

A NITROCARBURISING AND LOW-TEMPERATURE CHROMISING DUPLEX SURFACE TREATMENT

D.M. Fabijanic, G.L. Kelly, J. Long, P.D. Hodgson

Deakin University, School of Engineering and Technology, Waurn Ponds, Victoria, 3217

ABSTRACT

A duplex surface treatment has been developed involving the pre-treatment of hardened and tempered AISI H13 chromium hot-work tool steel by a ferritic nitrocarburising process, and a subsequent treatment of the nitrocarburised surface by a low-temperature chromium thermo-reactive deposition process. The process formed a thin and hard chromium carbonitride surface layer above a hardened diffusion zone, and the low processing temperature allowed the properties of the core material to be retained. It is expected this surface treatment will find application in the treatment of tooling used for aluminium forming operations.

1. INTRODUCTION

A surface layer designed for wear or corrosion resistance should possess a high *incompatibility* with the contacting counter-face or the working environment. Simultaneously the surface layer and the underlying substrate should possess a high *compatibility* to develop an effective interfacial bond strength, promote alloying, and to minimize the variation in key properties such as hardness, elastic moduli, and thermal expansion coefficients across the interface [1, 2].

Combining these two requirements in a single layer can be difficult and typically there is a sharp step-like discontinuity in properties and composition at the interface. For example, the interface between a hard PVD coating and a steel substrate can have an order of magnitude variation in hardness and highly contrasting elastic moduli. As a result, elastic flexure in the substrate during operation or high contact pressure can cause a loss of adhesion and delamination of the coating [1, 3, 4]. Duplex surface engineering is a technique that is gaining increasing application to improve the property gradient across an interface.

Duplex surface engineering combines two surface engineering techniques. A common duplex surface treatment involves thermo-chemically treating a steel substrate prior to the deposition of a hard surface coating. Thermo-chemical treatments, such as nitriding and carburising, inherently form a graded hardness from the surface to the substrate, which creates a gradual transition in interfacial properties and provides a tough and supportive sub-surface for the hard coating [1, 5]. There are numerous examples in the literature of the benefit of nitriding, nitrocarburising or carburising steels prior to the formation of a hard layer by physical or chemical vapour deposition [1, 5-14].

Another aim of duplex surface engineering is the combination of surface engineering techniques to form particular surface microstructures and compounds. For

example, enriching a steel surface with chromium by a thermo-chemical treatment [15] or by an electroplating process [16] prior to the diffusion of nitrogen by a plasma nitriding process. These duplex processes form a chromium nitride surface layer with a higher hardness and improved wear and corrosion resistance compared to the untreated substrate, and the chromium and nitriding surface treatments alone [15, 16].

The aim of this work was to develop a new duplex surface engineering process involving a ferritic nitrocarburising pre-treatment of hardened and tempered chromium hot-work tool steel substrates (AISI H13) and a low-temperature (575°C) chromium thermo-reactive deposition (TRD) surface treatment of the nitrocarburised surface. This duplex process is designed to form a hard chromium carbonitride surface layer by a diffusion alloying reaction between the nitrogen from the nitrocarburised surface and the deposited chromium metal. By processing at a low temperature the hardness of the core material is retained and distortion minimised. This paper describes the developed duplex process and characterizes the resulting surface layer.

2. FLUIDISED BED PROCESSING

Both processes were performed in a fluid-bed reactor (Fig. 1), which is a vessel containing a bed of dry, finely divided particles (1). A gas flow, introduced through a diffusion plate (2) at the bottom of the bed results in each individual particle becoming microscopically separated from each other. This allows the bed to have characteristics that have close resemblance to a liquid. An analogy in the natural world of solid particle fluidisation is the phenomenon of quicksand [25, 26]. The gases available for fluidisation in the present work were ammonia (NH₃), carbon dioxide (CO₂), nitrogen (N₂), and hydrogen chloride (HCl).

A layer of coarse grit alumina (3) was used to separate the fine bed material from the diffusion plate. This also allows the atmosphere to mix and reach the processing

temperature before entering the reaction zone. The bed was heated by external resistance that consisted of ceramic elements (4) in an insulating refractory housing (5), and the processing temperature was thermostated and monitored externally by a calibrated N-type thermocouple (6). The samples (7) were fixed to a centrally located jig, which was attached to the furnace lid. The output gas was extracted, treated by a scrubber system (8) and burned by a pilot flame.

