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RESEARCH ARTICLE

CORROSION WEAR AND MICROSTRUCTURE ANALYSIS OF SURFACES COATED BY HARDFACING ELECTRODE AND NITRIDING

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ABSTRACT

Cotton 30MnB5 quality steel (EN 10083:2006), used in agricultural machinery production, was employed in this study. Some of the components in agricultural tools are prone to abrasion during soil tillage. Processes of hardfacing with coated electrode fillet weld and surface hardening through nitriding, employed commonly for increasing abrasion resistance of such material used for digging components, were studied. A 2 mm thick deposit was formed on 8 mm thick, boron containing, heat treated and tempered steel surface using NiMo and Citomangan Hardfacing Electrodes. Also, liquid nitriding process was applied at 650 C for 3 hours on this material. The mass loss of the new material formed with such methods was measured and abrasion tests thereof were conducted. Abrasion tests at 0.186 m/s rotational speed for a period of 60 hours were applied on the abrasion specimens prepared for this purpose in a container with mineral abrasives. The smallest mass loss was measured for specimens made with Citomangan hardfacing electrode. In addition, corrosion resistances of the specimens were assessed in a 0.5 mol NCL and 29.22 gr double distilled corrosive environment. Surface hardness and wear loss values do not match, which is thought to be influenced by the elemental contribution resulting in harder phases or microstructures during the testing. Agricultural tools facing severe soil wear have been surface modified by using liquid nitriding, Citomangan and NiMo hardfacing electrodes. Hardfacing electrodes are comparatively more efficient in terms of wear loss compared to liquid nitriding. Agricultural tools facing severe soil wear have been surface modified by using liquid nitriding, Citomangan and NiMo hardfacing electrodes. Hardfacing electrodes are comparatively more efficient in terms of wear loss compared to liquid nitriding. Surface hardness and wear loss values do not match, which is thought to be influenced by the elemental contribution resulting in harder phases or microstructures during the testing.

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INTRODUCTION

Hardfacing is defined as a coating on the parent material to reduce wear or reduce material lost due to wear mechanisms (Serdar Atamert, 1988 and Kenchi Reddy, 2014). Fusion arc welding is one of the most commonly used techniques in the hardfacing industry extending service life of industrial products (Palanikumar, 2015). Some sections of the machinery parts produced for an industrial purpose, whether intentional or not, wear out due to the effect of one or more of abrasive mechanisms such as abrasion, adhesion, erosion or corrosion. Repairing parts that have lost their dimensions or broke during the course of work or by being affected from atmospheric conditions with welding also entails many advantages (Efremenko, 2013). When depositing hardfacing alloys on metal surface, the weld type and hardfacing alloy should be selected in accordance with relevant standards (Efremenko, 2013).

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There are three methods commonly used in hardfacing, which are done by using either one of fusion or solid state welding methods or by flame spraying method. Welding or thermally sprayed coating are methods used often during maintenance or production of new machinery parts (Seiji Kuroda, 2008; Zhang, 2015). The selection and use of any of these methods is associated with the magnitude of abrasion and the abrasion performance of the hardfacing deposit forming after the method is applied. Hardfacing applications performed through any fusion welding method are used commonly for resizing of overly worn machinery parts. However, the flame spraying methods stand out in terms of formation of thin wear resistant layers and thus increasing corrosion resistance without requiring any secondary processes (Milanti, 2016). Today many methods are utilized to make the surface resistant against wear and improve the service life of the matrix. To minimize the damage resulting from working conditions is priority when matrix material cannot function on its own. Low friction coefficient values, high wear resistance and improved corrosion resistance can be achieved by improving the surface of materials (Milanti, 2016 and Bin Han, 2013). Installation and uninstallation times and loss of efficiency following the wear of parts hinder effective operation of facilities and equipment and result in the loss of millions of dollar every year (Lekan Taofeek Popoola, 2013). One of the effective methods for improving the surface wear resistance is to increase wear resistance by hardfacing deposits formed on surfaces containing nickel and chromium. Nickel has very little effect on abrasive resistance. It promotes austenite on the parent metal surface over which it acts as a thermal stress barrier and metallurgically tolerant layer (Vineet Shibe, 2013). S. Chatterjeeet et al. revealed the possibility of obtaining similar wear resistance with higher chromium and carbon without adding niobium and molybdenum (Chatterjee, 2003). Hardfacing is applied to gray cast iron mill roller surfaces in the sugar cane sector to reduce wear and to improve wear resistant properties of surfaces. The reason for this is that such rollers work under the impact of a higher force using idlers to aid the crushing of sugar cane (Chatterjee, 2003). The reasons for selecting the shielded metal arc welding method “SMAW” are its cost-effectiveness and more effective accumulation of filler metal deposit (Dayana Beatriz Carmona Garcia, 2011). Wear behavior of AISI H13 hot work tool steel and 722M24 tool steel specimens at room temperature and at higher temperatures during plasma nitriding process at various nitriding temperatures and for different durations were investigated (Zagonel, 2012). It was reported that with the increasing nitriding temperature, even though surface roughness decreased, friction coefficient increased (Hakan Aydın, 2013). Nitrided layer obtained after long processing time had a lower wear rate than the layer obtained at short process time. Özdemir and Erten (Özdemir, 2003), noted that the resulting hardness and wear resistance in the deposited material from the effects of alloy elements in hardfacing electrodes, such as Cr, Mn, Co, Ni, V, Mo, and W, was due to the hard carbide formed by such elements or the cold deformation emerging as the parts operate during service as reported (Dayana Beatriz Carmona Garcia, 2011). Materials cannot maintain wear resistance on their own and therefore, surface coating filler alloys can be applied where the wear is critical (Patricio, 2014). This is study is related with the widely used 30MnB5 quality steel (EN 10083:2006), agricultural equipments which are faced with severe soil wear. Therefore, enhancing the wear behavior is important for the equipment service life. A hardfacing layer was formed on the material surface through nitriding method using commercial filler electrodes containing various alloys.

