

Formation of Molybdenum Boride Cermet Coating by the Detonation Spray Process

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The effects of the powder particle size and the acetylene/oxygen gas flow ratio during the detonation spray process on the amount of molybdenum phase, porosity, and hardness of the coatings using MoB powder were investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM), etc. The results show that the presence of metallic molybdenum in the coating results from decomposition of MoB powder during thermal spray. The compositions of the coatings are metallic Mo, MoB, and Mo₂B, which are different from the phases of the original powder. The amount of molybdenum phase increases monotonously with the oxygen/acetylene ratio, but the increasing rate for the fine powder is faster than that for the coarse powder. The porosity and hardness of the coating are related to the amount of molybdenum phase. The phase constitution of the coating is discussed.

Keywords acetylene, coating, detonation spray, molybdenum, molybdenum boride

1. Introduction

Molybdenum carbide and boride coatings have been extensively used for a variety of engineering applications,^[1] and they exhibit high hardness, good wear, and scuffing resistance. The phase constitution of the coatings is extremely important for the different applications. Molybdenum carbide and boride, such as MoC and MoB, have high melting points (MoC: 2650 °C, and MoB: 2600 °C), which make it difficult for them to form coatings by the high-velocity oxy-fuel (HVOF) thermal spray method and easy for them to decarburize^[2] during the spray process by plasma or HVOF spray. Regulating the detonation gas compositions could control the deoxidizing atmosphere in detonation thermal spray, which is propitious to forming a good coating of molybdenum carbide and boride during the spray process. Plasma spray coatings of molybdenum carbide and its wear resistance have been reported already,^[2] but the formation of molybdenum boride coatings, in particular directly from MoB powder, has not been reported. In the present study, two powders, fine and coarse of primary phase MoB with other phases such as MoB₂ and Mo₂B₅, were used in the detonation spray process. The effect of the gas flow conditions during detonation thermal spraying on the microstructure, porosity, and phase constitution of coatings was investigated.

2. Experimental Methods

2.1 Powders for Spray

Figure 1 shows the scanning electron micrographs of the powders, where it can be seen that the particle sizes are about 5

to 10 μm and 10 to 30 μm. X-ray diffraction (XRD) was performed under the conditions of Cu K_α radiation, 50 kV voltage, and 40 mA current. Figure 2 shows the XRD patterns of the powders and indicates that the main phases are α-MoB, β-MoB, and some MoB₂, for the fine powder, and metastable β-MoB and MoB₂ phases for the coarse powder. Other phases corresponding to the peaks of 2θ = 32.5 and 38.4° shown in the XRD pattern cannot be identified from the JCPDS cards. Neither powder contains molybdenum metal or low boron phase Mo₂B.

2.2 Coating

The powders were sprayed onto a low-carbon steel substrate of 10 × 10 mm area, degreased, and grit blasted with coarse alumina just prior to the detonation spray process. A Ukraine detonation gun spray (DGS) was used, and the process parameters are given in Table 1.

The temperature of the detonation process depends on the composition of the combustible gases. This is important for the properties of the coatings formed from these powders, because the phase constitution of the coatings strongly depends on thermal spray conditions. An advantage of the detonation spray method is that its temperature and combusted gases can be controlled over a larger range and the deoxidization atmosphere can be maintained through controlling the flow ratio of oxygen/acetylene and nitrogen dilution. An oxygen/acetylene ratio from 1.1 to 1.4 and nitrogen dilution of 10 to 25% were supplied in this experiment.

Phase constitution on the coating surface was examined by XRD, and the quantity of molybdenum in the coatings was calculated from the intensity ratio of the XRD peaks. The microstructure on cross sections of the coatings was observed by optical microscopy and scanning electron microscopy (SEM). The porosity of the coatings was determined from sectioned specimens by image analysis and statistical averaging techniques. The hardness of the coatings was measured by a diamond pyramid hardness tester model of HV-6 (Heng-yi, made in Shanghai, China) at a load of 300 gf.

