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Microstructural characteristics of high velocity oxy-fuel thermally sprayed Al-12wt.%Sn-1wt.%Cu alloys

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ABSTRACT: High velocity oxy-fuel thermal sprayed Al-12wt.%Sn-1wt.%Cu alloy coatings have been characterised both in the as-sprayed condition and following heat treatment in air at 300°C for periods up to 5 hours. The as-sprayed microstructure comprises principally nanoscale Sn-rich particles embedded in an Al-rich matrix. The Sn-particles coarsen and the alloy microhardness decreases with increasing time of heat treatment.

1. INTRODUCTION

The excellent tribological properties of Al-Sn alloys have led to their extensive use in automotive shell bearings. Al-Sn alloys possessing good anti-friction characteristics also need to be capable of withstanding cyclic loading, corrosion and temperatures in excess of 150°C in modern engines (ASM Metals Handbook, 1980). Al-Sn alloys have limited fatigue strength and this necessitates the introduction of additional elements such as copper to strengthen the alloy. Another possible way of producing Al-Sn alloys with higher strength is to use the high velocity oxy-gaseous fuel (HVOGF) spraying technique, instead of casting and roll bonding, to create nanoscale tin particle dispersions by rapid solidification. This can achieve high quality coatings under rapid solidification conditions with high density and good adherence to the substrate (Harris et al, 2000). This paper describes the microstructural evolution of thermally sprayed AlSnCu alloys as a consequence of using the related high velocity oxy-liquid fuel (HVOLF) technique to spray the deposit and subsequent heat treatment of coatings.

2. EXPERIMENTAL PROCEDURE

Sprayed coatings were produced from gas atomised Al-12wt.%Sn-1wt.%Cu feedstock powder, of size range 38-106 μm, supplied by Phoenix Scientific Industries Ltd. using a Met Jet II HVOLF thermal spray system. Kerosene fuel was mixed with oxygen and the resultant combustion provided the thermal and kinetic energy to spray the powder onto 2mm thick, mild-steel coupon substrates that were grit-blasted prior to deposition. The oxygen and kerosene flow rates were 13.8 and 6.5×10^{-3} ls^{-1}, respectively, while the powder was injected into the combusted gas with a feed rate of 0.40 gs^{-1} using a nitrogen carrier gas. The substrates were mounted on the circumference of a horizontal turntable and rotated with a tangential velocity of 1 ms^{-1} while the HVOLF thermal spray gun located at a distance of 356 mm from the substrate was traversed vertically at 5 mm s^{-1}. Coatings up to 400μm thick were deposited in ~ 20 passes of the gun.

After spraying, the coatings were heat-treated in air at 300°C for a range of times between 15 minutes and 5 hours. Microhardness was determined using a Leco M400 tester with loads of 200g. The as-sprayed and heat-treated coatings were hot mounted, ground and polished under non-aqueous conditions for metallographic examination using a JEOL 6400 SEM. X-ray diffraction (XRD) was carried out using a Siemens D500 diffractometer using CuK_α radiation, while more detailed microstructural analysis was performed using a JEOL 2000FX TEM.

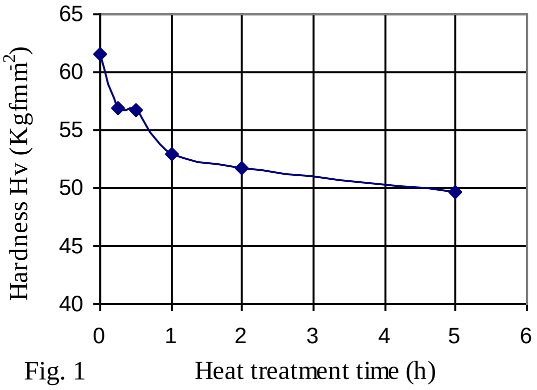
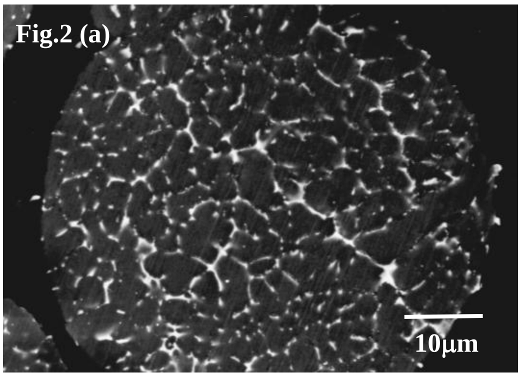
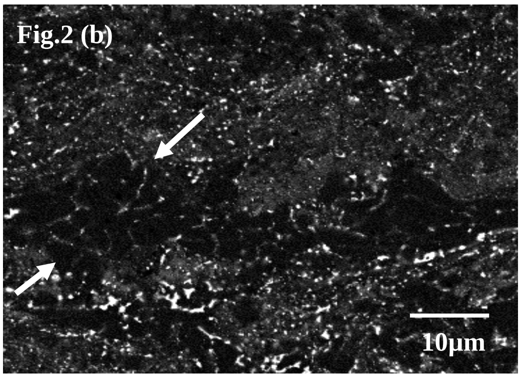