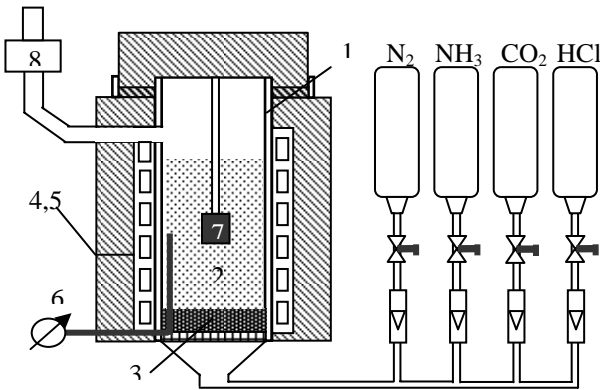


Figure 1: Schematic representation of the fluid-bed reactor used in all experiments.

3. FERRITIC NITROCARBURISING

Nitrocarburising is a thermo-chemical surface treatment applied to a wide range of ferrous substrates. The principle mechanism is the interstitial diffusion of both atomic nitrogen and carbon into the surface of a ferrous substrate matrix to form a surface structure consisting of a compound layer above a diffusion zone [17]. The role of nitrocarburising in this duplex process was to form a supportive sub-surface for the hard surface layer, create transitional interfacial properties, and supply nitrogen for the formation of chromium carbonitride at the surface.

Samples of hardened (1020°C for 1 hour, air quench) and double tempered (575°C, 45 minutes per temper) AISI H13 tool steel with final hardness of 551 ± 16 Hv_{500gf} were surface polished to 500-grade SiC paper finish and cleaned in acetone prior to nitrocarburising. The primary alloying elements of AISI H13 are summarised in Table 1.

Table 1: Chemical composition of AISI H13

| | C | Mn | Si | Cr | V | Mo |
|------|------|------|------|------|------|------|
| wt % | 0.32 | 0.45 | 1.07 | 4.58 | 0.72 | 1.11 |

All nitrocarburising was performed at 575°C in a bed consisting of 120-mesh alumina (Al₂O₃). A fluidizing atmosphere consisting of nitrogen-bearing gas (NH₃), carbon-bearing gas (CO₂) and inert carrier gas (N₂) was supplied to the bed. Samples were nitrocarburised in various atmosphere compositions (designated NC1, NC2, and NC3 in Table 2) for times between 10 minutes and 5 hours. The resulting surface structure was examined by optical and SEM examination and the

surface composition determined by Glow Discharge Optical Emission Spectrometry (GD-OES). The following are the key results from this nitrocarburising study.

Table 2: Nitrocarburising atmosphere compositions (percent volume)

| | NH ₃ | CO ₂ | N ₂ |
|-----|-----------------|-----------------|----------------|
| NC1 | 30 | 5 | 65 |
| NC2 | 60 | 5 | 35 |
| NC3 | 15 | 5 | 80 |

It was found that porosity formed in the region of the compound layer (CL) adjacent the surface when the thickness of the compound layer exceeded 10 μm (greater than 3 hours of nitrocarburising time). This porosity appears dark under optical examination (Fig. 2b) and is seen in more detail in the SEM image in Fig. 2c. Porosity is a common phenomenon in nitrocarburised compound layers and is attributed [18, 19, 20] to the metastability of the phases in the compound layer, which causes the dissolution and recombining of two diffused nitrogen atoms to form nitrogen gas.

