



Review on Effective Parameters on Fabrication of Aluminum Matrix Composite reinforced by Manganese Oxides

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Abstract

Most recently, manganese (Mn) oxides materials including MnO and MnO₂, are one of several types of ceramics are used as reinforcement elements to manufacture aluminum metal matrix composites (AMMC's). AMMC's are gaining widespread acceptance for household supplies, automobile, aircraft and many other industrial applications because of their essential properties such as low density, environment resistance, high strength and adequate mechanical and physical properties. The current article explores a detailed overview of the parameters effect on fabrication of AMMC's reinforced by Mn-oxides adopted by many researchers through methodologies, including solid, semi-solid and liquid techniques. Based on the literature review, research work has also focused on exploring the morphology, microstructure and properties of AMMC's reinforced with Mn-oxides. Mn-oxides, including MnO and MnO₂, can be used as reinforcement to manufacture In-situ Al-Al₂O₃-AlMnO_x (MnO₂, MnO) composite. The energy density of manganese oxide (Na_xMnO₂) cathode materials for rechargeable sodium batteries can be enhanced by the incorporation of aluminum, where these materials showed a significantly higher initial discharge capacity and superior cycling performance. The produced composite is highly dependent on parameters of manufacture technique. Temperature, reinforcement particles size and reinforcement volume ratio (RVR) have a remarkable effect on the morphology and properties of AMMC's reinforced by Mn-oxides. In-situ AlMnO_x particles are characterized by porous structure, which gives them a large surface area that could improve the related properties such as the heat storage capacity.

Keywords: Aluminum metal matrix composites, Ceramic reinforcements, Manganese oxides.

1. Introduction

Due to their unique characteristics, such as: high strength to weight ratio, environment resistance, low economic and an adequate mechanical and physical



properties, Aluminium metal matrix composites (AMMC's) are significantly important in the various demanding fields modern industrial applications, Wiley, J. (1992). There are several types of ceramics such as SiC, SiO₂, Al₂O₃, MgO, ZnO, BeO, MnO₂, TiO₂, TiC, etc. are utilized as reinforcement elements to manufacture metal matrix composites [MMC's]. Superior properties of these materials such as refractoriness, high compressive strength and hardness, excellent wear resistance, etc. make them appropriate for use as reinforcement materials in MMC's, Khedera, A. (2011); Ramesh, D. (2011); William, D. (2007); Surappa, M. (2003). In AMMC's one of the constituent is aluminium, which forms percolating network and is termed as matrix phase. Pure Aluminium and Aluminium alloys, such as the 2000, 5000, 6000 and 7000 alloy series are the most commonly used materials in composite manufacture, the other constituent is embedded in this aluminium and serves as reinforcement. Mono filaments, whiskers, fibers or particulate types are widely used as reinforcement phases. In recent years, Al based composites have gained significance in aerospace, automotive and structural applications due to their enhanced mechanical properties and good stability at high temperature, Kala, H. (2014).

1.1 Manganese Oxides

Manganese (Mn) is the second most abundant transition metal in the earth's crust and exists in a variety of crystallographic phases in nature. Manganese oxide refers to a variety of Mn oxides and hydroxides. There are more than 30 Mn oxide / hydroxide minerals that have been discovered. They consist of a variety of structures, chemistries, and microscopic and macroscopic morphologies. Mn is characterized by diverse oxidation states ranging from -3 up to +7, but is generally observed as +2, +3, and +4 in surface environments. Modeling predict the chemical and thermodynamic properties of Mn-oxide minerals and preparing of their synthetic analogues depend on a detailed understanding of their crystal structures. Since many Mn oxide minerals occur only as fine grained, poorly crystalline aggregates and coatings, so this makes crystal structure study extremely challenging. In the last few years, new techniques such as TEM, Rietveld refinements using powder diffraction data, extended x-ray absorption, fine structure spectroscopy and single crystal studies using charge coupled device detectors and synchrotron sources, have started and are continuing to discover numerous inner secrets of Mn oxide minerals, Post, J. (1999). Manganese oxides exhibit good electro-catalytic properties, has lower costs and easier availability and has environmental compatibility and chemical stability. They are primarily used as cathodes in alkaline batteries, Sotgiua, G. (2014). Mn oxides is one of the most important group of



materials in energy storage science. By precise control of their properties such as particle size, surface area and Mn_{x+} oxidation state, they can be fully leveraged for their application potential.

