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Development of superabrasive stone for mechanochemical superfinishing

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ARTICLE INFO

Article history: Received 19 November 2007 Received in revised form 3 March 2008 Accepted 17 March 2008 Available online 22 May 2008

Keywords:
Mechanochemical superabrasive stone
Cerium oxide
Thermodynamic analysis
Oxide layer
Synergistic effect
Smooth superfinished surface

ABSTRACT

One of the effective methods for obtaining an ultra-precision surface is utilization of the mechanochemical reaction that occurs at the interface between a tool and a workpiece. A thermodynamic analysis suggested that cerium oxide CeO_2 in contact with steel oxidizes the steel surface. Then, steel specimens embedded in CeO_2 powder were heated to 773 K in a vacuum, and their surfaces were closely analyzed by X-ray diffractometry. As a result, peaks of Fe_3O_4 together with α -Fe were recognized by their diffraction patterns. On the basis of this finding, vitrified superabrasive stones containing CeO_2 , i.e., cBN/CeO_2 stones, were made and their performances were evaluated through the superfinishing of bearing steels. Experiments showed that cBN/CeO_2 stone is superior in surface finish to conventional cBN stone because of the synergistic effect of the mechanical action of the cBN abrasive and chemical action of the CeO_2 abrasive.

1. Introduction

The roughness of rolling bearings operating under a mixed or boundary lubrication region is detrimental to the fatigue life of the bearings. Thus, their surfaces are finished to increase the elastohydrodynamic lubrication (EHL) oil film parameter which is defined as the ratio of the EHL oil film thickness to the composite RMS surface roughness. But, the current view supported is that smooth surfaces with negative skewness, i.e., ones with valleys, lengthen the bearing life [1].

However, such a surface topography cannot be produced by conventional mechanical superfinishing because a smoothing action on the top surface would be required. By combining the rubbing action by soft and reactive abrasives with the scratching action by hard abrasives, it is possible to produce a smooth surface with valleys. In order to realize this process with a vitrified-bonded superabrasive stone, fundamental and practical experiments below were carried out.

First, the soft abrasive reaction with the steel was examined by considering the degree of chemical equilibrium. Second, basic

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experiments were performed to check whether the abrasive chosen reacts with the steel in actual procedure. And last, in order to examine whether the expected surface topography could be produced, superfinishing experiments were conducted using superabrasive stones made by mixing the reactive abrasive with the superabrasive, which were named "mechanochemical superabrasive stones".

2. CeO₂ abrasive chosen and its chemical reaction

2.1. Fundamental principle

Ceria (CeO₂) is used as a catalyst for the exhaust gas purification of automobiles because it has the great advantage of storing oxygen, and releasing and uptaking oxygen due to the following reversible reaction [2]:

$$2CeO_2 = Ce_2O_3 + \frac{1}{2}O_2 \tag{1}$$

Taking this reaction into consideration, it is expected that the reduction of CeO_2 to Ce_2O_3 and oxidation of Fe to FeO, Fe_3O_4 or Fe_2O_3 occur simultaneously when CeO_2 is in contact with Fe. For example, the reaction could be represented by the following chemical equation.

$$x_1 \text{CeO}_2 + x_2 \text{Fe} = x_3 \text{Ce}_2 \text{O}_3 + x_4 \text{FeO}$$
 (2)

where x_i is the number of moles.

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It is necessary to probe the reactive possibility of ${\rm CeO_2}$ with Fe based on thermodynamic principles. In the chemical reaction, the system moves spontaneously from a state of higher Gibbs free energy to a state of lower energy. The direction and stability of a chemical reaction at a specified condition can be predicted by the difference between the energies of the left and right sides of the reaction equation. In brief, when the Gibbs free energy change ΔG_T° is a negative quantity, the reaction proceeds from the left to right sides of the reaction equation.

The value of ΔG_T° for the reaction is given as a function of temperature T[3]:

$$\Delta G_T^{\circ} = \Delta H_T^{\circ} - T \Delta S_T^{\circ}$$

$$= \Delta H_{298}^{\circ} + \int_{298}^{T} \Delta C_p dT - T \Delta S_{298}^{\circ} - T \int_{298}^{T} \frac{\Delta C_p}{T} dT$$
(3)

where ΔH° is the standard enthalpy change, ΔS° is the standard entropy change, and ΔC_p is the difference between the heat capacities of the reactants and products at constant pressure. The variation of the heat capacity with temperature for a substance is given by the below expression:

$$C_p = a + bT + cT^{-2} \tag{4}$$

where a, b and c are constants that are determined empirically.

