Microstructure and Phase Composition of NiCrBSi-TiB₂
Vacuum Furnace Fused Flame-Sprayed Coatings

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Abstract. Several studies have revealed that NiCrBSi reinforced with different intermetallic compounds exhibits characteristics that allow the material to be successfully used as a thermally sprayed coating for applications that require wear and corrosion protection. One of such materials is TiB₂, as it has an elevated melting point, high elasticity modulus, increased hardness and good thermal stability. NiCrBSi was mechanically mixed with 5%, 10%, 15% and 20% vol. TiB₂, flame sprayed and subsequently fused in a vacuum furnace. A remelting process under controlled atmosphere offer important advantages like good gas extraction and precise adjustment of temperature. The best performing batch of samples were selected for further analyse of microhardness and porosity measurements. The experimental results show that the thermal cycle created with the aid of the data offered by differential thermal analysis lead to a reduced porosity without affecting the hardness. X-ray diffractometry was used to characterize the phase composition while scanning electron microscopy was employed to investigate the microstructure and phase distribution. Further theoretical aspects regarding the influence of the phase composition on the coatings properties, like hardness or sliding wear conclude the work.

1. Introduction
Patented in 1909 by the Swiss inventor Max Ulrich Schoop [1], thermal spraying developed as a widely used technology in applications like heat exchangers, extruders, pistons, pipes or laminators [2-4]. The research in the area of Ni-based alloys began almost five decades ago [5] and shows that this type of materials can be used for a large range of technologies like flame spraying [6], Atmospheric Plasma Spray (APS) [7] or High Velocity Oxy Fuel (APS) [8].

Among the most well-known Ni-based alloys is NiCrBSi, a material used with industrial applications in respect of wear and corrosion protection [9-11]. Regarding its chemical composition, Ni as the main element influences the alloy’s mechanical properties, mainly its ductility and hardness. The role of Cr is to improve the corrosion resistance while B and Si lowers the melting temperature of the material [12]. The content of B helps improving the hardness. One of the possible reinforcements for the Ni-based alloys is TiB₂, which because of its characteristics, is a suitable candidate for thermal spraying depositions. This material exhibits a high hardness, 3460 HV, low density, 4.52 g cm⁻³, and an excellent resistance to oxidation, which goes up to 1000°C [13].
The NiCrBSi thermally sprayed products show moderate adhesion to the substrate, relatively high porosity and unwanted trapped gasses in the coatings [14]. A fusing process is therefore necessary to enhance the characteristics of the depositions and mitigate the above mentioned defects. Besides the properties previously described, B and Si also reduce the melting interval of the alloy [12], which has a positive impact for the coating post-treatment. Vacuum furnaces have recently started to be applied for such post-treatments as they offer reproducibility, the possibility of maneuvering products with complex geometries and a relative low cost with a short recoupment period [15].

The aim of the research work was to investigate the microstructure and phase composition of NiCrBSi-TiB₂ flame sprayed and vacuum fused coatings. NiCrBSi powder was mechanically mixed with TiB₂ in different volumetric concentrations, flame-sprayed and post-fused. Powder analysis, heat-treatment, microhardness measurement, porosity calculation, microstructure and phase composition examinations were all considered in the elaboration of the present work.

2. Experimental procedure

The Ni-based alloy was provided by Karl Schumacher GmbH and the NiCrBSi-TiB₂ powder was deposited on an S355JR carbon steel with 0.22% C and 1.6% Mn at the same German company. A successful deposition on a widely used steel in industry will offer the coating a larger applicability.

2.1. Feedstock powder and methods for characterisation

As one can see, Figure 1(a) shows the SEM micrograph of the NiCrBSi mixed with TiB₂. The spheroidization of Ni-based powder produced through water atomization helps the flowability through the spraying equipment. The EDX spectrum in Figure 1(b) shows the main element Ni, the hard carbide forming element Cr and Si, which promotes the wettability of the coating during deposition. The spectrum in Figure 1(c) shows Ni and the hard element Ti. The chemical composition and the size ranges of the two powders can be found in Table 1. Four sets of mechanically mixed powder with 5% (NTB5), 10% (NTB10), 15% (NTB15) and 20% (NTB20) vol. TiB₂ were prepared.

