DOE Award Number: DE-NE-0000538

Recipient: North Carolina State University

Project Title: Nanostructured Fe-Cr Alloys for Advanced Nuclear Energy Applications

PI: Professor Ronald O. Scattergood scatter@ncsu.edu 919-515-7843

Project Period: 10/1/2012 to 01/31/2016

Report Submission Date: 4/30/2016

Reporting Period: 10/1/2012 to 01/31/2016

Abstract

We have completed research on the grain-size stabilization of model nanostructured Fe14Cr base alloys at high temperatures by the addition of non-equilibrium solutes. Fe14Cr base alloys are representative for nuclear reactor applications. The neutron flux in a nuclear reactor will generate He atoms that coalesce to form He bubbles. These can lead to premature failure of the reactor components, limiting their lifetime and increasing the cost and capacity for power generation. In order to mitigate such failures, Fe14Cr base alloys have been processed to contain very small nano-size oxide particles (less than 10 nm in size) that trap He atoms and reduce bubble formation. Theoretical and experimental results indicate that the grain boundaries can also be very effective traps for He atoms and bubble formation. An optimum grain size will be less than 100 nm, ie., nanocrystalline alloys must be used. Powder metallurgy methods based on high-energy ball milling can produce Fe-Cr base nanocrystalline alloys that are suitable for nuclear energy applications. The problem with nanocrystalline alloys is that excess grain-boundary energy will cause grains to grow at higher temperatures and their propensity for He trapping will be lost. The nano-size oxide particles in current generation nuclear alloys provide some grain size stabilization by reducing grain-boundary mobility (Zener pinning – a kinetic effect). However the current mitigation strategy minimizing bubble formation is based primarily on He trapping by nano-size oxide particles. An alternate approach to nanoscale grain size stabilization has been proposed. This is based on the addition of small amounts of atoms that are large compared to the base alloy. At higher temperatures these will diffuse to the grain boundaries and will produce an equilibrium state for the grain size at higher temperatures (thermodynamic stabilization – an equilibrium effect). This would be preferred compared to a kinetic effect, which is not based on an equilibrium state. The PI and coworkers have developed thermodynamic-based models that can be used to select appropriate solute additions to Fe14Cr base alloys to achieve a contribution to grain-size stabilization and He bubble mitigation by the thermodynamic effect. All such models require approximations and the proposed research was aimed at alloy selection, processing and detailed atomic-level microstructure evaluations to establish the efficacy of the thermodynamic effect. The outcome of this research shows that appropriate alloy additions can produce a contribution from the thermodynamic stabilization effect. Furthermore, due to the oxygen typically present in nominally high purity elemental powders used for powder metallurgy processing, the optimum results obtained appeared as a synergistic combination of nano-size oxide particle pinning kinetic effect and the grain-boundary segregation thermodynamic effect.

Final Scientific/Technical Report

Background

The motivation for stabilization of grain size at high temperatures is based on the premise that grain boundaries would be effective sinks for irradiation produced He. This will help mitigate the production of large He bubbles that produce swelling. The development of Fe14CrYTX ODS alloys is based on nanoscale oxides that can trap He and mitigate swelling. Nanoscale oxides can also help prevent grain growth at higher temperatures by Zener pinning, and there will be a contribution to He bubble mitigation by grain boundary trapping. High-temperature stabilization of grain boundaries is therefore of interest for mitigating the production of large He bubbles. Grain boundary stabilization at high temperatures can be achieved using the Zener mechanism. Grain boundary mobility is restricted by the pinning effect when grain boundaries contact nanoscale oxide particles. This is a kinetic effect and can be overcome by thermally activated breakaway of grain boundaries from pinning particles. Thermodynamic stabilization is an alternate means of stabilizing grain boundaries at high temperatures. In this case small additions of non-equilibrium solutes is made to Fe-14Cr base alloys such that these migrate to grain boundaries and produce a stable equilibrium state by minimization of the excess Gibbs free energy due to grain boundaries. The DOE proposal is based on investigation of the efficacy of the thermodynamic stabilization effect. This is evaluated using models developed by us. A binary model was initially developed (Fe + stabilizer solute). A more suitable ternary model (Fe14Cr + stabilizer) was subsequently developed and modified in the initial stage of this DOE program. These are the basis for alloy selections made during the course of the DOE research. Processing of the alloys is done using high-energy SPEX ball milling to allow for a wide range of candidate alloys. Although the premise was to isolate the thermodynamic effects, the outcomes in the DOE research include possible combinations of kinetic and thermodynamic stabilization. As we recognized subsequently after the initial stages of the investigation, this can result from the commercially available high purity elemental powders obtained from vendors, which contain a significant amount of oxygen (not given in powder chemistry specifications). Our results therefore provide focus on the combined effects of these stabilization mechanisms. The summary of our research results in the following sections is framed in context with the alloy systems chosen for investigation.

