UCRL-BOOK-202251

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December 7, 2003

ASM Metals Handbook Volume 13B “Corrosion: Materials, Environment, Industries

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

07 December 2003
Article to be published in ASM Metals Handbook Volume 13B “Corrosion: Materials, Environment, Industries”

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INTRODUCTION

Environmentally Assisted Cracking (EAC) is a general term that includes phenomena such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), sulfide stress cracking (SSC), liquid metal embrittlement (LME), etc. EAC refers to a phenomenon by which a normally ductile metal looses its toughness (e.g. elongation to rupture) when it is subjected to mechanical stresses in presence of a specific corroding environment. For EAC to occur, three affecting factors must be present simultaneously. These include: (1) Mechanical tensile stresses, (2) A susceptible metal microstructure and (3) A specific aggressive environment. If any of these three factors is removed, EAC will not occur. That is, to mitigate the occurrence of EAC, engineers may for example eliminate residual stresses in a component or limit its application to certain chemicals (environment). The term environment not only includes chemical composition of the solution in contact with the component but also other variables such as temperature and applied potential. Nickel alloys are in general more resistant than stainless steels to EAC. For example, austenitic stainless steels (such as S30400) suffer SCC in presence of hot aqueous solutions containing chloride ions. Since chloride ions are ubiquitous in most industrial applications, the use of stressed stainless steels parts is seriously limited. On the other hand, nickel alloys (such as N10276) are practically immune to SCC in presence of hot chloride solutions and therefore an excellent alternative to replace the troubled stainless steels. Nonetheless, nickel alloys are not immune to other types of EAC. There are several environments (such as hot caustic and hot hydrofluoric acid) that may produce embrittlement in nickel alloys (Crum et al, 2000) (Table 1). The conditions where nickel alloys suffer EAC are highly specific and therefore avoidable by the proper design of the industrial components.

Commercial Nickel

Commercially pure nickel is not susceptible to stress corrosion cracking, except in the heavily cold worked conditions in the presence of high temperature (>250°C) concentrated caustic solutions. Commercial nickel is not susceptible to hydrogen embrittlement since the solubility and diffusivity of hydrogen in nickel are low and this material has low mechanical strength. The yield stress (YS) of annealed Ni-200 at room temperature is 190 MPa, the ultimate tensile stress (UTS) is 465 MPa, the elongation to rupture is 50% and the Rockwell B hardness is only 60.

Nickel-Copper Alloys

As in the case of Ni 200, alloy 400 is not very susceptible to stress corrosion cracking (SCC) probably because it has low mechanical strength. The yield stress of annealed alloy 400 at room temperature is 260 MPa, the ultimate tensile stress is 550 MPa, the elongation to rupture is approximately 50% and the Rockwell B hardness is 72. Alloy 400 was found to be susceptible to SCC in acidic solutions containing mercury salts, in liquid mercury, in hydrofluoric acid and in fluosilicic acid (The International Nickel Company, 1968). In hydrofluoric acid the cracking is transgranular and the highest susceptibility occurs in the vapor phase, especially in the presence of air (Pawel, 1994). Reduction of aeration reduces the susceptibility to cracking in hydrofluoric acid. Using U-bend specimens, it has been reported that the crack propagation rate in Alloy 400 exposed to the vapor phase of 20% HF for 240 h decreased as the temperature increased from 66°C to 93°C, probably because less oxygen was available in the vapor phase as the temperature increased (Rebak 2000). In the same study, U-bends of Alloy 400 were found free from cracking while immersed in the liquid phase (Rebak 2000, Rebak 2001).

It has also been reported that highly stressed alloy 400 suffers SCC in ammonia vapors at 300°C (Theus et al., 1982). Heat treatments that eliminate residual stresses and cold worked microstructures greatly reduce the susceptibility of alloy 400 to all types of environmentally induced cracking.

