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MECHANICAL PROPERTIES AND MICROSTRUCTURE OF VACCUM PLASMA SPRAYED Cr_3C_2 – 25(Ni20Cr) COATINGS

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Summary:

This paper analyzes vacuum plasma spray VPS - Cr_3C_2 - 25(Ni20Cr) coatings. Commercial powder marked Sulzer Metco Woka 7205 is used. The powder is deposited with a plasma gun F4 at a distance of 340 mm from the substrate. The main objective of the study was to eliminate, at the reduced pressure of inert gas Ar, the degradation of primary Cr_3C_2 carbide into $Cr_{23}C_6$ carbide which significantly reduces the microhardness and mechanical properties of the coating. The coating is deposited with a thickness of 100 - 120 µm on a steel substrate. The microhardness of the coating was tested by $HV_{0.3}$. The microhardness values were in the range of 1248 - 1342 $HV_{0.3}$. The bond strength of the coating was tested by tension. It was found that the bond strength between the substrate and the coating has a value of 89 MPa. The microstructure of the coating was tested by the light microscopy technique. The structure of the coating consists of an NiCr alloy base with a dominant primary Cr_3C_2 carbide phase. In addition to the Cr_3C_2 phase, the Cr_7C_3 phase is also present. The coating etching was done with the reagent 1HNO_3 : 4HCl : 4H_2O that primarily dissolves nickel to *enable the distribution of the carbide phase to be clearly seen in the coating. Etching the coating with this reagent revealed the presence of the largely undegraded primary Cr_3C_2 carbide phase which provides high hardness values to the coating.*

Key words: *vacuum, substrates, strength, property, phases, microstructures, microhardness, mechanical properties, coatings, carbides.*

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Introduction

Vacuum plasma spraying (VPS) is usually referred to as LPPS due to low pressure. At low pressure, a plasma jet becomes longer and smaller in diameter and with the use of convergent / divergent nozzles it has a higher rate of ions. Eliminating oxygen in the chamber and a possibility to preheat the substrate enable the creation of denser coatings with higher tensile bond strength and without the oxide content. For high performance applications, plasma spraying is carried out in a vacuum chamber at a reduced pressure of inert gas Ar. The vacuum plasma spray process (VPS) produces high-quality coatings, especially those sensitive to oxygen. One such coating is a cermet coating - Cr_3C_2 - 25(Ni20Cr) sensitive to oxygen due to the reaction of carbon from the carbide with the oxygen from the surrounding atmosphere. The VPS application process prevents the decarburization of the primary Cr_3C_2carbide, so that coatings of high hardness are deposited. Traditionally, these coatings were deposited by APS and HVOF processes. In the last decade, a number of researchers have published results concerning the structure and properties of the deposited coatings by the HVOF process (Guilemany, et al., 2006, p.2998), (Guilemany, et al., 2002, p.207), (Ji, et al., 2006, p.6749), (Li, et al., 2005, p.229), (Picas, et al., 2006, p.477). In this process, as in the APS process, the main problem was the loss of carbon during deposition. The results clearly show that the major loss of carbon occurs during the process of depositing particles due to the surrounding atmosphere. It was also found that the initial size of carbide powder particles have a significant impact on the carbon loss during the deposition of Cr_3C_2 - 25(Ni20Cr) coatings in the HVOF process (Li, et al., 2002, p.137). In VPS coatings, the dominant phase is the Cr_3C_2 carbide phase with a hardness of 1600HV and a less significant phase is the Cr_7C_3 phase with a hardness of 1300HV (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699-704). In the coatings there is no the $Cr_{23}C_6$ carbide phase with a hardness of 1000HV, which, in APS and HVOF carbide coatings, reduces the coating hardness. Tomita, T. and other researchers have found that the 75Cr_3C_2 - 25(Ni20Cr) coating deposited by the VPS process has a higher hardness than the coatings deposited by APS and HVOF processes (Tomita, et al., 2001, pp.699–704). The hardness of the VPS Cr_3C_2 - 25(Ni20Cr) coating is HV1243 ± 80, which is much higher than the one of HVOF coatings with a hardness of HV958 ± 44 (Tomita, et al., 2001, pp.699–704). The tensile bond strength of the coating deposited by the VPS process is greater than 80 MPa with a porosity content of less than 5% (ASM Metals Handbook, 1987, p.367). Cr_3C_2 - NiCr plasma spray coatings have a high resistance to abrasive wear and a low friction coefficient, from room temperature to 850°C, due to their high thermal stability and resistance to oxidation