Fig. 1





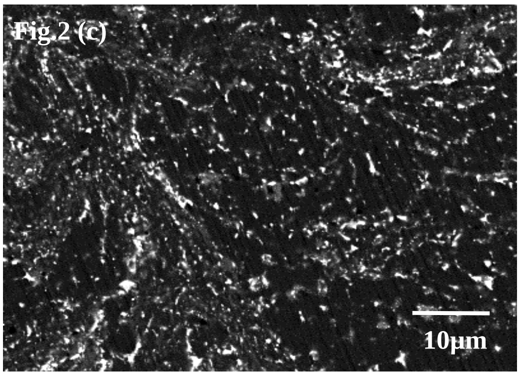


Fig. 1 The relationship between microhardness and time of heat treatment at 300°C.
Fig. 2 BSE images of Al-12wt.%Sn-1wt.%Cu alloys: (a) atomised powder; (b) as-sprayed coating, (e.g. cell structure arrow) and (c) coating heat-treated at 300°C for 1 hour.

3. RESULTS AND DISCUSSION

Fig. 1 shows the relationship between microhardness and heat treatment time at a temperature of 300°C. The microhardness decreases as the time of heat treatment increases, with a rapid drop during the first hour of treatment. XRD spectra revealed no obvious differences in phases present to explain the change in microhardness.

Backscattered electron (BSE) micrographs of the gas atomised powder, and cross-sections through as-sprayed and 1 hour heat-treated coatings are shown in Figures 2a to 2c, respectively. The powder adopts a characteristic dendritic structure of an Al-rich matrix (dark) and a Sn-rich interdendritic phase (bright) (Fig. 2a). In the as-sprayed condition, melted and resolidified powder appears grey in the BSE image, while unmelted parts of the powder retain their original dendritic structure (Fig. 2b, arrowed). In this context it is noted that gas atomised powders cool at $\sim10^4$ Ks^{-1} whereas the thermal spraying cooling rate is $\sim10^7$ Ks^{-1} (Moreau et al, 1991). The Sn-rich phase coarsens within all regions of the sample following heat treatment (Fig. 2c), which makes the dendritic structures of the initially unmelted deposit less obvious.

The TEM micrographs of Figs. 3a,b illustrate the fine-scale microstructure of the melted part of as-sprayed coating, whilst Figs. 3c,d are taken from the coating heat-treated at 300°C for 1 hour. The as-sprayed coating revealed principally equiaxed Al grains in the size range ~ 0.2 - 2µm (Fig. 3a), many with a fine dispersion of 5-50nm Sn particles sometimes associated with complex tangles of dislocations (e.g. Fig. 3b). The weak beam image of Fig. 3b additionally illustrates a fine distribution of dislocation loops within the Al grain. Larger 20-200nm Sn particles were additionally distributed along Al grain boundaries, with distinct precipitate free zones (Fig. 3a, arrowed). Extended intergranular structures of Sn particles were also observed, commensurate with BSE observations of lacy Sn-rich networks.

