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Wear Behaviors of Plasma-Sprayed Coating Layers in Mo and Co-based Alloy

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몰리브덴늄 및 코발트 합금을 플라즈마 용사한 피막 층의 마모거동

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요 약

자동차엔진의 피스톤-링에 응용할 목적으로 플라즈마 용사 기술로 피막한 몰리부덴늄 및 코발트 합금 피막 층의 마모성질을 비교 조사하였다. Ball-on-disc 형태의 마모기를 사용하여 상온 및 대기 중에서의 마모 및 마찰 거동에 대하여 조사하였다. 용사 층의 미세경도 시험도 행하였으며, 용사층의 결정구조를 알기 위해 용사층을 x-선 회절 방법으로 분석하였다. 주사전자현미경을 사용하여 마모면의 표면 형상을 관찰하였다. 여러 용사조건으로 만든 용사층의 미세경도치와 마모거동과의 상관관계를 이해하려고 시도하였다. 주사전자현미경과 EDX를 사용하여 마모시 화학반응층과 마모기구를 규명하고자 하였다. 모리부덴늄 및 코발트 합금 분말을 각각 플라즈마 용사층의 단면을 관찰하여 마모기구을 비교하였다.

1. Introduction

Surface coatings are classified as PVD, CVD, electroplating, and plasma spray coating. The spray coating has more advantages among the above techniques. The cheap substrates can be used. The substrates can be utilized relatively at low temperature. The sizes and shapes of substrates are not limited. The coating thickness can be controlled easily. The coating formation speed is fast. The powders required for spray coating are metal, cermet, and ceramics.

The plasma spray coating technique has been applied to the prevention of corrosion, wear resistance, and heat resistance. Currently the components in the electronic industry (such as VTR head), in the automobile industry, and in the heavy industry or power plants are the major utilization. The components of automotive engine (for examples ; cylinder, cylinder liner, piston ring, valve, crank-shaft, and tappet) has been coated with the plasma spray technique, which raises the fuel efficiency and improves the life time. Also rollers used in the textile industry were coated with this technique in order to improve the wear resistance.

Piston ring coatings consisting of molybdenum and chromium carbide mixtures had been used to extend the life of internal combustion engines. Houck and Whisenant[1] had studied several molybdenum-based alloy coatings that showed superior wear properties in comparison to conventional materials. Wayne and Sampath[2] described that for automotive applications, flame-sprayed molybdenum wire coatings were widely used in the production of piston rings for internal combustion engines due to their excellent scuff resistance. These coatings possess high hardness, attributed to the formation of MoO_2.

Investigation into the wear properties and frictional behavior of Mo coatings and Co-based coatings have been made primarily for tests. The results of this investigation can give the optimal coating conditions for recommending in a wide range of applications. A number of wear tests were evaluated by using the reciprocal tribometer.

Wear characterization was examined to get the correlation with the mechanical properties of the coating layers depending on the spraying conditions. Therefore, the hardness tests were carried out to analyze mechanical properties, and microscopy was utilized to evaluate the coating structure. All coating layers were ground down with using a 1000 mesh emery paper prior to the hardness testings. SEM and metallographic evaluation of the coating layers were also performed in order to determine the level of microsturctural interactions in the wear results.

2. Experimental procedures

In this study, wear resistance of the sprayed coating layers was evaulated at room temperature for the application into the piston ring coating in automotives. A holder of specimen was prepared to get the uniform layer even under high gas pressure of gun in the process of the plasma spray coating.

The powders used for the plasma spray coating were M64 and M66. The physical properties of the powders were shown in Table 1. M64 powder is pure molybdenum particle. M66 powder consists of 62% cobalt and 28% molybdenum. These powders were manufactured by the American METCO company. The purchased powders were analyzed with laser diffraction method to find out the size, shapes, and density of particles. The average sizes of M64 and M66 are 58.4㎛ and 40㎛, respectively. The densities are 1.62g/cc and 3.41g/cc, respectively.

A plasma spray gun used in this study was the METCO MBN gun with the maximum capacity of 40kW. The operating gas were Ar and H_2. The operation parameters were varied to determine the optimal coating condition ; the amount of gas, the current density of gun, and the spraying distance from the gun to the specimen. The plasma-spray gun was moved in the bi-axial mode of X-Y axis. The thickness of the sprayed coating was tried to be approximatively 300㎛ in average. The coating condition

Table 1. Characteristics of the initial powders for plasma spray coatings.

POWDERS	COMPOSITION	SIZE DIST.	M.P (℃)	PROP. OF COATING LAYER		
				DPH_{300}	POROSITY	BONDING STRENGTH
M66	Co:62% Mo:28% Cr: 8% Si: 2%	~45㎛ +15㎛	1230℃~ 1600℃	450±50 (DPH_{300})	< 5%	7,000psi
M64	Mo	~90㎛ +44㎛	2610℃	460±70 (DPH_{300})	< 2%	3,500psi

Table 2. Plasma spray coating conditions.