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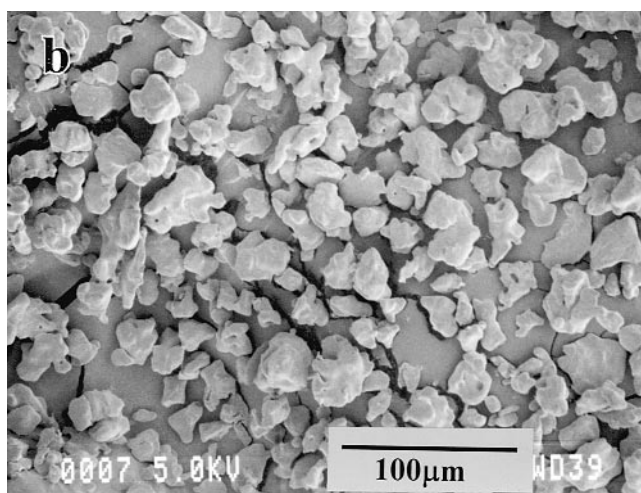
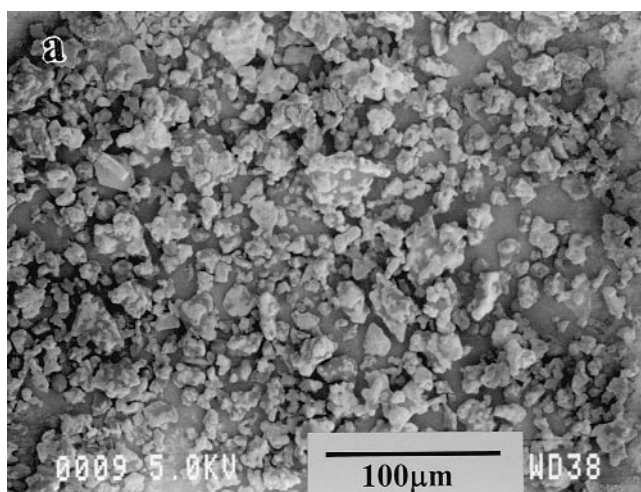


Fig. 1 SEM morphology of the fine and coarse powders used for detonation spray coating: (a) fine powder and (b) coarse powder

Table 1 The process parameters for molybdenum boron coating

Powder feed rate	80 g/min
Supplied gases	Acetylene, oxygen, and nitrogen
Nitrogen dilution	15, 20, and 25%
Oxygen-acetylene ratio	1.1–1.35

3. Results and Discussions

3.1 Phases of the Coatings

X-ray diffraction patterns of the sprayed coating are shown in Fig. 3, in which the numbers represent the oxygen/acetylene ratio during spraying. The main phases on the coatings are MoB, Mo₂B, and metallic Mo, which are different from the phases of powders whose primary phase is MoB. It is reasonable that the formation of Mo and Mo₂B phases in the coatings by the deto-

