CHAPTER 5

EFFECT OF POST TREATMENTS ON DRY SLIDING WEAR BEHAVIOUR

5.1 Introduction

It is found that the microstructure of plasma sprayed coatings is of foremost significance to the wear behaviour of the coatings. The microstructure is characterised by small sized inter lamellar porosity, larger pores, cracks of varying size and occasional unmelted particles. The porosity is widely considered as the major cause to the low mechanical and wear performance of sprayed coating. Hence, a number of post treatments have been used to reduce the porosity. One being laser remelting of the coating and other means used to fill the pores and cracks are electro-deposition technique and immersion of the coating in plastic resins, molten metal or aluminium phosphate.

In view of the effect of above cited post treatments process on the microstructure of sprayed coating, a need for detailed and systematic study of their effect on wear performance of coating is contemplated. In the present chapter, experimental results pertaining to the effect of post treatments on dry sliding wear are discussed.
5.2 Effect of Sealing on dry sliding wear behaviour

5.2.1 Effect of sealing on surface and subsurface

Figure 5.1 (a) Top surface of plasma sprayed molybdenum coating (b) Subsurface of plasma sprayed molybdenum coating. (c) Subsurface of sealed plasma sprayed molybdenum coating.
From Figure 5.1 (a) and (b) a splat structure noticed both in the subsurface and on top surface, most splats being surrounded by micro cracks. Some semi melted particles also were found. After sealing treatment, the pores and micro cracks were found to be filled with Ni throughout the thickness of Mo coating. The Figure 5.1 (c) shows presence of Ni across the cross section of sealed plasma sprayed molybdenum coating.

5.2.2 Effect of sealing on Porosity

The porosity of the unsealed coating was found 10.81%. The porosity of the sprayed coating was reduced (1.54%) by means of sealing with electro-deposited Ni. Thus original open porosity and micro cracks could be eliminated, without the closed pores in the coating. EDAX pattern (Figure.5.2) clearly shows the presence of Ni across the cross section of the coating thickness.
5.2.3 Effect of sealing on surface and subsurface microhardness

The hardness of sealed plasma sprayed molybdenum coating significantly increased. The hardness of the sealed plasma sprayed molybdenum coating was about 754HV₀.₁ higher than the unsealed plasma sprayed molybdenum coating as shown in Figure 5.3. It is believed that part of the resistance to indentation is due to the intrinsic hardness of the molybdenum and part is due to internal friction between molybdenum particles caused by relative movement. When the coating has been sealed with Ni, the internal friction between Mo particles is replaced by shear of the metallic Ni. It provides a larger resistance to shear during indentation than the friction between self mated Mo (Westergård and Hogmark, 2004a), hence it gives a higher hardness for sealed coating.

At the surface of the both the sealing and unsealing coating the microhardness is more. The microhardness of the coating as moving towards the substrate material is decreases (subsurface). This decrease in microhardness in the subsurface region may be due to change in lamella cooling rate. The thermal properties of the surface beneath the impinging particles change as the coating builds up; the lamella cooling
rate is expected to vary accordingly. In fact, for the first impinging particle, its cooling rate depends on the substrate thermal conductivity, the thermal interfacial resistance between the lamella and the substrate material, the wetting behaviour of the molten particle on the substrate material. The subsequent particles impinge on previously deposited lamellae and, thus, the properties of the underlying material and at the interface are different (Moreau and Lamontagne, 1992; Zimmer, 2010).

