INFLUENCE OF COPPER ON THE SACRIFICIAL BEHAVIOUR OF Al-Sn ALLOYS

S J Harris, D G McCartney, A J. Horlock and A H. Dent
Department of Materials Engineering and Materials Design
University of Nottingham
UK

ABSTRACT

Thermally sprayed aluminium alloy coatings containing additions of tin and indium can show sacrificial properties and can protect aluminium alloy substrates susceptible to stress corrosion. Two alloy powders Al-12wt%Sn and Al-12wt%Sn - 1wt%Cu have been used as feed materials for high velocity oxy-fuel (HVOF) spraying on to an aluminium alloy substrate. It has been demonstrated that the binary alloy coating was extremely reactive in distilled water in the as-spray condition. The coating containing copper did not react with water. Corrosion tests were carried out in 0.1M NaCl and this demonstrated that the copper containing alloy still corroded at an appreciable rate. Heat treatment at 450°C improved the corrosion behaviour of both coatings. As the time of heat treatment increased the corrosion rate of the copper containing coating decreased and evidence of passivation began to appear. SEM/TEM/XRD observations were made on the coatings to provide evidence of insolubility of tin in aluminium in all coating conditions and the coarsening of tin particles with heat treatment time. It was demonstrated that the coarsening of the insoluble tin particles are influenced, by the presence of copper.

Keywords: *Thermal Spray, Coating, Sacrificial Corrosion, Microstructure*

INTRODUCTION

To protect high strength structural aluminium alloys, particularly those fabricated by welding into portable bridge constructions or land based transport equipment, attempts have been made to use aluminium coatings. Thermally sprayed coatings can help prevent stress corrosion problems in structural parts fabricated in aluminium alloys. Spraying with commercially pure aluminium may be considered, but this would provide a "barrier" type protection. Early work by Birley et al.[1] demonstrated that an aluminium-4.5wt% zinc coating could act sacrificially but that zinc loss during spraying reduced the ability of the coating to act in this way. The possibility of using additions of mercury, indium or tin to aluminium was then considered. These elements can act as 'activators' and have been added to aluminium alloys used in the cathodic protection of structures[2]. Of these elements mercury shows the greatest effect, followed by indium and then tin. A quarternary alloy Al-1wt% Zn-0.1wt% Sn-0.18wt%. In was developed by Holroyd et al.[3] which can be drawn into a wire form and from which arc and flame sprayed coatings can be produced. Such processes permitted high rate of deposition on to larger surface areas. Work by Harris et al.[4] and Hepples et al.[5] using the Al-Zn-Sn-In wire in arc and flame spraying demonstrated that the coatings were indeed sacrificial to a 7000 series aluminium alloy and gave effective protection.

In this paper attempts are made to show how the selection of feedstock powder alloy for thermal spraying by the High Velocity Oxy-fuel (HVOF) system can influence the corrosion behaviour of the resultant coatings in the as-sprayed and heat treated conditions. Whilst Reboul et al.[6] attempted to explain the influence of mercury and indium on the corrosion behaviour of aluminium in terms of the breakdown of the protective oxide film, no understanding of the breakdown exists. With the small additions of these elements (<0.2wt%)

it has proved difficult hitherto to show how they are incorporated in the sprayed alloy. With the low level of solubility of indium and tin in aluminium, possibilities exist for either supersaturated solid solution due to the fast cooling after spraying or the formation of fine precipitates either during coating preparation and/or heat treatment. Tin is needed in greater concentrations to promote sacrificial behaviour even though it is not lost by evaporation during thermal spraying due to its high boiling point. Two alloy feedstock powders have been used, Al-12wt%Sn and Al-12wt%Sn-1wt%Cu to prepare the coatings by HVOF spraying and the coatings have been characterised by, XRD, TEM and SEM to demonstrate tin particle and copper distributions. Corrosion behaviour has been assessed in dilute sodium chloride solutions by potentiodynamic means.