Ni-Mo Alloys

Ni-Mo alloys are resistant to chloride induced cracking in boiling magnesium chloride solutions (Kolts, 1982; Hodge, 1983). When B-2 alloy and, to a lesser extent B-3 alloy, are exposed to temperatures in the range 550°C to 850°C, they loose ductility due to a solid phase transformation which forms ordered intermetallic phases such as Ni_4Mo. The precipitation of these ordered phases changes the deformation mechanisms of the alloys making them susceptible to EAC such as hydrogen embrittlement. In B-2 alloy, the precipitation of intermetallic phases can occur in the heat-affected zone (HAZ) during welding. It has been reported that B-2 alloy failed by intergranular stress corrosion cracking of the HAZ when exposed to organic solvents containing traces of sulfuric acid at 120°C (Takizawa and Sekine, 1985). It has also been reported that B-2 alloy was prone to transgranular stress corrosion cracking in the presence of hydroiodic acid (HI) above 177°C (Sridhar and Cragnolino, 1992).

Stress corrosion cracking studies of B, B-2 and B-3 alloys in acidic solutions were carried out under laboratory and plant conditions (Nakahara and Shoji, 1996). The effects of the electrochemical potential, cold work produced by drilling, and two different aging processes (that would simulate welding and the subsequent cooling cycle) were investigated. At anodic potentials (200 mV above the free corrosion potential) Nakahara and Shoji found transgranular fissuring in all three alloys both for mill annealed and aged materials. At cathodic potentials (100 mV and 400 mV below the free corrosion potential) they found intergranular cracking only for the aged (sensitized) alloys. Since the amount of intergranular brittle cracking increased at the lower applied cathodic potential, this environmentally induced cracking was attributed to hydrogen embrittlement (Nakahara and Shoji, 1996).

U-bend specimens of mill annealed B-3 (N10675) alloy were found to suffer stress corrosion cracking in the presence of vapor and liquid phase of a 20% HF solution at 66°C, 79°C and 93°C

(Rebak et al. 2001). The cracking susceptibility of N10675 increased with the temperature and the liquid phase was more aggressive than the vapor phase.

Ni-Cr-Mo Alloys

One of the major limitations of stainless steels is that these alloys are susceptible to chloride induced localized attack such as crevice corrosion, pitting corrosion and stress corrosion cracking. Ni-Cr-Mo alloys are the most resistant Ni based alloys to the classic chloride induced localized corrosion that troubles the stainless steels. In some cases SCC was reported in high strength materials; however, cracking only occurred in very aggressive conditions, such at temperatures higher than 200°C, pH lower than 4 and presence of hydrogen sulfide (Kolts, 1987). U-bend specimens of C-2000, C-22 and C-276 alloys were not susceptible to cracking in boiling (154°C) 45% $MgCl_2$ solution after 1008 h of testing (Rebak 2000). C-276 and C-4 alloy were free from cracking in a 25% NaCl solution at 232°C; however, these alloys were susceptible to cracking in a $MgCl_2$ solution of same chloride content at the same temperature (Kolts, 1982). C-22 alloy was immune to SCC in 20.4% $MgCl_2$ solution up to 232°C, even in the 50% cold reduced condition and in the 50% cold reduced plus aged at 500°C for 100 h condition.

Laboratory testing using U-bend specimens (ASTM G 30) had shown that Ni-Cr-Mo alloys such as C-276, C-22 and C-2000 alloy were susceptible to SCC in wet HF at both in the liquid and vapor phase (Figure 1) (Rebak 2000, Rebak et al. 2001). The most resistant of the Ni-Cr-Mo alloy to cracking in wet HF was C-2000 (N06200) probably because the beneficial effect of 1.6% Cu content. Just in opposite behavior to Ni-Cu Alloy 400, Ni-Cr-Mo alloys were less susceptible to cracking in the vapor phase than in the liquid phase, suggesting that the presence of Cr is beneficial for HF vapor phase applications (Rebak et al. 2001).

Nickel based alloys are known to be susceptible to caustic cracking. Under slow strain rate conditions, C-276 alloy was susceptible to transgranular cracking in 50% NaOH at 147°C (Asphahani, 1979). On the other hand, mill annealed and aged for 24 h at 677°C C-shape specimens (ASTM G 39) of C-22 alloy did not exhibit cracking after immersion in 50% NaOH solution at 147°C for 720 h.

