

# IN SITU FABRICATION OF Al 2024-Mg<sub>2</sub>Si COMPOSITE BY SPARK PLASMA SINTERING OF REACTIVE MECHANICALLY ALLOYED POWDER

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**Abstract:** In situ Al2024- Mg<sub>2</sub>Si composite was fabricated by spark plasma sintering (SPS) of reactive powder. Reactive powder was obtained from mechanical alloying (MA) of elemental powders. Clad layers of in situ composite were fabricated on Al substrates by spark plasma sintering (SPS). Structural evolution during MA process and after SPS was investigated by X-ray diffractometry (XRD). Scanning electron microscopy (SEM) was utilized to study the microstructure of sintered samples. Hardness and tensile behavior of sintered samples were investigated. The results showed that SPS of mechanically alloyed unreacted powder can result in the in situ formation of Mg<sub>2</sub>Si and Mg<sub>2</sub>Al<sub>3</sub> within the Al matrix. SPSed clad layer showed a sound and clear interface to the Al substrate with a hardness of about 140 HV. Sintered in situ composite exhibited a tensile strength of 288 MPa.

**Keywords:** Al composite, Mg<sub>2</sub>Si, Mechanical alloying, Spark plasma sintering.

## 1. INTRODUCTION

Ex-situ methods for the fabrication of metal matrix composites (MMCs) suffer from a few drawbacks such as agglomeration and inhomogeneous distribution of the reinforcements and the weak interfacial bonding between the reinforcing particles and the matrix [1-2]. As a solution in situ synthesizing of MMCs has been developed that involves the production of reinforcement within the matrix during composite fabrication. This method presents highlighted advantages such as more homogenous microstructure. Moreover, the reinforcements made by in situ reactions show a clean interface to the matrix and smaller size resulting in better mechanical properties [3-4].

In situ Al-Mg<sub>2</sub>Si composites, as a well-known class of ultra-light materials for aerospace and other advanced engineering applications, has attracted the attention of material scientists and design engineers [6-7]. These composites are good candidates for many industrial applications because of the presence of Mg<sub>2</sub>Si compound with a low density (1.99 g/cm<sup>3</sup>), low thermal expansion coefficient (7.5×10<sup>-6</sup> K<sup>-1</sup>) and reasonable hardness (450 HV) [8]. Different in

situ methods based on casting techniques have been developed to synthesize Mg<sub>2</sub>Si reinforced Al matrix composites [8-10]. However, in these processes the presence of coarse primary Mg<sub>2</sub>Si particles in the matrix has been reported to result in poor mechanical properties. The large Mg<sub>2</sub>Si particle size, brittle Al-Mg<sub>2</sub>Si eutectic structure and the inhomogeneous distribution of Mg<sub>2</sub>Si in the composites produced by the casting processes are mainly responsible for degraded mechanical properties of these composites. Therefore, some research efforts have been focused on the refinement of primary and eutectic Mg<sub>2</sub>Si phases in Mg<sub>2</sub>Si reinforced composites and modifying their morphology and distribution, to improve the properties of these composites. Many efforts have been focused on modifying of Mg<sub>2</sub>Si structure by the addition of elements or compounds during casting processes [8, 10]. On the other hand advanced processing techniques, such as rapid solidification processing, severe plastic deformation and MA have been utilized to improve the microstructure and properties of these composites [11-13].

MA as a solid state powder processing method has been considered for fabricating in situ MMCs [5]. MA has an advantage over other in situ

fabrication routes as it is capable of producing nano structured composite powders with high uniformity [5, 14]. Furthermore it is possible to obtain reactive powders by MA of elemental powders that are capable of reaction during high temperature processing such as sintering or thermal spraying [15].

Long time exposure at high temperature sintering in conventional methods, often results in severe grain growth, particularly in MAed powders. To overcome the problem of coarsening, a few sintering methods such as hot-pressing, shock consolidation, sintering with the application of AC currents, pulsed electric current and spark plasma sintering (SPS) have been introduced and investigated [16]. SPS provides fast densification with minimal grain growth in a short sintering time. It is proven that enhanced sinterability of powders subjected to SPS mainly associated with particle surface activation and increased diffusion rates on the contact zones caused by applied pulse current [17]. This method has been lately proposed as a cladding method for the fabrication of surface clad layers [18].

In this study a reactive powder consisting Al 2024 alloy, Mg and Si has been attained by double step MA method. The reactive powder was sintered by SPS technique to fabricate in situ composite clad layer on Al substrate. Structural evolutions and mechanical properties of the SPSed samples were studied.