(Guilemany, et al., 2006, p.2998). These deposits are extensively used for coating parts and components for energy conversion, such as steam and gas turbine engines (Matthews, et al., 2003, p.4267). Recently, it was established that these coatings can improve the resistance to thermal fatigue and wear resistance under severe conditions of load and extend the life of components (Guilemany, et al., 2002, p.207). Thermally sprayed cermet coatings Cr_3C_2 - 25(Ni20Cr) appeared as a good solution for a wide range of applications in machine parts. Because of the extended service life of parts, coatings based on chromium carbides are widely used for many applications in gas turbines, steam turbines and aircraft engines to improve slip resistance, abrasion and erosion wear (Hillery, 1986, pp.2684-2688). Thermally sprayed cermet coatings are a good alternative to hard chromium, when high wear resistance is required (Erning, Nestler, 1999, pp.462–466), (Sahraoui, et al., 2004, pp.654–660), (Ko, Robertson, 2002, pp.880–893), (Savarimuthu, et al., 2000, pp.1095–1104). When compared to WC coatings, Cr_3C_2-NiCr coatings offer greater resistance to corrosion and oxidation, and also have a high melting point and maintain high hardness, strength and wear resistance up to 900°C (Beczkowiak, et al., 1999), (Blatchford, 2001), (Doi, Yoshiaki Suda, 2000), (Liu, 1998), (Loubiere, et al., 1995, pp.1535–1546), (Staia, et al., 2001, pp.553–562). Corrosion resistance is primarily provided by the NiCr alloy base, while wear resistance is mainly provided by the hard Cr_3C_2 carbide phase (He, Lavernia, 2000, pp.555–564). So, Cr_3C2 carbide-based coatings are applied to a wide range of industrial components, including various accessories used in steam and gas turbines. Thermal spraying is an effective method to apply thin and thick coatings on mechanical components to change their surface properties (Erja Turunen, et al., 2006, pp.4987-4994), (Wang, et al., 2000. p.69.). APS plasma spray processes and VPS are used in a wide range of applications including automotive, aerospace industry, chemical processing equipment, pulp and paper, orthopedic and dental components, etc. (Erja Turunen, et al., 2006, pp.4987-4994), (Mrdak, et al., 2013, pp.559-567), (Mrdak, 2013, pp.69-88), (Mrdak, 2012, pp.182-201), (Mrdak, et al., 2009, pp.27-32), (Vencl, et al., 2006, pp.151-157), (Vencl, et al., 2011, pp.1281-1288). The plasma spray process has been used for more than four decades in manufacturing protective coatings based on metals, ceramics and even composite materials for various applications (Chuanxian Ding, et al. 2003, pp.455-458). Despite the long period of application of the plasma spray process, there is still a great interest among scientists in the development of new materials for coatings and in the study of their behavior under working conditions (Leblanc, 2003, pp.291-299).

This paper presents the results of the experimental investigation of the influence of the VPS - vacuum plasma spray process on the mechanical properties and the microstructure of the Cr_3C_2 - 25(Ni20Cr) cermet coating. The main objective of the study was to avoid, at the reduced pressure of Ar inert gas during deposition, the degradation of the primary Cr_3C_2 carbide into a much softer $Cr_{23}C_6$ carbide and to deposit coating layers with the microstructure with the dominant Cr_3C_2 carbide phase which gives better performance in the coating operation. The tests have shown that the - Cr_3C_2 - 25(Ni20Cr) VPS coating has higher hardness and bonding strength than APS and HVOF coatings, which are in accordance with the coating microstructure dominated by the primary Cr_3C_2 carbide phase.

Materials and experimental details

The Sulzer Metco Woka 7205 powder was used for coating production (Material Product Data Sheet, 2012, Woka 7205 Chromium Carbide - 25% Nickel Chromium Powders, DSMTS-0031.1, Sulzer Metco). The Woka7205 powder contains 75%Cr_3C_2 carbide and 25%(Ni20Cr) alloy. The Cr_3C_2 - 25(Ni20Cr) powder particles are spherical, produced by agglomeration and the sintering technique with a range of powder granules from 10 to 38 μm. Fig. 1 shows a scanning electron micrograph (SEM) of the powder particle morphology. A spherical Cr_3C_2 - 25(Ni20Cr) powder particle can be seen, consisting of sintered Cr_3C_2carbide particles (dark blue) and 25(Ni20Cr) alloy particles (light blue).

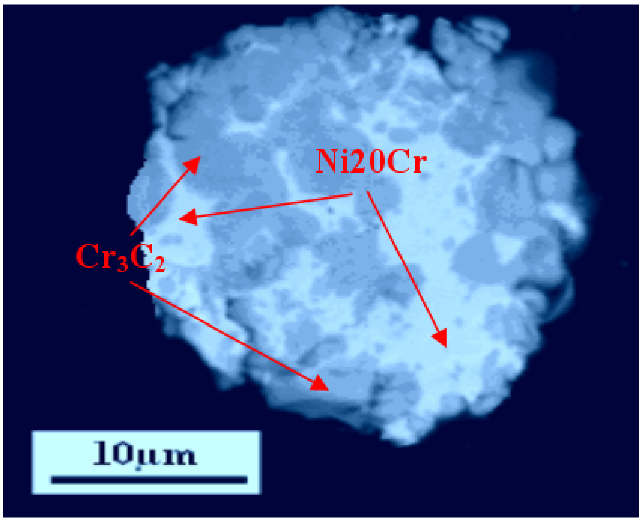


Figure 1 – (SEM) Scanning electron micrograph of Cr_3C_2 - 25(Ni20Cr) powder particles
Slika 1 – (SEM) Skening elektronska mikrografija čestica praha Cr_3C_2 - 25(Ni20Cr)
Рис. 1 – (SEM) Электронная микрография частиц порошка Cr_3C_2 - 25(Ni20Cr)

The substrates on which the coatings were deposited for micro hardness testing and microstructural evaluation were made of steel Č.4171 (X15Cr13 EN10027) in the thermally unprocessed state with the dimensions 70x20x1.5mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Also, the substrates for testing the bond strength are made of steel Č.4171 (X15Cr13EN10027) in the thermally unprocessed state with the dimension Ø25x50 mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

The mechanical and microstructural characterizations of the coatings were made according to Pratt & Whitney (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). The evaluation of the mechanical properties of the layers was done by the hardness testing method $HV_{0.3}$ and by bond strength tensile testing. The hardness testing was done in the direction along the lamellae, in the middle and at the ends of the sample. Five readings at three places were obtained and the paper presents the hardness range from the minimum to the maximum value.

The method of bond strength testing is a method of tensile testing. The testing was done at room temperature with a strain test rate of 1cm/60s. Three specimens were used, and the mean value is shown in the paper.