Specimen Number	Powder	Spray Distance(㎜)	Gun Current(Ampere)	Gas flow(ℓ /min)
M 64-1	Metco 64	100	400	80
M 64-2	Metco 64	75	400	80
M 64-3	Metco 64	150	400	80
M 64-4	Metco 64	100	300	100
M 64-5	Metco 64	100	400	100
M 64-6	Metco 64	100	500	100
M 66-1	Metco 66F-NS	100	500	150
M 66-2	Metco 66F-NS	75	500	150
M 66-3	Metco 66F-NS	150	500	150
M 66-4	Metco 66F-NS	100	500	100
M 66-5	Metco 66F-NS	100	400	175
M 66-6	Metco 66F-NS	100	500	175

was illustrated in Table 2.

Wear tests were conducted using a ball-on-flat wear test apparatus. The tribometer is Cameron Plint TE77. DC motor controlled the sliding speed. The sliding speed was 0.036 m/s. The sliding time was one hour. The steel balls of 5mm in diameter were used. The applied load was 20N. The frictional forces were measured with an attached torque transducer. The wear volume was calculated by measuring the differences between the weight of the unworn specimen and that of the worn specimen. The indentation time was 10 second. The hardness value was averaged with ten indentations.

3. Results and discussion

The XRD analysis was performed to investigate the crystalline structure of coating layers. Fig. 1 shows mainly peaks of Mo phase, and a

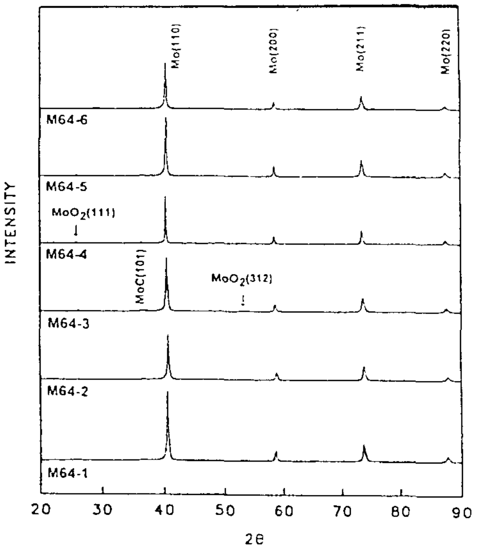

Fig. 1 XRD patterns of M64 coating layers.

small amount of MoC and MoO$_2$ pesks from the M64 powders. Fig. 2 shows the compound phases of Mo and Co mixtures from the the M66 powder. M66 coating layers illustrate amorphous phases, which appear to be independent on the coating parameters used in this study. Nertz and his coworkers3) indicated similarly that the cobalt is in an amorphous state or is characteristics of micro-crystalline materials. The amorphous phase would be recrystallized into various cobalt containing phases if heated to a sufficient temperature. The exothermic reaction is inherent to the coating, giving strong evidence that the reaction was the recapitalization of the amorphous materials formed during spraying.

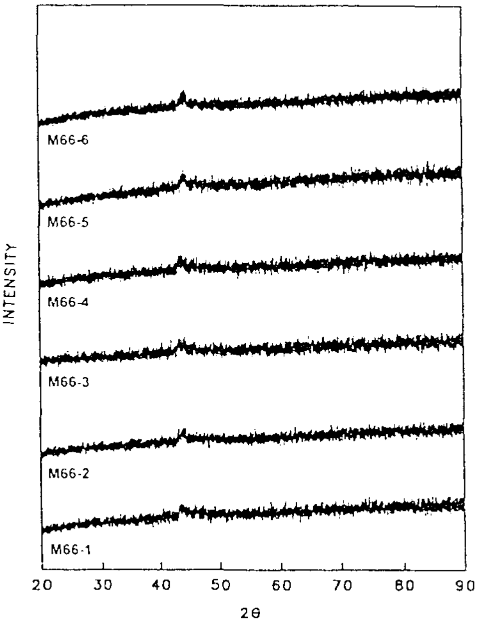

Fig. 2 XRD patterns of M66 coating layers.

Fig. 3 shows the SEM micrographs of M64 coating layers. Fig. 4 shows the SEM micrographs of M66 coating layers. M64 coating layers show that the spherical particles were agglomerated each other. M64 shows more porous structure compared to M66. There are several cracks and pores on the M64 coating layers. Most layers of M66 expect M66−1 do not show the presences of cracks and pores.

Fig. 5 shows the variation of hardness values with the various operating conditions. M66−2 shows about 580kg/mm^2. M66−1 shows about 540kg/mm^2. The others show the similar values except M64−4. M64 samples can not be measured because of extremely porous surface. The end of indentation tips on the coating layer could not be found. SEM micrographs as shown in Fig. 2 and 3 can indicate the good agreements of the wear testing results with the microhardness values.

