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Research Article

The Effect Of Thin Film CrC Coating On Microstructure And Microhardness Properties Of Manganese Steel Surface

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ARTICLE INFO **ABSTRACT**

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1. INTRODUCTION

Especially in the machinery and manufacturing industry, metal parts are faced with negativities such as wear and corrosion depending on the environment in which they are used. One method of extending the service life of the parts is the improvements to be made on the surface. These improvements on the surface are applied to improve one or more properties such as mechanical and chemical properties such as hardness, fatigue, wear and corrosion [1]. Under these conditions, various surface coating methods have been developed to provide the desired surface performance of the materials [2]. Laser, TIG (Tungsten Inert Gas), PAW (Plasma Arc Welding), HVOF (high-velocity oxygen fuel), plasma spray, CVD (Chemical Vapor Deposition) methods are frequently used by researchers in coating studies [3-7]. Among these methods, especially Laser and CVD methods have limited their use due to their expensive equipment and special environment requirements. In the TRD method process, the coating process is more convenient, cost-effective and suitable for industrial use compared to other methods [8]. Coatings containing VC, NbC and CrC in thicknesses of 1-15 μm, created on the surface with TRD, provide surfaces with high hardness and good wear resistance [9-10].

In this study, the microstructure and microhardness properties of manganese steel coated with chromium carbide (CrC) using Thermo Reactive Diffusion (TRD) method at 900℃ and 1100℃ for 4 hours were investigated. The surface morphology of the coating was characterized by scanning electron microscopy (SEM), elemental distribution, X-ray spectroscopy (EDS). Microhardness properties were determined using the Vickers method. Microstructural properties and microhardness results were characterized. The microstructure results showed that the coating process at 1100℃ was metallurgically more uniform. The minimum coating thickness was 14.95 μm at 900℃ and the maximum thickness was 24.1 μm at 1100℃. In EDS measurements, while CrC was dense in the coating region, Fe density increased towards the substrate. In the microhardness measurements, the highest value was measured as 2371 HV0.5 in the sample coated at 1100℃. Based on these results, it is thought that CrC coating forms a better coating layer especially at high temperatures.

> In previous applications, it was determined that the amount of coating attached to the surface increases with increasing temperature [11].

> It has been stated by the authors that increasing the coating time and temperature increased the coating thickness by 311.40%.[12].

> However, an important point in this method is that the C content of the steel-based substrate to be coated must be at least 0.3% or higher for the TRD process to take place [13].

> In this study, the surface of manganese steel was coated with CrC by TRD method. Microstructure characterization was performed after coating. Microhardness measurements of the coating layer were made and the results were characterized by microstructure.

2. MATERIAL AND METHOD

Diffusion thin film coating of manganese steel surface with CrC using TRD method. Manganese steel (%C: 1.375, %P: 0.047, %Si: 0.356, %S: 0.005, %Mo: 0.261, %Ni: 0.104, %Cu: 0.110, %V: 0.047, %Mn: 17.590, %Al: 0.013, %Cr: 0.977, %B: 0.002 and Fe) were cut to 12x12mm. The surface was polished with 1200 mesh SiC sandpaper before coating. The polished samples were cleaned from dirt and impurities on the surface in an ethanol bath. 45%CrC 45%Al2O3 and 10% NH4Cl were

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used as coating powder. Al2O3 as inert filler and NH4Cl as activator were used to prevent the powders from sintering with each other during the coating process. Al2O3 was used as plastering material before the coating powders into the crucible. After the plastering process was completed, the mixture powder was poured into the crucible and then the samples were buried in the mixture powder. After placing the samples in the crucible, the crucible was tightly closed and the outer wall was plastered with heat resistant paste. The process steps are shown in Figure 1.

Figure 1. Processing steps

The crucibles were placed in the oven at 900℃ and 1100℃ and kept for 4 hours. After the completion of the process, the crucibles were removed from the oven and cooled in water. After cooling, the scale on the surface of the coating material was removed. The coating samples were subjected to metallographic processes for optical microscope, SEM and EDS analysis. Coating surfaces were rough polished with 400- 1200 mesh SiC abrasives and final polishing was carried out with a fine polisher. After polishing, the prepared 4% nital etchant was dipped. After the etching process was completed, the coating microstructure and elemental distribution were examined by optical microstructure with an image system consisting of a Nikon Eclipse MA 100 type light microscope mounted with a Clemex type digital camera, SEM and EDS examinations were performed using SEM JEOL JSM-5600 device. Microhardness measurements were performed using Future Tech FM-700 model digital hardness tester.