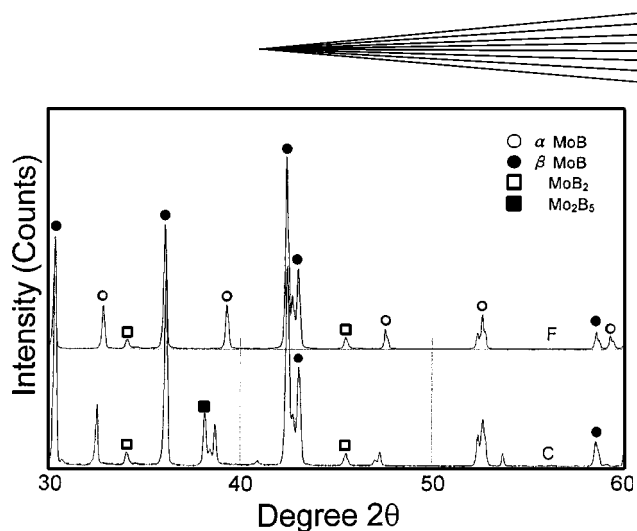


Fig. 2 XRD patterns of the phase constitution for the fine and coarse powders

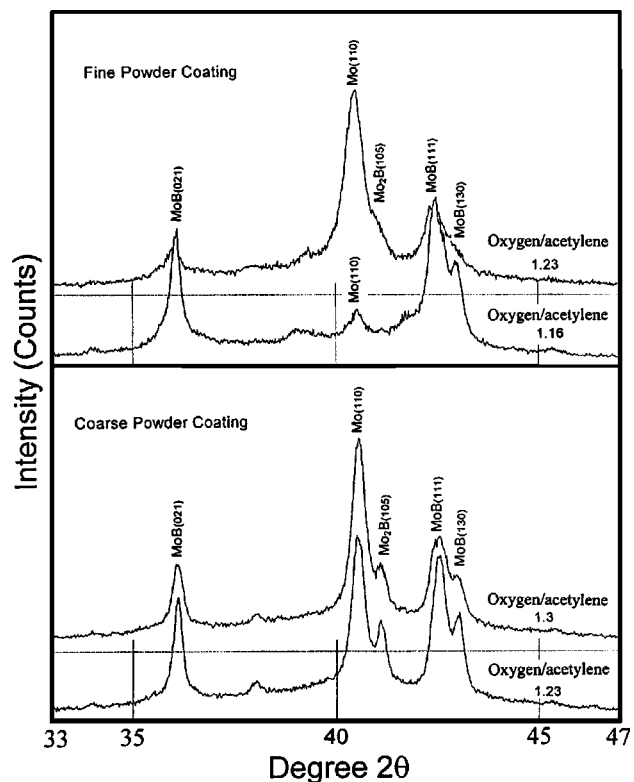


Fig. 3 XRD patterns of the sprayed coating with different powders at different oxygen/acetylene ratios

nation process results from the deboronization reaction between the detonation gases and the powder MoB.

Although the formation of the MoB phase in the coating was considered possible according to the heat of formation and the phase diagram, precise XRD studies on the coating suggest the following process. If there is a low partial oxygen pressure in the detonation gas, boron on the surface of the MoB particles is most often oxidized to B₂O₃, which would be vaporized before impacting on the substrate. This results in the loss of boron from

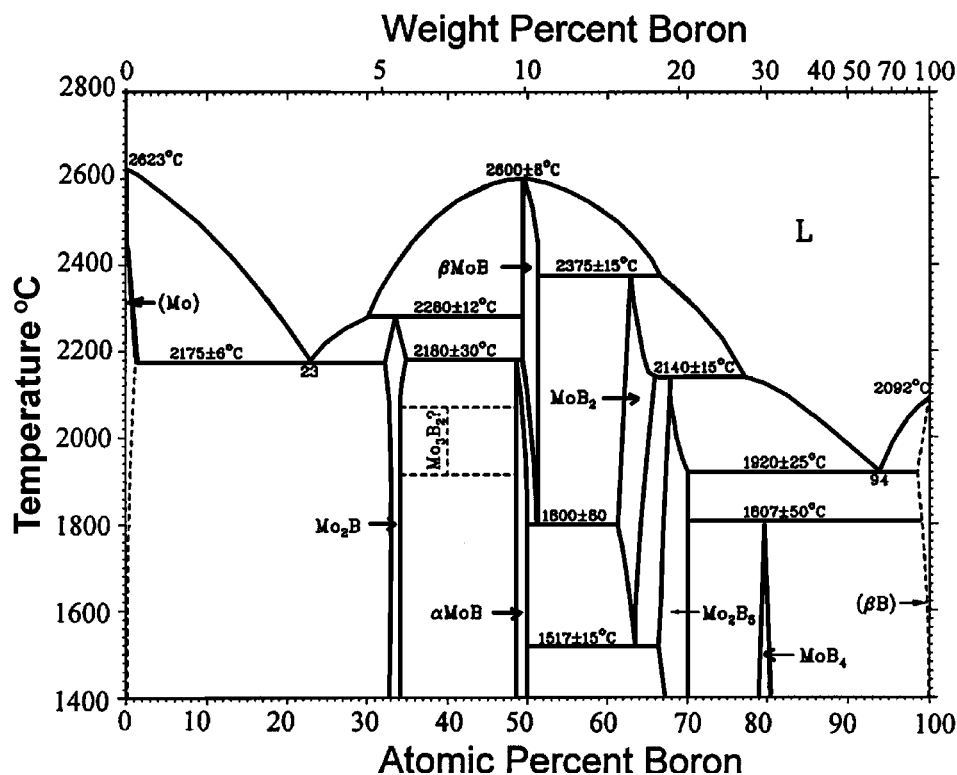


Fig. 4 Mo-B binary phase diagram^[3]

the surface of the MoB particles, which would cause the melting temperature to decrease and form particles of Mo₂B, Mo, or Mo₂B-Mo eutectic alloys, as expected with the Mo-B binary system^[3] in Fig. 4. These factors enable the detonation process of MoB with a gas mixture of a relatively low temperature, although MoB has a high melting point of 2600 °C. The relative amounts of molybdenum phase in the coatings are calculated by using the direct comparison method^[4,5] of integrated intensities of MoB (021), MoB (111), and Mo (110) peaks in XRD patterns as follows:

$$\text{Mo}\% = \frac{I(110)_{\text{Mo}}}{I(021)_{\text{MoB}} + I(110)_{\text{Mo}} + I(111)_{\text{MoB}}} \quad (\text{Eq 1})$$

