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A novel Zr-1Nb alloy has begun development based on a working model that takes into account the hydrogen permeabilities for zirconium and niobium metals. The β-Nb secondary phase particles (SPPs) in Zr-1Nb are believed to promote more rapid hydrogen dynamics in the alloy in comparison to other zirconium alloys. Furthermore, in the case of the Zr-1Nb alloys, some hydrogen release is possible at the lower temperatures corresponding to outages when the partial pressure of H_2 in the coolant is less. These characteristics lessen the negative synergism between corrosion and hydriding that is otherwise observed in cladding alloys without niobium. In accord with the working model, development of nanoscale precursors was initiated to enhance the performance of existing Zr-1Nb alloys. Their characteristics and properties can be compared to oxide-dispersion strengthened alloys, and material additions have been proposed to zirconium-based LWR cladding to guard further against hydriding and to fix the size of the SPPs for microstructure stability enhancements. A preparative route is being investigated that does not require mechanical alloying, and 10 nanometer molybdenum particles have been prepared which are part of the nanoscale precursors. If successful, the approach has implications for long term dry storage of used fuel and for new routes to nanoferritic and ODS alloys.

I. INTRODUCTION

In some respects, there is no strong motivation for new alloy development for cladding materials in LWRs. The costs to introduce a lead test assembly are high, so that substantial cost benefits must be realizable for such an investment to be undertaken. Furthermore, some economic analyses indicate there is little or no incentive for extending burnups beyond 60-70 GWD/MT, and an average burnup of this magnitude appears achievable with existing Zr-1Nb alloys coupled to advanced fuel management methods.[1,2] Enrichments greater than 5% will be needed to extend burnup beyond 70 GWD/MT, and the cost will be great to equip and license all operations to handle the higher enrichments. Other reasons, however, can motivate new alloy development for cladding.

Uprates are always appealing for existing capital investment, but uprates bring higher temperatures, faster corrosion, and can bring increased hydriding rates that exacerbate the hydride rim structure. A potential drawback is increased cladding failure. Cladding alloy improvements may help in this aspect. Cladding alloy improvements may help with fretting failure, which has been a leading cause;[3] and they can still help, with lesser incentive, with raising the average burnup to 60-70 GWD/MT. Lastly, for non-recycle fuel operations, such as in the U.S., cladding alloy improvements may benefit long-term dry storage of used fuel, especially with regard to radial versus circumferential hydride deposits, if the alloy improvements are founded in a model that can be leveraged to develop and optimize processes for extracting hydrogen from the assemblies going into dry storage.

A working model is here described for cladding alloy improvements that recognizes cladding improvements already reported in the literature. While the common perception for the role of niobium in the Zr-1Nb alloys is improved performance against corrosion, this working model takes into account the permeability of hydrogen in zirconium and niobium. A key feature of the working model is the capacity for the alloy to release some of the hydrogen as H_2 into the coolant at the lower temperatures occurring during outages. Since both metals have a decreasing enthalpy of solution (for hydrogen) with increasing temperature, hydrogen can diffuse down a temperature gradient toward a higher hydrogen concentration (the coolant side).[4] However, the H-permeability for niobium is more sensitive toward temperature than it is for zirconium (Figure 1).[5,6] As a result, some of the dissolved H atoms can recombine as H_2 and be released into the coolant, at the lower partial pressures of H_2 corresponding to the lower temperatures for an outage (e.g., with less corrosion occurring). Thus this working model holds that Zr-1Nb alloys, with β-Nb and minor amounts of dissolved niobium in the α-Zr matrix, support the release of H_2 to a greater extent than other zirconium alloys without niobium, because of differences in the permeability. The stability of the entire system can thereby be enhanced with a slower overall growth of hydrogen content and oxide thickness, as will be discussed in the context of various reports.

Based on the above observations, a new alloy can be proposed that seeks several key properties:[7]

- a uniform dispersion of niobium within the alloy having even smaller dimensions than existing Zr-1Nb alloys (targeting dimensions as small as 10-20 nm as fabricated)
- stabilizing agents that help reduce alloy processing such as heat treatments and cold working
- stabilizing agents that promote high niobium contents in the β-Nb SPPs (second, or secondary phase particles) to enhance hydrogen permeability
- stabilizing agents that pin the niobium, preventing SPP growth under irradiation
- stabilizing agents that also may increase the stability of the ZrO_2 corrosion layer.