## 2. EXPERIMENTAL PROCEDURE

Commercially available Mg (99.9%), and Si (99%) powders were used as starting materials. Powder mixture consisting Al (99.8%), Cu (98%), Mn and Zn with the nominal composition of Al2024 alloy (Al-4.5Cu-0.5Mn-0.2Zn-1.9Mg-0.5Si) was tailored as the matrix. Elemental powders were mechanically alloyed by a double step process to attain Al2024 alloy containing excess amount of Mg and Si to synthesize 10 wt.% Mg<sub>2</sub>Si. Powder mixtures of Al2024-Mg and Al2024-Si were milled by a high energy planetary ball mill having a rotating speed of 400 rpm, separately for 5h. Balls to powder weight ratio was chosen to be 10 and the diameter of

each chromium steel ball was 15 mm. The hardened chromium steel vial was evacuated and filled with pure argon to prevent oxidation during mechanical alloying. In order to avoid severe adhesion of aluminum powder to the balls and the vial surfaces, 1 wt% zinc stearate was added to the mixture as the process controlling agent. Resultant powder mixtures were mixed and milled for further 5h (a total MA time of 10h).

FCT spark plasma sintering machine (FCT System GmbH, Germany) was utilized to consolidate the MAed powders. Powders were consolidated to samples of 40 mm diameter and 10 mm thickness or on Al substrates of 40 mm diameter using graphite punches and die. The SPS was carried out at 550 °C with a heating rate of 50 °C min<sup>-1</sup> and holding time of 2 min under argon atmosphere. Uniaxial pressure was applied to the powder mass throughout the SPS cycle and this reached a maximum value of 40 MPa during sintering process. The total processing time from loading of the powder filled graphite die into the SPS chamber to ejection of sintered pellet from the die was about 20 min. A schematic illustration of powder processing and sintering is presented in Fig. 1.

Differential scanning calorimetry (DSC) experiment was conducted on MAed powder under argon flow with a heating rate of 15 °C min<sup>-1</sup> over the 25-575 °C temperature range. A SEIFERT X-ray diffractometer employing monochromatic Cu K $\alpha$  radiation ( $\lambda$ = 0.15406 nm) was used to investigate the structural changes during mechanical alloying and after thermal processing. XRD scans were performed with a step size of 0.05° and a dwell time of 2 s. The cross-sectional microstructures of SPSed samples together with spot analysis were studied with the aid of a LEO1450VP scanning electron microscope (SEM) at an accelerating voltage of 15 kV equipped with an energy dispersive X-ray spectrometer (EDX). Density of the SPS pellets was measured using Archimedes' principle. Sintered bulk sample was subjected to microhardness test at 50 g load by Zwick macrohardness machine using ASTM E92 standard method. Tensile behavior at ambient temperatures was studied by a Hounsfield H50KS S machine at a strain rate of 0.001 s<sup>-1</sup>

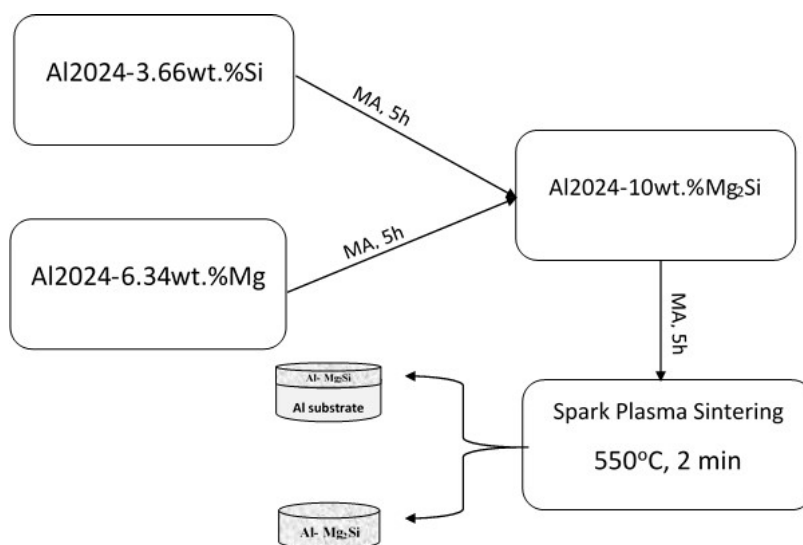


Fig. 1. schematic illustration of powder processing and bulk sample preparation.

using ASTM E8M standard test method for tension testing of metallic materials.

