Microstructure dependence of abrasive wear behavior in electrodeposited nanocrystalline Ni – P alloy

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Received: 28 December 2016; Revised: 17 February 2017; Accepted: 24 May 2017

Abstract

Effect of microstructure on two-body abrasive wear behavior in electrodeposited Ni – 4.4 mass% P alloy was investigated to obtain a clue to development of nanocrystalline materials with high wear resistance. The as-electrodeposited nanocrystalline Ni – 4.4 mass% P alloy, which was in a supersaturated solid-solution, transformed into a dual phase alloy composed of Ni and Ni₃P grains as a result of the precipitation of Ni₃P phase by annealing. The Hall-Petch relationship between the hardness and average grain size was maintained in the annealed dual phase alloy specimens with average grain size ranging from 50 nm to 1230 nm. The wear rate of the annealed specimens decreased with decreasing average grain size accompanied by hardening. The wear rate of the annealed specimens containing hard Ni₃P grains was lower than that of the as-electrodeposited specimen with the similar hardness. Although the very fine grain size induced smooth wear grooves, the conventional grain size induced rough wear grooves with turning of Ni phase. The hardness dependence of wear resistance in Ni – 4.4 mass% P alloy specimens was weaker than that obtained in the case of pure metal specimens with different hardness.

Keywords : Nanocrystalline nickel alloy, Precipitation, Electrodeposition, Two-body abrasive wear, Wear resistance

1. Introduction

The electrodeposited nickel – phosphorus (Ni-P) alloys with P contents less than 5 mass% have nanocrystalline (nc) grain structure and show very high hardness of about HV 660 (Safranik, 1986). Their hardness is further increased up to HV970 by annealing at above 573 K, because of the precipitation of the Ni₃P phase from the as-electrodeposited solid solution (Safranik, 1986). Therefore, the nc Ni-P alloy has been expected to apply as wear resistance coatings and structural materials. Abrasive wear is one of main wear mechanism of materials which subjected to sliding contact. Abrasive wear occurs by penetration of hard particles or surface asperities of a harder material into the surface of a softer material. Thus, the harder material must show the higher abrasive wear resistance (Archard, 1953, Khruschov, 1974). Khruschov (1974) reported that the wear resistance of fully annealed pure metals is linearly proportional to their specific hardness. Wear resistance of quenched and tempered steels having various carbon contents increased with increasing hardness (Richardson, 1967). However, it is possible that the harder material showed a lower wear resistance in brittle materials such as white cast iron (Gahr and Doane, 1980). They have suggested that the abrasive wear was controlled not only by hardness, but also other mechanical properties such as ductility and fracture toughness.

For the effect of microstructure on wear properties, Hutchings (1994) investigated that the relationship between wear rate and volume fraction of martensite in steels. He reported that a higher volume fraction of martensite induced a lower wear rate. Tyagi et al. (2002) demonstrated that age-hardening has a slight effect on wear resistance of Al-Mg-Si and Fe-Ni alloys. Modi et al. (2003) investigated the effect of interlamellar spacing on abrasive wear properties in high carbon steel. They found that the wear rate decreased with decreasing interlamellar spacing, although the effect of microstructural control on the wear resistance seemed to be much weaker than that of kinds of materials.
The studies on the wear resistance of nc materials have been drawing an increasing interest of many researchers (Farhat et al., 1996, Jeong et al., 2001 and 2003, Schuh et al., 2002, Apachitei et al., 2002, Mishra et al., 2004, Han et al., 2008, Rupert and Schuh, 2010, Li et al., 2012, Wasekar et al., 2012, Fu et al., 2015). Farhat et al. (1996) reported on the sliding wear behavior of nc aluminum films with average grain sizes ranging from 15 nm to 100 nm against stainless steel. The wear rate of nc aluminum linearly increased depending on the square root of the grain size. Wasekar et al. (2012) demonstrated that the wear rate and the coefficient of friction of nc nickel decreased with decreasing grain size. Recently, Fu et al. (2015) revealed that the wear resistance in vacuum of the nc Fe80Si12 alloy was improved by decreasing grain size because of change in wear mechanism. For the abrasive wear of nc materials, Jeong et al. (2001) and Schuh et al. (2002) revealed that the wear rate of electrodeposited nc nickel specimens decreased with decreasing average grain size. Therefore, it is found that the wear resistance of metallic materials is generally improved by nanocrystallization. However, the predominance of nanocrystallization for the improvement of wear resistance over other methods has not been fully clarified.