EXPERIMENTAL

The powders (Al-12wt%Sn and Al-12wt%Sn-1wt%Cu) were prepared by gas atomisation, the size range of the Al-Sn powders was in the range 50-160μm and those of the Al-Sn-Cu powder were in the range 40-110μm. A Miller Thermal/UTP spray system, was used. The substrate took the form of 2mm thick aluminium coupons which were grit-blasted prior to deposition. The samples were mounted on to a horizontal turntable and rotated with a surface speed of ~1m/s with the HVOF gun being transversed vertically at 5mm/s. The spray distance was 254mm and the gun was operated with a 3 mm combustion chamber.

Spray coated samples were heat treated at 450°C for various periods up to 20h in air and then slowly cooled. Coatings in the as-sprayed and heat treated condition were then immersed in distilled water at 20°C for periods up to 1h to determine the chemical reactivity of the coating.

More aggressive corrosion tests were carried out in 0.1M sodium chloride solution (adjusted to pH 7$\bigcirc$0.2) at 25°C. As sprayed and heat-treated samples were again hot mounted and ground to a 1200 grit finish on SiC papers. Sample edges were also masked off with Fortilac lacquer. The corrosion tests were potentiodynamically controlled using an ACM Gill 8ac potentiostat. Tests were run from -1500 to -400mV at a sweep rate of 20mV/minute. Prior to each test the solution was sparged with oxygen free nitrogen.

The SEM was used to examine the surface of polished samples with both secondary electron (SEI) and (BEI) modes being employed. Non-aqueous grinding and polishing media were used to prepare these surfaces in order that no specific attack took place. A Joel 2000FX transmission electron-microscope (TEM) was used to investigate the fine structure of the as-sprayed deposits. The thin films for the TEM study were prepared by a non-aqueous method. X-ray diffraction (XRD) spectra were produced on coating samples using a Siemens Krystalloflex D500 analyser. For comparison purposes XRD data was also produced on aluminium and aluminium 12wt% tin powder in the as received and annealed conditions.

RESULTS

Reaction in water

Small pieces of as-sprayed Al-12Sn coatings were immersed into water and this led to fragmentation in ~4 minutes and complete reaction after 11 minutes. During the reaction the coating effervesced and at the end only small quantities of pre-oxidised material remained. After heat treatment at 450°C the Al-12Sn coating showed no sign of effervescence in the water and no significant material loss took place. With the Al-12Sn-1Cu sample as sprayed and then heat-treated at 450°C, no reaction took place in the water.

Corrosion tests

The Al-12Sn coatings were immersed in deaerated 0.1M NaCl solution and subject to polarisation, the resultant curves are plotted in fig. 1. A curve was not obtained for the Al-12Sn coating in the as-sprayed condition due to rapid reaction which took place between coating and solution during the setting up of the sample. A minimum of 15 minutes heat treatment at 450°C was necessary before a stable polarisation curve could be obtained. Thereafter very similar plots (Fig. 1) were obtained for heat treatment for up to 2h at 450°C. It was noted that the corrosion potential (Ecorr) for all the coatings except the one heat treated for 20h was ~ -1300mV vs SCE.

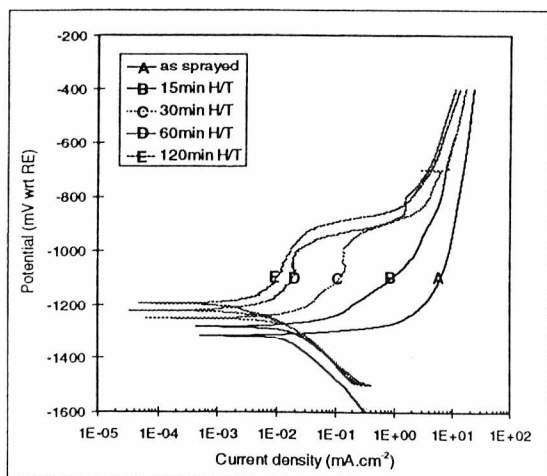
Fig. 1 Anodic polarisation curves for Al-12Sn coatings heat treated for various times at 450°C The tests were performed in deaerated 0.1M NaCl at a sweep rate of 20mV/min.
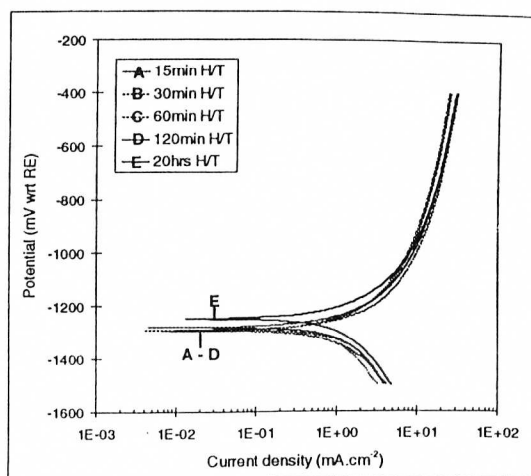
Fig. 2 Anodic polarisation curves for Al-12Sn-1Cu coatings heat treated for various times at 450°C The tests were performed in deaerated 0.1M NaCl at a sweep rate of 20mV/min.