The oxidation process related to different MnO_x species was observed by in situ X-ray diffraction (XRD) measurements showing time- and temperature-dependent phase transformations occurring during oxidation of the Mn(II) glycolate precursor to α - Mn_2O_3 via Mn_3O_4 and Mn_5O_8 in O_2 atmosphere, Augustin, M. (2015). Mn oxides are widely used for energy storage devices due to low cost, high energy density, environment pollution free and nature abundance, Hu, y. (2013). Manganese oxides were used in thermochemical heat storage for concentrated solar power. The engineering and economic feasibility of using thermochemical cycle based multivalent solid oxides for TES has been investigated. The concept is based on a pair of reduction and oxidation (REDOX) reactions which forms a thermochemical cycle (TC). Laboratory measurements and literature data showed that Mn_2O_3 and Mn_3O_4 have demonstrated reversibility in their REDOX behavior under ambient conditions. Additional laboratory measurements revealed that re-oxidation kinetics improvements were needed for Mn_2O_3 for them to be used as TES media, Wong, B. (2011). Mn- oxides, including MnO, MnO_2 and Mn_3O_4 , are used in wastewater treatment, catalysis, sensors, supercapacitors, and in alkaline and rechargeable batteries. Particularly, MnO and MnO_2 nanomaterials have attracted great interest as anode materials in lithium-ion batteries (LIBs) for their high theoretical capacity, low cost, environmental benignity, and special properties, Liu, X. (2013). By reduction of manganese oxide, such as MnO and MnO_2 , to manganese in molten aluminum, we can synthesize aluminum-manganese alloys, King, W. (1976). A new discovery for enhancing the energy density of manganese oxide ($NaxMnO_2$) cathode materials for sodium rechargeable batteries by incorporation of aluminum was reported. Results showed a much higher initial discharge capacity and superior cycling performance, Martin et al. (2010).

1.1.1 Manganese Oxide Mesoporous Solids (MOMS)

Porous materials can be classified into several types by their size. According to IUPAC notation, these materials are classified into microporous, macroporous and mesoporous materials. The microporous materials have pore diameters of less than 2 nm, the macroporous materials have pore diameters of greater than 50 nm and the mesoporous category thus lies in the middle. Some common kinds of silica and alumina are typical mesoporous materials. Oxides of niobium, zirconium, tantalum,



tin and cerium have also been reported as mesoporous materials, which can be disordered or ordered in a mesostructured.

Another ceramic is manganese oxide which is abundantly available in nature with various applications as oxidizing catalyst and as an electrode material, Ernesto, B. (1999); Rouquerol, J. (1994). Mixed valence Manganese oxides with general formula of Al_xMnO_2 often crystallize into microporous structures. These layered Manganese Oxide structures exhibit a variety of microporous structures with tunnels ranging of different degrees, thus giving versatile chemical behavior. Manganese oxide mesoporous solids (MOMS) are gaining popularity and are characterized by a high surface area mesoporous and /or microporous mixed oxidic solid, Sebastian, S. (1998); Scott, M. (2004).

2. Investigative Review on Manganese Oxides Particulate Al-Composites

Al- Al_2O_3 (MnO_2) hybrid MMC's are fabricated by liquid metallurgy through stir casting method using the in-situ and ex-situ processing. Al_2O_3 and MnO_2 particles were used together. Investigators showed that fine Al_2O_3 particles result from the reduction of MnO_2 particles by aluminum. As a result of release of manganese (Mn) in the matrix, intermetallic compound of Al-Mn precipitated in the matrix in different phases. Results showed that the porosity was evident in the micrographs and with increase in Al_2O_3 - MnO_2 wt%, the strength improved and the ductility decreased, Agarwal, A. (2012). Cast In-situ Al (Mg, Mn) – Al_2O_3 (MnO_3) composite can be synthesized by stirring manganese dioxide (MnO_2) particles into molten aluminum alloy. The unreacted MnO_2 particles lead to a sufficient enhancement in strength and hardness of the composite. The released Mn also reacts with the molten Al and forms intermetallic participates of aluminum and manganese $MnAl_6$, which is hard and brittle. Addition of Mg improved the wettability of MnO_2 with molten aluminum and thus increased the amount of reinforcing phase in the composite, Chandraveer, S. (2012).

Al1100-Mg alloy reinforced with different wt. % of MnO_2 (1, 3, 6, 9 and 12) and particle size of (1- 25) μm was fabricated by melt stirring route. commercially pure Al 1100 was melted and superheated to a 900°C. The weighed amount of MnO_2 particles was added into melt at the rate of 6-8 g/min. Mg of 2 wt. % was added to improve the wettability of the melt. A noncontact type speed sensor was used to measure the constant stirring speed of 300 rpm. Results showed that Fine Al_2O_3 particles are formed as a result of reduction of MnO_2 particles by Al and Mn is released in the matrix after the reduction of MnO_2 by Al. SEM analysis indicated that porosity in cast composites increases with increasing addition of MnO_2 powder.



