J Mater Sci (2006) 41:6116–6118
DOI 10.1007/s10853-006-0484-y

LETTER

A feasibility study of plasma nitriding of steel with an oxide layer on the surface

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Received: 7 April 2006 / Accepted: 31 May 2006 / Published online: 12 August 2006

In a traditional DC plasma nitriding furnace, the component to be treated serves as the cathode and forms an integral part of the DC plasma system [1]. It is, thus, an essential requirement that the component to be nitrided is clean and electrically conductive. Components with non-conducting materials such as an oxide layer, contamination of oil or lubricant, ink or paint marks on the surface cannot be directly plasma nitrided due to the risk of arcing and instability of the DC glow-discharge plasma. On the other hand, these non-conductive substances on whole or part a surface of an engineering component are almost unavoidable in industry. For example, oxidation of steel can occur during casting, forging and heat treatment. To facilitate plasma nitriding with the existing DC plasma technology, a component to be treated has to be ground or machined all over to remove the oxide layer before plasma nitriding treatment. This is in spite of the fact that in most cases only the working section of a part needs to be treated, e.g., bearing surfaces of a joint, tooth of a gear and inner wall of a cylinder. For parts with simple geometry, overall grinding/machining incurs extra production cost and time. For parts with complex geometry, machining or grinding throughout can be difficult if at all possible. The problem could be addressed by the newly developed active screen plasma nitriding (ASPN) technology [2], since in an ASPN furnace the components to be treated can be placed in a floating potential or subjected to a relative small bias power and thus electrical conductivity of the component is not critical [3]. This letter presents the experiment results of a recent feasibility study on ASPN of a low alloy steel samples with and without oxide layer on the surfaces.

The materials used was a hardened-tempered 3 wt% Cr–Mo low alloy steel (722M24). Disc samples of about 7 mm thick were cut from a 25 mm diameter bar. The flat surfaces of the disc samples were wet ground with SiC papers from 240 grit down to 1200 grit. Part of the samples were left in the as-ground state for reference, and part were heated in an air furnace at 800 and 600 °C for 2 h to produce an oxide layer on the surface. The temperatures and time of the heating are those typically employed in heat treatment of steel such as during hardening, annealing and tempering. The samples were identified as *Gr* for ground reference sample, *T6* for 600 °C oxidised and *T8* for 800 °C oxidised samples.

As expected, heating in air furnace produced an oxide layer on the 722M24 steel sample surface. XRD patterns in Fig. 1 shows that the oxide layer on the 600 °C heated surface (T6) was mainly Fe_2O_3, and that on the surface of 800 °C heated surface (T8) consisted of Fe_2O_3 and Fe_3O_4. High intensity α-Fe peak in the XRD pattern for sample T6 suggested that the oxide layer was thin so that the X-ray used for phase analysis penetrated through the oxide layer and reached the α-Fe substrate. No peak from the substrate α-Fe appeared in the XRD pattern for sample T8, confirming that the oxide layer on the higher temperature heated surface was thick.

Plasma nitriding was carried out with an industrial scale AS plasma nitriding unit (working chamber of ~1,000 mm diameter and ~1,000 mm height). The

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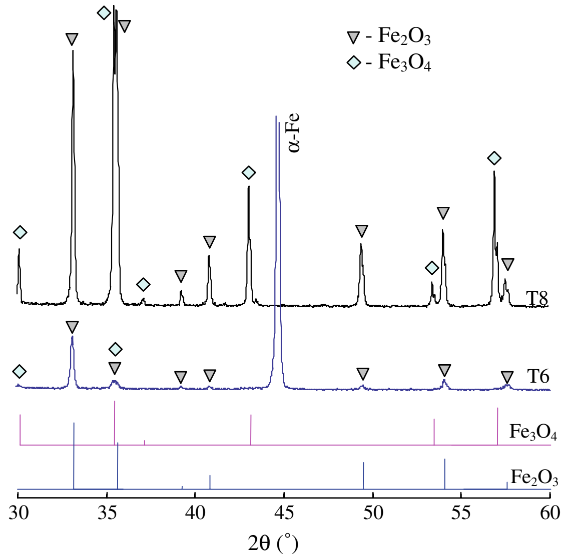

