Surface Hardening Titanium with Carbon Monoxide
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ABSTRACT
Titanium has very poor tribological properties and cannot be used for applications like drive train components. Various coatings can be used, for example TiN and DLC, to improve them, but the loading is limited by the low strength of the substrate. In recent years thermochemical diffusion treatments have been developed. To produce a layer that is sufficiently thick to support a load in a reasonable time, these treatments have to be carried out at high temperatures: 950°C and 1050°C for oxidation and nitriding processes respectively. The high treatment temperature degrades the core properties to such an extent that they must be heat treated again after the surface layer has been produced.

An alternative is desirable that would give a substantive load bearing layer with good wear properties at a treatment temperature of 850°C or lower. The use of such technology would allow the manufacture of a gear box that was 40% lighter than its steel equivalent. An initial study had shown that the layers formed using carbon monoxide were the most promising at lower temperatures and these were studied further. The effects of some of the treatment variables were determined, along with some of the characteristics of the optimised ceramic layer.

INTRODUCTION
Titanium has very poor tribological properties that limit its applications [1]. Many attempts have been made to improve them with thermochemical treatments, diffusing in mainly oxygen [1-6] and nitrogen [7-10]. In general, if these treatments are to produce sufficient case depth for general engineering applications within a reasonable time (24 hours), then the treatment has to be at high temperature – above the α→β transition temperature. This however degrades the core properties of the titanium (typically Ti-6Al-4V). Recently reported work has suggested that multi-element diffusion treatments might have advantages, both in terms of treatment temperature and case properties [11-13].

To achieve the desired results at low treatment temperatures, the availability of the reactants has to be very closely controlled. Previous experiments used very small samples and a continuous high flow of gas in a very small tube furnace [1]. However, when larger samples were treated the relatively small volumetric gas flow possible resulted in an uneven case. Therefore, for the experiments in this study employed a furnace with a higher volume to ensure uniform treatment. Feedback control was used to give a constant and consistent atmosphere composition.

EXPERIMENTAL
The samples were treated in a small Boye pit furnace (Figure 1), that had previously been used for carburising treatments. It was therefore thoroughly burnt out first, together with the loading jig, to ensure that no residues – particularly carbon – were present that might affect the results. This was done by passing air passed through the furnace at 850°C for some hours while the carbon dioxide was monitored. Burnout was considered complete when the carbon dioxide fell below the detectable limit.

Figure 1. The highly instrumented Boye pit furnace used in the trials

The samples of T-6AI-4V were in the form of polished cubes, 10mm per side. They were placed in the cold pit furnace, which was then heated under a flow of argon. When the processing temperature was reached, the processing gas mixture was introduced. At the end of the processing time the atmosphere was replaced by argon and the furnace cooled to below 150°C before the samples were removed.

Because of the very small flow rate of addition gas(es) required, it proved impossible to achieve a stable addition gas concentration using pure addition gases and a Tylan General DynaMass Flow control system. Premixed cylinders of standard gases were
therefore used to supply the addition gas to the mixer.

Preliminary screening runs at 850°C for 24 hours using several different addition gases or mixtures of gases containing oxygen, nitrogen and carbon indicated that treatments using carbon monoxide were worth further study [14]. A range of addition levels, treatment temperatures and times was investigated. The composition of the near surface layers was analysed by XRD.

RESULTS
The carbon monoxide level, as measured in the outlet gas stream, varied slightly during a given treatment, so all the results are expressed with reference to the average level over the treatment period.

THE EFFECT OF CARBON MONOXIDE ADDITION LEVEL
The effect of the carbon monoxide concentration in the treatment atmosphere for treatments carried out at 850°C is shown Figure 2. As expected, the case depth and surface hardness were relatively insensitive to the carbon monoxide concentration. Once the oxygen potential at the surface is sufficiently high to form TiO₂, the effective oxygen potential is fixed at that value and the driving force for diffusion cannot be increased further. Figure 3 shows the presence of a ceramic surface layer on a sample treated with a carbon monoxide concentration of 78 ppm. There is no such layer on samples treated at 45 ppm.

Figure 2. The effect of carbon monoxide concentration on surface hardness and case depth (400HV) at 850°C

Figure 3. The near surface microstructure of Ti-6Al-4V treated in 78 ppm carbon monoxide for 24 hours

THE EFFECT OF TREATMENT TIME
Samples were treated for 24 and 48 hours at 800°C using a carbon monoxide concentration of 55 ppm. The resultant case depths of 0.13 and 0.18 mm respectively were exactly in agreement with those predicted by Fick’s Law.

Figure 4. The effect of treatment temperature on case depth at 400 HV

THE EFFECT OF TREATMENT TEMPERATURE
Figure 4 shows that the case depth achievable in 24 hours is strongly affected by the treatment temperature. These results have been corrected for the small differences from the nominal 50 ppm level in the measured carbon monoxide concentration that occurred during the treatments.

Another effect of the treatment temperature is structural coarsening. Figure 5 shows clearly the significant coarsening of samples treated at 900°C, compared with those treated at 750°C. The effect is
not significant for processing temperatures of 850°C and below for Ti-6Al-4V.

Figure 5. The core microstructure of Ti-6Al-4V after 24 hours treatment at (a) 750°C, (b) 800°C, (c) 850°C and (d) 900°C

Discussion

Although wear testing was not part of this study, it might be expected that the optimal carbon monoxide level for the treatment of Ti-6Al-4V to improve wear would be close to the 78 ppm level. A thin ceramic surface layer like that found on top of the diffusion case in this sample is known to have enhanced tribological properties [15]. The XRD analysis showed that both carbon and oxygen from the carbon monoxide have been incorporated into the layer (Figure 6). Comparison with a fully characterised microstructure developed using carbon monoxide by Kim et al. suggests that the light outer part of the ceramic layer is TiO₂ and the inner dark part TiC [13]. If this is the case then it might well affect the tribological properties [16].

