

EFFECTS OF PHOSPHORUS AND MOLYBDENUM ON THE CAUSTIC STRESS CORROSION CRACKING OF NiCrMoV STEELS

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ABSTRACT

This paper presents a study of the effects of phosphorus and molybdenum on caustic stress corrosion cracking of 3.5NiCrMoV rotor steels. The results will show that phosphorus segregation to the grain boundaries substantially lowers the resistance of the steel to caustic cracking. Removal of molybdenum provides some improvement in the resistance to caustic cracking.

KEYWORDS

Steels; stress corrosion; grain boundary segregation.

INTRODUCTION

The susceptibility of low alloy rotor steels to intergranular stress corrosion cracking is well recognized and is often a serious problem to the power generating industries. These cracks usually occur in those parts of the rotors which are highly stressed and conducive to formation of crevices (Kalderon, 1972; Gray, 1972; Hodge and Mogford, 1979; Lyle and Burghard, 1982; McCord and co-workers, 1976). The environment responsible for this type of intergranular stress corrosion cracking is not well defined, although caustic solutions have been proposed as candidates (Lyle and Burghard, 1982; McCord and co-workers, 1976; Parker and Sadler, 1975). Laboratory tests have shown that stress corrosion cracking of mild and low alloy steels can occur in hydroxides (Diegle and Vermilyea, 1976; Doig and Flewitt, 1977; Reinoehl and Berry, 1972), nitrates (Flis and Scully, 1968; Henthorne and Parkins, 1967; Parkins, 1952;), carbonates (Sutcliffe and co-workers, 1972), phosphates (Parkins, Holroyd and Fessler, 1978), acetates (Parker and Pearce, 1974), high-purity water and moist steam (Gray, 1972; Hodge and Mogford, 1979; Kalderon, 1972; Lyle and Burghard, 1982; Parker and Sadler, 1975). In almost all cases, the stress corrosion cracks were found to propagate along prior austenite grain boundaries. However, very few attempts have been made to correlate this intergranular stress corrosion cracking to actual grain boundary composition.

A number of factors can affect the susceptibility of the steels to stress corrosion cracking. First, the data in the literature suggest that changes in the alloy composition can either improve or impair the steel's resistance to stress corrosion cracking. Roberts and Greenfield (1979) have reported that an Fe-3%Ni alloy is more resistant to stress corrosion cracking in steam and pure water than those that contain molybdenum and chromium. Parkins and co-workers (1981) have shown that additions of molybdenum to ferritic steels increased the susceptibility of these steels to caustic stress corrosion cracking. Secondly, the residual impurity elements, when segregated to the grain boundaries, can also affect the steel's resistance to stress corrosion cracking. Although these elements usually have a low bulk concentration, at the grain boundaries their concentrations can be as high as 2-5 atomic percent (McMahon and Marchut, 1978). Atkinson and co-workers (1980), and Woodward and Burstein (1983) have shown that impurity segregation can have a large effect on the caustic cracking susceptibility of 3CrMo steels at $-400 \text{ mV}_{\text{Hg/HgO}}$. The present authors (Bandyopadhyay and Briant, 1982) demonstrated that grain boundary impurity segregation of phosphorus increases the susceptibility of NiCr steels to caustic stress corrosion cracking at a potential of $-400 \text{ mV}_{\text{Hg/HgO}}$. A number of workers (Lea and Hondros, 1981; Kupper, Erhart and Grabke, 1981; Moloznik, Briant and McMahon, 1979) have shown that phosphorus segregation lowers the resistance of iron base alloys to stress corrosion cracking in nitrate solutions.

This paper presents the results of an investigation into the effects of molybdenum and phosphorus on the caustic cracking of 3.5NiCrMoV rotor steels.

EXPERIMENTAL

The compositions of the steels used in the present study are given in Table 1. Heat A is a high purity 3.5NiCrMoV rotor steel. Heat B is similar to heat A in composition, but it does not contain molybdenum. Heats C and D have compositions similar to heats A and B respectively, but they are doped with phosphorus.

The samples were austenitized at 950°C for 4 hours followed by water quenching. They were subsequently tempered at 600°C for 20 hours and water quenched. This produced a tempered martensite microstructure with grain sizes equivalent to ASTM number 6 to 7. Samples given only these heat treatments will be referred to as quenched and tempered. Some of the samples were given an additional step-cooling heat treatment (Powers, 1956) to produce increased amounts of impurity segregation to the grain boundaries. The mechanical properties of these steels are shown in Table 2. It should be noted that the step-cooling treatment did not alter either the microstructure or the mechanical properties of these steels.

