Nano-composite coatings with improved mechanical properties and corrosion resistance by thermal spraying

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Abstract. This paper reports the synthesis and characterization of nanostructured coatings. To improve the mechanical properties and oxidation resistance of the materials, two new types of nanostructured coatings including CoNiCrAlY-MoSi2 and Ni60-TiB2 were designed. The nanocrystalline feedstock powders were prepared by high energy ball milling (HEBM). The particle size, morphology and grain size of the feed stocks were investigated. The preparation, microstructure, mechanical properties, and anti-oxidation behavior of the nanostructured CoNiCrAlY-MoSi2 and Ni60-TiB2 coatings are presented. With a lamellar and compact structure, the optimized nano-composite CoNiCrAlY-MoSi2 coatings is metallurgically bonded with the substrate. It exhibits low porosity, high fracture toughness and excellent thermal shock resistance. The nanostructured Ni60-TiB2 composite coatings also exhibited better mechanical properties and wear-corrosion resistance than those of its conventional counterpart. This work is expected to play an important role in the preparation and application of high performance nanostructured coatings.

1. Introduction
In the field of surface engineering, thermal spray coating is widely used as overlay to protect components against wear, corrosion and high temperature oxidation. Thermal spraying can provide thicker coatings (>20 µm) over a larger area at higher deposition rates as compared to other coating processes such as electroplating, physical and chemical vapor deposition. The microstructure and properties of the coating depend on the thermal and momentum characteristics of the impinging particulate [1], which are determined by both the spraying methodology and the type of feedstock materials employed.

The variations of thermal spraying are distinguished as flame spraying (FS), detonation spraying (DS), wire arc spraying (WAS), plasma spraying (PS), high velocity oxy-fuel coating spraying (HVOF), and et al., among which PS and HVOF are the most popular and effective technique used to prepare metal matrix composite coatings (MMCs), such as WC–Co [2], Cr3C2–NiCr [3] or TiB2–NiCr [4,5], due to its flexibility, low cost and high velocity.

Because of the catastrophic oxidation of WC at high temperature, WC-based coatings are usually used below 450 °C [6,7]. Although Cr3C2-based coating can be satisfactorily applied at the temperatures up to 900 °C, its hardness and wear resistance are worse than those of WC-based coating [5]. Thus, development of novel types of coating with excellent properties at high temperature is in need.
TiB\textsubscript{2} has high hardness (34 GPa), low density (4.52 g/cm\textsuperscript{3}) and excellent oxidation resistance up to 1000 °C [4,5,8,9]. In recent work, TiB\textsubscript{2}- containing MMCs such as Fe(Cr)–TiB\textsubscript{2} and Ni(Cr)–TiB\textsubscript{2} coatings have been prepared by HVOF with the excellent abrasive resistance [4,5,8]. However, the high brittleness and low fatigue resistance for TiB\textsubscript{2} have become the main restrictions for the conventional TiB\textsubscript{2}-based coatings. In addition, with a high melting point (2030°C), moderate density (6.24g/cm\textsuperscript{3}) and excellent high temperature oxidation resistance, MoSi\textsubscript{2} has also become a promising high temperature protection coating for the superalloys. However, the occurrence of “Pesting” phenomenon in the temperature range from 400 to 600°C and the large difference of thermal expansion coefficient between coating and substrate severely limit its widespread application. To solve above problems, we suggest a new approach to improve the properties of TiB\textsubscript{2}- or MoSi\textsubscript{2}-containing coatings by achieving nanostructure in these films.

In this works, CoNiCrAlY–MoSi\textsubscript{2} and Ni60–TiB\textsubscript{2} nano-composite feedstocks were prepared by high energy ball milling. CoNiCrAlY–MoSi\textsubscript{2} nano-composite coating was deposited on superalloy GH4169 substrate by plasma spraying technology. Ni60–TiB\textsubscript{2} composite coatings were prepared by HVOF. The microstructure and properties of the two types of coatings were investigated in details.

