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5. M_3B_2 Boride Cermet Coating by Sintered Powder

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The boride cermet composed with M_3B_2 (M: metal)-system complex borides and metals have attained superiority over carbide cermets in various mechanical properties. However, their sintered materials have put into only the limited uses due to the cost. Therefore, two sorts of the boride cermet coating have been developed. Thermal spray coating of the boride cermet was investigated. The sprayed powder was prepared by low temperature sintering, and the spraying was performed by HVOF. Microstructure of the sprayed layer was finer, and its hardness was superior than sintered body in vacuum having the same compositions. Overlay of the boride cermet was investigated using sintered powder. Plasma transfer arc was selected as a welding method. The suitable compositions were not same between overlay and thermal spraying owing to the deference of provided heat in process.

1. Introduction

In this decade, sintered boride cermets composed with M_3B_2 - type ternary boride and iron group metal were developed[(1)~(3)], and have been put in practical uses[4)]. Because a boride cermet of Mo_2NiB_2 and Ni ("Mo_2NiB_2-Ni cermet" in this report) has some useful features, it is giving sufficient effects in several uses. For example, this cermet is especially suitable for forging moulds[(5)] in semi-hot process due to high strength and toughness at 773-1073K, and is very useful as various parts to cast aluminum products, i.e. a shoot sleeve in die-casting[(6)], a gate part for reduced casting[(7)] etc., due to high resistance to molten metals. However, this sintered body of Mo_2NiB_2-Ni cermet has been enjoyed in limited industries, because the shapes and dimensions of such hard sintered material are restricted. As a result, the boride cermet coating on metal body has been desired sincerely.

In this report, two sorts of coating, to use sintered powder as starting material, are represented. One is a thermal spray and the Other is a overlay by welding (overlay)[(8)]. High mechanical properties of coating layer and easiness of fabrication can be expected in case of thermal spray process, and high bonding strength and thick coating can be expected in the overlay process.

2. Experimental Procedure

2.1 Preparation of sintered powder

Sintered powders for thermal spray and overlay were prepared with the same way essentially. Raw powders of boride ceramics and metal were prepared at first, and these powders were milled in solvent by ball mill. Used powders are listed in **Table 1** for the both cases. The milled powder was agglomerated by spray drying in nitrogen. After the agglomeration, heating in vacuum and sieving were performed. Primary fine powders were sintered each other in agglomerated particle by the heating (see **Fig.1**). These sintered powders were applied for coating process. Particle size was 25-75 μm in diameter for thermal spray, and 75-225 μm in diameter for overlay.

2.2 Coating process

The high velocity oxygen fuel process (HVOF) was selected for thermal spray, because splayed layer was denser than other process. In general, HVOF is most suitable to cermets. The plasma transferred arc welding process (PTA) was carried out in case of overlay. Its process is controllable

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relatively, and diffusion of elements from substrate to coating layer is less than other welding process.

Table 1 Compounding Ratio of Raw Powders. (wt%)

	T.Spray	Overlay	Supplier
MoB	40	19	Japan New Metal
WB	12		Japan New Metal
CrB		15	Japan New Metal
TiB_2		1	Japan New Metal
Ni	40		Inco
Fe		39	ISP
Mo	8	26	Japan New Metal

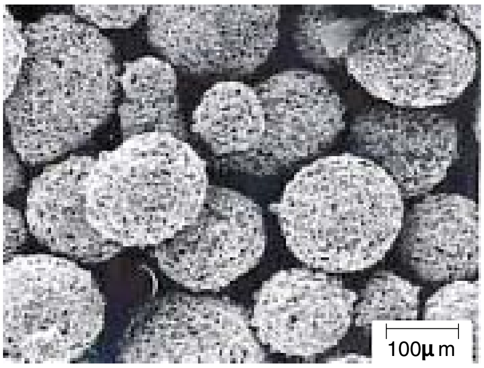

Fig. 1 Sinteded powders for overlay.

