Comparison on corrosion performance of waste-based multi-hybrid structure high carbon steel and high Cr cast steel

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Abstract

Series of protective layer on high C steel have been successfully developed through transforming various wastes. While high Cr cast steel (HCCS) offers excellent properties of toughness, hardness and corrosion resistance. In this research, the focus on characterisation methods of HCCS were conducted by SEM/EDS, TEM, XRD, Tafel and EIS curves. Results have revealed that modified surface high C steel performed higher corrosion resistance than 16.0–16.5%Cr steel. This finding has opened the new context of using wastes as a source for producing protective layer on the surface of high C steel that integrated profitability of steel products, thus, minimising production cost.

Keywords High C steel · Waste · Protective layer · High Cr cast steel · Corrosion

1 Introduction

In recent years, the demand of high C steel has been substantially increased, due to its superior properties from combination of strength-hardness ratio [1, 2] and low-cost steel that is continuously used in aviation, chemical and mining industries [3, 4]. With its mediocre level of corrosion resistance, it can inevitably lead to the loss of materials or failure on machineries and applications and should be further enhanced. Furthermore, in mining environment, water is very essential at almost every stage of its process and the main assets of the mining sites are located at water-stressed area, which has forced to find an alternative solution to resume the mining operation [5]. The used of sea water is one of the effective solutions, but with chloride content in the water that can increase the propensity towards corrosion attack of high C steel applications.

Recently, extensive researches have been devoted on resistance to corrosion by selecting and adding alloying element such as Cr in composition of steel. This method has been proven to be effective in significantly prevent

corrosion degradation. For instance, the high Cr cast steels (HCCS) have been widely covered various sectors and industrial applications, due to its excellent properties of toughness, hardness, wear and corrosion resistance that suit to use in corrosive environment. Their superior properties result mainly from emergence of high-volume fraction hard Cr-rich M_7C_3 carbides [6, 7]. However, it has a major drawback, due to its high addition of alloying element, Cr (typically exceed 12 wt%) content in steel [8, 9], which is typically expensive, the cost-efficient of this grade of steel is highly unlikely to be achieved. The microstructure contained different constituent phases that have direct influence on its chemical and mechanical properties. Transition metal carbides such as precipitation of M_7C_3 carbide in high Cr content steel, can dramatically affect its properties [6, 7]. This includes the crystal orientation, transition metal carbide stability and its thermodynamic properties [6, 7]. The carbides are commonly formed in HCCS that have few complicated crystal structures, and its chemical formulas usually correlate on C, Cr and other alloy element concentrations [10]. Nevertheless, to achieve certain properties

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that high C steel can offers, it requires the use of energy, resource and time through adding complex heat treatment process, thus, corresponding to higher production cost. Note to mention that these attempts have limited success.

To achieve the desire properties that high C steel has offers, an economical solution can be implemented through used of different type of wastes to generate multi-hybrid layer on the surface of high C steels to improve its corrosion resistance in single step-controlled heat treatment system at low temperature without altering bulk properties, which have been studied in recent research. Every year, millions of tonnes of wastes such as slag from steelmaking industry typically generated by electric arc furnace (EAF) [11], non-recyclable glass from laminated or tempered glasses and heterogenous mixture of plastics from automotive sector, especially automotive shredder residue (ASR) were discarded in the landfills. Disposed of these wastes has ignored the potential applications as value-added or supplementary materials, such as Fe, Si, C, Ti [12, 13], instead of using new resource excavated from the mining. The aim of this study is to overview and compare to what extend this generated multi-hybrid layer on high C steels, that able to compare with costly HCCS alloys in terms of corrosion resistance perspective.

2 Experimental procedures

2.1 Materials preparation

High C steel with nominal composition of 1.1%C, 0.15%Mn, 0.40%Si, 0.65–0.70%Cr, 0.02 Mo and balance, units are in wt%, was utilised in this investigation. Different multi-hybrid layer has been successfully bonded on the surface of high C steel samples, derived from various wastes from the previous studies [14–16]. The evidence of the existence of multi-hybrid layer of the steels with different mixture of wastes approach and in-depth characterisations of the coatings were clearly described in these previous researches [14–16]. The corrosion resistance that HCCS alloys with similar composition with different Cr content (18.5–19.0%Cr on sample-A and 16.0–16.5% Cr on sample-B) have been used to overview and compared its corrosion resistance properties in 3.5% NaCl solution condition. All steel samples were cut by Struers Accutom-50 at low speed rate to avoid heat transfer that can have direct impact on microstructure changes, grinded using SiC paper by Struers Tegramin-30, finely polished using diamond suspension and colloidal silica by Struers Rotopol-22, cleaned by ultrasonic cleaner, dried and stored into desiccator to minimise oxidation. The used of 2% nital solution to reveal the microstructures of high Cr steels.