EXPERIMENTAL PROCEDURES

Stick electrode arc welding and nitriding methods were used to deposit hardfacing layer in this study. A 2 mm hardfacing deposit was formed on the surface of 8 mm thick 30MnB5 material by using Citomangan and EIS 410 type commercial electrodes at a current of 155 A. Fillet weld was performed by establishing 20 mm seam width at 4.5 cm/min welding rate. Coated electrodes with a dimension of 4.00x350 (mm) were supplied from the producer. Interpass temperature of weld seams deposited with Citomangan hardfacing electrode and EIS 410 electrode were 385°C and 450°C, respectively. The dimensions of specimens used in nitriding are given in Figure 1a. In this process, liquid nitriding bath containing standard salt and activation salt in a pot made of stainless steel were used. While standard salt provided the bath environment, activation salt carried out nitriding. In the process, specimens were held at approximately 650^{o}C for 3 hours. The circulation of the liquid bath was enabled by providing compressed air into the bath. The specimens taken out of nitriding pool were cooled by submerging into water tanks at room temperature.

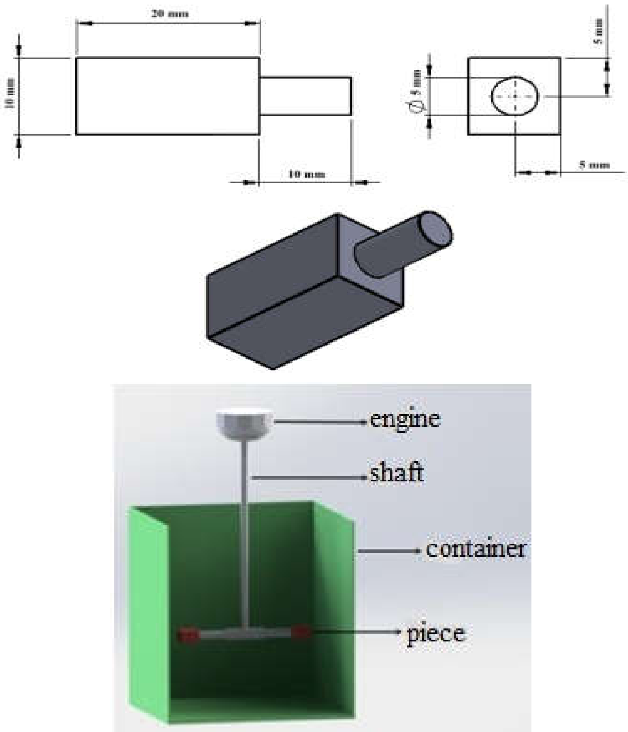


Figure 1. a) Wear test specimen dimensions
b) Abrasion test assembly

Abrasion test was carried out on a speed controlled columnar drill workbench shown in Figure 1b, which contained moisturized molding sand as an abrasive medium of 10 kg distributed load on abrasive sand. This process was performed at 50 rot/sec rotational speed for 1800 minutes. Specimens were later removed from the container and its mass loss value was calculated using a 0.01mg precision balance. The steel, produced with hot rolling of 5630 Erdemir quality steel, is also known as 30MnB5 quality steel according to DIN EN 10083-3:2006 standards. These quality steels are generally used for digging tips of agricultural tools for soil tillage. Chemical compositions of the used steel and filler alloy electrodes are given in Tables 1, 2 and 3.

