Increasing the Coefficient of Sliding Friction of NiCr at Low Loads by Interstitial Surface Hardening

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Abstract. Low-temperature interstitial hardening of NiCr alloys by gas-phase carburizing and nitriding increases the coefficient of sliding friction (COF) at low loads by as much as 50%. While the substantial surface hardening provided by the very high concentrations of interstitial carbon or nitrogen tends to decrease the COF, the presence of these interstitial solutes also decreases the thickness of the air-formed surface oxide layer, which tends to increase the COF. The overall result is an increase in COF.

Keywords: sliding friction; hardness; diffusion treatments; metal alloys

1. Introduction

NiCr alloys are of technical interest for vibrational damping structures operating at high-temperature (> 1000 C) [1]. For this purpose, woven wire meshes have been developed that consist of NiCr alloy (Ni–20Cr) wires. The inter-wire forces in these structures are estimated to be about 0.05 N [2]. Increasing the coefficient of sliding friction (COF) between the wires at these loads would improve the damping behavior.

It has been reported that hardening metal alloys without changing the composition decreases COF. For example, implanting martensitic steel with carbon or nitrogen increases hardness by about two times and reduces the COF (in air) by a factor of 8 [3]. Work hardening of an aluminum alloy doubles the hardness and decreases the COF from 1.4 to 0.9 [4]. Annealing a CuZrAl bulk metallic glass raises the hardness from 480 HV to 530 HV and reduces the COF from 0.5 to 0.4 [5].

Interstitial hardening of stainless steel by low-temperature gas-phase carburizing, in contrast, has previously been found to increase the COF [6]. In this technique, carbide formation is inhibited kinetically, since the low processing temperatures effectively immobilize the substitutional elements, and a “colossal” supersaturation – over 10^4 times the equilibrium solubility at the treatment temperatures – of interstitially dissolved carbon is achieved [7]. In

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particular, low-temperature carburizing of 316L stainless steel, which increases the surface hardness from 2.0 GPa to 7.6 GPa, increases the COF by 37% (from 0.51 to 0.70), as measured by a rotating ball-on-disk test at room temperature using 9.5 mm diameter balls and a 5 N load [6]. In addition, the wear rate decreases by over 98%.

A potential explanation for this unexpected result arises from the fact that on smooth samples, interstitial hardening can increase the surface roughness. The large stresses that develop due to the high concentration of interstitials cause severe near-surface plastic deformation that results in uneven uplift of the surface. The influence of surface roughness on friction has been the subject of extensive investigation [8-13], and its effect is complicated by many factors, including ductility, shear strength, and ambient conditions [14].

Further, low-temperature carburizing and nitriding can increase COF by reducing the thickness of the native, air-formed oxide layer on 316L stainless steel [15,16]. Low-temperature carburizing, in particular, reduces the oxide layer thickness from ≈ 1.5 nm to ≈ 1.0 nm. It was postulated that the strong Cr–C bonds make the surface less reactive and less prone to form Cr_2O_3 [15].

Increased surface oxide thickness decreases the COF of metals. For example, the COF at room temperature of a freshly cut Cu surface decreases substantially after forming a 50 nm thick surface oxide layer [17]. The COF of a Fe–19Cr alloy at room temperature decreases with increasing oxygen partial pressure in the testing ambient [18]. At elevated temperatures (800°C to 1050°C), the COF of 1018 mild steel decreases as the oxide thickness increases from 0.015 mm to 1.59 mm [19]. The COF of 304L stainless steel at room temperature decreases after oxygen ion implantation into the near-surface [20]. Therefore, a treatment that leads to a reduced surface oxide thickness should increase the COF.

In this work, we have investigated whether interstitial hardening, by low-temperature gas-phase carburizing or nitriding, alters the COF of NiCr at 0.05 N load, and whether the COF correlates with a change in the thickness of the air-formed surface oxide layer. Since this is a gas-phase process, the intricate geometry of a woven wire damping structure would not hinder complete conformal treatment of all surfaces. At very high temperatures, the interstitial atoms would react to form carbides and nitrides. Therefore, long-term operating temperatures of treated structures would be limited to less than $\approx 500^\circ\text{C}$.