2.2 Analytical methods

Optical microscope—Nikon ME-600 was adopted to observe and compare different microstructure characteristic on HCCS alloy samples. XRD analysis was conducted to provide quantitative data of presence of different phases in which were strongly presented in the steels, by using Empyrean (PANalytical) that equipped with HighScore Plus software. The Co-K α radiation was chosen for this experiment to avoid strong florescence influence from Cu radiation and to receive high precision spectrum, at 45 kV and 40 mA to measure different intensity in 2θ angle position between 20 ° and 130 °. High-resolution SEM images and EDS micro-analysis by JEOL-70001F to observe elemental composition of phase or presence of any secondary phase that can be considered on its effect to corrosion resistance. TEM—Philips CM200 was used to observe presence of Mo and V carbides in the HCCS. A reliable corrosion rate measurement through Tafel polarisation technique—Versatile Multipotentiostat VSP-300 has been implemented to compare the overall corrosion rate between multi-hybrid layer steels and HCCS against the base-material high C steel. Three electrodes (saturated calomel electrode (SCE)—reference, platinum (Pt) electrode—auxiliary and steel samples—working). Open circuit potential (OCP) mode was used in the experiments, with 1 cm² diameter as tested surface area of steels for 4 h. Tafel plot was recorded between – 250 mV and + 250 mV with scan rate of 0.25 mV/s. Therefore, corrosion potential, E_{corr} and current density, i_{corr} can be defined. Electrochemical impedance spectroscopy (EIS) method was used with OPC mode at corrosion potential 10 mV, frequency range between 100 kHz and 0.01 Hz with 24 hour time.

3 Results and discussions

3.1 Optical microscopy

In Fig. 1, it showed polarised light microscopy images of microstructures of HCCS at different magnification, in comparison with the previous study of multi-hybrid structure high carbon steel, sample HCS-C [14]. The dark colour represented martensite (M) phase, whereas ferrite (F) phase in bright colour. It can be observed that with higher Cr percentage, it refined both martensite and ferrite phases on sample-A over sample-B. Furthermore, X-ray spectrums in Fig. 2 suggested that in this microstructure, the presence of mostly eutectic chromium, Cr-rich (M_7C_3) carbides dispersed in the martensite

Fig. 1 Optical imaging of different high Cr content in steel on **a** sample-A and **b** sample-B with its different magnification on **a1** and **b1** respectively

Fig. 2 XRD diffraction spectra for HCCS alloys on **a** sample-A and **b** sample-B, where martensite (M) and ferrite (F)

phase matrix. The presence of less interconnected M_7C_3 carbides and ferrite promoted combination of abrasion resistance [17] and toughness [18] properties, respectively. With high alloying elements such as Cr in cast steel will significantly improve its corrosion resistance, thus, reduced the propensity of corrosive degradation, but it can be a costly steel product. Existence of molybdenum, Mo-rich (M_6C) and vanadium, V-rich (MC) carbides [19, 20] were detected in very low concentration of XRD spectrum in both steels, this can be due to very low amount of Mo and V elements in steels. However, further investigation on its micro-analysis through SEM/EDS analysis will be implemented to prove this assumption.

3.2 SEM/EDS analysis

The element distributions inhibited on each steel was better appreciated in SEM in back-scatter electron (BSE) mode and EDS mapping analysis in Fig. 3 for sample-A and sample-B. It can be clearly observed that grain boundary of martensite and ferrite phases have been performed through BSE, with Cr-rich of M_7C_3 carbides in the martensitic phase on both HCCS. Additionally, it has been shown that Mo-rich and V-rich carbides were existed in very low concentration on the tested steels. These secondary phases can downgrade the corrosion resistance of steel as it will promote intergranular corrosion attack [21, 22] and can cause pit growth, but with low volume fraction of

Fig. 3 SEM (BSE mode) images and EDS micro-analysis on Cr, Fe, C, Mo and V elements of HCCS alloys for **a** sample-A and **b** sample-B

these inclusion, will not have significant impact on overall corrosion resistance. In this microstructural analysis, a slightly different in size of constituent phases can lead to direct impact on the corrosion resistance properties of steels.

A reference SEM and EDS analysis of the waste-based multi-hybrid structure high carbon steel is referred to the previous study [14]—sample HCS-C, where the multi-hybrid layer composed from chromium nitride (CrN), magnesium nitride (Mg_3N_2) and other metallic phases, such as TiN and TiO_2 , in comparison with the current results of HCCS alloys. In-depth analysis to observe the presence of Mo and V carbides in HCCS is presented in Fig. 4 below through the TEM analysis.