The heat-treated coating shows that Sn particles within the grains agglomerate and coarsen into larger particles of size ~ 10 – 200 nm (Fig. 3c). Other regions of Al grains free of embedded particles

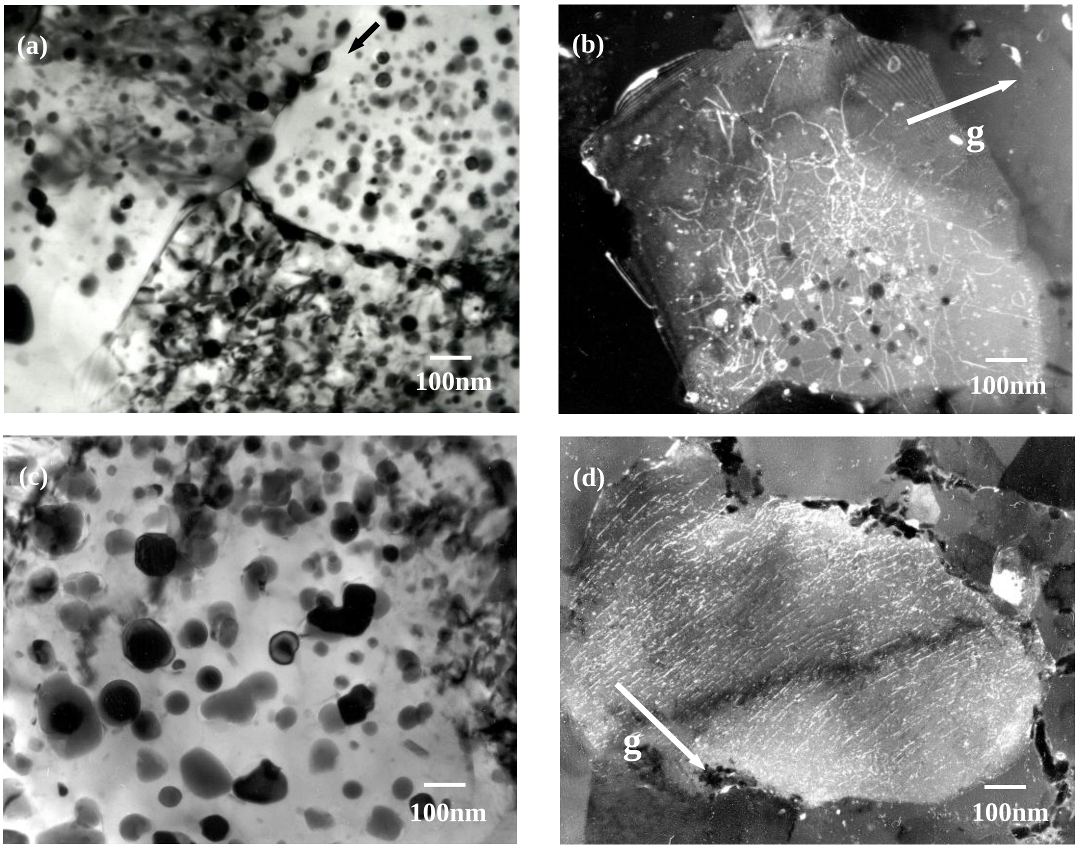


Fig. 3 TEM micrographs of Al-12wt.%Sn-1wt.%Cu coatings. As-sprayed (a) many beam bright field image and (b) weak beam image. After 1h heat treatment at 300°C (c) many beam bright field image, and (d) weak beam image.

exhibit aligned striations of dislocations (Fig. 3d). Further, some probably unmelted regions of the sample after heat treatment exhibit clusters of weakly scattering particles (Fig. 4a) that are believed to be an Al-Cu phase, as indicated by the EDX spectrum of Fig. 4b. XRD spectra do not reveal the presence of this compound due to its small overall volume fraction within the alloy in general.

During the HVOLF thermal spray process, molten and semi-molten powder particles impinge on the substrate with high velocity to form thin splats. In the as-sprayed condition it is evident that parts of the coating maintain the same dendritic structure as the original atomised powder. In particular, the string-like Sn structures revealed in BSE (arrowed, Fig 2b) and TEM reflect the original distribution of Sn throughout the atomised powder. The regions of grey contrast identified in BSE are attributed to compositional averaging of the fine dispersion of Sn particles within Al as revealed by TEM.