These features may be achievable with a zirconium alloy that includes minor amounts of tin, niobium, and molybdenum along with trace amounts of an oxide such as Y_2O_3 or Nd_2O_3. Since molybdenum is not soluble in α-Zr, [8] and since niobium forms a fairly ideal solid solution with molybdenum, [9] it is expected that the niobium will more readily precipitate out of the zirconium as compared to zirconium alloys without molybdenum. This characteristic is intended to promote the H-permeability via a uniform nanodispersion of β-Nb SPPs in the cladding alloy. Trace level additions of yttria (or other suitable oxides) are intended for their association with niobium because niobium is oxophilic, and because its chemistry supports the formation of suboxides such as NbO and NbO_2. The desired uniform nanodispersion may therefore consist of particles containing niobium, molybdenum, niobium suboxides, yttria, and possibly complex oxides; and the alloy overall will present properties and microstructural characteristics of oxide-dispersion strengthened type (ODS-type) alloys such as those involving Cr, Ti, TiO_x, and Y_2O_3, and complex oxides. [10] The incorporation of molybdenum, niobium, their oxides and suboxides, and yttria in the alloy is directed toward facilitating hydrogen transport through the oxide layer, stabilizing the alloy microstructure, and stabilizing the ZrO_2 corrosion layer to some extent.

ODS-type alloy production has been largely empirical for the last 100 years, and typically it is costly compared to traditional alloy fabrication methods. [11] Mechanical alloying is often employed to mill the ODS agents (such as Y_2O_3) with the metals for long periods of time, and development efforts are practically entirely Edisonian. Scale-up requires extensive development to reproduce the desired properties discovered at laboratory scale. In addition, the inherent nature of the uniformly distributed ODS particles have precluded conventional fusion welding and joining due to agglomeration in the weld zone during liquefaction. A primary interest then is to develop nanoscale precursor agents that can be processed in a way that either allows their dispersive characteristics to be preserved during handling or allows for the dispersive characteristic to be recovered during melting and freezing. With this aim, a few nanoscale precursor agents have been identified, such as yttria-coated molybdenum, and early achievements are here reported for the production of 10-nm sized particles of molybdenum.

In what follows, the background for the working model is discussed, then proposed alloy constitutions, proposed alloy fabrication, progress to date, and finally some conclusions.

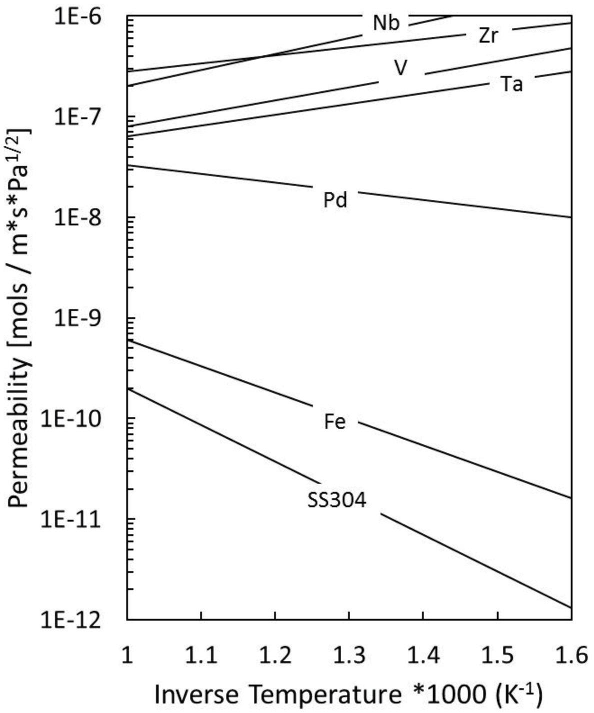

Fig. 1. Permeability of Hydrogen in Selected Metals. Redrawn from Refs 5, 6.

