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Hydrogen measurement during steam oxidation using coupled thermogravimetric analysis and quadrupole mass spectrometry

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A B S T R A C T

An analytical technique is presented with the goal of measuring reaction kinetics during steam oxidation reactions for three cases in which obtaining kinetics information often requires a prohibitive amount of time and cost. The technique presented relies on coupling thermogravimetric analysis (TGA) with a quantitative hydrogen measurement technique using quadrupole mass spectrometry (QMS). The first case considered is in differentiating between the kinetics of steam oxidation reactions and those for simultaneously reacting gaseous impurities such as nitrogen or oxygen. The second case allows one to independently measure the kinetics of oxide and hydride formation for systems in which both of these reactions are known to take place during steam oxidation. The third case deals with measuring the kinetics of formation for competing volatile and non-volatile oxides during certain steam oxidation reactions. In order to meet the requirements of the coupled technique, a methodology is presented which attempts to provide quantitative measurement of hydrogen generation using QMS in the presence of an interfering fragmentation species, namely water vapor. This is achieved such that all calibrations and corrections are performed during the TGA baseline and steam oxidation programs, making system operation virtually identical to standard TGA. Benchmarking results showed a relative error in hydrogen measurement of 5.7–8.4% following the application of a correction factor. Finally, suggestions are made for possible improvements to the presented technique so that it may be better applied to the three cases presented.

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1. Introduction

The steam oxidation behavior of any cladding material to be used in nuclear reactor systems must be understood so that informed decisions may be made in materials selection and engineering controls. The ultimate goal of material selection in designing nuclear reactor systems is to prevent the release of radioactive fission products to the environment during normal conditions as well during severe accidents. Because failure of the fuel cladding is generally accepted to result in the release of much of the gaseous and volatile fission product inventory to the reactor coolant, this condition must be avoided [1–6]. Further, this has the potential to release material to the reactor containment vessel, and ultimately, to the environment.

The first line of defense in minimizing the possibility of fission product release is in ensuring the integrity of the fuel cladding is maintained. Exposure of these cladding materials to high temperatures in the presence of steam commonly results in steam oxidation reactions taking place [3–12]. The effects of these steam oxidation reactions are twofold. First, the material is oxidized, and thus, the integrity of the cladding becomes compromised due to embrittlement and loss of ductility [2–5]. It is crucial that

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the cladding integrity remains intact, especially during severe accidents, so understanding these degradation mechanisms is important to cladding design. The second effect is that steam oxidation reactions can produce significant volumes of potentially explosive hydrogen gas [3,4,7–11]. Perhaps nowhere was this demonstrated so dramatically as in the hydrogen explosions during the Fukushima Daiichi nuclear disaster.

The technique presented in this paper attempts to couple mass change with hydrogen generation data so that the combined data may be used to study steam oxidation reactions. This coupling has the potential to allow one to gather continuous, real-time kinetics data on steam oxidation in the presence of gaseous impurities, steam oxidation with hydride formation, and the steam oxidation of systems with a volatile species. The method presented in this paper seeks to improve upon and complement the work performed by others to overcome many of the challenges involved in the study of steam oxidation reactions. Some of these challenges include measuring steam oxidation kinetics in the presence of gaseous impurities such as oxygen or nitrogen, measuring the steam oxidation kinetics for materials that are known to form hydrides, and determining the kinetics for systems containing a volatile oxide species.

2. Mathematical treatment

Simultaneous, real-time measurement of mass change and hydrogen generation during steam oxidation reactions has the potential to provide more information to the researcher than was previously available and in a more efficient manner. For example, it may be possible to gain access to subtle kinetics mechanism changes that would otherwise be overlooked. The technique presented in the experimental section relies on coupled thermogravimetric analysis (TGA) and quadrupole mass spectrometry (QMS) to gather this information. Three cases are presented below which demonstrate the possible uses of such a combined technique.

2.1. Case 1 – competing mass gain mechanisms

First, the situation of competing mass gain mechanisms through more than one reacting species is considered. It can be assumed that the environment seen by cladding materials during a severe accident will rarely be composed of pure steam, and that the non-steam gaseous species will affect the behavior of the material in question. Indeed, it has been found that steam oxidation of reactor materials is significantly influenced by gaseous impurities such as oxygen, nitrogen, and hydrogen [6,12–14]. Many of these studies rely on discrete data collection methods in which acquiring continuous behavior is both time consuming and the very act of observation may affect the material in unknown ways [3,4,6–11,15,16]. The TGA technique is attractive due to its ability to provide *in situ* determination of a sample's mass change during exposure to thermodynamic stimuli. Although this is far more powerful than

arrested tests to examine the mass change and evolved microstructure, TGA alone does suffer from limitations.

An example is in differentiating between mass gains from oxygen through steam oxidation and mass gains from nitrogen impurities. Thermogravimetric analysis can readily discern the weight change of a sample but no detail is available regarding the cause outside of thermodynamic judgment or additional characterization. Competing mass gains may be differentiated through microscopy and spectroscopy, but such an approach inherently limits the fidelity of collected data. Further, the material must be perturbed through cooling, followed by the mounting and polishing procedure which is often required for microscopy. Barring the use of radioactive tracers, it is impossible to differentiate between mass gains from steam oxidation and mass gains from oxidation by molecular oxygen impurities. It therefore becomes difficult to determine how the steam oxidation reaction kinetics and mechanisms are changed by the addition of these species.

In order for this coupled technique to be applicable for this case, it must be assumed that all hydrogen measured using QMS is produced through steam oxidation, and that one mole of atomic oxygen is added to the sample material for every mole of molecular hydrogen measured. This assumption is reasonable for testing conditions which are relatively pure, and for which hydride formation contributes little to the sample mass gain.

The mass gain caused by steam oxidation and impurities may be individually calculated by starting with the following equation;

$$\Delta m(\text{TGA}) = \Delta m(\text{X}) + \Delta m(\text{QMS}) \tag{1}$$

where $\Delta m(\text{TGA})$ is the mass gain as measured by the TGA instrument, in this case $\Delta m(\text{X})$ is the mass gain from impurities such as oxygen and nitrogen, and $\Delta m(\text{QMS})$ is the mass gain from the steam oxidation reaction as calculated by the QMS hydrogen measurement using the assumptions mentioned above. The $\Delta m(\text{QMS})$ term is determined by measuring the molar flow rate using QMS. The full procedure is presented in a later section, but the basic equation is shown as Eq. (2), where M_{O} is the molar mass of atomic oxygen. This equation may also be interpreted as being the mass gain due to steam oxidation for this first case.

$$\Delta m(\text{QMS}) = mol(\text{H}_2) \times M_{\text{O}} \tag{2}$$

Combining Eqs. (1) and (2) results in an equation corresponding to the mass gain caused by impurities.

$$\Delta m(\text{X}) = \Delta m(\text{TGA}) - mol(\text{H}_2) \times M_{\text{O}} \tag{3}$$

2.2. Case 2 – oxide and hydride formation

The next situation to be considered is that in which there are competing oxide and hydride mass gain mechanisms. Study of steam oxidation behavior in zirconium alloys is complicated due to zirconium's affinity for hydrogen [2,8–10,17]. The formation of hydrides in these materials is important in understanding and ensuring the mechanical integrity of the material during a severe nuclear accident. It is widely accepted that formation of hydride platelets is a major contributor to the degradation