Figure 1. SE micrograph (a) of the NiCrBSi-TiB₂ mechanically mixed powder along with two EDX spectra demonstrating the chemical composition of the (b) NiCrBSi and (c) TiB₂ powder.

| Table 1. Chemical composition and size range of the NiCrBSi and TiB₂ powder |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| NiCrBSi         | bal.| 6   | 1   | 4   | 1.5 | 0.3 | 45-106 |
| TiB₂            | bal.| min. 30 | max. 0.1 | 0.5 | max. 1.1 | 6.5-10 |

Ni, titanium, chromium, boron, silicon, iron, carbon, oxygen, size range in µm. 

2.2. Coating deposition and remelting
A careful thermal analysis of the powder was performed with a Netzsch STA 449F1 instrument. The DTA curve shows that all the examined powders exhibit a similar melting temperature at about 1030°C. This result has to be taken into account when selecting the fusion cycle as a temperature close to the melting point provides a densification of the coating without spilling it [16]. The surface was activated through grit blasting prior the deposition, this being a highly recommended step for a good adherence of the coating [17]. The fusion of the deposition was realised in a HITERM 80-200 vacuum furnace. Figure 3 represents the performed heating cycle which lasted a total of 288 min. with a maximum heating temperature of 1090°C with a holding time of 45 min. The ramps were set up to avoid changes during the heating and cooling steps that could have induced stress or cracks.

![Figure 2. DTA curve highlighting the liquidus temperature of the NiCrBSi and NTB powders.](image1)

![Figure 3. Vacuum furnace heating cycle of the as-sprayed samples.](image2)

2.3. Sample microhardness measurement and porosity calculation
The improvement of the post-treatment of the applied coatings was done considering the porosity and the microhardness of the samples. The porosity of the coatings was calculated on five different regions on micrographs using the image analysis software ImageJ. The microhardness tests were performed on the coating region at a load of 0.3 kgf using a Zwick/Roel ZHVµ-S machine.

2.4. Microstructure and phase composition
The quality of the coating was measured through several methods. The micrographs taken for the preliminary porosity calculation test were taken with a Leica DM-RME light microscope. The morphology, microstructure and chemical composition was studied using a Philips XL 30 SEM combined with EDX spectroscopy. The phase composition was determined using a Philips X'Pert X-ray diffractometer using a Cu K-α radiation source scattering the 2θ angle between 20° and 100°.

3. Results and discussions

3.1. Sample porosity and microhardness
The porosity level and the microhardness were chosen as the two eliminating criteria after the post-treatment of the samples. Both factors are commonly employed as excluding responses in thermal spraying [18,19] as they are directly influencing the mechanical properties of materials. Figure 4(a) represents an as-sprayed sample where a porosity level of approximately 25% in all coating batches prior the post-treatment process was measured. Figure 4(b) shows the post-fused NTB15 sample etched in a 3% HNO₃ solution. One can observe a drastic decrease of porosity, with an improved roughness, a good adhesion and no visible major defects. Porosity calculations of post-treated NTB5, NTB10, NTB15 and NTB20 can be consulted in Figure 4(c), Figure 4(d), Figure 4(e) and Figure 4(f). The NTB10 and NTB20 exhibited close mean values at 6.5±0.5% and 7.5±0.5%, respectively. The NTB5 and NTB15 performed better, showing average values of 1.5±0.5% and 0.8±0.5%, comparable
results to APS or HVOF processes. The decrease of porosity in the case of the fused samples may be attributed to the characteristics of the furnace to control and maintain the temperature, leading to the wetting of the surface offering a good gas extraction and void closure. The porosity of the coating is affected as well through the control of B and Si as they offer wettability [2] and act as fluxing agents.

Figure 4. Light microscopy micrographs in cross-section of the a) NTB15 as-sprayed coating, b) NTB15 post-treated coating and c) NTB5, d) NTB10, e) NTB15, f) NTB20 porosity measurements.

The microhardness of the deposited coatings was evaluated realizing seven imprints along the coating, the distribution being presented in Figure 5. The NTB10 and NTB20 coatings have both showed differences of over 30% between the extreme points of the measurement. The NTB5 coating exhibited a mean value of 225HV. The NTB15 samples showed smaller variations, the mean calculated value being 310HV. The variations of the measurements may be attributed to the different containing phases in the coating. The topography of a microindentation of the NTB15 sample presented in Figure 6 shows plastic deformation with no crack appearance, denoting a good phase bonding and low residual stresses.

Figure 5. Graph highlighting the variation of the HV0.3 microindentation along the coating.

Figure 6. HV0.3 microindentation of the NTB15 sample.
Considering the porosity of under 1% and the rather constant microhardness with crack-free imprints, the NTB15 post-fused coating was chosen to be further analysed regarding its microstructure and phase composition.