### 3. RESULTS AND DISCUSSION

Mechanical alloying of Al-Mg-Si powder mixture with the nominal composition of Al2024- 10Mg<sub>2</sub>Si resulted in an exothermic reaction when the vial was opened in air after 5 h of milling. The existence of Mg and Si with the stoichiometric ratio can be considered as a source to provide the energetic requirements for a self propagating high temperature reaction. Thermodynamically the formation of Mg<sub>2</sub>Si ( $\Delta G_f^\circ = -76.782$  kJ/Mol) from elemental powders is a favored exothermic reaction ( $\Delta H^\circ = -79.287$  kJ/Mol) [19]. The activation energy for this reaction can be provided from the fast oxidation of the clean and active surfaces of the Al powder particles leading to the initiation of a self-sustaining reaction between Mg and Si. Such behavior has been reported during the MA of Al-Ti-B powder mixture, too [20]. Therefore, to prevent SHS reaction between Mg and Si during mechanical alloying a double step route was tailored as described in experimental procedure. Fig. 2 shows the x-ray patterns obtained from the powder after mechanical alloying at different

steps. After 5 h of milling in the first step the peaks related to Al, Cu, Mg and Si can be observed on the XRD patterns (Fig. 2-a and b). Fig. 2-c shows the XRD pattern of Al-Cu-Mg-Si powder mixture after 5 h of milling in the second step (a total milling time of 10 h). The peaks corresponding to Cu have been disappeared from the XRD pattern that according to the literature can be attributed to the dissolution of Cu in Al matrix [21]. From the existence of some low intensity Si and Mg peaks it can be realized that Si and Mg are still unreacted and undissolved in the aluminum matrix. No excess peaks related to other phases appeared in the XRD pattern after 5 h of milling in the second step, which means there has not been any excessive reaction between the elements in the powder mixture.

The powder was evaluated by DSC analysis after a total milling time of 10 h to investigate the thermal behavior during further consolidation processing. The DSC trace of powder particles in Fig. 3 represents an apparent exothermic peak at 335 °C standing for the occurrence of a reaction in the powder. XRD pattern of the powder after DSC analysis up to 575 °C shown in Fig. 4 revealed the formation of Mg<sub>2</sub>Si matched with ICDD PDF# 00-034-0458. Also a peak appeared in the XRD pattern that can be attributed to

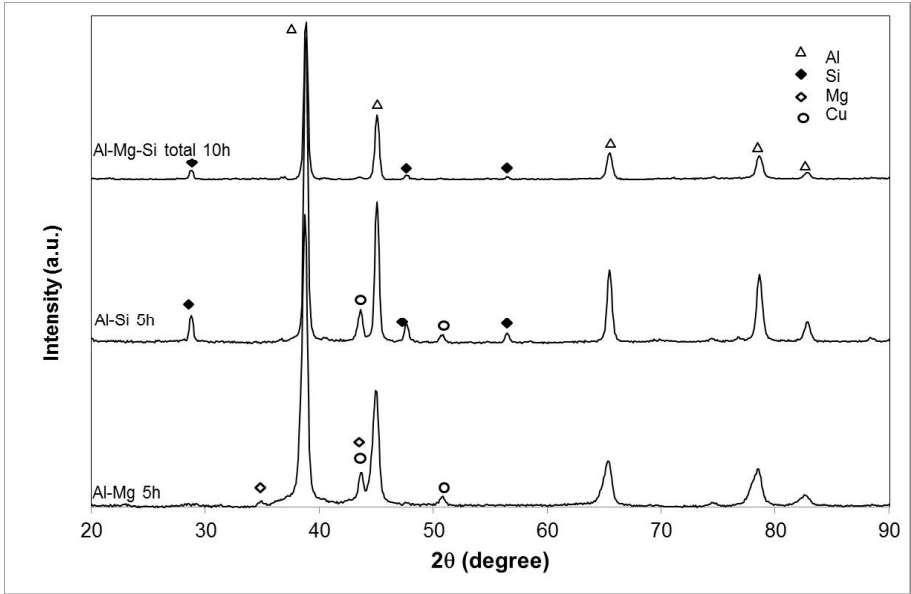


Fig. 2. XRD patterns of the powder after different times of double step MA method at 400 rpm.