The morphology of powder particles was examined on the SEM - Scanning Electron Microscope. The analysis of the share of pores in the coating was done by processing 5 photos at 200X magnification. Through tracing paper, micro pores are labeled and shaded, and their total area was calculated related to the total area of the micrograph. This paper presents the mean value of the share of pores. The microstructural analysis of the coating was performed under a light microscope. In order to determine the distribution of the carbide phase in the coating, the coating etching was done with the reagent $1HNO_3$: $4HCl{:}4H_2O$. The microstructure of the coating after etching was examined by the light microscopy technique.

The Cr_3C_2 - 25(Ni20Cr) powder was deposited at a low pressure of Ar inert gas in the VPS system of the Plasma Technik AG company. An F4 plasma gun was used for the powder deposition. The process involves cleaning the substrate surface by the transferred arc and the powder deposition at low pressure. A program for Cr_3C_2 - 25(Ni20Cr) powder deposition was designed in the microprocessor unit of the robot of the VPS Plasma Technik AG system. The program set and time-synchronized all process parameters such as: chamber vacuuming, plasma gas flow, cleaning the substrate by the transferred arc, powder flow, coating deposition, substrate cooling and ventilation of the vacuum chamber. The cleaning of the substrate surface and the powder deposition were performed with a mixture of Ar-He plasma gases. The VPS parameters of the deposition of Cr_3C_2 - 25(Ni20Cr) powder on the samples are shown in Table 1.

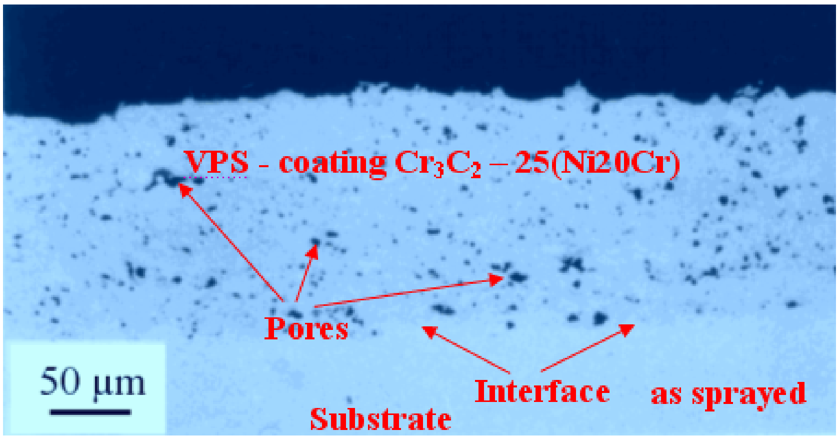
Table 1 – Plasma spray parameters
Tabela 1 – Plazma sprej parametri
Таблица 1 – Характеристики плазменного напыления

Parameters	Values	
	Cleaning arc	Spraying
Plasma current, I (A)	700	700
Plasma Voltage, U (V)	74	74
Primary plasma gas flow rate Ar (l/min)	50	50
Secondary plasma gas flow rate He (l/min)	20	140
Carrier gas flow rate Ar (l/min)	--	5
Powder feed rate (g/min)	--	45
Stand-off distance (mm)	320	340
Chamber pressure (mbar)	30	70
Nozzle diameter (mm)	8	8
Speed of the gun (mm /s)	12	12

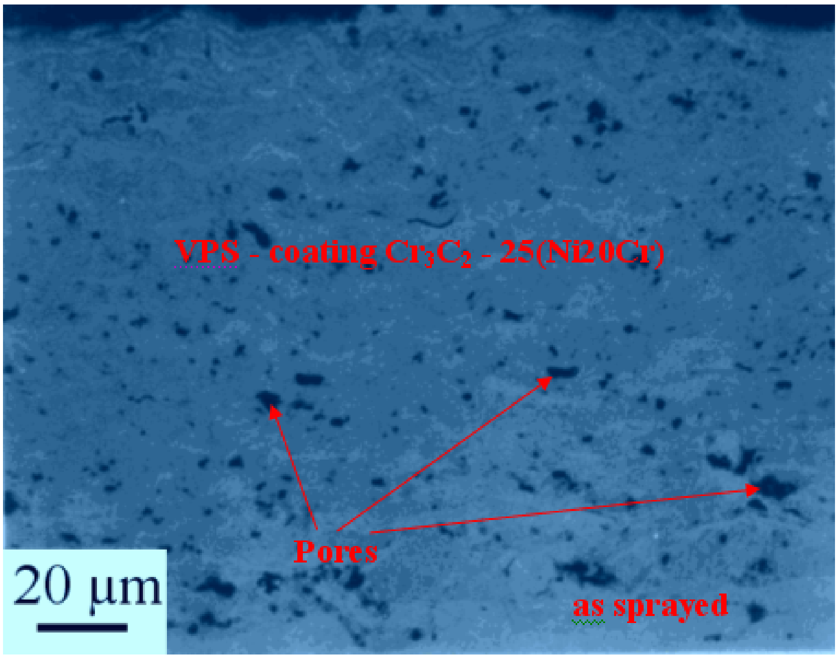
Results and discussion

In the Cr_3C_2 - 25(Ni20Cr) coating layers along the cross-section, the hardness values of 1248 to 1342 $HV_{0.3}$ were measured. The obtained hardness values indicate that a greater proportion of the degradable primary Cr_3C_2 carbide phase is present in the microstructure, due to the inert atmosphere of Ar at low pressure (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699–704). The range of hardness of the deposited layers is caused by the presence of micro pores in the coating layers. The tensile bond strength between the substrate and the coating was 89 MPa which is typical for VPS coatings. The cleaning of the substrate surface with the transferred arc resulted in better adhesion of the deposited coating layers, which resulted in obtaining high values of bond strength. The values of the microhardness and tensile bond strength were correlated with their microstructures.