II. BACKGROUND FOR WORKING MODEL

While the success of Zr-1Nb alloys is related to their improved performance against corrosion, improved performance is also observed for hydriding, dimensional stability, and creep in Zirlo™, E110, and M5® alloys.[12,13,14,15,16,17,18] As H_2 is generated by the reaction of water with zirconium, a fraction of the H_2 is picked up by the cladding. The hydrogen dissolves, and upon exceeding its low solubility, the δ-phase precipitates as platelets. In the simplest model, more extensive corrosion produces more hydrogen and a greater uptake, although the hydrogen pickup fraction may not be constant over time.

Some authors have noted the potential for a negative, synergistic interaction between the accumulation of hydrogen and the growth of the oxide layer.[19,20,21] High oxidation rates, and even differential rates of oxidation with temperature variations, can produce non-uniform hydrogen distributions in the cladding. The pickup of hydrogen will therefore be incommensurate with the growth of the oxide layer at the metal oxide interface. Subsequent migration of hydrogen during outages (see below) can produce volumetric changes in the metal incommensurate with the oxide layer, thereby introducing cracks and defects in the oxide that can spur further corrosion, especially on return to power.

Clearly the Zr-1Nb alloys are exceptional performers, and their improved properties may be related not only to corrosion, but also to the physicochemical properties of the alloys. It is possible that one cladding alloy can respond more quickly than another in its drive toward a steady-state dynamic for the hydrogen concentration gradient dictated by the thermal gradient. Then any volumetric changes in the alloy resulting from hydrogen pickup are more readily manifest at the same tempo as changes in the oxide layer, eliminating some fraction of the negative, synergistic interaction. Likewise, a fraction of hydrogen may be released from the cladding as H_2 during outages when the temperature is lowered, less corrosion is occurring, and the partial pressure of H_2 in the coolant is less. Here again, one cladding alloy may be more facile than another in releasing H_2 under such conditions. In fact, the permeability of hydrogen in niobium is higher than it is for zirconium, and the permeability is more sensitive to temperature in the case of niobium. This property may be responsible in part for the improved performance of Zr-1Nb alloys, together with the improved corrosion performance.

Permeability of a solute is influenced by the product of coefficients of solubility and diffusivity. The hydrogen permeabilities in niobium and zirconium are both increasing with decreasing temperature. This property results from the increasing enthalpy of solution with decreasing temperature, and it can drive hydrogen diffusion toward a region with a greater hydrogen concentration when the temperature is lower. The permeability of hydrogen in niobium however is significantly higher than it is in zirconium at reactor temperatures, a factor of two at approximately 400 ºC with an increasing margin toward lower temperatures (Fig. 1). This difference can support a more rapid dynamic in the Zr-1Nb alloys because of the uniform dispersion of β-Nb SPPs, and possibly to a lesser extent because of the low levels of niobium dissolved in the zirconium.

Two significant thermal excursions occur for the cladding over its lifetime: outages and restarts. During an outage, the cladding should be expected to give up some of its dissolved and δ-phase hydrogen to the coolant as H_2, because the hydrogen content is high at the metal-oxide interface and because the temperature is lower so that less H_2 is being produced (giving a lower partial pressure of H_2). This behavior should be expected for both zirconium and niobium, because of their hydrogen solution enthalpies. However, the zirconium will respond more slowly than niobium because of its lower permeability, and consequently zirconium will better retain hydrogen. More dissolved hydrogen can also migrate *toward the fuel side* in the case of zirconium, because its permeability is less sensitive to temperature. Now even though the cladding is not pure niobium and the β-Nb can have a range of zirconium concentrations,[22] the hydrogen transport dynamics are improved because the uniform dispersion of β-Nb does not sit interior to grains and hydrogen transport along grain boundaries should be more rapid than across grains.

