Stochastic Approach to the Effect of Alloying Elements on the Pitting Resistance of Ferritic Stainless Steels*

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Synopsis

Birth and death stochastic processes are confirmed to operate in pitting corrosion of ferritic stainless steels containing Cr, Mo, Ti and Nb. Birth process corresponds to pit generation and death process to pit repassivation, each rate being determined as a function of potential by the analysis of survival probability vs. time curves based on the stochastic theory. Pitting potential is found to shift to the noble value with the addition of all the alloying elements examined. The cause of the shift, however, differs for each element. The shift by alloying Cr, Ti and Nb is caused by a decrease in the pit generation rate, while the pit repassivation rate remains constant. In contrast, the addition of Mo enhances the rate of repassivation and decreases the pit generation rate. These changes of both rates are contributing to the observed shift in pitting potential to the noble value.

I. Introduction

Ferritic stainless steels is attracting considerable attention recently for the significant technological advance in achieving quite low levels of impurities which improve the ductility of the steel. Beneficial effect of alloying elements such as Cr and Mo on pitting resistance has been recognized for a long time, but its exact mechanism is still uncertain.

The very distinct nature of pitting corrosion is of random occurrence which causes some trouble for a detailed discussion on the mechanism due to the scattering of experimental data. Evans *et al.*¹⁾ had pointed out that this randomness is due to an intrinsic probabilistic nature included in the pitting corrosion process.

The stochastic theory of pitting corrosion²⁻⁵⁾ had been successfully introduced for analyzing statistical variation of pitting potential⁶⁾ and induction time for pit generation. The theory simply assumes that pit generation events occur by a pure birth stochastic process. Recently we have found⁷⁾ that the exact pitting process is a combination of birth and death stochastic process. The former birth process cor-

responds to pit generation and the latter death process to pit repassivation.

In this paper, the effect of Cr, Mo, Ti and Nb additions in the ferritic stainless steel on the improvement of pitting resistance is discussed through the determination of the rate of pit generation and pit repassivation, based on the birth and death stochastic theory of pitting corrosion.

II. Experimental

Chemical compositions of ferritic stainless steels used are shown in Table 1. Two series of ferritic steels, *i.e.*, 17Cr and 18Cr steels with addition of Ti, Mo and Nb were studied. The first series were commercial steels and the second were laboratory melts.

A large number of pitting potential and induction time is required in order to analyze pitting process based on the stochastic theory, so that a multichannel pitting corrosion testing apparatus^{3,8)} was used. Details of the apparatus and experimental procedure had been described elsewhere.³⁾ Testing solution was 3.5 % NaCl solution saturated with nitrogen gas, and temperature was 30 °C except for few experiments.

III. Results and Discussion

1. Distribution of Pitting Potential

Distributions of pitting potential which was determined by using the potential sweep method are plotted in normal probability paper as shown in Fig. 1. Each distribution nearly obeys normal probability. The mean value, or median, E_M , of the distribution is determined at 50 % probability. This value characterizes the distribution and is simply called the pitting potential.

Table 1. Chemical compositions. (%)

SUS designation	C	Si	Mn	P	S	Cr	Mo	Ti	Nb
SUS430, 17Cr	0.049	0.512	0.55	0.032	0.005	16.39	0.004	0.001	
430R, 17Cr-0.2Ti	0.006	0.150	1.32	0.037	0.005	16.69	0.003	0.184	
SUS434, 17Cr-1Mo	0.053	0.402	0.54	0.034	0.007	16.46	1.038		
18Cr	0.008	0.01	0.021	0.003	0.004	18.5			
SUS444, 18Cr-2Mo	0.011	0.01	0.010	0.002	0.004	18.8	1.95		
18Cr-2Nb	0.011	0.01	0.014	0.004	0.004	18.5			1.93

* Presented to Symposia of the 104th ISIJ Meeting, September 1982, A199, at Hokkaido University in Sapporo, and to the 3rd USSR-Japan Seminar on Corrosion, October 1982, at Karpov Institute of Physical Chemistry in Moscow. Manuscript received February 14, 1983. © 1983 ISIJ

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2. Dependence of Pitting Potential on the Potential Sweep Velocity

The pitting potential thus determined is found to increase with the square root of potential sweep velocity $V^{(9)}$ as far as V is not slower than 16.7 mV/min as shown in Fig. 2. That is, the relation between E_M and V is expressed as

$$E_M = (V/\alpha)^{1/2} + E_{crit} \dots\dots\dots(1)$$

where, E_{crit} , α : constants.
The constant α is determined from the dependence of pit generation rate on the potential as will be mentioned later in Section III. 4, and theoretical meaning of Eq. (1) had been discussed in the previous papers.^{3,4)} E_{crit} is a measure of pitting resistance of the steel.