Initially, wear resistant coatings are identified by employing bench test techniques which simulates reciprocating motion of a piston ring. Fig. 6 shows the variation of wear volume with the various coating conditions. M64−4 shows relatively the highest wear volume of 0.195mm^3.

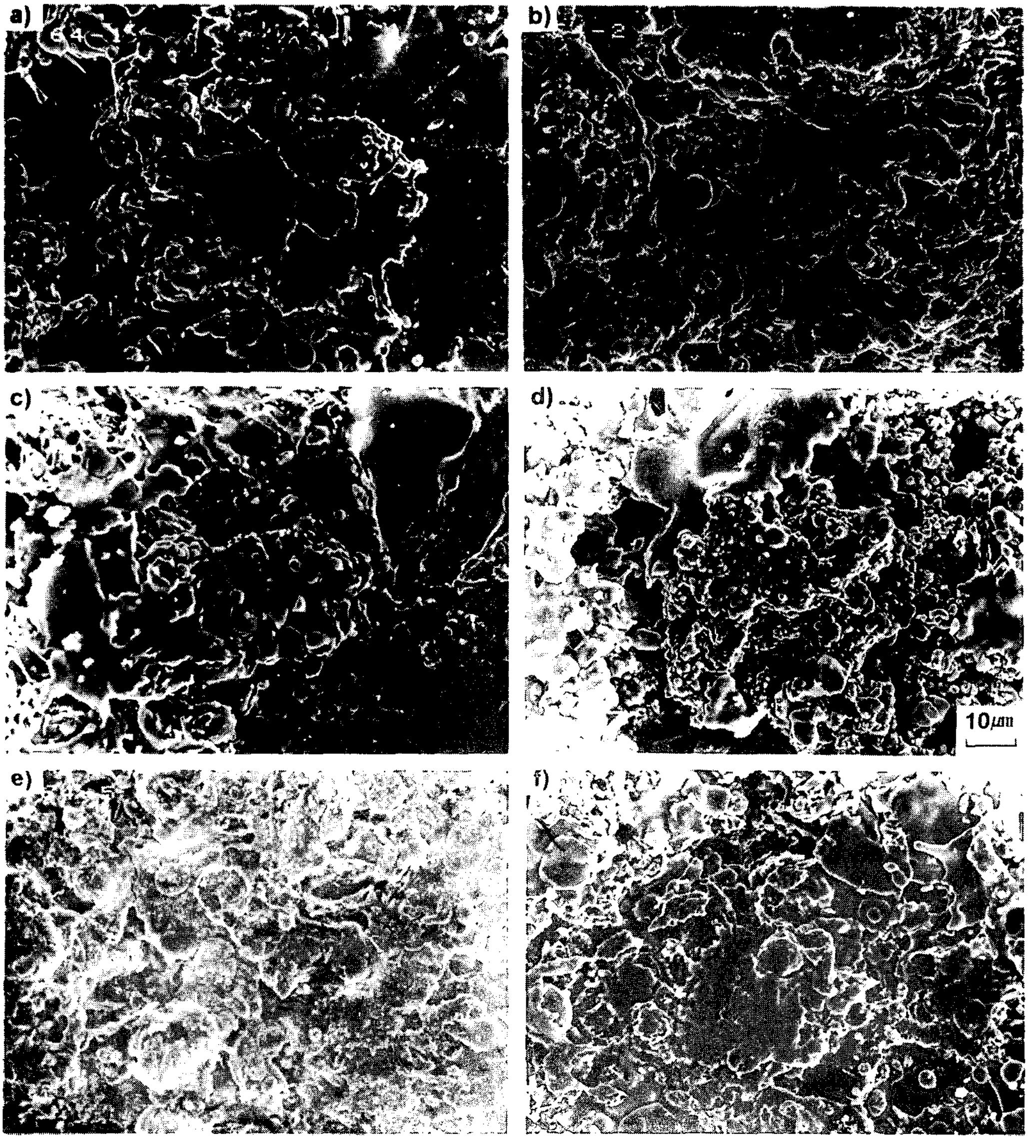

Fig. 3 SEM micrographs of M64 coating layers:
(a) M64-1, (b) M64-2, (c) M643, (d) M64-4, (e) M64-5, (f) M64-6.

