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Hydrogen embrittlement of 4340 steel due to condensation during vaporized hydrogen peroxide treatment

Mobbassar Hassan Sk, Ruel A. Overfelt*, R. Lance Haney, Jeffrey W. Fergus

National Center of Excellence for Research in the Intermodal Transport Environment, Materials Engineering, Auburn University, Auburn, AL 36849, United States

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ABSTRACT

Hydrogen peroxide vapor has been proposed as a sterilant/decontaminant for usage in buildings and transportation vehicles including emergency vehicles, buses, trains and aircraft. Although the efficacy of the process has been demonstrated, questions regarding the compatibility of vaporized hydrogen peroxide treatments with the many diverse materials of construction have been raised. This paper presents results on the embrittlement of high strength AISI 4340 steel as a result of condensation of the vapor during exposure to vaporized hydrogen peroxide. Notched four point bending samples of AISI 4340 steel were tested using the standard test methods of ASTM F519-06 to quantify susceptibility to hydrogen embrittlement in this aggressive service environment. No embrittlement effects were observed for samples exposed to strictly vapor phase hydrogen peroxide for concentrations up to 1000 ppm H_2O_2 and exposure times of 4.8 h. Higher concentrations of 1300 and 1600 ppm H_2O_2 led to the condensation of the vapor throughout the process chamber and brittle fracture of samples. These results were confirmed by examination of the fracture surfaces of samples using scanning electron microscopy. Samples that were not considered embrittled possessed dimpled fracture surfaces consistent with ductile failure. Embrittled samples exhibited inter-granular fractures along prior austenitic grain boundaries near the root of the notch – a common characteristic of hydrogen embrittlement.

1. Introduction

Vaporized hydrogen peroxide biodecontamination treatments provide rapid sterilization, intrinsic environmental friendliness (i.e., simple by-products composed of only water and oxygen), ease of usage and general compatibility with many materials and systems. Vaporized hydrogen peroxide technology has been utilized for 20 years to sterilize medical and pharmaceutical instruments, devices and clean rooms [1,2].

A schematic of a typical, closed-loop hydrogen peroxide vapor generation system and process isolation chamber is shown in Fig. 1(a). Most hydrogen peroxide vapor generators use 35% (by weight) H_2O_2 in water solution and flash vaporize the solution on a heated plate. Flash vaporization ensures that the concentration of H_2O_2 in the generated vapor is the same as that in the original solution. As shown in Fig. 1(b), typical sterilization/decontamination cycles consist of an initial phase where the temperature of the process chamber is stabilized and the relative humidity decreased to a predetermined level. During this dehumidification phase, warm, dry HEPA-filtered air flows into the enclosure to lower the relative humidity which allows a higher concentration of hydrogen peroxide vapor to be injected into the enclosure without condensation. The next phase is to flash vaporize the hydrogen peroxide and water solution to rapidly increase the amount of hydrogen peroxide vapor to the desired concentration as well as minimize the total cycle time. During the sanitization/decontamination phase, a steady concentration of hydrogen peroxide vapor (typically 250 ppm for 90 min) is maintained to give the desired sanitization/decontamination cycle as often measured by the 6-log kill (i.e., 10^6 reduction) of a commercial biological indicator (BI) spore population of *Geobacillus stearothermophilus*. Once the sanitization/decontamination phase is completed, the enclosure is then aerated with fresh air while any residual hydrogen peroxide vapor breaks down into environmentally benign water and oxygen.

Unger-Binczok et al. [3] note that the literature contains considerable disagreement on the optimum process conditions for vaporized hydrogen peroxide treatments. The levels of hydrogen peroxide and relative humidity in the process chamber are particularly important for antimicrobial efficacy. Unger-Binczok et al. found that the higher the levels of H_2O_2 vapor, the less important was the actual level of relative humidity. Conversely, high microbe inactivation rates were found at low levels of H_2O_2 vapor when the levels of relative humidity were high. In fact, sub-visible levels of microcondensation were found to be necessary for high microbial inactivation rates. Unger-Binczok et al. note that sub-visible levels of microcondensation are associated with the formation of a

* Corresponding author. Tel.: +1 334 844 5940; fax: +1 334 844 3400.
E-mail address: overfra@auburn.edu (R.A. Overfelt).

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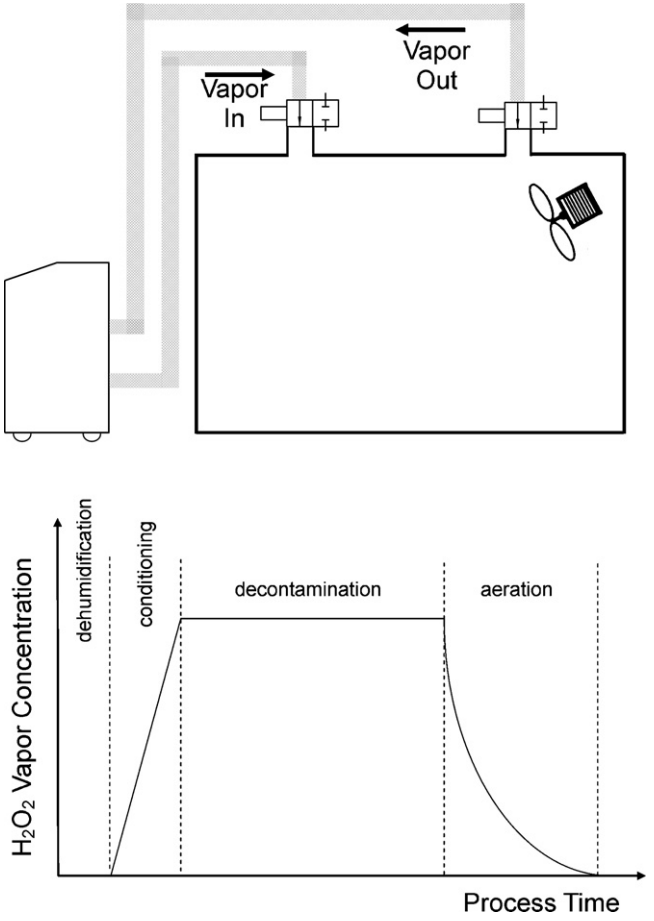