2.2. Calculation results

Various chemical equations that represent the reaction of Fe with CeO $_2$ in an aqueous solution have been formulated and the ΔG_T° values have been calculated. Fig. 1 shows ΔG_T° in the oxidation of iron by CeO $_2$ as a function of the atmospheric temperature. Since $\Delta G_T^\circ < 0$ in this figure, it can be predicted that CeO $_2$ forms various iron oxides in association with O $_2$ dissolving in water. Moreover, since $\Delta G_T^\circ < 0$ at temperatures higher than 450 K or 800 K, it can be predicted that CeO $_2$ together with H $_2$ O produces the iron oxide. Thus, it was confirmed in principle that CeO $_2$ oxidizes Fe in conditions in which oxygen is in short supply. Nevertheless, it is necessary to confirm whether such chemical reactions actually occur; therefore, simple experiments were performed.

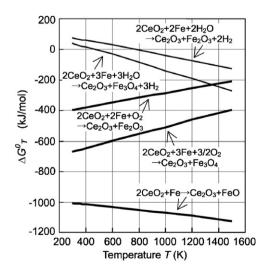


Fig. 1. Change in Gibbs free energy in reduction of CeO₂ and oxidation of Fe.

3. Experiments on reaction of bearing steel with CeO₂

3.1. Experimental procedures

The experiments on Fe oxidation by CeO₂ were performed in two different ways. The ferric specimen was high-carbon chromium ball-bearing steel SUJ2. First, two specimens were allowed to stand for 6 h in water heated to 333 K; one specimen was in contact with CeO₂ powder, and the other was not. After the treatment, there was evidence of corrosion only on the specimen surface that had been in contact with the CeO₂ powder. The corroded specimen surface was analyzed by energy dispersive X-ray spectrometry.

Next, two more specimens were heated at 773 K for 6 h in a high vacuum of 4.2×10^{-3} Pa; one specimen was embedded in CeO₂ powder, but the other was not. Although the specimen surface only heated was hardly damaged, the one heated inside CeO₂ powder cracked and scales came off, as shown in Fig. 2. From this finding, it is obvious that the scale formation in the vacuum was caused by the release of oxygen from CeO₂. The scales were analyzed by X-ray diffractometry to determine the type of ferric oxide.

3.2. Results and discussion

Fig. 3 shows the energy dispersive X-ray spectroscopy (EDS) spectra of two ferric specimens which were allowed to stand in water. The spectra indicate that the oxygen is occluded only on the surface corroded by CeO₂ powder. Hence, it can be easily supposed that an oxide layer is formed on the specimen surface.

Fig. 4 shows the X-ray diffraction pattern of the scale that was formed by heating in a vacuum. The number of peaks used in the estimation of the scales was 3, which was considered enough to make a good quantitative estimation. In the diffraction pattern, peaks of Fe₃O₄ together with α -Fe are seen, so it is concluded that CeO₂ powder in contact with the steel forms a magnetite oxide layer under the oxygen-lean condition. The diffraction pattern also gives vital information about the chemical change of CeO₂. Three diffraction peaks are seen at the diffraction angles 2θ = 28.20°, 32.68° and 46.80°, which relate to the interplanar spacings d = 3.162 Å, 2.738 Å and 1.940 Å, respectively. These interplanar spacings differ from those of Ce2O3 [4] and are slightly larger than those of the original CeO₂ powder. Therefore, the peaks are thought to be an oxide of cerium in the range of CeO_2 - $CeO_{1.714}$, i.e., oxygen-deficient non-stoichiometric oxide [2]. Many predictions have been made as to the formation of magnetite by CeO₂, as depicted in Fig. 1. The process can be represented in the following equation:

$$4CeO_2 + 3xFe \rightarrow 4CeO_{2-x} + xFe_3O_4$$
 (5)

4. Superfinishing characteristics of mechanochemical superabrasive stone

4.1. Test stones

Mechanochemical superabrasive stones were made experimentally by mixing CeO₂ powder, called CeO₂ abrasive in this paper, with cubic boron nitride (cBN) abrasive, tamping in a mold, drying and firing. As the CeO₂ abrasive is thermally unstable, a vitreous bond with a low melting point less than 1000 K especially developed was used. In addition to the above cBN/CeO₂ stone, a conventional vitrified cBN stone and a vitrified CeO₂ stone that consists of only bonded CeO₂ abrasive were prepared in order to investigate the effect of the CeO₂ abrasive on the superfinishing characteristics. The composition of these three stones is illustrated in Fig. 5. They are the straight cup-shaped abrasive

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