When Ni-Cr-Mo alloys are aged at temperatures higher than 600°C for long time, long range ordering reactions and precipitation of an intermetallic μ phase can occur. The occurrence of these solid state reactions during aging would reduce the ductility of Ni-Cr-Mo alloys. For example, for annealed C-276 alloy, the yield stress (YS) at room temperature is 360 MPa, the ultimate tensile stress (UTS) is 807 MPa, the elongation to rupture is 63%; however, for a C-276 alloy that was aged for 16,000 h at 760°C, the YS increases to 476 MPa, the UTS increases to 894 MPa and the elongation to rupture decreases to 10%. It has been reported that aged C-276 alloy was susceptible to hydrogen induced cracking in environments containing hydrogen sulfide (H_2S) (Kane et al., 1977; Sridhar et al., 1980).

Ni-Cr-Mo alloys were also found to suffer environmentally induced cracking in conditions associated to super critical water oxidation (SCWO). It has been reported that both C-276 (N10276) and Alloy 625 (N06625) suffered intergranular cracking when exposed to various aqueous solutions in the vicinity of the critical point of water (374°C) (Mitton et al. 1998, Kritzer et al. 1998, Alley and Bradley 2003).

Because of its excellent resistance to stress corrosion cracking and other types of localized corrosion, Alloy C-22 (N06022) was selected by the Department of Energy (U.S.A.) to fabricate the inner wall of the high level nuclear waste containers that are going to be buried permanently at the Yucca Mountain site (U. S. DOE 2001, Gordon 2002, Cragnolino et al. 2002).

Alloy C-22 is being extensively tested for its susceptibility to SCC in a variety of environments, mainly at GE Global Research, Southwest Research Institute and Lawrence Livermore National Laboratory (LLNL). This alloy was found extremely resistant to EAC in many different solutions at the corrosion potential, at all the tested temperatures from ambient 110°C [Andresen et al. 2003, Dunn et al. 2002, Pan et al. 2000 and Estill et al. 2002). Tests were carried out using cyclic loading, constant load and slow strain rate tests in solutions from 14 Molal $MgCl_2$, to basic saturated water (BSW) to simulated acidified water (SAW). Similarly, U-bend specimens of N06022 and other nickel alloys such as C-4 (N06455), G-3 (N06985), 825 (N08825) and 625 (N06625) are being used to characterize the stress corrosion cracking susceptibility in a variety of environments [Fix et al. 2004). Gas Tungsten Arc Welded (GTAW) and non-welded U-bend specimens were exposed for more than 5 years at the corrosion potential to the vapor and liquid phases of three different solutions (pH 2.8 to 10) simulating up to 1000 times the concentration of ground water both at 60°C and 90°C. None of these alloys suffered any indication of environmentally induced cracking [Fix et al. 2004].

Alloy C-22 was found susceptible to EAC when SSRT was performed on mill annealed specimens in hot simulated concentrated water (SCW) at anodic applied potentials (Fix et al. 2002, King et al 2002, King et al. 2004). SCW is a multi-ionic alkaline solution approximately 1000 times more concentrated than Yucca Mountain ground water. It is likely that the presence of fluoride ions in this solution contributed to the cracking of C-22 [King et al. 2004]. The susceptibility to cracking was strongly dependent on the applied potential and the temperature of the solution. The highest susceptibility to EAC was found at around 90°C at +400 mV in the saturated silver chloride (SSC) electrode scale (Figure 2). At the corrosion potential, C-22 was free from EAC even at 90°C. Similarly, at anodic applied potentials, C-22 was free from EAC at ambient temperatures and as the temperature increased the time to failure in the tests decreased (Figure 3).

It has also been reported that Alloy C-22 (N06022) may suffer embrittlement when slow strained under cathodic applied potentials (or currents) (Kesavan 1991, Scammon 1994, King 2004). The maximum susceptibility to cracking under cathodic conditions seemed to occur at ambient temperatures suggesting a hydrogen related failure mechanism.

