Effect of surface attrition on hardness on the hardness and wear properties of 304 stainless steels

S K Alias\textsuperscript{1*}, M N Halmy\textsuperscript{1}, M A M Shah\textsuperscript{1}, N N Ahmad\textsuperscript{1}, S A Sulaiman\textsuperscript{1}, H.F. Pahroraji and B Abdullah\textsuperscript{2}

\textsuperscript{1}Faculty of Mechanical Engineering, Universiti Teknologi Mara Pasir Gudang
\textsuperscript{2}Faculty of Mechanical Engineering, Universiti Teknologi Mara Shah Alam

*khadijah_alias@uitm.edu.my

Abstract. The occurrence of wear in austenitic stainless steel is inevitably unavoidable due to the presence of high chromium content and other alloying elements that hinder the implementation of surface treatment process. This process is usually used to improve the hardness and wear properties of steels and alloys by diffusing hard protected layer on the surface of the material. This paper investigates the effect of surface attrition on the hardness and wear properties of paste boronized 304 stainless steel. Surface attrition treatment was applied onto the surface of 304 stainless steel before paste boronizing was conducted at temperature of 850°C for 8 hours holding times. The microstructure of the boronized samples before and after surface attrition treatment was then observed and recorded in order to compare the phase constituent and boride layer thickness. The hardness of each phases was then evaluated using Vickers microhardness test and the wear resistance test of both paste boronized sample and surface attrited samples after boronizing was performed using pin on disk test. The microstructure results show that there are presences of both FeB and Fe\textsubscript{2}B phases on the surface of Pa-B850 and Pa-SB with boride layer thickness improvement of 3 times compared to untreated samples. This lead to enhancement of both hardness and wear resistance of the paste boronized samples due to better protection on the surface of the 304 stainless steel. The improvement of wear and hardness properties of 304 stainless steel could introduce new application that could be exposed to environment containing friction and wear.

1. Introduction

Generally, 304 stainless steel is the most common type of stainless steel that are widely used in automotive and oil & gas parts due their excellent corrosion resistance, high strength-to-weight ratio in conjunction to whole weight reduction and excellent formability [1-2]. Unfortunately, this material exhibited resistance to hardness and wear properties which restricted their usage in application that are exposed to constant loading and friction. Although there are many available surface treatments that enhanced the tribological behavior of steel, these treatments are ineffective to 304 stainless steel due to the presence of high alloying element contents that obstruct the formation of protective layer on their surface. Hence, a newly modified surface treatment should be implemented in order to develop dispersion of boride layer, thus promoting better wear resistance in 304 stainless steel.

Boronizing, which is a thermochemical method that formed protective boride layer that act as shielding layer on the steel’s surface is used to enhance of hardness and wear behavior of steel [3]. However, the boride layer formation which exhibited combination of FeB and Fe\textsubscript{2}B phase might not be
attained in 304 steel as the existence of high alloying elements impede the creation of this phase, thus resulting in poor hardness and wear properties [4]. As there are presences of carbon and other alloying elements, for example chromium and vanadium in 304 stainless steels, the diffusion of boride layer phase may require longer time to form as the carbon and alloying elements will typically gathered at the boron diffusion zone [5-6]. In conjunction to that, the thickness of Fe₂B diffusion layer is significantly dependent on the selection of boronizing time and temperature which can be exceeded to more than 10 hours holding times. In conventional method, longer boronizing time are required in order to fully diffused Fe₂B and FeB layer with saw tooth morphology that have a minimum thickness of 50µm [7]. The alteration of surfaces layer by layer implemented shot blasting treatment are essential as it culd lead to reduction of boronizing parameters which are temperature and time. Decreasing the boronizing temperature and time are also important as it will effect in cost reduction without compromising the minimum thickness of FeB and Fe₂B layers.