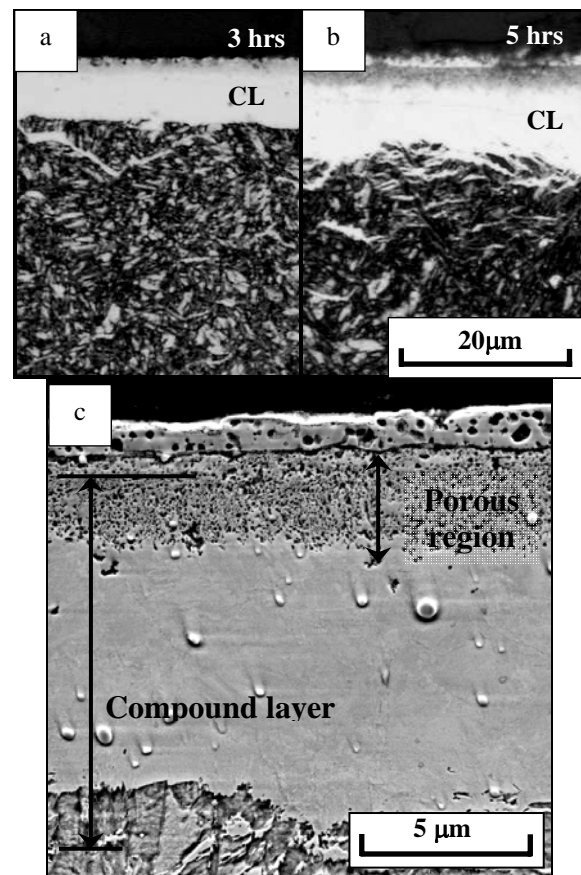


Figure 2: Optical micrographs of the compound layers after a) 3 and b) 5 hours of nitrocarburising (x1000, 2% nital etch). The porous region is shown in greater detail in the SEM image c) (x20 000, EHT: 5kV, aperture: 60 μm, working distance: 10 mm, 2% nital etch).

During the chromium thermo-reactive deposition (TRD) process the compound layer supplies nitrogen to the surface to form a chromium carbonitride layer. Typically TRD treatments are performed above 900°C and applied to carbon-bearing substrates to form alloy carbide surface layers. In these processes it has been found [21, 22, 23] that increasing the carbon content of the substrate increases the thickness of the alloy carbide layer formed. Therefore, it was aimed to maximise the nitrogen content of the compound layer. Increasing the ammonia content of the nitrocarburising atmosphere from 15 percent volume to 30 percent volume had a positive effect on the nitrogen content of the compound layer, seen in the quantitative depth profile obtained by GD-OES analysis (Fig. 3). However, no significant effect on the nitrogen content of the compound layer occurred by further increasing the ammonia content to 60 percent volume.

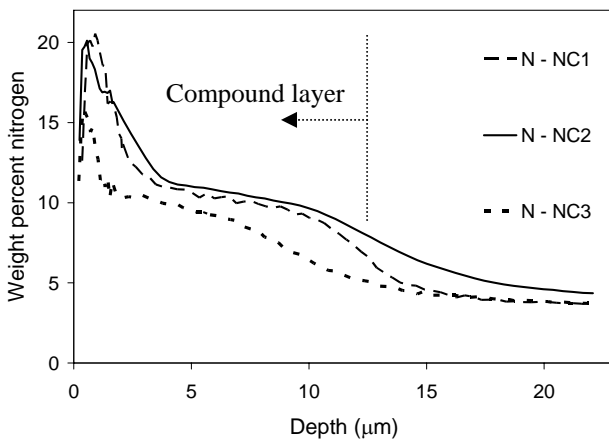


Figure 3: Quantitative depth profiles for nitrogen in the compound layers formed after 5 hours of nitrocarburising in NC1, NC2, and NC3 atmospheres.

The microstructure of the hardened and tempered AISI H13 substrate consists of alloy carbides in a tempered martensite matrix. During nitrocarburising the diffusing nitrogen penetrated into the alloy carbides, which resulted in their conversion to nitrides and the release of carbon into the steel matrix. This conversion is based on the higher affinity alloy elements such as chromium, vanadium, and molybdenum have for nitrogen relative to carbon [20, 24], and evidence of this is observed in the quantitative depth profile for nitrogen and carbon in the diffusion zone (Fig. 4).

Here the carbon released by the alloy carbides is observed as a carbon peak located at the substrate side of the diffusion zone-substrate interface. That is, the liberated carbon is pushed ahead of the advancing nitrogen diffusion front. This preferential formation of alloy nitrides over alloy carbides is important to the second stage of the developed duplex process and is discussed further in the Section 4.

