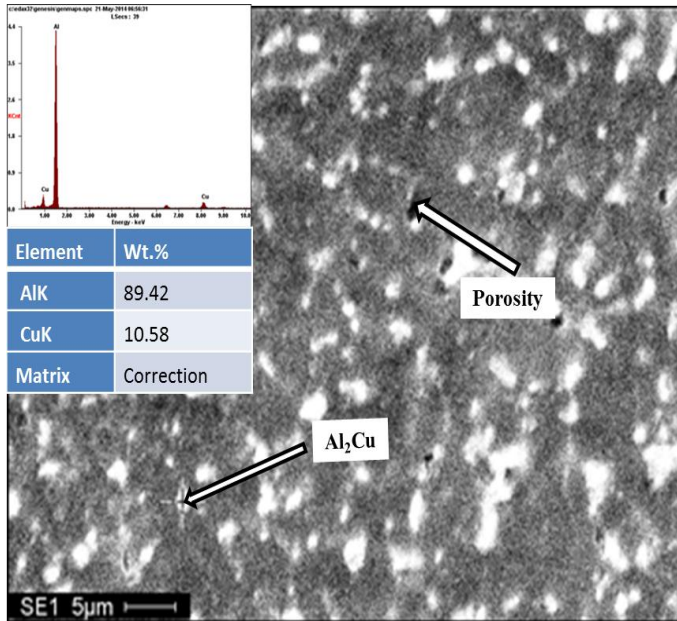| Element	Wt.%
AlK	89.42
CuK	10.58
Matrix	Correction

Fig. 11 EDAX Results of SPS Al-4.5 wt. % Cu alloy sintered at 500^0C a) at 30 MPa b) at 40MPa c)at 50 MPa

Fig. 12 Hardness V/S sintering pressure.

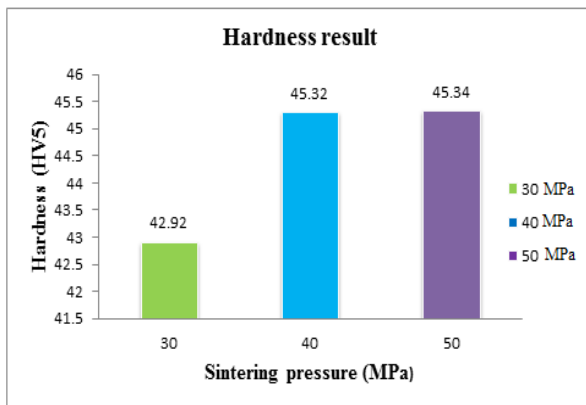Fig. 13 The compression graphs for different sintering pressure at (a) 30 MPa, (b) 40 MPa and (c) 50 MPa.

