

# Effect of nano-crystallization of high velocity oxy-fuel-sprayed amorphous NiCrBSi alloy on properties of the coatings

Chang-Jiu Li,<sup>a)</sup> Yu-Yue Wang, and Hua Li<sup>b)</sup>

State Key Laboratory for Mechanical Behavior of Materials, Welding Research Institute,  
School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049,  
People's Republic of China

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NiCrBSi self-fluxing alloy coatings were deposited by high velocity oxy-fuel (HVOF) spraying. Annealing treatment was applied to the as-sprayed coatings to develop the microstructure of the Ni-based coating. The microstructure of the coating was characterized using optical microscopy, x-ray diffraction and transmission electron microscopy. The crystallization behavior of the amorphous coating was also characterized by differential scanning calorimetry. The properties of the coating were characterized by microhardness and abrasive wear tests. The results showed that the as-sprayed HVOF coating deposited by well melted spray particles exhibited a dense microstructure of amorphous phase. It was revealed that the crystallization of the amorphous phase in HVOF NiCrBSi coating occurs at a temperature of about 502 °C. Annealing at temperature a little higher than recrystallization temperature leads to the formation of the nano-crystalline microstructure. The subsequent nanostructured Ni-based coating presents higher microhardness and excellent wear performance. With the further increase in annealing temperature, the growth of the nano-crystalline grains occurs and, accordingly, the microhardness of the coating and the wear performance decrease. Thereafter, the microstructure and properties of the Ni-based self-fluxing alloy coating can be controlled through postannealing treatment. © 2004 American Vacuum Society. [DOI: 10.1116/1.1776183]

## I. INTRODUCTION

Owing to the relative low melting point and the ability of self-fluxing during postspray fusing process, nickel-based self-fluxing alloy coatings can be reheated by fusing process up to over their melting point, which is well below the melting point of iron-based substrates to achieve dense coatings with excellent metallurgical bonding with the substrate. Therefore, since they were developed in the early 1950's, such materials and their coatings have been widely used in various industry fields for their excellent wear resistance and corrosion resistance.

The high velocity oxy-fuel (HVOF) process has become very popular to deposit dense coatings with excellent adhesion and mechanical performance.<sup>1-3</sup> Several studies showed that a Ni-based self-fluxing alloy coating with comparable microhardness and wear resistance to traditional spray-fusing coatings can be produced through the HVOF process.<sup>4-6</sup> Therefore, it is obvious that HVOF process can be utilized as an alternative to the spray-fusing process for some applications. Moreover, Ni-based self-fluxing alloy materials usually contain a certain amount of metalloids such as boron which promote formation of amorphous phase. Accordingly, an amorphous phase can be formed in the coating.<sup>7,8</sup> It was reported that the formation of a mixed amorphous/nano-crystalline Ni-rich matrix by HVOF likely

contributes to the high hardness of the coating.<sup>9</sup> Studies also showed that annealing treatment of amorphous phase under a temperature higher than the recrystallization temperature can increase coating hardness.<sup>10,11</sup> Those facts mean that the controlling of the formation of amorphous structure and subsequently crystallization may modify the coating performance.

In the present article, a Ni-based alloy coating containing substantial amorphous phase was formed by HVOF process based on a previous study.<sup>12</sup> The crystallization behavior of the amorphous phase in the coatings was studied using x-ray diffraction (XRD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The effect of crystallization of the amorphous phase on the mechanical properties of the coating was investigated.

## II. MATERIALS AND EXPERIMENTAL PROCEDURES

The nickel-based self-fluxing alloy powder used was a NiCrBSi alloy with a particle size from 37 to 73  $\mu\text{m}$  (Xi'an Banglin Co.). The chemical composition of the powder is shown in Table I. This powder was designed to form a NiCrBSi bulk coating of a nominal hardness HRC 60 through the conventional spray-fusing process. Mild steel was used as a substrate.