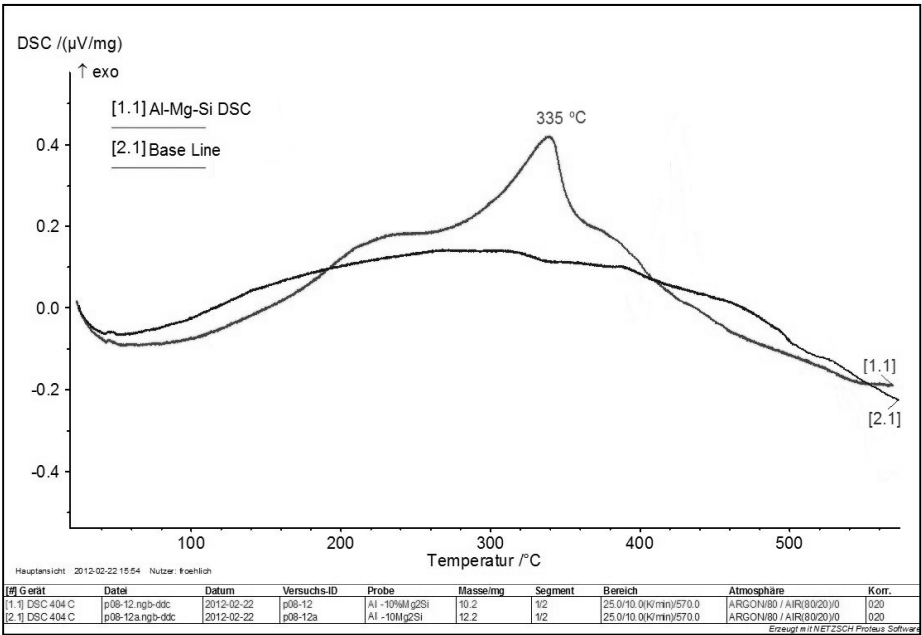


Fig. 3. DSC trace obtained from the powder after a total 10 h of double step MA at 400 rpm.

$\text{Mg}_2\text{Al}_3$  intermetallic compound (ICDD PDF# 00-001-1132). Therefore it can be concluded that the powder obtained from double step MA method is capable of reaction at high temperature

exposure.

The powder obtained from a total 10 h of MA was sintered by SPS technique, on Al substrate, as a clad layer. Bulk samples were also sintered

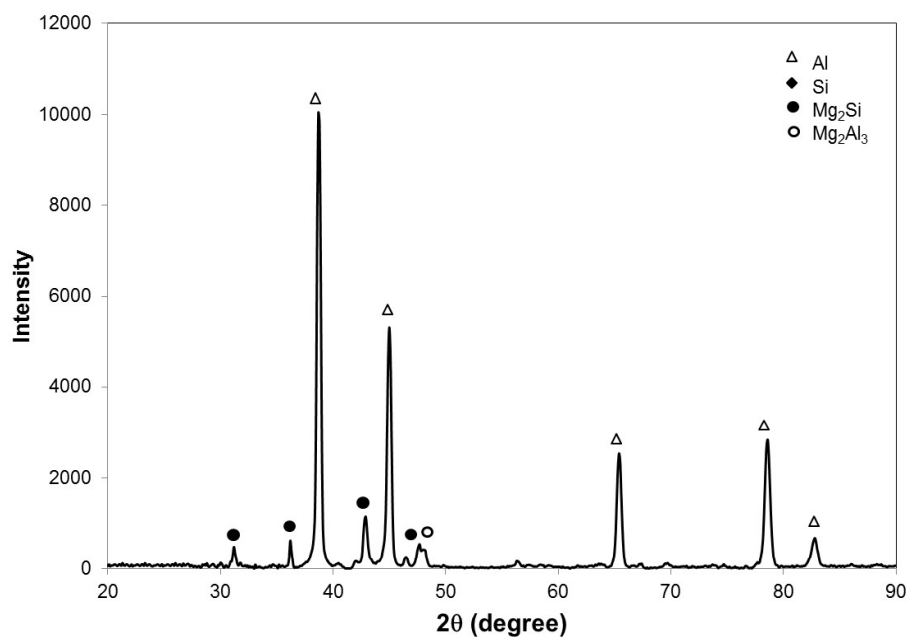


Fig. 4. XRD pattern of the powder obtained from 10 h of double step MA at 400 rpm after DSC up to 575°C.