Ni-Cr-Fe Alloys

This is one of the largest groups of nickel-based alloys since it covers Inconel 600 (N06600), Incoloy 825 (N08825) and 800 (N08800) and Hastelloy G-30 (N06030) type alloys. Since Alloy 600 has been used to fabricate the tubes of steam generators in nuclear power plants, it has been by far the most studied nickel alloy regarding its stress corrosion cracking behavior, especially in hot water. Alloy 600 has been found to suffer stress corrosion cracking in high temperature pure water (> 300°C) both in service and in the laboratory. Due to its importance for the nuclear industry, the stress cracking of alloys 600 and 690 in pure water and in caustic solutions has been extensively researched in the last three decades (Szklarska-Smialowska and Rebak, 1996, Staehle and Gorman 2003) and more than one thousand papers were published in this subject. In general, alloy 690 is more resistant to cracking than alloy 600, probably due to its higher content of chromium (29%). The susceptibility to cracking of alloys 600 and 690 depends strongly on environmental factors such as temperature, level of tensile stresses, presence of hydrogen gas, solution pH and electrochemical potential, and metallurgical factors, such as the amount of cold work and heat treatment. Cracking in alloy 600 could be intergranular or transgranular.

Alloy 600, like other nickel based alloys, also suffers stress corrosion cracking in hot caustic solutions (150°C-200°C). Alloy 690, which has double the amount of chromium in Alloy 600 has been found to be more resistant than Alloy 600 to high temperature cracking in pure water and in caustic solutions. Due to its high content of nickel (76%), alloy 600 is resistant to stress corrosion cracking in chloride containing solutions; however, Alloy 600 was susceptible to localized attack in hydrofluoric acid containing environments (Pawel, 1994).

Alloy 800 is also used in the nuclear power generation. It was shown that Alloy 800 (N08800) was also susceptible to caustic cracking (Mignone et al., 1990) and even more susceptible than Alloy 690, probably because of the higher Cr content of the latter (Yang et al. 2001).

Alloy 825 is more resistant to stress corrosion cracking than for example 316 stainless steels due to its higher content of nickel. Slow strain rate tests and U-bend tests have shown that alloy 825 was susceptible to transgranular stress corrosion cracking in 45% $MgCl_2$ solutions at temperatures above 146°C.

Data on the stress corrosion cracking behavior of G-30 alloy is scarce. It has been reported that G-30 components used in the industrial production of hydrofluoric acid suffered cracking (Rebak 2000). U-bend specimens of G-30 alloy did not crack after exposure for 500 h in 45% $MgCl_2$ solution at 154°C. It has been found that G-30 as well as other nickel alloys would suffer cracking in the aggressive conditions encountered in super critical water oxidation (SCWO) treatments.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U. S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract N° W-7405-Eng-48. This work is supported by the Yucca Mountain Project, LLNL

REFERENCES

Alley, D. W. and Bradley, S. A. [2003], Paper 03351, Corrosion/2003 (Houston, TX: NACE International, 2003)

Andresen, P. L. [2003], Emigh, P. W., Young, L. M. and Gordon, G. M., Paper 03683, Corrosion/2003 (Houston, TX: NACE International, 2003).

Asphahani, A. I. (1979) in Stress Corrosion Cracking - The Slow Strain Rate Technique, ASTM STP 665, p. 279 (ASTM: Philadelphia, USA).

Cragnolino, G. A., Dunn, D. S. and Pan, Y. - M. [2002] in Scientific Basis for Nuclear Waste Management XXV, Vol. 713, pp. 53-60 (Warrendale, PA: Materials Research Society 2002).

Crum, J. R. [2000], Hibner, E., Farr, N. C. and Munasinghe, D. R., "Nickel-Based Alloys" Chapter 7, p. 287 in Casti Handbook of Stainless Steels and Nickel Alloys (Edmonton, Alberta: CASTI Publishing Inc., 2000).