In this work, the effects of the grain size and the morphology of Ni3P precipitates on two-body abrasive wear behavior in electrodeposited Ni-P alloy were investigated to obtain a clue to development of nc materials with high wear resistance. The Ni –4.4 mass% P specimens whose grain size distribution were greatly changed by electrodeposition and subsequent annealing were subjected to pin-abrasion tests on silicon carbide (SiC) abrasion paper in the absence of a lubricant. Moreover, the effectiveness of control of nc grain structure for improving wear resistance of the Ni-P alloy was discussed in comparison with wear resistance for various pure metals with largely different hardness.

2. Experimental procedure

The nc Ni –4.4 mass % P alloy was produced by electrodeposition using an electrolytic bath composed of 150 g l⁻¹ nickel sulphate, 45 g l⁻¹ nickel chloride, 80 g l⁻¹ phosphoric acid and 4 g l⁻¹ phosphorous acid with pH 1.5 (Kobayashi and Kashikura, 2003). The electrodeposition was carried out onto a Ti substrate whose dimensions of 50 mm length, 6 mm width and 1 mm thick, at 338 K and a current density of 2.0 mA/mm² for 10.8 ks. The Ni –4.4 mass % P alloy thin sheets were mechanically stripped from the Ti substrate. The thickness of Ni-P alloy thin sheet was about 300 μm. They were annealed in an evacuated (1 × 10⁻¹ Pa) SiO₂ tube at 673 K – 1073 K for 60 s –1.8ks, and subsequently air-cooled to room temperature. The wear specimen with the contact area of 4 mm x 4 mm was cut from the as-electrodeposited and annealed Ni –4.4 mass % P alloy thin sheets. The surface of wear specimens was mechanically polished using abrasion papers of 600 – 1500 grade and 0.06 μm alumina powder slurry. The surface roughness of all the specimens was about 0.04 μm in arithmetic roughness (Rₐ). This value of the surface roughness was much smaller than the particle size of the abrasion papers for abrasive wear tests.

An X-ray diffractometer (XRD) measurement was employed to evaluate the average grain size and crystal structure of the as-electrodeposited Ni –4.4 mass % P alloy specimen and the specimen annealed at relatively low temperature of 673 K. The average grain size was determined from the full width at half maximum of (111) reflection by the Scherrer formula (Cullity, 1978). Quantitative evaluation of the microstructure of annealed specimens was carried out using a scanning electron microscope (SEM). Moreover, the SEM observations of worn surface were performed to reveal the effect of microstructure on two-body abrasive wear behavior in the nc and submicron-grained Ni –4.4 mass% P alloy specimens. The relationship between the morphology of wear grooves and the microstructure was investigated.

Vickers hardness tests were carried out at an indentation force of 0.49 N for 15 s. The indentation left on the specimen surface was about 2.5 μm in depth, which was sufficiently shallow to the specimen thickness of 300 μm. Five measurements were averaged to determine the hardness of each specimen.

Two-body abrasive wear tests were performed using a pin-abrasion type tribometer. The Ni-P alloy specimens were worn to one-way on the virgin surface of SiC abrasion paper at room temperature without lubrication in air and at a wear speed of 15 mm/s, so the effect of free SiC abrasion particles on wear mechanism was removed. The average particle sizes of the SiC abrasion paper were 68 μm, 110 μm and 150 μm. A constant nominal pressure of 0.06 MPa was applied normal to the specimen surface. This pressure was sufficiently lower than the yield stress of about 1.6 - 2.0 GPa in the Ni –4.4 mass% P alloy specimens with different average grain size (Kobayashi and Kashikura, 2003). The volume loss and wear rate of the specimens were calculated by the following equations:
\[ V_L = \frac{M_0 - M_1}{\rho} \]  
\[ W = \frac{V_L}{L} \]  

where \( V_L \) is the volume loss, \( M_0 \) the specimen mass before the wear test, \( M_1 \) the specimen mass after the wear test, \( \rho \) the density of Ni – P alloy, \( W \) the wear rate and \( L \) the wear distance.

Scratch tests were performed to reveal the effect of grain refinement on abrasive wear behavior in more detail. The specimens were scratched by a SiC rider having an indentation angle of 130° and the radius of curvature of the indentation tip of about 50 \( \mu \)m and at an applied force of 0.98 N. The relationship between the morphology of wear grooves and the microstructure was investigated.