3. RESULT AND DISCUSSION

3.1. Microstructure

The optical microstructures of CrC coating on manganese steel surface at 900℃ and 1100℃ for 4 hours are shown in Figure 2 In Figure 2a and 1b optical images of the coating at 900 °C, there is a clear contrast difference between the coating and the substrate. The veneer layer is lighter while the substrate is darker. The veneer layer is indented and protruding in tooth form. There is a homogeneous bond between the veneer and the substrate. No pores and discontinuities were observed. The minimum coating thickness was 14.96μm and the maximum was 20.72μm. Figure 2 (2a,2b) coating made at 1100℃ was homogeneous and non-porous. There is a distinct color difference between the veneer and the substrate. The plating layer is lighter while the substrate is darker. The reason for the marked color difference between the coating layer and the substrate at the interface is attributed to the ability of iron in the matrix to dissolve chromium [14]. The lowest coating thickness was 22.39μm and the highest was 24.1μm. When the coating thicknesses were compared, the highest thickness value was obtained in the sample made at 1100℃. It was determined that the coating temperature has a significant effect on the thickness. In the coating studies carried out by different researchers with TRD method, it was observed that the coating thickness increased with increasing temperature [15].

Figure 2. Optical microstructure image of CrC (1a, b) coating performed at 900 °C for 4 hours and CrC (2a, b) coating performed at 1100 °C for 4 hours

Figure 3 shows the SEM-EDS images and results of the sample coated at 900℃. There is a homogeneous bonding between the coating and the substrate. The coating layer is dispersedly bonded to the substrate. The upper part of the coating layer looks like a cloud. As you go towards the substrate, slats similar to martensite slats are formed. When the EDS results were evaluated, it was determined that the ratio of carbon and chromium decreased and iron increased as you move towards the bottom layer of the coating. At the 1st point, the network was analyzed as 11.93% C, 61.15 Cr, 26.95 Fe, at the 2nd point as 27.88% C, 46.74 Cr, 25.38 Fe, and at the 3rd point as 9.48% C, 8.49 Cr, 82.04 Fe. When the mapping results of the coating sample at 900℃ are evaluated in Figure 4, it is observed that the color concentration of C and Cr decreases from the coating to the substrate while Fe increases.

Figure 4. SEM-EDS images of CrC coating performed at 900 ℃ for 4 hours

Figure 3 Mapping image of CrC coating performed at 900 ℃ for 4 hours

Figure 5 shows the SEM-EDS images of the sample coated at 1100℃. The coating layer exhibited a smooth and homogeneous structure. There is a distinct color concentration between the coating and the substrate. The interface between the substrate and the coating layer is more pronounced compared to the sample at 900℃. As the temperature and processing time increased, the amount of elements passing to the surface increased as the time required for diffusion was sufficient. As a result, the surface layer was more uniform and the transition/substrate interface was more homogeneous than other coating methods [16]. The coating layer at 1100℃ exhibited a more uniform structure than the sample at 900℃. No pores or discontinuities were observed in both samples. When the EDS results of the sample were evaluated, it was determined from the analysis results that at the 1st point, 6.68% C, 58.08 Cr, 32.94 Fe, 8.22% C, 46.91 Cr, 39.49 Fe, 3.54% C, 4.24 Cr, 80.25 Fe at the 3rd point. It can be seen that the phase formation also depends on the percentage of carbon atoms. As the diffusion process progresses, the amount of carbon atoms on the surface increases and Cr7C3 phase is formed [17]. Ghadi et al. They stated that carbon diffusion plays a very important role in the coating process and affects the type of phase formed. [18]. When the EDS results obtained are evaluated together with the Fe-Cr-C ternary phase diagram in Figure 6, they point to Cr23C6 and Cr7C3 phases. Özel 2023 carried out a coating study with Cr3C2 and Fe powder. After the work, Cr3C2 and Cr7C3 compounds were formed and hardness increased due to these compounds. Depending on the values in EDS analysis, he stated that it may indicate CrxCy type carbides [19].