Generally, there are many types of boronizing technique and each can be implemented with different medium and purposes [8]. In liquid boronizing, mixture of crystallized Boraks and boric acid was often used as the boronizing medium and improvement of wear resistance and mechanical properties could be achieved at lower and shorter boronizing temperature and time compare to pack boronizing [9-11]. Regardless to that, the limitation of this method is the need for additional process of removing the salt layers formed on the surfaces of boronized samples, which can be tedious and expensive. Past research on gas boronizing indicated that this method formed thicker boride layer than conventional boronizing methods at similar temperatures as the results of more chemical reactions were activated during the treatment [10]. Despite to the advantages given by this approach, high toxicity of the precursor and requirement of complex boronized unit set-up are the limitations of this method. Out of all the methods, paste boronizing is the most cost-effective method and offer better dispersion quality compared to powder form.

Paste boronizing will be implemented as boron in paste form offer better dispersion quality compared to powder form [6,12]. It is expected that with the successfulness of Fe₂B formation on the surface of 304 stainless steel will lead to enhanced tribological behaviour, thus introducing new and innovative applications for this material. It would be beneficial if a new approach could be implemented, in order to increase both boron diffusion. Thus, this study focused on the effect of surface attrition on the improvement of hard-ness and wear properties of 304 stainless steel.

2. Research Work
The samples used in this study are Grade 304 stainless steel, which is in a form of rod with diameter of 10mm and plate with dimension of 75mm X 25mm X 8mm. Surface attrition treatment as conducted using Finimac shot blasting machine implementing ceramic Silison Carbide (SiC) ball with 2mm diameter and velocity of 70 m/s, in order to induce plastic deformation on the surface of stainless steel. In paste boronizing, the samples (Pa-850) was coated with the boron paste comprising of 5% B₄C as donor, 90% SiC as the diluents and 5% KBF₄ which act as an activator with thickness of approximately 2mm and heated at temperature of 850°C for the 8 hours holding time.

The wear test was performed through Ducom Wear and Friction Pin on Disk TR-20LE tester using 125mm diameter rotating disk of hardened 316 stainless steel with speed of 200 r.p.m. load of 20N and sliding distance of 80 for 1 hour sliding time. The hardness value of all types of samples was evaluated and calculated through Mitutoyo MVX-H1 Vickers microhardness tester as per ASTM E-384 applying 10N load.

Table 1 shows the chemical composition of 304 stainless steel samples which was obtained from Spectro Maxx Spark emission machine. The microstructural observation and SEM observation analysis were performed via Olympus B X 41M microscope with IMAPs 4.0 edition and Scanning electron microscopy (SEM) analyzer using SMARTSEM software respectively. The energy dispersive X-Ray (EDX) spectrometry also conducted to determine the percentage of boron in each phase of the boride layer. The samples were compared before (Pa-B850) and after (Pa-SB850) surface attrition process.
3. Research Finding

Table 1. Chemical composition of 304 stainless steel samples.

| Wt (%) | C   | Mn | Si  | P   | S   | Cr  | Mo | Ni | Fe   |
|--------|-----|----|-----|-----|-----|-----|----|----|------|
| 304    | 0.065 | 1.8 | 0.75 | 0.04 | 0.03 | 18.5 | 0.0 | 8.5 | Bal   |

3.1. Microstructure Analysis

Figure 1 (a) shows the micrograph of 304 stainless steel sample (Pa-850B) after paste boronizing. It could be seen that there are presence of boride layer consisting of FeB and Fe2B phases with thickness of approximately 43 μm was produced after the boronizing process. The microstructure of boronized stainless steel sample after surface attrition process was shown in Figure 1 (b). It could be observed that an improvement of boride layer thickness which is approximately 120 μm had been successfully achieved after implementation of surface attrition treatment before boronizing process. This value indicated that surface attrition treated samples attained boride layer thickness of more than 100 μm and three times the value of thickness layer of boronized stainless steel with the value of 43 μm without surface deformation at the same temperature. It was also noted there are vast enhancement on the thickness layer of the diffusion zone of boronized samples after surface attrition process.