3. Experimental results
3.1 Microstructure and thermal stability of electrodeposited nc Ni -4.4 mass % P alloy specimen

Figure 1 shows the XRD profile for the as-electrodeposited Ni -4.4 mass% P alloy specimen. The as-electrodeposited specimen was composed of only Ni phase, although the P content of 4.4 mass% is much higher than the solubility limit of P in Ni (< 0.17 mass%). Hentschel et al. (2000) revealed that the P atoms in the electrodeposited Ni -3.6 at% P (Ni -1.9 mass % P) alloy segregated at the grain boundaries of Ni matrix, because the volume fraction of grain boundaries becomes considerably high in nc materials with grain size less than 100 nm. The as-electrodeposited Ni-P alloy specimen obtained in the present work was in solid solution, although the specimen had the higher P content of 4.4 mass %. The average grain size of the as-electrodeposited specimen evaluated by the Scherrer formula was 37 nm. The surface of the as-electrodeposited specimen was strongly oriented to around (111).

In general, nc grain structure is thermally unstable owing to the high density of grain boundaries and triple junctions. It has been reported that the grain growth in nc pure Ni occurs even at 353 K (0.2\( T_m \); \( T_m \) is melting point) (Klement et al., 1995). Mehta et al. (1995) demonstrated that the grain structure in Ni -1.2 mass % P alloy has been shown to be stable at temperatures up to 633 K (0.38\( T_m \)). The thermal stability of grain structure in Ni-P alloy is improved by increasing P content. Fig. 2 shows the differential scanning calorimetry (DSC) curve of the as-electrodeposited Ni -4.4 mass % P alloy specimen. Two processes of exothermic reactions appeared in the DSC curve of the as-electrodeposited nc Ni -4.4 mass % P alloy specimen. The first and second exothermic reaction occurred at about 380 K and 658 K in onset temperature, respectively. It seemed that the first exothermic reaction was associated with grain boundary migration in the nc Ni solid solution. The second exothermic should be related to precipitation of
Ni₃P phase. Fig. 3 shows the XRD profile of Ni -4.4 mass % P alloy specimens annealed at 673 K for 1.8 ks. It is found that the precipitation of Ni₃P phase occurred in the specimen annealed at 673 K. The average grain size was slightly increased from that of as-electrodeposited specimen. Moreover, the {111} texture of Ni phase which formed by electrodeposition was weakened by annealing. The thermal stability of the nc Ni was improved by addition of P atoms. In particular, the nc grain structure was maintained even at relative high temperature of 673 K, owing to the precipitation of Ni₃P grains.

3.2 Microstructure evolution in electrodeposited Ni -4.4 mass % P alloy specimens by annealing

Figure 4 shows SEM images of Ni -4.4 mass % P alloy specimens annealed at different conditions. The specimens were in dual phase alloy composed of Ni and Ni₃P grains, which appear as black and white grains in the SEM images, respectively. The grain size of Ni₃P precipitation phase was similar to that of Ni matrix. The Ni and Ni₃P grains were equiaxed in all specimens and they formed the respective clusters in which some specific grains were interconnected. It is found from the SEM images that the connectivity of Ni₃P grains in their cluster decreased with increasing grain size.

Figure 5 shows relationship between grain size and annealing time in Ni -4.4 mass % P alloy specimens annealed at 873K, 973K and 1073K. In this figure, the data of grain size were obtained from both Ni and Ni₃P grains, because the Ni₃P grains were rapidly precipitated and grew to the same order in grain size of the Ni grains, as shown in Fig. 4. The as-electrodeposited nc grains rapidly grew up to submicron-order in grain diameter at the initial stage of annealing within 60 s, and the grain growth became negligible after annealing for 600 s. The higher annealing temperature induced faster grain growth at the initial stage.
The superior hardness of Ni–P alloy is resulted from the precipitation of hard Ni₃P grains. Therefore, the area fraction of Ni₃P grains in the specimen surface must dominate the wear resistance of Ni-P alloy. Fig. 6 shows the area fraction of Ni₃P grains in the specimen surface as a function of average grain size. The area fraction of hard Ni₃P grains decreased with increasing average grain size depending on annealing temperature. It was found that the area fraction of Ni₃P grains tended to be increased by annealing at higher temperature when the specimens had similar grain size.

Fig. 4  SEM images of Ni–4.4 mass % P alloy specimens annealed at different conditions. The specimens has the dual phase structure composed of Ni and Ni₃P. The connectivity of Ni₃P grains tended to decrease with increasing grain size.

Fig. 5  Relationship between grain size and annealing time in the Ni–4.4 mass % P alloy specimens annealed at different temperature. The initial nc grain structure immediately coarsened to submicron-grained structure by annealing.