RESULTS AND DISCUSSIONS

Hardness, wear and microstructure characterization

In order to report the properties before abrasion test, the micro hardness value of 30MnB5 quality steel was measured as 179.66 $HV_{(0.5)}$ by taking the average of hardness values recorded from different parts of the material. It is seen in Figure 2a that the hardness values of NiMo (EIS 410) filler welded specimen increase from the parent metal to filler deposit. This increase becomes twice the hardness of the parent metal at the side of deposited weld. While the hardness values of other filler alloy electrode (Citomangan) displayed less increase from base metal towards deposited weld when compared to EIS electrode; the hardness at deposited region increases up to two folds, but then rapidly decreases (Figure 2b). The hardness change in hardfacing deposited surface begins in the transition area, i.e. HAZ and reaches its highest value in deposited layer. The highest hardness value was measured in the layer made with NiMo (EIS410) filler alloy electrode. Wear and hardness values between nitride and hardfaced specimens were also compared. The wear resistance in nitride specimens was measured to be relatively high and appears to be decreasing with low hardness value. as dispersed in a softer eutectic (Khanlar, 2015). Also it is confirmed in other studies that primary carbides determined as a result of SEM / EDXA analyses and hardness values depend on carbides of M_7C_3' (Saha, 2015).

Table 1. The chemical composition of 5630 quality steel (%)

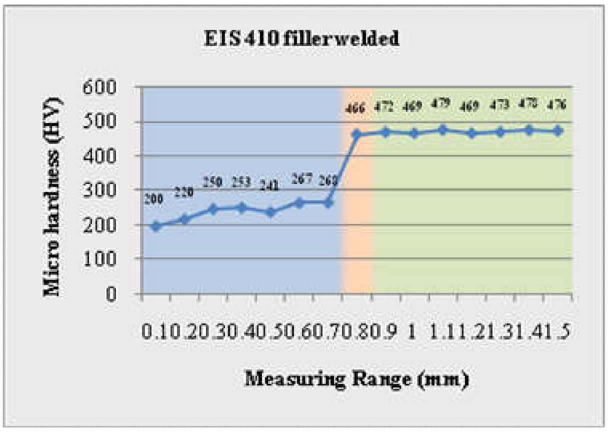
C	Mn	P max.	S max.	Si max.	Cr	Ti	B
0.27 - 0.33	1.15 - 1.45	0.025	0.035	0.40	0.05 - 0.30	0.015-0.060	0.0008-0.0050

Table 2. The chemical composition of EIS 410 NiMo stainless steel filler rod (%)

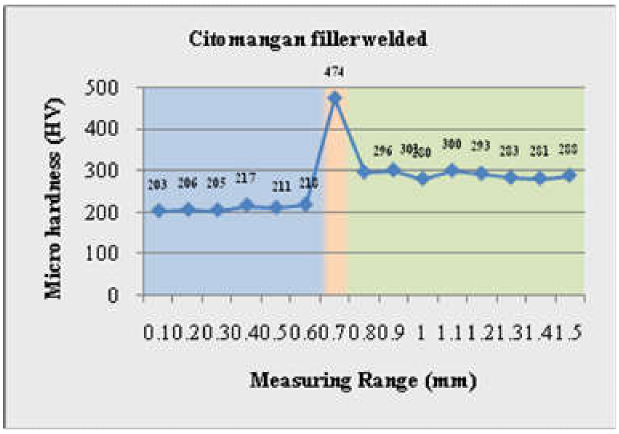
C	Si	Mn	Cr	Ni	Mo
0.06	0.75	0.80	12.00	4.00	0.50

Table 3. The chemical composition of Citomangan hardfacing electrodes (%)

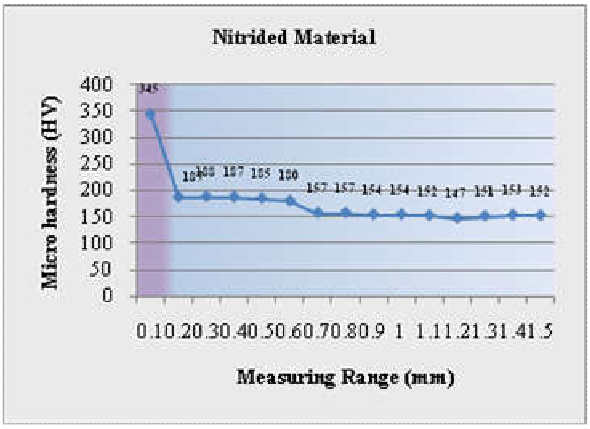
C	Mn	Ni	Fe
0.70	12.00	3.00	Remaining



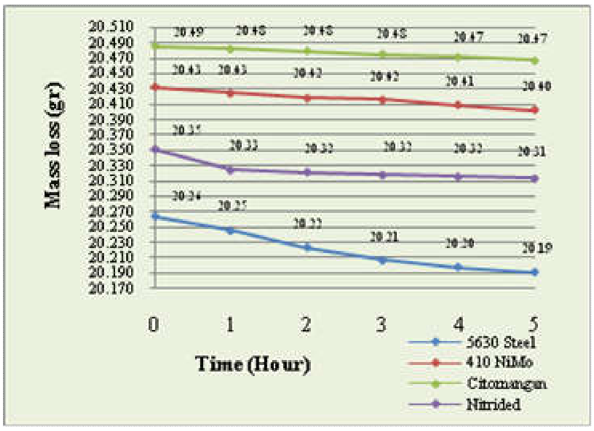
a)



b)



c)



d)