M66-1 shows the lowest wear volume of 0.05mm^3. Wear volume of M66-5 is close to that of M66-1. Typically M64-4 shows the lowest wear resistance. The M66 series shows relatively better wear resistance compared to the M64 series. The sliding load was 20N. The sliding time was 1 hour. The sliding speed was 0.036m/s. The wear testing temperature was room temperature. Fig. 7 shows the friction behaviors of M64 series. Fig. 8 shows that of M66. The coefficients of friction in the steady state stage are ranged from 0.6 to 0.8. In the initial stage the coefficients of friction are differently illustrated. The frictional trends were not well matched

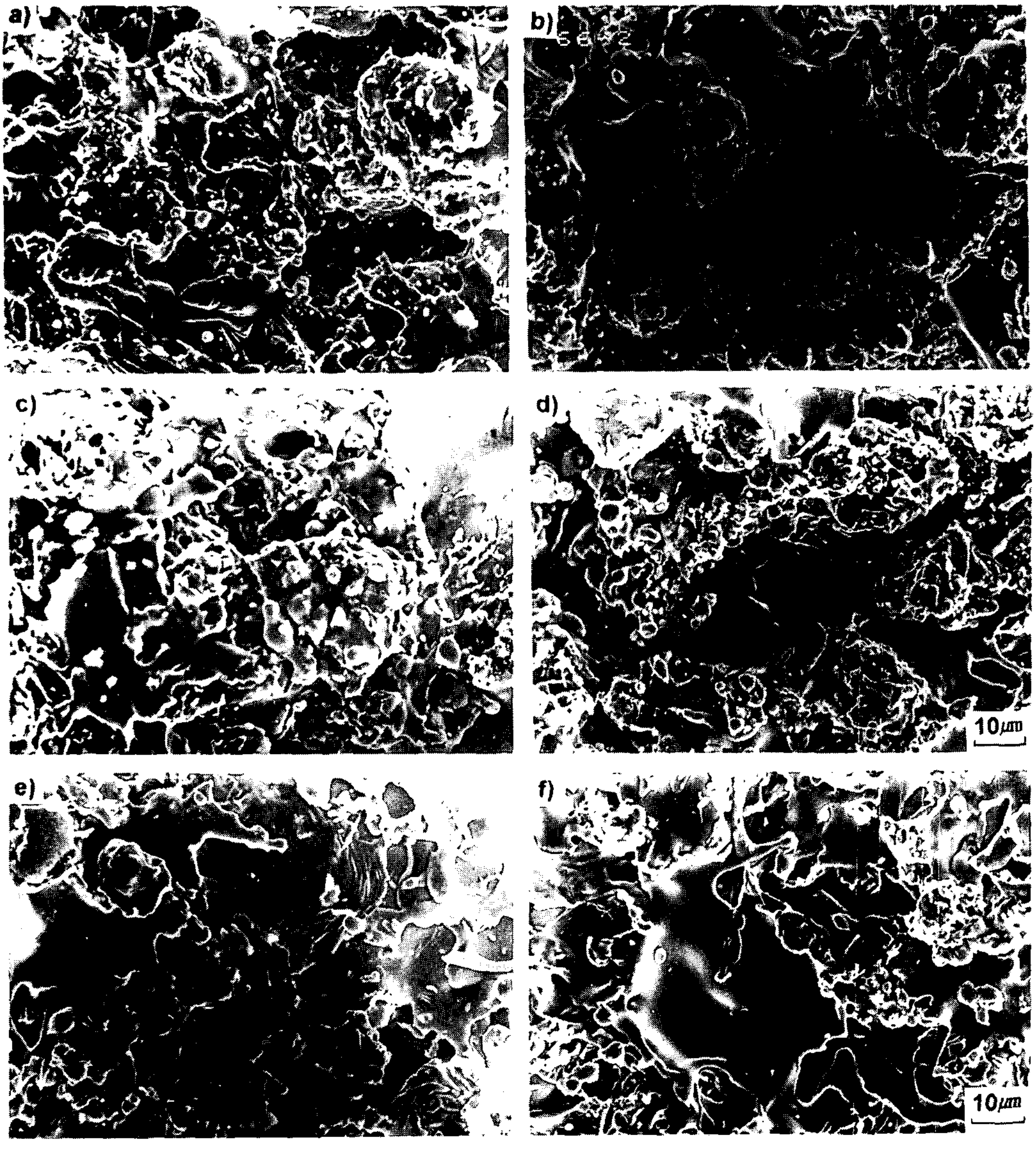

Fig. 4 SEM micrographs of M66 coating layers:
(a) M66-1, (b) M66-2, (c) M66-3, (d) M66-4, (e) M66-5, (f) M66-6.

with the wear trends. Smith and his coworkers4) reported TiC reinforced NiCr matrix coatings may reduce the adhesive failure, thereby, preventing "micro-welding" of surface asperities, but may contribute to the couple's abrasive wear as the oxide films rupture and enter the wear track. Thus oxide inclusions in the plasma-sprayed coating layers may act to initially provide the lower coefficient of friction, however, on later these oxides may increase the abrasive wear as the oxides fracture under the load of the wear element.