3.4.2 Hardness conversion from HV to MPa

There is now a trend towards reporting Vickers hardness in SI units (MPa or GPa) particularly in academic papers. Unfortunately, this can cause confusion. Vickers hardness (e.g. HV/30) value should normally be expressed as a number only (without the unit's kgf/mm2). Rigorous application of SI is a problem; most Vickers hardness testing machines use forces of 1, 2, 5, 10, 30, 50 and 100 kgf. To convert Vickers hardness number the force applied needs converting from kgf to Newton and the area needs converting from mm² to m² to give results in Pascal's. To convert HV to MPa multiply by 9.807 and to GPa multiply by 0.009807. The obtained test results in MPa are 420.9±0.04, 444.5±0.904 and 444.60±0.217 for 30, 40 and 50 MPa respectively.
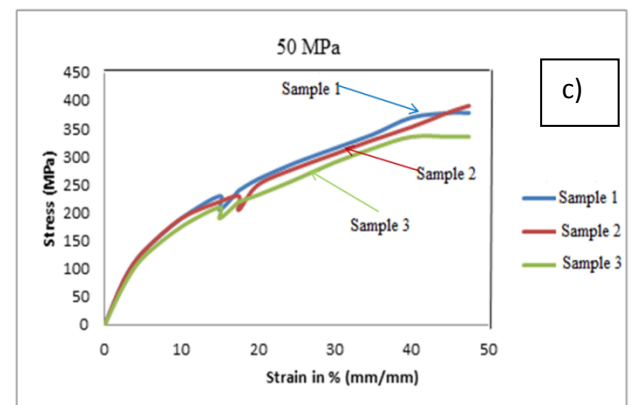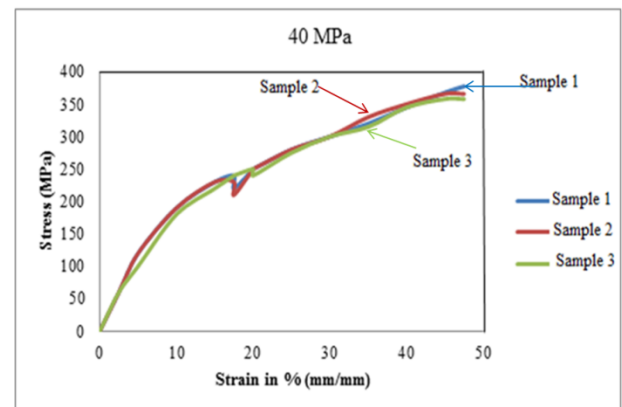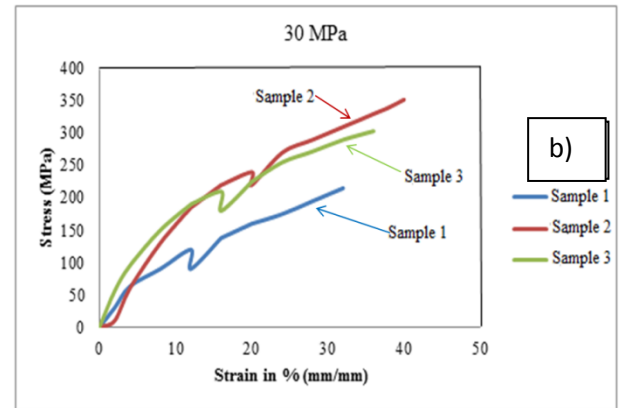
3.4.3 Compressive strength

The compression test samples are obtained as per the ASTM standard of aspect ratio 1.5. The each sintered cylindrical compact of diameter 30 mm and height 15mm can be cut by using EDM wire cut to obtain the three test samples (9*9*14). And the compression test was carried out at a strain rate of 1.47×10^{-2} S^{-1} (Universal testing machine, its capacity 100 tone's) so the average ultimate compressive strength was absorbed to be 278±0.90, 366±0.21 and 368±0.31 MPa respectively with respect to the 30, 40 and 50 MPa sintering pressures. Figs. 13 (a), (b) and (c) shows the compression graphs for different sintering pressures of 30, 40 and 50 MPa respectively. The 30 MPa test sample shows varying compression strength due to presence of porosity and voids while other two samples show uniform

varying graphs it leads to the dense and uniformly distribution of grains. While the sintered compact at 40 MPa and 50 MPa exhibited the highest compression strength since the microstructure was characterized by fine distribution of precipitates, large fraction of sub-micron grains and completes metallurgical bonding. This increased strength can be attributed to the uniform distribution of the Cu particles in the aluminum alloy and better interfacial bonding between the Aluminum and Cu alloy powder. 4.5 wt. % Cu with aluminum gives higher mechanical properties like hardness and compression strength imparts better mechanical properties to sintered compact, when good interfacial bond is formed between Al-4.5 wt. % Cu alloy powder particles through spark plasma sintering process.

4. CONCLUSION

In this study optimizing the process parameters (Sintering temperature of 500°C, sintering time 5 min, and varying compaction pressure from 30-50 MPa, heating rate 50 °C/min, pulsated current and voltage under controlled atmosphere) were used for compaction of the SPS Al-4.5 wt. % Cu alloy powder. From the obtained results the conclusions are as follows:

1. Spark plasma sintering is an effective way to obtain the samples with homogenous microstructure, exceptional physical and mechanical properties at 500ºC and 40, 50 MPa sintering pressures.

2. Micrographs reveals the uniform and homogenous microstructure confirms second phase particles are well dispersed in the interior of the grains and even rarely presence of secondary phase along the grain boundaries results in good compact and porosity-free materials it indicates that full densification is achieved at higher sintering pressures.

3. The EDAX reports confirm the presence of Aluminum, Copper and Al_2Cu phase in the compact.

4. Fully dense Al-4.5 wt. % Cu alloys compacts are obtained through spark plasma sintering with almost uniform density values.

