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Metallurgical Bonding of Plasma Sprayed Tungsten on Hot Molybdenum Substrates

Molybdenum substrates are completely recrystallized when preheated substrate temperatures range between 2200 and 3700° F

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ABSTRACT. Metallurgically bonded plasma sprayed tungsten was applied on metallographically polished and preheated molybdenum substrates. The substrates were preheated to 1750° F or higher immediately before spraying. The preheating and spraying operation was performed in a nitrogen atmosphere.

Metallurgical bonding occurred when the preheated substrate temperature ranged between 2200 and 3700° F. At these temperatures the molybdenum substrates completely recrystallized even though the total time for preheating, spraying and cool down to 400° F was only about 30 sec.

Cross sections of the coating and substrate indicate that the coating-to-substrate bond is the result of substrate grains growing into the coating.

Introduction

The relationship between the performance of a coating-substrate system and the quality of the bond between them is well known and has been studied extensively for many coating techniques. Little attention, however, has been given to the characterization of the bonding mechanisms that exist during plasma spraying and to the improvement of the quality of the bonding of coatings applied by this technique. In a previous investigation the authors reported the establishment of a true metallurgical bond and complete continuity of grain structure between plasma-sprayed tungsten and hot tungsten substrates.[1] Since this type of bond occurred in a system where the lattice parameters of the sprayed particles and the substrate were equal, the system may be considered to be an ideal case. Therefore, an effort was made to determine the applicability of the original technique to dissimiliar metal systems.

This paper reports the results of spraying tungsten on hot molybdenum substrates. These materials were selected, because they are of interest to the aerospace program and because they form a complete series of solid solution alloys. The main effort was directed toward determining if this system would also exhibit metallurgical bonding by continuation of the substrate grains and by concurrent elimination of the coating substrate interface as occurred in the tungsten-tungsten system.

Apparatus and Procedure

Small coupons of as-received 0.020 in. molybdenum sheet were metallographically polished and subsequently plasma sprayed with tungsten powder in a high-purity dry nitrogen atmosphere using techniques developed in an earlier investigation.[1] Substrate temperatures in the range of 1750 to 2950° F were continuously monitored by platinum platinum – 13% rhodium thermocouples and read out on a millisecond response recorder. A typical spray cycle is shown in Fig. 1.

Results and Discussion

The substrate temperatures that were obtained as a result of preheating the specimens with the plasma gas varied with torch-to-substrate distance. This is shown in Fig. 2, which also shows the temperature of the substrate during the actual spraying operation. The velocity of the powder particles was nearly constant over the range of distances examined in this investigation.[2]

For the torch-to-substrate distances investigated (2 to 7 in.), the tungsten particles exhibited a

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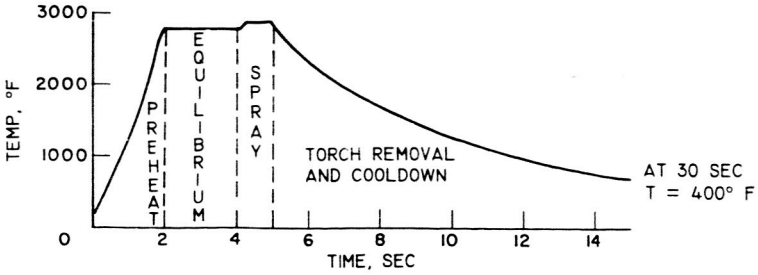