Dunn, D. S. [2002], Pan, Y.-M. and Cragnolino, G. A., Paper 02425, Corrosion/2002 (Houston, TX: NACE International, 2002)

Estill, J. C. [2002], King, K. J., Fix, D. V., Spurlock, D. G., Hust, G. A., Gordon, S. G., McCright, R. D., Gordon, G. M. and Rebak, R. B. Paper 02535, Corrosion/2002 (Houston, TX: NACE International, 2002)

Fix, D. V. [2004], Estill, J. C., Hust G. A., Wong, L. L. and Rebak, R. B. Paper 04549, Corrosion/2004 (Houston, TX: NACE International, 2004)

Gordon, G. M. [2002], Corrosion, 58, 811 (2002).

Kane, R. D., Watkins, M., Jacobs, D. F. and Hancock, G. L. (1977), Corrosion-NACE, 33, 309

Kesavan, S [1991], Ph.D. Dissertation, The Ohio State University (1991)

King, K. J [2002], Estill, J. C. and Rebak, R. B. in 2002 PVP-Vol. 449, p. 103 (New York, NY: American Society of Mechanical Engineers, 2002)

King, K. J [2004], Wong, L. L., Estill, J. C. and Rebak, R. B, Paper 04548, Corrosion/2004 (Houston, TX: NACE International, 2004).

Kolts, J. (1982), Paper 241, Corrosion'82 (NACE: Houston, USA).

Kolts, J. (1987), in Metals Handbook Ninth Edition, Volume 13, p. 647 (ASM International, Metals Park, Ohio, USA).

Kritzer, P. [1998], Boukis, N. and Dinjus, E., Paper 415, Corrosion/98 (Houston, TX: NACE International, 1998)

Mignone, A. [1990], Maday, M. F. , Borello, A. and Vittori, M., Corrosion, 46, 57 (1990).

Mitton, D. B. [1998], Zhang, S-H, Quintana, M. S., Cline, J. A., Caputy, N., Marrone, P. A. and Latanision, R. M, Paper 414, Corrosion/98 (Houston, TX: NACE International, 1998)

Nakahara, M. and Shoji, T. (1996), Corrosion, 52, 634.

Pan, Y.-M. [2000], Dunn, D. S. and Cragnolino, G. A. in Environmentally Assisted Cracking: Predictive Methods for Risk Assessment and Evaluation of Materials, Equipment and Structures, p. 273 (West Conshohocken, PA: ASTM, 2000).

Pawel, S. J. (1994), Corrosion, 50, 963 (1994)

Rebak, R. B. [2000], in Environmentally Assisted Cracking: Predictive Methods for Risk Assessment and Evaluation of Materials, Equipment and Structures, p. 289 (West Conshohocken, PA: ASTM, 2000).

Rebak, R. B. [2001], Dillman, J. R., Crook, P. and Shawber, C. V. V., Materials and Corrosion, 52, 289 (2001).

Scammon, K. M. [1994], MS Thesis, University of Central Florida (1994)

Sridhar, N. and Cragnolino, G. A. (1992) in Stress Corrosion Cracking, p. 131 (ASM: Materials Park, Ohio, USA).

Sridhar, N., [1980] Kargol, J. A. and Fiore, N. F., Scripta Metall., 14, 1257.

Staehle, R. W. and Gorman, J. A. [2003], Corrosion, 59, 931 (2003)

Szklarska-Smialowska, Z. and Rebak, R. B. (1996) in Control of Corrosion on the Secondary Side of Steam Generators, p. 223 (NACE International: Houston, USA).

Takizawa, Y. and Sekine, I. (1985), Paper 355, Corrosion/85 (NACE: Houston, USA).

The International Nickel Company (1968), Corrosion Engineering Bulletin CEB-5 (Inco: New York, USA).

Theus, G. J.[1982], Emanuelson, R. H. and Russell, J., Paper 209, Corrosion/82 (NACE: Houston, USA).

U. S. Department of Energy [2001], Office of Civilian Radioactive Waste Management, Yucca Mountain Science and Engineering Report, DOE/RW-0539, Las Vegas, NV, May 2001.