Our initial development of the thermodynamic stabilization model was based on binary Fe-X alloys, for example Fe-2at%Zr (Fe-Zr) where Zr is the stabilizer. This is a regular solution based model that supersedes previous models and provides a rigorous basis for minimization of the excess Gibbs free energy with respect to both grain size and grain boundary solute concentration. The binary model was developed in earlier research. An extended ternary version of the model was developed and modified for use in the DOE program. This will target possible stabilizer solutes for an Fe-14Cr-X base alloy. The modeling work gained further recognition, and we submitted an invited review paper on thermodynamic stabilization during the first program year, which is cited in the publication list at the end of this report. Based on modeling predictions and subsequent experimental work, several ODS alloys with different stabilizer solutes and related effects have been investigated. The results with appropriate specific publications are summarized in the following sections. Full details are presented in the publications. Our research has shown that nanoscale grain size stabilization of the model ODS alloy by selected stabilizer additions can be effective. Stabilization in our alloys, which contain excess oxygen, is a synergistic combination of thermodynamic and kinetic mechanisms. The role of complex nano-oxides and excess stabilizer solute produce a range of complex multiscale microstructures. The significant outcomes with corresponding publications are summarized in the following sections. Key references are included in the sections. A complete list of publications for the duration of the project is attached at the end of this report.

Ternary Model and Predictions

The ternary model [1] is a significant advance over binary models due to the fact that there are additional critical interactions. In a binary model there is one elastic size misfit and three mixing enthalpies whereas in a ternary model there are two elastic size misfits and six mixing enthalpies. Most relevant to the results described in this report is the fact that Hf is predicted to be a somewhat stronger stabilizer in Fe-14Cr-X compared to Zr. In both cases, it is predicted that there will be significant excess amounts of stabilizer X remaining in solution at the equilibrium grain boundary segregation for the stabilizer at a given temperature (excess values on the order of 30-50%). If this excess exceeds the equilibrium solubility, which is the case in these systems, one must expect additional precipitation reactions in addition to thermodynamic stabilization. Combined thermodynamic and kinetic stabilization can thus be realized. A third possibility for stabilizer X that was considered is Sc. This is unique in that there is minimal excess Sc at thermodynamic stabilization and it shows only minimal entropic destabilization as temperature increases. In addition, pure Fe has some equilibrium solubility for Sc at elevated temperatures.

Yittria (Y_2O_3) additions to ODS Alloys - Size Effect

Yittria is one of the key additions to ODS alloys. It is a primary component of the nanoscale oxides (< 10nm) that can increase strengthening at higher temperatures, and can contribute to irradiation resistance. Two scenarios have been proposed to explain the formation of nanoscale Y_2O_3 particles in as-milled powders. In one case it is proposed that fragments produced by ball milling are incorporated into the microstructures. The alternate scenario contends that Y_2O_3 particles have been completely dissolved in the matrix during milling and re-precipitate during annealing. Models have been proposed for these possible mechanisms, but direct evidence obtained by TEM on as-milled particulates has not been previously reported. Sample preparation is challenging. Although a sidelight to the main theme of our research it is an important aspect for applications. We attempted and were successful in preparing FIB lift-out TEM samples of as-milled 14YT powders prepared using SPEX mills. The analysis and results are reported in [3]. TEM/SAD, HAADF-STEM and STEM-EDS maps were used for structure-chemical analysis. With additions up to 1 wt% Y_2O_3 there are no Y_2O_3 fragments present in as-milled powder and complete solution is obtained (0.25 wt% is typical in ODS alloys). Furthermore, identical results were obtained using nano-scale or micron-scale starting Y_2O_3 powder materials. With additions of 10 wt% there are fragmented Y_2O_3 particulates in the as-milled powders. Heat treatments for as-milled powders (0.25 wt% Y_2O_3) showed identical trends for nano vs. micron size starting powders. One practical outcome of this work is that milling can be done and effective results obtained using micron scale Y_2O_3 starting powders. These are more easily obtained and handled during processing and we have taken advantage of this outcome in some of our research.

