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Oxidation effects during laser cladding of aluminium with SiC/Al powders

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Aluminium substrates were covered with a layer of an Al–SiC powder mixture. The surface was scanned with a laser beam during which the surface was melted. The top layer of the laser tracks contained oxide plates apart from some large SiC particles. In the bottom layer a cellular network was found with aluminium cells and silicon-rich cell walls.

1. Introduction

Although aluminium and its alloys are widely used, they cannot be applied in situations where a hard surface is needed. This problem can be circumvented by applying a coating, for example for wear-resistant applications on aluminium [1] and also on steel [2], composite coatings of a metal and carbide particles are useful. Suitable defect-free layers can be produced using a high-power laser for the application of such coatings [1, 3, 4] or to remelt plasma-sprayed coatings [5].

Laser cladding is usually done in the air, and although the aim is to prohibit contact between oxygen and hot material by an inert gas stream, this is very difficult to accomplish, especially in industrial circumstances. So far this subject has not been extensively reported in the literature. In addition, there is often little attempt to identify the different phases found after the cladding [2–5], although it is sometimes suggested that oxygen from the air affects the process [1].

In this study a layer of aluminium and SiC powder is melted by a laser beam on an aluminium substrate, and investigated, paying special attention to the identification of the different phases.

2. Experimental procedures

The substrate material was ground and ultrasonically cleaned. Powder material was deposited on it by making a suspension of the powder in methanol, submersing the sample in this suspension and evaporating the methanol. A coarse-grained SiC powder (particles between 0.5 and 40 μm) and a fine-grained SiC powder (50% of particles $< 0.5\,\mu$m, 90% $< 1.8\,\mu$m) were used. The grain size of the aluminium powder was 5 to 10 μm. The different preparations of the samples used in the experiments are listed in Table I. The powder layer thickness is given assuming no porosity.

The samples were scanned by the beam of a 1.5 kW CW–CO_2 laser (Spectra Physics 825) under an argon atmosphere. The laser passes were well separated to inhibit influences of adjacent laser scans. The Gaussian beam was deflected by a molybdenum mirror and focussed by a ZnSe lens with a focus distance of 127 mm. The focus point lay 5 mm above the surface. At the surface the power of the beam was 1300 W. The scanning velocities were between 1 and 25 cm sec^{-1}. After the laser treatment, cross sections were made of the different passes and were analysed by light microscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Energy-dispersive spectometry (EDS) was also performed on the cross sections to obtain information about the distribution of the different elements in the melt pool.

3. Results

In the laser tracks two different zones were found. The lower 50 to 70% of a cross section of the track consisted mainly of a cellular microstructure, and the upper 50 to 30% of plates which sometimes protrude in the cellular microstructure (Fig. 1). Only with a coating thickness of 20 μm were no plates found. Using the fine SiC powder no SiC particles could be found after the laser treatment, but with the coarse SiC powder some large particles containing silicon and carbon, presumably SiC, were found near the interface between the plate-rich and cellular zones (Fig. 2). Perpendicular to the SiC particles, plates were grown (Fig. 3).

The cellular structure was extensively studied by TEM. It was found that the cells contained pure aluminium. To identify the phases of the cell walls, the diffraction pattern from this region was analysed (Fig. 4). Apart from the diffraction spots of aluminium from the cells, a set of rings of tiny spots was found originating from the cell walls. It was concluded

TABLE I Preparation of samples

Sample	Powder layer thickness (μm)	Composition	Type of SiC powder
1	20	50% SiC, 50% Al	Coarse
2	50	50% SiC, 50% Al	Coarse
3, 4	100	50% SiC, 50% Al	Coarse
5	150	50% SiC, 50% Al	Coarse
6	100	50% SiC, 50% Al	Fine
7	100	25% SiC, 75% Al	Fine
8	100	75% SiC, 25% Al	Coarse

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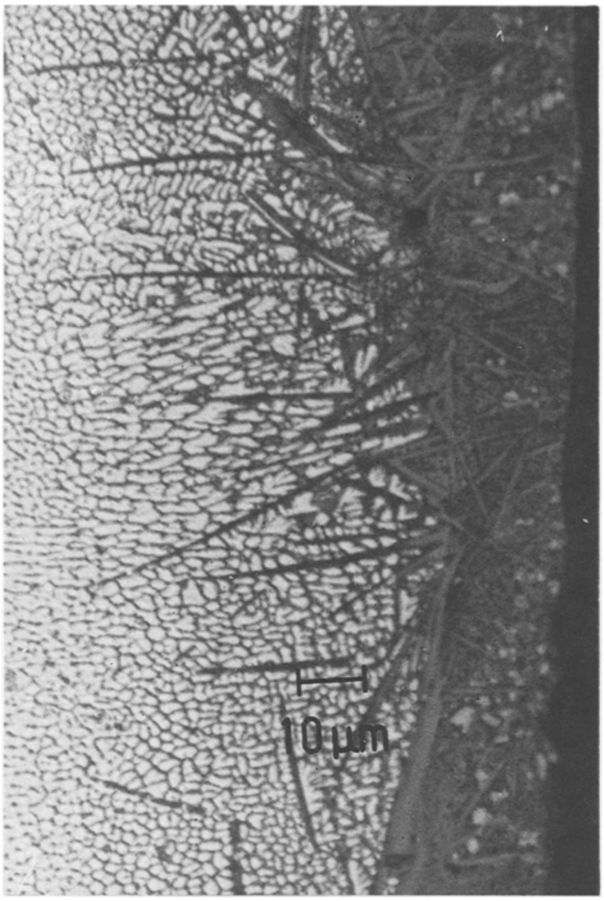