Fig. 9 shows the SEM micrographs of the worn track area. The wear mechanism seems to

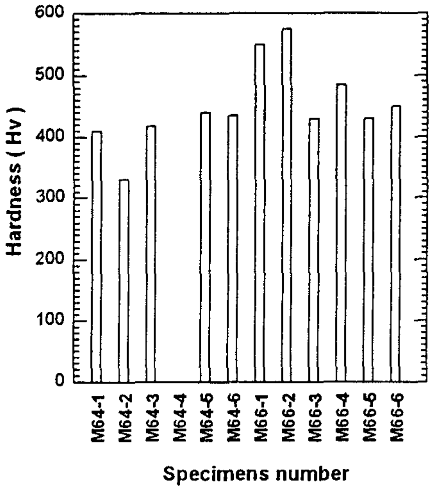

Fig. 5 Hardness of M64 and M66 coating layers.

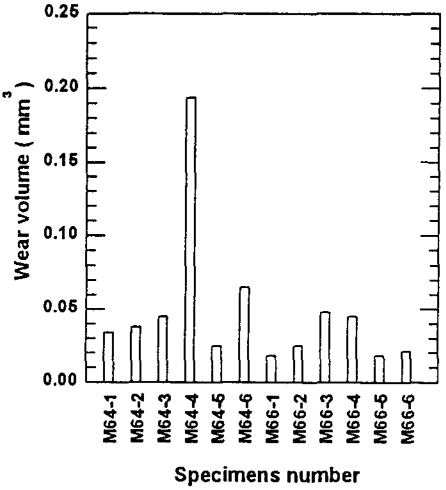

Fig. 6 Wear volume of M64 and M66 coating layers.

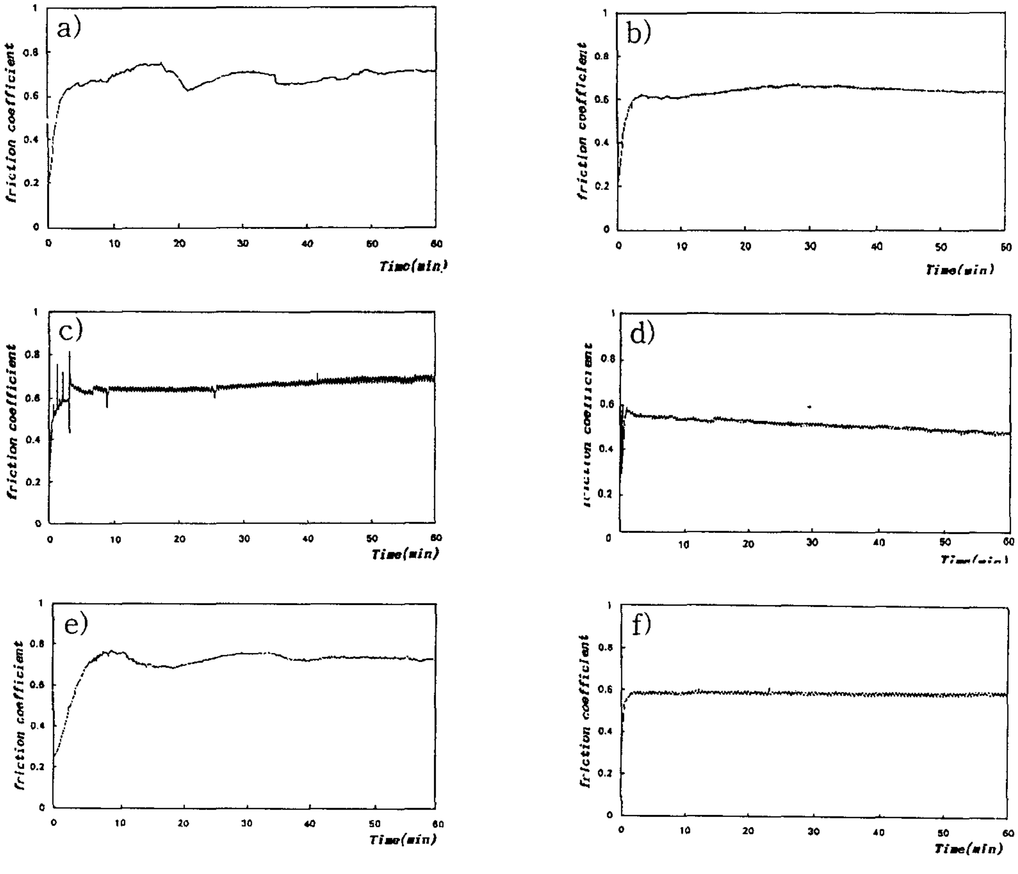

Fig. 7 Friction coefficient of M64 coating layers:
(a) M64-1, (b) M64-2, (c) M64-3, (d) M64-4, (e) M64-5, (f) M64-6.