Figure 2. Micro hardness and mass change a) 410 EISA filler welded b) Citomangan filler welded c) nitriding d) wear mass change)

In hardfacing layers, it was seen that the wear resistance also decreased in parallel to the decrease in hardness value (Figure 2d). Although the filler alloy used led to an increase in the hardness of the current material, the carbon value of the parent material plays an important role in hardness increase of the hardfacing layer. In a similar study, the wear behaviors of hardfaced deposits produced by Fe-Cr-B alloy based commercial electrodes were tested on gray cast iron surface (Buchanan, 2008). Alloy composition of layers on which hardfacing electrodes are formed, usually have a known composition. Primary carbides are formed during welding process and increase the wear resistance of the matrix structure

It was calculated that the hardness value of the layer formed on nitrided material was nearly three times the hardness value of the base metal. Since the atomic diameter of the nitrogen in the liquid bath used in nitriding is 0.71nm, it can easily penetrate to the iron lattice easier when compared to carbon which has an atomic diameter of 0.77nm (Çelik, 1996). Nitrogen diffuses very quickly in solid phase of austenite at high temperatures, As a result of nitrogen compounds (i.e. nitride) forming on the surface, it leads to the formation of a fragile layer on the surface (Chemkhi, 2013). In addition, due to austenite-ferrite transformation, a change in volume occurs and the nitrogen diffuses into ferrite.

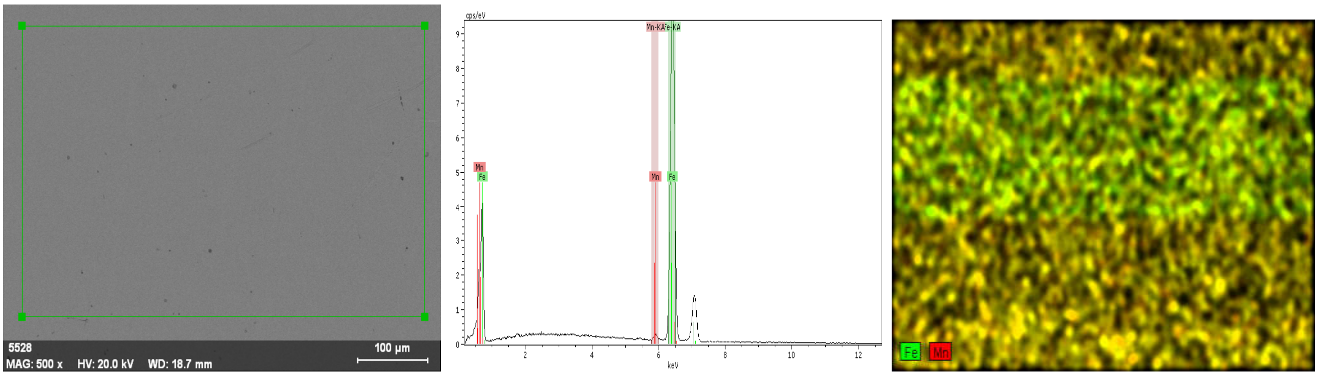


Figure 3. SEM microstructure analysis of 5630 quality material

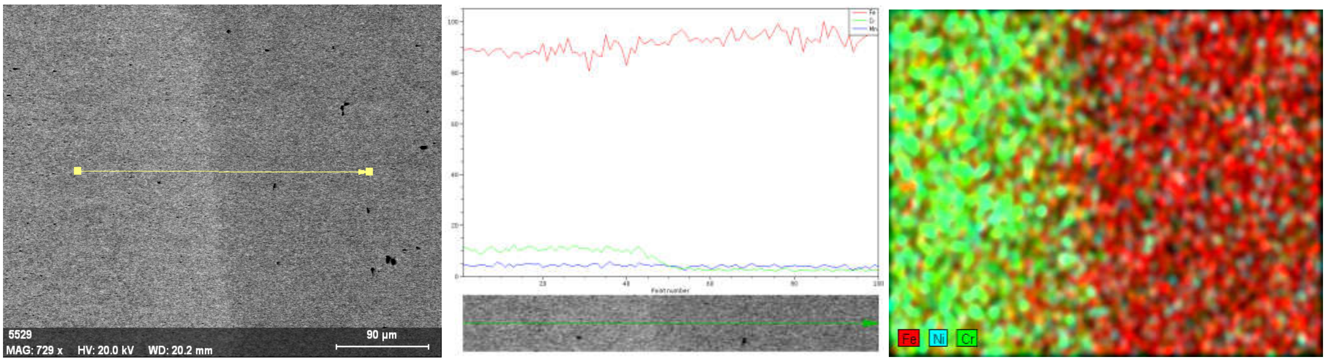


Figure 4. SEM microstructure analysis of EIS 410 NiMo hardfacing deposit structure

