2021 Award Nomination

Title of Innovation:
Innovative & Safe Halogen Corrosion Test

Nominee(s)
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Category:

Coatings and Linings	Instrumentation
Cathodic Protection	**Testing**
Materials Design	Modeling/Risk Assessment
Chemical Treatment	Other—fill in

Dates of Innovation Development:
September 2014 – September 2017

Web site: https://www.cpp.edu/engineering/cme/

Summary Description:

The innovation is a method and system for an economical and safe approach to conducting high temperature halogen gas corrosion tests on metallic alloys. This eliminates the need for the use of dangerous, flowing halogen gas systems and the attendant safety issues. The test setup consists of a two-compartment ampoule where a vestibule connects these two compartments. A pre-selected mixture of salts is placed in one compartment to generate a specific partial pressure of halogen gas; and a metallic alloy is placed in the other compartment. The ampoule is then heated to a pre-determined temperature and held at this temperature for the desired time. A halogen gas of a specific partial pressure is generated from the mixture of salts and because the ampoule creates a sealed environment, the metallic alloy is under constant halogenation during the pre-determined time period. The metallic alloy is removed for examination when the pre-determined time period expires.

Full Description:

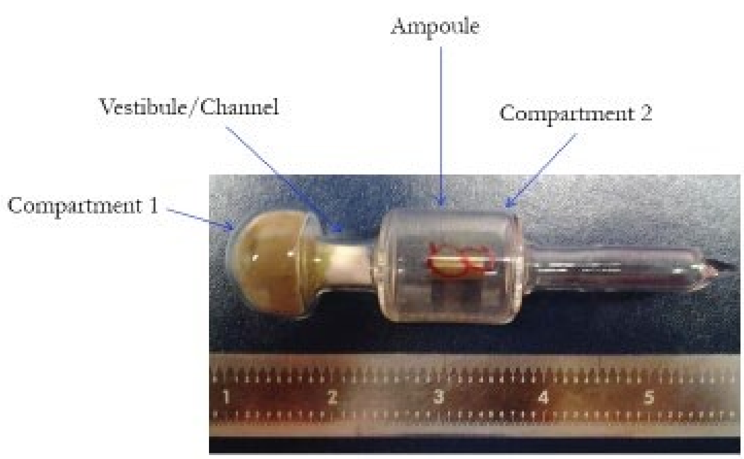
(Please provide complete answers to the questions below. Graphs, charts, and photos can be inserted to support the answers.)

1. What is the innovation?

The innovation is a method and system for an economical and safe approach to conducting high temperature halogen gas corrosion tests on metallic alloys. This eliminates the need for the use of dangerous, flowing halogen gas systems and the attendant safety issues.

2. How does the innovation work?

The present invention involves exposing a metallic alloy to a halogen gas of a known partial pressure at a pre-determined temperature over a pre-determined time period. Flowing gases can be used to set up the desired partial pressures in the atmosphere. However, these pose significant safety issues and require scrubbing systems. In the present invention, an innovative closed system was devised, thereby eliminating the necessity for an external, continuous flow system with its associated safety concerns. This innovation provided the necessary gaseous environment to which the metal or alloy was exposed while eliminating safety concerns. In one embodiment, as shown in Fig. 1, a sealed container 1, e.g., an ampoule, having two compartments (2 and 4) is disclosed. These two compartments (2 and 4) are connected via a channel 3, e.g., a vestibule. Fluids (gases or liquid) may flow freely between these two compartments. The sealed container 1 should be heat conductive. Preferably, the sealed container 1 is purged with an inert gas, such as argon. In some embodiments, the sealed container 1 is made of glass or quartz.