Yang, W. [2001], Lu, Z, Juang, D., Kong, D. Zhao, G. and Congleton, J., Corr. Sci., 43, 967 (2001).

Table 1
Environments that may cause EAC in nickel alloys

Nickel Alloys	Example UNS	Environments which may produce EAC
Commercial Nickel	N02200	Not especially susceptible
Nɨ Cu Alloys	N04400	Hydrofluoric acid (especially in the vapor phase containing oxygen)
Nɨ Mo Alloys	N10675	Cathodic and anodic acidic solutions (especially near welds), Wet HF solutions
Nɨ Cɍ Mo Allloys	N10276, N06022	Hot Caustic, SCWO, Hot Liquid HF solutions
Nɨ Cɍ Fe Alloys	N06600, N08825	Hot water, Hot Caustic, high chloride high temperature

FIGURE 1: SCC of Alloy C-276 (N10276) U-bend specimen immersed in liquid 20% HF solution at 93°C for 240 h. Magnification X100.

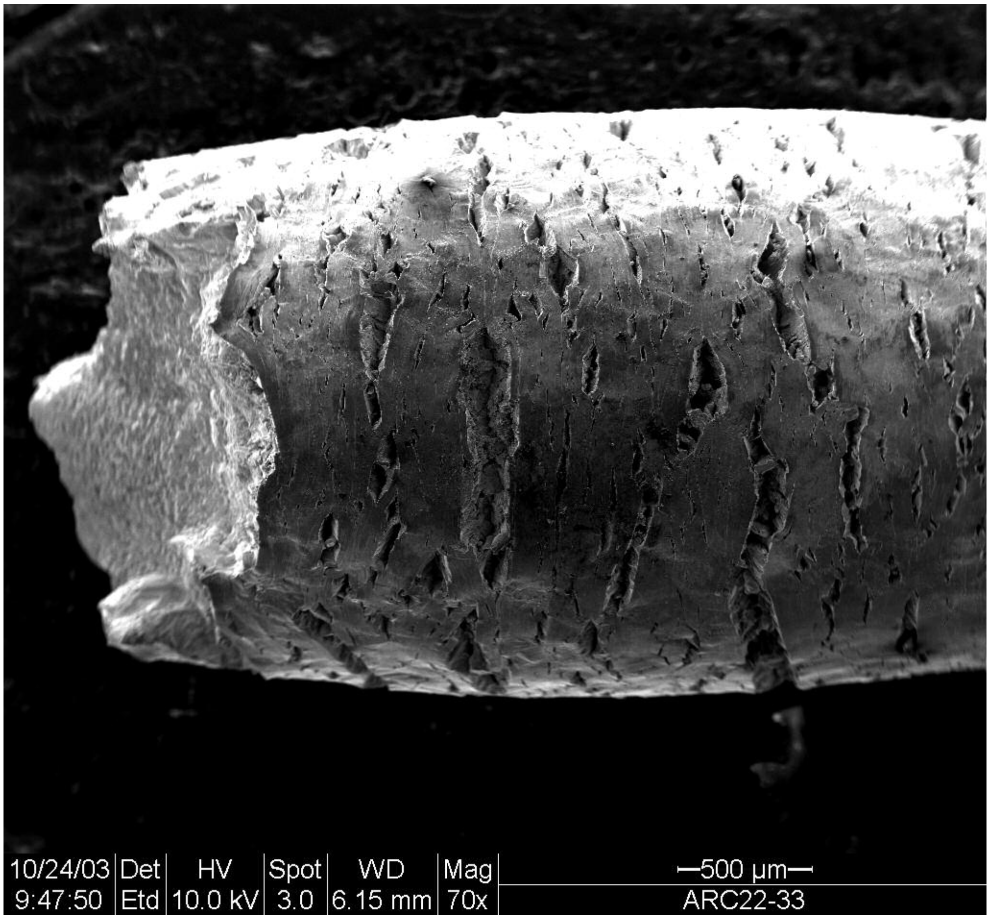

FIGURE 2: Alloy C-22 strained in 86°C SCW solution at +400 mV SSC applied potential.