Figure 5 shows the relationship between the oxygen/acetylene gas ratio and the amount of molybdenum phase in the coatings at a nitrogen dilution gas of 20%. The presence of metallic molybdenum in the coating results from decomposition of MoB powder during thermal spraying, and the amount of the molybdenum phase in the coatings increases monotonically as the oxygen/acetylene gas ratio increases. The increasing proportion of molybdenum phase coatings sprayed with the fine powder is greater than that with coarse powder under the same spraying conditions. It is impossible to form a coating using coarse powder at oxygen/acetylene ratios lower than 1.1, since both temperature and partial oxygen pressure are not sufficiently high. If a coarse powder with an oxygen/acetylene ratio more than 1.35 were used, the powder would be deposited on the liner of the gun. A gas condition map for the successful molybdenum boron coating is shown in Fig. 6.

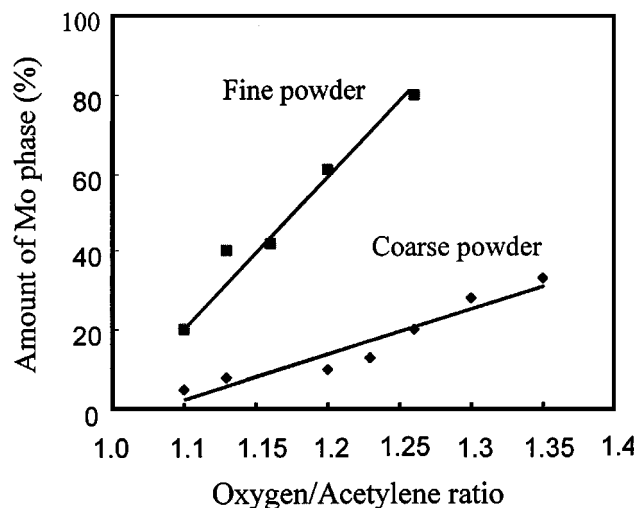


Fig. 5 Relationship between the oxygen/acetylene ratio and the amount of the molybdenum phase on the coatings

3.2 Porosity and Hardness

Figure 7 shows the relationship between the porosity measured on the cross section of the coatings and the amount of the molybdenum phase. The porosity decreases from 1 to 0.4% when the amount of the molybdenum phase is increased from 20 to 42%. The porosity increases rapidly from 0.5 to 4% when the amount of the molybdenum phase is over 50% for the fine pow-

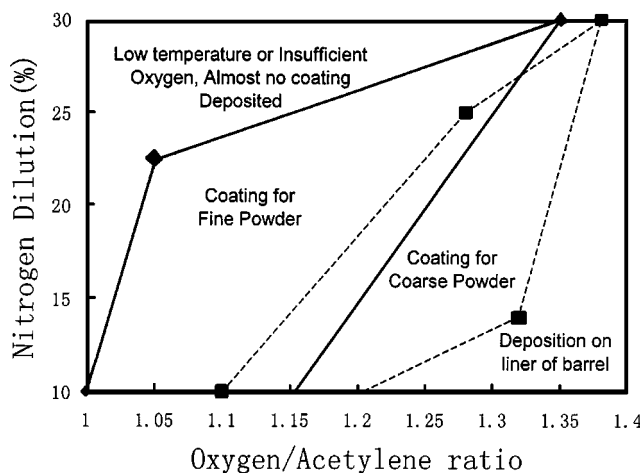


Fig. 6 Gas condition map for successful Mo-B coating

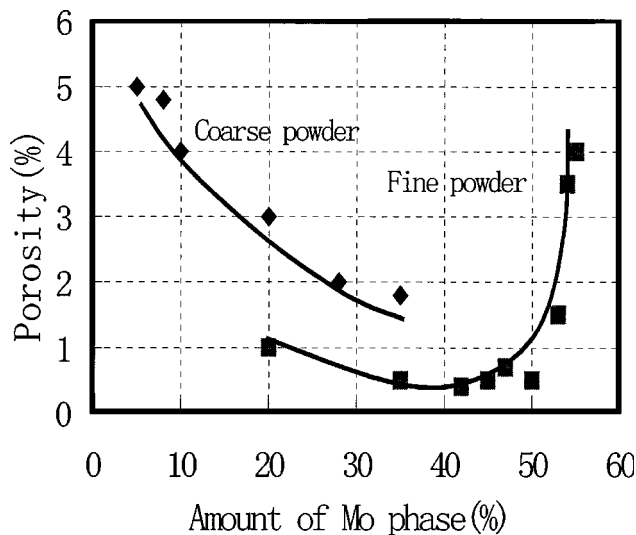


Fig. 7 Relationship between the amount of the molybdenum phase and the porosity measured on the cross section of the coating

