

EFFECT OF TENSILE STRENGTH ON PITTING CORROSION RESISTANCE AND HYDROGEN DESORPTION PROFILE IN AUTOMOBILE SPRING STEELS

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ABSTRACT

Three kinds of automobile spring steels, which have three different levels of tensile strength, respectively, were prepared to understand an effect of strength level on the pitting corrosion resistance and the hydrogen absorption with pitting corrosion. The changes in corrosion resistance and hydrogen desorption profile were evaluated by electrochemical anodic polarization curve measurements and wet-dry cyclic corrosion tests and thermal desorption spectroscopic analyses, respectively. Experimental results revealed that the pitting potentials showed no significant changes with tensile strength, resulting in the independence of strength. However, their values were slightly different depending on the kind of steel, namely, the chemical composition. The sizes of corrosion pits measured after the wet-dry cyclic corrosion tests also showed almost no variation with tensile strength, as well as the pitting potential. The hydrogen desorption profiles with peak temperature of 250 °C were measured on all spring steels after the corrosion tests. The amount of desorbed hydrogen increased linearly with increasing number of cycles of corrosion test. However, it was difficult to declare a clear correlation between the strength level of steel and the hydrogen absorption.

1 INTRODUCTION

Suspension spring steels for automobile suffer possible degradation of mechanical properties attributable to wet-dry cyclic corrosion in a solution containing chloride ions. The ions result from road salts (sodium chloride, calcium chloride, etc.) scattered on road for melting ice and/or snow in winter. The susceptibility to this environmental embrittlement increases with increasing strength level of steel. This increase in susceptibility hinders the practical application of high strength spring steels to automobile suspension, which is essential for reducing a weight of automobile. The reasons for the degradation are classified into two factors. One is a corrosion pit as a geometric damage. The other is hydrogen generated with the formation of corrosion pits.

In our previous study (Kobayashi [1]), the resistance to pitting corrosion was investigated by electrochemical method using six different automobile spring steels with various tensile strength. The pitting potential, V_{pc} , decreased monotonously with increasing strength level (Fig. 1). This result indicated that the tensile strength was one of the most important controlling factors of pitting corrosion. The possibility that the difference in microstructure (dislocation density) affected the corrosion resistance was undeniable in that study. However, it was also very difficult to conclude that the resistance to pitting corrosion was strongly dependent on the tensile strength, because not only strength but also chemical compositions of the steels were different from each other. In this study, the three kind of spring steels, which have three different levels of tensile strength, respectively, were prepared to clarify an effect of strength level on the pitting corrosion resistance. The steels were subjected to the anodic polarization curve measurement and wet-dry cyclic corrosion test in a sodium chloride solution for evaluating their corrosion resistance. Moreover, hydrogen desorption profiles were measured on the steels subjected to the wet-dry cyclic corrosion tests by the thermal desorption spectroscopic analysis for investigating the dependence of strength level on the hydrogen absorption due to pitting corrosion.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

The materials used in this study were three different automobile spring steels, namely, SUP12, HDS13 and HDS13M. Their chemical compositions are summarized in Table 1. As show in Table 2, the tensile strength of each steel was adjusted to three different levels of around 1600, 1800 and 2000 MPa by controlling the tempering temperature.

2.2 Electrochemical measurements

The block-type specimen, 15×5×5^t mm, were connected to a lead wire and then covered with epoxy resin, except for the measurement area (12×4 mm). The measurement surfaces were mechanically polished to a 0.05 μm finished. The anodic polarization curve measurement was performed in a 5 mass% sodium chloride solution at 35 ± 0.5 °C in accordance with the Japanese industrial standard (JIS) G 0577 which is standardized for stainless steels. The potential of the specimen was scanned from the corrosion potential to the anodic direction at a sweep rate of 20 mV/min. The pitting potential is defined as the potential where the current density reached 100 μA/cm².