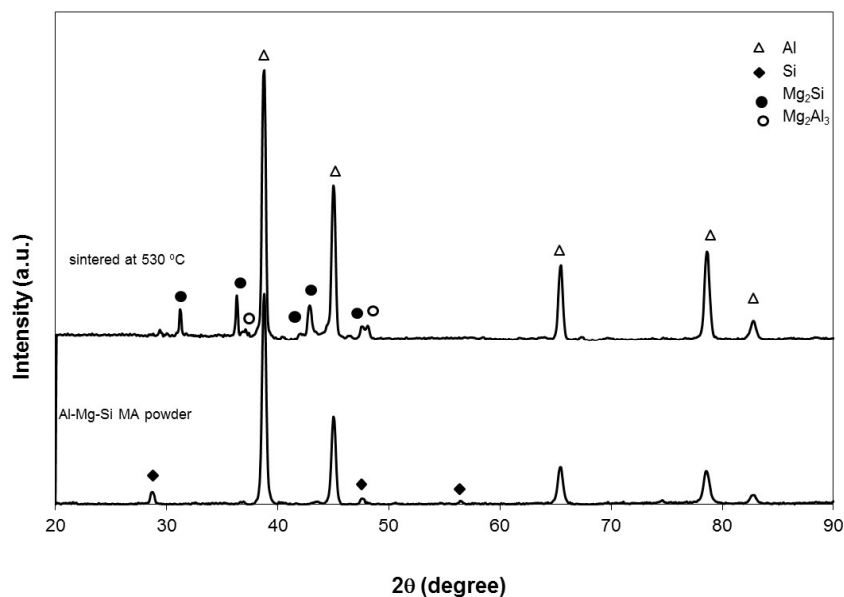
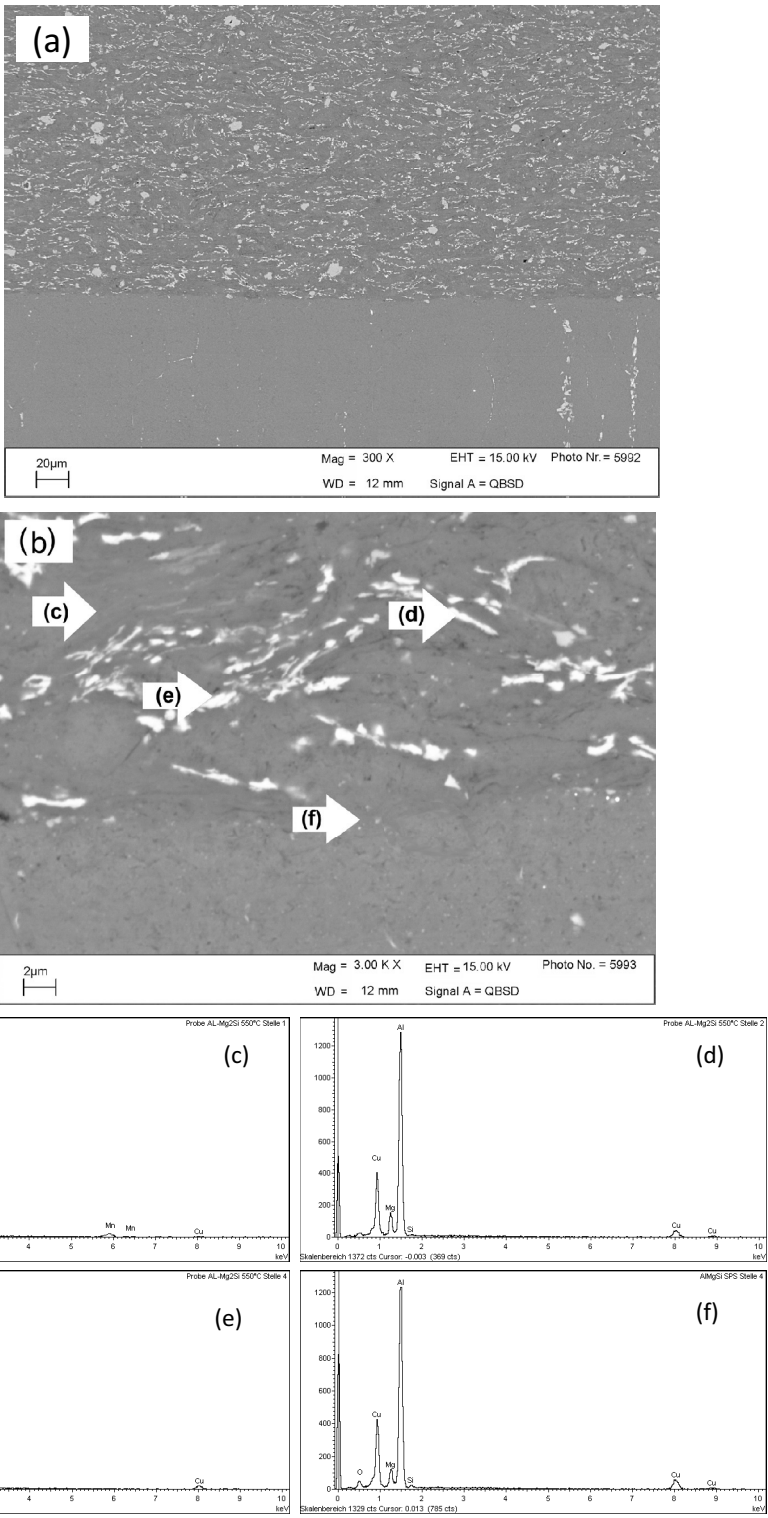


Fig. 5. XRD pattern of consolidated sample after SPS at 550 °C.

by SPS at similar process parameters to evaluate the density and for the preparation of tensile test specimens. The density of the SPSed sample was

determined to be 2.775 g/cm<sup>3</sup> which is 99 % of the theoretic density. Fig. 5 shows the XRD pattern of the clad layer compared to the MAed powder.



**Fig. 6.** Cross-sectional SEM micrographs of the clad layer obtained from SPS of MAed powder at 550 °C, a) clad layer b) clad layer-substrate interface, c-f) EDS microanalysis of selected points.