These arguments suggest that some hydrogen may be released from cladding during outages; this possibility follows from Le Chatelier's principle. In the case of niobium-free alloys, perhaps only a small amount of hydrogen, if any, is released, with activation energy provided by decay processes. The Zr-1Nb alloys however may be expected to have a more effective release of hydrogen (a higher release fraction) than the zircaloys because of the higher permeability arisiong from the niobium. While SPPs in the cladding possibly act as hydrogen traps for the zircaloys, β-Nb in the Zr-1Nb alloys can act to convey hydrogen with its increased permeability and grain boundary location.[23] These arguments are also consistent with hydrogen transport in the oxide films, especially along pathways including oxides of the SPPs in the oxide because of their increased uniform content.[24,25] It is not clear if the hydrogen would be transported as hydrogen atoms or protons in the oxide layer. The step-wise characteristics associated with behaviors described in this report, i.e., between surface oxidation and volumetric cladding changes, also appear to be consistent with the cyclical (on-off) oxidation behavior that has been reported.[26]

II.A. Proposed Alloy Compositions and Preparation

A report by Sabol et al. for simple binary systems indicates there is a critical size range and critical concentration for the SPPs.[27] They investigated multiple alloys within the Zr-Mo, Zr-Nb, and Zr-V systems and compared their corrosion behaviors of heat treated alloys to the corrosion of Zircaloy-4. They found superior performance for corrosion in steam at 427 C, and they found the performance was related to a critical concentration and critical size range for the SPPs as boundary precipitates. These observations support the working model described above, and the pursuit of further improvements to SPP characteristics somewhere in the size range of 10-80 nm.

The alloy compositions being studied include minor amounts (on the order of 1 wt%) of tin, niobium, molybdenum along with trace to low amounts of yttria or rare earth oxides (on the order of 0.25%). Other alloy additives such as iron and chromium can be added at a later time, if the progress warrants it. As indicated, molybdenum is insoluble in α-Zr,[28] and the molybdenum can be expected to precipitate as uniform fine dispersion with heat treatment. Niobium forms an ideal solid solution with molybdenum, [29] so that β-Nb can be expected to be composed primarily of niobium and molybdenum with low levels of zirconium. These initial compositions are directed toward improving the hydrogen permeability of the β-Nb and facilitating more rapid hydrogen transport.[30] It may be mentioned that the Excel alloy (Zr-3.5Sn-0.3Mo-0.8Nb) [31] has been observed to give higher terminal solid solubilities for hydrogen in comparison to all zirconium alloys in use (which give rather similar hydrogen solubilities),[32] and this difference could instead be detrimental.

Nanoscale precursors are being formulated from molybdenum cores, and the cores will be coated with a suitable oxide such as yttria. The Y_2O_3-Mo particles may then be contacted with molten tin in proportions conducive to downstream processing. Some concern exists whether the tin will wet the oxide-coated particles; however, both temperature and alternate oxides can be varied in the attempt to produce a usable intermediate material. The tin encapsulated mixture may then be subjected to one or more extrusions through the ECAP (equal channel angular pressing) process in the interest to produce a more uniform mixture, if necessary. After this, the tin mixture can be reacted with niobium at low to moderate temperature to produce a brittle Nb-Sn intermetallic intimately mixed with the oxides,[33] similar to a cermet. This final intermediate material may then be pulverized and mixed with sponge zirconium and any additional niobium and tin in accord with established arc melting procedures.

In an alternative scenario, the use of molybdenum may be omitted, and the nanoscale precursor structure can be inverted. In this case, the cores are made of yttria (or another suitable oxide) and niobium is used to coat the yttria cores. These particles can then be reacted directly with tin at low temperature to moderate temperature to produce the brittle Nb-Sn intermetallic phase for pulverizing. In both scenarios, the oxide is expected to remain associated with the niobium because it is oxophilic, and the tin is expected to be associated with the niobium at least until arc melting with zirconium. This alternative scenario is very appealing because minor amounts of molybdenum in niobium have been found to lower the hydrogen permeability, while minor amounts of zirconium in niobium have been found to increase the hydrogen permeability.[34] Likewise, as mentioned above, the Excel alloy contains some molybdenum and exhibits a higher solid solubility for hydrogen, which may be undesirable. Other process variations can be envisaged and attempted in an effort to optimize the alloy. In any case, the oxophilic character of niobium and the stability of its suboxides are expected to cause the niobium to associate with the rare earth oxides particulates, thereby preventing or inhibiting the dissolution, migration, and re-precipitation of niobium during irradiation and outages.