5. The macro hardness of spark plasma sintered samples increases with the increase of compaction pressure from 30 to 50 MPa and reaches the values from 42.92 ± 0.31 to 45.34 ± 0.43 HV it confirms the increased higher sintering pressure not much influence on hardness.

6. Compressive strength of spark plasma sintered samples increases with the increase of compaction pressure from 30 to 50 MPa and reaches the values from 278 ± 0.90 to 368 ± 0.31 MPa.

5. REFERENCES:

[1] J.M. Silcock, T.J. Heal and H.K. Hardy, Journal of international metals. 82, 1954, 239.

[2] S.C. Wang and M .J. Starink, International material review. 50, 2005, 193.

[3] G. Baumeister, B. Okolo and J. R.Anger, Journal of microstructural technology. 149, 2008, 1647.

[4] W. Chen, U. Anselmi-Tamburini, J.E. Garay, J.R. Groza, Z.A. Munir, Material science engineering. 394, 2005, 132.

[5] German, Randall M. Powder Metallurgy and Particulate Materials Processing. Princeton: Metal Powder Industries, 2, 2005, 253.

[6] D. Bernache-Assollant, Chimie-physique du frittage (Ed:D. Bernache-Assollant), Hermes FORCERAM Collection, Paris. 7, 1993, 168.

[7] T. Hungrı´a, Jean Galy and Alicia Castro Adv. Powder metal particulate material. 11, 2009, 8.

[8] K. Vanmeensel, A. Laptev, J. Hennicke, J. Vleugels, O. Vander Biest, Densification and strength evolution in solid-state sintering, Journal of material science. 53, 2005, 4379.

[9] J.L. Li, L.J. Wang, G.Z. Bai, W. Jiang, journal of powder metallurgy structural materials. 52, 2005, 867.

[10] Williams, W. C., and G. C. Stangle. "Fabrication of Near-Net-Shape Al2O3-Fiber-Reinforced Ni3Al Composites by Combustion Synthesis." Journal of Materials Research 7, 1995, 1736.

[11] Sikka, V. S., S. C. Deevi, and J. D. Vought. "Exo-Melt: A Commercially Viable Process." Advanced Materials Processing 147, 6, 1995, 29.

[12] Dunand, D. C. "NiAl Formation by Annealing of Infiltrated Aluminum-Nickel Precursors." Journal of Materials Science 29, 1994, 4056.

[13] Je´re´my guignard, Misha Bystricky and Fre´de´ric be´jina, Dense fine grained aggregate prepared by SPS. Journal of material science 23, 2011, 323.

[14] Nouari Saheb International Journal of Minerals, "Spark plasma and microwave sintering of Al6061 and Al2124 alloys" 20, 2013, 152.

[15] Th. Schubert , A. Zhu, Y. Horita, Z. Koch, C.C. and Holesinger, T.G. Processing and characterization of nanostructured Cu-Carbon nanotube composites. Materials Science and Engineering 523, 2009, 60.

[16] S.Devaraj, S.Sankaran and R kumar "Influence of SPS temperature on densification, microstructural and mechanical properties of Al-4.5 Wt.% Cu alloy" 26, 2013, 761.

[17] Z.A. Munir and Dat V. Quach, J. Am. microstructural and mechanical characterization of ceramics by SPS. Ceramic society. 94, 2011, 1.

[18] M.S. Motta, P.K. Jena, E.A. Brocchi, I.G. Solorzano, journal of Material science and engineering. 15, 2001, 175.

[19] Parvin, & Rahimian,M.- "The characteristics of alumina particle reinforced pure Al matrix composites". Proceedings of the international congress on Advances in applied physics and material science, 61, 2011, 197.

[20] C. Padmavathi, A. Upadhyaya and D. Agarawala, Microwave sintering of aluminum alloys, Journal of Materials Chemistry and physics. 130, 2011, 449.

[21] Zhao-Hui Zhang*, Fu-Chi Wang, Lin Wang, Shu-Kui Li "Ultrafine-grained copper prepared by spark plasma sintering process" 476, 2008, 201.

[22] R. Trivedi, F. Jin and I. E. Anderson, Acta Materialia. 51, 2003. 289.