Similar to paste boronized sample, implementation of surface attrition also produced FeB and Fe2B phases. However, it could be seen that the formation of Fe2B phase was thicker in surface attrition treated sample as compared to the as received sample. The thickness of FeB layer is 50 μm while Fe2B layer attains a thickness of approximately 70 μm. The addition of surface attrition process created surface deformation such as atomic displacement and void which move the atom and allowing the boron atom to be diffuse onto the surface of boronized stainless steel. The formation of Fe2B phase is essential in producing excellent strength and tough-ness to boride layer thickness, thus delivering prominent protection to the surface of boronized samples. A similar trend was obtained by past researchers [13-14] which indicated that alteration of the surface region by applying a permanent plastic deformation are beneficial in enhancing diffusivity of case hardening and thermochemical methods such as boronizing, carburizing and nitriding on both low alloy and high alloy steels. Other significant effects of surface deformation are occurrence of dislocation at both grain boundaries as well as within the grain, all in which are the justified reasons of major improvement in the case depth of boronized layer.

The presence of FeB and Fe2B phases was validated through XRD analysis at 2 Theta angles of 37°[1 1 9], 62°[4 3 4] and 80°[6 1 1] for FeB phase and 35°[2 0 8], 42°[0 1 1] and 82°[7 1 6] for Fe2B phase for Po-B850 samples. The validation of FeB phase in surface attrited boronized samples are...
performed by XRD analysis at 2 Theta angles of 37 [1 3 4], 42 [0 3 9] and 80 [5 2 3] while for Fe2B phase at angles of 35 [3 2 1], 58 [0 3 9] and 80 [2 5 2].

Figure 2. X-Ray Diffraction pattern of paste boronized stainless steel (a) before (Pa-B850) and (b) after (Pa-SB850) surface attrition process.

3.2. Microhardness

The microhardness values for paste boronized stainless steel before and after surface attrition is depicted in Figure 3. The microhardness of Pa-B850 sample was averaged at 1550 Hv. The diffusion layer started from the outer layer of FeB phase, which contained the highest microhardness value to Fe2B phases which contained adequate strength and toughness and diffusion layer which is the area in between the Fe2B phases and the substances. The substances generally portrayed the microhardness value of the material. Pa-SB850 sample exhibited excellent microhardness with the maximum value of 1800 Hv at FeB phases with increment of 6 times or 600% the microhardness as compared to the substrate. Achievements of hard, but brittle nature of FeB phase is related with the boron composition of two times the value of Fe2B phase which is 16.23 wt. %. This was also supported by past researchers indicating that FeB is much harder than more ductile Fe2B phase in boronized steels [15-16]. Reduction of microhardness values was observed on the Fe2B region of approximately 1550 Hv and at diffusion zone further decrement with average of 580Hv was perceived.

Pa-SB850 accomplished highest microhardness compared to other samples as thickest boride layer was obtained. The deformed surface acquired atom dislocations, thus creating small voids for the boron to diffuse at deeper thickness. Comparably, the microhardness values of boronized sample increased proportionately with the increment of boride layer thickness [17]. At substrate region, minimum microhardness values were obtained as compared to another region with an average of about 257 Hv for all types of samples. After surface attrition, there are noticeable improvements on microhardness as the values increased to an average of 330Hv. Although surface attrited samples attained the same austenitic structures, the size of grain plays important role in improvement of microhardness. After surface attrition, the grain sizes reduced tremendously through the impact given by blast media that created surface deformation.

Likewise, the improvement of residual stress at the applied surfaces through surface modification also leads to the microhardness enhancement apart from improvement of thicker boride layer [18]. Similarly, Arifvianto et al. [19] found that the steel slag ball blasting treatment increases the microhardness of samples surface and subsurface of 316L stainless steel. The slag balls are nearly spherical but with a bit irregular surface. Microhardness tester was used to measure the microhardness distribution on the samples cross-sectional area. The measurement was conducted from the closest point to the surface down into the bulk of the samples with an indenting load of 4.9 N for 0 to 600 sec.
Arifvianto et al. [19] demonstrated that the use of bigger slag balls for the treatment also produces a harder surface layer and thicker hard layer.