Grain size stabilization for Fe-14Cr-X alloys (X = Zr, Hf)

Initial work was done on Fe-14Cr-Zr alloys, some of which preceded our DOE results as noted in [4]. However, with implementation of the ternary model, Hf is predicted to be a better stabilizer and could therefore be preferred. Results for hardness and grain size vs. annealing temperature for both of these alloys are reported in [4] (the paper focuses primarily on Hf, however comparative results for Zr are included and the trends for Hf vs. Zr are similar). Compared to base Fe-14Cr alloy, Zr and Hf show improved stability with respect to grain growth and hardness decrease as temperature is increased. Hf is more effective than Zr as was anticipated from the ternary model predictions Additions of the stabilizer solutes up to 4 at% show increasing microstructure stability as can be expected based on the thermodynamic modeling results. Lattice parameter data indicate that for annealing temperatures (1 hr isochronal annealing) above 600˚C, the (oversize) Zr and Hf stabilizer solutes are no longer in metastable solid solution. TEM results for Fe-14Cr-4Hf indicated 52 nm nanoscale grain size for 900˚C anneals, increasing to 143 nm at 1100˚C. These results follow the trend predicted by the ternary model, but are larger suggesting that thermodynamic stabilization is only partially effective. Also, one can expect additional microstructural components with Hf/Zr stabilizers due to nano-oxide formation. The TEM and SAD results indicate the presence of nanoscale second phase particles with nominal size on the order of 20 nm, but this was not characterized at high resolution. One approach to gaining further insight was illustrated in the published results. Creating a baseline Hall-Petch (HP) plot for Fe-14Cr alloys allows the grain size contribution to the hardness of the Fe-14Cr-Hf alloys to evaluated. Excess hardness obtained from the experimental data is attributed to Orowan hardening, which in turn predicts the volume fraction of nanoscale second phase particles and the Zener pinning contribution to grain size stabilization. If this is larger than the TEM grain size, the difference can be attributed to thermodynamic stabilization with the caveat that thermodynamic stabilizer by solute segregation to grain boundaries was not directly verified by the resolution of the TEM results obtained in this case. The results reported in this paper do imply a contribution from thermodynamic stabilization in this context.

Characterization of nanoscale microstructure in Fe-14Cr-1.5Zr

As anticipated in the previous discussion, grain size stabilization by stabilizer solutes such as Zr and Hf can result from concurrent thermodynamic and kinetic stabilization contributions. This is expected from the ternary model predictions with respect to solute excess. Further verification and insight into these effects requires high-resolution electron microscopy analysis. The characterization results reported in [5], obtained on our aberration-corrected FEI Titan (G2) with X-FEG source and ChemiSTEM technology, operated in STEM mode represent this approach. The results reported were obtained for a 1.5 at% Zr alloy annealed at 900˚C for 1 hour. The relatively narrow grain size distribution histogram spans the range of 10 – 80 nm with a mean grain size of 44 nm. The significance of these results is that, based on thermodynamic stabilization model results, no stabilization should be expected above 600˚C. Any stabilization must be a result of Zener pinning and would therefore be attributed to Fe-Cr-Zr intermetallic nanoparticles. The relevance of the detailed microstructure characterization results reported in

[5] is that the notably effective stabilization in this case can be attributed to Zener pinning by nano-sized (3.7 nm average size) highly dispersed ZrO_2 particles (as opposed to possible intermetallics). The ZrO_2 particles also show coherency with the matrix similar to Y_2O_3 in ODS alloys. In addition, the level of oxygen needed is significant, on the order of 0.2 wt % oxygen. Subsequent chemical analysis of our Fe powder used routinely for SPEX ball milling was found to contain over 0.3 wt % oxygen as a contaminant. Although significant oxygen content and oxide reactions were not initially anticipated for this study, the formation of nanoscale oxides with strongly oxidizing stabilzer additions such as Zr or Hf provided additional and effective routes to nanoscale grain size stabilization by the kinetic mechanism, in conjunction with some contribution from thermodynamic stabilization.

Characterization of nanoscale microstructure in Fe-14Cr-xHf alloys

The effects of oxygen introduced during ball milling are further revealed in a detailed characterization of the microstructures produced in Fe-14Cr-xHf alloys where the Hf content varied from 1 to 4 at%. Based on thermodynamic stabilization modeling results, effective stabilization at higher temperatures would require 3 – 4 at% Hf and about half the Hf content would be excess and subject to reactions producing intermetallic and/or oxide phases. The oxygen content should modify this scenario since Hf is a strong oxide former (as also are Zr, Y and Sc). The microstructures for alloys containing X = 1, 2 and 4 at% after annealing for 1 hr at 900˚C were characterized in detail using aberration corrected scanning electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS). The grain size for 1% Hf was bimodal containing ultrafine grains (100-300 nm) and micron scale grains. Nanoscale grain size distributions were maintained for 2% and 4% Hf (average grain size of 66 nm and 57 nm, respectively). The microstructures contained combinations of larger Fe-Cr-Hf intermetallics and nanoscale Hf oxides in the size range of about 4 nm. Fe-Cr-Hf intermetallics in the size range 50-150 nm were found at 4% Hf but not at lower contents. HAADF-STEM imaging and EDS mapping detected Hf segregation to grain boundaries for the 4% Hf alloy, but not at lower Hf contents. Grain boundary segregation at 4% Hf is consistent with a contribution from thermodynamic stabilization as also are the presence of the intermetallics. However the nanoscale oxides make a significant additional contribution to the grain size stabilization over the range of Hf content and the extent of thermodynamic stabilization cannot be directly extracted. Nonetheless the combination of nanoscale oxides (kinetic stabilization by Zener pinning) with additional contribution from thermodynamic stabilization is significant. In addition, carbide phases with complex chemistry and size ranging from 20 to 150 nm were detected. The introduction of C is a result of contamination from the milling media (stainless steel balls and vials). The carbide phases would not be effective grain size stabilizers compared to the nanoscale Hf oxides.