Stress corrosion tests were performed in 9M NaOH solution at 98°C . The solution was held in a Teflon cell and was constantly de-aerated with nitrogen during the test. The tests were run at a controlled potential of -400 mV with respect to a $\text{Hg/HgO}/9\text{M NaOH}$ reference electrode. The samples were unnotched tensile samples with a gauge diameter of 0.254 cm and a gauge length of 2.54 cm. They were tested in a constant load configuration.

RESULTS AND DISCUSSION

(a) Effect of Phosphorus

Figure 1 shows the stress corrosion test results for the phosphorus-doped NiCrMoV steel in the quenched and tempered condition and the step-cooled condition. The figure shows that the step-cooled samples, which had more P segregation, failed much more rapidly than the quenched and tempered samples at any given initial stress. Also included in the same figure are the stress corrosion test results for a high purity NiCrMoV steel which was also given a step-cooling heat treatment. Because of the absence of any impurity segregation, the high purity steel, even in the step-cooled condition, showed more resistance to caustic cracking than the phosphorus doped steel in either heat treated condition. However, in all cases the corrosion cracks were intergranular.

Figure 2 shows a representative Auger spectrum from a grain boundary of a step-cooled sample of the phosphorus-doped NiCrMoV steel. The segregation of phosphorus to the prior austenite grain boundaries is quite substantial as shown in the figure. Attempts to obtain intergranular fracture inside the Auger chamber were unsuccessful for the high-purity and quenched and tempered phosphorus-doped NiCrMoV steels, a result which suggests that there is much less phosphorus segregation for these steels. Additional etching experiments confirmed this fact (Bandyopadhyay and Briant, 1983).

(b) Effect of Molybdenum

Figure 3 compares the stress corrosion test results of the step-cooled samples of the high-purity NiCrMoV and high-purity NiCrV steels in 9M NaOH at 98°C and at a controlled potential of $-400 \text{ mV}_{\text{Hg/HgO}}$. Comparison between these two steels will determine if molybdenum has any intrinsically bad effects. At this point one must note that the yield strength of the molybdenum-free steel is somewhat lower than that of the molybdenum-containing steel. Therefore, when a comparison is made at a certain percentage of the ultimate tensile strength, the molybdenum-free steel will actually be subjected to a lower stress. However, the present authors have also found that the stress corrosion behavior is not solely or clearly dependent on the yield strength of the material. Figure 3 shows that the removal of molybdenum from the high-purity NiCrMoV steel does cause some minor improvement in the stress corrosion cracking susceptibility of these alloys. However, because of the absence of any impurity segregation, both show very good resistance to caustic stress corrosion cracking at this potential. Figure 4 compares the stress corrosion test results for the step-cooled samples of the phosphorus-doped NiCrMoV and the phosphorus-doped NiCrV steels. Here the removal of molybdenum from the phosphorus-doped NiCrMoV steel does produce a substantial improvement in the resistance to caustic cracking. Thus, it would appear that in the absence of molybdenum, the presence of phosphorus is less detrimental.

The results are more striking when one examines the fracture surfaces of these two steels. Figures 5a and 5b show scanning electron micrographs of the fracture surfaces of the molybdenum-containing, phosphorus-doped steel and the molybdenum-free phosphorus doped steel, respectively. The fracture path in both cases is predominantly intergranular. However, the fracture

surfaces of the molybdenum containing steel shows relatively smooth grain boundary facets, Fig. 5a, whereas the individual grain facets in the molybdenum-free steel are very rough and have received substantial general corrosive attack, Fig. 5b. The implications of these results for the mechanism of stress corrosion cracking are discussed in detail elsewhere (Bandyopadhyay and Briant, 1983; Bandyopadhyay, Briant, Emigh and Ford, 1983).

CONCLUSION

1. Grain boundary segregation of phosphorus greatly enhances the susceptibility of NiCrMoV steels to caustic stress corrosion cracking at an electrode potential of $-400 \text{ mV}_{\text{Hg/HgO}}$.
2. Removal of molybdenum from the steel improves the resistance to caustic stress corrosion cracking. High purity steels, both with and without molybdenum, show excellent resistance to stress corrosion cracking.

