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COMPOSITE HARDFACING COATING

RESEARCH ARTICLE

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Corresponding author:

Liudmyla Melakh liudmyla.melakh@taltech.ee

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Plasma-transferred arc-welded composite hardfacings with ZrB₂ and TiC reinforcements

Liudmyla Melakh^a, Andrei Surzhenkov^a, Kristjan Juhani^a, Mart Viljus^a, Rainer Traksmaa^a and Dmytro Vedel^b

- ^a Department of Mechanical and Industrial Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
- ^b Department of Structural Ceramics and Cermets, Frantsevich Institute for Problems of Materials Science, Omelyana Pritsaka 3, 03142 Kyiv, Ukraine

ABSTRACT

The traditional approach to prolonging the lifetime of wear parts is to use wear-resistant materials. One such material is hardfacing, which, in addition to its primary function, contributes to sustainability objectives by preventing the failure of wear parts and allowing them to be used more efficiently. The present study focuses on hardfacings that are free of critical raw materials (CRM) and are based on materials that are non-harmful to health and the environment, in line with the European Union policy on material supply chains, availability, and safety (REACH legislation). The present study used plasma-transferred arc welding (PTAW) to produce a 316L stainless steel-based hardfacing reinforced with non-CRM components ZrB₂ and TiC. Pre-applied mixtures of matrix powders and ceramic components on a soft S235 steel substrate were remelted using optimized PTAW parameters, specifically with a welding current of 115 A and 135 A and a linear torch velocity of 0.7 mm/s. Microstructure analysis and phase identification were conducted using the scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods on pre-prepared cross-sections. The Vickers hardness (HV) was measured under different indenter loads. Due to the interaction between the iron-based allow and ceramic components under PTAW, carbide-boride phases with a complex composition were formed, contributing to the increased hardness of the material. The highest hardness value (HV5) was observed in the hardfacing with the composition of (ZrB₂ + TiC) + 60 vol% 316L stainless steel, processed with a welding current of 135 A. These results demonstrate the potential for applying ceramic-reinforced stainless steel hardfacing in industrial applications.

Introduction

Due to their properties, 316L stainless steel-based materials reinforced with borides, nitrides, or carbides find practical application in various industries, where high demands are placed on corrosion resistance, wear resistance, and mechanical properties [1]. Introducing titanium or zirconium borides into the steel matrix increases hardness and elastic modulus and favorably affects the wear resistance of composites [2,3]. The growing interest in such systems is driven by the desire to improve material supply chains, the availability of critical raw materials (CRM) [4], and their safety (REACH legislation) [5], taking into consideration the health and environmental issues. The present study focuses on hardfacings that are free of CRM and are based on materials that are non-harmful to health and the environment. Using hardfacings supports sustainability by preventing the failure of wear parts and reusing them more efficiently. One effective method for making such materials is plasma-transferred arc welding (PTAW), which can extend the life of parts and reduce production time. Due to its high temperature, excellent arc stability, low thermal deformation of the workpiece, high cladding speed, and high energy exchange efficiency, this method can work with various materials, making it versatile for multiple industrial applications.

In the existing studies on the production of claddings based on a metal matrix with ceramic components, the focus is mainly on the synthesis of borides or carbides in the PTAW process and their influence on the mechanical properties of the resulting cladding. In [6], the interaction of iron with titanium and zirconium carbides under PTAW was investigated. It was shown that the use of metal oxides in PTAW leads to the formation of metal carbides. The formed structure consisting of small polygonal

Table 1. Characteristics of the powders used to fabricate the investigated composition

Powder (manufacturer)	Elements, wt%											Particle
	0	C/C _{free}	Cr	Ni	Mo	Si	Mn	Ν	Fe	ZrB ₂	TiC	size, µm
ZrB ₂ (H.C. Starck)	0.6	0.11/-	-	—	-	-	-	-	-	bal.	-	0.6–5.1
TiC (Pacific Particulate Materials Ltd.)	0.29	-/0.08	-	-	-	_	-	0.02	-	-	bal.	1–3
AISI 316L (Castolin Eutectic)	-	0.03/-	16.5-18.5	10-13	2.0-2.5	1.0	2.0	0.1	bal.	_	Ι	10-45