Figs. 2 and 3 show the microstructures of the VPS Cr_3C_2 - 25(Ni20Cr) coating layers in the deposited condition.



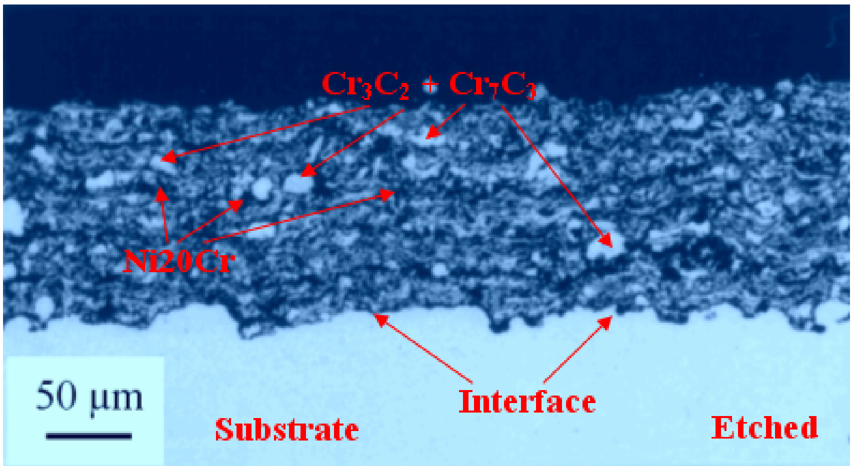
Slika 2 – Microstructure of the Cr_3C_2 - 25(Ni20Cr) coating in the deposited state
Slika 2 – Mikrostruktura Cr_3C_2 - 25(Ni20Cr) prevlake u deponovanom stanju
Рис. 2 – Микроструктура покрытия Cr_3C_2- 25 (Ni20Cr) в нанесенном состоянии



Slika 3 – Microstructure of the Cr_3C_2 - 25 (Ni20Cr) coating in the deposited state
Slika 3 – Mikrostruktura Cr_3C_2 - 25(Ni20Cr) prevlake u deponovanom stanju
Рис. 3 – Микроструктура покрытия Cr_3C_2 - 25 (Ni20Cr) в нанесенном состоянии

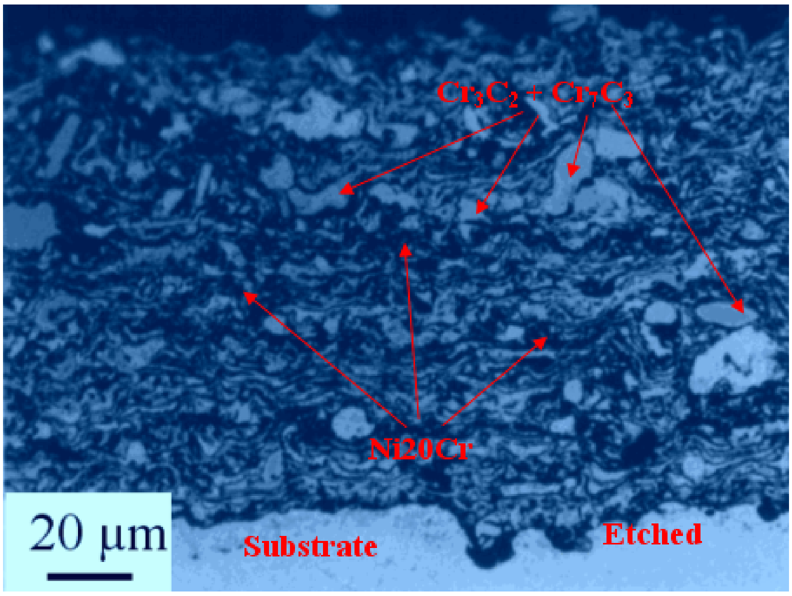
The qualitative analysis showed that at the interface between the substrate and the deposited coatings there are no defects such as discontinuities of the deposited layers on the substrates, microcracks, macrocracks and separation of the coating from the substrate. The boundaries on the interface between the substrate and the coating layers are very clean, which indicates a good cleaning of the substrates with the transferred arc. Through the coating layers, micropores of spherical and irregular shapes can be seen (marked with red arrows). There are no unmelted particles and precipitates in the coating layers. Microcracks are not present in the structure. Oxide lamellae cannot be observed through the layers of coatings. The VPS - vacuum plasma spray process allows depositing layers without oxide content in the coating, which is a big advantage over the APS and HVOF processes.

Figs. 4 and 5 show the microstructures of the VPS Cr_3C_2 - 25(Ni20Cr) coating in the etched condition.



Slika 4 – Microstructure of the Cr3C2 - 25 (Ni20Cr) coating in the etched state.
Slika 4 – Mikrostruktura Cr_3C_2 - 25(Ni20Cr) prevlake u nagrizenom stanju.
Рис.4 – Микроструктура покрытия Cr_3C_2 - 25 (Ni20Cr) в протравленном состоянии

The microstructure of the coating clearly shows the two phases. The dark blue phase represents the lamellae of Ni20Cr alloy and the light blue one shows the primary Cr_3C_2 undegraded carbides and the secondary Cr_7C_3 carbides which give high values of microhardness to the coating (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699–704). The Cr_3C_2 and Cr_7C_3 carbide phases are evenly distributed in the coating structure. The structure of the coating is quite uniform in the cross-section, with no history of micro and makrocracks.