3.3 Tafel polarisation methods

Corrosion tests have been conducted through Tafel polarisation method to measure and compare its corrosion rate and calculated the percentage of protection efficiency, η_p . The Tafel curves of multi-hybrid layer high C steel and HCCS alloys against the base-material high C steel is

presented in Fig. 5. From this graph, the difference properties of corrosion resistance on tested steels were defined by low i_{corr} value and more positive E_{corr} value toward noble side. A summary of Tafel quantitative data is presented in Table 1. It can be observed that highest Cr cast steels—sample-A owned the highest corrosion resistance contributed to 64.43%, followed by multi-hybrid layer steel about 51.98% and sample-B respectively around 36.89%, lastly base-material of high C steel as reference to calculation of η_p . A very significant improvement of both i_{corr} and E_{corr} on multi-hybrid layer steel than base-material high C steel and was closed to 18.5–19.0%Cr cast steel—sample-A. On the other hand, sample-B performed higher i_{corr} value and more negative E_{corr} value than multi-hybrid layer steel, meaning that waste-integrated inputs as source for production of multi-hybrid layer steels has corrosion resistance behaviour somewhere between these HCCS alloys. Furthermore, in these dual-structure steels, preferential corrosion degradation on ferrite then followed by martensite, this was mainly due to the C content is higher in martensitic phase that led to phase stability than Fe-rich ferrite phase [23, 24]. Meaning that martensite performed

Fig. 4 TEM analysis on the presence of Mo-rich and V-rich carbides on the HCCS

Fig. 5 The comparison of Tafel curves on base-material, different Cr percentage in cast steel—sample-A and sample-B and multi-hybrid layer high C steel

Table 1 Summary of Tafel parameters of multi-hybrid layer high C steel and HCCS against the base-material high C steel

Sample-ID	E_{corr} (mV vs. SCE)	i_{corr} (mA/cm ²)	η_p (%)
fBase-material high C Steel	− 742	0.0158	–
Sample-A	− 326	0.00562	64.43
Sample-B	− 529	0.00997	36.89
Multi-hybrid layer steel	− 369	0.00759	51.98

cathodic behaviour and ferrite exhibited anodic behaviour [24, 25]. Other factor that can influence this preferential degradation on one phase than another, was because of iron atoms dissolutions. With controlled heat treatment process, the bulk properties remained unalter to maintain its original properties for multi-hybrid layer steel.

Corrosion mechanism of these steels were grain boundary corrosion [26], pitting corrosion [27] and intergranular corrosion [28]. Grain boundary corrosion was mainly due to the dual-structure of constituent phases—martensite and ferrite that have difference in potential energy between contacted surface area or interface of both phases [26]. Additionally, it can be caused by different size, shape, distribution and stability of each phase in the steel that determined the overall corrosion degradation. Pitting corrosion or well-known as localised corrosion because of the depassivation of certain area on the surface of steels that caused anodic and cathodic half

reaction to occur, promoting electromigration of aggressive anions and potential gradient that formed pit holes with limited numbers of diffusion of ions [27]. Intergranular corrosion was caused by deterioration along the grain boundaries due to thermodynamic effect for corrosion is higher at grain boundaries than at the inner grain boundaries in which exposure of certain crystalline on materials, impurity or secondary phase and difference in composition at a particular environment (electrochemical or chemical) that can initiate this type of corrosion [28, 29]. Therefore, it can be concluded that corrosion resistance of high C steel has been enhanced through multi-hybrid layer that able to match with costly HCCS.

Further analysis was performed by utilising the electrochemical impedance spectroscopy (EIS) method to confirm the finding in the Tafel polarisation curves above. EIS method has proven to be an effective tool to analyse the corrosion process of steels in different conditions. In Fig. 6, the Nyquist curve is presented, with higher corrosion resistance property, the size of the high-frequency (HF) loop is expanded, and the disappearance of inductive loop occurred. The increasing in diameter of the capacitive loop has proven to be reduced in the charge-transfer resistance and corrosion current density value. Therefore, the corrosion resistance property of the sample-A is the highest, followed by multi-hybrid layer steel, sample-B and base material high C steel.

Fig. 6 The Nyquist curve from the EIS experimental data for base-material high C steel, multi-hybrid layer steel and HCCS samples

4 Conclusions

Corrosion resistance of low-cost high C steel has been improved through the production of multi-hybrid layer derived from various wastes—slag, non-recyclable glass and heterogenous mixture of plastics from ASR, via heat treatment. Microstructural and crystallography analysis by polarised light microscopy, SEM/EDS and XRD have proved the presence of eutectic Cr-rich, M_7C_3 carbide in the martensite matrix on both HCCS. The presence of Mo-rich (M_6C) and vanadium, V-rich (MC) carbides were detected using a TEM analysis. Although HCCS can significantly enhance corrosion resistance properties with good combination of toughness, hardness and wear resistance, but they are not cost-efficient. Results have revealed that this type of multi-hybrid layer steel was able to compete with 18.5–19.0%Cr cast steel, which contributed to 51.98 and 64.43% improvement in corrosion resistance properties respectively than in base-material high C steel. This study has opened a new opportunity to utilised wastes as source for production of protective layer of low-cost high C steel to save production cost, reducing the dependency on new resources and minimising the impact to the environment through disposed of wastes into landfills.

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Author contributions WH designed and performed experiments and data analysis. FP performed experiments and critically analysed the data. VS supervised the study and gave recommendations to revise manuscript. WH wrote the manuscript and all authors analysed data, discussed the results, read and approved the final manuscript.

Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request

Compliance with ethical standards

Conflicts of interest The authors declare no conflicts of interest.

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