der coatings. The porosity decreases from 5 to 1.8% when the amount of the molybdenum phase for the coarse powder coatings is increased. Consequently, when the amount of the molybdenum phase in the coating is small, most of the porosity in the coatings appears in MoB particles that melted insufficiently. The porosity increases rapidly when the amount of the molybdenum phase is beyond 50%. The higher spray temperature results in a few larger holes in the coatings for the fine powder, which suggested that the small MoB particles overmelt at the condition of the high oxygen/acetylene ratio. Compared with the fine powder, significant porosity was distributed between the MoB particles for the coating formed from the coarse powder.

Coating hardness also depends on the amount of the molybdenum phase (Fig. 8). When the amount of the molybdenum phase is less than 8%, the MoB particles do not melt sufficiently and the contact between MoB particles is poor and directly results in low coating hardness. On the other hand, when the

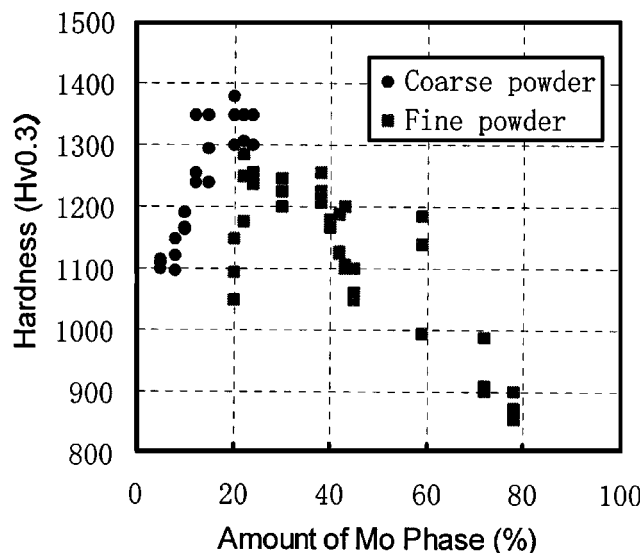


Fig. 8 Relationship between the hardness and the amount of the molybdenum phase on the coatings

amount of the molybdenum phase is larger than 20%, since the hardness of metallic molybdenum is much lower than that of MoB, the increase of the amount of the molybdenum phase in the coating also results in a hardness decrease.

3.3 Microstructure

Figure 9 shows the SEM microstructure with different amounts of the molybdenum phase in the coatings formed from the coarse powder. The black regions are mostly composed of porosity, while the dark and bright areas, respectively, consist of MoB or Mo₂B and metallic molybdenum.

Different phases can form in the coatings by controlling the oxygen/acetylene gas ratio and using molybdenum boron powders in the detonation spray process. In this study, the oxygen/acetylene gas flow ratio is 1.0 to 1.4. Such an atmosphere is excess in acetylene gas, since the oxygen/acetylene ratio necessary for complete reaction is 2.5, which can be calculated from the reaction equation



The process conditions of detonation spraying for lower porosity and the best optical microstructure (Fig. 10) are listed in Table 2.

Conclusions

- Coatings composed of Mo, MoB, and Mo₂B are formed by the detonation spray process. The Mo phase present in coatings results from deboronization. The phase constitution of the coatings can be controlled by the flow rate of the gases.
- The amount of the molybdenum phase increases monotonically with the oxygen/acetylene ratio. However, the Mo phase increase is greater for the fine powder.

