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Effect of Multifunctional Composite Infringement on the Electrochemical Propagation and Characterization of Al-Mg-Si/TiO₂-SnO₂ Composite by Stir Casting Method

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ABSTRACT

In this paper, the performance evaluation of aluminum alloy, their microstructural and mechanical properties associated with the change in induced composite particles were studied. The influence of $TiO_2.SnO_2$ metal composite in the range of 5-10% wt as inoculant on Al-Mg-Si series alloy and its corrosion resistance mechanism has been explored by liquid metallurgy and investigated in 3.65% NaCl solution using linear potentiodynamic polarization technique. The composite alloyed compositions and phase change were determined with (SEM/EDX and XRD). The surface structure of the alloy samples shows that $TiO_2.SnO_2$ particles were dispatched along the interface. The addition of $TiO_2.SnO_2$ to the alloy led to the precipitation and modification of complex intermetallic particles like Al_2SnTiO and AlSiSn which also indicate a fairly good interfacial interaction. This phase orientation further reduces the possibility of corrosion penetration within the intermediate. It was found that the addition of dispersed composite in the melt provide feasible improvement on the hardness behavior.

1. Introduction

The significant role of aluminum and its alloy to national development and industries are enormous due to its physical, mechanical and corrosion $% \left\{ 1\right\} =\left\{ 1\right\} =$ properties. It has found a widespread use in various industrial capacities such as construction, automotive, and aircraft industries [1-9]. Worldwide demand for aluminum from literature has proven that over 22 million of new aluminum products are aluminum scrap due to economic and environmental value with no variance in superiority between virgin and reprocessed aluminum alloys [1, 5-8]. Aluminum is softer in nature, possesses ductile behavior, and has corrosion resistant with high electrical conductivity. Aluminum efficiency are well explore with combinations of other alloying metal to provide an advantageous properties such as strength, high corrosion resistance and formability for ever-growing applications [10-15]. Formation of special advanced and advantageous behavior for Al can be obtained with incorporation of particles into liquid melt by physical dispersion thermal migration of particles know as inoculation.

Inoculation is the addition of solid particles to a metallic melt to act as nucleate catalysts for the formation of fine equiaxed, rather than columnar, grains [11, 12-18]. The utmost hand used refiners or alloyed for aluminum are with copper, zinc, magnesium, silicon, manganese chromium, titanium, zirconium, lead, bismuth and nickel [1, 9]. Combined system such as $Al[Ti[B]\ also\ give\ a\ typical\ composition.$ When $[Ti[B]\ added$ to the melt, the matrix melts and the dilution of the titanium content leads to rapid dissolution of the Al₃Ti, while the TiB₂ remains stable. Magnesium particle-inclusion in cast bath has been reported to induced crack and foster corrosion initiation instead of improving metal stability [1, 20]. Nickel particle as a refiner for ferrous and nonferrous castings has been subject of interest over years. Some report have shown that this metal help to promote the formation of passive films resulting into a reduction in corrosion rate [9, 21-22]. Although grain refiners has been used to enhance aluminum alloy properties, but the study of the corrosion resistance, mechanical and morphological behavior is also very essential in evaluating the performance of the alloy behavior [23-25].

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Of recent, composite inform of ceramics and oxide have found express entrance into material industries. These composite blends show particular physical and chemical properties, which cannot be achieved by each component separately. The use of additives is extremely important due to their influence on the growth and structure of the resulting melt in such away as they provide influence in physical and mechanical properties of cast such as grain size, brightness, internal stress, pitting and even chemical composition [11-16, 25-27]. The aim of the present work was to produce $\rm TiO_2/SnO_2\text{-}Al$ composite using liquid metallurgy technique. More so, to further investigate the effects of composite alloy concentrate on aluminum alloy, their corrosion resistance trend and mechanical behavior of the admixed alloy for advanced application.

2. Experimental Methods

2.1 Materials

The TiO_2 -SnO $_2$ materials used in this work is fine nano-sized powder. These particles are obtained from South Africa. The substrate used in this work is Al-Mg-Si alloy which was obtained from aluminum tower, Ogunstate, Nigeria; high purity compositions as shown in Table 1.

2.2 Equipment

The equipment used in this work included; moulding box, cylinder, crucible, Diamond hardness tester, polishing machine, scanning electron microscope, x-ray diffractogram.

