Standard Operating Procedure

(SOP)

for Improved Assessment of Chromium Evaporation Rates in Alloys

Test ID: HTE-P-28

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

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3. Procedures

a. Scope and Applicability

This document outlines the SOP for enhanced assessment of Cr evaporation rates in alloys. This procedure effectively addresses potential interferences arising from various sources: (1) the deposition of silicon deposits derived from the quartz furnace tube, (2) the adverse impacts of sodium species on the alloy oxidation process due to the use of sodium carbonate for improved capture of Cr oxyhydroxide species, and (3) the chemical interactions between Cr gaseous species and the alumina furnace tube. A schematic representation of the Cr evaporation test is depicted in Figure 1[1].

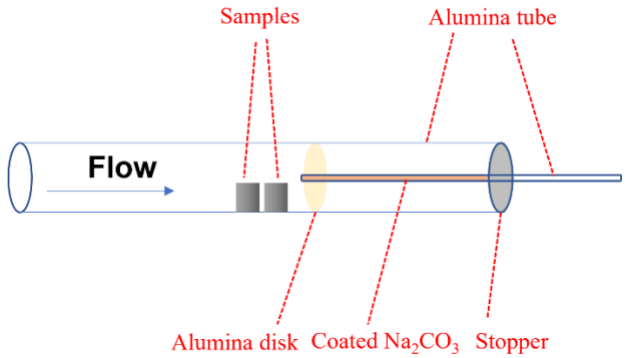


Figure 1 Schematic of the Cr evaporation test of alloys in sodium carbonate coated thin alumina tube.

b. Summary of Method

The humidity within the alumina tube is meticulously regulated through a combination of a gas flow meter, a PID temperature controller, and an MH-series humidifier. Subsequently, alloy samples are carefully positioned in an upright orientation within the alumina tube, with the wide side of the sample aligned with the direction of gas flow, after having undergone a standard grinding process. To facilitate the collection of evaporated Cr species emitted by the alloy, a thin alumina tube coated with Na_2CO_3 is employed. The absorbed Cr species are subsequently dissolved into the collected solution, which is then subjected to ICP-AES tests for analysis.

c. Definitions

- Chromium (Cr)
- Inductively coupled plasma atomic emission spectroscopy (ICP-AES)
- Deionized water (DI water)
- Proportional-Integral-Derivative (PID)
- Scanning electron microscope (SEM)
- X-Ray diffraction (XRD)

d. Health & Safety Warning

- High temperature tube furnace may cause fire hazard and severe burns.
- To protect against exposure to the toxic hexavalent gaseous Cr species, it is imperative to wear gloves and a mask when conducting the experiment.
- Adequate ventilation or a fume hood is essential for handling potential leaks of the toxic hexavalent gaseous Cr species.

e. Cautions

- The MH-series humidifier must be maintained with proper moisture levels to ensure the integrity of its permeable membrane[2].
- The alloy samples must be positioned in an upright orientation within the alumina tube to facilitate the flow of water vapor across the sample surface[1, 3].
- The coated Na_2CO_3 must be to be uniformly distributed along the interior wall of the thin alumina tube to reduce the reaction area where chromium species reacts with alumina tube[1]

f. Interferences

- Gas tightness-must be checked to eusure there is no leakage.
- Alloy samples orientation-must be aligned with the gas flow direction
- Humidity of inlet air-must be controlled consistent during the test
- Temperature- must be controlled consistent during the test
- Undissolved Na_2CO_3- must be all collected after the test

g. Personnel Qualifications / Responsibilities

The experimenter should possess a proficient understanding of the gas flow meter, PID temperature controller, MH-series humidifier, fittings of the system and wet chemistry. This is essential for effectively managing humidity control within the inlet air, guaranteeing gas tightness, and maintaining uniform Na_2CO_3 coating on the alumina tube.

h. Equipment and Supplies

- Water tank
- Gas flow meter
- PID temperature controller
- Thermocouple
- Heating strips
- Lab jacks
- MH-series humidifier
- DI water adding system
- Tube furnaces (e.g., MTI, GSL-1100X-NT-LD)
- Thin alumina tubes
- Alumina tube
- Alumina disk
- Alloy samples
- Stoppers
- Teflon tubes
- Filtering flasks
- Cooling systems (Hydrofarm, Model AACH10)

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization
  - Before initiating the heating process, it is imperative to conduct a leak test at room temperature and atmospheric pressure using air. The leak rate should not exceed 5% for compliance.

- The thin alumina tubes must be uniformly coated with $NaHCO_3$ and subsequently pre-heated at 250 °C for 2 h to ensure their transformation to Na_2CO_3.
- Ensure that the alloy samples are positioned vertically within the alumina tube, with their wide side aligned to the direction of gas flow.

