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Oxidation reaction during laser cladding of SAE1045 carbon steel with SiC/Cu alloy powder

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Laser cladding of SAE1045 carbon steel with SiC/Cu alloy powder was performed in air. The microstructures of the cross-section of the clad layer obtained were obviously divided into three laminae. Analysis results using X-ray diffraction, scanning electron microscope (SEM) and electron probe microanalysis (EPMP) indicate that there exist α-Cu, SiO_2 and Cu_5Si in the top layer. However, SiC particles (SiCp) originally added almost disappeared during laser cladding. To simulate the reaction taken place in the laser pool, differential thermal analysis was carried out by using a Perkin-Elmer DSC 7 in an atmosphere of Ar and O_2. This revealed that the SiCp is stable during heating in the atmosphere of Ar. However, intensive oxidation and decomposition of the SiCp were found when heating was undertaken in an O_2 atmosphere, which reasonably explains the formation of SiO_2 and Cu_5Si in the top layer.

1. Introduction

The formation of surface metal matrix composites (MMCs) by incorporation of ceramic particles to produce superior surface properties on various alloy substrates, which in general possess poor wear or oxidation resistance, has attracted increasing interest in recent years. Among the various processing techniques, laser cladding is more promising because it is often the case that only a limited area of a component requires additional modification, and the laser beam can be focused on the essential area, leaving the remainder untreated. Therefore, using laser cladding to make surface metal matrix composites will save energy and time.

Since silicon carbide (SiC) has good properties, such as high hardness and low density, it is usually used as strengthening phase in surface metal matrix composites. However, in most cases, the chemical composition, morphology and amounts of the silicon carbide particles (SiCp), added as a powder, are hardly remained unchanged. In some special cases, the SiCp will completely disappear in the surface layer. For example, Abboud and West [1] injected SiCp into a commercial purity titanium surface. They observed partial dissolution of the SiCp, which led to the enrichment of the matrix with silicon and carbon during solidification. Hu and Baker [2] preplaced SiCp on aluminium alloy surface and treated by laser melting. They found that the SiCp partially dissolved in the liquid and reprecipitated during the solidification. When cobalt and nickel alloys were used to produce surface metal matrix composites with SiCp, no SiCp was found in the molten zone [3, 4]. These results show that the SiCp is not stable enough in laser processing. Some important metallurgical reactions of the SiCp with environment must take place. Up to now, the interest has been focused on the dissolution of the SiCp and some reasonable explanations are obtained [2].

However, it is because the laser processing is usually carried out in air that more complex chemical reactions may take place. In fact, it is hard to prevent the oxygen and other gaseous elements in the atmosphere from entering the laser melt pool, even when inert gas shroud techniques have been used during the laser cladding. As one can easily image, a drastic oxidation reaction occurs in the most alloy systems because of the high temperature and the high flow speed of the molten fluid. Hegge reported that SiCp reacted with oxygen during laser cladding of aluminium with SiCp/Al powder even when they wanted to prohibit contact between oxygen and hot material by an inert argon stream [5].

What makes this reaction important is that both the chemical and microstructural states may be changed to a great extent [6]. Previously, only a few investigations were concerned with the reactions in laser pool. In the present study, a composite system of copper alloy with SiCp was selected to test the stability of the SiCp under the conditions of which produced little effect of the matrix copper alloy on the reaction during laser cladding. This is because the copper alloy is relatively insensitive to reaction with oxygen. More attention is paid to exploring the type of products and their distribution within the clad layer.

2. Experimental procedure

Laser cladding was carried out by employing a 2 KW CO_2 laser with multimode. The laser power, the beam size in diameter and the scanning velocity were fixed at 2 kW, 5 mm and 5 mm/s respectively. The laser cladding was undertaken in air. A plain-carbon steel, SAE1045, was used as the substrate of the specimen with 80 mm length, 30 mm width and 10 mm thickness. Powders of the copper alloy (~90 μm) and SiCp (~60 μm) were mixed to form the mixture for cladding, where SiCp was 25 wt-%. Then the powder mixture was pre-placed on the surface of the substrate with a chemical binder to a thickness of 1 mm. The chemical composition (wt-%) of the copper alloy used in this investigation is: Al 5.49, Fe 4.73, Si 0.3, Cu bal.