Grain size stabilization for 14YT-X alloys (X = Sc)

Based on thermodynamic modeling predictions, and as evidenced in the results discussed in the previous sections, it is found that excess stabilizer solute, ie., that which would remain in solution at stabilization, will lead to formation of additional phases which may or may not be beneficial. In contrast to Zr and Hf, the thermodynamic model predicts that Sc will segregate to grain boundaries, with essentially no solute excess (typically less than 0.001%). Also, there is only a minimal entropic destabilization effect of Sc over the temperature range of interest. Based on these possible outcomes, we investigated the effect of Sc stabilizer for base model ODS alloy, anticipating that it can be more effective than the choices of Zr or Hf. As noted earlier the alloys in this work were also synthesized with Fe powder containing O contaminant, as discussed in previous sections. Sc is a strong oxide former and the microstructures will include that effect. The grain size stabilization was remarkably effective in these alloys, with x-ray grain size remaining at about 70 nm after 1 hour annealing at 1100˚C in all cases. This is not conclusive since x-ray grain size does not include contributions from larger grains. TEM results showed that the grain size distribution was bimodal at 1% Sc, but with a larger fraction of nanoscale (< 100 nm) grains. Uniform nanoscale grain size distributions with mean grain sizes of 51nm and 32 nm for 2% and 4% Sc, respectively were maintained for 1100˚C anneals. VHN values between 5 and 6 GPa were maintained for the 2% and 4% Sc alloys even after annealing at 1200˚C. HRTEM analysis and EDS mapping of the 2% and 4% Sc alloys indicated the presence of coherent nanoscale particulates in the size range 3-4 nm. This impressive stabilization is attributed to the formation of oxide-based nanoparticles formed from Y and Sc. Their similar formation energies lead to a competition between these. However in the 4% Sc alloy the concentration difference between Sc and Y is significant with nearly all the O consumed by Sc. It is also found that the difference between 14YT-Sc and conventional ODS alloy is the lack of large precipitates such as TiO_2 and intermetallic compounds. The role of Sc grain boundary segregation and concomitant contributions from thermodynamic stabilization were not disclosed in these results, however the driving force for Sc segregation to grain boundaries would facilitate the nanoscale oxide clustering that is observed on such grain boundaries. The additional O introduced in the Fe powder must also be a beneficial contribution.

Irradiation Damage and Nanoscale Microstructures

Nanoscale microstructures, and in particular nanocrystalline grain boundaries and/or nanoparticles, can provide sinks to ameliorate the effects of irradiation damage. One component of the DOE proposal is to conduct irradiation tests on selected nanoscale microstructures. The microstructures and their development using modeling and processing routes were part of the DOE proposal. The irradiation testing was done at LANL. We have made samples and identified test conditions in conjunction with colleagues at LANL. Our contribution is to characterize the irradiated samples in terms of microstructures, damage profiles and hardness variations. This is done using high resolution TEM characterization and nanoindentation testing. These key results and outcomes of the DOE research wre discussed in more detail in the following sections. References pertinent to the previous sections are listed below based on the publication dates appropriate at the time submitted. The final listing of publications in print or pending for the 3-year duration of the DOE are given at the end of this report.

1. M. Saber, H. Kotan, C.C. Koch, R.O. Scattergood, "A Predictive Model for Thermodynamic Stability of Grain Size in Nanocrystalline Ternary Alloys" Journal of Applied Physics 2013; 114: 103510.
2. M. Saber, C. Koch, R. Scattergood, "Thermodynamic Grain Size Stabilization Models: An Overview" Materials Research Letters, DOI: 10.1080/21663831.2014.997894.
3. M. Saber, W. Xu, L. Li, Y. Zhu, C. Koch, R. Scattergood, "Size Effect of Primary Y2O3Additions on the Characteristics of the Nanostructured Ferritic ODS alloys: Comparing