Fig. 1 XRD patterns of 722M24 steel after heating in an air furnace at 800 °C (T8) and 600°C (T6) for 2 h. The standard patterns for Fe_3O_4 and Fe_2O_3 are also shown

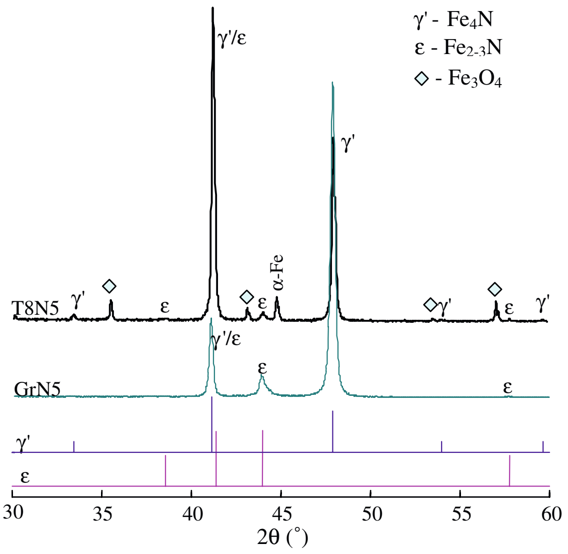

Fig. 2 XRD patterns showing plasma nitriding produced iron nitrides of γ' and ϵ on the surfaces of sample Gr (reference) and T8 (800 °C oxidised)

oxidised samples and the ground reference sample were placed on the working table side by side in the AS plasma furnace and nitrided for 500 °C for 10 h. The treatment gas was 25%N_2 + 75%H_2 and the chamber pressure was 125 Pa. Such a combination of plasma nitriding of oxidised samples and ground samples in the same batch was regarded as a simulation of plasma nitriding a partly machined component with oxide layer remaining on the un-machined surface. It was found that the oxidised samples did not disturb the plasma nitriding process—there was no arcing; the plasma was stable and the treatment proceeded as if there were no oxidised samples in the furnace. After 10 h treatment, the samples were slow-cooled down to room temperature in the vacuum chamber. The 500 °C plasma nitrided samples were identified as *GrN5, T6N5* and *T8N5*, respectively, according to their pre-nitriding surface condition.

XRD result: XRD analysis revealed that a compound layer of γ'-Fe_4N and ϵ-$Fe_{2\text{-}3}N$ was formed on the ground reference surface after nitriding (Fig. 2), suggesting that the reference sample was nitridied as normal. Surprisingly, it was noticed that after nitriding the oxidised surfaces were changed to an appearance very similar to the nitrided reference sample (GrN5). This was particular evident for sample T6 since the as-oxidised surface was red brown (the colour of iron oxide), whilst after plasma nitriding it became dark grey as observed on a nitrided steel surface. XRD results revealed that iron nitrides also formed on the oxidised surfaces so that iron nitride diffraction peaks dominated the XRD patterns for both samples of T8N5 and T6N5. This can be seen from the XRD pattern for T8N5 shown in Fig. 2. Although small diffraction peaks of Fe_3O_4 were still detected for sample T8N5, no peak of iron oxide appeared in the XRD pattern for sample T6N5. This is probably because the original oxide layer on the surface of sample T6 was very thin.

The transformation of iron oxides to iron nitrides could be caused by the deposition of iron nitrides on the oxidised surfaces according to "sputtering-deposition" model for nitrogen mass transfer in AS plasma nitriding [4]. It could also be possible that certain reactions occurred between the oxidised surfaces with the active species in the plasma atmosphere. Further mechanism investigations are being carried out.

Microhardness results: Microhardness (HV) tests were performed on the sample surface with a Mitutoyo MVK-H Microhardness Tester at 1 kgf. It was found that surface hardness of the reference sample was increased from 300 HV1.0 to more than 900 HV1.0 after plasma nitriding, Fig. 3. Such a considerably increased surface hardness indicated that placing the oxidised samples inside the plasma chamber appeared to have no negative influence on plasma nitriding hardening of the ground reference sample.

