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ScienceDirect

Wear 263 (2007) 625–628

WEAR

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Short communication

Characterisation of nitrogen-bearing surface layers on Ni-base superalloys

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Received 2 September 2006; received in revised form 22 November 2006; accepted 7 January 2007

Abstract

Nitrogen plasma immersion ion implantation (PI^3) of a commercial Ni-base alloy (Inconel 601) was performed to assess the effects of such treatments on the alloy's wear and corrosion resistance. After 5 h treatment at 350 and 400 °C a super-saturated fcc phase was formed. At 450 and 525 °C CrN precipitates were formed in the nitrided layer. The hardness initially increased with increasing temperature from 6.83 ± 1.43 GPa at 350 °C to 15.05 ± 0.53 GPa at 450 °C. At 525 °C however a lower hardness of 9.40 ± 0.69 GPa was recorded. The hardness of the untreated alloy was 2.94 ± 0.16 GPa.

All of the nitrided samples showed superior corrosion resistance to the untreated alloy in 3.56 wt.% NaCl but corrosion of the untreated core occurred at grain boundaries and especially at triple points on the nitrided surfaces. Unlike austenitic stainless steels, the presence of CrN in the nitrided layers did not cause a dramatic reduction in corrosion resistance. Unlubricated reciprocating pin-on-disc wear tests against an alumina ball showed that the PI^3 treatment in all cases reduced wear (by as much as 3 orders of magnitude) and friction compared to the untreated alloy. Despite having the second lowest hardness the sample nitrided at 525 °C showed the lowest wear and friction.

Keywords: Nickel-base alloys; Nitriding; Expanded austenite; S-phase; Corrosion; Sliding wear

1. Introduction

Nitriding of Ni-base alloys has been much less widely studied than nitriding of austenitic (fcc) stainless steels despite the similarity in structure and shortcomings (susceptibility to localised corrosion and poor tribological performance) for the two alloy systems. Nitriding experiments (using both gaseous [1,2] and plasma transport media [3]) on binary Ni–Cr alloys at temperatures above 500 °C has shown that CrN precipitates are formed in a Cr-depleted fcc–Ni matrix. The nitride precipitates become finer as the temperature decreases with uniform layers formed below 700 °C in which individual precipitates are not resolvable by optical or scanning electron microscopies [1–3]. For a given temperatures the nitride dispersion also becomes finer with increasing Cr content and once a critical Cr content (approximately 30 wt.% for temperatures of 900 °C and above) continuous CrN layers can be formed [1,4]. Similar results have been reported for nitriding of commercial Ni–Cr alloys (for example, see [5–7]).

It is now well known that low temperature (<500 °C) nitriding of austenitic stainless steels can produce a supersaturated fcc phase that combines high hardness and good corrosion resistance (above 500 °C hardness is increased at the expense of corrosion resistance). This phase is known as s-phase or expanded austenite (for example, see [8–10]). Due to the similarities between the austenitic stainless steels and Ni–Cr alloys it is reasonable to expect an analogous phase to be formed in Ni–Cr alloys. Williamson et al formed just such a phase (also termed expanded austenite, γ_N) in a binary Ni–20Cr alloy by low energy ion implantation at 400 °C, simultaneously confirming the possibility of a γ_N phase in Ni–Cr alloys and the key role played by Cr in the formation of such phases [10]. This was followed by further studies forming γ_N in binary Ni–Cr alloys [11] as well as commercial Ni-base alloys (for example, see [12–15]).

This research seeks to increase the limited knowledge regarding the tribology and corrosion behaviour of nitrided Ni-base

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doi:10.1016/j.wear.2007.01.089

alloys and in particular to compare and contrast the properties of nitrided layers comprising nitride precipitates and supersaturated solid solution phases.

2. Procedure

A series of Inconel alloy 601 (IN601—Ni–23Cr–14Fe–1.5Al) coupons were cut from 3 mm thick sheet and polished to an Ra of better than 5 nm. These polished samples were nitrided using the plasma immersion ion implantation facility at the ANSTO Advanced materials Division, NSW, Australia. The samples were heated up to treatment temperature in an argon/hydrogen plasma with 20 kV ion bombardment to assist in cleaning the surfaces (total time 1 h). The samples were then processed for 5 h in a nitrogen plasma with a constant nitrogen dose rate of 2.25×10^{14} N/cm^{2}s at 35 kV. The treatment temperature was maintained with the aid of a heating element below the working table. The samples were nitrided at a range of temperatures to determine the different surface phases formed as a function of temperature.