Similar kinds of dispersed microstructures have previously been identified by TEM within Al-based alloys formed by melt spinning (Kim and Cantor, 1991), ion implantation (Johnson et al, 2000) and mechanical alloying (Zhang et al, 1991). The Al-Sn system undergoes a eutectic reaction, in a similar fashion to the Cu-Co and Fe-Co systems (Nakagawa, 1958), with a metastable liquid miscibility gap below a long flat liquidus (Kim and Zhang, 1991). When liquid is under-cooled below the miscibility line it separates into Al-rich and Sn-rich liquids. As the Al-rich liquid solidifies and grows, it entraps a fine dispersion of Sn-rich liquid that in turn solidifies. This results in a fine scale random distribution of Sn particles throughout the Al grains. Al and Sn have identical rates of thermal expansion of $23.5 \times 10^{-6}\ K^{-1}$ (Brandes and Brook, 1992) and this explains the absence of strain fields around the embedded particles. During the later stages of solidification, some Sn-rich droplets may be pushed ahead of the Al growth fronts and coarsen at the grain boundaries, thus encouraging denuded zones of Sn around the grain boundaries.

The HVOLF thermal spray process imparts high kinetic energy to the sprayed partially molten powder leading to splatting / deformation of the powders when they impinge at the substrate followed by rapid cooling. This will plastically deform the solid introducing irregular tangles of

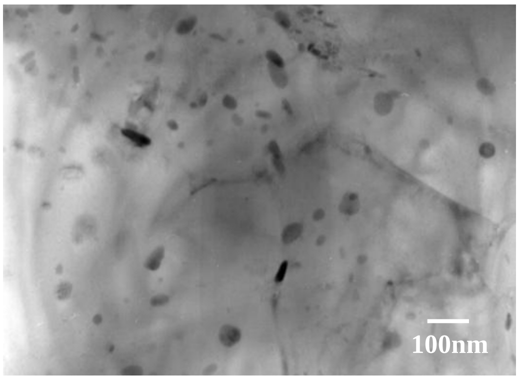


Fig. 4a TEM micrograph of Al-Cu precipitates produced after 1 hour of heat treatment at 300°C

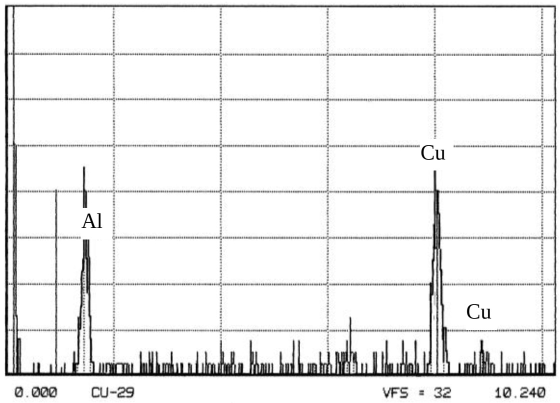


Fig. 4b EDX spectrum confirming an Al-Cu

dislocation (Fig. 3b). In addition, during the rapid cooling associated with HVOLF spraying, the very high concentration of vacancies that are known to be associated with Al-Sn (Kimura and Hasiguti, 1961) might be expected to agglomerate and form dislocation loops (Fig 3b). Any glide of dislocations through the grains would also be expected to leave a trail of vacancies in their wake. Heat treatment might also be expected to lead to recovery process as well as deformation induced dislocated structures in cooling depend upon the presence of fine Sn particles, e.g. by glide along a specific slip system, within Al grains free of Sn particles (Fig. 3d).

It is considered that there are several components related to the decrease in micro-hardness following increasing time of heat treatment at 300°C. The string-like Sn particles coarsen at the grain boundaries, while the nanosized Sn particles embedded within the Al grains also coarsen and agglomerate. Both processes imply that elemental Sn dispersed in a metastable state throughout the Al matrix is used to feed particle growth. Continuation of this process coincides with stabilisation of the alloy microhardness. EDX analysis indicates that localised Al-Cu contain precipitates form in the matrix. The Al-Cu phase diagram [Porter, 1981] indicates that an Al-1%Cu alloy heat-treated at 300°C would be expected to produce a small amount of θ′ that might reduce solid solution strengthening without promoting much precipitate hardening. Heat treatment might also be expected to release the thermal and mechanical stresses generated during spraying and this might be the important factor causing a decrease in microhardness.

In summary, atomised powders of Al-12wt.%Sn-1wt.%Cu have been investigated following HVOLF spraying and heat treatment. The dynamic evolution of the coatings is characterised by a coarsening of Sn particles within deformed Al grains and at grain boundaries, and the reduction of thermal and mechanical stresses, that is associated with a reduction in the alloy microhardness.

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