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STUDY OF RUST PREVENTIVE CHARACTERISTICS OF RUST PREVENTIVE OIL FROM POLARIZATION CURVE MEASUREMENT

BADANIE WŁAŚCIWOŚCI PRZECIWRDZEWNYCH OLEJU Z POMIARU KRZYWEJ POLARYZACYJNEJ

Fe-Cu-C sintered steels are widely used as powder materials, because of its small volumetric shrinkage. However, Cu, which acts as cathode enhance formation of rust $Fe_2O_3 \cdot xH_2O$ during fabrication. To prevent formation of $Fe_2O_3 \cdot xH_2O$ rust preventive oils are widely used. High viscosity of those rust preventive oils decrease workability. While, low viscosity degrade rust preventive performance. Therefore, it is necessary to develop new rust preventive oils with contradictory properties of low viscosity and superior rust prevention. In this study, we developed technique to quantitatively evaluate rust prevention ability by measuring polarization curve through thin corrosive solution on Fe-Cu-C sintered steels coated with rust preventive oils. The electrochemical measurements were carried out in corrosive solution of 0.35 mass % NaCl. Using a double capillary was added dropwise to the specimen. From the experimental, it is possible to evaluate the corrosion rate quantitatively in the surface of specimen, which was coated with rust preventive oil through thin corrosive solution. From the measurement results, Corrosion rate is reduced by coating the rust preventive oil. Especially, corrosion rate of the specimen coated with oil that showed best performance indicated 10000 times better than that of without oil ones. Zn addition negative correlation between corrosion rate and period of potential oscillation.

Keywords: sintered steel, polarization curve, rust preventive oil

Spiekane stale Fe-Cu-C są szeroko stosowane jako materiały proszkowe, ze względu na mały skurcz objętościowy. Jednak miedź, która zachowuje się jak katoda, wpływa na zwiększone powstawanie rdzy $Fe_2O_3 \cdot xH_2O$ w procesie wytwarzania stali. Aby zapobiec tworzeniu się $Fe_2O_3 \cdot xH_2O$ stosuje się oleje ochronne. Jednak wysoka lepkość olejów zmniejsza ich urabialność, natomiast niska lepkość zmniejsza ich właściwości ochronne. Z tych względów konieczne jest opracowanie nowego typu olejów przeciwrdzewnych charakteryzujących się zarówno niską lepkością jak i dobrymi właściwościami ochronnymi. W niniejszej pracy opracowano metodę ilościowej oceny właściwości ochronnych olejów za pomocą pomiaru krzywej polaryzacji poprzez cienką warstwę roztworu korozyjnego na spiekanych stalach Fe-Cu-C pokrytych olejami ochronnymi. Pomiary elektrochemiczne zostały przeprowadzone w roztworze korozyjnym NaCl (0,35 %wag.). Roztwór został naniesiony na próbkę za pomocą kapilary. Na podstawie wyników eksperymentalnych można ilościowo oszacować szybkość korozji zachodzącej na powierzchni próbki. Badania wykazały, że olej ochronny zmniejsza szybkość korozji. Olej dla którego otrzymano najlepsze wyniki wykazał poprawę właściwości ochronnych 10000 krotnie w porównaniu z próbkami bez oleju. Dodatkowo stwierdzono korelację pomiędzy szybkością korozji a okresem oscylacji potencjału.

1. Introduction

Fe-Cu-C sintered steel can be easily controled the volumetric change by sintering, and it has about 80% of quantity of production in the field of powder metallurgy [1–8]. However it is easily rusted, because of existing of many Cu and C which act as the cathode site on their surfaces. Especially, during their m anufacturing process, the rust of Fe_2O_3 would be generated on their surface, under high temperature and/or humid climate. Thus they are coated with rust preventive oils (RPOs) to prevent the rust formation. While, there exists anothe problem. High viscosity of these RPOs decrease workability, and low viscosity of it's deteriorate rust preventive performance. Therefore, it is necessary to develop new RPOs with contradictory properties of low viscosity and superior rust prevention. However, precise methodology to evaluate rust prevention ability has not been established. In this study, we developed new technique to quantitatively evaluate rust prevention ability by polarization curves measurement through thin corrosive solution on Fe-Cu-C sintered steels coated with rust preventive oils. As a result, the ability for rust prevention can be measured quantitatively. The aim of this study, therefore, is to evaluate the rust prevention ability of three kinds of representative rust prevention oils by using this newly-developed measuring method [9].