5.2.4 Evaluation of sealed and unsealed coating performance

5.2.4.1 Dry Sliding Wear Behaviour

5.2.4.1.1 Effect of load on sliding wear

![Graph showing volume loss of sealed and unsealed coatings with respect to applied load]

**Figure 5.4** Volume loss of sealed and unsealed coating with respect to applied load

The volume loss of sealed and unsealed sprayed molybdenum coatings increases with increase in applied load at a constant sliding speed of 3.53 m/s and sliding distance of 5000 m as shown in Figure 5.4 and similar results were observed by Khedkar et al., (1997), Hwang et al., (2005) and Uyulgan et al., (2003). This is because; loosely adhere semi melted splats detached from coating surface and acts as an abrasive particle. Elongated micro cracks may occur when highly concentrated
stresses are imposed by abrasive particles especially in the case of brittle materials. Unsealed coating consists of open pores which allow easier crack propagation. Such phenomena of micro cracking and crack propagation vary with wear load and greatly influence the wear rate (Ahn et al., 2005; Normand et al., 2000; de Portu et al., 2007; Siu and Li, 2000).

**Figure 5.5 (a)** Worn surface of sealed plasma sprayed molybdenum coating at lower load (30N).

**Figure 5.5 (b)** Worn surface of sealed plasma sprayed molybdenum coating at higher load (90N).

The Figures 5.5 (a) and (b) are the SEM micrographs showing worn surfaces of sealed coatings at an applied load of 30N and 90N, speed of 3.53m/s and a sliding
distance of 5000m. Figures 5.5 (a) and (b) shows the distinct abrasive wear mode which is responsible for formation of grooves and delamination. As the applied load increases the intensity of splat delamination also increases along with formation of tribofilm. It is evident from Figure. 5.5(b) is that the worn surface was covered by tribofilm and increased intensity of delamination. Thus, the sealed plasma sprayed Mo coatings surface worn mainly by detachment of tribofilm and splats.

5.2.4.1.2 Effect of sliding distance on sliding wear

![Graph showing volume loss of sealed and unsealed coating at increasing sliding distance.]

**Figure 5.6** Volume loss of sealed and unsealed coating at increasing sliding distance.

The Figure 5.6 shows the variation of volume loss with sliding distance at a constant applied load of 50 N and for a constant sliding speed of 3.53m/s. The volume loss of sealed and unsealed coating increases with increase in sliding distance. Usmani and Sampath, (1999) and Khedkar et al., (1997) also noticed that material loss of the sprayed coating increases with increase in the sliding distance. When the sliding between coated pin and steel disc starts, the asperities of the coated pin plow into the harder moving parts, debris will be generated. Hence, initially the generation of wear debris take places primarily due to plowing. Due to continuous sliding and fatigue of coating, micro cracks are generated in coating surface. These micro cracks
are responsible for extensive delamination from coating surface and are causes for further generation of wear debris. Because of this reason material loss is higher at higher sliding distance (Usmani and Sampath, 1999).

Figure 5.7(a) Worn surface of sealed plasma sprayed molybdenum coating at lower sliding distance (2000m).

Figure 5.7(b) Worn surface of sealed plasma sprayed coating at higher sliding distance (6000m).

It is evident from Figure.5.7(a) at lower sliding distance the wear debris were generated mainly due to plowing. From Figure. 5.7(b) it has been noticed that
formation of plow, debris and micro cracks at higher sliding distance. The formation of micro cracks are accountable for widespread delamination of coating surface. Because of this motive higher volume loss was observed at higher sliding distance.

5.2.4.1.3 Effect of sliding Speed on sliding wear

![Graph showing volume loss vs sliding speed]

