ABSTRACT


The complex process-structure-property relationship is the basic theme of materials science and engineering. Hence, through engineering the microstructure, desired properties can be achieved. Nanostructured materials exhibit superior properties such as high strength due to their small grain size (<100 nm). Oxide dispersion strengthened (ODS) steels show good irradiation-resistance owing to the presence of numerous nanoclusters. The objective of this research is to develop new nanostructured ferritic alloys with a dispersion of nanosized oxide particles in the nanoscale matrix. The interfacial area provided by both nanometer oxides and grain boundaries could improve the irradiation resistance while maintaining high strength for structural applications in advanced nuclear energy systems. However, nanostructured alloys are highly unstable at elevated temperatures. This thesis focuses on studying the thermal stability of nanocrystalline ferritic alloys through solute additions.

Oversized solute atoms tend to segregate to the grain boundaries or form precipitates, which can reduce grain growth thermodynamically or kinetically. The addition of Hf was compared with that of Zr, where Hf showed better stabilizing effect on Fe-14Cr base alloys. The nanoscale matrix was maintained up to 1000 °C with 4 at.% Hf addition. Zener pinning, one of the kinetic stabilization approaches, was considered as the major contribution to high temperature stability of nanocrystalline ferritic alloys. Based on the thermodynamic stabilization model for ternary alloys, Hf solute was predicted to be strong segregator, which contributes to the grain size stabilization as well. A deviation of predicted grain size from the actual grain size in Fe-14Cr-4Hf was found, suggesting the presence of grain boundary segregation. Further study of Fe-
14Cr-4Hf/Zr using HRTEM, directly observed Hf and Cr co-segregation on the grain boundaries. The grain size and nano-oxide effects on the evolution of irradiation-induced hardening were investigated through nanoindentation tests.

In addition to Hf/Zr solutes, Sc was found to be a good stabilizer. Only 1 at.% Sc addition can retain grain size of ODS steel in the nanometer range and microhardness of 5.6 GPa at temperature of 1000 °C. Large second phases such as titanium oxides were not observed compared to conventional ODS steels. This is likely due to the consumption of Ti atoms by Sc and O, forming a more complex nanofeature [SiTiO]. The presence of extremely small nanoclusters and the disappearance of large second phases stabilized the microstructure at high temperatures. Mechanical properties were also investigated.

Long-term thermal stability of ODS steel with Sc addition has been further studied at 1000 °C up to 60 hours. Grain growth was observed as a function of time through characterization techniques such as XRD, FIB and TEM and the growth rate could be obtained. More complex nano oxides of [SiTiYO] were detected from EDS elemental mapping in long-term annealed samples compared to ternary nanofeatures of [SiTiO] in short time annealed samples. The mechanisms of nanoscale precipitates formation were also investigated.
Increasing Stability of Nanocrystalline Ferritic Alloys at High Temperatures and Long Times for Advanced Nuclear Energy Applications

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Materials Science and Engineering

Raleigh, North Carolina 2015

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DEDICATION

To my dear parents, Wei and Yanhong.

To my respected grandma, Xuqin.
BIOGRAPHY

Lulu Li was born in Hunan, China on August 16th, 1990 to Wei and Yanhong. She got admission to Central South University (China) in 2008, majoring Materials Science and Engineering. During the undergraduate study, Lulu was selected in the program of Innovation Lab supervised by Prof. Shengdan Liu. She completed the undergraduate thesis under the supervision of Prof. Zhengqing Ma and earned the Bachelor degree in 2012. After that, Lulu came to US and continued her education at North Carolina State University. There, she joined Prof. Ronald O. Scattergood and Prof. Carl C. Koch group and worked on the thermal stability of nanocrystalline ferritic alloys.
ACKNOWLEDGMENTS

I sincerely thank all the people I have met during my Ph.D. life.

First, I would like to express my deepest gratitude to my advisors Professor Ronald O. Scattergood and Professor Carl C. Koch for their greatest supervision, support and kindness during the past three years. Many thanks to Dr. Korukonda L. Murty and Dr. Yuntian T. Zhu for being members of my Ph.D. committee and sharing insightful thoughts throughout my graduate study.

I am also thankful to Roberto Garcia and Dr. Stephen Podowitz-Thomas from Analytical Instrumentation Facility of NCSU for their useful training and services for the experimental work.

Financial support from the Department of Energy, Grant DE-NE0000538, is gratefully acknowledged.

I wish to express my appreciation to Dr. Mostafa Saber and Dr. Weizong Xu for their kind help, patience and invaluable suggestions during the research work. And thank all the members in my research group who share their knowledge and happiness: Dr. Hasan Kotan, Dr. Alexander Zaddach, Dr. Peiman Shahbeigi Roodposhti, Min Fan, and Peter Feldtmann. A special thanks goes to Edna Deas for her help from my admission until graduation.