Fig. 6  Relationship between area fraction of Ni₃P grains and average grain size in the specimens annealed at different temperature. The area fraction of Ni₃P grains tended to decrease with increasing average grain size.
3.3 Change in hardness of Ni -4.4 mass% P alloy specimens with different grain structure

The five specimens with largely different grain structure were selected to reveal the effect of nanocrystallization on the two-body abrasive wear property of the Ni -4.4 mass% P alloy specimens which produced by electrodeposition and subsequent annealing. Figure 7 shows the relationship between the Vickers hardness and the inverse of the square root of the grain size. The annealed Ni/Ni₃P dual phase alloy specimens with average grain sizes between 50 nm and 1230 nm obeyed the Hall-Petch relationship, while the hardness of as-electrodeposited solid-solution specimens with an average grain size of 37 nm largely deviated from the Hall-Petch relationship. The scatter in the hardness data of five measurements taken for each specimen was small. In the annealed specimens, the hardness was increased from HV 330 to HV 970 when the grain size decreased from 1230 nm to 50 nm. It was found that the hardness of Ni – P alloy specimen was strongly affected by the precipitation of Ni₃P grains as well as grain size.

![Fig. 7 The Hall-Petch plot of grain size dependence of the Vickers hardness in as-electrodeposited and annealed Ni -4.4 mass% P alloy specimens. The hardness of the annealed Ni/Ni₃P dual phase alloy specimens linearly increased with decreasing average grain size, according to Hall-Petch relationship. However, the as-electrodeposited solid-solution specimen deviated from the linear relationship between the hardness and the average grain size.](image)

3.4 Effect of microstructure on two-body abrasive wear property of Ni -4.4 mass% P alloy

Figure 8 shows the relationship between the wear rate and the inverse of the square root of the grain size in Ni -4.4 mass % P alloy specimen. The scatter in data of wear rate was negligible even when the specimens were worn by different size of abrasion particles. The wear rate decreased with decreasing average grain size in the annealed Ni/Ni₃P dual phase specimens, although the wear rate of the specimen with the average grain size of 1230 nm was deviated from the linear relationship between wear rate and grain size ($\bar{d}^{-1/2}$). Moreover, the wear rate of as-electrodeposited solid-solution specimen was higher than that of annealed Ni/Ni₃P dual phase alloy specimens, although the as-electrodeposited specimen had smaller average grain size than annealed specimens. This result suggested that the effect of precipitation of Ni₃P grains on wear resistance is more significant than that of nanocrystallization.

The worn surfaces of specimens with different grain structures were examined, in order to reveal the cause of the grain size dependence of abrasive wear property in Ni –4.4 mass% P alloy. Figs. 9 (a), (b) and (c) are SEM images of worn surfaces of specimens whose average grain sizes are 37 nm, 50 nm, and 1230 nm, respectively. These specimens were worn by SiC abrasion particles of 150 μm in diameter and up to 2.0 m in wear distance. In the case of the as-electrodeposited specimen (Fig. 9 (a)), a smooth worn surface and ductile wear debris were formed. The annealed specimen with an average grain size of 50 nm also yielded a smooth worn surface (Fig. 9 (b)). On the other hand, the annealed specimen with an average grain size of 1230 nm showed a rough worn surface with turning and fracture.

To understand the differences in abrasive wear behavior of the specimens with different grain size in more detail, the scratch tests were performed using a SiC rider. Figs. 10 (a), (b) and (c) show the SEM images of scratched grooves on specimens with average grain sizes of 37 nm, 50 nm and 1230 nm, respectively. The as-electrodeposited specimen
Fig. 8  The Hall-Petch plot of grain size dependence of the wear rate in electrodeposited and subsequently annealed Ni -4.4 mass% P alloy specimens. The wear rate of the annealed specimens with the average grain size of less than 420 nm was linearly decreased with decreasing grain size. The specimen with average grain size of 1230 nm showed considerably high wear rate. The as-electrodeposited specimen showed high wear rate independently of the results of annealed specimens.
Fig. 9  The SEM images of specimen surface after abrasive wear tests. (a) The as-electrodeposited specimen and (b) the annealed specimen with nanocrystalline structure showed smooth worn surface. On the other hand, (c) the annealed specimen with microcrystalline structure showed the rough worn surface accompanied with turning of specimen surface.

Fig. 10  The SEM images of specimen surface after scratch tests. (a) The as-electrodeposited specimen and (b) annealed nanocrystalline specimen showed the sharp groove. (c) The annealed specimen with microcrystalline structure showed brittle wear groove accompanied with turning of Ni grains by dragged hard Ni₃P grains.