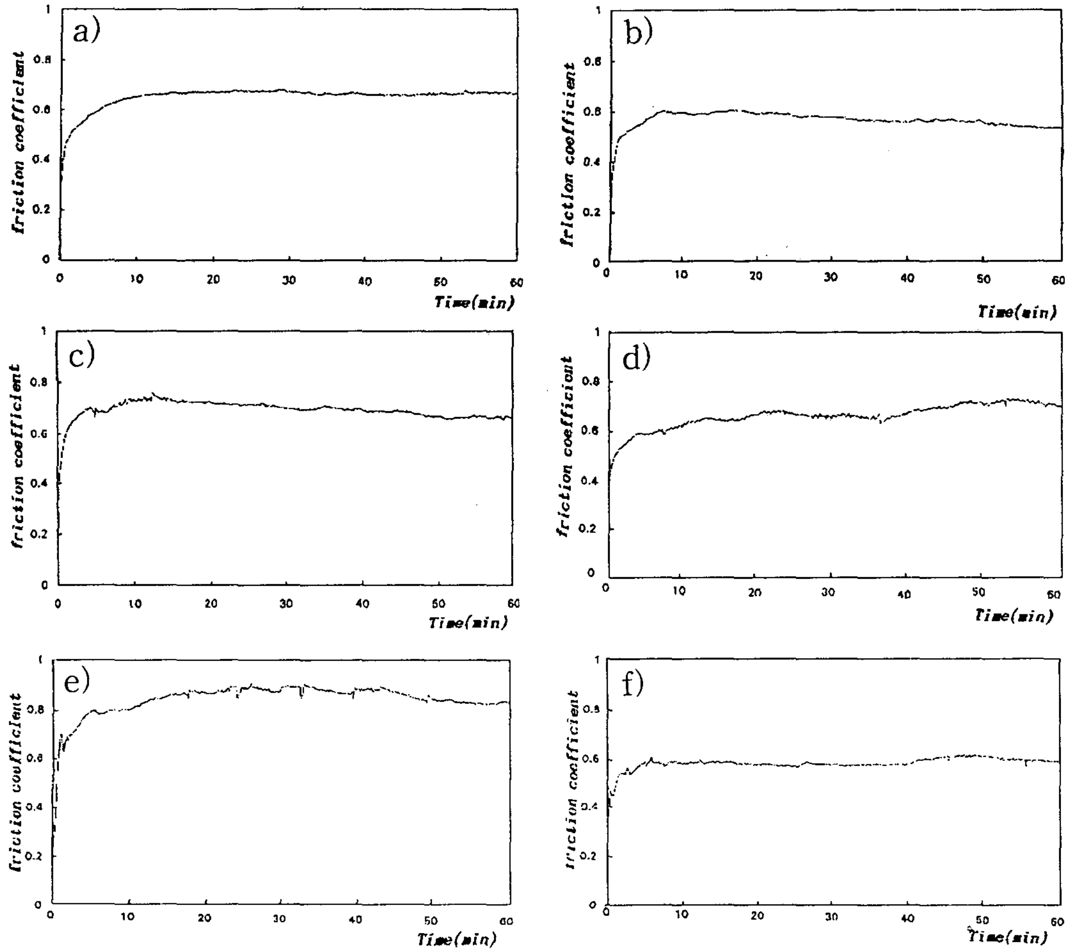

Fig. 8 Friction coefficient of M66 coating layers:
(a) M66-1, (b) M66-2, (c) M66-3, (d) M66-4, (e) M66-5, (f) M66-6.

be abrasive mode even with the different coating layers and the different plasma-sprayed coating parameters. M66, which consists of and Co, high Mo, alloy, had excellent tribological properties. Generally there are two important factors which influence tribological properties of the wear resistant coatings, i.e., interlamellar bond strength and mechanical properties of the individual lamellas, which are both influenced by powder characteristics and deposition process. Wayne and Sampath[2] reported that plasma sprayed unalloyed-Mo is relatively soft and prone to fracture and delamination during sliding contact. That was evidenced by the response of plasma-sprayed Mo to the single-point scratch test and pin-on disk sliding conditions. In both tests, fracture and delamination of Mo lamellar occurred. Fig. 10 shows the EDX analysis of the wear debris and wear tracks, which illustrates the peak of Fe. This peak represents the abraded particles come from steel ball as the counterpart. Peaks of Mo or Co, and Cr de