- Sample Collection

  Transfer the collected solution into a 5-liter beaker. Proceed to utilize this collected solution to entirely dissolve the Na_2CO_3 coating present on the thin alumina tube. During this process, be sure to record the volume of the collected solution. Alloy samples are subsequently subjected to SEM and XRD analysis.

- Sample Handling and Preservation

  A portion of the collected solution is transferred into a centrifuge tube and subsequently analyzed using ICP-AES test.

- Sample Preparation and Analysis
  - Prior to the Cr evaporation testing, all surfaces of the specimens are mechanically ground to 800 grit, then all specimens are ultrasonically cleaned in acetone and dried by a dryer. The final dimension of each sample was approximated to 25mm * 20mm * 1mm with an exposed surface area approximately to 11 cm^2.
  - To maintain a stable flow field during the oxidation process, a thin alumina plate with a width similar to the interior diameter of the alumina tubes is prepared. It featured a rectangular slot measuring 20 × 1 mm^2, allowing the samples to stand upright inside the alumina tubes[4].

Figure 2 Thin alumina plate with slots (top view)

- Troubleshooting

  Several factors that might introduce interferences into the Cr evaporation tests include:
  - Inaccurate gas flow rate

- Inaccurate temperature
- Low water level in the water tank
- Gas leakage
- Undissolved sodium carbonate

- Data Acquisition, Calculations & Data Reduction Requirements

  Following the ICP-AES test, the concentration of Cr in the collected solution was determined. This value was then multiplied by the volume of the solution to calculate the quantity of evaporated Cr. To obtain the Cr evaporation rate (Unit: kg/(m^2·s)), this quantity was divided by the specific surface area of the alloys and the specific duration of the operation.

- Computer Hardware & Software

  Not applicable for this SOP

j. Data and Records Management

Not applicable for this SOP.

4. Quality Control and Quality Assurance Section

- Prior to Cr evaporation experiments, all surfaces of the specimens are mechanically ground to 800 grit, then all specimens are ultrasonically cleaned in acetone and dried by a drier.
- A 20 × 1 mm^2 slot is drilled on a thin alumina plate to hold a sample upright in the alumina tubes to maintain a stable flow field during the Cr evaporation test.
- Thin alumina tubes are uniformly coated with $NaHCO_3$ and subsequently pre-heated at 250 °C for 2 h to ensure their transformation to Na_2CO_3.
- Prior to heating up, gas tightness test is carried out to ensure a leak rate lower than 5%.
- The humidified air is not pumped in until the tube furnace reaches the designated temperature at a heating rate of 3 °C/min.
- The coated Na_2CO_3 on the thin alumina tube must be fully dissolved in the collected solution.
- Rigorous standard quality assurance procedures are implemented to ensure the accurate evaluation of the Cr concentration in the collected solution during the ICP-AES test.

5. Reference Section

[1] L. Zhou, W. Li, M.P. Brady, Z. Zeng, L. Ma, Y. Wang, S. Hu, X. Liu. Improved Assessment of Chromium Evaporation Rates in Solid Oxide Cell Balance of Plant Component Alloys. *High Temperature Corrosion of Materials* **2023**. DOI: 10.1007/s11085-023-10207-w.

[2] L. Zhou, Z. Zeng, M.P. Brady, D.N. Leonard, H.M. Meyer, Y. Yamamoto, W. Li, G. Collins, X. Liu. Chromium evaporation and oxidation characteristics of alumina-forming austenitic stainless steels for balance of plant applications in solid oxide fuel cells. *International Journal of Hydrogen Energy* **2021**, *46* (41), 21619-21633. DOI: 10.1016/j.ijhydene.2021.04.002.

[3] L. Zhou, M.P. Brady, W. Li, T.B. Eldred, R. Garcia, Z. Zeng, L. Ma, Y. Wang, S. Hu, X. Liu. Alumina-forming austenitic stainless steel for high durability and chromium-evaporation minimized balance of plant components in solid oxide fuel cells. *International Journal of Hydrogen Energy* **2022**, *47* (90), 38334-38347. DOI: 10.1016/j.ijhydene.2022.09.010.

[4] L. Zhou, W. Li, M.P. Brady, T.B. Eldred, R. Garcia, L. Ma, Y. Wang, S. Hu, W. Li, X. Liu. Long-term oxidation and chromium evaporation behavior of Al2O3-forming austenitic stainless steel for 900 °C balance-of-plant components applications in solid oxide fuel cells. *International Journal of Hydrogen Energy* **2023**. DOI: 10.1016/j.ijhydene.2023.10.041.