Figure 5. SEM-EDS images of CrC coating performed at 1100 ℃ for 4 hours

Figure 6. Fe-Cr-C triple phase diagram [20].

3.2. Microhardness

The hardness change table and graph of the coated samples depending on the process temperature are given in Figure 7. In both samples, it is seen that the hardness increases significantly as you go from the coating to the substrate. The lowest hardness value measured at 900℃ was 673 HV0.5 in the substrate and the highest value was 1823 HV0.5 in the coating layer. In the sample coated at 1100℃, the lowest hardness value was measured as 789 HV0.5 in the substrate, while the hardness value reached 2371 HV0.5 in the coating layer. The hardness value increased about 2.5 times in the coating layer compared to the substrate. In addition, a change in hardness measurement values with temperature change was also determined in the light of the data obtained. Based on these results, it can be concluded that the temperature-dependent diffusion in the TRD method is better and leads to the formation of harder carbide phases. Najari et al. investigated the possibility of chromium carbide layer formation on the surface of AISI W1 cold work tool steel by TRD method. They successfully obtained compact, adhesive, uniform and crackfree chromium carbide coatings ranging in thickness from 5.14 to 18.06 μm, mainly composed of Cr7C3, Cr23C6 and Cr3C2 on the substrate at 900℃ and 1000℃. The hardness of the coatings was in the range of 771 to 1600 HV, depending on the process conditions [21]. Ganji et al. used carbide coatings to extend the life of dies used for hot and cold forging, extrusion and powder metallurgy. They stated that a hardness value of

1782 HV was obtained in the chromium carbide layer after the process [22]. When compared with the results we obtained in the light of the literature, similarly high hardness measurements were obtained in the coating layer compared to the substrate.

Figure 7. Hardness table and graphic table of microhardness values of the coating

4. CONCLUSION

The manganese steel surface was coated with CrC using the TRD method. The following results were obtained after microstructure analysis and hardness measurements after the coating process.