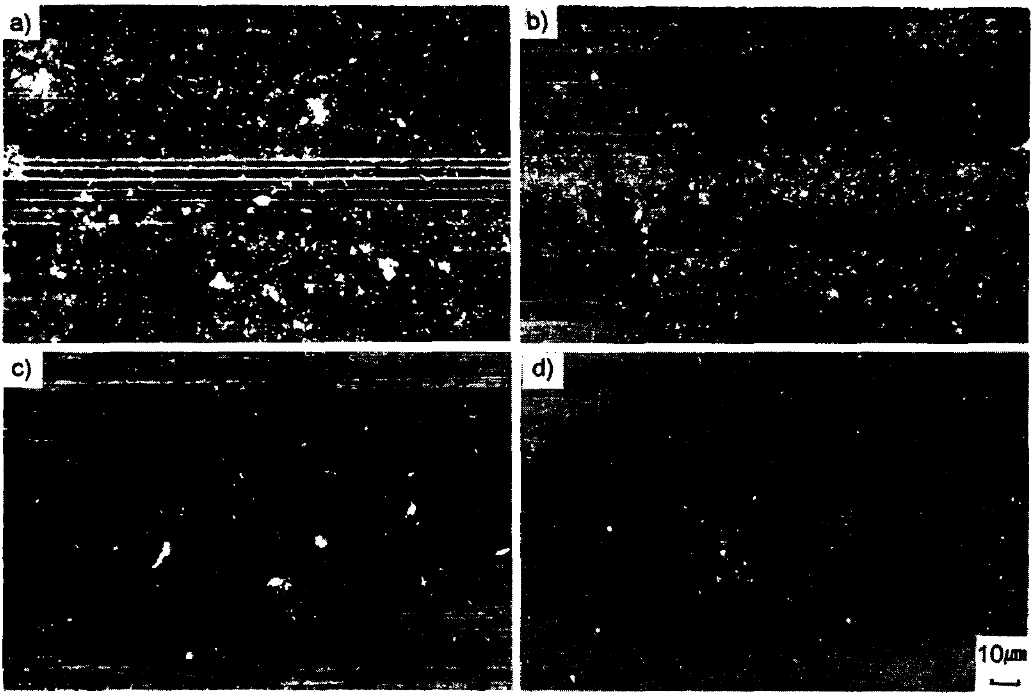

Fig. 9 SEM micrographs of wear tracks of M64 and M66 coating layers.
(a) M64-1, (b) M64-4, (c) M66-1, (d) M66-4.

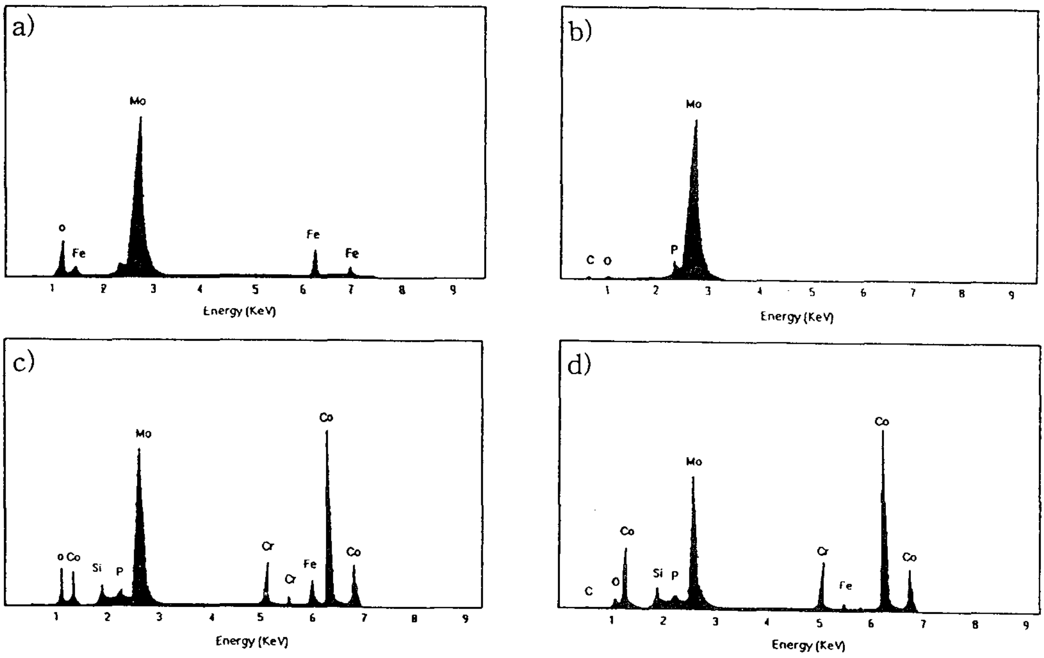

Fig.10 EDX analysis of worn surfaces of M64 and M66 coating layers:
(a) M64-1, (b) M64-4, (c) M66-1, (d) M66-4.