Figure 6. XRD analysis

There is obviously a trade-off between getting the maximum case depth and the structural coarsening that inevitably lowers core strength. This is more of a problem for larger components that require a deeper case. However, the structural coarsening observed is not severe for treatments at 850°C and below and would not be expected to significantly affect the core strength of Ti-6Al-4V.

Although carbon monoxide has been used previously to form diffusion layers in titanium alloys [12], the same technique as had previously used for oxygen diffusion layers was used [3]. This technique can be effective but it is expensive as it needs three separate treatment stages, reaction in atmosphere, diffusion in vacuum and surface layer formation in atmosphere. By using the technique described above and controlling the availability of the reactants, it is possible to do all three steps in a single treatment.

CONCLUSIONS

- Dilute mixtures of carbon monoxide in argon can be used to create hard diffusion layers rich in oxygen and carbon on Ti-6Al-4V.
- At low carbon monoxide concentrations no ceramic surface layer is formed, but at higher concentrations a ceramic layer
probably consisting of TiO₂ and TiC, thought to be optimal for wear, is produced.

- The process follows the usual axioms for diffusion treatments and there is no significant structural coarsening at treatment temperatures below 850°C.

**FURTHER WORK**

Further work is needed to determine the exact carbon monoxide level needed to form the optimum layer. This optimised layer should then be subjected to comparative wear testing to confirm that it is better than the layer produced by oxygen alone. It has been shown that for one treated α+β alloy the lubricated wear rate was better than hardened SUJ-2 steel [16].

**ACKNOWLEDGEMENTS**

The authors would like to thank Heike Plebich of the Linde Group metallography team for her work on the micrographs and hardness traverses.

**REFERENCES**


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Surface Hardening Titanium with Carbon Monoxide

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Introduction

• Titanium has very poor tribological properties that limit its applications to non-wearing parts
• Coatings can be used, but they cannot support high loads
• Attempts have been made to improve them with thermochemical treatments using oxygen or nitrogen
• To produce sufficient case depth for, say a gear, within a reasonable time - say 24 hours, then a high temperature must be used
  — above the $\alpha \rightarrow \beta$ transition temperature.
• This degrades the core properties of the titanium
  — typically Ti-6Al-4V
• It has been suggested that multi-element diffusion treatments might have advantages for treatment temperature and case properties
Introduction

• To achieve the desired results at low treatment temperatures, the availability of the reactants has to be very closely controlled.

• Previous experiments used very small samples and a continuous high flow of gas in a very small tube furnace. When larger samples were treated, the relatively small volumetric gas flow possible resulted in an uneven case.

• For these experiments a furnace with a higher volume was used to ensure uniform treatment.

• Feedback control was used to give a constant and consistent atmosphere composition.
The highly instrumented Boye pit furnace used in the trials
Experimental – furnace preparation

• The Boye pit furnace had previously been used for carburising treatments

• It was thoroughly burnt out, together with the loading jig, to ensure that no residues—particularly carbon—were present that might affect the results
• Samples of T-6Al-4V were polished cubes - 10mm per side

• Experimental procedure
  — samples placed in the cold pit furnace
  — heated under a flow of argon
  — processing temperature reached
  — processing gas mixture introduced
  — processing completed
  — Processing gas mixture replaced by argon
  — furnace cooled to below 150ºC
  — samples removed
• Very small flow rate of carbon monoxide were needed
• To get the required control premixed cylinders of standard gases were used to feed the mixer
• The carbon monoxide level, as measured in the outlet gas stream, varied slightly during a given treatment
• All the results are expressed as the average level over the treatment period
The case depth (to 350 HV) was insensitive to the carbon monoxide concentration.

Once the surface ceramic layer is formed the effective oxygen/carbon potential is fixed and the driving force for diffusion cannot be increased further.
Similarly the surface hardness was insensitive to the carbon monoxide concentration.
Results - the effect of carbon monoxide addition level

There is a ceramic surface layer on a sample treated with a carbon monoxide concentration of 78 ppm. There is only a very thin layer on samples treated at 45 ppm.
Results - the effect of treatment time

• Samples were treated for 24 and 48 hours at 800°C using a carbon monoxide concentration of 55 ppm
• The resultant case depths of 0.13 and 0.18 mm respectively were exactly in agreement with those predicted by Fick’s Law
Results - the effect of treatment temperature
Results - the effect of treatment temperature

- a - 750°C
- b - 800°C
- c - 850°C
- d - 900°C
Characterising the layer - XRD analysis
• There is obviously a trade-off between getting the maximum case depth and the structural coarsening that inevitably lowers core strength.
• This is more of a problem for larger components that require a deeper case.
• The structural coarsening observed is not severe for treatments at 850°C and below and would not be expected to significantly affect the core strength of Ti-6Al-4V.
• Higher strength beta alloys need investigation.
• Using surface hardened gears can potentially reduce the weight of a gearbox by 40%.
Alternative processes

• Carbon monoxide has been used previously to form diffusion layers in titanium alloys but the process route was tortuous.

• It is expensive as it needs three separate treatment stages:
  — reaction in atmosphere
  — diffusion in vacuum
  — surface layer formation in atmosphere

• Using the new technique it is possible to do all three steps in a single treatment.
• Dilute mixtures of carbon monoxide in argon can be used to create hard diffusion layers rich in oxygen and carbon on Ti-6Al-4V
• A ceramic layer probably consisting of TiO$_2$ and TiC, thought to be optimal for wear, is produced
• The process follows the usual axioms for diffusion treatments and there is no significant structural coarsening at treatment temperatures below 850°C.
Thank you for your attention

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