Fig. 1—Typical time-temperature history of substrate during spray treatment

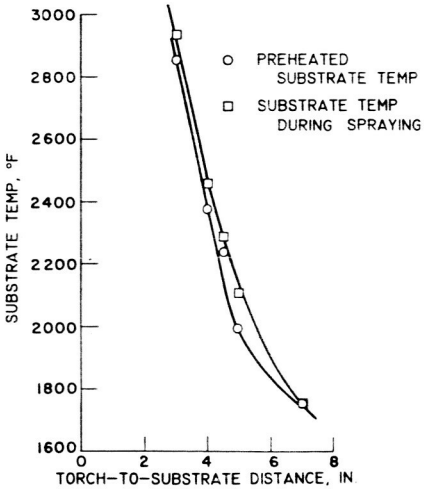

Fig. 2—Variation of substrate temperature with torch-to-substrate distance

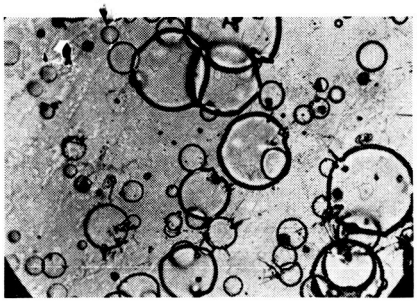

Fig. 3—As-sprayed view for 4 in. torch-to-substrate distance. Substrate temperature—2450° F; etchant—Murakami's reagent. X 250 (reduced 72% on reproduction)

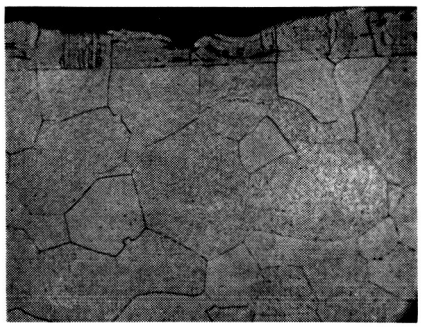

Fig. 4—Cross-sectional view for 3 in. torch-to-substrate distance. Substrate temperature—2950° F; etchant—Murakami's reagent. X 500 (reduced 67% on reproduction)

considerable amount of plasticity. This was demonstrated by their ability to deform into shapes similar to flat almost circular disks that had sufficient plasticity to flow over the previously deposited particles. A typical picture showing the sprayed particle configuration on the substrate for a 4 in. torch-to-substrate distance is shown in Fig. 3. Similar configurations were observed at the other spray distances.

The particle-substrate bonds resulting from spraying at torch-to-

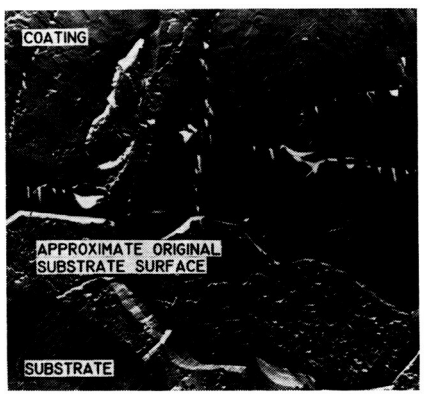

Fig. 8—Electron micrograph of cross section of tungsten coating on tungsten substrate for 4 in. torch-to-substrate distance. Substrate temperature—2750° F; etchant—Murakami's reagent. X 10,000 (reduced 60% on reproduction)

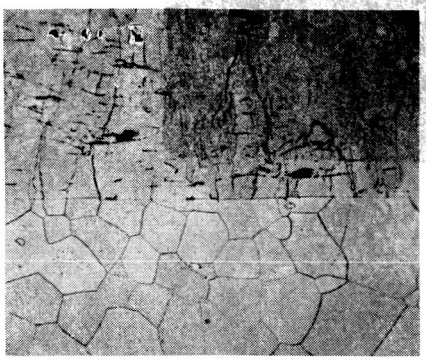

Fig. 5—Cross-sectional view for 4 in. torch-to-substrate distance. Substrate temperature—2450° F; etchant—Murakami's reagent. X 500 (reduced 65% on reproduction)

substrate distances of 3 and 4 in. are shown in Figs. 4 to 6, which are cross sections through the coating and the substrate. Figure 6 is an electron micrograph at a magnification of 10,000 for the 4 in. spray distance. The molybdenum substrates recrystallized as a result of preheating and spraying at distances up to 5 in., while at 7 in. the as-worked structure was retained. Spraying at distances of 5 and 7 in. resulted in a poorer particle-substrate bond.