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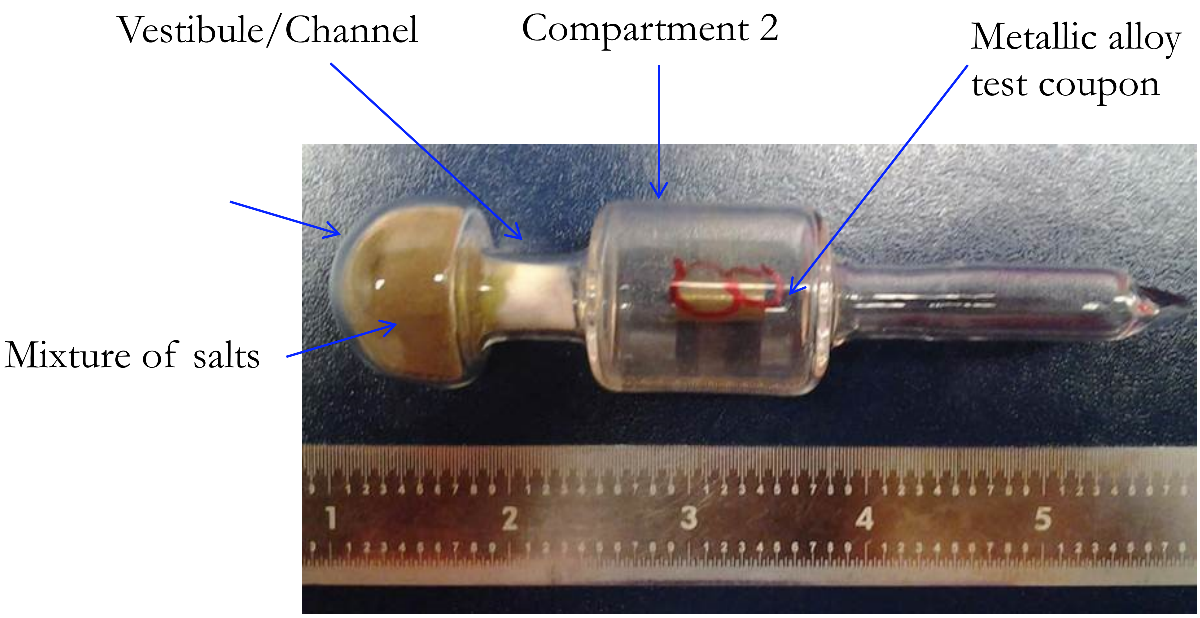


(2)

Figures 1 and 2. Test Ampoule and description of components

In the present invention, as shown in Fig. 2, a pre-selected mixture of salts 5, which is capable of generating a halogen gas at equilibrium, is placed in one compartment 2. In one embodiment, the pre-selected mixture 5 comprises an equimolar mixture of nickel (Ni) and nickel chloride (NiCl2), which at equilibrium generates chlorine gas of a known partial pressure according to the following thermodynamic equilibrium:

$$Ni\ (s) + Cl_2\ (g) \Rightarrow NiCl_2\ (s)$$

A metallic alloy element 6 is placed in the other compartment. In one embodiment, the metallic alloy element 6 is a metallic alloy coupon. The sealed container 1 containing the mixture 5 and the metallic alloy element 6 is then heated to a pre-determined temperature (e.g., 626°C) and held at this temperature for a pre-determined time period (e.g., 100. 250, 1,000 hours, etc.). At the pre-determined temperature, a halogen gas (e.g., chlorine gas) of a known partial pressure is generated from the mixture 5, which flows through the channel 3 and filled fills the entire sealed container 1. The amount of the mixture should be sufficient to generate sufficient halogen gas for the duration of the pre-determined time period. Therefore, the metallic alloy element 6 is constantly exposed to the halogen gas under the known partial pressure during the entire pre-determined time period. Upon expiration of the pre-determined time period, the metallic alloy element 6 is then removed from the sealed container 1 and cleaned (e.g., by ultrasonic cleaning) in order to be examined and determine the results of halogenation (e.g., corrosion rate) of the metallic alloy element 6.

The test coupon (6) may be analyzed in various ways including mass loss analysis and destructive metallography using optical and/or electron microscopy. In one embodiment, the mass of the metallic coupon is recorded before exposing to the halogen gas in the sealed container 1. The mass of the metallic alloy (6) is again recorded after exposing to the halogen gas in the sealed container 1 and after being cleaned. The mass change of the test coupon before and after exposing to the halogen gas is normalized to the density, surface area, and test duration can yield the corrosion rate in the appropriate units.

3. Describe the corrosion problem or technological gap that sparked the development of the innovation. How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

Many metals readily react with halogen gases at elevated temperatures to form metal halides. Some metal halides exhibit low melting points and some even sublime at relatively low temperatures. As a result, metallic alloys that readily form metal halides are potential candidates for high-temperature halogen corrosion. Industrial environments often contain halogen gases. Therefore, reactor vessels that are resistant to high temperature halogenation attack are often required. Hydrogen (H_2) and silicon-tetrachloride ($SiCl_4$) are used at temperatures between 950° to 1150° F (or 510° to 621°C) and at a relatively high pressure to produce solar grade silicon. The reaction between hydrogen and silicon-tetrachloride results in the formation of hydrochloric acid gas, HCl (g). The equilibrium between hydrogen gas and hydrochloric acid gas defines a partial pressure of chlorine gas (p_{Cl_2}) that can lead to high temperature chloridation attack on reactor vessels which are made of metallic alloys. Therefore, there is a need to determine the resistance of metallic alloys to environments containing halogen gases.