Table 2. Composition and cladding parameters

Sample grade	Composition, vol%	Current, A
115ZS	40 vol% ZrB ₂ +60 vol% 316L	115
135ZS		135
115ZTiS	$20 \text{ vol}\% \text{ ZrB}_2 + 20 \text{ vol}\% \text{ TiC} + 60 \text{ vol}\% 316\text{L}$	115
135ZTiS		135

or dendritic TiC or ZrC, which are uniformly distributed in the pearlitic matrix, results in improved abrasion resistance under low load abrasion. In [7,8], the interaction between zirconium, boron carbide, and iron resulted in a composite with inclusions of ceramic components in the form of boron carbide with better mechanical characteristics and wear resistance than the metallic component. A metal matrix composite hardfacing, reinforced with the ZrC–ZrB₂ phase, was successfully fabricated using an in-situ reaction of pre-applied mixed Zr, B₄C, and Fe powders by the gas tungsten arc welding (GTAW) cladding process [9]. The results show that the main phases of the composite coating produced by the GTAW process are ZrC, ZrB₂, and α -Fe, which also lead to higher hardness and better wear resistance of the produced hardfacing.

This work aimed to obtain wear-resistant hardfacing by PTAW, based on 316L stainless steel, and investigate the effect of TiC and ZrB_2 ceramic phases on the structure and hardness of hardfacing.

Materials and methods

The studied materials were produced using the following powders: ZrB_2 , TiC, and stainless steel AISI 316L. The substrate used was steel S235. Table 1 presents the characteristics of the raw powders used in the work.

The powders were ball milled in a horizontal ball mill for 72 hours, with a balls-to-powder ratio of 20:1, using isopropyl alcohol as the medium. A ball mill with a WC–Co lining and WC–Co balls as the milling media were used. The particle size after ball milling was averaged up to 2 μ m.

Two compositions were used in this study: $ZrB_2 + 60 \text{ vol}\%$ 316L and $(ZrB_2 + TiC) + 60 \text{ vol}\%$ 316L. A 6 wt% solution of paraffin in petrol was used as a binder to prepare the powderbased suspension, which was applied onto a substrate steel. These samples were dried in a vacuum for 30 minutes at a temperature of 310 °C. PTAW was performed using a EuTronic Gap 3001 DC (Castolin Eutectic) with a tungsten electrode (\emptyset 2.4 mm) to remelt the applied suspension layer. The cladding parameters were as follows: cladding current 115 A and 135 A, linear velocity of the plasma torch 0.7 mm/s, oscillation frequency 0.6 Hz, direction of oscillations perpendicular to the cladding speed vector, and square oscillation wave. The selection of parameters for the cladding was based on the knowledge obtained from previous experiments.

The marking, modes, and composition of mixtures are presented in Table 2.

Compact specimens were cut and subjected to standard metallographic preparation. The microstructure and elemental analysis of the obtained materials were examined using a Zeiss EVO MA15 scanning electron microscope (SEM) with an INCA energy-dispersive X-ray spectroscopy (EDS) device. Phase analysis was conducted using the Rigaku Smartlab with Cu-k α radiation. Hardness measurements were carried out using Indentec 5030 KV and Micromet 2001 with the Vickers pyramid at an indenter load of 0.5, 5, and 30 kg (4.9, 49.1, and 294.3 N, respectively) with a dwell time of 10 seconds.

Results and discussion

X-ray diffraction (XRD), SEM analysis, and an investigation of mechanical properties were conducted in the cladding sections of the samples' central part.