With Al-12Sn-1Cu coatings polarisation curves were obtained on the as-sprayed and those in the heat treated condition, see Fig. 2. The as-sprayed coating had a polarisation curve close in form to that obtained on the Al-12Sn after heat-treatment for 15 or more minutes with an Ecorr value of -1300mV. Heat treatment at 450°C then began to change the form of the plot as the time of treatment increased (see Fig. 2). The value of Ecorr became more anodic so that its value reached -1200mV after 120 minutes heat treatment. Also as the heat treatment time increased the anodic polarisation curve began to show signs of significantly reduced current densities in the potential range -900 to -1300mV. After 30 minutes heat treatment (curve C) some evidence of passivation is seen and this was enhanced as the treatment time increased up to 120 minutes. Evidence of a pitting potential (Epit) was noted in curves C, D and E at ~ -900mV. Comparison between the current densities at -1000mV between the Al-12Sn-1Cu heat treated for 120 minutes at 450°C and the as-sprayed version of the same coating as-sprayed showed three orders of magnitude change in this measure of corrosion rate. This indicates that a more stable form of passive film can be developed at this potential after heat treatment.

X-ray Diffraction Data

Fig. 3 shows a bar chart representing different measured lattice parameter values obtained from the XRD data. The lattice parameter of the as received Al-12Sn powder is shown to be greater than bulk high purity aluminium. Heat treating the powder at 200°C (in air or argon increases

the parameter marginally). Thermally spraying the powder to form a coating produces a change in parameter ie the Al-12Sn coating now has a value lower than that of bulk pure aluminium. This remains the case on annealing at 200°C and changes back to values measured on the powder when annealed at 450°C. This pattern of behaviour was also observed when aluminium powders were also sprayed and heat treated. Initially this would suggest that tin was dissolving in aluminium in the as-sprayed coating. Since the behaviour observed in pure aluminium coatings follows the same pattern, it would suggest that there was no significant solid solution of tin in aluminium in the post-spraying stage. The apparent increase in lattice parameter is probably due to residual thermal stresses. Subsequently heat treatment at 450°C is capable of reducing these stresses and the lattice parameter effect, see fig. 3.
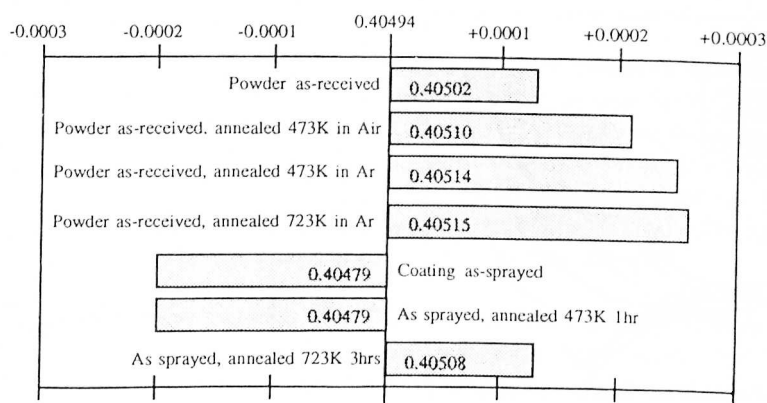

Fig 3. Comparison of lattice parameter measurements obtained on Al-12Sn powders and coatings with those of aluminium. The exact lattice parameter of pure Al is 0.40494nm. All values are in nm.