3. Results and Discussion

3.1 Thermal Spray

3.1.1 Effects of sintering

The compositions of several samples examined by X-ray diffraction analysis. **Figure 2** shows the diffraction charts of agglomerated powders and thermal sprayed layer with these powders. In this layer, the ternary borides are hardly observed and MoB is remaining. On the other hand, main composition of the thermal sprayed layer by sintered powders are the ternary boride : Mo_2NiB_2 similar to Mo_2NiB_2-Ni sintered body (**Fig.3**). The coated layer is porous in former case and dense in latter case. The sintering of Mo_2NiB_2-Ni cermet is due to two step of chemical reaction, formation of Mo_2NiB_2 by the reaction between MoB and Ni, and the appearance of liquid phase by partial solution of Mo_2NiB_2 to Ni. Because these both reactions are induced by heating, sufficient thermal energy is required to obtain this dense sintered material. It is thought that total thermal energy of thermal spraying process is not enough to generate this two step reaction. Therefore, the sintering process after agglomeration is important to obtain a dense coated layer of Mo_2NiB_2-Ni by the thermal spray.

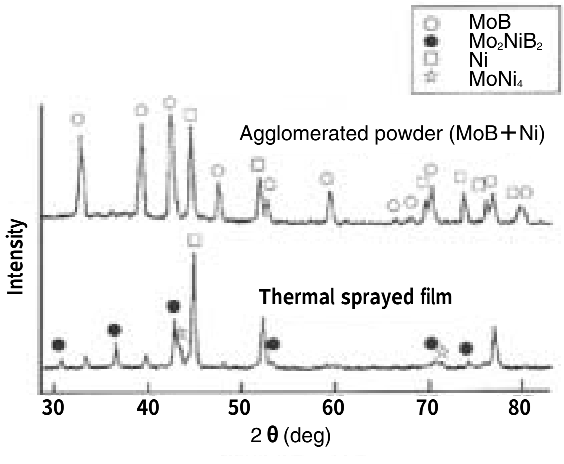

Fig. 2 The X-ray diffraction charts of agglomerated powder and sprayed layer.

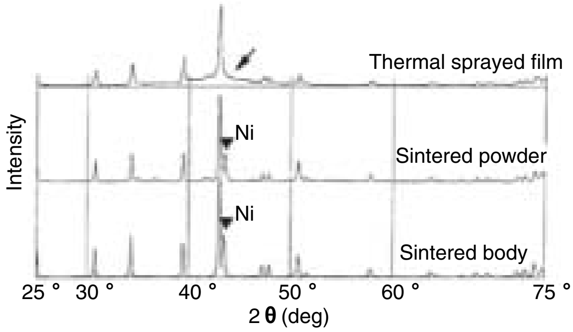

Fig. 3 The X-ray diffraction charts of Sintered powder, sprayed layer and sintered body.

Figure 4 shows microstructure of coated layer by the sintered powder. Fine ternary boride particles are dispersed uniformly and surrounded by Ni alloy phase. The average particle size of boride ceramic is about 2μm observed and is smaller than that of sintered materials (5-6μm). As this sprayed layer is well match to carbon steel substratum, ores and disordered reacted region are not bserved at boundary.

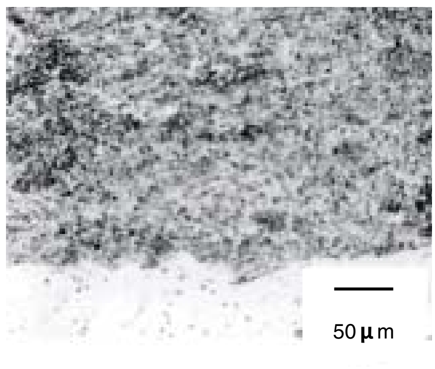

Fig. 4 Microstructure of sprayed layer by sintered powder.

3.1.2 Mechanical properties

The bonding strength of thermal sprayed Mo_2NiB_2-Ni layer on carbon steel is higher than sticking strength (70-80 MPa) of regulated adhesive resin for the pealing test in JIS method. The strength is similar to carbide cermets layer and is valuable sufficiently, because the bonding strength of ceramics layer sprayed with APS is 3,5-4 MPa commonly.