2. CoNiCrAlY-MoSi\textsubscript{2} nano-composite coatings

CoNiCrAlY-MoSi\textsubscript{2} with mass ratio of 1:1 powders were produced by mechanically mixing for 12h and the nanocomposite feedstock powders were prepared by ball milling the mechanically mixed powders for 5 to 40 h using a high energy planetary ball miller. The parameters of ball milling include the rotational speed of 300 rpm and ball/powder mass ratio of 15:1. The CoNiCrAlY-MoSi\textsubscript{2} nano-composite coatings were sprayed onto the superalloy GH4169 substrate by plasma spraying technology. Spraying powder, Spraying distance, main gas (Ar) flow rate, auxiliary gas (He) flow rate and gun moving speed were regulated as follows: 30kW, 70cm, 45 l/min, 5l/min and 500mm/s, respectively[10].

2.1 Microstructures of the starting powders

Figure 1a [11] shows the morphology of the mechanical mixing powders, which consists of the CoNiCrAlY powder with smooth surface and spherical and the MoSi\textsubscript{2} powder with small particle size. When the milling time increases to 30 h, it is difficult to distinguish between CoNiCrAlY particles and MoSi\textsubscript{2} particles, because both particles have nearly spherical morphology with similar particles size (Figure 1b). The cross-sectional SEM image of powders milled for 30 h is shown in figure 1c. It can be seen that a large number of dark gray particles (MoSi\textsubscript{2}) are uniformly and dispersedly distributed in a light-colored matrix (CoNiCrAlY).

Figure 2a shows the XRD patterns of the CoNiCrAlY-MoSi\textsubscript{2} powders milled for different times. The results show there is no new phase formed during the entire milling process, suggesting that neither impurity precipitation nor obvious oxidation phenomenon happens after high energy ball milling under argon atmosphere.

Figure 2b shows that the D\textsubscript{50} (the median diameter D\textsubscript{50} corresponding to the cumulative distribution value of 50%) value of CoNiCrAlY-MoSi\textsubscript{2} mixing powders gradually reduces, suggesting a reduction of powder granularity with the increase of milling time. While the D\textsubscript{50} value of powders milled for 40 h does not change much, revealing the crushing effect from grinding balls to powders is no longer significant after ball milling for 30 h.

The grain size of MoSi\textsubscript{2} phase milled for different times is shown in figure 2c. It is obvious that the grain size of MoSi\textsubscript{2} phase approximates to 53 nm only after milling for 5 h. Along with the increase of milling time, the value tends to decrease though the rate of reduction becomes slow, and it seems to be stabilized after milling for 30 h. It is worth noting that although the high energy ball milling can reduce the powder grain sizes to nanoscale, the particle sizes still remain micron scale.
2.2 Microstructure of as-sprayed coatings

Figure 3a shows that feedstock powders were overlapped to form a clear "stacking" shape configuration of MoSi$_2$-CoNiCrAlY nanostructured coatings. And nanoscale feedstock powders displayed a good molten effect, but a small amount of semi-molten or unmolten particles is still visible in the local magnification, as arrows pointed in the inset of figure 3a. The presence of these particles allows the coating has a high bonding strength and good wear resistance [12]. The cross-section image of the coating is shown in figure 3b, a typical thermal spray nanostructured coating with unique layered dense structure and less porosity is evident. Figure 3c shows the result of X-ray energy dispersive spectrum (EDS) line scanning of Co element. There is a high Co content in the regions of substrate near the coating, while there is no Co element in the original substrate matrix. This indicates that Co atoms diffuse into the substrate matrix through the interface during the thermal spraying. The diffusion behavior led to a certain metallurgical bonding between coated layer and the substrate, thus it should significantly improve the binding force between them.

Figure 3. Microstructure of coating and line scanning pattern: (a) surface morphology; (b) cross-section image; (c) distribution spectrum of Cobalt line scanning
2.3 Mechanical properties of as-sprayed coatings

2.3.1 Microhardness and fracture toughness

With a lamellar and compact structure, the optimized CoNiCrAlY-MoSi2 nanostructured coating is metallurgically bonded with the substrate. It exhibits low porosity (2.31±0.65%) and high fracture toughness (5.27 MPa·m$^{1/2}$, 50% higher than that of MoSi$_2$). The average values of microhardness is about 854.4±157HV$_{0.1}$[11].

2.3.2 Cycle oxidation behavior

The cycle oxidation kinetics curve of CoNiCrAlY–MoSi$_2$ coating measured under 500°C is displayed in figure 4a. The mass of the coating does not increase continuously in the process of oxidation. In other words, an incubation is needed for the linear increase and the incubation is about 36h. After oxidizing for 48h, the mass gain is substantially constant, the final mass gain is just 0.083mg/cm$^2$, indicating that the coating has good low-temperature oxidation resistance. Figure 4b shows that there is no “peesting” phenomenon occurring for the composite coating oxidizing at 500°C for 120h, indicating nano-composite coating can improve density and effectively suppress the low-temperature “peesting” phenomenon of MoSi$_2$.