1. In the microstructure results, the coating process at 1100℃ temperature was metallurgically more uniform.

2. The lowest coating thickness was 14.95μm at 900℃ and the highest thickness was 24.1μm at 1100℃.

3. In EDS measurements, while CrC was dense in the coating region, Fe density increased towards the substrate.

4. In the microhardness measurements, the highest value was measured as 2371 HV0.5 in the sample coated at 1100℃.

5. Based on these results, it is thought that CrC coating forms a better coating layer especially at high temperatures.

REFERENCES

- **[1]** Ş. Ertürk, F. Erzincanlı, "Investigation of Coating Properties and Machining Capability of Boron and Titanium Coated AISI D2 Cutting Tools by Thermochemical Method." DUBITED 8.1: 1095-1109, 2020.
- **[2]** S. Özel, "Yüzey Kaplama İşlemlerinde Kullanılan Isıl Püskürtme Yöntemleri." Bitlis Eren University Journal of Science 2.1: 88-97, 2013. **[3]** Ç. Dindar, M. Altay, & H. Aydın, " Laser Cladding Process and Process
- Parameters: A Review Uludağ University Journal of The Faculty of Engineering 26.2: 723-736, 2021
- **[4]** M. Kilic, A Imak, & I. Kirik, "Surface modification of AISI 304 stainless steel with NiBSi-SiC composite by TIG method." JMEPEG 30.2: 1411-1419, 2021.
- **[5]** M. Akkaş, "The mechanical and corrosion properties of WCCo–Al coatings formed on AA2024 using the HVOF method." *Materials Research Express(MRX)* 7.7: 076515, 2020.
- [6] H. Durmuş, M. Türkmen, & U. X6Cr17 Ferritic Stainless Steel Surfaces Coated with Al2O3 Powders Using Thermal Spray Method." DUJE 11.3: 1167-1173, 2020.
- **[7]** A. Aytaç, & U. Malayoğlu, "Comparison of PVD and JVD / DVD Thin Film Coatings by Physical Vapor Deposition Methods and a Conceptual, Academic and Theoretical Analysis on Industrial Applications of DVD Coating Technology." Journal of Defense Sciences 17.1: 131-164, 2018.
- **[8]** M. Kılıç, & E. Korkmaz, " Effect of Parameters on Coating Thickness." Batman University Journal of Life Sciences 13.2: 28-35, 2024.
- **[9]** B. Kurt, Y. Küçük, and M.S. Gök, Microabrasion wear behavior of VC and CrC coatings deposited by thermo-reactive diffusion technique, Tribol. Trans., 57, No. 2, pp. 345, 2014.
- **[10]** A. Toru, "Thermoreactive deposition/diffusion process for surface hardening of steels." *Steel Heat Treating Fundamentals and Processes*. ASM International, 725-740, 2013.
- **[11]** M. Kilic, (2020). "TiC coatings on an alloyed steel produced by thermal diffusion". *Materials Testing*, *62*(9), 909-912, 2020.
- **[12]** Çelik, Y. H., Ertem, M., Gür, A. K., Kurt, B., Caligulu, U., Özay, Ç., & Yildiz, T. (2021). Investıgatıon Of Mıcrostructure Propertıes Of Nbc–B Coated Hardox 400 Steel By Trd Method And Evaluatıon Of Wear Behavıor By Taguchı Method. *Surface Review and Letters*, *28*(12), 2150115.
- **[13]** S. Buytoz, B. Yılmaz, " Investigation of microstrucutural properties of TiC coating obtained by termoreactive diffusion process on AISI4140 steel." *Fırat University Journal of Engineering Sciences* 31.2: 473-480, 2019.
- **[14]** B. Kurt, Y. Küçük, & M.S. Gök, "Microabrasion wear behavior of VC and CrC coatings deposited by thermoreactive diffusion technique." *Tribology Transactions* 57.2: 345-352, 2014.
- **[15]** Y. Karaca, "Investigation of VC Coatability Of 1.2344 Hot Work Tool Steel With Box Cementation Method." *Nevşehir Journal of Science and Technology* 106-110, 2019.
- **[16]** M. Kilic, "TiC coatings on an alloyed steel produced by thermal diffusion." *Materials Testing* 62.9: 909-912, 2020.
- **[17]** F. E. Castillejo, D. M. Marulanda, J. J. Olaya& J. E. Alfonso, "Wear and corrosion resistance of niobium–chromium carbide coatings on AISI D2 produced through TRD." *Surface and Coatings Technology* 254: 104- 111, 2014.
- **[18]** A. Ghadi, H.Ebrahimnezhad-Khaljiri, & R. Gholizadeh, "A comprehensive review on the carbide-base coatings produced by thermo-reactive diffusion: microstructure and properties viewpoints." *Journal of Alloys and Compounds*, 171839, 2023.
- **[19]** S. Özel, " Microstructure and hardness investigation of fe matrix carbide layers alloyed by TIG welding method." KSU Journal of Engineering Sciences 27.2: 311-324, 2024.
- **[20]** A. V. Khvan, B.Hallstedt, & C. Broeckmann, "A thermodynamic evaluation of the Fe–Cr–C system." *Calphad* 46: 24-33, 2014.
- **[21]** M. R. Najari, S. A. Sajjadi, & O. Ganji, " Microstructural evolution and wear properties of chromium carbide coating formed by thermo-reactive diffusion (TRD) process on a cold-work tool steel " *Results in Surfaces and Interfaces* 8: 100059, 2022.
- **[22]** O. Ganji, S. A. Sajjadi, Z. G.Yang, M. Mirjalili, & M. R. Najari, "On the formation and properties of chromium carbide and vanadium carbide coatings produced on W1 tool steel through thermal reactive diffusion (TRD)" *Ceramics International* 46.16: 25320-25329, .

BIOGRAPHIES

Musa KILIÇ obtained his BSc degree in metal teaching from Fırat University in 2004. He received the MSc diploma in Metallurgy and materials training from the Fırat University and Phd degree in Graduate School of Science from Fırat University. His research interests are welding and coating. In 2014 he joined the Faculty of Technology, Batman University as a assistant professor doctor, where he is presently a Associate Professor.