2.3 Methods

The prepared 300 g Al in an ingot was liquefied by an electric furnace under a protective nitrogen census environment. At optimum temperature of 700 °C, TiO2.SnO2 particle were inserted in to the melt based and the prescribed in Table 2 with varying concentration. The process was allow for about 2-3 minutes for proper admixed and precipitation during which the temperature was sustained for super heating to occur. The processed liquid melts were then poured into permanent cast iron mould which was pre-heated to about 200 °C. Portions of the alloyed sample were further taken for machining and sectioning using diamond cutting disc at 6 rpm.

SEM/EDS and XRD was used to examine the structural properties and phase change respectively. The electrochemical performance was observed with the help of linear polarization method.

Table 1 Chemical analysis of the produced Al-Mg-Si Alloy

Element	Al	Si	Mg	Fe	Cu	Mn	Ti	Cr
Composition (wt%)	Balance	0.45	0.50	0.22	0.03	0.03	0.02	0.03

Table 2 Processing method and designation of samples

Sample	Admix	Bath composition
Blank	0	300g Al-Mg-Si + O
1	5% SnO ₂	300g Al-Mg-Si + 5% SnO ₂
2	10% SnO ₂	300g Al-Mg-Si + 10% SnO ₂
3	5% TiO ₂	300g Al-Mg-SI + 5% TiO ₂
4	10% TiO ₂	300g Al-Mg-Si + 10% TiO ₂
5	10% TiO ₂ + 10% SnO ₂	300g Al-Mg-Si + 10% TiO ₂ + 10% SnO ₂

2.4 Electrochemical Examination

The anti-corrosion properties were examined with the help of potentiodynamic polarization technique in 3.65% NaCl solution at room temperature (RT) in a static solution for a period of 30 minutes. The polarization curves were determined by stepping the potential at a scan rate of 0.003 V/sec. and potential from -1.5 V to +1.5 V. The polarization curves were plotted using Autolab data acquisition system model: AuT71791 and PGSTAT 30 with (GPES) package version 4.9.

2.5 Hardness Study

The micro-hardness behaviors of the samples were determined according to Dura scan Emco test standard. The indentations was taken along the surface of the alloyed sample using a load of 100 g for 10 s dwell time. The hardness was determined with 20 μm spacing between corresponding indentations and average mean values recorded were calculated.

3. Results and Discussion

The microstructure of as-received (cast Al without TiO_2 - SnO_2) by SEM with EDS are shows in Fig. 1 with spectra indicating Al presence.

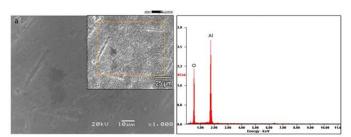


Fig. 1 SEM/EDS microstructure of A500 alloy

The morphology of the working metal indicates coarser and rather heterogeneous patches all over the sample. In Fig. 2, the effects of composite show reasonable uniform dispatches of the SnO_2 and some macro-residual and segregation in some region. The effect of small percentage of $5\%\ SnO_2\ shows\ a$ well harness Al solidified precipitate at the surface. Though the strengthening effect was not as preferred as TiO_2 single blend, reason been that $SnO_2\ solutes\ particles$ are expected to have oxidized to form blended clusters in the aluminum matrix.

The characteristic of sample 5 (10% $TiO_2 + 10\%$ SnO_2) change due to Sn and Ti composite in the Al melts. The presence of Ti in the alloy is revealed showing possible evenly intermetallic phases. Although [1, 9] stated in their report that structures of reinforced alloy will help to determine the strengthening properties of that material. With the admixed melt of TiO_2 concentrate for sample 3 and 4, a sound improvement was seen from other properties studied. This dendritic system is enclosed by the eutectoid precipitant of small Ti particle all through the interface with both 5 and 10% admixed. Agglomeration does not exist for TiO_2 unlike that of SnO_2 diffusion which might have initiate pitting and porosity. Therefore addition of 10% TiO_2 to the Al-Mg-Si alloy revealed a complex TiO_2 -based intermetallic compound within the aluminum solid melt. In fact, since

structural refinement takes place due to the reduction of grain size [1, 11, 27], particles of Ti might facilitate refinement and improved mechanical properties.

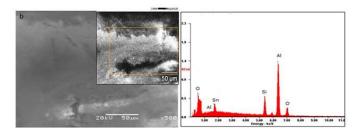


Fig. 2 SEM/EDS photomicrographs of 5% SnO2 inoculated A500

Noted that the serviceability of material which is alloyed is quantified to a huge extent by the conditioning addition and the metallurgical processes engaged [9]. Also, it has been attested to that refiners added to a melt cumulate in structural modifications resulting to establishment of intermetallic complex compounds [1, 27]. Most interestingly is the change in structure of the binary composite admixed in Fig. 3 (Al-Mg-Si + 10% TiO $_2$ + 10% SnO $_2$) with 10% each of the composite in the melt. Both functional particle of Ti and Sn were noticeable through EDX identification inappreciable quantity.