**Figure 5.8** Volume loss of sealed and unsealed plasma sprayed at increasing sliding speed

The Figure 5.8 corresponds to variation in volume loss with the sliding speed for the sealed and unsealed coatings. The volume loss of unsealed coatings uniformly increases and sealed coatings increased as the sliding speed increases up to 1.8 m/s, beyond 1.8 m/s the wear pattern of the unsealed coatings changes and it increases with increasing speed, however the same trend of increasing volume loss with increasing the speed was observed in sealed coatings. A drastic increase of volume loss was observed for unsealed coatings when the speed is increased from 2.8 m/s to 4.7 m/s. It is clear from the study that as the sliding speed increases, the volume loss of both the coatings are lower up to 1.8 m/s.
During plasma sprayed molybdenum coating process, the molybdenum combines with oxygen and forms a thin hard molybdenum oxide layer. The presence of MoO₂ can help to improve the dry sliding condition of the coating (Laribi et al., 2007; Khedkar et al., 1997; Niranatlumpong and Koiprasert, 2010). Due to this reason at lower sliding speeds the volume loss of sealed and unsealed coatings is very much lower. However, above a sliding speed of 1.8m/s volume loss of both the coatings increases with increase in sliding speed. Since, as the sliding speed increases the length of contact between pin and disc increases. This increase in contact would cause the rise in interface temperature. The oxides usually volatile at higher temperature (de Portu et al., 2007; Ozdemir et al., 2003). When the oxide volatilises, poorly adhered particles are removed from the coating surface and cause for increased volume loss (Gu et al., 2012; Basavarajappa et al., 2006).

In all the cases the sealed coating exhibits better wear resistance as compared to unsealed coating. This is because of detached splats that stay on the sliding track are crushed and compacted to form a tribofilm. The tribofilm properties are vital for the wear resistance.

A tribofilm made only of molybdenum is brittle in nature. It was confirmed by EDS analysis (Figure.5.9) that tribofilm was covered by Ni. Thus, tribofilm covered by Ni helps to reduce the brittleness of tribofilm (Westergård and Hogmark, 2004; Westergård et al., 2004). Another reason for reduced wear volume loss in sealed coating is because of the sealing treatment improves the cohesion between the splats and also between the splats separated by micro cracking. In the sealed coating, the crack propagation is impeded by the sealant. This impedance causes for fewer and smaller fragments detached from the coating surface.
Figure 5.9 EDAX pattern of worn surface
5.3 Effect of laser remelting on dry sliding wear

The laser remelting of the specimen is carried out using the laser setup shown in Figure 3.4

5.3.1 Characterization of laser remelted coating

5.3.1.1 Effect of laser remelting on the morphology of coating

Figure 5.10 Plasma sprayed molybdenum coating before laser remelting

(a) Top surface (b) Subsurface of coating

The Figure 5.10 (a) shows SEM image of the top surface of the plasma sprayed Mo coating. This sprayed coating surface is characterized by undulations comprising unmelted, partially melted and fully melted splats. The top surface also contains a large number of ubiquitous micro cracks originating from the spray process. Figure 5.10 (b) illustrates a cross-sectional micrograph of the plasma sprayed
Mo coating, where a lamellar microstructure of the coating can be seen. The micro pores and other structural defects can also be observed in Figure 5.10 (b). The presence of these microstructural defects decreases the density of the coating and reduces the adhesion.

**Figure 5.11** Plasma sprayed molybdenum coating after laser remelting (a) Top surface (b) Subsurface of coating (X). Magnified image (500X) of coating Subsurface
The Figure 5.11 (a) and (b) shows the morphology of the plasma sprayed Mo coating after laser remelting. The Figure 5.11(a) confirms that the undulations comprising unmelted, partially melted splats shown in Figure 5.10(a) were effectively remelted by laser. However, a large network of micro cracks are found on the laser remelted surface. The micro cracks are probably caused by shrinkage and thermal stresses arising during the rapid cooling after laser treatment. Figure 5.11 demonstrates a subsurface of the as sprayed Mo coating after laser remelting. The reduced number of micro pores and other structural defects can be observed. From the Figure 5.11(X) it is confirmed that lamellae of coating was remelted effectively by laser.