The peaks related to Si disappeared and new peaks corresponding to  $\text{Mg}_2\text{Si}$  (ICDD PDF# 00-017-0081) appeared in the XRD pattern of sintered clad layer. Moreover, other peaks appeared in the XRD pattern of sintered sample that matched the  $\text{Mg}_2\text{Al}_3$  phase (ICDD PDF# 00-001-1132).  $\text{Mg}_2\text{Al}_3$  is a low density, brittle intermetallic compound with strengthening effect when distributed in Al matrix as fine particles [22]. In situ sintering of reactive powders has been reported in metal matrix composites and ceramic materials [23-24].

Fig. 6-a presents the cross sectional SEM micrograph of the clad layer SPSed on Al substrate at a maximum temperature of 550 °C for 2 min. As can be seen the clad layer was sintered without obvious defects such as noticeable porosities or cracks. The clad layer exhibited a clear and sound interface with the substrate with no obvious evidence of interface defects. EDS point microanalysis conducted on selected regions of the interface (Fig. 6c-d), showed a metallurgical and diffusional thin transition region at the interface, containing substrate and clad layer elements.

by microhardness measurements on the cross section of SPSed sample from the substrate to the clad layer, as shown in Fig. 7. At the vicinity of the interface, hardness showed a sharp transition from about 78 VHN in the substrate to about 140 VHN in the clad layer.

Tensile tests were conducted on bulk samples sintered by SPS method. Average tensile strength of three sintered sample was 288 MPa without an obvious yielding point in the stress-strain curve. Typical curves obtained from tensile tests are presented in Fig. 8. The offset yield strength was determined to be about 200 MPa and the total elongation was 1.05 %. Several researchers have reported such a brittle behavior for the samples fabricated from mechanically alloyed powders [25-26]. In situ synthesized composites have been reported to show enhanced mechanical properties in comparison to ex-situ composites [5]. The tensile strength of SPSed sample is higher than that reported for in situ Al- $\text{Mg}_2\text{Si}$  alloy fabricated by centrifugal casting [6]. This may be attributed to finer distribution of the participated phases in the sample which has been sintered from MAed powder.

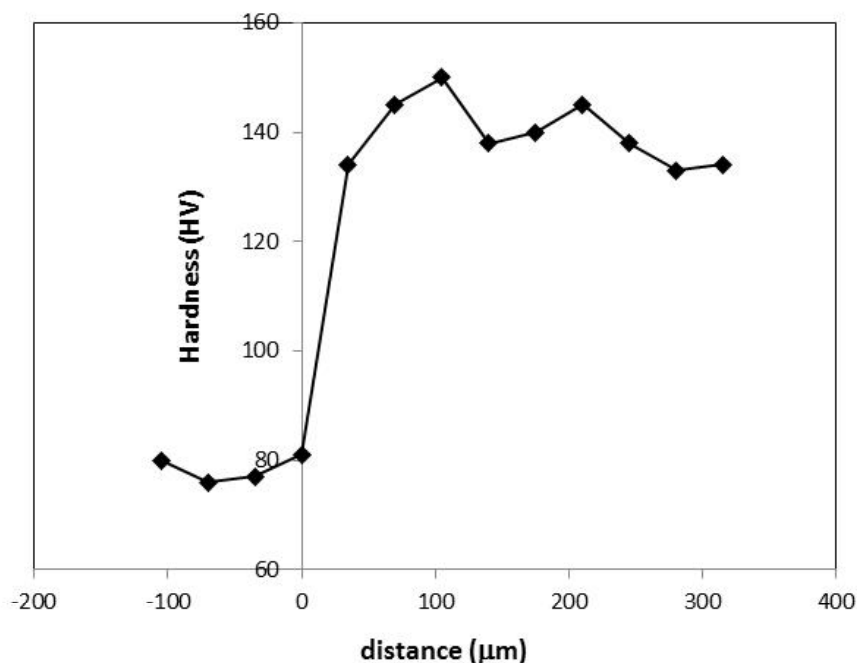
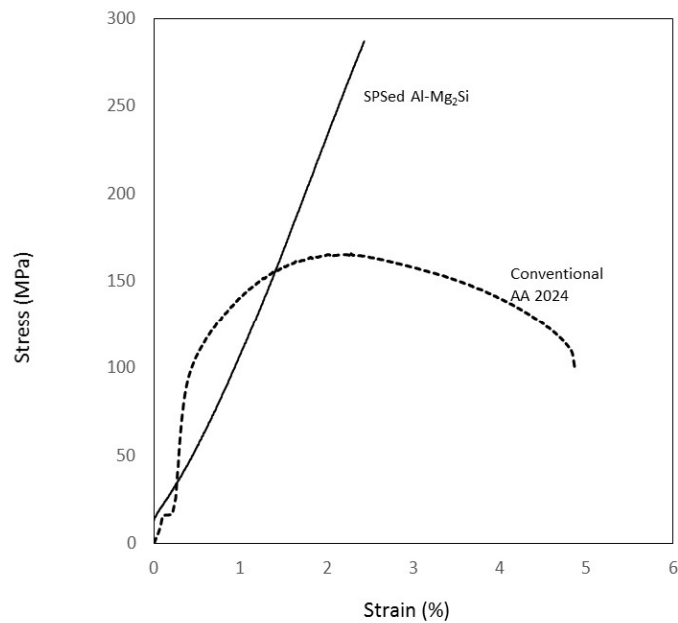