Hardness and abrasion properties of thermal sprayed Mo_2NiB_2-Ni layer are compared with Cr_3C_2-Ni/Cr sprayed layer, which is well known as a wear-resistance surface-finishing to present a sufficient effects at high temperature up to 923K in oxidation condition. Mo_2NiB_2-28%Ni is harder than Cr_3C_2-27%Ni/Cr at the range from room temperature to 1073K in vacuum, and the a advantage of the former in Hv hardness is about 2GPa at 973K (**Fig.5**). The wear-resistance is considered to be dominated directly by hardness. Wearing tests are carried out with flame spraying nozzle to inject ceramics powder. Thermal sprayed surfaces of samples, heated at 973K, are exposed to injection of Al_2O_3 powder sprinkled by propane-oxygen flame with spray-gun. The Al_2O_3 powder is sprinkled continuously for ten minutes in a cycle, and the sample is weighed on the instant. Consequently, a worn volume is calculated by the weight loss. **Figure 6** indicates that a wear-resistance at high temperature of the Mo_2NiB_2-Ni layer comes up to our expectation and is superior to Cr_3C_2-Ni/Cr.

3.2 Overlay by welding

3.2.1 Composition of welded layer

At the beginning, the overlay of $(Mo,W)_2NiB_2$-Ni cermet was investigated. However, this overlay was abandoned immediately because of notable grain growth. It is thought that this rapid grain growth is due to anisotropic feature of Mo_2NiB_2 crystal. Therefore, subsequent investigations were focused to $Mo_2(Fe,Cr)B_2$-Fe/Cr cermet, because Mo_2FeB_2 is more isotropic than Mo_2NiB_2.

Microstructure composed with ceramics particles and metal matrix was observed successfully by PTA (**Fig.7**). Mean particle size of ceramics is about 10-15 μm, to be 5-7 times of particles in the thermal

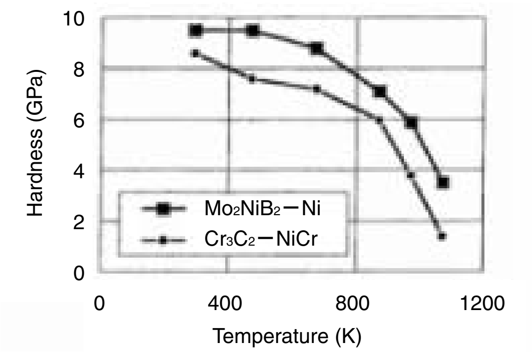

Fig. 5 Effect of temperature to Hv hardness of the sprayed layers.

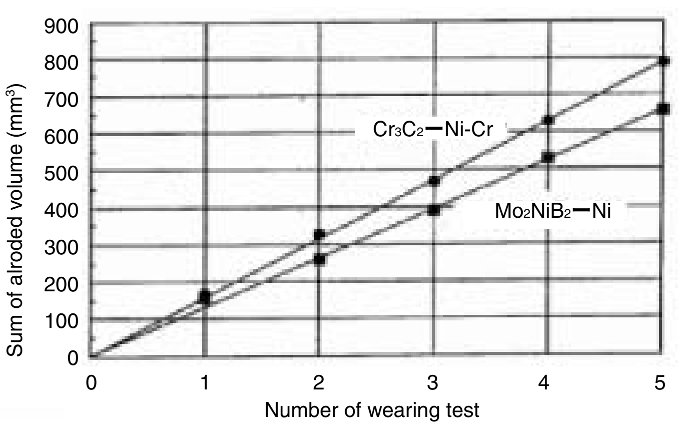

Fig. 6 Comparison of abrasive volume of the Mo_2NiB_2-Ni and Cr_3C_2-Ni/Cr sprayed sample.

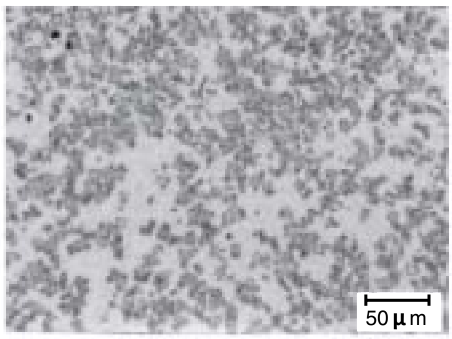

Fig. 7 Microstructure of welded layer with Mo_2 (Fe, Cr) B_2-Fe/Cr powder.