Figure 1 Cross section of laser pass with scan velocity 2 cm sec^{-1} on sample 2.

that the cell walls contained silicon after correction for relativistic effects. For a comparison of our experimental spacings and the tabulated spacings, see Table II (Joint Committee on Powder Diffraction Standards). Very little aluminium was found in the cell walls.

Because the laser tracks were rather inhomogeneous, no exact relations could be determined between the laser parameters and the different features. Cell size diminished with higher laser velocity from 2 to 1 µm, and was almost independent of the powder-layer thickness or the type of SiC powder.

The plates in the top layer were 2 to 5 µm thick and 10 to 30 µm long, sometimes stretching out to 80 µm or more. There was a tendency for the concentration of plates to be higher with larger sizes at higher silicon concentration or at lower laser scan velocities.

With EDS, only aluminium, silicon and oxygen could be detected in the plates. The ratios between the three elements differed from plate to plate. although the atomic percentages were always of the same order. The largest plates in the top of the layer were more-or-less perpendicularly oriented to the surface, and sometimes protruded to the bottom of the melt bath. The plates lying in a lower zone were randomly oriented.

TABLE II Comparison of atomic spacings

Measured spacings (nm)	Tabulated spacings for silicon (nm)
0.317	0.313
0.193	0.193
0.165	0.164
0.136	0.136
0.125	0.125
0.111	0.111
0.105	0.105
0.096	0.096
0.092	0.092

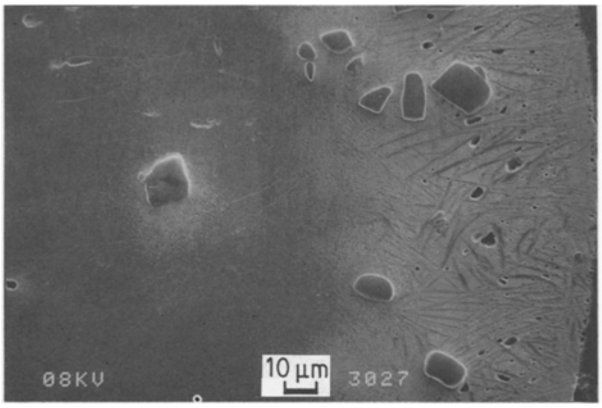

Figure 2 SiC particles in melted and resolidified area (scan velocity 2 cm sec^{-1}, sample 5).

Between the plates the same cellular structure was found as in the lower parts of the melt bath. The contact angle between the cell walls and the plates was high, often 90°. There seemed to be no relation between the cells at one side of the plate and those at the other side.

4. Discussion

The most important result of this investigation is the fact that only if large powder particles are used, SiC is retained after the laser treatment. After depositing the powder layer, an open structure is formed with a thickness a few times that of a massive layer of a material of the same mass, suggesting a large volume of pores. Even at room temperature, SiC is not stable with respect to oxidation. However, normally an SiO_2 layer is formed which prohibits further contact with oxygen [6]. At higher temperatures (2100° C at an

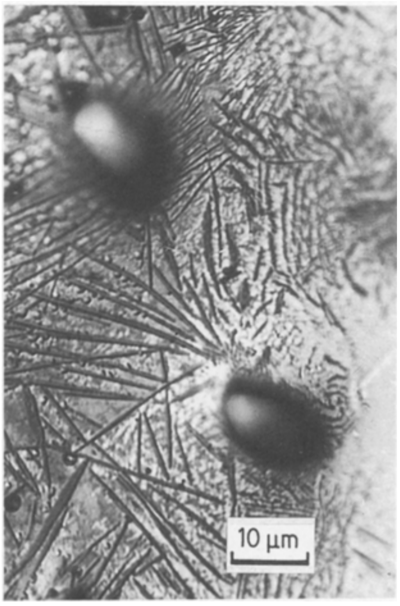

Figure 3 Growth of plates around SiC particle.