The microstructures of the clad layer were observed in the optical microscope and using a JSM-35C scanning electron microscope. The composition distributions were analyzed by using a JXA-8800R electron probe microanalyser (EPMP). The laser-treated specimens were also examined by using a D/MAX-III C X-ray diffractometer with Mo K α. To simulate the reaction taking place in the laser pool, differential thermal analysis was performed by using Perkin-Elmer DSC 7. Measurements were made using a ramp rate of 20 °C min^{-1} in the temperature range from 20 °C to 1200 °C in an atmosphere of Ar and O_2.

3. Results

3.1. Microstructural characteristics

The microstructures of the vertical cross-section of the clad layer were clearly divided into three laminas, i.e., the top layer (marked by I), the bright zone (marked by II) and the heat effect zone (marked by III), as shown in Fig. 1. At higher magnification, the particles with regular spherical shapes were uniformly distributed in the top layer with a copper rich matrix. The sizes of the particles vary from 1 micrometer to over ten micrometers. The distributions of composition of the particles were analyzed by EPMA. The results are given in Fig. 2, from which we can see that the particles, as shown in Fig. 2a, are rich both in silicon and in oxygen (Fig. 2b, c). Combining the results obtained by the X-ray diffraction phase identification, an unambiguous conclusion may be drawn that the particles presented within the top layer are SiO_2, as shown in Fig. 3. The X-ray diffraction spectrum obtained from the as-laser clad surface was indexed in terms of α-Cu, SiO_2 and Cu_5Si. This result indicates SiCp has almost oxidized, decomposed or dissolved into the matrix during laser cladding. The EPMA analysis showed that the silicon content increased from 0.3 wt-% to 2.3 wt-% in the matrix of the top layer.

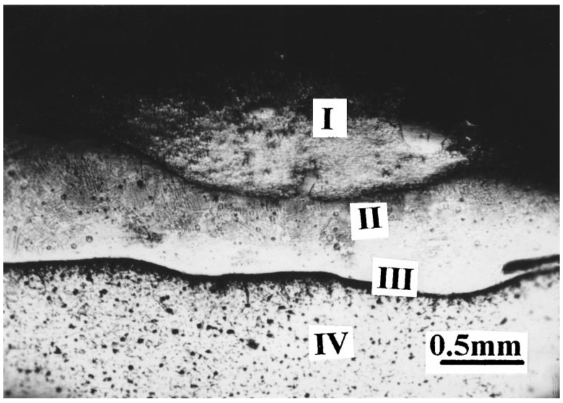

Figure 1 A cross-section of a laser-clad specimen. The top layer, bright zone, heat-effected zone and steel substrate are marked by I, II, III and IV, respectively.

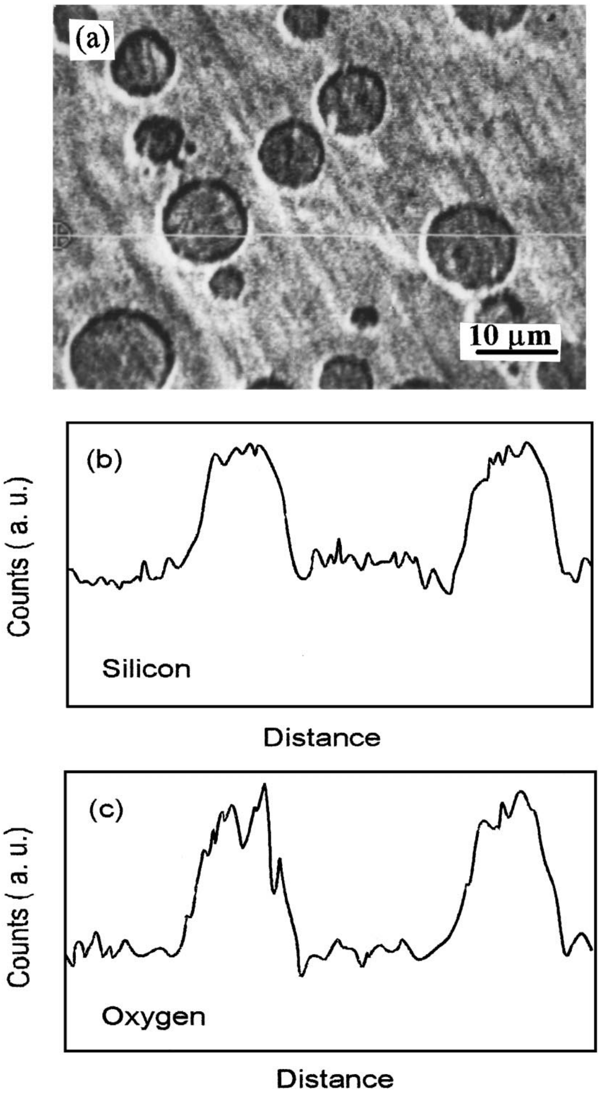

Figure 2 Particle morphology (a), silicon (b) and oxygen (c) composition distribution in the top layer.