Traditionally, metallurgical corrosion testing involves creating an accelerated simulated environment for corrosion testing using extensive laboratory equipment and constant monitoring to ensure safety. In the case of halogen attack, this involves the setup of elaborate and expensive safety protocols with the need for continuous monitoring and with the ever-present danger of a safety incident. Clearly, a need exists for a safe and lower cost approach to high temperature halogen corrosion testing.

Therefore, the present invention fills a technical need while preserving safety and reducing costs for testing.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the

innovation.

Yes, this innovation has been reduced to practice and tested in the laboratory. Various alloys have been tested in this test setup. Examples of the macrophotographs of Alloys UNS N08120 and UNS N12160 for 1000 hours at 626°C (Figure 3). Below the macrographs is an example of the corrosive attack in these environments. The cross-sectional images shows the attack with compositions at selected points (Figure 4).

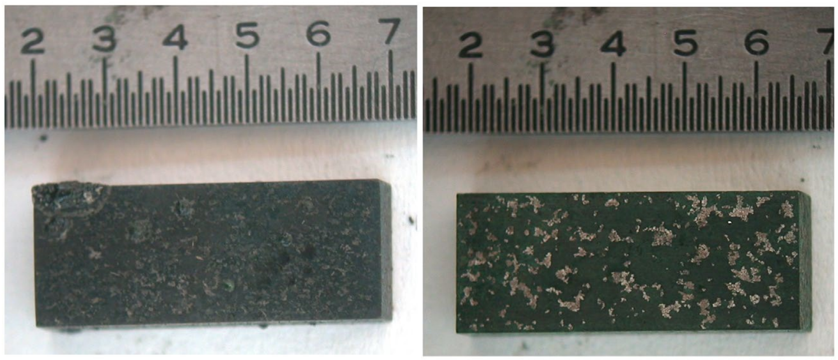
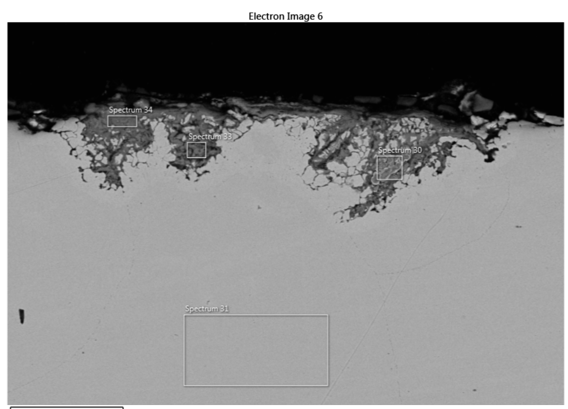


Figure 3. Surface appearance of selected samples of Haynes 120 and Haynes 160 exposed for 1000 h at 626°C.



Spectrum #	O	Al	Si	Cl	Cr	Co	Ni
30	48.34	0.38	5.36	0.48	20.19	6.02	19.24
31	-	-	6.16	-	29.91	28.12	35.35
33	61.42	0.87	7.02	0.68	26.3	1.99	1.1
34	59.01	0.32	5.39	0.53	28.09	2.24	2.36

Figure 4. EDS results from the identified location in the Back Scattered Electron Image from the internal corrosion reaction product in the HR160 test specimen.

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?

Corrosion control and prevention activities start with the proper recognition of the role of the material and the environment in which it is supposed to function. Predicting the lifetime of the materials becomes key to assuring the customer of the functionality of the equipment for a guaranteed period of time. The development of innovative laboratory testing protocols is a key component in the overall corrosion control and prevention strategies. High temperature halogen corrosion testing protocols are fraught with danger and safety is a primary concern.

This invention provides a method for testing metallic alloys in a halogen-containing environment with ease and reduced safety concerns. Moreover, this invention provides a method that allows for long term exposure of metallic alloys in order to conduct testing of said metallic alloys in a halogen-containing environment.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?

This innovation is available for licensing. Reaching potential customers of this technology innovation is challenging. One of the approaches to reach the appropriate uses is through the industrial sponsor of this work. Other approaches to bringing this technology innovation to the attention of potential customers is to be recognized through awards such as these.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

Yes - A US patent was issued for this work. US Patent No: 9,869,629 B1 issued on January 16, 2018. The inventors on the patent are: Vilupanur A. Ravi, Juan C. Nava and Shahan S. Kasnakjian.