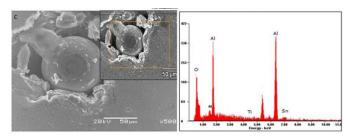


Fig. 3 SEM/EDS photomicrographs of 10% each of TiO_2 -Sn O_2 inoculated A500

From the XRD analysis in Fig. 4, improved phase transformation, homogenization and suitable cluster of Al phase matrix of AlSn₂, Al₂Sn₂and AlSn₂O₁₂Si along the cast surface exist. SnO₂ lumps and agglomeration causes micro-segregation thus establishing eutectic within the zone [14-16, 19].

In Fig. 5, more solid bound alloy phase system of Ti/Sn matrix formation of complex intermetallic compounds was seen. The nucleation and wild spread of the composite particle combined phase could be ascribed to the satisfactory sites for the nucleation offered by the aluminum particles that are formed on solidification.

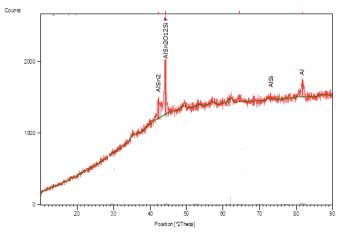


Fig. 4 XRD pattern of 5% SnO₂ inoculated A500-Al-Si

According to the reported works [1, 9, 11], to enhance heterogeneous nucleation and achieve grain refinement, the nucleation substrates not only need to be potent, but also need to have an adequate proper particle size and a narrow size distribution. In view of this, understanding the grain refinement attained by the liquid melt and the interfacial diffusion of the Ti/Sn composite can be well described in term of their heterogeneous nucleation and phase bond as seen in figure 5 with Ti, Al:SiTi, AlSn₂O₁₃Ti.

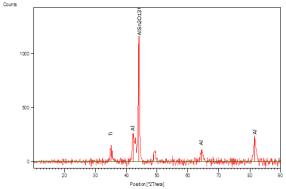


Fig. 5 XRD pattern of 10% each of TiO2-SnO2 inoculated A500-Al-Si

3.1 Electrochemical Studies

Fig. 6 and 7 show the linear potentiodynamic polarization curves of all the conditioned alloys indicated in Table 2. The effect of composite particulate and their synergistic blend on as cast alloy are seen from the potential/current trend. As cast Al-Mg-Si alloy was used ascontrol toother alloy enhanced composite admixed melt. From observation, all particles inoculated provide good active-passive behavior except for $10\%\ SnO_2$ (Table 3). Although, literature attested that not all refiners or inoculant perform at their best on condition of application. In some case when intermediate precipitations are partly coherent with immediate matrix, defect tends to be obvious and provide such material less polarized with current densities finding its way aggressively into the passive region.

In view of this, the influence of trace composite particulate and their synergistic blend on Al has great effect on the growth, nucleation and the passivation potential as observed in Fig. 7. In order word, this behavior can be attributed to the perfect interaction, and the stability of this inoculant on the vacancies site. From the linear scan, the corrosion potential of the inoculated sample at; 5% SnO₂ was -0.61085 V,10% SnO₂ is -0.65013 V, 5% TiO₂ is -0.68609 V, 10% TiO₂ is -0.79953 V, 10% TiO₂ + 10% SnO₂ is -0.6925 V while that of as-cast Al is -0.85214 V.

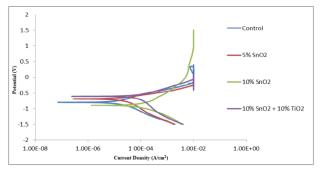


Fig. 6 Linear potentiodynamic polarization curves for as-cast A500-Al-Si and SnO₂ (TiO₂-SnO₂) inoculated in 3.65% NaCl solution

The corrosion rate (CR) follows the same trend. Sample 5 have; $0.001913 \ mm/y$, sample 4 is $0.002503 \ mm/y$ sample 3 is $0.005451 \ mm/y$ sample 2 is $0.00669 \ mm/y$, sample 1 is $0.00556 \ mm/y$ and $0.00599 \ mm/y$ for as-received sample. The decrease in deterioration behavior of the composite alloy was far encouraging with about four time difference in magnitude ($4.077X10^{-3}$) when compare with control sample.