The CH-2000 HVOF system developed in Xi'an Jiaotong University was used to deposit coating. A detailed description of the spray system can be found elsewhere.<sup>13</sup> Propane was used as fuel gas. According to the previous systematical investigation on the effect of HVOF parameters on the coating properties,<sup>12</sup> the operating pressures of oxygen and propane were set to 0.55 and 0.4 MPa, respectively, while the

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: licj@mail.xjtu.edu.cn

<sup>b)</sup> Present address: School of Mechanical and Production Engineering, Nanyang Technological University, Singapore.

TABLE I. Nominal composition of NiCrBSi powder used.

| Elements | B | C   | Si  | Cr    | Fe | Ni   |
|----------|---|-----|-----|-------|----|------|
| wt%      | 4 | 0.6 | 5.3 | 20–22 | 5  | Bal. |

flow rates of both gases were set to 479 l and 41.4 l min<sup>-1</sup>, respectively. Nitrogen was used as powder carrier gas, which was operated at the pressure of 0.35 MPa and the flow rate of 32 l min<sup>-1</sup>. The spray distance was fixed at 170 mm. The substrate temperature was controlled during deposition with compressed air jets to keep the temperature lower than 200°C.

The as-sprayed HVOF NiCrBSi coatings were annealed under different temperatures from 200 to 800°C at ambient atmosphere and kept for 30 min at each elevated temperature in a heat treating furnace.

The microstructure of the coatings was examined using optical microscopy and TEM. The crystalline structure and recrystallization behavior of the coating upon heat treatment were characterized by XRD and DSC. XRD was performed using the CuK<sub>α</sub> radiation.

The mechanical properties of the coatings were characterized by microhardness measurements and abrasive wear tests. The microhardness of the coating was measured under a load of 200 g and an average of ten tests was used as an indicator of the hardness of the coating. Abrasive wear was estimated using a dry-sand rubber wheel abrasive-wear tester according to the American Society for Testing and Materials -G65-91 standard. During the test, 120 mesh alumina was used as abrasives. The test was performed under a load of 13 N at a rotation speed of 50 rpm. The weight loss of the sample was measured after 10 min testing. The surface of the specimen was ground before the wear test in order to obtain the same roughness for all specimens. Three test specimens were tested for each coating and the average weight loss of the coating was used to estimate the wear performance of the coating.

### III. RESULTS

#### A. Microstructure of as-sprayed HVOF NiCrBSi coating

Figure 1(a) shows the typical optical microstructure of the as-sprayed HVOF NiCrBSi coating. The coating presents a dense microstructure. The etched cross-sectional microstructure of the coating illustrated in Fig. 1(b) shows that the coating exhibits well-layered structure. Such a microstructure indicates evidently that most spray droplets were completely melted before impact on the surface of the substrate.

Figure 2(b) shows the XRD pattern of the as-sprayed coating compared with that of starting powder (a). Evidently, a very large broad peak maximized at 2θ of about 45° can be observed for the as-sprayed coating. This result clearly indicates that the as-sprayed coating consisted of amorphous phase, although some small peaks were superimposed on the broad shallow peak. The appearance of such small peaks resulted from the partially melted particles embedded in the

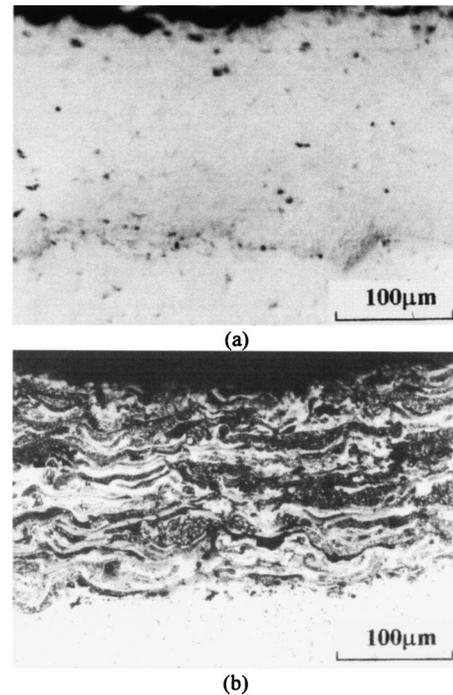


FIG. 1. Typical optical microstructure of the as-sprayed HVOF NiCrBSi coating (a) and microstructure of the as-sprayed NiCrBSi coating in etched condition (b).

coating, especially the unmelted core-central fraction of the spray particle. TEM examination of the as-sprayed coating confirmed the formation of an amorphous matrix phase.