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TABLE 1 Chemical Compositions of Steels

Steel	(Wt. %)										
	C	Ni	Cr	Mo	V	Mn	Si	P	S	Sn	Al
A: (Pure: 0.6% Mo)	0.19	3.30	1.57	0.69	0.12	-	0.30	0.004	0.003	-	0.53
B: (Pure: 0% Mo)	0.19	3.47	1.46	<0.02	0.12	<0.02	0.12	0.003	0.006	<0.02	0.30
C: (P-doped: 0.6% Mo)	0.19	3.49	1.53	0.58	0.12	<0.02	0.12	0.012	0.003	<0.02	0.30
D: (P-doped: 0% Mo)	0.19	3.39	1.48	<0.02	0.10	<0.02	0.11	0.018	0.004	<0.02	0.29

TABLE 2. Mechanical Properties of Steels

Steel	Heat Treatment	0.2% Offset Yield Stress		Ultimate Tensile Strength	
		KSi	MPa	KSi	MPa
A	Quenched and Tempered +Step-cooled	138.9	957.7	154.6	1066.0
B	Quenched and Tempered	112.2	773.6	131.0	903.3
B	Quenched and Tempered +Step-cooled	117.8	812.2	131.9	909.4
C	Quenched and Tempered	138.8	957.0	155.3	1070.7
C	Quenched and Tempered +Step-cooled	139.2	959.8	153.1	1060.5
D	Quenched and Tempered	101.9	702.6	120.0	827.4
D	Quenched and Tempered +Step-cooled	99.1	683.3	116.0	719.8

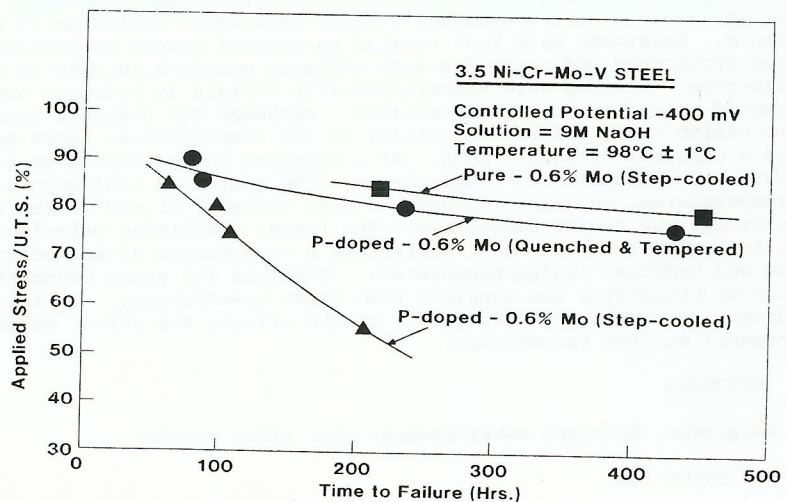


Fig. 1. Variation of time to failure with the initial applied stress for pure (steel A) and P-doped (Steel C) NiCrMoV steels in the quenched and tempered and step-cooled conditions.

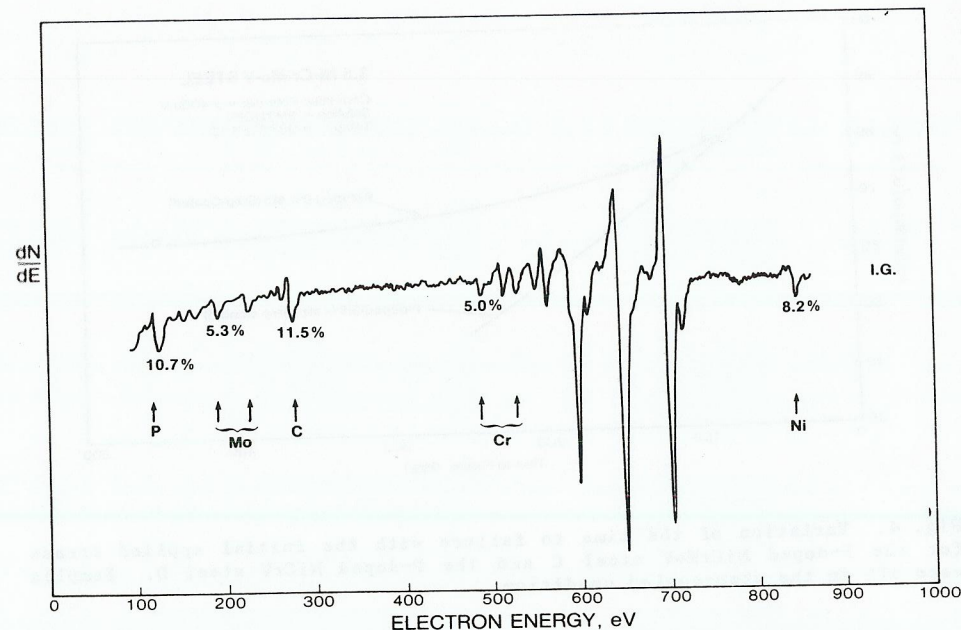


Fig. 2. Representative spectrum taken by Auger electron spectroscopy of a grain boundary in a step-cooled sample of the P-doped NiCrMoV steel C. This spectrum shows the derivative in the number of electrons of a given energy plotted as a function of the electron energy. The peaks in the spectrum correspond to certain elements and they are identified on the figure.