II.B. Early Progress Results

Molybdenum nanoparticles were produced under contract with Nanomaterials Company (Malvern, Pennsylvania). The characterization results obtained by the vendor gave two different average sizes by using two methods. Particle size analysis indicated the average size to be approximately 20 nm (Figure 2), while line-broadening X-ray diffraction indicated the average size to be approximately 10 nm (Figure 3). The vendor indicated the particle size analysis results could have been caused by some agglomeration of the primary particles. It may be mentioned that their characterization was performed soon after production of the nano-molybdenum.

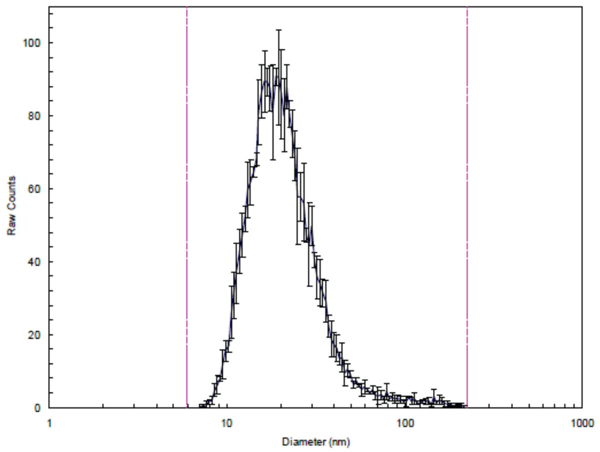

Fig. 2. Distribution of molybdenum particle sizes.

The vendor subsequently prepared a sample of the nano-molybdenum in epoxy, and this sample was examined at the Idaho National Laboratory the TEM (FEI Tecnai F30) at CAES (Center for Advanced Energy Studies). For a large number of particles examined, the primary particle size averaged on the order of 12 nm, and agglomerates were evident (Figures 4a and 4b). These results show that the nanoscale molybdenum cores can be produced.

It may be mentioned that there was a difference in the solution characteristics for the nanoparticles. The molybdenum nanoparticles were stored under degassed, dry toluene, and when the solution was first prepared, a swirled solution became inky and opaque, and required some time before settling. On the other hand, the sample prepared in epoxy and examined in CAES was aged for approximately two months. This solution when swirled settled much more rapidly, the top of the liquid becoming clear in less than a minute. As a result of these observations, some agglomeration is attributed to the aging time in solution, which is consistent with the TEM images observed.

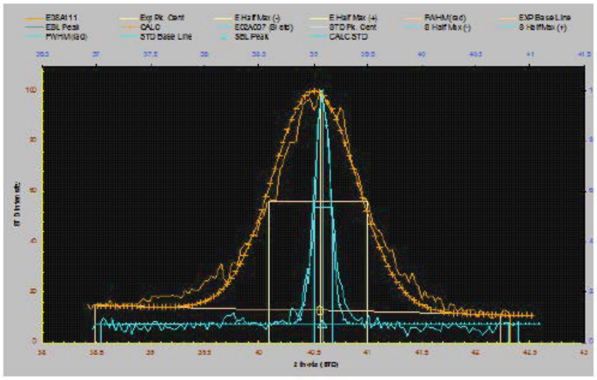

Fig. 3. Line-broadening X-ray diffraction pattern. Brown: experimental and fitted peaks for Mo at approximately 40.56 2θ; blue: experimental and fitted peaks for Si at about 39.08 2θ. Data reduction led to an estimated primary particle size of 10 nm.

Some difficulties were encountered in the production of the nano-molybdenum such that the yield decreased over time. These difficulties are being addressed by the vendor.

II.C. Discussion

Many uncertainties still exist regarding the method described here, and doubts can be easily raised because the 100 year-old ODS-type materials are still in their infancy as to predictive process knowledge. Even so, the approach described here does rely on thermodynamic and transport data as its springboard. The approach then relies on recent advances in nanomaterials and in metal processing for its accomplishment.

Since molybdenum is known to depress the H-permeability of niobium, and zirconium is known to enhance it, it will be interesting to evaluate the two kinds of precursor agents described above: one with and one without molybdenum. It is difficult to predict the behavior of β-Nb SPPs if they contain both molybdenum and zirconium; however, the Excel alloy (Zr-3.5Sn-0.3Mo-0.8Nb) was noted to have a higher hydrogen solubility compared to other zirconium alloys, which is possibly detrimental to long-term cladding performance. This research should also be directed at producing nanoscales precursors at two or three different median sizes between 10 to and 70 so that the effect of size can be evaluated.