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2. Experimental

Fe-Cu-C sintered steel (Fe, 2.0 mass % Cu and 0.8 mass % C) was used as a specimen in this experiment. Dimensions of the specimens were 3.4 ×4.9 mm^2. The wire lead was attached to this specimen and it was resin-mounted to make an electrode for specimen. Dry type polishing was carried out on the electrode surface to No. 2000 of emery paper, and it was dried after degreasing with acetone. Then, fabricated electrode for specimen was dipped in the beaker containing RPO, and it was held for 15 min in the vacuum desiccator to remove bubbles from the surface of this specimen electrode. We employed three kinds of test oil named oil A, B and C. (oil A: conventional rust preventeve oil, oil B: without the rust inhibitor and without two types of oil film modifier from the oil A, oil C: containing differ oil film modifiers from the oil A). The 0.35 mass % NaCl aqueous solution of its pH is 5.76 was used for the test evaluating rust prevention ability by polarization curve measurement through thin corrosive solution (newly developed testing method) [10]. The schematic diagram of the newly developed testing method is shown in Fig. 1. Using a double capillary was added dropwise to the specimen. The polarization curve measurement through thin corrosive solution on the specimen was used, Ag/AgCl (3.33 kmol /m^3KCl) as a reference electrode, platinum wire as the counter electrode, respectively Polarization curves were registered after 30 min of exposure to aqueous solution in order to allow corrosion potential (E_{corr}) stabilization. All the polarization experiments were carried out, from – 200 mV vs. E_{corr}, to +200 mV vs. E_{corr} at a sweeping rate of 0.5 mV/s.

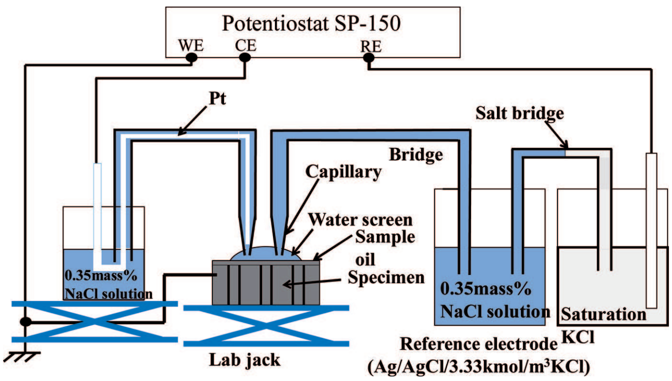

Fig. 1. Schematic diagram of apparatus for the polarization curve measured

3. Results and discussion

Figure 2 shows the result of corrosion potential measured in the condition of coated with the oil A. In the period from 0 ks to 140 ks, the vibration behavior of the potential was recognized in initial stage [10]. The vibration behavior of the potential was reported by K. Arai in water/1-octanol/water (including surfactant) system. According to their experiment the potential oscillation mechanism was found to be due to the repetitive formation and destruction of a surfactant layer adsorbed at the octanol/water interface. the results of our experiment shows good agreement with their model. In this initial stage, surfactant, included in the RPO was coated to the specimen surface was gradually aligned to the oil / water interface, and then thin corrosive solution vibration phenomena of the potential observed. Concentration of surfactant at the interface crowded with time course. It is thought that the interface might be gradually wavy at that time and the potential was gradually increased. The phenomena correspond to schematic diagram of Fig. 2(b) and (c). Formation of micelles on surfactant, which surround water in the thin corrosive solution when this concentration is higher than the critical micelle concentration (Fig. 2(d)). Potential increases to the critical micelle concentration, the potential decreases significantly at the moment micelles might to be formed as shown in Fig. 2 (d). Corrosive solution is soluble in oil by formation of micelles.

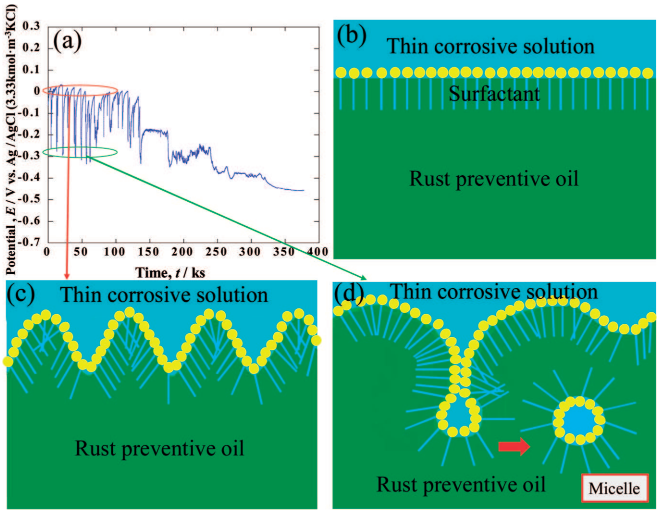

Fig. 2. (a) Corrosion potential of sintered Fe-Cu-C alloy measured with oil A in thin corrosive solution[10] and schematic diagram of formation micelle: (b) the initial stage, (c) the second stage, (d) the third stage