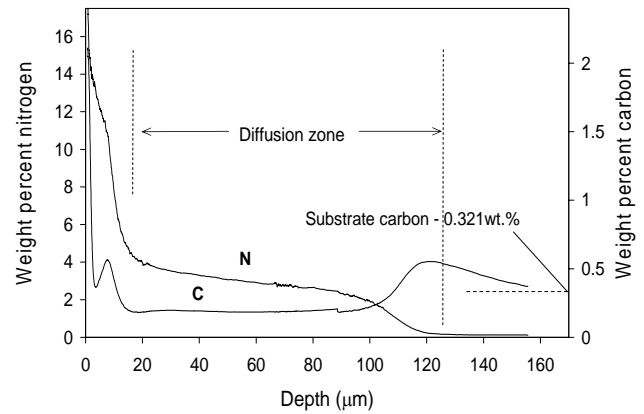


Figure 4: Quantitative depth profile for nitrogen and carbon in the compound layer and diffusion zone after 3 hours of nitrocarburising in a NC1 atmosphere.

Based on these results, all nitrocarburised samples prepared for chromium TRD treatment were processed for 3 hours to produce compound layers of 10 μm thickness having minimal porosity. A NC1 atmosphere was chosen for all samples to maximise the nitrogen content of the compound layer.

4. LOW-TEMPERATURE CHROMIUM THERMO-REACTIVE DEPOSITION

The nitrocarburised samples were placed in a bed consisting of 120-mesh alumina and 75-mesh chromium metal powder and heated to 575°C under an inert N₂ atmosphere. Gaseous hydrochloric acid was added to the fluidising flow which allowed reaction with the chromium metal powder to produce gaseous chromium chloride (CrCl_{2(g)}) according to Reaction 1 [25] (Fig.5). The evolved CrCl_{2(g)} was adsorbed [21] onto the nitrocarburised surface and was reduced by the hydrogen produced by Reaction 1 to deposit chromium (Reaction 2). This process is called thermo-reactive deposition (TRD) or chromising when chromium is the depositing species.

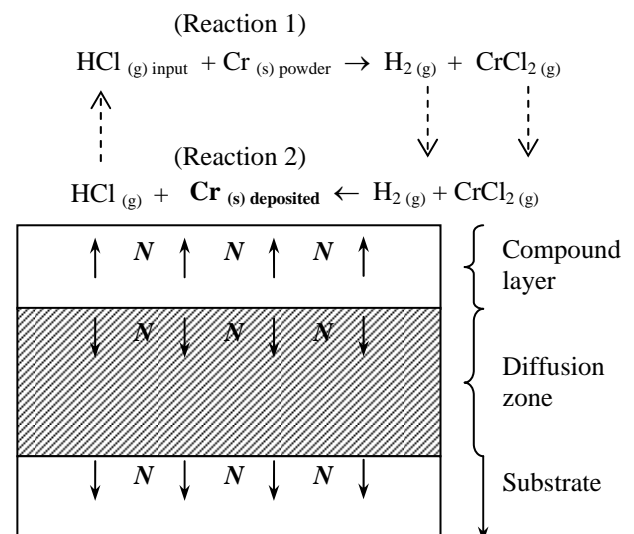


Figure 5: The deposition of chromium and the direction of nitrogen diffusion during TRD.

During chromium TRD the free-nitrogen content in the compound layer and diffusion zone diffused towards the surface (Fig.5). A diffusion alloying reaction occurred between the nitrogen and the chromium to form a distinct surface layer. In high temperature TRD processes where alloy carbide layers, the driving force for the diffusion of carbon towards the surface is the low free energy of carbide formation at TRD processing temperatures [21, 22]. For the developed process, it is assumed that the driving force for nitrogen diffusion is the low free energy for chromium nitride formation at 575°C.

After 16 hours of chromium TRD treatment at 575°C a surface layer of 2.5 μm thickness was formed (refer to the optical micrographs in Fig. 6). It is seen that the original compound layer has decomposed (Fig. 6a) and that the diffusion zone has increased in depth by approximately 40 μm due to the inward diffusion of nitrogen (compare Fig. 6b and c). The original tempered martensite core structure is retained.