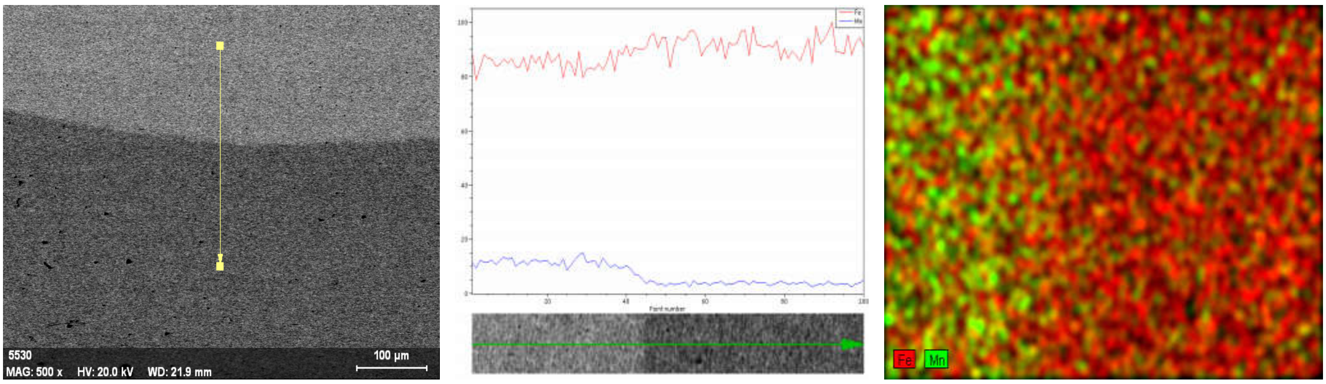


Figure 5. SEM and EDX analysis of microstructure of Citomangan hardfacing deposit structure

In the meantime, a rather thin and fragile structure of nitrides forms in the region containing nitrogen. Alloy nitrides precipitate on cooling, which will lead to a high hardness value even higher than the hardness of martensite (Bobadilla, 2015). Wear test results are given in Figure 2d and micro hardness values are also shown in Figures 2a, b and c. When wear curves are examined, it is clearly seen that the amount of wear increases with time. The common characteristic for each specimen is the increase in total mass change for all specimens with respect to time. It can be said that electrodes used for hardfacing are under the impact of additives such as manganese and chromium and this is related to electrodes being more resistant against wear. Phases formed on hardfacing deposits and their particle and grain sizes are important factors that affect mechanical properties (Junfeng Gou, 2016). In microstructure images given in Figure 4and Figure 5, it is seen that hardfacing deposited and heat affected zones are different when compared to the parent metal. Microstructure images of weld zones provide information on the cooling characteristic of the melting filler deposit.

In this case cooling of sections near HAZ zone appears to be faster because columnar martensite structure is formed due to fast cooling. Direction throughout the length of the columns formed on weld metal points from the welding pool to the direction of the heat flow (Mohsen Mokhtabad Amrei, 2016). Hardface zone closet to HAZ contains a columnar particle structure, whereas center of the weld has dendritic grains (Kenchi Reddy, 2014; Çelik, 2000). In Figures 4, 5, dentritic and ferritic microstructures due to high alloying can be observed in the microstructure of hardfaced specimens at the grain borders in the area bordering the parent metal. Nickel, chromium and manganese in the composition of the filler electrode used can be suggested as the reason of such changes in microstructure. Hardfacing alloys usually have a highly alloyed certain composition and therefore primary carbides are formed during welding process and precipitate in the matrix of which its hardness and wear resistance increase by their presence in the microstructure (Jae Hyun Jeong, 2015). Manganese steels are employed in hardfacing welding. Its resistance against impacts is high and the hardness of weld metal increases with cold welding.

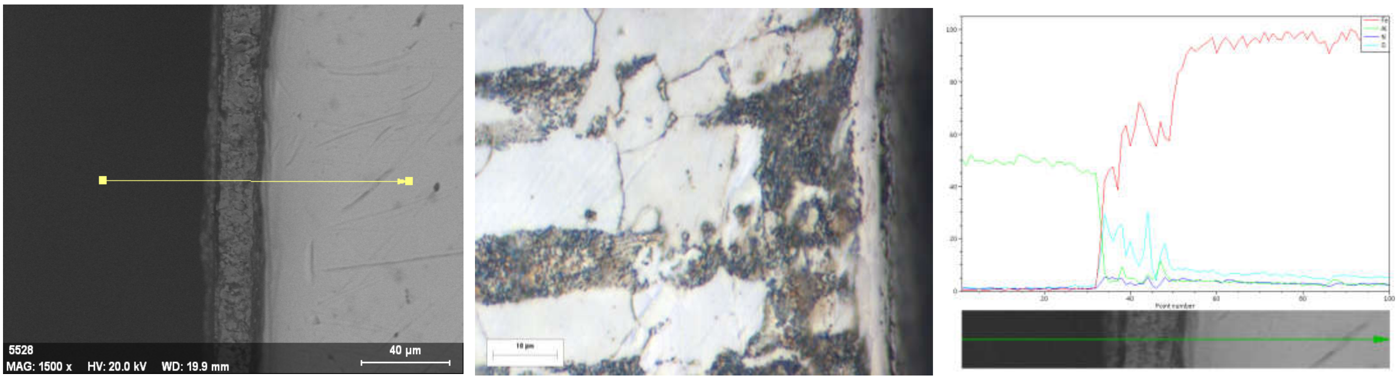


Figure 6. Microstructure images of material, surface of which is coated with nitriding method