#### B. Effect of annealing on the microstructure of HVOF NiCrBSi coatings

Figure 3 illustrates the XRD patterns of HVOF NiCrBSi coatings annealed under different temperatures from 200 to 800°C for 30 min at ambient atmosphere. From those patterns, it can be found that no evident change occurred in the XRD pattern when the coating was annealed under the temperature of 400°C. However, when the coating was annealed at temperatures above 600°C, the broad peak disappeared in the XRD patterns. This fact indicates that the crystallization of the amorphous phase has occurred in the coatings. More-

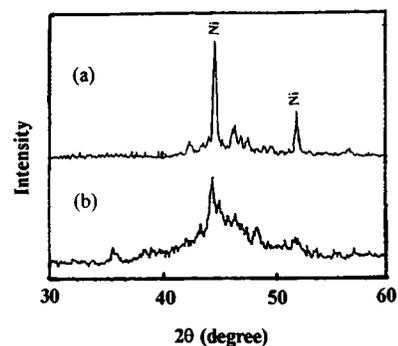


FIG. 2. XRD patterns of NiCrBSi powder (a) and of the as-sprayed coating (b).

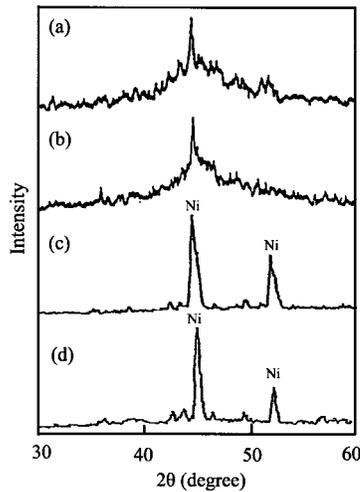


FIG. 3. Effect of annealing temperatures on the XRD patterns of HVOF NiCrBSi coating (holding time: 30 min). (a) 200°C; (b) 400°C; (c) 600°C; (d) 800°C.

over, it was found that the main phase in the crystallized coating was a nickel-based solid solution, although it can be considered that the precipitations of carbide or boride occurred during annealing treatment.<sup>14</sup>

The DSC analysis of the coating, as illustrated in Fig. 4, showed that there were two main exothermic peaks which correspond to two exothermic reactions during the annealing of the as-sprayed coating up to 550°C. Taking into consideration the XRD analysis results, it can be considered that the second reaction occurring at the temperature of 501.8°C corresponds to the crystallization of the amorphous phase in the coating. The exothermic peak appearing at about 300°C may be due to the precipitation of elements such as carbon which were supersaturated in the nickel matrix solid solution resulting from rapid cooling of deposited splats.

Figures 5(a) and 5(b) show the TEM images of the coatings annealed at 400 and 500°C. At 400°C the matrix of the amorphous phase remains unchanged when compared with the XRD results. At 500°C, the recrystallization of the matrix phase occurred, which resulted in nano-crystalline grains distributed in the amorphous matrix. This fact clearly confirms that the exothermic reaction at 501.8°C revealed by the DSC analysis corresponds to the crystallization temperature of the amorphous phase in the coating.

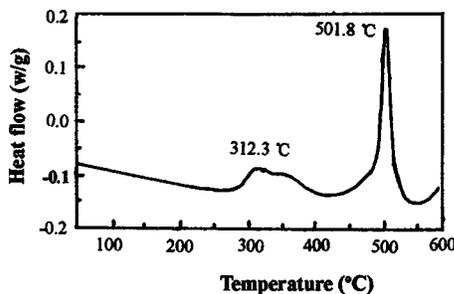


FIG. 4. DSC analysis result of the as-sprayed HVOF NiCrBSi coating.