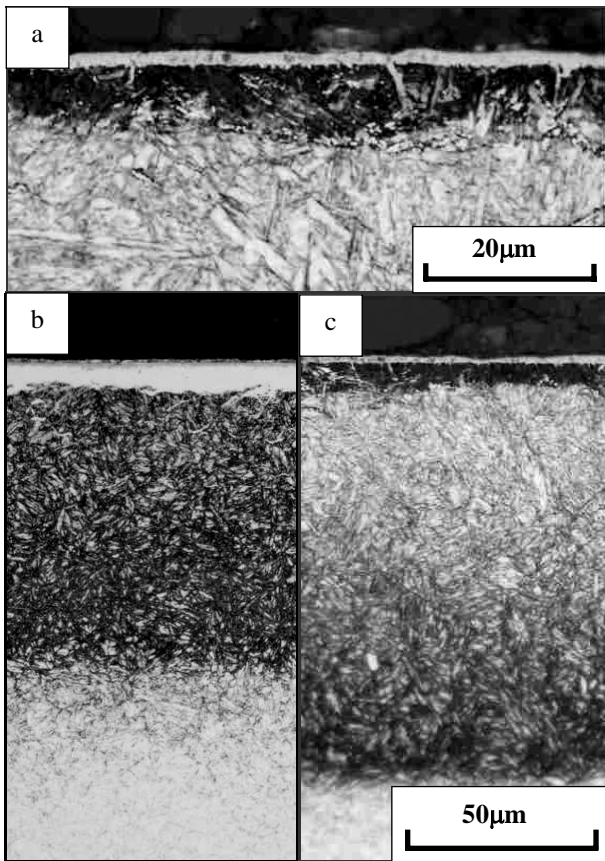


Figure 6: a) The microstructure of duplex treated AISI H13 after 16 hours of chromium TRD treatment at 575°C (x1000) and the comparison of b) nitrocarburised and c) duplex treated microstructures (x500) (2% nital etch).

GD-OES quantitative depth profiling (Fig. 7) revealed that the surface layer was rich in chromium and nitrogen, with smaller quantities of carbon, iron and oxygen present. The depth of the chromium concentration profile correlated with the thickness of the layers measured by optical examination. X-ray

diffraction (XRD) profiling showed that the major phase of the surface layer was chromium nitride (CrN) (Fig. 8). The iron peaks are due to the penetration of the X-rays through to the underlying substrate. Arai et al. [26] and Ohta et al. [27] have formed similar layers by salt-bath nitrocarburising-TRD duplex processes and have suggested alloy nitride phases in layers containing carbon should be expressed as alloy carbonitride layers. This terminology has been adopted in this investigation, with the layers formed referred to as chromium carbonitride layers.

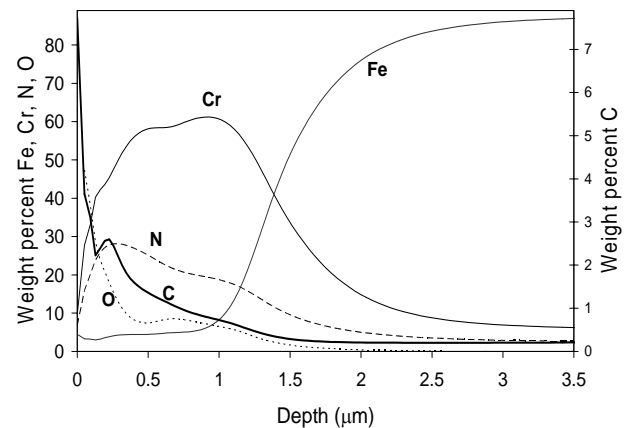


Figure 7: Quantitative depth profile of a duplex treated surface after 16 hrs at 575°C.

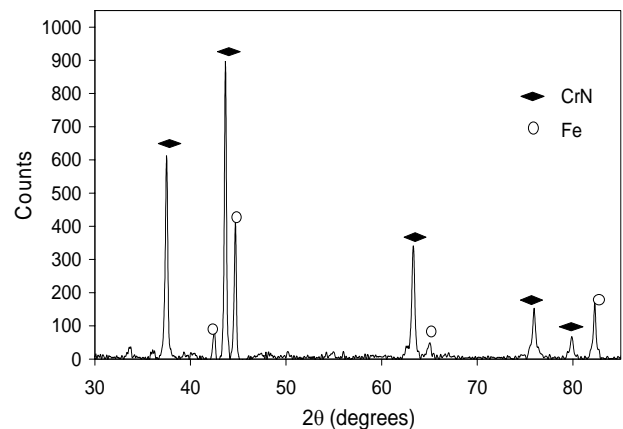


Figure 8: XRD analysis of the surface layer (Cu-K α source)