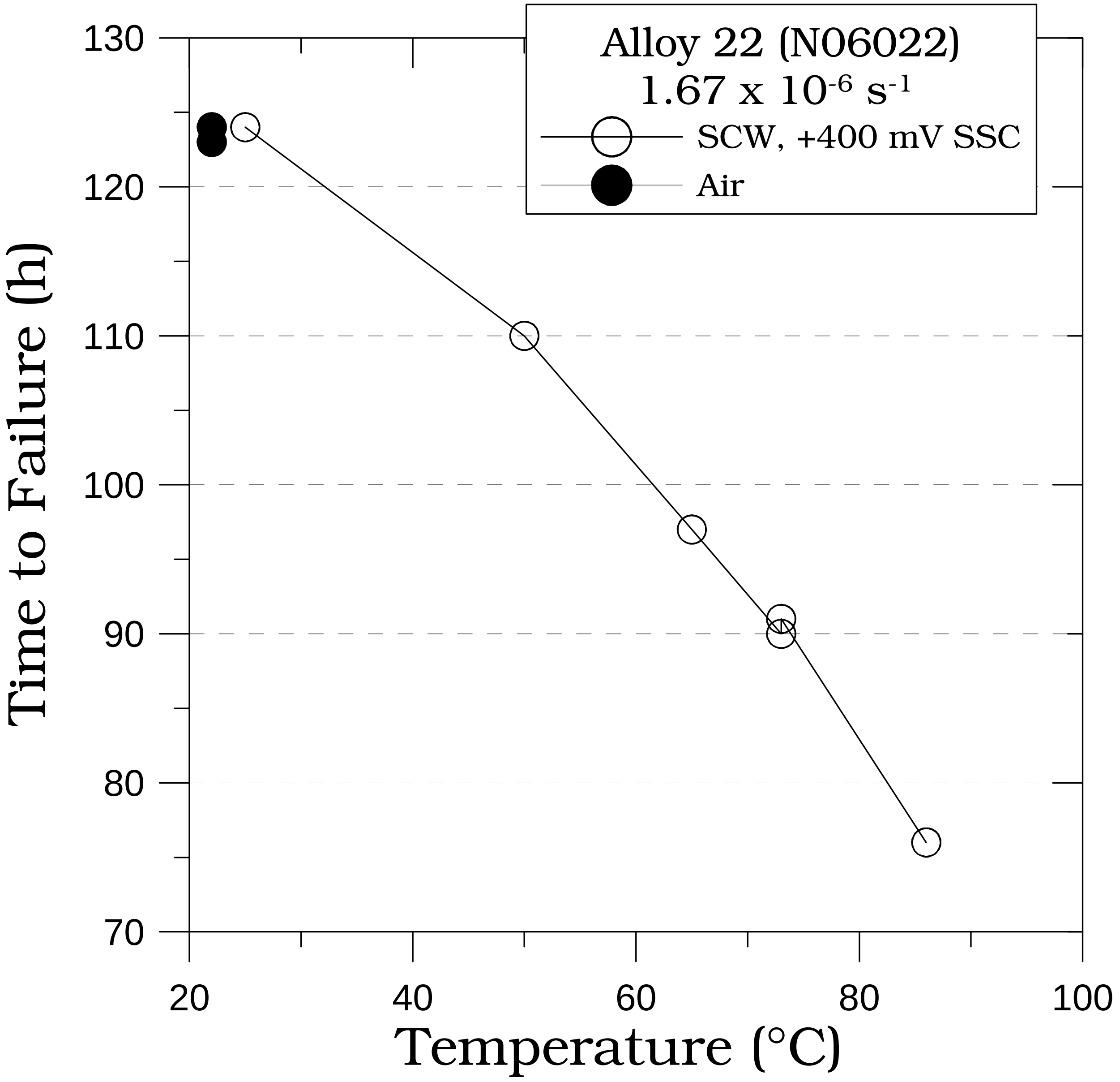

FIGURE 3: Effect of temperature on the SCC susceptibility of N06022 in SCW at an applied potential of +400 mV.