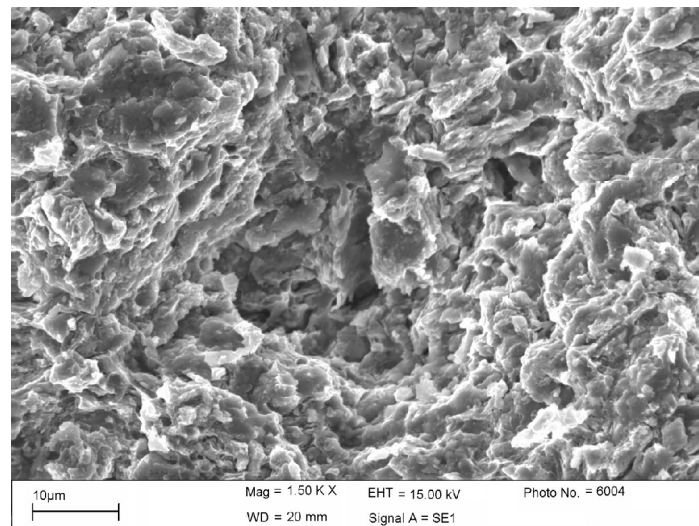
Fig. 7. Vickers microhardness profile through the cross-section of SPSed sample, from Al substrate to the clad layer.

Hardness profile of the clad layer was obtained

SEM fractography of tensile specimen tested



**Fig. 8.** typical stress- strain curve obtained from tensile testing of SPSed samples compared to the conventional 2024 Al alloy.



**Fig. 9.** Fracture surface morphology of SPSed sample.

at the strain rate of 0.001 mm/s is presented in Fig. 9. Fracture surface morphology showed a dimple fracture which has been mostly transgranular. Such a microscopic ductile behavior has been previously observed in bulk composites obtained from sintering of MAed

powders [25,27]. As mechanical alloying results in finer microstructures, the size of intergranular dimple feature reduces in comparison to conventional fabrication methods like casting [28].

#### 4. CONCLUSIONS

SPS of mechanically alloyed unreacted powder can result in the in situ formation of  $Mg_2Si$  and  $Mg_2Al_3$  within the Al matrix. SPSed clad layer showed a sound and clear interface to the Al substrate with a hardness of about 140 HV. Sintered in situ composite exhibited macroscopic brittle behaviour with a tensile strength of 288 MPa.