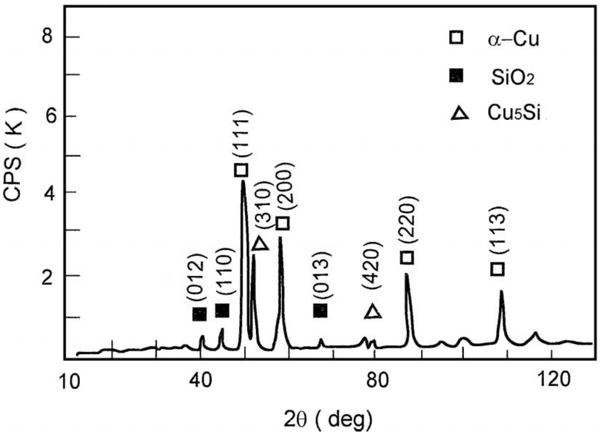

Figure 3 X-ray diffraction spectrum of the laser clad sample.

In bright zone, the microstructures mainly consist of the particles and the martensite-like matrix. The particles are divided into two types, one with a larger size

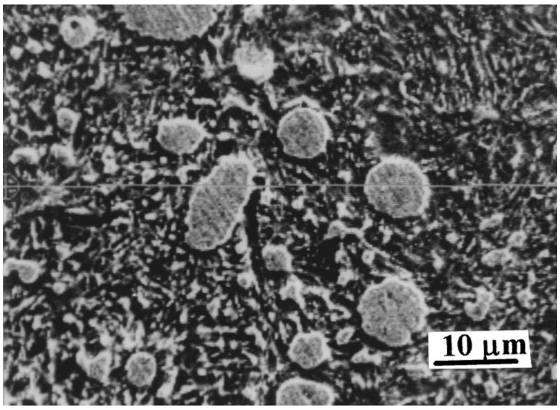

Figure 4 Particle distribution in the bright zone.

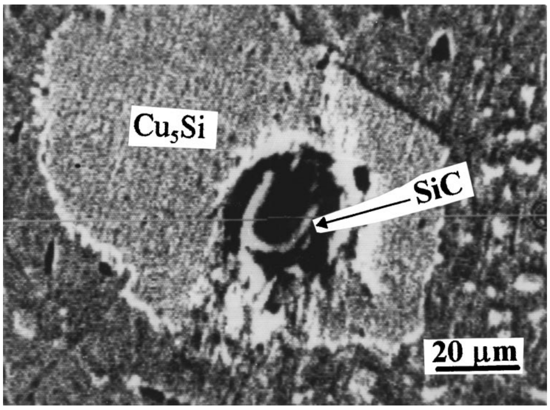

Figure 5 The retained SiC particle as a nucleus of Cu$_5$Si.

(1–10 micrometer in diameter) and near spherical in shape, the other with a smaller size, less than 1 micrometer, as shown in Fig. 4. The elemental distribution analysis showed that the particles with the larger size are rich in copper, aluminium and silicon. We may reasonably infer that these particles are the metallic compound Cu$_5$Si, in which aluminium atoms were dissolved. Cu$_5$Si was deposited as a primary phase during solidification.

Minor retained SiC was occasionally observed. The retained SiC particles acting as nucleus for Cu$_5$Si is illustrated in Fig. 5, in which the morphology of Cu$_5$Si is around a small SiC particle. It is very interesting to note that the size of the Cu$_5$Si particle nucleated at the retained SiC particle is much larger than that of the particles having not external nucleus. Therefore, the retained SiC particles have a great effect on the nucleation and growth dynamics of the Cu$_5$Si primary phase in solidification. A similar important result is obtained on the effect of the solidified Cu$_5$Si particle on the reprecipitation of SiC from the liquid matrix. As shown in Fig. 6, around the Cu$_5$Si particle, there are many small SiC particles that are precipitated from the liquid matrix. This indicates that the SiC particles added to the composite powder are partially decomposed and dissolved into the matrix during the laser cladding. In the solidification, the matrix supersaturated with silicon and carbon will precipitate the SiC particles.