5.3.1.2 Effect of laser remelting on the porosity

The degree of porosity measured by the image analyser is greatly reduced after laser treatment, decreasing from 10.98% to 1.34%. The reduction in porosity is due to remelting of the molybdenum coating, which enhances the densification of the structure and allows a large quantity of pores in the as sprayed coating to coalesce and escape.
5.3.1.3 Effect of laser remelting on the microhardness

The Figure 5.12 shows the variation of microhardness of laser treated and plasma sprayed coatings vs. distance from the outer edge on the cross-section of samples. It is seen that the microhardness of the laser treated samples is higher than that of the as sprayed ones. After laser treatment, a graded distribution of hardness in the coating can be attributed to the formation of three regions: the remelted zone, the heat affected zone and the substrate (Fu et al., 1997). The melting layers become much denser, pores and other defects are substantially reduced or even eliminated after laser treatment. Thus the microhardness of the melting layers of the Mo coatings has been greatly enhanced and similar results were observed by Liang et al., (2000) and Yuanzheng et al., (2000).

The microhardness at the surface of the both the laser treated and untreated coating more. The microhardness of the subsurface towards the substrate material is decreases. This decrease may be due to change in lamella cooling rate. The thermal properties of the surface beneath the impinging particles change as the coating builds up and the lamella cooling rate is expected to vary accordingly. Due to variation in the
cooling rate, the properties of the subsurface of coating is different (Moreau and Lamontagne, 1992; Zimmer, 2010).

5.3.2 Evaluation of coating performance by sliding wear tests

5.3.2.1 Effect of load on dry sliding wear volume loss

![Figure 5.13 Variation of volume loss at different loads](image)

The wear data shows (Figure 5.13) that the volume loss increases with increasing load but the increased rate of volume loss of the plasma sprayed coatings with increasing normal load is much higher than that of the laser treated specimens. Under a load of 10 N, the volume loss of the plasma sprayed coating is about four times higher than that of the laser treated coatings and, with a load of 50 N, the volume loss of plasma sprayed coating is about 3 times as high as that of the laser treated coatings and similar kind of results were observed by Fu et al., (1997). The results from Figure 5.13 indicates that laser treatment can improve the wear resistance of the plasma prayed coating significantly. This is due to an improvement in bonding strength and the significant decrease in porosity after laser treatment. The small increase in microhardness and the improvement in the surface roughness of the laser treated coatings also contribute to the enhanced wear resistance.
**Figure 5.14** Worn surface of plasma sprayed Mo coating showing larger area of spallation.

**Figure 5.15** Detached wear particle on the worn surface of the plasma sprayed Mo coating.

**Figure 5.16** A crack passing around an unmelted particle on the worn surface of the plasma sprayed Mo coating.
The worn surface of a plasma sprayed Mo coating is presented in Figure 5.14 to Figure 5.17. From Figure 5.14 the spallation of the coating at its surface is very apparent. The spallation of the plasma sprayed Mo coating can be attributed to the combined effects of a large porosity, poor bonding strength and low ductility. During the wear process, cracks that are either present in the plasma sprayed coating or newly emerge in the coating during the wear process propagate rapidly and eventually interconnect leading to the removal of a large wear particle. Figure 5.15 shows a particle which has detached from the coating. Cracks are often found to pass through the unmelted particles in the coating; an example is shown in Figure 5.16. The Figure 5.17 illustrates delaminated particles and spalled coating fragments become wear particles which subsequently plough the coating. Therefore the dominant wear mechanism for plasma sprayed coating is spallation of the coating. The other mechanism is abrasive wear.

Figure 5.17 Ploughing and wear tracks on the worn surface of plasma sprayed Mo coating

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The wear behaviour of the laser treated coating is very different. Figure 5.18 shows that the worn surface of the laser treated coating is characterized by ploughing track and smooth areas with small wear particles which are about to detach. The severe plastic flow at the edge of the ploughing track is shown in Figure 5.18. It indicates the presence of a high temperature during wear, where Mo splat adjacent to the local contact area is softened and rendered plastic.

The Spallation of the coating can also be observed in laser treated coating as shown in Figure 5.19, but it is not extensive, even though there are many cracks in the coating. It can be concluded that the main wear mechanisms of laser treated specimens are ploughing and abrasive wear.
5.3.2.2 Effects of sliding distance on wear volume loss

It is observed from the Figure 5.20 that the volume loss of laser remelted plasma sprayed coating is increases with increase in sliding distance. Kato, (2000); Rao and Das, (2011) and Khedkar et al., (1997) also observed that material loss of the sprayed coating increases with increase in the sliding distance.