![Figure 4. Oxidation kinetics curve of coating (a) and macrograph of coating before and after oxidation (b) [10]. (Note: Comparison sample is the original sample with coatings before oxidation.)](image)

2.3.3 Thermal shock behavior

Figure 5 shows the macrographs of coating surface after different thermal shock cycles. The initial sample surface was gray metallic luster, and there is no apparent unmelted particles. When the thermal shock cycle reach to 13 times, the sample surface begins to darken and a small area is peeling at the corners (figure 5b), which is due to larger stress concentration at the corners of rectangular specimen. Microcracks begin to appear in the center of specimens when the thermal shock testing recycled 18 times (figure 5c), and the crack gradually extended with increasing the number of cycles. When the testing is cycled 22 times, the coating is separated from the substrate and showed an apparent warp (figure 5d). Continued to cycle 27 times, large area peeling appears in the coating along the direction of crack propagation (figure 5e). Therefore, the thermal shock fracture initiation life of the CoNiCrAlY-MoSi$_2$ nanostructured coating is 18 times, thermal shock failure life is 27 times.
3. Ni60-TiB2 nano-composite coatings

Ni60–40wt.%TiB2 powders were prepared by mechanically mixing for 12 h. The nanocomposite feedstock powders were produced by ball milling the mechanically mixed powders for 5 to 40 h using a high energy planetary ball miller under argon atmosphere. The parameters of ball milling include the rotational speed of 400 rpm and ball/powder mass ratio of 10:1. The Ni60–TiB2 composite coatings were sprayed onto the 45 carbon steel substrates by HVOF thermal spray system (Metallisation MET-JET II). During the HVOF spray, propane and nitrogen were used as the fuel gas and the powder carrier gas, respectively. The spraying parameters were detailed in Ref.[13].

3.1 Microstructures of the starting powders

The SEM micrograph of the mechanically mixed powders (figure 6a) presents the spherical shape of Ni60 spray powders and the small polygonal shape of TiB2 particles. These TiB2 particles may reduce the fluidity of mechanically mixed powders. Figure 6b shows the surface morphology of a single milled particle with spherical structure. It is clear that the milled particle is an aggregate composed of many smaller spherical particles with mean size of 50–100 nm. Figure 6c displays the cross-sectional microstructure of the as-polished ball milled powder. Obviously, the ball milled powders are composed of two regions with different contrast which were identified as γ-Ni metallic matrix (white region) and TiB2 ceramic reinforcing phase (dark gray region). The fine TiB2 ceramic reinforcing particles evenly dispersed in the γ-Ni metallic matrix.

Figure 7 [12] shows the XRD patterns of the Ni60-TiB2 powders milled for different time and the milling time dependence of the grain size for TiB2 in Ni60-TiB2 powders. The results shows that no new phase formed during the whole high-energy ball milling process and the milled powders exist in the form of polycrystalline structure composed of nano-sized grains.
3.2 Microstructure of as-sprayed coatings

Figure 8 shows the microstructure of the Ni60-TiB2 composite coatings by HVOF with mechanically mixed and ball milled powders, respectively named conventional and nanostructured composite coating. The nanostructured coating exhibits a compact and uniform structure. The fine TiB2 particles are homogeneously distributed in γ-Ni metallic matrix, as shown in figure 8a. However, the microstructure of the conventional coating is not uniform. Micro-sized TiB2 particles accumulated around the γ-Ni metallic matrix and are separated by the γ-Ni lamellae (figure 8b).

The bright field image in figure 9a presents a uniform, nanoscale microstructure of the composite coating. With an average value of about 45.7 nm, the maximum grain size is around 72.4 nm. As shown in figure 9b, the diffraction patterns are also typical polycrystalline rings which are characterized the crystallographic plane diffractions of γ-Ni and TiB2. It is evident that the nanostructure characteristics of both metal matrix γ-Ni and ceramic reinforcement particles TiB2 were successfully preserved during HVOF spraying.