The heat effect zone of the clad layer is an alloyed layer of the composite powder with the steel substrate. In this zone, a great amount of iron will enter the clad layer. The thickness of the zone is sensitive to the laser cladding process parameters, e.g., the laser power, the beam size and the scanning velocity.

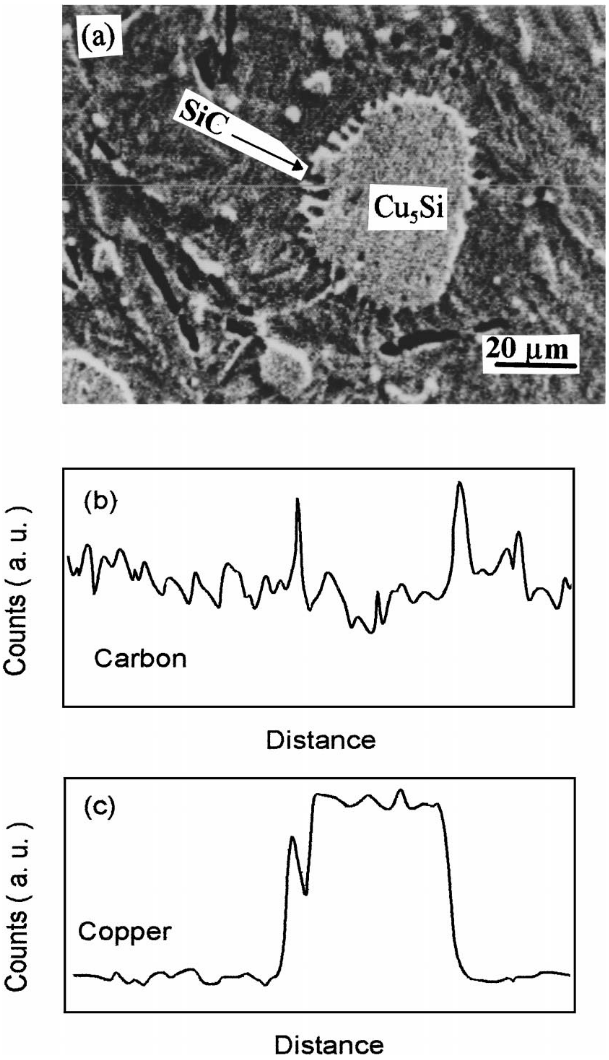

Figure 6 (a) SEM micrograph of the precipitation of SiC around Cu$_5$Si, (b) carbon (c) copper composition distribution.

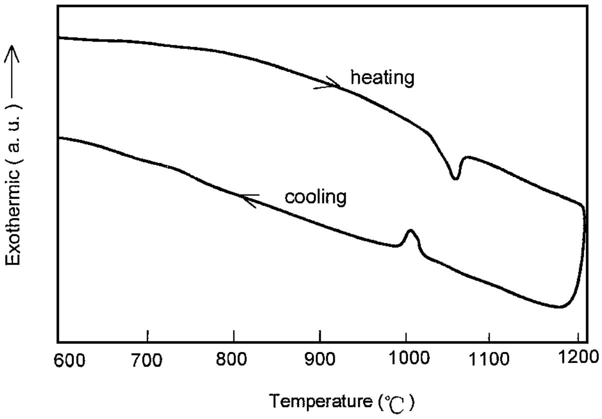

Figure 7 DTA curves in DSC mode of 25 wt-% SiCp/Cu alloy in an atmosphere of Ar.

3.2. Simulation of the reaction taken place in the laser melt pool

Fig. 7 shows the DTA curves in DSC mode of the sample measured in an atmosphere of Ar. There is one endothermic peak in the heating curve. The endothermic

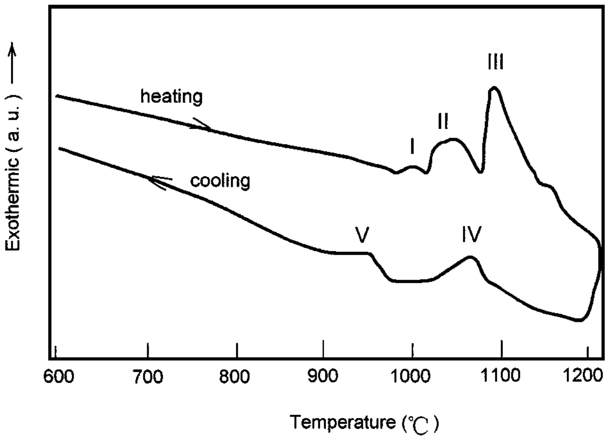

Figure 8 DTA curves in DSC mode of 25 wt-% SiCp/Cu alloy in an atmosphere of O_2.