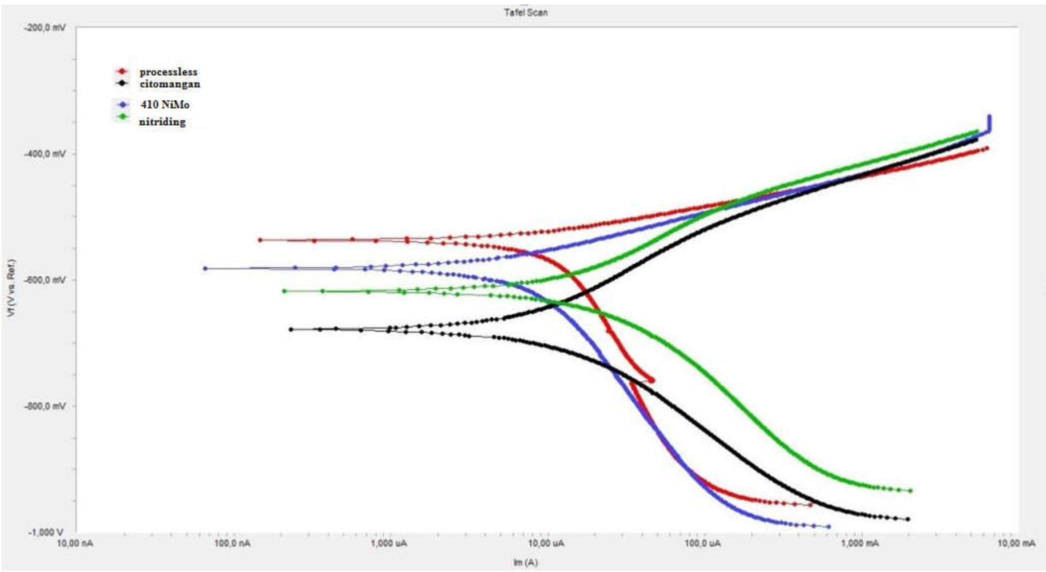


Figure 7. Tafel curves obtained in 0.5 mol NCL corrosive environment

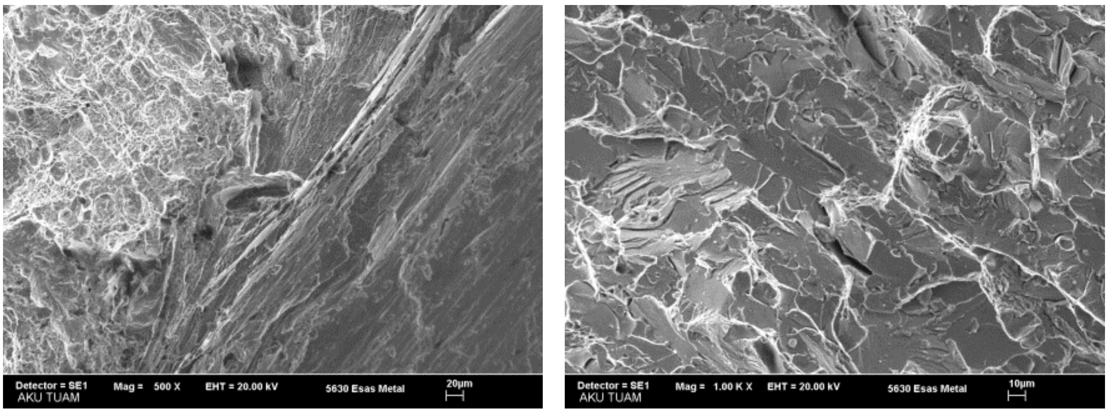


Figure 8. SEM image of fractured surface of parent metal

It is particularly suitable for hardfacing welding of components that have been abraded due to severe impact and shocking strains (Örtülüelektrotlar, 2016). Alloy material used for hardfacing can be reprocessed later. The welded surface may harden when submitted to cold welding. More than one pass of hardfacing weld can be done successively without requiring buffer. Hardfacing welding can be used for crusher jaws, cone crusher mantles and worn excavator buckets. For nitrogen concentration to be 0.42% solid solution of nitrogen in α-Fe should be raised up to a 590°C eutectoid temperature. At room temperature, this solubility drops to C>O.l5. γ phase is a Fe_4N based solid solution. γ phase contains 5.7-6% N at 450°C. ε phase is a Fe_3N based solid solution that contains 8.25-11.2% N. At the maximum amount of nitrogen for ε phase, there is also γ phase over 590°C. At 590°C α and γ phases undergoes eutectoid fragmentation. This structure containing 2.35% N is composed of a mixture of α and γ phases. Nitrogen dissolves both in α and γ iron; in addition, only a portion of the atomic nitrogen forming as a result of breakup of the ammonium gas sent to the system diffuses onto the surface of the steel (Akbulut, 2014). At nitration temperature ammonium gas breaks up as follows:

2NH3 => 2N + 3H2……………………..1

4Fe N => Fe_4N………………………….. 2

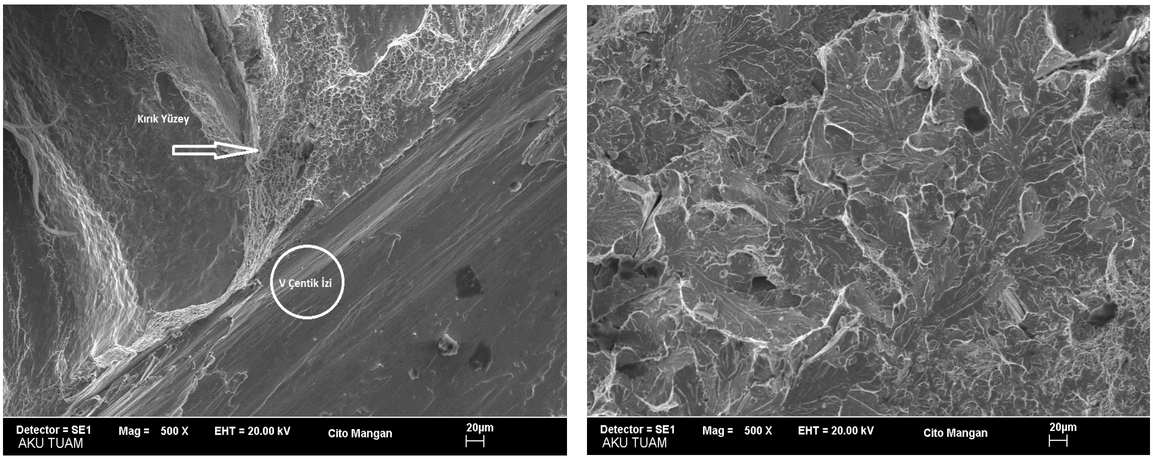


Figure 9. SEM image of fractured surface of coating made with Citomangan hardfacing electrode

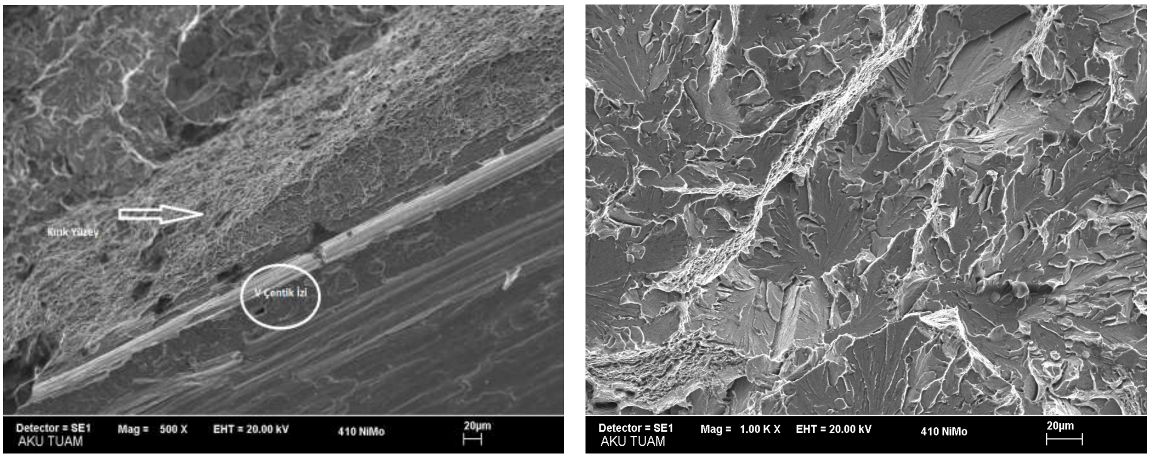


Figure 10. SEM image of fractured surface of coating made with NiMo hardfacing electrode