2.3 Wet-dry cyclic corrosion tests

The specimen measuring 3×3×10 mm was subjected to the wet-dry cyclic corrosion test. One

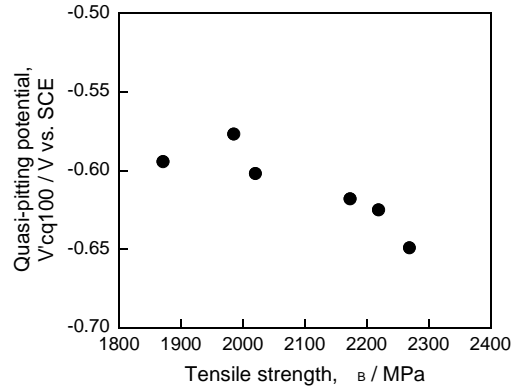


Figure 1: Relationship between tensile strength and quasi-pitting potential.

Table 1 Chemical compositions (mass%) of steels used in this study.

	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Al	Nb	V	Ti	B	N
SUP12	0.59	1.44	0.75	0.017	0.004	0.04	0.75	0.01	0.09	0.028	-	-	-	-	-
HDS13	0.49	1.47	0.61	0.013	0.003	1.46	0.98	0.77	0.10	0.028	0.025	0.11	-	-	-
HDS13M	0.50	1.57	0.40	0.007	0.004	0.49	1.49	0.35	0.26	0.020	0.020	0.08	0.027	0.003	-

Table 2 Heat treatments and mechanical properties of steels.

	Quenching	Tempering	Vickers hardness, HV	Tensile strength, MPa
SUP12-A	900 -30min/OQ	415 -30min/AC	586	2019
SUP12-B		450 -30min/AC	534	1830
SUP12-C		500 -30min/AC	482	1617
HDS13-A		415 -30min/AC	597	2000
HDS13-B		470 -30min/AC	532	1830
HDS13-C		625 -30min/AC	454	1560
HDS13M-A		400 -30min/AC	584	1970
HDS13M-B		500 -30min/AC	534	1840
HDS13M-C		575 -30min/AC	477	1570

cycle of the corrosion test consisted of immersion of the specimen in a 5 mass% sodium chloride solution (35 ± 0.5) for 3 h and subsequent drying in an atmosphere of 35 ± 0.5 and 95% relative humidity for 21 h. After 20 cycles, size and number of corrosion pits were measured on the specimen surface by an optical microscope.

2.4 Thermal desorption spectroscopic (TDS) analyses

The TDS analysis was applied to the above corroded specimen for investigating the amount and distribution of hydrogen, which had generated with corrosion and absorbed into the specimen. It was carried out from room temperature to 800 using the heating rate of 100 /h. The desorbed hydrogen carried with high purity argon gas was detected by a gas chromatograph every 5 min. The flow rate of the argon carrier gas was fixed at 1.2×10^{-5} m³/min throughout the analysis. The hydrogen evolution rate was defined as the amount of hydrogen desorbed in one minute per one gram of the specimen.

3 RESULTS AND DISCUSSION

3.1 Effect of tensile strength on pitting corrosion resistance

Figure 2 shows the pitting potentials plotted as a function of tensile strength, σ_B . In this figure, the pitting potential is termed “quasi-pitting potential”, because the present electrochemical method is not standardized for spring steels but for stainless steels. As can be seen in this figure, the pitting potentials show no significant changes with tensile strength, resulting in the independence of tensile strength for all steels. However, their values are slightly different depending on the kind of steel. The pitting potential of the SUP12 is the lowest in the three steels, and the HDS13 has the highest potential to the contrary. This result suggests that not tensile strength but chemical composition governs the resistance to pitting corrosion of the spring steels. The excellent pitting corrosion resistances of the HDS13 and HDS13M are likely to result from the additions of Ni, Cr, Cu and B, which have been reported to be the effective elements to improve the corrosion resistance of low alloy steels (Fukuzumi [2]).