Slika 5 – Microstructure of the Cr3C2 - 25 (Ni20Cr) coating in the etched state
Slika 5 – Mikrostruktura Cr_3C_2 - 25(Ni20Cr) prevlake u nagrizenom stanju
Рис.5 – Микроструктура покрытия Cr_3C_2 - 25 (Ni20Cr) в протравленном состоянии

This indicates that the coating layers are deposited evenly. Micropores are present in the coating structureand seen as dark fields in Figs.2 and 3. The porosity of the coating was determined by the image analysis technique, where 5 fields were analyzed at 200X magnification in the coating cross section. The average value of the porosity was 4%. Primary Cr_3C_2 carbide particles and secondary Cr_7C_3 carbides phases are located in the interlamellar regions of the Ni20Cr alloy (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699–704). Due to coating etching, Ni is dissolved from the solid solution of the Ni20Cr alloy while Cr_3C_2 and Cr_7C_3 carbides are raised in the light blue relief. Since the incident light falls obliquely onto the sample surface, and casts a shadow over the raised carbide phases, the Ni20Cr alloy phase is dark blue.

Conclusion

In this paper, the vacuum plasma spray - VPS procedure is used to deposit Cr_3C_2 - 25(Ni20Cr) cermet coatings with cleaning the substrate surface with the transferred arc at a distance of 320mm of the F4 plasma gun from the substrate and deposit powder particles at a distance of 340mm of the plasma gun from the substrate. The paper investigated the mechanical properties and the microstructure of the coatings in the deposited and etched state in the reagent 1HNO_3: 4HCl: 4H_2O. The investigation came to the following conclusions.

The VPS Cr_3C_2 - 25(Ni20Cr) cermet coating had high hardness values from 1248 to 1342 $HV_{0.3}$ along the cross-section. The measured hardness values indicate the presence of a large share of the nondegraded primary Cr_3C_2 carbide phase in the coating microstructure. The range of the hardness of the deposited layers is a consequence of the presence of micro-porosity in the coating layers. The tensile bond strength of the Cr_3C_2 - 25 (Ni20Cr) coating had a high value of 89 MPa. The cleaning of the substrate surface with the transferred arc resulted in better adhesion of the deposited coating layers, which resulted in obtaining high values of bond strength. The values of the microhardness and tensile bond strength correlated with their microstructures.

The microstructure of VPS 75Cr_3C_2 - 25(Ni20Cr) cermet coatings is lamellar. Micro pores with a share of 4% are present in the deposited layers. Through the deposited layers,unmelted powder particles and precipitates cannot be observed. The microstructure of the coating in the etched condition clearly shows the dark layers of the Ni(Cr) alloy in which light fields of evenly distributed primary Cr_3C_2 carbide phases can be seen as well as the secondary Cr_7C_3 carbide phases. in the coating layers deposited at low pressure in an inert atmosphere of Ar, there are no Ni and Cr oxide phases.

The tests have shown that the VPS - Cr_3C_2 - 25(Ni20Cr) cermet coatings have higher hardness and bond strength values than the APS and HVOF coatings, which are in accordance with the coating microstructure. The deposition of powder in a protective atmosphere at low pressure enabled the deposition of the coating layers with the prevailing primary Cr_3C_2 carbide phase which provides better performances to the coatings in operation.

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МЕХАНИЧЕСКИЕ СВОЙСТВА И МИКРОСТРУКТУРА ПОКРЫТИЯ Cr_3C_2 - 25(Ni20Cr) НАНЕСЕННОГО МЕТОДОМ ВАКУУМНОГО ПЛАЗМЕННОГО НАПЫЛЕНИЯ.

ОБЛАСТЬ: химические технологии
ВИД СТАТЬИ: оригинальная научная статья
ЯЗЫК СТАТЬИ: английский

Резюме:

В данной работе анализируется метод вакуумного плазменного напыления покрытия Cr_3C_2 - 25(Ni20Cr) с использованием промышленного порошкового состава Sulzer Metco Woka 7205 при применении плазматрона F4 на расстоянии 340мм от основания.

Основной целью работы является проверка утверждения, что при пониженном давлении инертного газа исключается распад первичного карбида Cr_3C_2 до карбида $Cr_{23}C_6$, который значительно снижает микротвердость и механические свойства.

Покрытие толщиной 100 – 120 μm наносилось на стальное основание. Испытания покрытия на микротведость проводились по методу $HV_{0.3}$. Значения показателей микротвердости на-

ходятся в промежутке 1248 - 1342 $HV_{0.3}$. Испытание адгезии покрытия к основанию проводилось методом натяжения, полученное в результате испытания значение составляет 89 MPa.

Изучение микроструктуры покрытия, методом световой микроскопии показало, что покрытие состоит из основного сплава NiCr с преобладанием первичной карбидной фазы Cr_3C_2 и присутствием фазы Cr_7C_3.

Травление покрытия проводилось с использованием реагента $1HNO_3$: 4HCl: $4H_2O$, растворяющего в первую кочередь никель, что позволяет увидеть распределение карбидной фазы в покрытии. Травление покрытия показало, что в слое преобладает карбидная фаза Cr_3C_2, обеспечивающая высокое значение микротвердости покрытия.