As-Milled and As-Milled/ Annealed Alloys Using S/TEM" Journal of Nuclear Materials 2014; 452: 223.
4. L.L Li, M. Saber, W.Z. Xu, Y.T. Zhu, C.C. Koch, R.O. Scattergood, "High-Temperature Grain Size Stabilization of Nanocrystalline Fe-Cr Alloys with Hf Additions" Materials Science and Engineering A 2014; 613: 289.
5. W.Z. Xu, L.L. Li, M. Saber, C. Koch, Y.T. Zhu, R.O Scattergood, "Nano ZrO2 Particles in Nanocrystalline Fe-14Cr-1.5Zr Alloy" Journal of Nuclear Materials 2014; 452: 434.
6. W.Z. Xu, L.L. Li, M. Saber, C. Koch, Y.T. Zhu, R.O Scattergood, "Microstructures and Stabilization Mechanisms of Nanocrystalline Iron-Chromium Alloys with Hafnium Addition" Metallurgical and Materials Transaction A, Under Review, 2014-2015.
7. L.L Li, M. Saber, W.Z. Xu, Y.T. Zhu, C.C. Koch, R.O. Scattergood, "Influence of Scandium Addition on the High-Temperature Grain Size Stabilization of Oxide-Dispersion-Strengthened (ODS) Ferritic Alloy" Materials Science and Engineering A, Under Review, 2014-2015.
8. M. Saber, W. Xu, L. Li, Y. Zhu, C.C. Koch, R.O. Scattergood, "Microstructural investigation of precipitates in ODS ferritic alloys" Oral presentation in MRS 2013 Fall meeting.
9. M. Saber, W. Xu, L. Li, Y. Zhu, C.C. Koch, R.O. Scattergood, "Grain Growth Mitigation in nanostructured Fe-Cr Alloys at High-Temperature Applications" Oral presentation in MS&T 2014 meeting.
10. W.Z. Xu, L.L. Li, M. Saber, C. Koch, Y.T. Zhu, R.O Scattergood, "Formation of ZrO_2 Nano Particles in Nanocrystalline Fe-14Cr Alloys with Zr Additions" Oral presentation in MRS 2014 Fall meeting.
11. R. O. Scattergood, C. C. Koch, Y. Zhu, M. Saber, L. Lu, and W. Xu, Fe-Cr Alloys for Advanced Nuclear Energy Applications", Webinar presentation, Aug. 19, 2014.

Characterization of Irradiation Effects

The following sections summarize the final phases of the research activities. Somewhat more detail is given these results. It includes He-ion irradiation that was done at LANL and the characterizations that follow therefrom. This is was a primary impact for the motivation and execution of the research activities.

Nanoindentation Testing

We initially proposed to carry out shear-punch testing to further characterize the mechanical properties of the irradiated samples vs. the unirradiated properties. After considerable effort, the results were not acceptable to the difficulty in compacting processed powder samples sufficiently free of flaws with our hot punch-die pressing facilities. In place of this, we developed a nanoindentation method for characterizing the hardness depth-profiles in compacted samples produced and irradiated. This is possible since nanoidentation can be done on individual powder particles. This gives a different and useable perspective on the hardening effects. The first batch of materials selected to undergo He irradiation were Fe-14Cr base alloys annealed at different temperatures and times to achieve different grain size, and also a Fe14Cr1.5Zr annealed sample. The ion irradiations were performed at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. We used a Hysitron Ubi-1 nanoindenter and a NorthStar cube corner tip with radius less than 40 nm for the study. The continuous stiffness measurement method was not used in this case due to instrumentation limitations, noting also possible uncertainties associated with this method. A modeled P-h relationship during the unloading process was obtained using power law fitting results from non-irradiated samples in muti-cycling tests. This is shown schematically in Figure 2 along with testing results. A continuous loading nano-hardness profile is obtained from the intersections (P*) of the model unloading curves and measured loading curves, divided by the tip contact area A_{hc}. The purpose this research segment was to characterize the evolution of microstructure and hardness depth profiles after irradiation. This can indicate whether our high temperature stabilized alloys could improve irradiation resistance, He bubble size and void swelling volume. The data in Figure 1 implies that the Fe-14Cr-1.5 Zr sample exhibits the best irradiation hardening resistance compared to Fe-14Cr base alloys. This is explained by the formation of nano ZrO_2 oxides that can increase irradiation-induced defect recombination and reduce void swelling.