As-Sprayed and Heat Treated Microstructure

Coatings were examined in the SEM, care being taken to ensure that non-aqueous polishing etc. was used prior to this work. The Al-12Sn coating, again prepared in non-aqueous media, showed evidence of only a minor amount of the white tin phase in the BEI photomicrograph see Fig. 4a. Heat treatment of Al-12Sn coating for 15 minutes at 450°C produced copious amounts of white phase see Fig. 4d. In comparison, the Al-12Sn-1Cu coatings in the as-sprayed condition showed more evidence of the white tin phase (see Fig4c). Heat treatment for 5 minutes at 450°C also coarsened the white phase, see Fig 4d.

TEM images of Al-12Sn and Al-12Sn-1Cu coatings in the as-sprayed condition are shown in Figs. 5 (a and b). In the Al-12Sn there was clear evidence (Fig. 5a) of a high volume fraction of tin particles ~15nm in size evenly distributed throughout the aluminium matrix. With the Al-12Sn-1Cu coating the tin particles were not evenly distributed, some finer particles (15nm) existed in the grains and coarse particles 0.2μm were to be found at boundaries, see Fig. 5b. There was also evidence of fine precipitate free zones.

TEM was also carried out on both coatings after heat treatment at 450°C for 1h, see fig. 5c. Al-12Sn coating, the size of the tin particles had increased to 60nm and there was now more evidence of precipitate free zone at boundaries and coarse tin particles at grain boundaries. For the Al-12Sn-1Cu coating, coarsening had gone much further, with tin precipitated only at grain boundaries at a size of ~0.5μm.