![Variation of volume loss at different sliding distances](image)

**Figure 5.20** Variation of volume loss at different sliding distances

The Figure 5.21 shows the worn surface of laser remelted Mo coating tested at different sliding distances. The micrograph illustrates a groove running parallel to the direction of sliding direction. These attributes are characteristic of adhesive wear. At lower sliding distance, the hard particles entrapped between the pin and disc, plough or cut the pin, causing wear by the elimination of the small fragments of a material as shown in Figure 5.21(a). These findings are agree with the previous studies (Usmani and Sampath, 1999; Fernhdez and Cuetos, 1996; Mateos et al., 2000). The worn surface shows (Figure.5.21 (a) and (b)) that the surfaces are covered by fine oxide layer. Frictional heating during sliding causes oxidation of the surface. Due to that the volume loss of coating is mild at lower sliding distance and the wear is oxidative wear (Ramachandran et al., 2012). As the sliding distance increases there is a gradual transition in the wear behaviour of the coating occurred from an oxidation wear to
delamination wear as shown in Figure 5.21 (b). The penetration of hard asperities of the counter surface to the softer pin surface increases. The deformation and fracture of asperities of the softer surface also increases.

Figure 5.21 Worn surface of laser remelted Mo coating at (a) lower sliding distance (b) higher distance
5.3.2.3 Effect of sliding speed on wear volume loss

The Figure 5.22 illustrates that the wear volume loss of laser remelted plasma sprayed Mo coating is very much lower than untreated plasma sprayed Mo coating. The defects connected with plasma spray coating could be eliminated or reduced by laser remelting. The laser remelting provides a dense and a pore free microstructure. The better tribological performance of laser remelted plasma spray coating was basically due to the presence of a metallurgical bond between the splats.

The Figure 5.22 also illustrates that the volume loss of laser remelted plasma spray coating increases as the sliding speed increases. The plasma sprayed coatings usually fail along the interface of the splats. Certainly, the temperature gradient built up between the substrate and the coating as the sliding speed increases and causes for stress development. The stress development in the coating weakened the interface bond between splats and leads to failure of coating.
Figure 5.23 Worn surface of laser remelted Mo coating at (a) lower sliding speed (1.17 m/s) (b) higher speed (5.89 m/s)

The Figure 5.23 illustrates worn surfaces of the laser remelted plasma sprayed Mo coating tested under different speeds. Figure 5.23(a) shows fractured splats, plough and the traces of tribofilm formation on the worn surfaces of laser remelted plasma sprayed Mo coatings.

As the sliding speed increases the temperature at the contact surface also increases and it leads for thermal softening. Because of this much more intense ploughing was observed (Figure 5.23 (b)) at higher speed. The sharp thermal stress develops in the surface layer of coating due to the high frictional heat. the thermal
stress that occurs in the surface layer of the coating leads to the formation of microcracks (Zhao and Ye, 2013). The microcracking intensifies with increasing sliding speed. The propagation of the microcracks is responsible for the delamination of the coating. The Figure 5.23(b) exhibits delamination and ploughing which is responsible for the severe wear.

The inherent defects associated with plasma sprayed coatings such as high surface roughness, porosity, poor bond strength could be rectified by laser remelting, which provided a dense and a pore free microstructure. The results from Figure.5.13, Figure 5.20 and Figure 5.22 demonstrated that the laser remelted Mo coating exhibits better tribological behaviour as compared to the sealed and untreated Mo coatings. The improved tribological performance of laser remelted coatings was essentially due to the presence of a metallurgical bond between the substrate as well as between splats and significant decrease in the porosity. The small increase in microhardness and the improvement in the surface roughness of the laser treated coatings also contribute to the enhanced wear resistance.