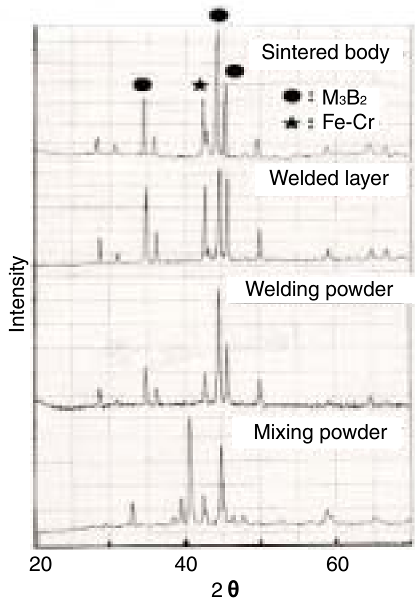

Fig. 8 XRD charts of powders, welded layey and sintered body having same compositions.

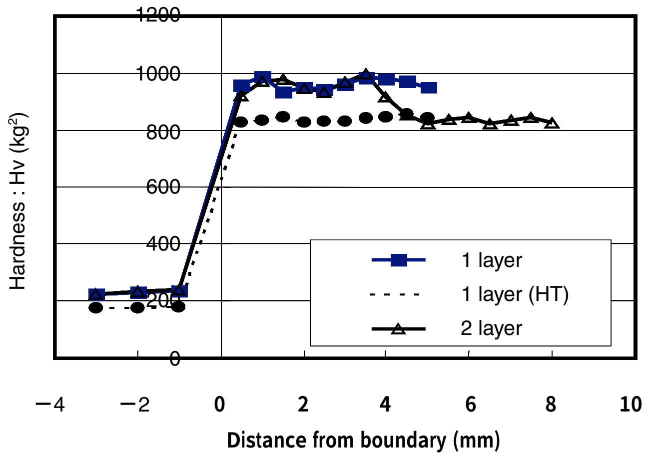

Fig. 9 Hardness distributions of Mo_2 (Fe, Cr) B_2-Fe/Cr overlay as welded and after annealing.

splayed layer shown at 3,1. Composed phases of the mixing powder of raw powders, welding powder, welded layer and sintered body of mixing powder were studied by XRD (**Fig.8**). It can be recognized that composed phases of welded layer are Mo_2(Fe,Cr)B_2 and Fe-Cr. The sintered body is not similar to the welding powder but the welded layer. These results suggest the high stability of microstructure in welded layer. However, homogenizing of its micro-structure is more difficult than the thermal spray due to the diffusion of elements from substratum. It is necessary to control welding conditions exactly in matching to heat capacity of substratum.

3.2.2 Mechanical properties

The Mo_2(Fe,Cr)B_2-Fe/Cr cermet layer with 5mm thickness was welded successfully on a Stainless-steel plate by PTA. Rectangular specimens (4×4×40) were obtained from the welded layer, and bending strength of the cermet was measured. Its bending strength (TRS) is 1.4 GPa at 293K and 1.2 GPa at 873K respectively. Furthermore, effect on hardness of the welded layer was investigated. **Fig.9** show hardness distributions in coated layers of as welded and after annealing (1073K×3h). The high stability of this cermet layer can be recognized with these results and their strength and hardness are high sufficiently in practice uses for wear resistance.

4. Conclusion

Sintering of agglomerated powder is effective to the attainment of the ternary boride cermet in thermal spraying and overlay by welding.

The (Mo, W)$_2$NiB_2 cermet layer was obtained successfully by HVOF thermal spraying. The layer is superior to Cr_3C_2-Ni/Cr thermal sprayed layer in hardness and wear resistance at high temperature.

The overlay of Mo_2(Fe,Cr)B_2-Fe/Cr cermet was obtained successfully by PTA. The phases of this cermet are stabile and the hardness is high sufficiently in practice uses for wear resistance.

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