Ключевые слова: *вакуум, основание, прочность, свойства, микроструктура, механические свойства, покрытие, карбиды.*

MEHANIČKA SVOJSTVA I MIKROSTRUKTURA VAKUUM PLAZMA NAPRSKANE Cr_3C_2 - 25(Ni20Cr) PREVLAKE

OBLAST: hemijske tehnologije
VRSTA ČLANKA: originalni naučni članak
JEZIK ČLANKA: engleski

Sažetak:

U radu je analizirana vakuum plazma sprej prevlaka VPS – Cr_3C_2 - 25(Ni20Cr). Upotrebljen je komercijalni prah oznake Sulzer Metco Woka 7205. Prah je deponovan sa plazma pištoljem F4 na odstojanju substrata od 340 mm. Glavni cilj rada bio je da se na smanjenom pritisku inertnog gasa Ar eliminiše razgradnja primarnog karbida Cr_3C_2 u karbid $Cr_{23}C_6$ koji bitno umanjuje mikrotvrdoću i mehaničke karakteristike prevlake. Prevlaka je deponovana debljine od 100 do 120 μm na čeličnom substratu. Mikrotvrdoća prevlake ispitana je metodom $HV_{0.3}$. Vrednosti mikrotvrdoće bile su u rasponu od 1248 do 1342 $HV_{0.3}$. Čvrstoća spoja prevlake ispitana je metodom na zatezanje. Utvrđeno je da čvrstoća spoja između substrata i prevlake ima vrednost 89 MPa. Mikrostruktura prevlake ispitana je tehnikom svetlosne mikroskopije. Struktura prevlake sastoji se od osnove NiCr legure sa dominantnom primarnom karbidnom fazom Cr_3C_2. Pored Cr_3C_2 faze prisutna je i faza Cr_7C_3. Nagrizanje prevlake urađeno je reagensom $1HNO_3$: 4HCl: $4H_2O$ koji prvenstveno rastvara Ni da bi se videla raspodela karbidne faze u prevlaci. Nagrizanjem prevlake reagensom utvrđeno je da je u slojevima prevlake u velikom udelu prisutna primarna nerazgrađena karbidna faza Cr_3C_2 koja prevlaci daje visoke vrednosti mikrotvrdoće.

Uvod

Vakuum plazma prskanje (VPS), zbog niskog pritiska, obično se naziva i LPPS. Na niskim pritiscima mlaz plazme postaje veće dužine i manjeg prečnika sa upotrebom konvergentnih/divergentnih mlaznica i ima veću brzinu jona. Eliminisanje kiseonika u komori i mogućnost primene predgrevanja substrata omogućuje izradu gušćih prevlaka, više zatezne čvrstoće spoja bez sadržaja oksida u prevlaci. Primenom VPS procesa sprečava se dekarburizacija primarnog karbida Cr_3C_2, tako da se deponuju prevlake visoke tvrdoće. U poslednjoj deceniji veliki broj istraživača publikovao je rezultate koji se odnose na strukturu i svojstva prevlaka deponovanih HVOF procesom (Guilemany, et al., 2006, p.2998), (Guilemany, et al., 2002, p.207), (Ji, et al., 2006, p.6749), (Li, et al., 2005, p.229), (Picas, et al., 2006, p.477). Kod ovog procesa, kao i kod APS procesa, glavni problem bio je gubitak ugljenika tokom taloženja prevlake. U VPS prevlakama dominantna je karbidna faza Cr_3C_2 tvrdoće 1600HV sa manjim udelom faze Cr_7C_3 tvrdoće 1300HV (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699-704). U prevlaci nije prisutna karbidna faza $Cr_{23}C_6$, tvrdoće 1000HV, koja u APS i HVOF karbidnim prevlakama umanjuje tvrdoću prevlaka. Tvrdoća VPS Cr_3C_2 - 25(Ni20Cr) prevlake je HV1243 ± 80, što je mnogo veće od HVOF prevlake sa tvrdoćom HV958 ± 44 (Tomita, et al., 2001, pp.699–704). Zatezna čvrstoća spoja prevlake deponovane VPS procesom veća je od 80 MPa sa sadržajem poroznosti manjom od 5% (ASM Metals Handbook, 1987, p.367). Plazma sprej prevlake Cr_3C_2 - NiCr imaju visoku otpornost protiv abrazionog habanja i nizak koeficijent trenja, od sobne temperature do 850°C, zbog visoke termičke stabilnosti i otpornosti na oksidaciju (Guilemany, et al., 2006, p.2998). Nedavno je utvrđeno da ove prevlake mogu poboljšati otpornost na toplotni zamor i otpornost na habanje u teškim uslovima opterećenja i produžiti radni vek komponentama (Guilemany, et al., 2002, p.207). Termički naprskane kermet prevlake dobra su alternativa tvrdom hromu, kada se zahteva visoka otpornost na habanje (Erning, Nestler, 1999, pp.462–466), (Sahraoui, et al., 2004, pp.654–660), (Ko, Robertson, 2002, pp.880–893), (Savarimuthu, et al., 2000, pp.1095–1104). Plazma sprej procesi APS i VPS koriste se u širokom spektru aplikacija, uključujući automobilsku industriju, avionsku industriju, hemijsku procesnu opremu, industriju celuloze i papira, ortopedskih i stomatoloških komponenti i dr. (Erja Turunen, et al., 2006, pp.4987-4994), (Mrdak, et al., 2013, pp.559-567), (Mrdak, 2013, pp.69-88), (Mrdak, 2013, pp.182-201), (Mrdak, et al., 2009, pp.27-32), (Vencl, et al., 2006, pp.151-157), (Vencl, et al., 2011, pp.1281-1288). Plazma sprej proces koristi se više od četiri decenije za izradu zaštitnih prevlaka na bazi metala, keramike i čak kompozitnih materijala za različite aplikacije (Chuanxian Ding, 2003, pp.455-458). Uprkos dugom periodu primene plazma sprej procesa, među naučnicima je još uvek prisutno veliko interesovanje za razvoj novih materijala za izradu prevlaka i istraživanje njihovog ponašanja u radnim uslovima (Leblanc, 2003, pp.291-299).