Figure 3 shows the results of corrosion potential which were coated with RPOs and without oil. In the case of without oil {Fig. 3 (a)}, potential was decreasing in a monotone manner. In the case of coated with Oil A, the vibration behavior of the potential was recognized in initial stage and second stage {Fig.3(b)}. In the Oil B, the potential shows similer manner to that of without oil. From these results, it is strongly suggested that the potential oscillation is derived from a rust inhibitor or oil film modifier. Thus, the species of base oil do not derive the vibration manner. In the condition of coated with Oil C, the potential oscillation was maintained longer than that of coated with Oil A. Therefore, oil film modifier of the Oil C is better than that of the Oil A. Table 1 shows Icorr and Ecorr obtained by polarization curve measurement(9 and the period when potential oscillation continued. The Oil B shows worst improvement in corrosison resistance among those coated with RPOs. It shows good agreement with the results of corrosion potential obtained by polarization curve measurement. The results of other RPOs are also consistent with the corrosion rate which was obtained by polarization curve measurements. Figure 4 shows the relationship of the period of potential oscillation and corrosion rate coated with RPOs and without oil. As shown in Fig. 4 negative correlation between corrosion rate and period of potential oscillation.

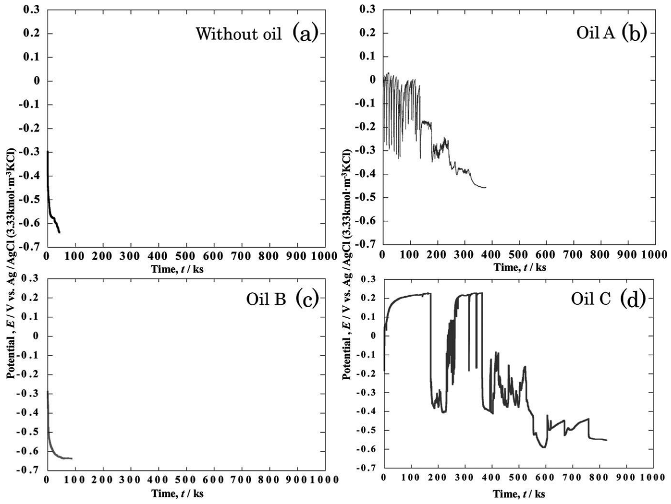

Fig. 3. Corrosion potential of sintered Fe-Cu-C alloy measured in thin corrosive solution (a) without oil, (b) coated with Oil A, (c) coated with Oil B and (d) coated with Oil C

TABLE 1

Corrosion rates obtained from the polarization curves(9

	Without Oil	Oil A	Oil B	Oil C
I_{corr}(A/cm^2)	2.78×10^{-4}	4.64×10^{-7}	4.64×10^{-6}	2.53×10^{-8}
E_{corr}(V)	-0.41	-0.20	-0.40	-0.16
Duration of potential oscillation(ks)	42.8	377.4	86.4	824.9

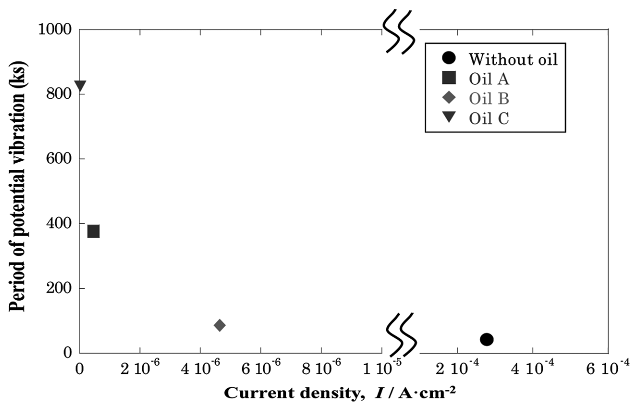

Fig. 4. Negative correlation between corrosion rate and period of potential oscillation

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4. Conclusion

The results of this study are summarized as follws.

1. The potential oscillation caused by adding rust inhibitor and oil film modifier to oil.
2. There is a negative correlation between corrosion rate and period of potential vibration.
3. Our method of polarization curve measurement evaluate the corrosion rate quantitively and the value is consistent with the period of potential oscilation.

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