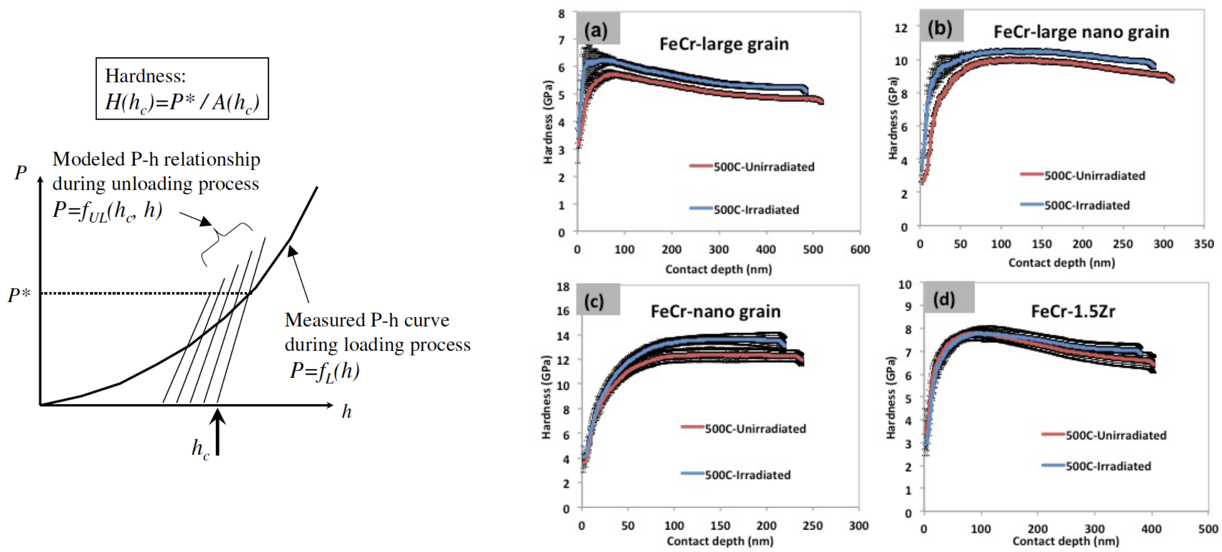

Figure 1. Left: Schematic illustration of the hardness profiling method. Right: Nano-indentation hardness vs. depth curves obtained for He irradiated and non-irradiated FeCrX base alloys.

He Irradiation Effects and Thermal Stabilization in Fe14Cr-Zr or Hf Alloys (Xu)

New nano-size oxide candidates of ZrO_2 and HfO_2 in the Fe-14Cr alloy system were developed in this research. These new oxide species have many similarities to Y-Ti-O enriched particles in ODS alloys, regarding their nano size and distribution in the ferritic matrix. The Y-Ti-O enriched particles are known to play a critical role in controlling irradiation damage of ODS alloys subject to neutron and ion irradiation. Considering the similarity of ZrO_2 and HfO_2 species to the Y-Ti-O enrich particles, their effectiveness in the irradiation enhancement is particularly interesting in materials development in the context of new irradiation tolerant materials.

Systematic studies were made on Fe-14Cr based alloys with Zr or Hf additions. The scope of the research ranges from microstructural characterization and evolution, nano-oxide formation and particle size, relationships to irradiation resistance properties, and statistical analysis of He bubble size and distribution when subject to 200KeV He irradiation at elevated temperatures. In particular six Fe-14Cr based alloy samples were synthesized by mechanical alloying using a SPEX 8000M Mixer/Mill, followed by subsequent annealing. These were Fe14Cr2Hf_700C1h, Fe14Cr_500C1h, Fe14Cr1.5Zr_800C1h, Fe14Cr_500C26h, Fe14Cr1.5Zr_900C1h, and Fe14Cr_900C1h.

A strong emphasis was put on the microstructural characterization and statistical analysis after irradiation tests. Ion irradiation tests were performed at 500 °C using the Ion Beam Materials Laboratory Facility at Los Alamos National Laboratory. Our samples were irradiated with 200 keV He ions (perpendicular to the sample surface) to a fluence of 6.5×10^{20} ions/m^2 and a flux of 2.2×10^{17} ions/m^2s. In order to accurately determine the bubble size, density and distribution along a 700 nm sample depth region, we modified the FIB sample preparation method. This includes (1) coating a sample with an (oversize) thick layer of Pt to protect the specimen from bending (2) gradient reduction of milling energy down to 2kV for non-intrusive milling. The improved methods help thin down the specimen to less than 50 nm with minimal damage for quantitative analysis. In this work, we utilized the advance aberration corrected microscopy facilities installed in NC State to reveal the microstructure details with unprecedented spatial resolution. Nano-scale chemical analysis from EDS and EELS spectrometer were conducted in the same instrument at the same time.

The effect of different nano-oxide particles on the resistance of He irradiation in Fe-14Cr base alloys was characterized. High densities of nano-size ZrO_2 particles are found in the ferritic matrix with one or more He bubbles existing near-by, showing a strong He trapping effect by nano ZrO_2 particles coupled with good stability of nano ZrO_2 particles when subjected to 200 keV He irradiation. He bubbles and nano HfO_2 particles evolve into core-shell structures and thus reduce void swelling by suppressing the growth of He bubbles, as shown in Figure 2. Chromium oxide particles are also found in Fe-14Cr based alloys. It is suggested that these nano oxide particles acted as effective sites for He bubble formation.