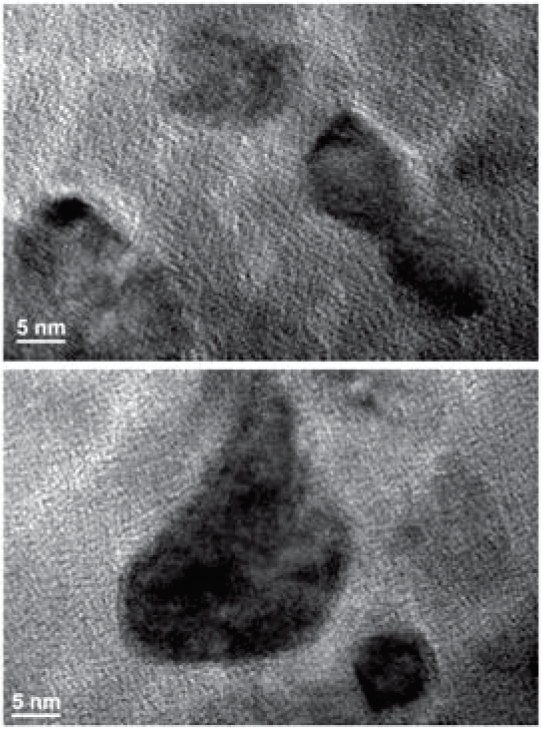

Fig. 4. Figure 4a (top) and 4b. TEM images for molybdenum nanoparticles mounted in epoxy.

Since the inverse temperature relationship with H-permeability is not common for most metals, it seems reasonable that SPPs in zircaloys may act as hydrogen traps while β-Nb SPPs in Zr-1Nb alloys may act as conduits. The rapid H-transport is not necessarily detrimental for hydriding; the rapid transport could enhance the approach to steady state and mitigate step-wise production of mismatches at interfaces. The presence of niobium may allow for the release (equilibration) of some hydrogen with the coolant during outages. Furthermore, the H-permeabilities of other metals are not only correlated with temperature, they are quite low in comparison to that for niobium.[35] These features along with other considerations for the working model suggest the ongoing experiments described here are warranted for cladding improvements.

Whether or not a new alloy is successfully developed for cladding applications, the physicochemical properties cited here are interesting also for evaluating issues related to used fuel disposition. Long-term storage of used fuel assemblies can benefit from research along these lines, if the working model holds up for niobium-bearing alloys.

In particular, experimental data from these types of alloys can be assessed to build models that identify additional experiments needed, and finally that identify alloy-specific conditions for removing hydrogen or rearranging hydride deposits prior to dry storage. It may be noted that test alloys do not need to be prepared by this method in order for this type of evaluation to proceed. Lastly, this approach is general enough that it may find application in the development of nanoferritic alloys and other ODS-type materials, which have broad technological interest. In fact, one alloy composition has been identified that holds promise for allowing conventional fusion welding.

III. CONCLUSIONS

It is believed that predictive, purposeful, alloy development with a nanodispersion of stabilizing agents is possible, and an approach to a zirconium cladding alloy has been developed. Nanoscale precursor agents are being developed with the intent of processing the alloy using conventional methods. The approach makes use of the differential solubility of alloying components and the oxophilic characteristics of the alloying components to force precipitation of metal alloying agents along with oxides on the grain boundaries. While much remains to be demonstrated, the method outlined has a sound basis in thermodynamic and transport theory, it is consistent with the extant literature, and early progress has demonstrated that 12 nm-sized molybdenum precursors can be produced.

Immediate future efforts will be directed toward obtaining the oxide-coated molybdenum and downstream processing to produce small alloy buttons by arc melting as funding permits. Of course, a strong interest exists to characterize the alloys with regard to heat treatments, etc., and to extrude these materials as warranted by the microstructures of the as-cast and heat treated ingots. It is worth noting that, even if a zirconium alloy such as this is never adopted, the approach may be perfectly general and suitable for adaption with other materials such as steels.

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