U radu su predstavljeni rezultati eksperimentalnih ispitivanja uticaja VPS – vakuum plazma sprej procesa na mehaničke karakteristika i mikrostrukturu kermet prevlake Cr_3C_2 - 25(Ni20Cr). Glavni cilj rada bio je da se na smanjenom pritisku inertnog gasa Ar u procesu depozicije izbegne razgradnja primarnog karbida Cr_3C_2 u mnogo mekši karbid $Cr_{23}C_6$ i deponuju slojevi prevlake sa mikrostrukturom u kojoj će biti dominantna karbidna faza Cr_3C_2 koja daje bolje performanse prevlaci u eksploataciji. Ispitivanja su pokazala da VPS – Cr_3C_2 - 25(Ni20Cr) prevlaka ima veće vrednosti mikrotvrdoće i čvrstoću spoja od APS i HVOF prevlaka, koje su u saglasnosti sa mikrostrukturom prevlake u kojoj dominira primarna karbidna faza Cr_3C_2.

Materijali i eksperimentalni detalji

Za izradu prevlaka koristio se prah firme Sulzer Metco s oznakom Woka 7205 (Material Product Data Sheet, 2012, Woka 7205 Chromium Carbide - 25% Nickel Chromium Powders, DSMTS-0031.1, Sulzer Metco). Prah Woka7205 sadrži 75%Cr_3C_2 karbida i 25%(Ni20Cr) legure. Čestice praha Cr_3C_2 - 25(Ni20Cr) sfernog su oblika, proizvedene tehnikom sinterovanja i aglomeracije sa rasponom granulata praha od 10 do 38 μm.

Osnove na koje su deponovane prevlake za ispitivanje mikrotvrdoće i za procenu mikrostrukture napravljene su od čelika Č.4171 (X15Cr13 EN10027) u termički neobrađenom stanju, dimenzija 70x20x1,5mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Takođe, osnove za ispitivanje čvrstoće spoja napravljene su od čelika Č.4171(X15Cr13EN10027) u termički neobrađenom stanju dimenzija Ø25x50 mm (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA).

Mehaničke i mikrostrukturne karakterizacije prevlaka urađene su prema standardu Pratt & Whitney (Turbojet Engine – Standard Practices Manual (PN 582005), 2002, Pratt & Whitney, East Hartford, USA). Procena mehaničkih osobina slojeva urađena je ispitivanjem mikrotvrdoće metodom $HV_{0.3}$ i čvrstoće spoja ispitivanjem na zatezanje. Ispitivanje mikrotvrdoće urađeno je u pravcu duž lamela, u sredini i na krajevima uzorka. Urađeno je pet očitavanja na tri mesta, a u radu je prikazan raspon mikrotvrdoće od minimalne do maksimalne vrednosti.

Metoda ispitivanja čvrstoće spoja je metoda ispitivanja na zatezanje. Ispitivanje je urađeno na sobnoj temperaturi sa brzinom zatezanja 1cm/60s. Za ispitivanje su upotrebljene tri epruvete, a u radu je prikazana srednja vrednost.

Morfologija čestica praha urađena je na SEM – skening elektronskom mikroskopu. Analiza udela mikropora u prevlaci urađena je obradom 5 fotografija na uveličanju 200X. Preko paus papira mikropore su označene i osenčene, a njihova ukupna površina računala se na ukupnu površinu mikrofotografije. U radu je prikazana srednja vrednost udela mikropora. Mikrostrukturna analiza prevlaka urađena je na svetlosnom mikroskopu. Radi utvrđivanja raspodele karbidne faze u prevlaci rađeno je nagrizanje prevlake u reagensu $1HNO_3:4HCl:4H_2O$. Mikrostruktura prevlake posle nagrizanja ispitana je tehnikom svetlosne mikroskopije.

Depozicija praha Cr_3C_2 - 25(Ni20Cr) izvršena je na niskom pritisku inertnog gasa Ar u VPS sistemu firme Plasma Technik AG. Za depoziciju praha korišćen je plazma pištolj F4. Proces obuhvata čišćenje površine substrata transferovanim lukom i deponovanje praha na niskom pritisku. Na mikroprocesorskoj jedinici robota VPS sistema Plasma Technik AG urađen je program deponovanja praha Cr_3C_2 - 25(Ni20Cr). U programu su zadati i vremenski sinhronizovani svi parametri procesa kao što je: vakuumiranje komore, protok plazma gasova, čišćenje substrata transferovanim lukom, protok praha, depozicija prevlake, hlađenje substrata i ventilacija vakuum komore. Čišćenje površine substrata i depozicija praha urađena je sa mešavinom plazma gasova Ar-He.

Rezultati i diskusija

U slojevima prevlake Cr_3C_2 - 25(Ni20Cr) duž poprečnog preseka su izmerene vrednosti mikrotvrdoće od 1248 do 1342 $HV_{0.3}$. Dobijene vrednosti mikrotvrdoće ukazuju da je u mikrostrukturi u većem udelu prisutna nerazgrađena primarna karbidna faza Cr_3C_2, što je omogućila inertna atmosfera Ar na niskom pritisku (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699–704). Raspon mikrotvrdoće deponovanih slojeva je posledica prisustva mikroporoznosti u slojevima prevlake. Zatezna čvrstoća spoja između substrata i prevlake bila je 89 MPa, što je karakteristično za VPS prevlake. Čišćenje površine substrata transferovanim lukom uticalo je na bolje prijanjanje deponovanih slojeva prevlaka, što se odrazilo na dobijanje visoke vrednosti čvrstoće spoja. Vrednosti mikrotvrdoće i zatezne čvrstoće spoja bile su u korelaciji sa njihovim mikrostrukturama.