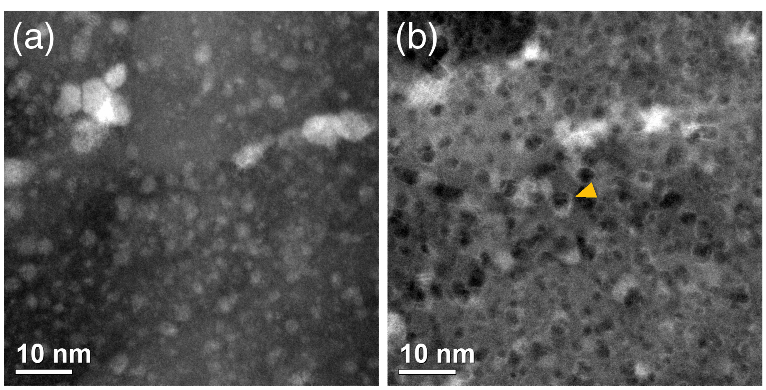

Figure 2. The change of the HfO_2 particle distributions is shown for a Fe14Cr2Hf_700C1h sample subject to 200 keV He^+ irradiation at a total fluence of 6.5×10^{20} ions/m^2 at 500 °C. HAADF-STEM image in (a) non-irradiated area and (b) irradiated area at the depth of 550-600 nm. As marked by the yellow arrow, the morphology of HfO_2 particle evolves to a shell structure around the He bubble.

A new software program was developed to conduct statistical analysis of void swelling, bubble size and density from a series of HRTEM images. Our (open) code enables the quantitative analysis of large number of bubbles with regard to their size and distribution along the specimen depth. By statistically analyzing 700-1500 He bubbles at the depth of about 150-700 nm from a series of HRTEM images for each specimen, we have established the variation of average He bubble size, He bubble density, and swelling percentage along the depth, and found them to be very consistent with the He concentration profile calculated from the SIRM program. As shown in Figure 3, with decreasing oxide particle size, swelling percentage drops. *What might appear as a slight decrement of nano oxide particle size at about 2 nm is in fact a 30% reduction of the swelling percentage (Figure 3d). This is attributed to the nano-grain size effect for He bubble trapping.* Effective oxide particles sizes are suggested to be less than 3.5-4 nm for enhancing radiation resistance. Such size effects for nano-oxide particles are found to play a significant role in controlling the void swelling percentage in the studied Fe-14Cr alloys subject to 200 keV He irradiation at 500 °C. This will also help design ODS alloys that can include alternative oxide candidates. Most notably the grain size effects related to the irradiation resistance are observed when the average grain size becomes sufficiently small.

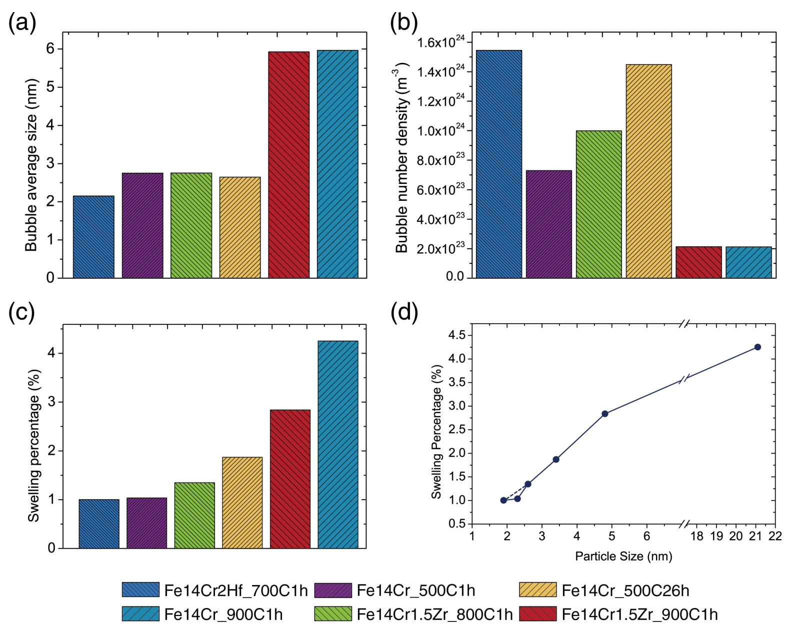

Figure 3. Comparison of the maximum value of (a) void swelling, (b) He bubble size and (c) bubble density among Fe14Cr2Hf_700C1h, Fe14Cr_500C1h, Fe14Cr1.5Zr_800C1h, Fe14Cr_500C26h, Fe14Cr1.5Zr_900C1h, and Fe14Cr_900C1h alloy samples subject to 200 keV He irradiation. (d) The relationship between nano-oxide particle size and the void swelling in Fe-14Cr alloys.