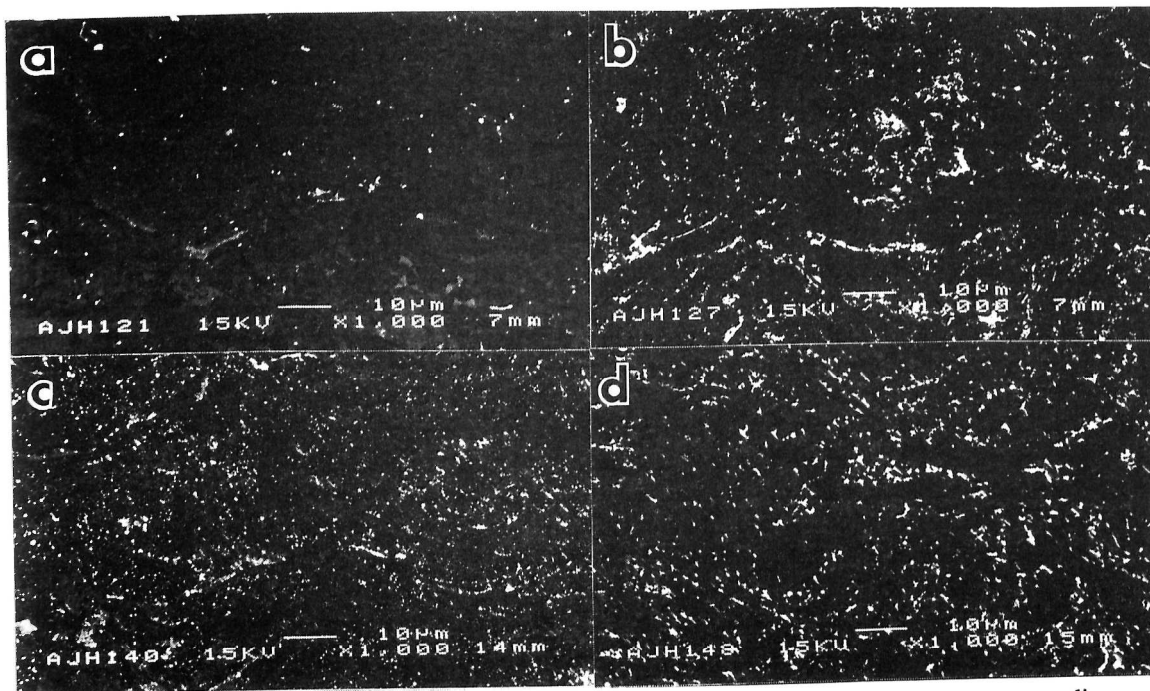
Fig.4 SEM/BEI micrograph of coatings after grinding and polishing in a non-aqueous media; (a) Al-12Sn in the as-sprayed condition. (b) Al-12Sn after heat treatment at 450°C for 15 minutes. (c) Al-12Sn-1Cu in the as-sprayed condition. (d) Al-12Sn-1Cu after heat treatment at 450°C for 5 minutes.
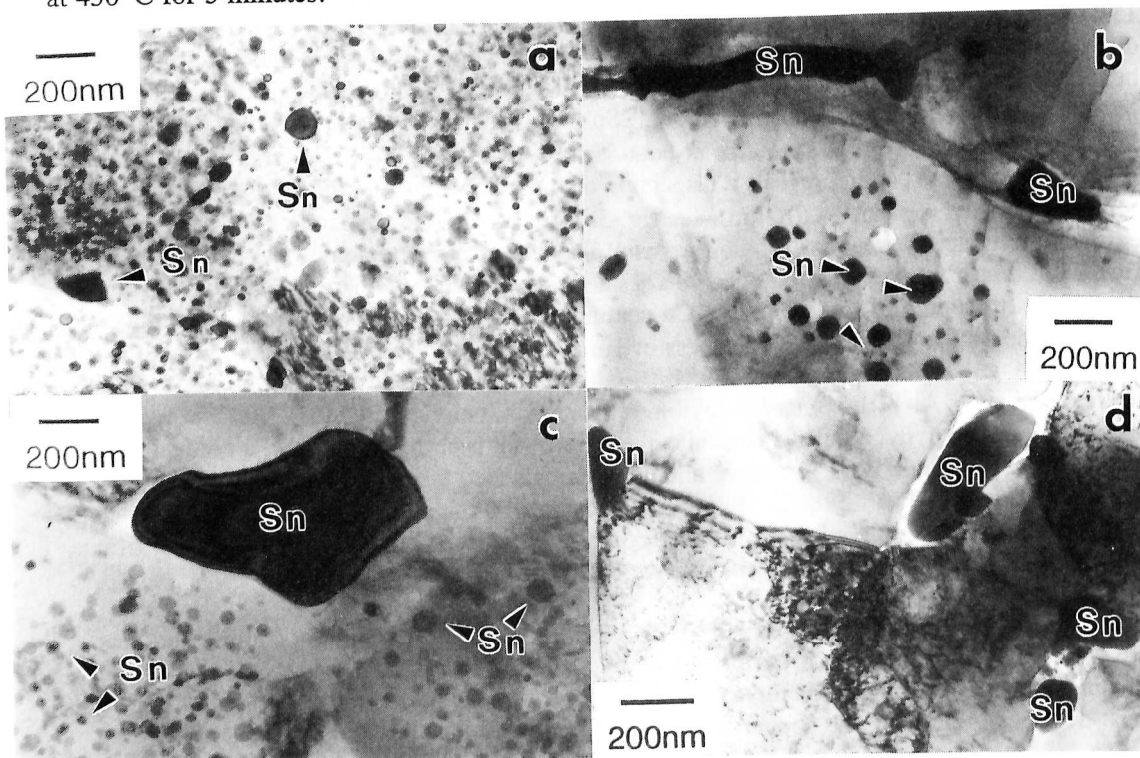

Fig.5 TEM micrographs of foil prepared from as-sprayed coatings by non-aqueous methods: (a) Al-12Sn, (b) Al-12Sn-1Cu and as sprayed and annealed for 1h at 450°C: (c) Al-12Sn. (d) Al-12Sn-1Cu

DISCUSSION

Examination of the XRD data on as-sprayed coatings suggests that the lattice parameter aluminium is changed by the thermal spray process. The presence of tin in the sprayed all does not modify the lattice parameter significantly above that found in the aluminium coating. Since the change in parameter can be reversed by heat treatment at 450°C it is assumed the residual stress is the major reason for this in the sprayed deposit. This information demonstrates that tin does not exist in a supersaturated solid solution even though a fast cooling has been applied. The back scattered images obtained from the SEM on the as-sprayed coatings show very little evidence of a white tin phase indicating that if it is present it must in a very fine dispersed form. TEM evidence, see fig. 5a, demonstrates that a high volume fraction of fine 15nm tin particle exists in an even distribution in the aluminium matrix with a few large particles at grain boundaries.