3. Effect of Alloying Elements on the Pitting Resistance

From Fig. 2, E_{crit} or the pitting resistance of the steel is found to be in the order of

$$17Cr < 17Cr-0.2Ti < 17Cr-1Mo < 18Cr \\ < 18Cr-2Nb < 18Cr-2Mo.$$

More quantitative expression is obtained by a multiple regression analysis for a correlation between E_{crit} and the amount of alloying elements. Result is expressed as a linear regression equation in terms of the equivalent amount of Cr, i.e., Cr_{eq} , with the multiple correlation coefficient of 0.98:

$$E_{crit} = -1.284 + 0.0769 Cr_{eq} \\ = -1.284 + 0.0769(Cr + 4.98 Ti \\ + 1.39 Mo + 0.55 Nb) \dots\dots\dots(2)$$

which is plotted in Fig. 3.

It should be noticed that all of the elements examined contribute to raise pitting potential, and especially Ti and Mo play a decisive role to improve the pitting resistance of this steel.

4. Determination of the Rates of Pit Generation and Pit Repassivation

In order to clarify the role of these alloying elements to raise pitting potential, change in survival probability of specimen with time, or histogram of induction time, is analyzed and the rates of pit generation and pit repassivation are determined based on the death and birth stochastic theory.

A histogram of induction time for pit generation of 17 Cr at the constant potential of 0.02 volt vs. SCE is shown in Fig. 4. In contrast to the distribution of pitting potential, this distribution for induction time is not symmetrical but distorted to the left side. This characteristic feature can be explained rationally by assuming that pitting events occur randomly with birth of pits and/or their death. This process is called the birth and death stochastic process which can be schematically shown in the Shanon diagram of Fig. 5. The upper figure in Fig. 5 demonstrates that there are two processes operating during pitting, one destroying the passive state to generate pit, and the

Fig. 1. Distributions of pitting potential for various steels, measured by the potential sweep method and plotted in normal probability paper.

Fig. 2. Pitting potential expressed as a function of the square root of potential sweep velocity.

Fig. 3. Effect of alloying elements on critical pitting potential, expressed by the linear regression equation.

other recovering from the pit generated state to the original passive state by pit repassivation. Between two states, transitions occur randomly with time from the no pit formed state to the pit formed state, or

Fig. 4. Histogram of induction time for pit generation at the constant potential of 0.02 V for 17 Cr steel.

Fig. 5. Shanon diagram showing the birth and death stochastic process, each of which corresponds to the pit generation and the pit repassivation respectively illustrated in the upper figure.

vice versa, with transition probability of λ and μ . The basic probability differential equation to describe the above process is given by

$$dP/dt = -\lambda P + \mu(1-P) \dots\dots\dots(3)$$

- where, P: probability of no pit formed specimen, or survival probability
- λ : the transition probability of birth process corresponding to the rate of pit generation
- μ : the transition probability of the death process corresponding to the rate of pit repassivation.

The integration of Eq. (3) leads to

$$P = \mu/(\lambda + \mu) + \lambda/(\lambda + \mu)(\exp(-(\lambda + \mu)(t - t_0))) \dots\dots\dots(4)$$

When $\mu=0$, Eq. (4) reduces to the following simple equation,

$$P = \exp(-\lambda(t - t_0)) \dots\dots\dots(5)$$

which just describes only one process, that is, the birth process operating. This type of equation had been found for various processes such as fracture of glass,

Fig. 6. Change in survival probability with time for 17 Cr steel. Curve fitting gives the value of λ , μ and t_0 in Eq. (4).