Fig. 1. (a) Schematic of a vaporized hydrogen peroxide bio-decontamination system. (b) Typical concentration profile of vaporized hydrogen peroxide during a decontamination cycle.

thin film of condensate on surfaces prior to the actual appearance of visible droplets. Microcondensation can be detected with optical dew point sensors. Higher levels (i.e., visible levels) of condensation apparently did not increase the antimicrobial efficacy.

Watling et al. [4] investigated the thermodynamics and mass transport conditions for the binary H_2O_2–H_2O liquid/vapor system. These researchers show that the maximum concentration of H_2O_2 vapor in the process isolation chamber can be increased when the initial humidity in the chamber is reduced. The upper limit on H_2O_2 vapor concentration is reached when liquid begins to condense from the vapor solution. This limit is the primary reason for the initial dehumidification step as shown in Fig. 1(b). Condensation is considered to be problematical and can result in nonuniform decontamination as well as prolonged aeration times when porous materials are involved. A hydrogen peroxide vapor treatment process that is designed to avoid condensation is often referred to as a "dry" process.

Watling et al. [4] note that the concentrations of the initial bead of condensed liquid can be as high as 50–75 wt.% H_2O_2 even though the original flash vaporized liquid was only 35 wt.% H_2O_2. Such high concentrations of the condensate can naturally lead to the very high microbial inactivation rates seen by Unger-Binczok et al. [3]. Commercial systems have been developed that control the temperature, humidity and hydrogen peroxide vapor concentrations so that the decontamination process provides so-called "micro-condensation" on the surfaces being cleaned [5]. A hydrogen peroxide vapor treatment process that is designed to provide minute levels of condensation is often referred to as a "wet" process.

Vaporized hydrogen peroxide treatments have been investigated for possible usage in disinfection/decontamination of buildings [6], spacecraft [7], aircraft [8,9] and railcars [10]. The aircraft studies used vaporized hydrogen peroxide concentrations in the range of 150–600 ppm and cycle times of 80–120 min. Maximum concentrations of hydrogen peroxide vapor were carefully controlled to avoid condensation in cool locations within the large aircraft cabins.

Previous studies of the compatibility of vaporized hydrogen peroxide exposures as well as 35% liquid hydrogen peroxide exposures to a range of aerospace grade metals (2024-T351, 2024-T6, 7075-T6 and 304 stainless steel) indicated that the 0.2% offset yield strength, ultimate tensile strength and % elongation to failure were unaffected by the exposures [11,12]. Compatibility tests on aerospace grade composite materials (carbon fiber/epoxy, glass fiber/carbon fiber epoxy and FR4 printed circuit board materials) exhibited no significant changes in flexural strength or flexural strain at peak load after 10 sequential 4.8 h exposures to 450 ppm vaporized hydrogen peroxide. However, some mechanical degradation in the composite samples was observed after a 168 h exposure to 35 wt.% liquid hydrogen peroxide. Delamination of the 1B31 acrylic conformal coating was observed on FR4 printed circuit board materials when exposed to 35 wt.% liquid hydrogen peroxide. Finally, crazing of acrylics was also detected when the vapor process conditions enable condensation to form [11].

Compatibility test results with textiles have been more complex due to the ease of absorption of both hydrogen peroxide and water molecules in typical textiles. Absorbed water is known to decrease the strengths and increase the elongations of many textiles. The tensile strength of nylon was minimally degraded (<10% loss), polyester was slightly degraded (~10% loss), and wool was moderately degraded (~20–30% loss) by exposure to 450 ppm vaporized hydrogen peroxide. The tensile strength and the elongation to failure of leather were severely degraded (~50% loss) by exposure to 450 ppm vaporized hydrogen peroxide. The tensile strength and the elongation to failure of Nomex® were unchanged by exposure to 450 ppm vaporized hydrogen peroxide [13,14].

Finally, the compatibility of vaporized hydrogen peroxide treatment with construction materials of buildings has been recently evaluated [15] and minimal deleterious effects were found.

The specific motivation for the present investigation was to evaluate the resistance of high strength 4340 steel to hydrogen embrittlement from exposure to a range of potential decontamination cycles using conventional vaporized hydrogen peroxide technology.

2. Methods and materials

Aerospace grade, low alloy high-strength AISI 4340 plate (thickness 63.5 mm, AMS 6359, see Table 1) was acquired from Lukens Steel (Coatesville, PA) and machined by Metal Samples Company (Munford, AL) into round tensile bars and square blanks for 4-point bending samples. The original longitudinal orientation of the plate was maintained in the machined tensile bars and the 4-point bend-

Table 1
Composition of test specimens of AISI 4340. Certified compositional data provided by vendor.

Element	C	Cr	Mn	Ni	P	Si	S	Al	Fe
Composition (wt.%)	0.39	0.88	0.65	1.69	0.005	0.25	0.1	0.03	Bal