Grain boundary continuity across the coating-substrate interface is evident in Figs. 4 to 6 and is most apparent in Fig. 6. Figure 7 shows an area where a continuity of etch markings exists across the interface, which gives evidence of an orientation continuity between the coating and substrate. From these illustrations it is apparent that there is a metallurgical bond at the coating-substrate interface.

These observations on coating-substrate grain continuity are similar to those obtained when tungsten was deposited on hot tungsten substrates with the same spray conditions.[1] A representative picture of the coating-substrate

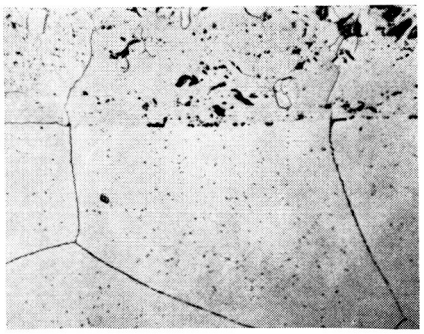

Fig. 9—Cross-sectional view for 2 in. torch-to-substrate distance. Substrate temperature—3700° F; etchant—Murakami's reagent. X 500 (reduced 66% on reproduction)

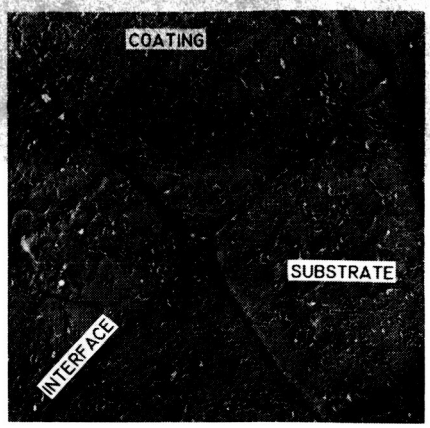

Fig. 6—Electron micrograph of cross section of coating and substrate for 4 in. torch-to-substrate distance. Substrate temperature—2450° F; etchant—Murakami's reagent. X 10,000 (reduced 56% on reproduction)

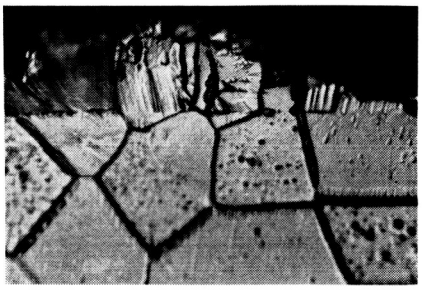

Fig. 7—Result of etching on interface structure of specimen sprayed at 3 in. torch-to-substrate distance. Substrate temperature—2950° F; etchant—boiling Murakami's reagent. X 1000 (reduced 65% on reproduction)

cross section for tungsten on tungsten is shown in Fig. 8. In Fig. 8 it is apparent that not only is there a continuity between the grains in the coating and those in the substrate, but also that the original interface between them has been eliminated. Since molybdenum is very similar to tungsten, it was felt that the same

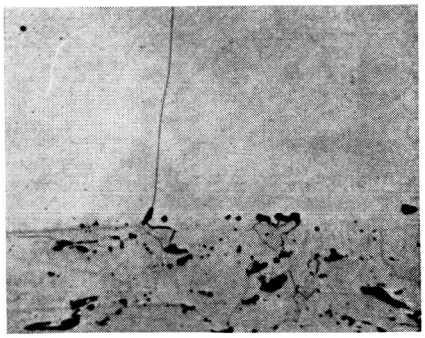

Fig. 10—Result of subsequent diffusion treatment of interface structure for specimen sprayed at 3 in. torch-to-substrate distance. Substrate temperature—2950° F; specimen heat treated at 2700° F for 3 hr plus 3700° F for 1 hr; etchant—Murakami's reagent. X 500 (reduced 60% on reproduction)