Figure 3. Microhardness of Pa-B850 and Pa-SB850 samples from the diffusion zone until the outer surface.

3.3. Wear properties
It was evaluated that boronizing using paste medium provides favourable benefits as the COF obtained was much lower with the average value 0.458 of than powder boronized samples that attained the value of 0.611 with improvement of 25%. This was associated with the formation of deeper boride layer of 43 μm on Pa-B (850°C) as compared to 15 μm samples. As paste medium produced higher activation energy, the diffusion occurs at a faster rate compared to powder boronized samples, thus provide better diffusion thickness of the boronized layer.

The formation of thicker FeB layer with thickness of 30 μm which is almost three times the thickness of Fe2B layer which is 13 μm. Although there are major improvement of the overall thickness of boride layer from 15 μm in Po-B850 sample to 43 μm in Pa-B850 sample, the enhancement of FeB layer thickness increased the brittleness of the layer, thus resulted in insignificant improvement of COF with the variation of only 25% as compared to Po-B850 sample. Paste medium exhibited smaller grain sizes than powder medium, the formation of boride layer of the outer surfaces are smoother, and thus it is harder for particles to be removed initially during the pin on disc test. Paste medium also produces a denser outer layer, which reduce the brittleness of the boride layer. This provides better protection to the surfaces, thus better wear quality was produced, indicated by the lower COF value.

Past researcher performed modifications on the properties of boronizing medium by adding chromium and rare earth elements and established that lower COF values was produced [20]. This was because the addition of these elements reduced the brittleness of the boride layer by enhancing the
density of the layer. As the layers produced are denser, it restricted the action of wear during pin on disc test.

Figure 4 shows the results for coefficient of friction for Pa-SB850 sample as compared to Pa-B850 sample. The lowest COF values, indicating the highest wear resistances were achieved by combining surface attrition and paste boronizing at temperature of 850°C to the samples which is Pa-SB850 samples at the average value of 0.353 as compared to Pa-B850 sample with the value of 0.458 with improvement of 30%. This was mainly because of enhancement of boride layer thickness of Pa-B850 sample from 43 μm to 120 μm in Pa-B850 after surface attrition process.

Additionally, the improvement of COF may also contribute by the formation of Fe2B phase is generally thicker with the thickness of 70 μm as compared to 50 μm in FeB phase. This indicates that a combination of paste boronizing and surface attrition successfully improved the wear resistance with the COF value of more than two times as compared to the COF as received grade 304 stainless steel which is 0.856, as more than 100 μm thicknesses of boride layer was produced. Theoretically, surface attrition enhanced the thickness of boride layer by enabling the boron atom to diffuse deeper, occupying by grain size refinement and density defect formation [21]. As a conclusion, it can be said that the values of COF increased in opposition to the boron diffusion layer thickness. It also relates that boronizing automotive parts with modification of the roughness parameters could enhance the wear resistances of the parts by 30 to 40% [22].

![Figure 4. Coefficient of friction for Pa-SB850 sample as compared to Pa-B850 sample.](image)

### 4. Conclusion

In this study, the influence of surface attrition process on the hardness and wear properties of boronized stainless steel was investigated and the following conclusion could be obtained:

Surface attrition process had increased the boride layer thickness of boronized stainless steel up to 3 times from 43 μm to 120 μm due to the surface deformation effect that allow the boron atom to be dispersed deeper into the deformed surface.

Pa-SB850 samples exhibited higher hardness and better wear resistance as the addition of surface attrition before boronizing process produced deeper and harder boride layer produce which allowed more surface protection to the material.

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