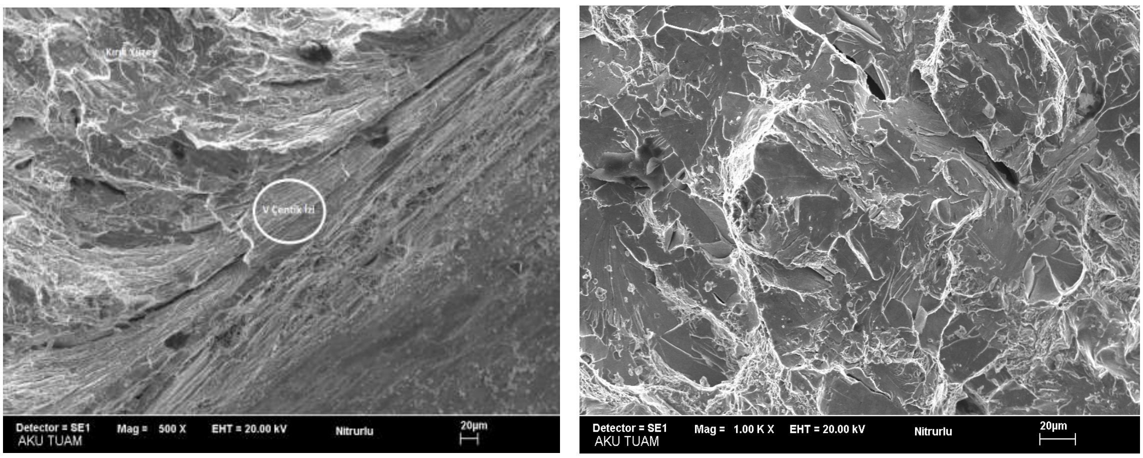


Figure 11. SEM image of fractured surface of coating made with nitriding

The reaction starts turning left at 595 C, however it is not fast under 580 C

$2Fe + N \Rightarrow Fe_2N$…………………………3

Resulting atomic nitrogen diffuses into the iron. If nitration process is carried out under eutectoid point, α phase would form at the first moment of saturation on the surface. After α phase reaches maximum saturation at the given temperatures, fragile phase would start forming at the same temperature (γ phase) (Akbulut, 2004). Nitriding process is performed on components, for which it is desired that geometrical shapes such as precise, finely detailed, sharp corners are not lost and wear resistance thereof is high. Nitriding processes do not damage the surface of the material under suitable conditions. By submerging into a nitride bath, it is showing its effect on all surfaces that have come into contact with the liquid. After nitriding, the rolling lines formed on the microstructure of 5630 quality steel during production display completely the same properties. In the SEM line analysis N concentration decreasingly continues towards the depth of parent metal. As seen in the analysis reflects from the base used in SEM device (Figure 6). While the lowest Icorr value was obtained in specimen in which 410-NiMo hardfacing electrode was used, the highest Icorr value was obtained in the nitrided specimen. 410-NiMo and Citomangan hardfacing electrode increased the corrosion resistance of the specimens. However, corrosion resistance of the nitrided specimen was reduced. The results obtained from Tafel curves are observed to be directly proportional to Rp values (Figure 7). SEM images of surfaces formed after Charpy impact toughness experiment are given in Figures (7-10). In Figure 7, the highest fracture toughness energy was calculated for non hardfaced 5630 quality steel. It is suggested that in the production of this steel, reduction in grain size due to hot rolling and existence of rolling bands in the microstructure causes high impact toughness. The lowest fracture toughness energy was for EIS 410 NiMo welded steel. Even though Ni present in filler alloy reduced ferrite formation in the weld zone, it accelerated martensite formation due possibly to fast cooling (Figure 9). In Figure 8, it is suggested that the perlitic phase is formed on Citomangan hardfacing electrode not changing and also the effect of Manganese additive contained in filler alloy may cause the increase in impact toughness.

Conclusions

- While microstructure and phase changes occurred at HAZ zone for Citomangan and EIS 410 NiMo hardfacing welded specimens compared with 5630 quality steel, for specimens submitted to nitriding at lower temperature phase changes resulting from diffusion can be seen on the surface of the material.
- In the weld zone, dentritic areas progress into the parent metal and due to the effect of recrystallization resulting from high temperature, roll lines on the parent metal disappear. An approximately 0.1 mm thick nitride layer formed as a diffused straight line parallel to the surface of nitrided material. The nitride layer has an oxide layer that formed during cooling.
- Impact toughness is calculated as maximum in unprocessed 5630 quality steel and minimum in EIS 410 NiMo welded specimen.
- Micro hardness is measured to be the highest in the weld metal and hardness decreases from HAZ towards the parent metal. The hardness value for EIS 410 welded material continues at HAZ zone without any excessive decrease, whereas it decreases quicker in citomangan welded specimen. Even though the hardness value at the nitride deposit on the nitrided specimen is the highest, it displays a sudden drop down to the hardness value of the parent metal.
- As for the results of wear due to mass loss, the highest mass loss occurred in the parent metal i.e. 0.366%. The least mass loss was observed as 0.087% for specimens coated with Citomangan covered electrode. For the nitrided specimen, a rapid decrease due to the oxide deposit occurred on the surface was observed and then it was seen that the specimen displayed rather high wear resistance.

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