#### 5. ACKNOWLEDGEMENT

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#### REFERENCES

1. Ezatpour, H. R., Parizi, M. T. and Sajjadi, S. A., "Microstructure and Mechanical Properties of Extruded Al/ $Al_2O_3$  Composites Fabricated by Stir-casting Process". *T. Nonferr. Metal. Soc.*, 2013, 23(5), 1262-1268.
2. Kok, M., "Production and Mechanical Properties of  $Al_2O_3$  Particle-reinforced 2024 Aluminium Alloy Composites". *J. Mater. Process Technol.*, 2005, 161, 381-387.
3. Kumar, S., Sarma, V. S. and Murty, B. S., "A Statistical Analysis on Erosion Wear Behaviour of A356 Alloy Reinforced with In situ Formed  $TiB_2$  Particles". *Mater. Sci. Eng. A*, 2008, 476(1-2), 333-340.
4. Ai, T. T., "Microstructures and Mechanical Properties of In-situ  $Al_2O_3/TiAl$  Composites by Exothermic Dispersion Method". *Acta Metall. Sinica*, 2008, 21(6), 437-443.
5. Tjong, S. C. and Ma Z. Y., "Microstructural and Mechanical Characteristics of In situ Metal Matrix Composites. *Mater*". *Sci. Eng. R*, 2000, 29(3-4), 49-113.
6. Zhang, Z. M., Xu, C. J., Guo, X. F. and Jia, S. Z., "Reciprocating Extrusion of In situ  $Mg_2Si$  Reinforced Mg-Al Based Composite". *Acta Metall. Sinica*, 2008, 21(3), 169-177.
7. Qin, Q. D., Zhao, Y. G., Zhou, W. and Cong, P. J., "Effect of Phosphorus on Microstructure and Growth Manner of Primary  $Mg_2Si$  Crystal in  $Mg_2Si/Al$  Composite". *Mater. Sci. Eng. A*, 2007, 447(1-2), 186-191.
8. Georgatis, E., Lekatou, A., Karantzalis, A. E., Petropoulos, H., Katsamakis, S. and Poulia, A., "Development of a Cast Al- $Mg_2Si$ -Si In Situ Composite: Microstructure, Heat Treatment, and Mechanical Properties". *J. Mater. Eng. Perform.* 2013, 22(3), 729-741.
9. Zhang, J. T., Zhao, Y. G., Xu, X. F. and Liu, X., "Effect of Ultrasonic on Morphology of Primary  $Mg_2Si$  in In-situ  $Mg_2Si/Al$  Composite". *T. Nonferr. Metal. Soc.*, 2013, 23, 2852-2856.
10. Emamy, M., Khorshid, R. and Honarbakhsh Raouf, A., "The Influence of Pure Na on the Microstructure and Tensile Properties of Al- $Mg_2Si$  Metal Matrix Composite". *Mater. Sci. Eng. A*, 2011, 528, 4337-4342.
11. Qin, Q. D. and Zhao, Y. G., "Nonfaceted Growth of Intermetallic  $Mg_2Si$  in Al Melt During Rapid Solidification". *J. Alloys Compd.*, 2008, 462, 28-31.
12. Bian, L., Liang, W., Xie, G., Zhang, W. and Xue, J., "Enhanced Ductility in an Al- $Mg_2Si$  In situ Composite Processed by ECAP Using a Modified BC Route. *Mater*". *Sci. Eng. A*, 2011, 528, 3463-3467.
13. Sagamata, M., Shiina, K., Kubota, M. and Kaneko, J., "Properties of Mechanically Alloyed P/M Composites of Al- $Mg_2Si$ -Oxide Systems". *J. Alloys Compd.* 2009, 483, 350-354.
14. Kubota, M. and Cizek, P., "Synthesis of  $Al_3BC$  from Mechanically Milled and Spark Plasma Sintered Al- $MgB_2$  Composite Materials". *J. Alloys Compd.*, 2008, 457, 209-215.
15. Horlock, A., Sadeghian, J. Z., McCartney, D. G. and Shipway, P. H., "High-Velocity Oxyfuel Reactive Spraying of Mechanically Alloyed Ni-Ti-C Powders". *J. Therm. Spray. Technol.* 2005, 14(1), 77-84.
16. Viswanathan, V., "Challenges and Advances in Nanocomposite Processing Techniques", *Mat. Sci. Eng. R*, 2006, 54, 121-285.
17. Mamedov, V., "Spark Plasma Sintering as Advanced PM Sintering Method". *Powder Metallurgy*, 2002, 4 (45), 322-328.
18. Zohari, S., Sadeghian, Z., Lotfi, B. and Broeckmann, C., "Application of Spark Plasma Sintering (SPS) for the Fabrication of In situ Ni-TiC Nanocomposite Clad Layer". *J. Alloy. Compd.*, 2015, 633, 479-483.
19. Barin, I., "Thermodynamical Data of Pure

- Substances”, Wiley- VCH, Weinheim, 1989.
20. Sadeghian, Z., Enayati, M. H. and Beiss, P., “In situ Production of Al-TiB<sub>2</sub> Nanocomposite by Double-step Mechanical Alloying”. J. Mater. Sci. 2009, 44, 2566-2572.
21. Suryanarayana, C., “Mechanical Alloying and Milling”. Prog. Mater. Sci., 2001, 46, 1-184.
22. Singh, D., Suryanarayana, C., Mertus, L. and Chen, R. H., “Extended Homogeneity Range of Intermetallic Phases in Mechanically Alloyed Mg-Al Alloys”. Intermetallics, 2003, 11, 373-376.
23. Daoush, W., Francis, A., Lin, Y. and German, R., “An Exploratory Investigation on the In-situ Synthesis of SiC/AlN/Al Composites by Spark Plasma Sintering”. J. Alloy. Compd. 2015, 622(15), 458-462.
24. Wang, L., Zhang, J. and Jiang, W., “Recent Development in Reactive Synthesis of 103-112”.
25. Nie, C. Z., Gu, J. J., Liu, J. L. and Zhang, D. “Production of Boron Carbide Reinforced 2024 Aluminum Matrix Composites by Mechanical Alloying”. Mater. Trans. 2007, 48(5), 990-995.
26. Azimi, A., Shokouhfar, A. and Nejadseyfi, O., “Mechanically Alloyed Al7075-TiC Nanocomposite: Powder Processing, Consolidation and Mechanical Strength”. Mater. Design., 2015, 66, 137-141.
27. Tang, F., Hagiwara, M. and Schoenung, J. M., “Microstructure and Tensile Properties of Bulk Nanostructured Al-5083/SiCp Composites Prepared by Cryomilling”. Mater. Sci. Eng. A, 2005, 407(1-2), 306-314.
28. Meyers, M. A., Mishra, A. and Benson, D. J., “Mechanical Properties of Nanocrystalline Materials”, Prog. Mater. Sci. 2006, 51, 427-556.