After heat treating the Al-12Sn coating at 450°C for a short period e.g. 15-60 minutes the large changes in microstructure begin to take place, i.e. the tin particles become 50 time larger, as shown in the SEM (fig. 4b) and TEM (fig. 5c). Much of the tin now resides continuous films at grain and intersplat boundaries. Around the grains there are tin precipitate free zones, see fig. 5c. The coarsening of the tin due to heat treatment has also drastically reduced the area of the tin - aluminium interfaces and the reaction rate in the distilled water and in 0.1M sodium chloride. Coarsening produced after 15 minutes heat treatment reduces the extreme reaction of the as-cast coating and allows the test to be completed. No further change occurs until after holding for 20h at 450°C when more coarsening encourages a small shift towards lower current densities and a rise in potential, (sample E in fig. 1).

Introducing copper into the as-sprayed alloy prevents reaction with distilled water and allow the potentiodynamic test in chloride to be completed. As the heat treatment time increases from 15 minutes to 2h at 450°C then the potential-current density curves (A-E) in fig. 2 are displaced to lower current densities and evidence of passivation appears. This behaviour can be related to the initial size and distribution of the tin particles and the subsequent coarsening behaviour, see fig. 4 and 5. As sprayed Al-12Sn -1Cu coating also show evidence of white tin phase particles (0.2 μm) at intersplat boundaries, see fig. 4c. TEM observations of thin films from the same coating reveals a dispersion of fine tin (~5nm) in the centre of grains splats and of coarse particles (0.2μm), see fig. 5b. Tin precipitate free zone (~0.2μm wide existed at many grain boundaries. Copper would appear to have prevented the nucleation of fine 15nm tin particles close to grain boundaries and encouraged large particles at the boundary itself. Heat treatment of the Al-12Sn -1Cu coating at 450°C for a short period of 5 minutes coarsens the tin particles to sizes in excess of 1μm, see fig. 5d. These changes in precipitate distribution will effectively reduce the tin - aluminium interfacial area beyond the level achieved in the Al-12Sn binary alloy and thus it is believed reduces the amount of electrochemical activity. Whilst corrosion currents fall with heat treatment time, a gradual shift in corrosion potential (Ecorr) to move anodic potentials also takes place i.e. from -1325mV (as sprayed) to -1290mV (after 2h at 450°C). Then after 30 mins treatment at 450°C evidence of passivity appears in the range -1250 to -1050mV, see curve C in fig. 2. A protective film must now be forming to introduce the passive behaviour.

The influence of copper on the coarsening kinetics of the tin phase on initial cooling and heat treatment may only be one of the processes by which over reaction is prevented in these coatings. Copper distribution in the solid state may be an issue in the corrosion behaviour. By heat treating at 450°C all the copper will be in solution and then on cooling the small degree

of supersaturation does not allow significant amounts of copper to precipitate as θ (CuAl₂).

CONCLUSIONS

1. In the as-sprayed condition an Al-12Sn coating is very reactive even to distilled water, this behaviour can be accounted for by fine nanoscale dispersions of tin particles in the aluminium matrix.

2. Introducing 1% copper into the Al-12Sn coatings considerably reduces the rate of corrosive attack in water at least in part due to a change in tin particle distribution within the as-sprayed coating.

3. Heat treatment at 450°C coarsens the tin phase in both copper containing and copper free coatings and this reduces the corrosion rate in water and chloride containing solutions.

4. In copper containing coatings longer heat treatments at 450°C allows the formation of a protective passive film when the sample is introduced into a chloride solution.

5. A large interfacial area between aluminium and tin would appear to increase the corrosion rate. The presence of copper encourages a reduction in this area and the associated corrosion rate.

ACKNOWLEDGEMENTS

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