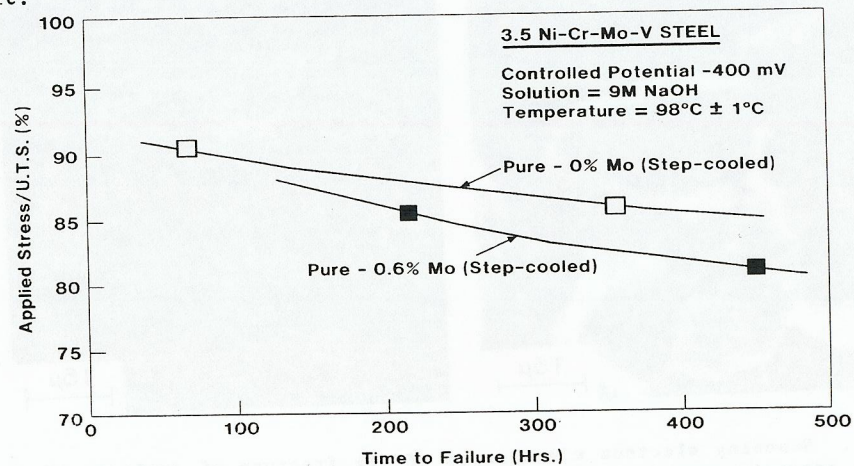


Fig. 3. Variation of the time to failure with initial applied stress for the pure NiCrMoV steel A and the pure NiCrV steel E. The samples were in the step-cooled condition.

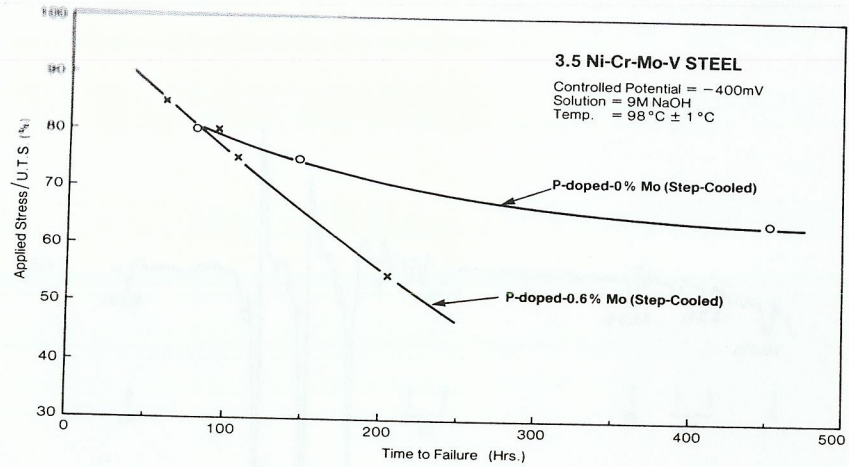


Fig. 4. Variation of the time to failure with the initial applied stress for the P-doped NiCrMoV steel C and the P-doped NiCrV steel D. Samples were all in the step-cooled condition.

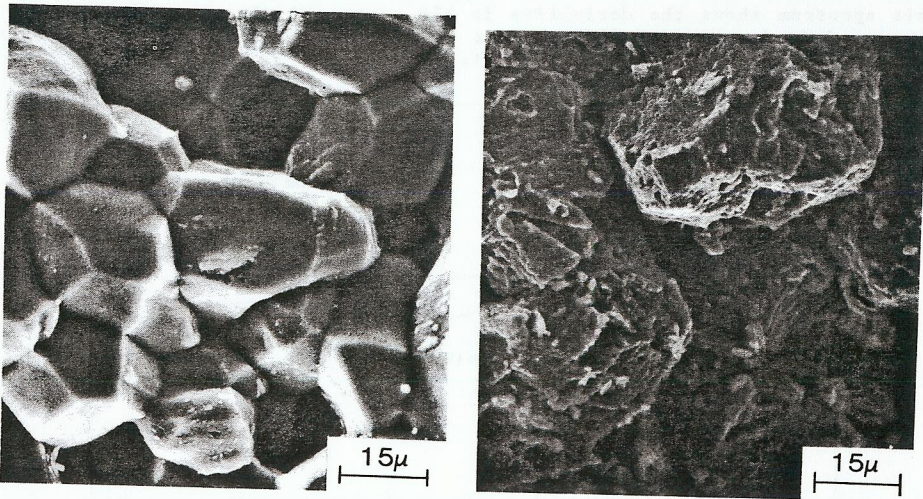


Fig. 5. Scanning electron micrographs of the fracture of surfaces of the stress corrosion samples of (a) P-doped NiCrMoV steel C and (b) P-doped NiCrV steel D.