After treatment the samples were characterised by glancing incidence X-ray diffraction (GXRD) using a Siemens D500 diffractometer with CoKα radiation at a fixed angle of incidence of 5°. Nanoindentation experiments were carried out with a Nano IIs nanoindenter using a maximum load of 50 mN.

Cyclic polarisation (CP) tests were carried out in freshly prepared, deaerated 3.56 wt.% NaCl solution at ambient temperature using an EG&G K0235 Flat Cell coupled to a computer controlled EG&G 263 potentiostat. After 1 h exposure to the electrolyte the free corrosion potential (U_{corr}) of the samples was recorded relative to the saturated silver–silver chloride (Ag/AgCl) reference electrode. The samples were then polarised potentiodynamically at 0.166 mV/s from U_{corr} until a corrosion current of 1 mA/cm^2 was obtained. The scan direction was then reversed until the U_{corr} was again reached. Knife-edge PTFE gaskets were used in all cases to make the seal with the sample surfaces. After completion of the corrosion tests the sample surfaces were examined by optical microscopy (OM).

Reciprocating pin-on-plate wear tests were conducted in ambient laboratory air (approximately 22 °C) using a tribometer in which the tested samples were fixed to a moving plate (operated by a crank-slider mechanism) that reciprocated under the stationary pin. A 7.94 mm diameter 99.5% alumina ball was used as the pin for all tests and the reciprocation stroke and frequency were set at ±7.5 mm and 1 Hz, respectively, giving an average sliding speed of 0.015 m/s. Tests were conducted at loads of 0.98 and 4.90 N for a duration of 60 min for the nitrided samples while the untreated sample was tested at 0.98 N only (the maximum Hertzian contact stress in this condition was approximately 50% of the yield stress as approximated from the hardness at 1.00 N). The friction force was collected continuously during the tests allowing the coefficient of friction (COF) to be calculated. The wear tests were periodically interrupted and the wear scars on both pin and plate examined by OM. At the end of the tests the wear scar volume was quantified using a WYKO optical light interferometer.

3. Results and discussion

3.1. Crystal structure and topography

After PI^3 treatment at 350 and 400 °C an expanded fcc solid solution phase (analogous to expanded austenite/s-phase in austenitic stainless steels and termed γ_N hereafter) was detected, Table 1. Substrate peaks were also observed and were of lower intensity with increasing temperature due to the increasing thickness of the γ_N layer. The Bragg angles for the γ_N phase at 350 and 450 °C were similar suggesting a similar nitrogen content. After treatment at 450 and 525 °C the GXRD peaks corresponded with those for CrN. Higher peak intensities for the 525 °C indicated a thicker layer than for the 450 °C sample.

This phase evolution (γ_N at 350 and 400 °C with CrN precipitation 450 °C and above) is similar to that reported by Collins et al for AISI 316 PI^3 nitrided under similar conditions [9]. Unlike the AISI 316 samples however CrN precipitation in nitrided IN601 was not associated with a change in crystal structure of the matrix.

3.2. Mechanical properties

All of the nitrided samples showed hardnesses greater than that of the untreated sample, Table 1. The measured hardness initially increased with increasing treatment temperature reaching a maximum of 15.0 GPa for the sample nitrided at 450 °C. For the sample nitrided at 525 °C the hardness was lower at 9.40 GPa. The lower measured hardness for the 350 °C sample compared to the 400 °C sample may have been due to the thinner surface layer for the former as hardness of γ_N typically depends on nitrogen content which according to the GXRD results was similar for both samples.

The mechanism behind the decrease in hardness between the samples nitrided at 450 and 525 °C is unclear but may be due to a coarsening of the CrN precipitates. There is general agreement in the literature that precipitate coarsening leads to a decrease

Table 1

Summary of phase composition, hardness and corrosion behaviour for nitrogen PI^3 treated Inconel 601 samples

Temperature (°C)	Phase	H (50 mN) (GPa)	$U_{\mathrm{corr}}/V_{\mathrm{Ag/AgCl}}$	$U_{\mathrm{pit}}/V_{\mathrm{Ag/AgCl}}$	$U_{\mathrm{prot}}/V_{\mathrm{Ag/AgCl}}$	Attack
–	γ	2.94 ± 0.16	−0.322/−0.168	0.327/0.373	0.078/0.182	Pitting + Crevice
350	γ_N, γ	6.83 ± 1.43	0.024/−0.012	0.280/0.287	−0.032	Blistering
400	γ_N, γ	12.7 ± 1.9	−0.086/−0.094	0.206/0.314	−0.046/0.007	Blistering
450	CrN, γ	15.0 ± 0.5	0.007	0.349	0.095	Blistering
525	CrN, γ	9.40 ± 0.69	−0.115	0.131	−0.116	Blistering