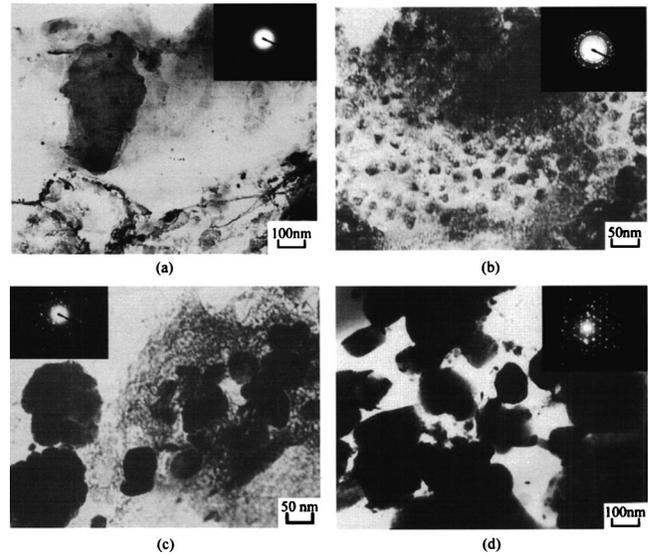


FIG. 5. Typical TEM microstructures of HVOF NiCrBSi coatings annealed under temperatures of 400°C (a), 500°C (b), 600°C (c) and 800°C (d).

The TEM examination of the microstructure of the coating annealed at 800°C, as shown in Fig. 5(d), revealed that the grain size of the matrix phase was increased to over 100 nm, boride and carbide particles being distributed in the matrix, compared with that in the coating annealed at 600°C (c). This fact suggests that the annealing at temperature over the crystallization temperature leads to the growth of the recrystallized nanocrystalline grains.

### C. Influence of the annealing temperature on the coating properties

The microhardness tests revealed that the as-sprayed HVOF NiCrBSi coating deposited under the present conditions yielded an average hardness of 905 Hv<sub>0.2</sub>. This value is higher than that of the NiCrBSi coating produced by conventional spray-fusing process with identical materials to the one used in the present study. This high hardness can be attributed to the formation of an amorphous phase in the coating. Figure 6 shows the effect of the annealing temperature on the microhardness. The microhardness of the coating tends to decrease with the increase in annealing temperature up to 200°C. With a further increase in annealing temperature, the microhardness increases and an average hardness of 1072 Hv<sub>0.2</sub> is observed when the coating is annealed at the temperature of 600°C. It can be considered that such an increase is due to the nano-crystallization of the amorphous phase as mentioned in the previous section and also to the precipitation of carbides and borides. With a further increase in annealing temperature, above 600°C, the hardness of the coating tends to decrease again. Evidently, such a decrease in hardness is due to the coarsening of the crystallized grains.

Figure 7 shows the effect of the annealing temperature on the abrasive wear weight loss of the coatings. It can be clearly recognized that there exists a significant effect of the annealing temperature on the wear resistance of the coating.

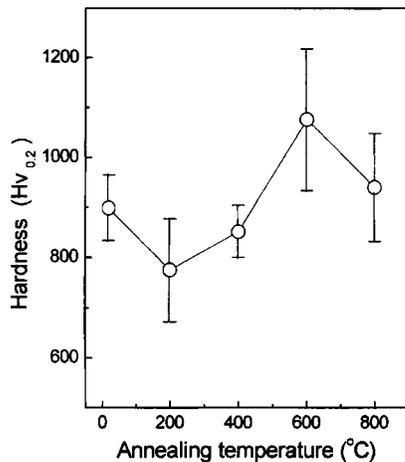


FIG. 6. Effect of annealing temperature on the microhardness of HVOF NiCrBSi coating.

The comparison of the results shown in Fig. 6 with those in Fig. 7 clearly shows a good correlation between microhardness and abrasive wear loss. Therefore, the abrasive wear weight loss is observed to decrease with the increase in the hardness of the coating. Corresponding to the maximum hardness observed in the present experiment, the optimum abrasive wear resistance of the coating can be obtained with an annealing treatment at 600°C.