Figure 3 shows the relationship between the tensile strength and the size of corrosion pits observed on the wet-dry cyclic corrosion test specimens. The corrosion test specimens were covered with a thick layer of rust after the corrosion test was repeated twenty times. The specimens were longitudinally cut into two halves without removing the rust. The average depth and radius of corrosion pits were measured on the cross sectional surfaces. Both of the depth and radius show almost no variation with tensile strength. The pit size in the SUP12 is the largest according to its low pitting corrosion resistance (pitting potential). To the contrary, the HDS13 seems to have the smallest size because of relatively high corrosion resistance, although there is no significant difference between the average radius of the HDS13 and that of HDS13M. In this way, the result of the wet-dry cyclic

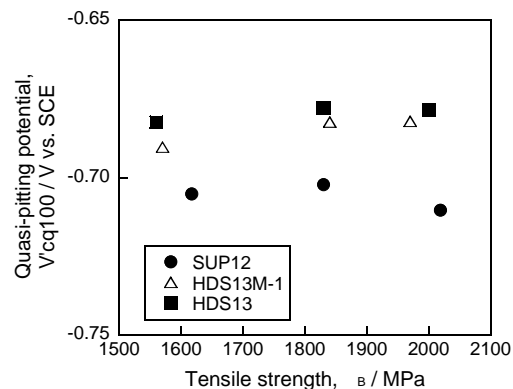


Figure 2: Quasi-pitting potential plotted as a function of tensile strength.

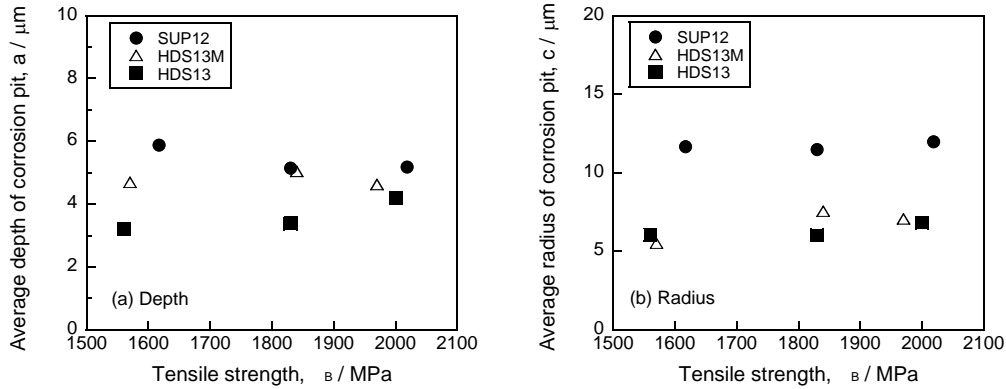


Figure 3: Average pit sizes plotted as a function of tensile strength.

corrosion tests is in relatively good agreement with that obtained from the electrochemical tests. Consequently, it can be concluded that the strength level of automobile spring steels has no influence on the pitting corrosion resistance, and they are determined by the chemical composition.

3.2 Effect of tensile strength on hydrogen desorption profile

Figure 4 shows examples of hydrogen evolution curves measured on the HDS13 steel, where the hydrogen evolution rate is plotted as a function of temperature. The corroded specimens were submitted to the TDS analysis without removing the thick layer of rust. Large hydrogen evolution peaks can be clearly seen at around 250 °C. This kind of hydrogen peak was not observed at all in the specimen, which had not been subjected to the corrosion test. Likewise, the SUP12 and HDS13M exhibited similar desorption profiles. It has been experimentally showed by the authors that hydrogen released from the inner rust formed the hydrogen desorption profiles with the peak temperature of 200-250 °C. On the other hand, hydrogen desorbed at the temperature range from 300 to 600 °C mainly corresponded to hydrogen released from the steel itself and the steel/rust interface. From Fig. 4, it can be seen that most of the hydrogen desorption originates from the rust layer. The amount of desorbed hydrogen was estimated by calculating the area under the hydrogen evolution curve.