2. Materials and methods

COF measurements were performed using ball-on-plate dry sliding tests in a Bruker/CETR UMT tribometer. **The laboratory humidity was not monitored.** The plates were NiCr (Ni–20Cr) and the 1.6 mm diameter balls were Hastelloy C276 (Ni–23Cr–14Mo–7Fe). The plates were purchased from Goodfellow, and polished with SiC grit paper through 1200 grit (P4000), which produces an arithmetic average roughness R_a of ≈ 20 nm [21]. The balls were purchased from Bal-tec, and were Grade 200, indicating a maximum R_a of 200 nm. **Balls made of NiCr were desired, but could not be obtained in the necessary size, and therefore Hastelloy C276 was chosen as an alternate material due to its compositional similarity.** Plates and balls were carburized and nitrided in a flowing-gas atmospheric pressure furnace built by CVD Equipment Corporation. Both treatment recipes included initial activation in HCl gas for 4 h at 325°C [22]. The carburizing treatment consisted of 20 h at 450°C in 30% CO / 45% H₂ / 25% N₂. The nitriding treatment consisted of 20 h at 440°C in 10% NH₃ / 10% CO / 40 % H₂ / 40 % N₂. The nitriding recipe contains CO gas, which leads to carbon interstitials, but previous investigations with 316L stainless steel [23,24] revealed that the carbon interstitials are located deeper into the sample, and only nitrogen interstitials are located close to the surface.

The furnace treatments could alter the surface roughness of the plates, either from plastic deformation caused by the carbon and nitrogen interstitials, or from etching by the HCl gas. Therefore, the plates were lightly re-polished with 1200 grit SiC paper after treatment.

COF measurements were performed at 0.02, 0.05, and 0.1 N loads. Assuming elastic Hertzian deformation, and using reported values of 210 GPa and 0.3 for Young's modulus and Poisson's ratio, respectively, for both ball and plate materials [25,26], the average contact pressures during testing were 180 MPa, 250 MPa, and 310 MPa for testing with 0.02 N, 0.05 N, and 0.1 N loads, respectively.

Microstructural and microchemical analyses were carried out in the Swagelok Center for Surface Analysis of Materials at Case Western Reserve University. The treated samples were investigated with X-ray diffractometry (XRD) using a Scintag X-1 diffractometer, and the concentration of interstitials and thicknesses of the surface oxide layers were measured with X-ray photoelectron spectroscopy (XPS, also called ESCA – electron spectroscopy for chemical analysis) using a Physical Electronics Versaprobe. Hardnesses were measured using a Buehler Micromet Vickers indenter, with a 0.25 N (25 gf) load.

3. Results

COF results for nontreated NiCr under unidirectional sliding as a function of sliding velocity are shown in Fig. 1a, and COF results for nontreated, carburized, and nitrided NiCr under reciprocating sliding as a function of load are shown in Fig. 1b. The standard deviations of the measured COFs are high, likely due to a noisy data acquisition system, but the data sets are sufficiently large for statistical testing (Student's t-test) to conclude that the improvement in COF at 0.05 N load is significant (real) for both treatments. Specifically, carburizing in all probability increases the COF by 50%, from 0.18 to 0.27, and nitriding increases the COF by 11%, to 0.20. Fig. 1c shows the time evolution of the COF data for the reciprocating sliding tests performed at 0.1 N.

Figure 1. COF results for (a) unidirectional sliding of nontreated NiCr at varying velocities, and (b) reciprocating sliding of nontreated, carburized, and nitrided NiCr at varying loads. The error bars represent one standard deviation. (c) COF as a function of testing time, averaged over 5 s intervals for the reciprocating sliding tests performed at 0.1 N.

Figure 2. (a) XRD scans for nontreated, carburized, and nitrided NiCr. **(b)** NiCr lattice parameters determined from the peak positions shown in (a).

The XRD results for the three NiCr samples are shown in Fig. 2. The scans in Fig. 2a do not reveal any precipitates after either treatment. Fig. 2b shows the lattice parameter determined from each of the 5 peaks identified in Fig. 2a. The systematic variations in the lattice parameter are caused by a residual compressive stress [27], which can be caused by either machining-induced deformation or interstitial solutes in solid solution. Fig. 2b shows that both treatments increase the lattice parameter by dissolution of interstitial elements, particularly nitrogen. The hardnesses were measured as 3.4 GPa, 5.0 GPa, and 6.4 GPa, for nontreated, carburized, and nitrided NiCr, respectively (Table I). Clearly, interstitial hardening occurred for both treatments.

