Microstructure, fatigue strength and erosion resistance of MAX-phase embedded Ti-Si-B nanostructured coatings on Ti-6Al-4V

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Abstract. Ti-Si-B nanostructured coatings were deposited on Ti-6Al-4V substrates by vacuum plasma processing with droplet separation. A composite Ti-Si-B cathode fabricated by self-propagating high temperature synthesis with subsequent hot pressing was used. The microstructure and mechanical properties of the obtained coatings were analysed by applying Auger-electron spectroscopy, X-ray diffraction and scanning electron microscopy methods accompanied by hardness measurements, fatigue strength and erosion resistance testing. It was established that Ti-Si-B nanostructured coating deposition leads to significant improvement of fatigue strength and erosion resistance of Ti-6Al-4V. A noticeable raise of the fatigue strength is attributed to presence of low dispersed Ti₃SiB₂ MAX-phase inclusions that suppress fatigue crack propagation.

1. Introduction

Ti-Si, Ti-Si-B, Ti-Si-C, Ti-Si-B-N and a wide range of other alike binary, ternary, quaternary and quaternary boride, nitride, carbide, carbonitride etc. systems have been extensively investigated for more than two decades, see [1–8] and references cited therein for recent trends in materials microstructure, phase and chemical compositions and manufacturing techniques. These materials demonstrate outstanding thermal stability, wear and high temperature oxidation resistance and therefore are considered as primary candidates for synthesis of advanced coatings capable of increasing the lifetime of cutting tools and/or improving their operational parameters (service properties).

Studying the microstructure and properties of advanced nanostructured ternary and quaternary Ti-based coatings originated from [1, 3, 8]. Hard coatings with microhardness of more than 40 GPa obtained there possess nanocrystalline microstructure with grain size ~2–5 nm and extremely low dry friction [8]. Along with atomic force microscopy the microstructure, chemical and phase composition of the coatings were analysed by Auger-electron spectroscopy (AES), transmission and scanning electron microscopy, (TEM) and (SEM), respectively, and X-ray diffraction (XRD).

A 3–4 µm thick Ti-Si-B coating was deposited by magnetron sputtering using composite targets produced by self-propagating high-temperature synthesis (SHS) [7, 8]. Being coupled with hot isostatic pressing (HIP) SHS provides a cost-effective opportunity of manufacturing dense sputter
cathodes of complex chemical compositions that can hardly be synthesised by employing other techniques [8].

Following the experimental work conducted in [3–5] and analytical tools applied there we have extended the developed method to vacuum plasma deposition of Ti-Si-B nanostructured coatings on Ti-6Al-4V alloy that is used for manufacturing of compressor blades of modern gas turbine engines. In contrast to industrial cutting tool applications a few essential prerequisites need to be matched to qualify the proposed approach for use in such a demanding area:

- A coating with high strength, fracture toughness, erosion resistance and fatigue performance while capable of withstanding oxidation and corrosion environment at wide range of temperatures is necessary. A Ti-Si-B nanostructured coating with embedded MAX phase inclusions is a promising option that fits this criteria;
- Harsh operational conditions require protective coatings with increased thickness of up to 20–25 µm;
- Vacuum plasma processing with droplet separation and ion beam assisted deposition (IBAD) of the coating is prescribed by the required high deposition rate, moderate production cost and environmental sustainability of the developed technology.

2. Materials and methods

Nanostructured Ti-Si-B coatings are deposited on test samples and high pressure compressor blades of a gas turbine engine made of Ti-6Al-4V industrial Ti-based alloy (Ti-6Al-4V). Exact chemical composition of Ti-6Al-4V alloy is provided in table 1. Ti-Si-B cathode for vacuum plasma processing of the samples was manufactured by SHS synthesis of Ti, Si and B powder mixture at T = 1500 °C in argon atmosphere with subsequent HIP treatment. The chemical composition of the cathode is Ti-15 mas. % Si-12 mas. %.

Table 1. Ti-6Al-4V alloy chemical composition.

| Fe  | C    | Si   | V    | N    | Ti   | Al   | Zr   | O    | H    | other |
|-----|------|------|------|------|------|------|------|------|------|-------|
| < 0.3 | < 0.1 | <0.15 | 3.5 - 5.3 | < 0.05 | base | 5.3 - 6.8 | < 0.3 | < 0.2 | < 0.015 | < 0.3 |

Ti-Si-B coatings were deposited in a trial sputter deposition rig. An experimental arc sputter with arched magnetic field and a combined universal source of fast neutral molecules coupled with argon beam sputter was employed. Prior to coating deposition substrate surfaces were cleaned by argon molecular beam followed by 10 minute pulse arc ion implantation of cathode constituent components at accelerating voltage of 25 kV, 0.1–1 mA/cm² current density in a pulse and 30 Hz pulse frequency. During Ti-Si-B coating deposition the substrates were negatively biased to 400 V. Processing of the samples for fatigue tests was performed at continuous rotation of the substrates. The compressor blades remained stationary during treatment. Only one side of the blades was plated.