#### IV. DISCUSSION

The present study showed that Ni-based self-fluxing alloy coatings mainly consisting of an amorphous phase can be formed by the HVOF process. This may be attributed to the boron contained in the powder and to the rapid cooling conditions of the completely melted spray particles at impact on the substrate. The analyses showed that the recrystallization of the amorphous phase occurs at a temperature around 500°C. This temperature is close to that reported by Dent *et al.* for a HVOF Ni-based alloy,<sup>15</sup> although the difference in the compositions of the alloy in the literature from that in this study leads to a little difference in the crystallization temperature.

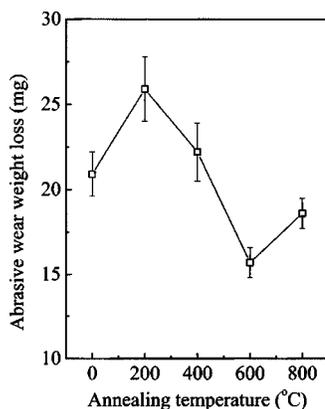


FIG. 7. Effect of annealing temperature on the abrasive wear weight loss of HVOF NiCrBSi coating.

The hardness of the as-deposited coating in this study reached about 905 Hv, which is higher than that of bulk coatings formed by the fusing process. This is also a higher value than those of HVOF Ni-based coatings reported by other investigators.<sup>16,17</sup> The difference can be attributed to the formation of an amorphous phase in the coating. A previous study<sup>12</sup> revealed that the microstructure and microhardness of the as-sprayed Ni-based self-fluxing alloy coating are significantly influenced by spray conditions. Under the spray conditions for which spray particles can substantially reach a molten state, as those used in the present study, the microstructure of the coating depends on cooling characteristics during splatting of the molten droplets. Accordingly, the amorphous phase will be the main matrix phase in the as-sprayed coating. On the other hand, when most of the spray particles only partially reach the melted state, only the melted fraction may form an amorphous phase while the unmelted fraction will keep the original microstructure of the starting powder. As a result, a mixed microstructure containing the amorphous phase and a fraction of the well-crystallized original structure of the powder is observed. The microhardness of the coating depends on the fraction of the amorphous phase in the coating, although the other microstructural features such as the lamellar structure with the limited bonded lamellar interface and porosity in the coating inherent to thermal spraying<sup>18</sup> will also affect the hardness of the coating. This may be the main reason for the difference in hardness of HVOF Ni-based coatings of similar compositions.

The annealing treatment of the amorphous coating at 600°C yielded the highest mean hardness (1072 Hv) and wear resistance. This result can be attributed to the formation of a nano-crystalline structure followed by the subsequent precipitation of borides in the coating. TEM examination of the microstructure confirmed that the coating annealed at 600°C for 30 min presented recrystallized grains 30–50 nm in size. As mentioned above, when the annealing temperature was further raised to 800°C, nanograins grew to over 100 nm. Therefore, it can be considered that the high hardness of the coating can be attributed to the transformation of the amorphous phase in the coating into a nanocrystalline phase. Therefore, through the controlling of the spray conditions and subsequent annealing treatment of the coating, the microstructure and, consequently, the performance of HVOF Ni-based self-fluxing alloy coating can be modified.

#### V. CONCLUSIONS

The microstructure of HVOF sprayed nickel-based alloy coatings and the effect of annealing temperature on the microstructure and properties of the coating were examined. The results revealed that the HVOF NiCrBSi coatings deposited with well melted particles exhibit an amorphous structure and that an annealing treatment results in the recrystallization of this amorphous phase. The crystallization temperature of this amorphous phase in the NiCrBSi coating is about 502°C. The crystallization resulted in the increase of the coating microhardness and in the improvement of the

abrasive wear resistance. Moreover, the crystallization of the amorphous phase into a nanostructured phase yielded the highest hardness. It was also clear that a large increase in the annealing temperature over the crystallization temperature led to the growth of the crystallized grains and to a decrease in coating hardness and wear resistance.

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