Hardness and strength of the cast composites are found to increase with increase in reinforcement content, Ghanaraja et al. (2022).

Dry sliding wear behaviour of the Al 6061 alloy reinforced with MnO₂ particles in 3, 6, 9, and 12 wt.% in four steps in stir casting process was investigated. The tests were achieved at varying loads from 0 to 15 N, track radius of 30 mm and constant speed of 1000 rpm. Tribological results revealed that wear rate is directly related with the load. The results showed that the wear resistance of the produced composite increased with increase in MnO₂ content, but decreases with increase in normal load, Harshith S. (2019).

Al/Al₂O₃ composite was fabricated via powder forging of aluminum and manganese oxide (MnO₂) powders. A mixture of Al-Al₂O₃ was compacted, forged and annealed. MnO phase was produced because of incomplete reduction of MnO₂ by Al and Al₆Mn compound was formed due to the release of manganese to the Al-matrix beyond the limit of solubility. Results revealed that Tensile strength and ductility for forged billet which are anneal at 600°C for 30 h. Annealing at higher temperature and for longer time results in decrease of tensile strength, Tachai et al. (2007).

Pure Al (AA-1070 with 99.77% purity) as matrix, MnO with particles size range from 188 µm to Reinforcement with 250 µm and pure Mg powder as wetting agent were used for production of Al-MnO composites having 15 wt.% of MnO via stir casting technique. The results revealed the presence of an in-situ formed finer alumina (Al₂O₃) particles and an intermetallic precipitate of Al-Mn as a result of chemical reaction between molten Al and manganese oxide (MnO) particles as well as generated porous in-situ AlMnO_x particles, Almadhoni, K. (2018).

Particulate Al-8Mg-MnO₂ composite was fabricated via stir casting technique. 3, 5 and 8 wt% of MnO₂ powder was added in Al-8Mg melt and subsequently hot forged at 400 °C. Results showed intermetallic precipitates containing Al, Mg and Mn at dendrite boundaries and embedded alumina and MnO₂ particles in the matrix. It was observed that the hardness enhanced with increasing the MnO₂ percentage from 3 to 8%. Results showed that similar in the forged samples, and an increase in tensile and yield strength was also there as the percentage of MnO₂ increased in cast composite. Forging has enhanced the yield and tensile strength further keeping the trend similar to that of as cast composite. Results showed that an increase in MnO₂ percentage has adverse impact on percentage elongation, forged samples also showed a similar trend of decrease in percentage elongation. Whereas forging has



improved the initial fracture toughness JIC. An increasing of MnO₂% in both the cast and the forged composites led to decreasing in JIC. They found that toughness, initiation fracture toughness and the growth toughness are directly affected by wt.% MnO₂ in composite, Naraina et al. (2019). Al₂O₃ composite was fabricated by powder metallurgy method. Results showed a generated Al₂O₃ in-situ particles because of the chemical reaction between Al and MnO₂ during annealing of forged specimen. Annealing temperature was 600°C, which is sufficiently high for chemical reaction between Al and MnO₂ to occur, but does not too severely soften the Al-matrix. Tensile strength and ductility reached 120 MPa and 8%, respectively, for specimen forged and annealed at 600°C for 30 h. Al, Al₂O₃, MnO, and Al₆Mn phases were found in the investigated specimen Luangvaranunt, T. (2007).

Al-Si alloy as matrix and MnO nanopowder as reinforcement were used to produce a composite by stir casting method. A composite samples content of 1.5 kg Al-Si alloy and 0.05 at. % MnO nanopowder with sintered time for 30 min and 60 min, and MnO doped in GO with sintered time for 60 min samples were synthesized. Result indicated that Al-Si with nanoreinforced MnO after sintering 60 min generated the highest tensile strength that was 14.7 kg/mm² and had brittle fractures compared to other specimens. This result fits with Al-Si nanoreinforced MnO after sintering 60 min hardness test at 128.7 HV number. Supported by the fact that the cast result micro photo showed an evenly spread grains with clear and smaller dendrites, small and tight grain structure, and high tensile strength and hardness, Puspitasari, P. (2019). The effect of magnesium concentration in molten aluminum produced from beverage cans on the process of aluminothermic reduction of Mn₂O₃ particles obtained from the cathodes of discharged alkaline batteries was studied by O. Dávila and others.