Figure 1 shows the results of the X-ray phase analysis of the obtained materials. It was determined that the composites of both compositions mainly consist of iron-based phases (strong lines in diagrams). Weak lines were identified as $Fe_{2}B$, $Cr_{v}Fe_{v}C_{z}$ (or $Fe_{v}C_{v}$) phases, $Fe_{v}Zr_{v}$, and ZrC in small amounts. However, zirconium boride and titanium carbide phases were not observed in the diffractogram, which may be due to their low concentration or small grain size in the matrix. This phenomenon is discussed in detail in the work of Bhaskar et al. [10]. In the study by Yöyler et al. [11], which involved the formation of Fe-based cladding and in-situ synthesis of TiC using the plasma-arc cladding method, identifying the carbide phases through XRD analysis proved to be challenging. A typical microstructure of the cladding is shown in Fig. 2. Comparison of the microstructures revealed two different areas within the matrix (grey and dark grey) and the presence of reinforcing components (white and black). ZS cladding is generally characterized by the uniform distribution of the reinforcing phase in the matrix, which provides dispersed strengthening of the material; also, borides tend to be located along the grain boundaries of the steel







Fig. 2. Microstructure (SEM) of ZrB_2 + 60 vol% 316L and (ZrB_2 + TiC) + 60 vol% 316L under different PTAW parameters.

matrix. Materials marked ZTiS have a coarser grain structure, and ceramic particles are located both along the boundaries and inside the grains. As a result, cladding formation at a current of 135 A forms a wider remelting zone for both compositions of the investigated claddings.

Figures 3 and 4 show the results of the EDS analysis with the distribution of the main elements (wt%). The microanalysis data show that the resulting material is a matrix with a high iron content. The data further indicate the presence of key alloying elements, such as chromium and nickel, and a

79.44

2.91

10.03

6.62

thin phase of similar composition but with a high content of boron and carbon. The observed increase in boron and carbon content can be attributed to the diffusion of these elements into the steel matrix due to the partial dissolution of ZrB2 and TiC particles [12]. Carbon and boron in the matrix suggest the possible formation of carbide and boride phases, such as Fe₃B or Fe₃C. It can be assumed that at the initial stage of PTAW, ZrB₂ reacted with Fe, Cr, and formed the (Fe, Cr)₂B phase. The interaction process between ZrB₂ and steel alloy is described in detail by Zhunkovskii et al. [13]. Further temperature increase leads to eutectic melt formation between Fe₃B and Fe at 1177 °C. During the crystallization process, the remaining ZrB₂ was uniformly distributed in the liquid phase, whereas its particles served as the centers of crystallization due to the highest melting temperature (3000 °C). The next crystallized phase was ferrite (α -Fe) due to the second-highest melting point (1538 °C). A eutectic microstructure (Fe₂B-a-Fe) trace was observed at the grain boundaries because it crystallized last.

These phases are usually formed during high-temperature processing and contribute to the material's hardness and wear resistance [14].

White-colored grains correspond to zirconium boride or similar phases containing insignificant amounts of iron (Fig. 3). In addition, significant amounts of zirconium, carbon, and, in some cases, boron can lead to the formation of eutectics based on zirconium carbide or carboboride and iron-based phases (Fig. 3, point 3). Tungsten was found in the white phase in the 2–3% range, due to contamination of WC–Co grinding

> **4** 30 μm

> > Ni

0.50

0.80

0.20

2.60

Fig. 3. Microstructures and corresponding EDS analysis of ZrB₂ + 60 vol% 316L cladding.

115ZS								135ZS 1 2								
<u>30 μm</u>								-	1.	Y	;	1	30			
	Zr	В	С	Fe	Cr	Ni	1		Zr	В	С	Fe	Cr			
1	—	—	2.01	95.79	1.30	0.90		1	_	4.21	5.21	89.48	0.40			
2	77.10	18.70	0.70	3.50	-	-		2	86.90	7.70	0.90	4.40	0.10			
3	35.00	-	5.90	56.60	0.50	1.20]	3	17.62	12.61	10.41	58.06	0.50			

4

8.51

6.71

81.28



Fig. 4. Microstructures and corresponding EDS analysis of $(ZrB_2 + TiC) + 60 \text{ vol}\% 316L$ cladding.