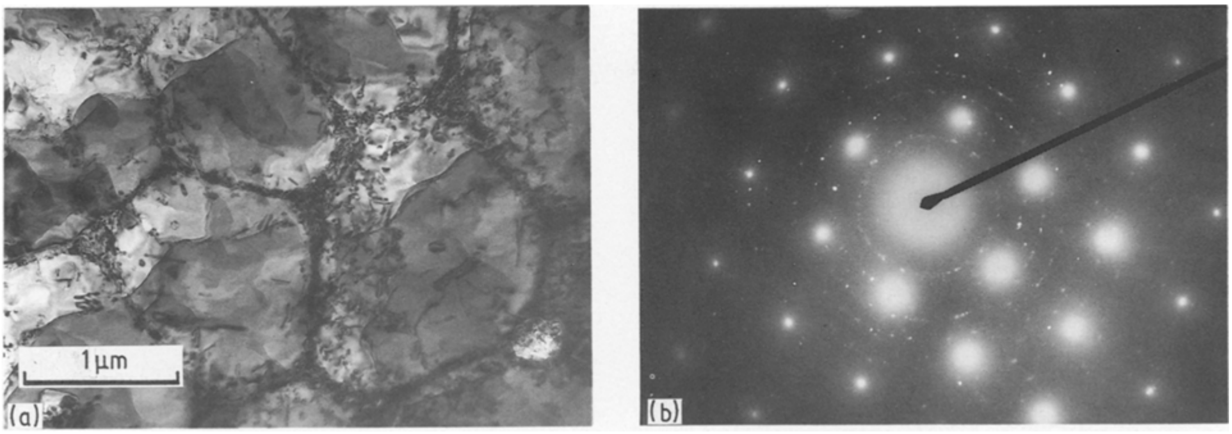

Figure 4 Cellular structure for (a) bright field, (b) diffraction pattern of cell walls.

oxygen pressure of 1 atm and 1350° C at an oxygen pressure of 10^{-5} atm) the formation not of SiO_2 but of SiO is energetically favoured [6]. In this temperature range Al_2O_3 reacts with SiC to form SiO, CO and other oxides [7]. Further, it is known that $Al_2O_3 \cdot SiO_2$ reacts with SiC to form SiO, Al_2O_3 and CO [8].

Liquid aluminium reacts with SiC to form Al_4C_3 and silicon. This reaction only proceeds due to the dissolution reaction of silicon in aluminium [9]. At higher temperatures Al_4C_3 oxidizes and sublimates [10]. SiO is formed as a gas above 1000 to 1250° C, and decomposes easily to silicon and SiO_2 [11]. SiO is sublimated as an amorphous solid, although in the literature there are references to a crystalline form. However, this conclusion is mainly based on X-ray analysis of mixtures of SiO and base materials (SiC, silicon) or decompositon products (silicon, SiO_2) [12].

In the present case the SiC and aluminium particles are surrounded with thin oxide layers, because the preparation of the samples was made in air. It is known that most of the time an inert gas stream does not cover the melt bath effectively enough to prohibit every contact with oxygen, so there is probably enough oxygen and oxides to oxidize SiC. Because oxide solidification products are found as plates, the temperature must have been high enough (around 2000° C) to melt these materials, to favour the reaction for SiO and to oxidize or sublimate Al_4C_3. Silicon is probably formed as decomposition product of SiO or as a product of the reaction between liquid aluminium and SiC. It is dissolved in the liquid aluminium.

During the laser treatment, the SiC particles oxidize rapidly. The small particles have a relatively large surface, which is the reason for complete oxidation in contrast to the powder with larger particles where some SiC particles are not completely oxidized.

Both the high temperatures, at which Al_2O_3 has a lower surface energy, and the reaction with SiC also probably cause fracturing of the oxide layer around the aluminium particles, oxidation of some aluminium, and a filling up of the pores with liquid aluminium. The cellular structure is a typical solidification structure [13] originating from the bottom of the melt. Silicon is solidified eutecticly with aluminium as the last part of the melt.

The plates developed in areas with a high oxygen content, and therefore also with a high aluminium oxide or silicon oxide content. Plates start to grow around retained SiC particles (Fig. 3) or are nucleated at the surface or homogeneously in the melt. Because the solidifying cellular structure is influenced, for example, plates divide the cellular structure into parts which have no orientation relation with each other, the plates must have been originated first. This is also indicated by the phase diagram of Al_2O_3–SiO_2, in which solidification temperatures between 1580 and 2050° C are found, much higher than the solidification temperature range of aluminium alloys [14]. After nucleation and growth of the plates and further cooling a cellular network of Al–Si is formed in the remaining fluid.

5. Conclussions

During the laser treatment of aluminium coated with a layer of aluminium and SiC, only after using large SiC particles (20 to 40 µm) is some SiC retained. Use of an inert gas stream is not always enough to prohibit sufficiently contact of air with the melt. During the laser treatment most SiC reacts with O_2, Al_2O_3 and SiO_2, forming among other reaction products silicon, which is taken up by the aluminium melt bath. In the lower layer of the melt bath, a cellular network of aluminium cells and eutectic-type Al–Si cell walls are found. In the upper layer, aluminium–silicon oxide plates are first formed, after which the remaining fluid is solidified as a cellular Al–Si network.

Acknowledgements

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