The thickness of the surface layer was increased by nitrocarburising prior to chromium TRD. Fig. 9 compares the quantitative depth profiles for chromium in nitrocarburised samples and untreated samples after 16 hrs of TRD treatment. The chromium concentration profile is indicative of layer thickness and it is seen that the prior nitrocarburised sample forms a layer approximately 5 times the thickness of the untreated sample. The untreated sample shows a carbon peak coinciding with the chromium peak indicating that a thin chromium carbide layer may have formed. This benefit to layer thickness provided by a prior nitrogen diffusion process may be attributed to the preferential formation of chromium nitride over chromium carbide at 575°C,

as observed by the conversion of the alloy carbides to nitrides in the steel matrix during nitrocarburising.

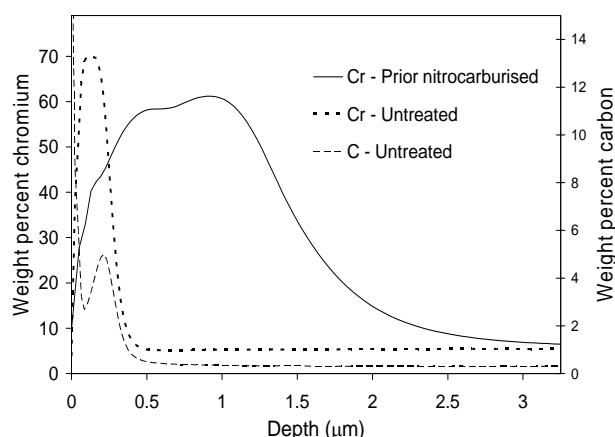


Figure 9: Quantitative depth profiles for chromium and carbon indicating the differing thickness of layers formed on untreated and nitrocarburised samples.

The layer hardness was determined to be 1520 ± 43 Hv using nanoindentation with a load of $10 \mu\text{N}$ and the hardness profile directly beneath the surface layer to the core was measured using micro-Vickers with a 25g load (Fig. 10). The retention of the nitrocarburised diffusion zone hardness after the chromium TRD process formed a gradual transition in hardness across the layer-substrate interface, which should provide a supportive sub-surface for the hard layer and result in good layer adhesion. Additionally, it is seen that the core hardness of the hardened tool steel is maintained after the duplex process.

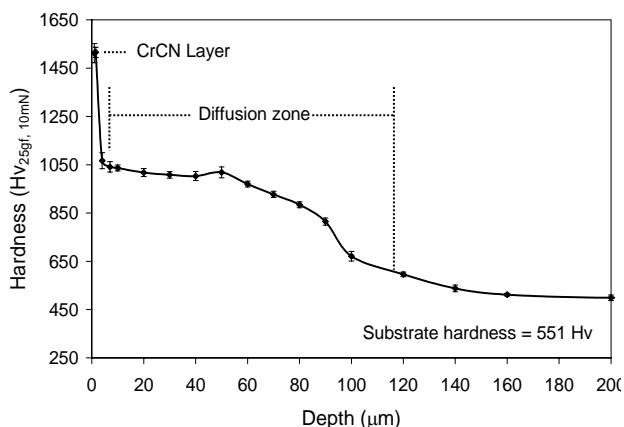


Figure 10: The surface to core hardness profile of duplex treated surface AISI H13.

Current research into this process aims to form chromium carbonitride layers of greater thickness and to determine the performance of duplex treated AISI H13 tooling used in aluminium forming operations.

5. CONCLUSIONS

A nitrocarburising and low-temperature chromising duplex surface treatment has been developed. The main

findings arising from the study of the nitrocarburising pre-treatment and the chromium TRD process were:

- To avoid porosity in the compound layer prior to TRD treatment the compound layer thickness should not be greater than $10 \mu\text{m}$
- The ammonia content of the nitrocarburising atmosphere had a slight influence on the nitrogen content of the compound layer, and to maximise the compound layer nitrogen content 30-volume percent ammonia has been used
- During the TRD process the nitrogen from the compound layer diffused to the surface causing the compound layer to decompose
- A hard and thin chromium carbonitride layer was formed above a hardened diffusion zone, which created a gradual transition in interfacial properties
- Prior nitrocarburising was beneficial to layer thickness, which may be attributed to the preferential formation of chromium nitride to chromium carbide at the processing temperature.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the guidance provided by Mr. Ray Reynoldson. Trials described in this paper were carried out at Quality Heat Technologies, the authors thank them for their support and access to facilities. This work was supported by the Australian Research Council.