A new ordered intermetallic phase in the Fe14Cr4Hf alloy was also found after 1 hour annealing in the temperature range of about 800-1000 °C. The detailed microstructures are characterized using Aberration corrected scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) analysis. Electron diffraction and composition microanalysis were used to assign a space group to the structure and determine the atomic positions. The ordered phase has an Fd-3m symmetry and has $Mn_{23}Th_6$-type crystal structure. The EDS elemental mapping results show that the new phase is expected to be a Fe-Hf enriched intermetallic. The atomic ratio of Fe to Cr to Hf is estimated to be 1:0.08:0.33. Such results could add important new information to the Fe-Hf phase diagram.

List of Journal Publications in Print

M. Saber, C. C. Koch, R. O, Scattergood, "Thermodynamic Grain Size Stabilization Models: An Overview" Materials Research Letters, DOI: 10.1080/21663831.2014.997894.

M. Saber, W. Xu, L. Li, Y. Zhu, C. Koch, R. Scattergood, "Size Effect of Primary Y2O3Additions on the Characteristics of the Nanostructured Ferritic ODS alloys: Comparing As-Milled and As-Milled/ Annealed Alloys Using S/TEM" Journal of Nuclear Materials 2014; 452: 223.

L.L Li, M. Saber, W.Z. Xu, Y.T. Zhu, C.C. Koch, R.O. Scattergood, "High-Temperature Grain Size Stabilization of Nanocrystalline Fe-Cr Alloys with Hf Additions" Materials Science and Engineering A 2014; 613: 289.

W.Z. Xu, L. Li, M. Saber, C. Koch, Y.T. Zhu, R.O Scattergood, "Nano ZrO2 Particles in Nanocrystalline Fe-14Cr-1.5Zr Alloy" Journal of Nuclear Materials 2014; 452: 434.

L Li, W Z Xu, M Saber, Y Zhu, C C. Koch, R O. Scattergood, Influence of Scandium Addition on the High-Temperature Grain Size Stabilization of Oxide-Dispersion-Strengthened (ODS) Ferritic Alloy, Materials Science and Engineering: A 636 (2015): 565-571.

WZ Xu, L Li, JA Valdez, M Saber, YT Zhu, CC Koch, RO Scattergood, Microstructures and stabilization mechanisms of nanocrystalline Fe-14Cr alloys with Hf addition, Metallurgical and Materials Transactions A, 2015, 46:4394-4404.

WZ Xu, L Li, M Saber, CC Koch, YT Zhu, RO Scattergood, Effect of nano-oxide particle size on radiation resistance of iron-chromium alloys, Journal of Nuclear Materials, 2016, 469:72-81.

L Li, WZ Xu, M Saber, Y Zhu, C C. Koch, R O Scattergood, Long-Term Stability of 14YT-4Sc Alloy at High Temperature, Materials Science and Engineering: A 647 (2015): 222-228.

Presentations

M. Saber, W. Xu, L. Li, Y. Zhu, C.C. Koch, R.O. Scattergood, "Microstructural investigation of precipitates in ODS ferritic alloys" Oral presentation - MRS 2013 Fall meeting.

M. Saber, W. Xu, L. Li, Y. Zhu, C.C. Koch, R.O. Scattergood, "Grain Growth Mitigation in nanostructured Fe-Cr Alloys at High-Temperature Applications" Oral presentation - MS&T 2014 meeting.

W.Z. Xu, L.L. Li, M. Saber, C. Koch, Y.T. Zhu, R.O Scattergood, "Formation of ZrO_2 Nano Particles in Nanocrystalline Fe-14Cr Alloys with Zr Additions" Oral presentation - MRS 2014 Fall meeting.

L.L. Li, WZ Xu, M Saber, Y Zhu, C C Koch, R O Scattergood, High temperature grain size stabilization of 14YT ferritic alloys, Materials for Nuclear Applications and Extreme Environments: Materials for Extreme Applications, MS&T15.

W.Z Xu, L Li, M. Saber, C.C Koch, R.O Scattergood and Y.T Zhu, Microstructures and Stabilization Mechanisms of Nanocrystalline Iron-Chromium Alloys with Hafnium Addition. Symposium of Nanostructured Materials for Nuclear Application - TMS 2016.

Participants

Professor R. O. Scattergood PI
Professor C. C. Koch coPI
Professor Y. T. Zhu coPI
Dr. Mostafa Saber Postdoc (currently Assistant Professor, Portland State University)
Ms. Lulu Li PhD Graduate Student
Mr. Weizong Xu PhD Graduate Student and Postdoc

PhD Theses Completed

Increasing Stability of Nanocrystalline Ferritic Alloys at High Temperatures and Long Times for Advanced Nuclear Energy Applications, Lulu Li, doctoral thesis, 2015.

Transmission Electron Microscopy Study of Defects and Microstructure Evolution in Metals, Weizong Xu, doctoral thesis, 2014.