Kvalitativna analiza je pokazala da na interfejsu između substrata i deponovanih prevlaka nisu prisutni defekti kao što je diskontinuitet deponovanih slojeva na substratima, mikropukotine, makropukotine i odvajanje prevlaka od osnove. Granice na interfejsu između substrata i slojeva prevlake izuzetno su čiste, što ukazuje na dobro čišćenje površine substrata transferovanim lukom. Kroz slojeve prevlake uočavaju se mikropore sfernog i nepravilnog oblika obeležene crvenim strelicama. U slojevima prevlake nisu prisutne nestopljene čestice i precipitati. U strukturi nisu prisutne mikropukotine. Kroz slojeve prevlaka ne uočavaju se oksidne lamele. VPS – vakuum plazma sprej proces omogućuje deponovanje slojeva bez sadržaja oksida u prevlaci, što je velika prednost u odnosu na procese APS i HVOF.

U mikrostrukturi prevlake jasno se vide dve faze. Tamnoplava faza su lamele legure Ni20Cr, a svetloplava faza su primarni nerazgrađeni karbidi Cr_3C_2 i sekundarni karbidi Cr_7C_3 koji daju prevlaci visoke vrednosti mikrotvrdoće (Marcano, et al., 2008, pp.4406–4410), (Tomita, et al., 2001, pp.699–704). Karbidne faze Cr_3C_2 i Cr_7C_3 su ravnomerno raspoređene u strukturi prevlake koja je dosta ujednačena po preseku, bez prisutnih mikro i makropukotina. To ukazuje da su slojevi prevlake ravnomerno deponovani. U strukturi prevlake prisutne su mikropore koje se vide kao tamna polja. Poroznost prevlake određena je pomoću tehnike analize slike, gde je 5 polja na uvećanju od 200X analizirano na poprečnom preseku prevlake. Prosečna vrednost poroznosti iznosila je 4%. Primarne čestice karbida Cr_3C_2 i sekundarne karbidne faze Cr_7C_3 nalaze se *u interlamelarnim regionima legure Ni20Cr (Marcano, et al., 2008, pp-p.4406–4410), (Tomita, et al., 2001, pp.699–704). Nagrizanjem prevlake Ni se rastvara iz čvrstog rastvora legure Ni20Cr, dok karbidi Cr_3C_2 i Cr_7C_3 stoje izdignuti u reljefu svetloplave boje. Pošto upadna svetlost koso pada na površinu uzorka i baca senku iznad izdignutih faza karbida, faza Ni20Cr legure je tamno- plave boje.*

Zaključak

U ovom *radu su vakuum plazma sprej – VPS postupkom deponovane kermet prevlake Cr_3C_2 - 25(Ni20Cr) sa čišćenjem površine substrata transferovanim lukom na odstojanju 320 mm plazma pištolja F4 od substrata i depozicija čestica praha na odstojanju 340 mm plazma pištolja od substrata. Ispitane su mehaničke karakteristike i mikrostrukture prevlaka u deponovanom i nagriženom stanju u reagensu $1HNO_3$:$4HCl$:$4H_2O$. Na osnovu izvršenih ispitivanja došlo se do određenih zaključaka.*

VPS kermet prevlaka Cr_3C_2 - 25(Ni20Cr) duž poprečnog preseka imala je visoke vrednosti mikrotvrdoće od 1248 do 1342 $HV_{0.3.}$ Izmerene vrednosti mikrotvrdoće ukazuju na prisustvo većeg udela nerazgrađene primarne karbidne faze Cr_3C_2 u mikrostrukturi prevlake. Raspon mikrotvrdoće deponovanih slojeva posledica je prisustva mikroporoznosti u slojevima prevlake. Zatezna čvrstoća spoja Cr_3C_2 - 25(Ni20Cr) prevlake imala je visoku vrednost od 89 MPa. Čišćenje površine substrata transferovanim lukom uticalo je na bolje prijanjanje deponovanih slojeva prevlaka, što se odrazilo na dobijanje visoke vrednosti čvrstoće spoja. Vrednosti mikrotvrdoće i zatezne čvrstoće spoja bile su u korelaciji sa njihovim mikrostrukturama.

Mikrostruktura VPS kermet prevlake $75Cr_3C_2$ - 25(Ni20Cr) je lamelarna. U deponovanim slojevima prisutne su mikropore sa udelom od 4%. Kroz deponovane slojeve ne uočavaju se neistopljene čestice praha i precipitati. U mikrostrukturi prevlake u nagriženom stanju jasno se vide tamni slojevi legure Ni(Cr) u kojoj se nalaze svetla polja ravnomerno raspoređene primarne faze karbida Cr_3C_2 i sekundarne faze karbida Cr_7C_3. U slojevima prevlake koje su deponovane na niskom pritisku u inertnoj atmosferi Ar nisu prisutne oksidne faze Ni i Cr.

Ispitivanja su pokazala da VPS - Cr_3C_2 - 25(Ni20Cr) kermet prevlake imaju veće vrednosti mikrotvrdoće i čvrstoće spoja od APS i HVOF prevlaka, koje su u saglasnosti sa mikrostrukturom prevlake. Deponovanje praha u zaštitnoj atmosferi na niskom pritisku omogućilo je da se u prevlaci deponuju slojevi sa dominantnom primarnom fazom Cr_3C_2 u kojoj dominira primarna karbidna faza Cr_3C_2 koja u eksploataciji daje bolje performanse prevlaci.

Ključne reči: *vakuum, substrat, čvrstoća, svojstva, faze, mikrostrukture, mikrotvrdoća, mehanička svojstva, prevlaka, karbidi.*

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