3.3. Mechanical properties of as-sprayed coatings

3.3.1. Microhardness and fracture toughness

Table 1 shows the results of average porosity, roughness, microhardness and fracture toughness of the Ni60-TiB2 composite coatings. Low porosity was obtained in the nanostructured coating, agreeing well with the microstructure shown in figure 8. The microhardness and fracture toughness of the nanostructured coating are also higher than those of the conventional coating. They are increased by 84.2% and 62%, respectively. The reason for property improvement can be attributed to the microstructural homogenization, grain refine strengthening and dispersion hardening of the nanosized...
TiB$_2$ particles in the composite coating sprayed by HVOF using ball milled powders.

**Table 1. Properties of the Ni60-TiB$_2$ composite coatings prepared by HVOF**

| Coating type   | Porosity (%) | Microhardness (HV$_{0.3}$) | Fracture toughness (MPa.m$^{1/2}$) | Roughness (μm) |
|----------------|--------------|----------------------------|-----------------------------------|----------------|
| Nanostructured | 0.96±0.18    | 1102±43                    | 3.5±0.2                           | 2.8±0.2        |
| Conventional   | 1.18±0.25    | 680±109                    | 1.9±0.4                           | 3.6±0.3        |

3.3.2. Sliding wear behavior
Average sliding wear coefficients under different applied loads are presented in figure 10 for nanostructured and conventional coatings. Obviously, the coefficient of the nanostructured coatings decrease with increasing applied load, while the sliding wear coefficient of the conventional coating first increases and then decreases with increasing applied load. Figure 11 displays the average volume loss of the two different types of coatings increases with increasing applied loads. It is clear that the nanostructured coating has better dry sliding wear resistance than the conventional coatings.

![Figure 10. Sliding friction coefficient of Ni60-TiB$_2$ composite coatings under different applied loads.](image)

![Figure 11. Variations of wear rate of Ni60-TiB$_2$ composite coatings under different applied loads.](image)

3.3.3. Cycle oxidation behavior
Figure 12 [13,14] presents the cycle oxidation kinetic curves of two types of composite coatings at 600°C and 800°C in static air. As expected, the cycle oxidation mass gain of the nanostructured composite coating is less than that of conventional composite coating. Both cycle oxidation kinetic behaviors of the composite coatings approximately follow the parabolic law. This indicates that the oxidation process is controlled by the diffusion mechanism. The oxidation rate constant of the nanostructured composite coating is about 1 order of magnitude lower than that of the conventional coating, which indicates that the nanostructured coating has better cycle oxidation resistance than conventional coating.

![Figure 12. Cycle oxidation kinetics of the Ni60-TiB$_2$ composite coatings [13,14].](image)
Figure 13 shows the cross-sectional microstructure of the composite coatings oxidized at 800°C. An adherent and thin oxide film with no crack formed on the nanostructured composite coating, which is reasonable for the low oxidation mass gain during cycle oxidation. For the conventional coating, the oxide film is mainly composed of TiO₂ [15] and is thicker than that of the nanostructured coating.

4. Summary
The synthesis and characterization of the nanostructured feedstock powders prepared by high energy ball milling and the nano-composite coatings prepared by plasma spray and HVOF are introduced. The results show that mechanical milling can be effectively used to synthesize nanostructured powders. The milled powders exist in the form of polycrystalline structure composed of nano-sized grains with the hard phase (nano-MoSi₂ or nano-TiB₂) uniformly dispersed in (CoNiCrAlY or NiCr) binder phase matrix. The prepared feedstock exhibits spherical morphology, uniform particle size and good thermal stability, which is expected to be used directly thermal spraying after sieving slightly.

Using nanostructured powders as feedstock powders, CoNiCrAlY-MoSi₂ and Ni60-TiB₂ nano-composite coatings have been successfully prepared and have shown improved performance. The as-sprayed nanostructured coatings are metallurgically bonded with the substrate and have compact structure and low porosity. CoNiCrAlY-MoSi₂ nanostructured coatings with a lamellar and compact structure exhibit low porosity, high fracture toughness and excellent thermal shock resistance, and the “pesting” phenomenon of MoSi₂ does not occur. The Ni60-TiB₂ nanocomposite coating exhibited better mechanical properties and wear-corrosion resistance than those of its conventional counterpart. Available experimental evidence suggests that nanostructured coatings have strong technological potential, and rapid industrial growth is expected over the next decade.

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