REFERENCES

1. R. Priestner and D.M. Priestner: Surface Engineering, 1991, vol. 7(1), pp 53-59.
2. K.N. Strafford, C. Subramanian and T.P. Wilks: J. Mat. Proc. Tech., 1993, vol. 38, pp 431 - 448.
3. K.N. Strafford and C. Subramanian: J. Mat. Proc. Tech., 1995, vol. 53, pp 393-403.
4. A. Mathews and A. Leyland, Heat Treatment of Metals, 2001. 3: p. 63-70.
5. S. Hogmark, S. Jacobson and M. Larsson: Wear, 2000, vol. 246, pp 20-33.
6. P. Panjan, V. Urankar, B. Navinsek, M.Tercelj, R. Turk, M.Cekada and V.Leskovesk: Surf. Coat. Tech., 2002, vol. 151-152, pp 505-509.
7. T. Bell, Surface Engineering, 1990, vol. 6(1), pp 31-40.
8. B. Navinsek, P.Panjan and F. Gorenjak: Surf. Coat. Tech., 2001, vol. 137, pp 255-264.
9. B. Navinsek, P. Panjan, I. Urankar, P. Cvahte and F. Gorenjak: Surf. Coat. Tech. ,2001, vol. 142-144, pp 1148-1154.
10. P. Kaestner, J. Olfe, J.W. He and K.T. Rie: Surf. Coat. Tech., 2000, vol. 142-144, pp 928-933.
11. H. Surm, O. Kessler, F. Hoffmann and P. Mayr: Proc. 5th Conf. on Heat Treatment and Surface Engineering, 2000, Gothenburg, Sweden, ASM International.
12. J. Vetter, T. Michler and H. Steuernagel: Surf. Coat. Tech., 1999, vol. 111(2-3), pp 210-219.

13. H.J. Spies, B. Larisch, K. Hock, E. Broszeit and H.J. Schroder: Surf. Coat. Tech., 1995, vol. 74-75, pp 178-182.
14. K. Hock, H.J. Spies, B. Larisch, G. Leonhardt and B. Buecken, Surf. Coat. Tech., 1996, vol. 88, pp 44-49.
15. D.Y. Chang, Y.L. Sang and S-S. Kang: Surf. Coat. Tech., 1999, vol. 116-119, pp 391-397.
16. E. Menthe and K.T. Rie: Surf. Coat. Tech., 1999, vol. 112(1-3), pp 217-220.
17. (37) T.Bell, ASM Handbook – Heat Treating: vol. 4, ASM International, Metals Park, Ohio, 1991, pp 425-436.
18. S. Li, R. Manory and J. Hensler: Surf. Coat. Tech., 1995, vol. 71(2), pp 112-120.
19. F. Chen and O. Teh: Materials and Manufacturing Processes, 1996, vol. 11(5), pp 803-819.
20. J. Slycke and L. Sproge: Surface Engineering, 1989, vol. 5(2), pp 125-140.
21. F-S. Chen, P-Y. Lee and M-C, Yeh: Material Chemistry and Physics, 1998, vol. 53, pp 19-27.
22. T. Arai: ASM Handbook – Heat Treating, vol. 4, ASM International, Metals Park, Ohio, 1991, pp 448-453.
23. B. Chicco, W.E. Borbidge and E. Summerville: Mat. Sci. Eng, 1999, vol. A266, pp 62-72.
24. E. Haruman, T. Bell and Y. Sun: Surface Engineering, 1992, vol. 8(2), pp 275-282.
25. F.J. Perez, M.P. Hierro, F. Pedraza, C. Gomez and M.C. Carpintero: Surf. Coat. Tech., 1999, vol. 120-121, pp 151-157.
26. T. Arai, H. Fujita, Y. Sugimoto and Y. Ohta, Industrial Heating, 1989, vol. 56, pp 30-34.
27. Y. Ohta, Y. Sugimoto and T. Arai: Japanese Heat Treatment Society, 1992, Kyoto, Japan.