Fig. 5. Vickers hardness of the surface and base of the materials under study with a load on the indenter of 5 kg.

balls during mixing. The dark and white dots (Fig. 4, points 2, 3) represent a solid solution with a complex composition based on Ti and Zr.

Figure 5 presents the average hardness values of the resulting cladding and substrate at an indenter load of 5 kg. The substrate exhibited hardness values ranging from 133 to 181, which are 1.3 to 1.7 times lower than those of the cladding. The 135ZTiS material demonstrated the highest hardness of all the materials investigated under different loadings. Thus, at an indenter load of 0.5 kg, its hardness was 367 ± 40 , and at 30 kg it was 332 ± 16 . It was also observed that increasing the indenter load resulted in only slight changes in the hardness of all investigated materials. This behavior suggests that the material has good resistance to indenter penetration under load, likely due to the presence of hard ceramic components.

Conclusions

The effect of ZrB_2 and TiC ceramic additives on the properties and microstructure of metal matrix claddings produced by PTAW was investigated. The following conclusions can be drawn from the results obtained:

- The interaction between ceramic components and stainless steel formed a relatively homogeneous iron-based structure containing complex carbide and boride phases. This has led to an increase in the hardness of the cladding.
- The hardness values of the hardfacing containing 20 vol% ZrB₂ + 20 vol% TiC were higher than those of the cladding containing only 40 vol% ZrB₂.
- 3. The maximum hardness was obtained for the ZTiS composition at a current of 135 A.

Data availability statement

All research data are contained within the article and can be shared upon request from the authors.

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Plasmapeale
sulatuse teel valmistatud $\rm ZrB_2$ ja TiC-ga tugev
datud komposiitkõvapinded

Liudmyla Melakh, Andrei Surzhenkov, Kristjan Juhani, Mart Viljus, Rainer Traksmaa ja Dmytro Vedel

Tööriistade ja masinaosade kulumise vähendamiseks kasutatakse traditsiooniliselt kulumiskindlaid materjale. Uurimistöö ülesanne lähtub Euroopa Liidu säästva majanduse, tarneahelate kindlustamise ja keskkonnahoiu eesmärkidest, mille kohaselt tuleb loobuda kriitiliste toorainete (CRM) kasutamisest ning eelistada keskkonna- ja tervisesõbralikke materiale vastavalt REACH määrusele. Seetõttu uuritakse töös kriitiliste toorainete vabade, plasmapealesulatuse (PTAW) teel valmistatud kõvapinnete struktuuri ja kõvadust. Uuriti 316L roostevaba terase baasil valmistatud kõvapindeid, milles tugevdava faasina kasutati tsirkooniumboriidi (ZrB₂) ja titaankarbiidi (TiC). S235 terasest alusmaterjalile kanti eelnevalt ette valmistatud pulbrisegu, mis koosnes terasmaatriksist ja keraamilistest lisanditest, ning sulatati ümber optimeeritud PTAW-režiimide alusel, kasutades keevitusvoole 115 A ja 135 A ning elektroodi lineaarse liikumise kiirust 0,7 mm/s. Mikrostruktuuri analüüsiks ja faaside tuvastamiseks kasutati skaneerivat elektronmikroskoopi (SEM) ja röntgendifraktsiooni (XRD) ning analüüs teostati pinnete ristlõigetelt. Valmistatud kõvapinnete Vickersi kõvadus (HV) määrati erinevate indentorile rakendatavate koormustega. Uuringust selgus, et rauapõhise sulami (316L) ja keraamiliste komponentide koos- toime tulemusena tekkisid plasmapealesulatuse käigus karbiid-boriidkoostisega faasid, mis tagavad kõvapinnete suurenenud kõvaduse. Suurim Vickersi kõvadus (HV5) saavutati kõvapindel koostisega (ZrB₂ + TiC) + 60 vol% 316L roostevaba terast, mis oli valmistatud keevitusvoolu 135 A abil. Tulemused näitavad, et uuritud keraamilise faasiga tugevdatud roostevabast terasest kõvapinded omavad tööstuslikes rakendustes kasutamise potentsiaali.