It was believed that, due to the formation of an iron nitride compound layer, the oxidised samples could also have been hardened after plasma nitriding. Indeed, microhardness tests showed that the as-oxidised surface of T6 had an average hardness of

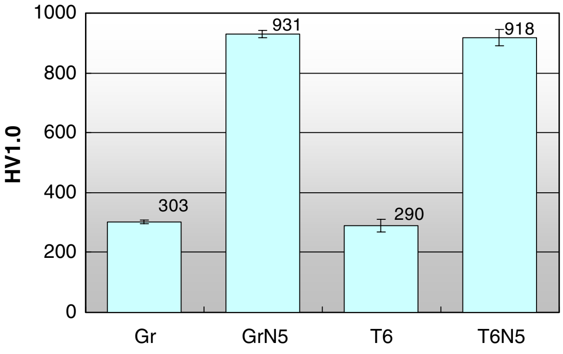

Fig. 3 Microhardness (HV1.0) of the ground (Gr) and 600 °C oxidised (T6) 722M24 steel before and after plasma nitriding at 500 °C for 10 h

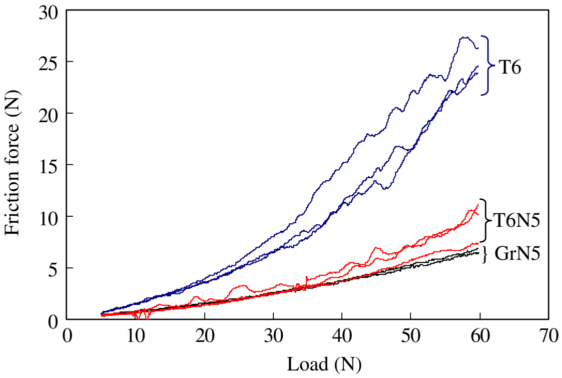

Fig. 4 Friction force against scratching load for the oxidised (T6) and nitrided (GrN5—reference, T6N5—pre-oxidised) samples

290 HV1.0. After nitriding, the surface hardness was increased to 918 HV1.0 which is comparable to the hardness of the nitrided reference sample, Fig. 3. However, microhardness tests on the surfaces of T8 and T8N5 were not successful since cracks formed around the Vickers indentation impression which made focusing and measurement difficult. Probably, nano indentation technique can be used to measure the hardness of the oxidised (T8) and nitrided (T8N5) samples.

Scratch test results: An ST3001 Teer Scratch Tester was used to evaluate the scratching properties of the oxidised (T6) and the nitrided (T6N5 and GrN5) samples. During the test, a Rockwell C diamond indenter of 0.2 mm tip radius was drawn across the sample surface under a normal load which was linearly increasing from 5 N to 60 N at a rate of 100 N/min. The friction force was recorded so that friction curves as shown in Fig. 4 were obtained. Three tests were performed for each sample.

A comparison of the friction curves in Fig. 4 revealed that friction force for sample T6 (as-oxidised) was high and quickly increasing with the scratch load. On the other hand, friction force for the nitrided reference sample (GrN5) was low and increasing very slowly. One of the three friction curves for nitridied sample of T6N5 overlapped with the curves for sample GrN5, and two other curves were slightly higher and more fluctuated. Nonetheless, the difference in friction force between T6N5 and GrN5 is much smaller than that between T6 and GrN5 at any scratch load. Further, morphological examinations revealed that scratch tracks on the surface of sample T6 were deeper and wider and those on the surfaces of T6N5 and GrN5 were narrower and shallower, suggesting that plasma nitriding increased the scratch resistance for both ground and the pre-oxidised samples.

The results above demonstrated that with AS plasma nitriding it is possible to nitride a partly machined components. In other words, it may not be necessary to remove the oxide layer/scale by throughout machining before plasma nitriding if only part of the surface is to be nitrided. In addition, it might be possible to modify the structures and properties of the oxide layer on the surface of a steel component with AS plasma nitriding. Further studies are being carried out to make this laboratory finding into an industrially viable technology.

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