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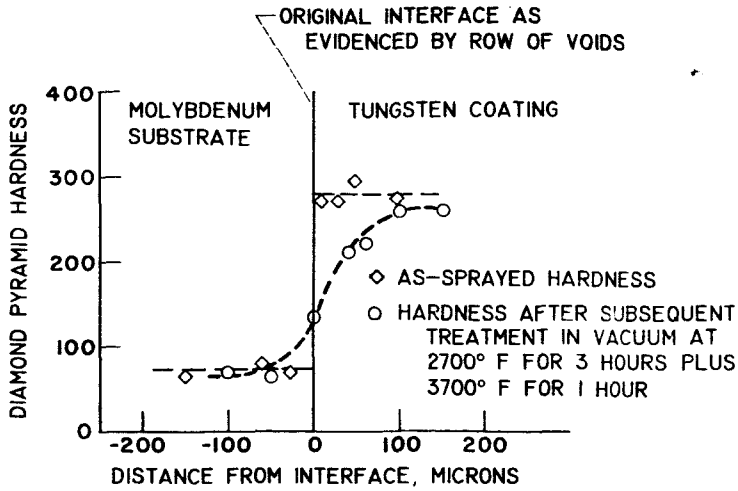

Fig. 11—Hardness as function of distance from original interface for specimen sprayed at 3 in. torch-to-substrate distance

type of interface should prevail in this system. Therefore, further experiments were undertaken to show that the coating-substrate interface obtained when tungsten was sprayed on hot molybdenum resulted from the chemical differences between the two materials at the interface.

Two approaches were taken to verify that the interface resulted from a chemical discontinuity. These approaches involved the use of a higher substrate temperature and diffusion treatments.

To evaluate the influence of a higher substrate temperature on the elimination of the apparent coating-substrate interface, an additional specimen was sprayed at a 2 in. distance. The substrate temperature at this distance was estimated to be approximately 3700° F. A cross section of this specimen appears in Fig. 9 and shows the grain boundary continuity across the interface. Even in this specimen, however, there is a slight line at the coating-substrate interface, although over most of the interface it appears to be the result of a color change.

Figure 10 shows a specimen that was sprayed at 3 in. and given a subsequent vacuum heat treatment of 2700° F for 3 hr plus 3700° F for 1 hr. After the 2700° F treatment there was no significant observable change in the interface discontinuity. After the subsequent 3700° F treatment, however, the apparent coating-substrate interface had been largely removed—Fig. 10.

Figure 11 is a hardness traverse across the coating-substrate interface It further substantiates that the heat treatment caused diffusion to occur as evidenced by the elimination of the original hardness discontinuity at the interface. It has been shown that the hardness of molybdenum is increased considerably by the addition of tungsten, whereas molybdenum additions to tungsten cause a decrease in the hardness of tungsten.[3,4] Therefore, the continuous hardness change across the reference interface after the diffusion treatment is verification that a significant amount of molybdenum has diffused into the original tungsten particle. Also, since the original interface is eliminated after this heat treatment (Fig. 10), it must have resulted from a sharp chemical gradient.

These results show that a metallurgical bond is obtained during the spraying of tungsten on hot molybdenum substrates similar to that obtained when tungsten is sprayed on hot tungsten. This bond is produced by the grains of the coating growing out of those in the substrate, and the apparent interface that results is due to the sharp chemical gradient that exists between the tungsten and molybdenum.

Conclusions

1. Metallurgically bonded tungsten coatings can be applied to metallographically polished molybdenum substrates by plasma spraying if the substrate is preheated to 2200° F or higher immediately before spraying in a nitrogen atmosphere.

2. The type of columnar grains that appear in the cross sections indicate that the coating-to-substrate bond is the result of substrate grains growing into the coating producing a coherent interface. This apparent interface is due to a chemical gradient only and can be eliminated by heat treatment.

3. The substrates that were preheated over the temperature range 2200 to 3700° F were completely recrystallized even though the total time for preheating, spraying and cooldown to 400° F was only about 30 sec.

References

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