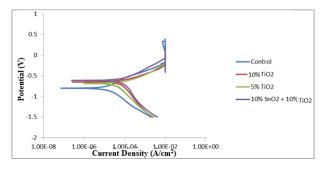


Fig. 7 Linear potentiodynamic polarization curves for as-cast A500-Al-Si and TiO_2 ($TiO_2\text{-SnO}_2$) inoculated in 3.65% NaCl solution

The best Rp value was for the synergistic blend (10% TiO₂-SnO₂) was 5449.7 Ω compare to that of as-received sample of 1164.8 Ω as shown in Table 3.

 $\begin{tabular}{ll} \textbf{Table 3} & \textbf{Potentiodynamic polarization data obtained from Tafel plot for as-cast Al-Mg-Si and alloyed Al-Mg-Si samples \end{tabular}$

Samples	ba (V/dec)	bc (V/dec)	E _{corr} (V)	jcorr (A/cm ²)	C _R (mm/y)	R _P (Ω)
S5	0.03833	0.033974	-0.69251	1.44E-06	0.001913	5449.7
S4	0.053398	0.039093	-0.79953	1.88E-06	0.002503	5218.8
S3	0.024302	0.041977	-0.68609	4.10E-06	0.005451	1522.2
S2	0.034288	0.015547	-0.65013	5.02E-06	0.00669	925.29
S1	0.026909	0.019544	-0.61085	4.17E-06	0.00556	1178.4
Blank	0.058467	0.009311	-0.85214	4.99E-06	0.00599	1164.8

In general, precipitation of two phases Ti/Sn could be said to improve strength and corrosion stability. Although micro-constituent has been affirmed to alter electrochemical corrosion process leading to non-uniform attached and initiation of corrosion region but in this study, reverse was the case. The magnitude of the dissolution does not depend on the percentage of the additive per say, but rather on the dispersion mechanism, and the activities of each constituent at the solid solution which help to stabilize the potential.

3.2 Microstructure Study

The microhardness (HVN) value of the Al-XTiO₂.SnO₂ alloy for each sample at different concentration of composite condition was measured. Fig. 8 shows the average microhardness profile for the matrix. From all indications, hardness increased from 42.56 HVN for base Al to approximately 65.5 HVN for Al-XTiO₂.SnO₂ about 23.04 HVN significant improvements. This characteristic follows for all incorporated sample of TiO₂ and SnO₂ at their respective percentage.

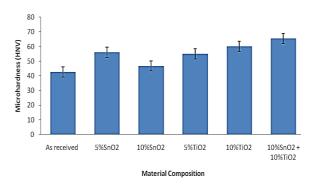


Fig. 8 Hardness behavior of as-received and conditioned alloys

The variation of microhardness as a function of distance from the substrate interface was examined and the average mean of all conditioned were examined. The tremendous improvement in hardness formost especially in the binary conditioned composite was attributed to the formation of Ti and Sn stable properties [11, 19, 27]. Attest that oxide, composite as affinity to form solid precipitation Interfacial diffusion which might results to fine-grained structure of the conditioned alloys and the dispersed particles in the fine-grained matrix which may obstruct the easy movement of dislocations, thereby given rise to higher hardness value.

4. Conclusion

From the structural behavior, XTiO₂.SnO₂ metal composite modified Al shown an overwhelming intermetallic phase of AlSn₂Ti and Ti₂SnAl₆ inform of eutectic segment which enhanced the stability of the passivation over the based aluminum.

The alloy behavior changed with the presence of $XTiO_2.SnO_2$ in all regard from the solidification to precipitation and thus presents significant degree of resistance to corrosion and surface degradation over the parent material except for $Al-10SnO_2$. Which experience little deterioration below the control.

The hardness of the composite coatings was significantly higher with the presence of $XTiO_2.SnO_2$ in both single and synergistic trend blend. The significant higher hardness of the coating was due to the fine-grained adherent conditioning properties of the alloy which obstructs the easy movement of dislocations and hence improves the hardness property.

The introduction of an $XTiO_2.SnO_2$ produced a multiphase structure consisting mainly aluminum-rich and $XTiO_2.SnO_2$ -rich phases. In addition, oxides films are formed on the surface of $XTiO_2.SnO_2$ -aluminum which extensively give rise to excellent corrosion resistance.

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