rived from the substrates. Because the wear debris of disc specimen is so small in the ranges of $0.1 \sim 0.5\mu m$, the wear particles can not be detected precisely. This EDX analysis means that there were no materials transfers each other. Bell and Delargy[5] described the influence of lubrication on the wear of piston-ring ceramic coatings. The possible influence of tribochemical film formed on the surface reacted by the lubricant gave lower wear than the unlubricated contact. The effectiveness of lubricant surface film is a factor that must clearly be taken with account when assessing the relative performance of wear resistance coatings. The incorporation of transfer of transition metals to promote surface film formation or by modifying the surface morphology, which is strongly affected by the microstructure, to encourage a more uniform distribution of such films over surface. Fig. 11 shows the comparison of the optical micrographs of the cross section of worn area for Mo and Co-alloy coating layers with different spray conditions. From these micrographs, it appears that the coating layers are removed by collapse around pores and also intersplats are broken. Fig. 5 indicated that hardness of M64-4 is very low and indentation diagonals were not measured by binocular. Hardness of M66-1 is relatively high. Therefore, the wear volume is low. Wear mechanism of these layers is abrasive mode as shown in Fig. 10. Hardness is dominant factors on wear mode of plasma coat-

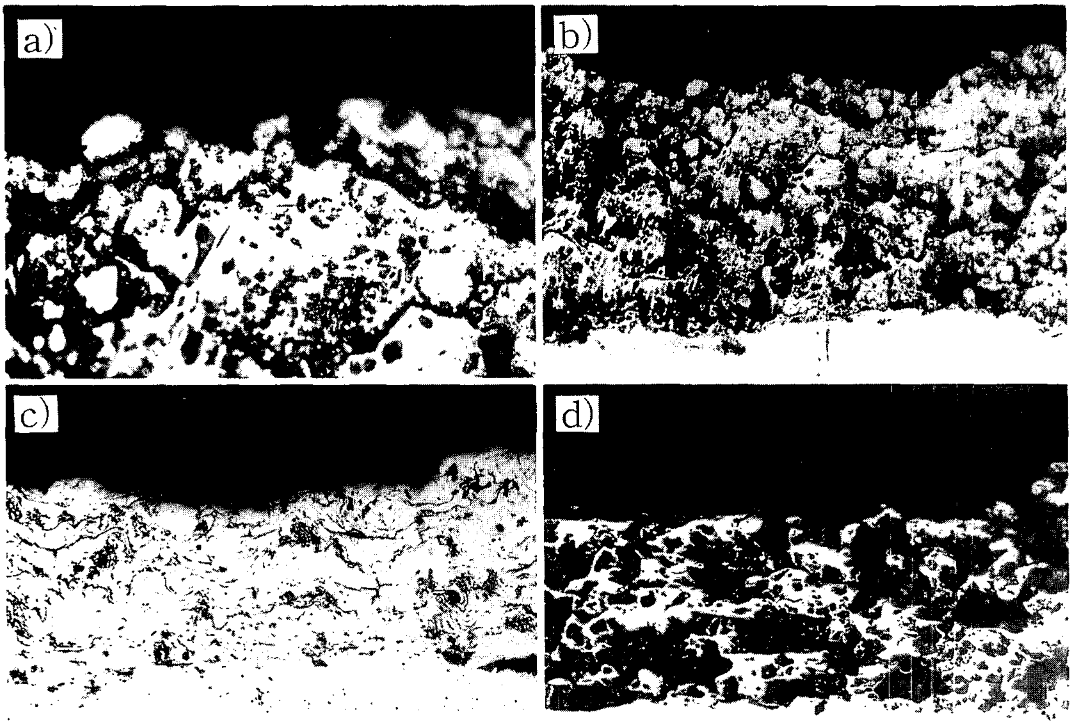

Fig.11 Optical micrographs of the cross section of the wear tracks: (a) M64-1, (b) M64-4, (c) M66-1, (d) M66-4.

ing layers of Mo and Co- alloy. The experimental results are matched partially as Hartfiel[6] suggested among four different wear mechanisms for the plasma sprayed coating materials. It is mainly due to effect of porosity and the bonding strength of the intersplats. In such case the porosity enhances the coating materials removal.

4. Conclusions

The plasma spray coating technique offers a great potential to precision tailor desirable morphological and tribological properties for wear resistant coatings. The basic processes and unique characterization of the plasma spray coating can be understood in order to explore their capabilities to perform the excellent wear resistance. The optimal processing parameters have yet to be established.

Plasma sprayed coatings are strongly dependent on their intrinsic materials such as hardness and microstructures. Processing condition of both the starting powder and the plasma spray method has been shown to change the important deposit characteristics. These coatings characteristics are directly interrelated with wear, friction behavior, and hardness.

Microstructures significantly changes with respect to porosity, size and shape of deposited powders and have been found to modify coating wear properties on the plasma sprayed coating layers. Material transfer from the steel ball sided little information of the coating performance with the presence of iron particles onto the coating layers.

Experimental results have indicated that the Co-based coating layer had better wear resistance compared to the Mo-based coating layer. This might be attributed to the different crystalline phases. Microstructure of the plasma sprayed coating layers controls the abrasive wear. Specifically the porosity enhances materials removal. The bonding strength of intersplats is very affective factor, which depends on phases among the intersplats such as oxides. Further analyses on the wear tracks such as TEM work allow a clue of wear mechanism in detail to determine phases among the intersplats.

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