Figs. 3a-c show XPS depth profiles for the three NiCr samples. Each shows a thin surface oxide layer. The oxide is enriched in Cr, compared to Ni, which is expected due to the highly negative Gibbs energy change associated with Cr_2O_3 formation. The carburized sample (Fig. 3b) contains 4 at.% carbon near the surface, while the nitrided sample (Fig. 3c) contains 8 at.% nitrogen near the surface. No interstitial carbon was detected in the near-surface region of the nitrided sample. The larger interstitial concentration in the nitrided sample agrees with its larger lattice parameter expansion.

Figure 3. XPS depth profiles for (a) nontreated, (b) carburized, and (c) nitrided NiCr. (d) The first five Cr scans from the depth profile of the nontreated NiCr.

The thicknesses of the surface oxide layers were determined from XPS Cr scans. As shown in Fig. 3d, the Cr 2p peaks reveal contributions from both metallic Cr and Cr bonded to oxygen. The difference in the binding energies allows the peak-fitting software to separate the signals into the two different contributions. The thickness of the surface oxide layer was taken as the depth at which the two contributions were equal, applying linear interpolation to the XPS data obtained from different depths. The surface oxide thicknesses were: 2.7 nm, 2.1 nm, and 2.6 nm nontreated, carburized, and nitrided NiCr, respectively (Table I).

Table 1. Hardness, COF, and surface oxide thickness results.

Treatment	NiCr Plate Hardness (GPa)	COF	Plate surface oxide thickness (nm)
Nontreated	3.4	0.18	2.7
Nitrided	6.4	0.20	2.6
Carburized	5.0	0.27	2.1

4. Discussion

The results for surface hardness, COF, and oxide thickness after low-temperature carburizing and nitriding are summarized in Table 1. Both carburizing and nitriding (i) significantly increase the surface hardness, (ii) reduce the thickness of the air-formed surface oxide that re-formed after polishing prior to friction testing, and (iii) increase the COF.

Since all three NiCr plates were polished in the same manner, we expect that they initially had similar surface roughness, and it seems unlikely that the roughness changed during the sliding friction test. Accordingly, the observed increase in COF cannot be attributed to differences in surface roughness, e.g. in the sense of Coulomb's theory [13].

According to expectation, increasing the surface hardness should decrease the COF [3-5], while reducing the oxide layer thickness should increase the COF [17-20]. Under the conditions of our experiments, apparently, the COF-increasing effect of reduced oxide layer thickness over-compensates the COF-decreasing effect of increased surface hardness.

The reduction in surface oxide thickness can be explained as follows: Cr atoms in the NiCr alloy have a strong affinity for both carbon and nitrogen. Cr is a strong carbide- and nitride former. When the carbon and nitrogen interstitials in the NiCr are in close proximity to Cr atoms, it is likely that strong bonding occurs between them. The air-formed oxides are Cr_2O_3 -rich, as shown in Fig. 3. Therefore, the decrease in the surface oxide thickness is likely due to a decreased reactivity (activity) of the Cr atoms in the alloy, analogous to what was earlier observed for 316L stainless steel [15]. According to previous research [17-20], the COF of metals depends particularly strongly on the surface oxide layer thickness in dry sliding friction under low loads, which is the regime investigated in this study.

It is expected that if the carburized or nitrided layers would be removed by wear, the COF would revert to the value observed for nontreated material. However, since the treated

layers are several micrometers thick, and the contact pressures are so low, the lifetimes of the treated layers will be extremely long.

5. Conclusions

The COF of NiCr under dry sliding conditions at low loads (0.02 to 0.1 N) was investigated in conjunction with gas-phase low-temperature carburizing and nitriding. The following conclusions have been drawn:

- (1) The COF of NiCr at 0.05 N load was increased 50% by carburizing, from 0.18 to 0.27, and 11% by nitriding, from 0.18 to 0.20.
- (2) The hardness of NiCr was increased by 47% by carburizing and by 88% by nitriding. This was induced by the infusion of ≈ 4 at.% carbon and ≈ 8 at.% nitrogen, respectively.
- (3) The air-formed surface oxide layer on NiCr was decreased by the treatments: from 2.7 nm for nontreated NiCr to 2.6 nm for nitrided NiCr, and to 2.1 nm for carburized NiCr. The reduction in oxide thickness, more pronounced for carburizing than for nitriding, is likely caused by the reduction of the reactivity of Cr in the alloy, and brings about the increase in COF.
- (4) The observed phenomenon of increasing COF by low-temperature carburizing or nitriding may have technical application for damping applications. In particular, carburizing increases the COF by 50% at 0.05 N loads.

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