Fig. 11  Schematic illustration of abrasive wear mechanisms of Ni–P alloy specimens with (a) nanocrystalline and (b) microcrystalline structure. The abrasive wear mechanism was probably changed by the difference in the relative size between the average grain size of the specimen and the abrasion particles.
3.5 Effectiveness of microstructure control for improvement of abrasive wear resistance of Ni-P alloy

The abrasive wear resistance of the Ni –4.4 mass% P alloy was improved by the precipitation of hard Ni₃P grains as well as grain refinement. In this section, the effectiveness of nanocrystallization for the improvement of abrasive wear resistance will be investigated through the comparison with the hardness dependence of abrasive wear resistance in some pure metals, according to the fundamental works on the relationship between two-body abrasive wear resistance and bulk hardness which was firstly demonstrated by Khruschov (1974). In general, the slope of the abrasive wear resistance versus the bulk hardness line for some alloys which hardened by microstructural change, such as precipitation, cold working and martensitic transformation, is smaller than that for annealed pure metals with different hardness (Khruschov, 1974, Mutton and Watson, 1978, Hokkirigawa et al., 1988, Larsen-Basse, 1990).

Figure 12 shows the relationship between the relative wear resistance and the Vickers hardness for the Ni -4.4 mass% P alloy specimens produced by the electrodeposition and subsequent annealing. In this figure, the relative wear resistance was estimated as wear resistance of specific specimen normalized by wear resistance of Pb with the highest wear rate. The results for fully annealed pure metal specimens such as Pb, Al, Cu, and Ni were added in this figure.

It is found that the relative wear resistance of pure metal specimens linearly increased with increasing their hardness. The similar trend was observed in the case of the annealed Ni/Ni₃P dual phase alloy specimens with various average grain size, although the relative wear resistance of as-electrodeposited specimen was lower than that of annealed specimen with a similar hardness. The hardness dependence of relative wear resistance for annealed Ni/Ni₃P alloy specimens was weaker than that for different pure metals. The microstructure near the wear grooves is certainly subjected to local deformation by sliding abrasion particles. In the Ni–P alloy specimens, the influence of nanocrystallization and precipitation of Ni₃P phase on the wear resistance may be weakened by the microstructural change such as dislocation pile up in grain interior during wear tests. On the other hand, the hardness dependence of the wear resistance for different kinds of pure metals can be hardly affected by the microstructural change owing to cutting by abrasion particles during abrasive wear tests, because the different kinds of pure metal has an intrinsically different hardness.

In the present work, it was revealed that the abrasive wear resistance of Ni–P alloy specimens was improved by nanocrystallization. The relative wear resistance was increased up to about 1.7 times when the average grain size decreased from 1230 nm to 50 nm. Moreover, it was suggested by obtained results that control of morphology of precipitated Ni₃P grains was quite important to improvement of the abrasive wear property as well as nanocrystallization.

![Fig. 12](image-url) Relationship between the relative wear resistance and the Vickers hardness for Ni -4.4 mass% P alloy specimens. The data of relative wear resistance for some fully annealed pure metals with different specific hardness were also shown in this figure. The relative wear resistance increased with increasing hardness in the annealed specimens. The hardness dependence of relative wear resistance for the annealed Ni/Ni₃P alloy specimens was weaker than that for the pure metals with different specific hardness.
4. Conclusions

The two-body abrasive wear property of electrodeposited nc Ni-4.4 mass% P alloy was investigated using the specimens with different grain structure, to obtain a clue to development of nc materials with high wear resistance. The effectiveness of control of nc grain structure for improving wear resistance of the Ni-4.4 mass% P alloy was discussed in comparison with wear resistance for pure metals with different specific hardness. The main results obtained are as follows.

(1) The wear rate of the annealed Ni/Ni₃P dual phase alloy specimens with the average grain size of less than 420 nm was linearly decreased with decreasing grain size, although the annealed specimen with average grain size of 1230 nm showed considerably high wear rate.

(2) The annealed Ni/Ni₃P dual phase alloy specimens with nc grain structure showed the ductile worn surface with smooth wear grooves. On the other hand, the specimen with microcrystalline grain structure showed the rough worn surface with turning and brittle fracture of Ni phase.

(3) The relative wear resistance increased with increasing hardness in the annealed specimens with nc and submicron grained structure. The hardness dependence of relative wear resistance for the annealed Ni/Ni₃P alloy specimens was weaker than that for the pure metals with different specific hardness.

Acknowledgements

The present work was financially supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number JP17760573.

References