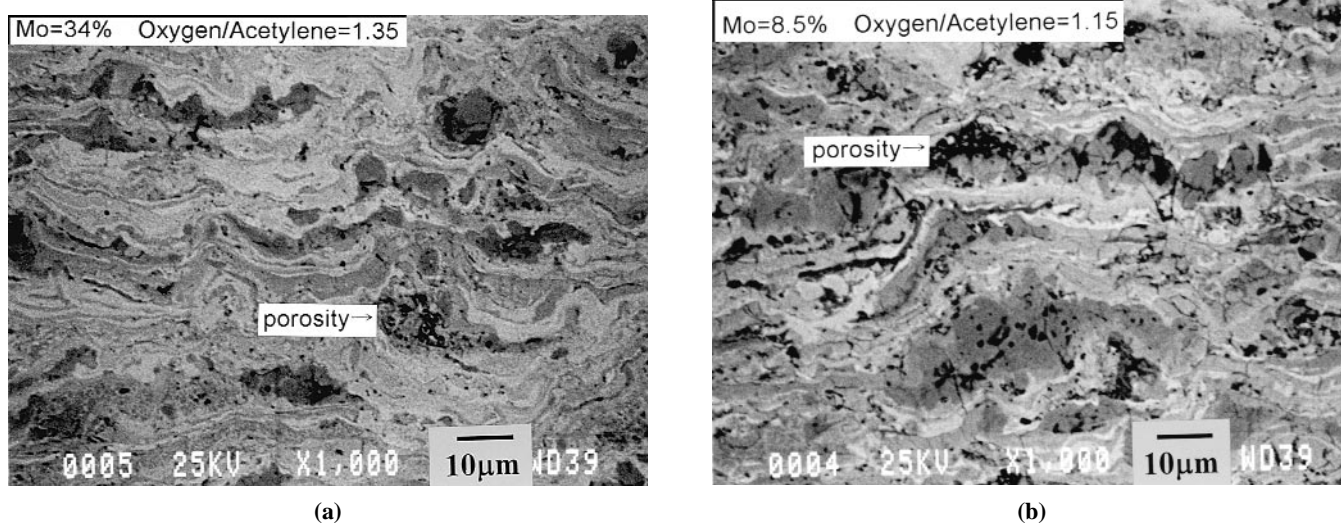


Fig. 9 SEM microstructure of the coatings with different amounts of the molybdenum phase for coarse powder

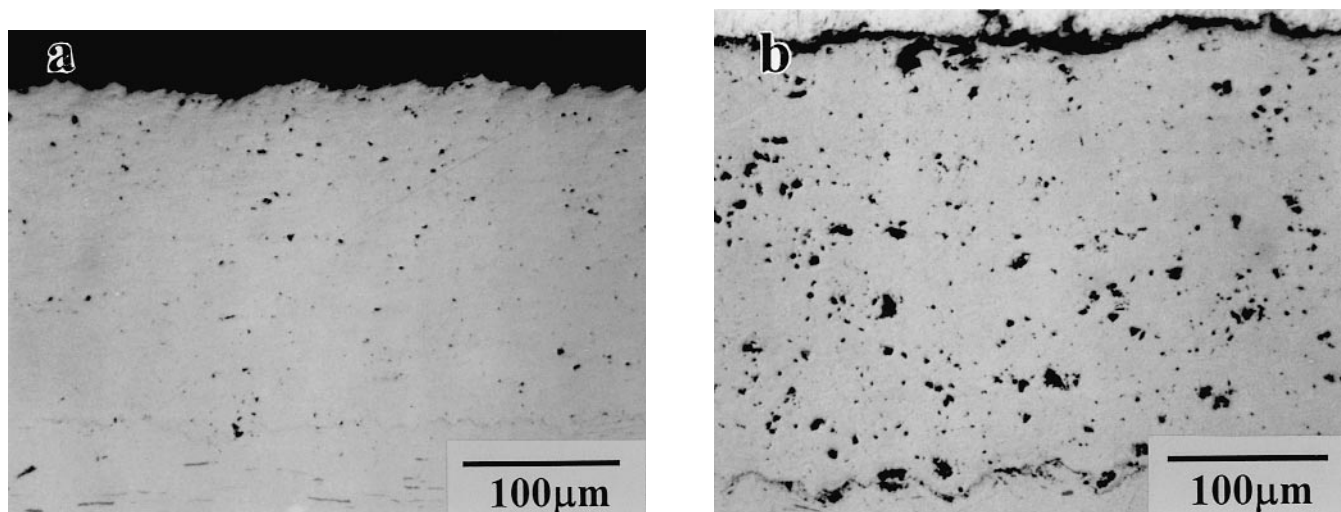


Fig. 10 Typical coating with the best optical microstructure: (a) fine powder and (b) coarse powder

Table 2 The process conditions to produce the coating of the best optical microstructure

Parameters	Fine powder	Coarse powder
Molybdenum contents	43%	19%
Hardness (kg/mm ²)	1250	1350
Porosity	1%	2.5%
Acetylene flow (m ³ /h)	1.8	2.0
Oxygen flow (m ³ /h)	2.07	2.7
Nitrogen dilution	20%	20%

- The porosity and hardness of the coating are related to the amount of the molybdenum phase.
- The fine powder (5 to 10 µm) undergoes a greater degree of deboronization than does the coarse powder.

Acknowledgments

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