reaction has a starting temperature of 1024 °C, an ending temperature of 1075 °C, and a peak temperature of 1056 °C where the enthalpy of the endothermic peak is 120 J/g. We believe this endothermic reaction relates to the melting of the copper alloy. After heating to 1320 °C the sample was cooled. Only one exothermic peak occurs in the cooling curve. The peak has a temperature span from 1025 to 983 °C with a peak temperature of 1006 °C. The corresponding exothermic enthalpy is 61 J/g. Obviously, this exothermic peak refers to the solidification of the copper alloy. These results indicate that the SiCp has no reaction with the copper alloy during heating and cooling in the atmosphere of Ar.

The DTA curves in DSC mode of the sample measured in oxygen are shown in Fig. 8. In this case, the curves show a quite different kind of behaviour. There are three exothermic peaks in the heating curve. The first peak (marked by I) has a temperature span from 981 to 1018 °C with a peak temperature of 1005 °C and an exothermic enthalpy of 7 J/g. The second peak (marked by II) occurs in the temperature ranges from 1018 to 1076 °C with a peak temperature of 1047 °C and an exothermic enthalpy of 144 J/g. The last peak (marked by III) is found between 1076 and 1149 °C, with a peak temperature of 1095 °C and exothermic enthalpy of 340 J/g. The three exothermic peaks may be referred to the oxidation reactions of the SiCp. Much to our surprise, there is no endothermic peak in the heating curve, which is the indication of the melting of copper alloy. The reasonable explanation is that the oxidation reactions of the SiCp are so intensive that the endothermic heat of the copper alloy melting is completely counteracted by the exothermic oxidation reaction.

In the cooling curve obtained under oxygen, two exothermic peaks may be observed, while only one exothermic peak has found under Ar. As shown in Fig. 8, the first exothermic reaction (marked by IV) occurs between 1143 to 982 °C, with a peak temperature of 1072 °C and exothermic enthalpy of 250 J/g. We deduce that this reaction is the precipitation of the primary phase of the metallic compound Cu_5Si from the liquid copper alloy. The second exothermic reaction is found in the temperature ranges from 982 to 895 °C, with a peak temperature of 954 °C and exothermic enthalpy of 74 J/g. Although this peak is shifted to a lower temperature in comparison with the peak which occurred in the cooling curve under Ar, we may infer that this reaction is the solidification of the copper alloy.

The results given above, clearly show that SiCp is not stable when heated in an oxygen atmosphere. A series of reactions may take place, as will be discussed further in the following section. This is the reason why the SiCp is rarely completely retained during laser cladding. If one wants to make SiCp reinforced surface metal matrix composites by laser cladding, careful protection against oxidation should be taken.

4. Discussion

The all results shown in the previous section indicate that the SiC particles almost disappeared during laser cladding, while the silicon oxide present in the top layer and also the silicon content of the matrix increase in the laser melt pool. A drastic oxidation reaction is thought to be responsible to explain why these results. Because the laser cladding was performed in an oxygen atmosphere, oxygen readily entered the melt pool and reacted with the SiC particles by the possible following reactions,

$$\mathrm{SiC} + \mathrm{O}_{2(g)} \rightarrow \mathrm{SiO}_{2(l)} + [\mathrm{C}] \quad (1)$$

$$2\mathrm{SiC} + \mathrm{O}_{2(g)} \rightarrow 2[\mathrm{Si}] + 2\mathrm{CO}_{(g)} \quad (2)$$

$$[\mathrm{Si}] + 2[\mathrm{O}] \rightarrow \mathrm{SiO}_{2(l)} \quad (3)$$

where (s), (l) and (g) refer to the reactants or the products in solid, liquid and gaseous states respectively, and the symbol [ ] denotes that the element is dissolved in the liquid matrix.