Figure 5 shows the change in the amount of hydrogen desorbed at the temperature range from room temperature to 600 °C with number of cycles of the wet-dry corrosion test. The amount of hydrogen increases almost linearly with an increase in number of cycles. The dependence of tensile strength can not be observed in the relationship between them. However, when the number of cycles is 20, the quantities of hydrogen in the steels with tensile strength of 1830 and 2000 MPa are larger than the other steel. Figure 6 shows the amount of hydrogen after 20 cycles plotted against the tensile

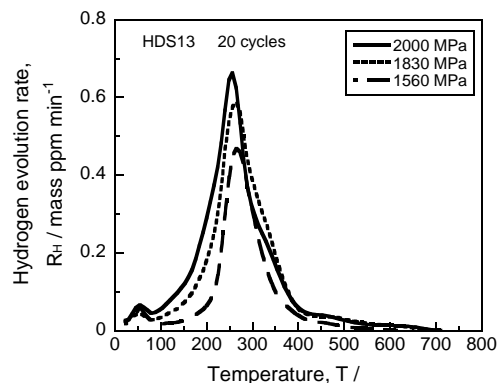


Figure 4: Examples of hydrogen desorption profiles measured on HDS13 steel.

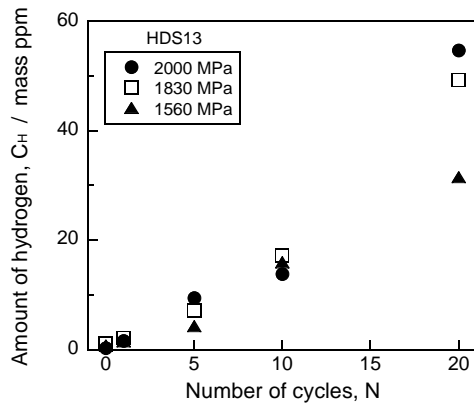


Figure 5: Hydrogen content plotted as a function of number of cycles.

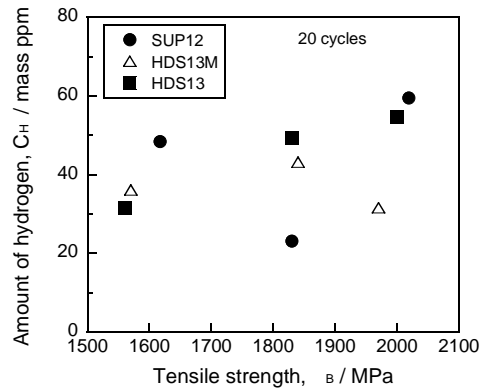


Figure 6: Hydrogen content plotted as a function of tensile strength.

strength. The amount in the HDS13 increases as the tensile strength increases. However, two other steels show no distinct dependences of tensile strength. It may be difficult to discuss the correlation between the strength level and the hydrogen absorption due to pitting corrosion by using the present results alone. Further researches would be necessary to obtain a conclusive remark on the above correlation and the relationship between the pitting corrosion resistance and the hydrogen absorption characteristics.

4 CONCLUSIONS

The three kinds of automobile spring steels (SUP12, HDS13, HDS13M), which have three different levels of tensile strength, respectively, were prepared to understand an effect of tensile strength on the pitting corrosion resistance and the hydrogen absorption with pitting corrosion. The changes in corrosion resistance and hydrogen desorption profile with strength were evaluated by electrochemical anodic polarization curve measurements and wet-dry cyclic corrosion tests and thermal desorption spectroscopic analyses after the corrosion tests, respectively. From the present investigation, the following conclusions can be drawn.

- (1) The pitting potentials of three steels show no significant changes with tensile strength, resulting in the independence of strength. However, their values are slightly different depending on the kind of steel, namely, the chemical composition. The pitting potential of the SUP12 is the lowest in the three steels, and the HDS13 has the highest potential to the contrary. The size of corrosion pits measured after the wet-dry cyclic corrosion tests also shows almost no variation with tensile strength, as well as the pitting potential.
- (2) The hydrogen desorption profiles with peak temperature of 250 °C are measured on all spring steels after the wet-dry cyclic corrosion tests. The hydrogen desorptions predominantly correspond to hydrogen released from the rust layer. The amount of desorbed hydrogen increases linearly with increasing number of cycles of corrosion test. However, it is difficult from the present results alone to declare a clear correlation between the strength level of steel and the hydrogen absorption due to pitting corrosion.

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