3.2. Microstructure and phase composition
The NTB15 sample presented in Figure 7 exhibits a heterogeneous distribution of the dark phases TiB$_2$ phases. The reason for a non-homogeneous distribution lies in the mixing process of the powders and the high melting temperature of TiB$_2$ [13] which resists to plastic deformation and solubility in solid solutions even at high temperatures [21]. An EDX spot analysis at the interface demonstrates diffusion of Ni into the substrate creating a metallurgical bonding instead of the commonly reached mechanical hooking [22], aiding the adhesion.

Figure 7. Cross-section SEM micrographs at lower magnification of the NTB15 sample.

Figure 8(a) shows four different regions with different chemical composition as detected by means of EDX spot analyses in Figure 8(b), Figure 8(c) and Figure 8(d). Corroborating the XRD spectra from Figure 9 with the EDX spot analyses, the matrix marked with b in Figure 8(a) mainly consists of the $\gamma$-Ni and BNi$_2$, similar eutectic phases being previously reported in Ni-based thermal sprayed coatings research [23-26]. Another component of the matrix is the $\sigma$-Cr$_3$Ni$_2$Si$_2$ phase, that can be found in the ternary Cr-Ni-Si diagram [27]. As previously reported by Schuster et al [28], the low Si content (4% in the present work) favours forming the $\sigma$ phase.

Figure 8. a) SEM micrograph of NTB15 sample along with the corresponding b), c), d), e) EDX spectra.
A confirmation that the heating cycle parameters were well chosen comes from the fact that it was not reached a temperature which transforms the Cr containing Cr$_3$Ni$_5$Si$_2$ hard phase into a Ni solution along with minor constituents [29]. Observing both EDX analysis XRD results, the region c in Figure 8(a) corresponds to the rest γ-Ni/BNi$_2$ phase. The area d on the SEM micrograph is represented by the hard TiB$_2$ phase which is expected to aid the wear resistance of the coating and partly the Ti$_3$O. The EDX spectrum of the e area is showing a diffusion at the interface between the matrix and the TiB$_2$. The diffusion process forms on the one side Ti$_3$SiC$_2$, conferring high temperature stability and high fracture toughness [30], and Ti$_2$FeNi. The crack free microindentations may be attributed to the presence of the ductile Ti$_3$SiC$_2$ phase which is binding the matrix and the TiB$_2$ particles together leading to a coating with low residual stresses. The Ti$_2$FeNi phase with the more known empirical formula FeNiTi$_2$ may be consulted in the ternary Fe-Ni-Ti diagram [27]. The data provided by Duarte el al [31] shows that the solid solubility of Ti in (Fe,Ni) varies in dependence with the Fe:Ni ratio and lowers with decreasing temperature.

As the maximum operating pressure of the furnace vacuum pump is 10$^{-6}$ mbar and the elimination of a large number of oxide and gases is successfully performed, Ti and Si have both according to the Ellingham diagram a high susceptibility of forming oxides until an oxygen partial pressure of about 10$^{-23}$ mbar [32] and the formation of Ti$_3$O and SiO$_2$ is therefore inevitable. Nevertheless, in the current case the presence of Ti$_3$O during sliding wear tests it is proved to activate a tribofilm on the contact surfaces, resulting a decrease of the wear rate and the friction coefficient of the tribological pair [33].

![Figure 9. XRD pattern of the NTB15 sample.](image)

4. Conclusions
Reinforcements and the improvement of self-fluxing alloys are a continuous topic in the coating industry. NiCrBSi-TiB$_2$ with 5%, 10%, 15% and 20% vol. concentration of TiB$_2$ have been successfully flame sprayed and vacuum furnace fused on a low alloyed steel. A coating with no visible major defects and a strong metallurgical bonded interface was obtained. Following the post-treatment process, considering the results of the microhardness tests and porosity measurements, the NiCrBSi-TiB$_2$ 85-15 was further analyzed. The microstructure exhibits a heterogeneous distribution of the TiB$_2$ in the coating. A complex structure, with a matrix mainly composed of γ-Ni and BNi$_2$ was observed. The hard TiB$_2$ particles are partly diffused in the matrix creating Ti-based phases which offer the coating ductile properties, resisting to deformations without generating cracks. Recent research show that the presence of Ti$_3$O might represent a positive aspect as during sliding wear tests it activates a tribofilm decreasing the wear rate of the tribological pair. Further research could be performed in the direction of examining the deposited coating in respect for their corrosion and wear behaviour.
5. References

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