SiC phase is stable enough under ambient pressure till the temperature reaches about 2830 °C. However, it has been reported that in the temperature region from 1000 to 1400°C, SiC is sensitive to oxidization [7]. Under the present experimental conditions, the temperature of the laser pool is not higher than 2000 °C, and this overlaps the temperature region of SiC phase in unstable state. Thus the SiO_2 will be produced accoring to Equations 1 or 3. It is calculated by Equation 3 that a release of heat of 890 kJ/mol will occur, while the calculations based on Equations 1 and 2 will give 800 and 78 kJ/mol, respectively, in the temperature range from 1000 to 1400 °C. A comparison of these data with the results obtained from Fig. 7, suggests that SiCp reacts with oxygen and forms SiO_2. Meanwhile silicon and carbon atoms are dissolved into copper alloy matrix. The dissolved silicon reacts further with oxygen and forms SiO_2, untill the SiCp is almost consumed.

The products of the reaction, i.e., the elements silicon, oxygen and carbon, will be dissolved into the liquid, which resulted from the SiC which precipitated around the existed particles, e.g., the Cu_5Si, during solidification, as observed in Fig. 6.

The possible reactions which existed in laser melt pool, as describing above, may give a reasonable explanation of the formation of silicon oxide and the increase of the silicon content in the matrix, as well as the formation of the metallic compound Cu_5Si. But, it is still not resolved how the distributions of these oxides within the clad layer can be explained? Why do the SiO_2 particles exist in the top layer? The application of dynamic analysis, dealing with the flow of a molten alloy containing a multiphase, is believed to be useful for the determination of the distribution of the oxide particles. At the very beginning, the velocity (V) of oxide particles within the liquid can be estimated using Stokes law [8] if we suppose the flow velocity of the liquid is omitted, therefore

$$V = \frac{2r^2(\rho_l - \rho_s)g}{9\mu} \tag{4}$$

where μ is the liquid copper viscosity, taken as 0.0341 kg/m·s, r the oxide particle radius, ρ_s and ρ_l the densities of oxide and liquid copper, and g the gravitational acceleration, respectively. The densities of SiO_2 and liquid copper are 2.32 and 7.93. Substituting these values into Equation 4, we can get the velocity of SiO_2 within the melt pool. The value is very small, for example, taking the radius of the oxide as 10 micrometer, $V_{SiO_2} = 3.58 \times 10^{-5}$ mm/s. Because the lifetime of the melt pool under the present experimental conditions is about one second ($=D/V_s$, where V_s is the scanning speed, D the beam size of laser), the upward migration distances of the SiO_2 particles are 3.58×10^{-5} mm. Obviously, the values are too small to explain the results obtained by the present experiment. In order to obtain a satisfactory explanation to the experimental results, another key factor, i.e., the movement of the liquid copper driven by the surface tension, must be considered.

There are many forces acting on the melt pool. One of the largest is that from the variation in surface tension due to the steep thermal gradients. The surface tension driven flow has been identified to be responsible for the distribution of the chemical composition and the particles with various different densities. By mathematical modeling of the flow in the pool, some very interesting and important results were obtained. For example, the recirculating flow could be observed clearly, the velocity of the flow near the surface for all cases was of one or two orders of magnitude higher than that of the scanning speed, and the melt pool would rotate approximately five times before solidifying [9]. Therefore, the velocity of the liquid copper near the melt pool surface will be ~50 mm/s, if we take it as one order of magnitude higher than that of the scanning speed. Suppose the migration velocity of the oxide particles is equal to the velocity of liquid copper, then most of the oxide particles produced will move upward to the top layer of the melt pool.

5. Conclusions

(1) There exists a drastic oxidation reaction during the laser cladding of copper alloys with SiC particles on the steel substrate SAE1045. SiC particles will be oxidized and SiO_2 formed within the melt pool. The X-ray diffraction spectrum obtained from the as-laser clad surface identified α-Cu, SiO_2 and Cu_5Si. This result indicates that SiCp has almost completely oxidized, or decomposed and dissolved into the matrix during laser cladding.

(2) SiCp is stable during heating in an atmosphere of Ar. However, extensive oxidation and decomposition of the SiCp was found when heating in an atmosphere of O_2, three exothermic peaks in the heating DSC curve and two exothermic peaks in the cooling DSC curve were observed, which reasonably explain the formation of SiO_2 and Cu_5Si in the surface layer.

(3) The migration velocity of the oxides estimated using Stocks law is too small to explain the experimental results. It is believed that the key factor to drive the movement of oxide to the surface layer is the surface tension driven flow of the molten matrix metal. In this case, most of SiO_2 particles within the melt pool can move upward to the top layer.

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