They found that the addition of Mg improves the wettability of solid particles by molten Al, thus increasing the reaction and its subsequent incorporation into the molten aluminum solution of Mn released from the reduction reaction. The results showed that the higher the initial Mg concentration in the molten Al, the higher the speed of the chemical reduction reaction of the Mn₂O₃ particles, Dávila, O. (2019). By milling a mixture of aluminum (Al) and manganese dioxide (MnO₂) powders were used to generate Al₂O₃ nanoparticles. The generated Al₂O₃ nanoparticles were reinforced in molten aluminum-magnesium (Al-Mg) alloy matrix via stir casting to synthesize nanocomposites. Results showed that the ball milling of reinforcement before adding to the melt brought considerable improvement in the integration and uniform dispersion of the milled particle in the Al-Mg alloy matrix melt, which led to improvement in the strength and ductility of the cast nanocomposites, Ravikumar, K. (2021).

2.1 Manganese Oxide Mesoporous Solids (MOMS)

Researchers have found that the surface area of Al_xMnO_2 is $711 \text{ m}^2/\text{g}$, while the mean pore diameter was 3.6 nm. Results showed that the extreme surface area value of Al_xMnO_2 is attributed to the existence of an open network interconnected particles forming features medium height with no preferential orientation, figure 2.1 shows an AFM image of Mn-Al- O_x , Kreysa, G. (2000).

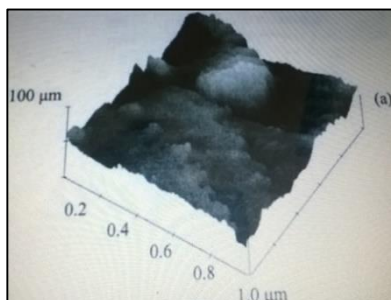


Fig. 2.1: AFM image of Mn-Al- O_x

MnAlO $_x$ catalysts with ordered mesoporous structure was prepared via evaporation-induced self-assembly (EISA) rout. It was designed for the selective catalytic reduction (SCR) of NO $_x$ with NH $_3$ at low temperature. Results indicated that with an increase in calcination temperature, the SCR activity of MnAlO $_x$ catalysts increased. Figure 2.2 shows TEM images of (A) MnAlO $_x$ -450 °C, (B) MnAlO $_x$ -550 °C, (C) MnAlO $_x$ -700 °C, (D) MnAlO $_x$ -800 °C, Qixiong, H. (2022).

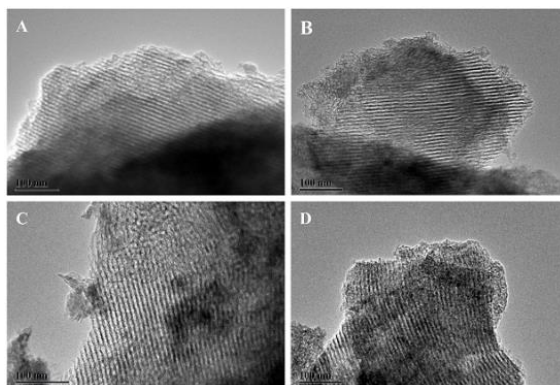


Figure 2.2 TEM images of (A) MnAlO $_x$ -450 °C, (B) MnAlO $_x$ -550 °C, (C) MnAlO $_x$ -700 °C, (D) MnAlO $_x$ -800 °C

3. Conclusion



The above review for the aluminum based metal matrix composites (AMMC's) reinforced by manganese oxides leads to the following conclusions:

- Manganese oxides materials, including MnO and MnO₂, can be used to manufacture In-situ Al-Al₂O₃-AlMnO_x (MnO₂, MnO) composite.
- In-situ Al₂O₃ and porous AlMnO_x particles are generated due to the chemical reaction between Al and (MnO, MnO₂), which also leads to precipitate Al-Mn intermetallic compound in the matrix.
- The degree of reduction of manganese oxide particles is highly dependent on temperature.
- Reinforcement particles size, weight percentage of reinforcement particles and parameters of manufacture technique have a remarkable effect on the morphology and properties of AMMC's reinforced by manganese oxide.
- Addition of Mg improves the wettability of solid particles by molten Al, thus increasing the reaction and its subsequent incorporation into the molten Al solution of Mn released from the reduction reaction.
- Higher the initial Mg concentration in the molten Al, the higher the speed of the chemical reduction reaction of the Mn-oxides particles.
- In-situ AlMnO_x particles characterized by porous structure, which gives them a large surface area and thus improves their related properties such as the heat storage capacity.
- Al-AlMnO_x composite has ability to store energy as sensible heat, and might be used for macro-encapsulation of PCM to improve the efficiency of the latent heat storage unit.

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