Fig. 7. The rate of pit generation, λ , and pit repassivation, μ , as a function of applied potential. Critical pitting potential, E_{crit} , just corresponds to the crossing point of two curves.

metals and other materials and also pit generation²⁻⁴⁾ of stainless steels. It should be pointed that Eq. (5) is an approximate expression for the case of pitting because only one process of pit generation is taken into consideration. Thus, the exact expression for pitting process should be Eqs. (3) and (4).

As can be seen from Eq. (4), survival probability, P, is a function of time, t, at the constant potential since λ and μ are constants which depend on applied potential. The constants λ and μ can be easily determined by a curve fitting, an example of which is illustrated in Fig. 6.

The rates of pit generation, λ , and pit repassivation, μ , thus determined for various alloys are plotted as a function of applied potential as shown in Fig. 7. From this figure the following important conclusions can be deduced. The first conclusion is that pitting potential, E_{crit} , just corresponds to the potential at which the rate of pit generation is equal to the rate of repassivation. This means that pitting potential is not an equilibrium potential but a kind of mixed potential determined by the rate of pit generation

and pit repassivation. Both processes of pit generation and repassivation at the pitting potential have the same numerical value of λ and μ , but proceed in the opposite direction. If the potential goes over the pitting potential E_{crit} , the rate of pit generation λ exceeds μ , resulting in the pit generation and growth. Thus, it is concluded that the pitting potential is determined by a dynamical balance of pit generation and pit repassivation. It is also interesting to note that the rate of pit generation increases with the increase of applied potential, while the rate of pit repassivation shows no dependence on the potential. Exact potential dependence of λ is expressed as

$$\lambda = \alpha(E - E_{crit}) \dots\dots\dots(6)$$

and, replacing the constant α thus determined into Eq. (1), a linear relation between E_M and $V^{1/2}$ was confirmed to fit the experimental data as shown in Fig. 2.

Another interesting behavior is the very characteristic dependence of each rate on temperature, an example of which is shown for 17Cr-1Mo in Fig. 8. Larger temperature dependence is observed for the rate of pit generation, while the rate of pit repassivation shows much smaller temperature dependence. Activation energy for the former is calculated to be 95 kJ/mol and 6.7 kJ/mol for the latter. Both behaviors of potential and temperature dependence suggest that the pit generation is controlled by a potential dependent activation process and the pit repassivation by a mass transport process.

5. Effect of Alloying Elements on the Rate of Pit Generation and Pit Repassivation

It is demonstrated in Fig. 7 that all of the alloying elements Cr, Ti, Mo and Nb make a shift to a higher pitting potential as mentioned before. The cause of the shift, however, is not the same, because change in λ and μ due to the alloying is quite different for each element. Alloying of Cr, Ti and Nb contributes to decrease the rate of pit generation, while the rate of pit repassivation is not influenced. On the contrary Mo has a strong effect to enhance the rate of repassivation in addition to decrease the rate of pit generation. Many studies¹⁰⁾ using surface characterization techniques demonstrate that Cr enriches in the passive film. It is no doubt that this enrichment of Cr is responsible for the decrease of the rate of pit generation observed for the steels containing Cr, Ti and Nb as well as the Mo containing steel. It is still uncertain whether Mo enriches in the passive film or not, but Mo in the steel plays a definite roll to enhance the rate of repassivation as demonstrated in this stochastic analysis.

IV. Conclusion

Birth and death stochastic processes are confirmed

Fig. 8. Effect of temperature on the rate of pit generation and pit repassivation for 17Cr-1Mo steel.

to operate in pitting corrosion of ferritic stainless steels containing Cr, Mo, Ti and Nb, and the rate of pit generation, λ , and pit repassivation, μ , are decided as a function of potential based on the stochastic theory. Pitting potential is found to shift to the noble value with addition of all the alloying elements examined, being expressed as the linear regression equation (2). It is demonstrated that the shift in the pitting potential for the steels containing Cr, Ti and Nb is brought about simply by a decrease in λ , while μ remains constant. In contrast, the shift for the Mo containing steel is caused by an increase in μ in addition to a decrease in λ . Mo in the steel is concluded to have a very characteristic role to enhance the rate of repassivation.

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