The thickness of the deposited coatings varies from 1 to 8 µm depending on process duration. Cutting-off EDM was employed to make 15×5 mm² test samples from the compressor blades for coating thickness measurements that were performed by optical microscopy (OM). The same samples were used for hardness testing. Along with microstructure analysis, phase and chemical composition of the obtained coatings and near-surface layers of the substrates were studied by applying AES, SEM, XRD and OM in polarized light. Fatigue samples were tested in air at room temperature and 2800–3000 Hz alternate loading frequency. Erosion resistance of the coatings was studied by employing MAI erosion test rig.

3. Result and discussion

The microstructure of the 2 µm deposited Ti-Si-B coating and adjacent surface layers of the processed high pressure turbine blade is shown in figure 1. It was found that the deposited coating replicates all notches, scratches and other imperfections of the substrate surface. The obtained 20 µm thick modified surface layer consists of two easily distinguished sub-layers. Top 1–6 µm thick deposited X-ray
amorphous layer produces two broad halos on XRD spectra, figure 2, at $30^\circ < 2\theta < 50^\circ$ and $60^\circ < 2\theta < 80^\circ$ that might reflect presence of Ti$_3$SiB$_2$, Ti$_5$Si$_3$ and TiB$_2$ phases. Formation of 8–12 $\mu$m thick sub-layer underneath can be attributed to SHS process at the substrate surface during coating deposition. Noticeable heat release and temperature increase above $\alpha \rightarrow \beta$ transition temperature followed by rapid cooling and quenching of high temperature microstructure after the end of the coating deposition. Possible SHS occurrence during ion beam treatment was pointed out a few decades ago. However, up to now it was impossible to initiate SHS process because of low current density during ion implantation (typically 10–100 uA/cm$^2$).

**Figure 1.** The microstructure of the surface layer of high pressure compressor blade made of Ti-6Al-4V industrial Ti alloy after deposition of Ti-Si-B coating by vacuum plasma processing.

**Figure 2.** XRD spectra of the surface of the compressor blade made of Ti-6Al-4V industrial Ti alloy before and after deposition of Ti-Si-B coating by vacuum plasma processing.

**Figure 3.** A fragment of AES spectra of the Ti-Si-B coating deposited on Ti-6Al-4V substrate by vacuum plasma processing. Position and shape of Ti peaks indicate presence of Ti$_3$SiB$_2$ MAX phase in the surface layer.
The results of fatigue and erosion tests of Ti-6Al-4V samples with deposited Ti-Si-B nanostructured coatings are provided in tables 2 and 3, respectively. Noticeable improvement of the service properties is apparent. Ti-6Al-4V samples with the deposited coatings have higher fatigue limit. The number of cycles to rupture of Ti-6Al-4V samples with 6 µm thick Ti-Si-B coating in fatigue tests exceeds that of the samples without coating by two orders of magnitude.

**Table 2.** Results of fatigue tests at 25 °C in air.

| Sample № | Coating thickness, µm | Number of cycles | Fatigue limit, MPa |
|----------|-----------------------|------------------|--------------------|
| initial  | n/a                   | 2x10⁷            | 250±20             |
| 1        | 1                     | 1.9x10⁸          | 350                |
| 2        | 1                     | 3x10⁵            | 372                |
| 3        | 4                     | 3.8x10⁷          | 367                |
| 4        | 4                     | 1.2x10⁷          | 382                |
| 5        | 5                     | 9.3x10⁵          | 371                |
| 6        | 5                     | 3.6x10⁷          | 390                |
| 7        | 6                     | 2x10⁹            | 387                |
| 8        | 6                     | 1.1x10⁹          | 390                |

**Table 3.** Results of erosion tests (blasting with 80 µm quartz particles; particle speed is 200 m/s with normal incident angle; erosion exposure of duration is equal to 30 s).

| Sample № | Coating thickness, µm | Material loss, µm |
|----------|-----------------------|-------------------|
| initial  | n/a                   | 3.5               |
| 1        | 1                     | 1.2               |
| 2        | 1                     | 1.0               |
| 3        | 4                     | 0.8               |
| 4        | 4                     | 0.9               |
| 5        | 5                     | 1.0               |
| 6        | 5                     | 0.8               |
| 7        | 6                     | 1.1               |
| 8        | 6                     | 1.0               |

**Figure 4.** SEM image of Ti-6Al-4V sample with deposited 8 µm thick Ti-Si-B coating after fatigue test.
4. Conclusion
Ti-Si-B nanostructured coating with embedded Ti$_3$SiB$_2$ MAX-phase inclusions has been deposited on Ti-6Al-4V by vacuum plasma processing with droplet separation. It has been found that along with the coating deposition the modified subsurface layer is formed by SHS heating and subsequent quenching. A comprehensive study of the microstructure and mechanical properties of the obtained system has been carried out by AES, SEM, OM and XRD techniques accompanied by hardness measurements, fatigue strength and erosion resistance testing. It has been established that deposition of the ternary Ti-Si-B nanostructured coating with embedded low dispersed Ti$_3$SiB$_2$ MAX-phase inclusions.

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