Finally, I would like to thank my family, who gave me endless courage, long-lasting support and unconditional love.
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1.1 Introduction

From the basic physics and chemistry of solids, it is expected that properties of solids depend on the microstructure, which is the result of synthesis and processing [1, 2]. Process-Structure-Properties are interrelated and changes in one are inseparably linked to changes in the other two. Fig. 1.1 gives a framework to explain the complex relationship.

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Fig. 1.1 A schematic framework explains the interrelationship in the field of mechanical behavior of materials based on Thomas’s iterative tetrahedron.
The development of different materials with a variety of properties is based on processing. The determination of micro/macro-structures and properties of materials is obtained by various characterization methods. The understanding of these consequent structures and properties is based on theory.

Nanocrystalline materials with unique microstructure (grain size <100 nm) were found to exhibit excellent properties such as high strength compared to their conventional polycrystalline counterparts [3-9]. Processing methods and parameters such as temperature, pressure, atmosphere, etc. for synthesizing nanostructured materials with high performance have been investigated and developed for many decades [10]. In this work, nanocrystalline ferritic alloys were produced by high-energy ball milling, introducing severe plastic deformation into the matrix.

The major challenge for the application of nanocrystalline materials is their thermal instability. Extensive grain growth has been observed in many nanostructured alloy systems at elevated temperatures due to their high Gibbs free energy provided by grain boundaries [11]. A consolidation process involving high temperatures and high pressures is necessary for turning mechanically alloyed powders into a bulk shape for further applications. During the grain coarsening process, the excess free energy in the system is reduced while the exceptional properties connected to the nanostructure are lost. Therefore, the study of thermal stability of nanocrystalline materials is imperative.

Grain growth can be suppressed kinetically [12] and thermodynamically [13, 14]. The kinetic stabilization approach reduces the mobility of grain boundaries but will eventually be overcome by higher temperatures [15]. The thermodynamic stabilization approach is based
on the driving force for grain growth. The driving force related to the grain boundary energy is lowered via solute segregation to grain boundary area. The background knowledge of nanocrystalline structures, grain growth and stabilization mechanisms is reviewed in Chapter 2. The experimental techniques measuring grain size and other mechanical properties are given in Chapter 3.

Based on the ternary thermodynamic model proposed by Saber et al. [16, 17], Zr, Hf and Sc are considered to be strong segregating solutes in the ferritic alloys due to their large atomic misfit when added into the Fe matrix. The influence of solute (Hf/Zr) additions on the thermal stability of Fe-Cr alloys is detailed in Chapter 4. Nanoscaled grain size was found maintained up to 1000 °C annealing temperature with 4 at.% Hf addition.

Oxide dispersion strengthened (ODS) steel is a good candidate for structural materials in Gen-IV reactors due to the high volume fraction of interfaces provided by the extremely small nanoclusters (NCs). The interface between oxides and matrix can significantly reduce irradiation damage such as swelling and irradiation hardening. Through combining the nanoscale matrix with the dispersed nanoclusters, a more irradiated-resistant structural material is expected. The knowledge of irradiation damage and ODS steel is reviewed in Chapter 2.

Chapter 5 reports the observation of nanofeatures [SiTiO] in ODS steel with Sc addition. The presence of these nanoparticles is the major source for stabilizing nanoscale-matrix at high temperatures. A following investigation on the stability of 14YT-4Sc for long time annealing is given in Chapter 6. Abnormal grain growth was observed while a large fraction of matrix retained nanograins. The stabilization mechanisms and microstructures in this alloy system
are carefully examined. Chapter 7 discusses the nanoindentation theory and the application of nanoindentation for studying the irradiated samples.

Chapter 8 is based on co-authored published papers studying the formation of nano ZrO₂ particles in nanocrystalline ferritic alloys with Zr additions; the effect of the size of starting powders; the Hf oxide dispersion and Hf/Cr grain boundary segregation in nanocrystalline ferritic alloys with Hf additions; the effect of nano-oxide size on irradiation resistance of nanocrystalline ferritic alloys.

Finally, Chapter 9 summarizes this work and suggests future plans.

1.2 References


2.1 Nanocrystalline Materials

Nanocrystalline materials are single phase or multiphase polycrystals with small crystal size on the order of a few (less than 100) nanometers in at least one dimension [1]. A large volume fraction of interfacial boundaries is a major structural characteristic of nanocrystalline materials. The average atomic density in the “boundary component” is 10-30\% less than that within the crystal [2], subsequently enhanced by free volume in the boundaries. The atomic structure of nanocrystalline materials is shown in Fig. 2.1. The boundary core region represented by open circles shows a reduced atomic density and the interatomic spacing deviates from that in the perfect lattice represented by black dots. This is also experimentally confirmed in high-resolution electron micrographs [3].
2.1.1 Properties

When the atomic structure changes, the structure-dependent properties will change accordingly. The properties of nanocrystalline materials deviate from conventional chemically identical polycrystalline materials. They are very often superior to them due to the numerous interfaces exhibited between adjacent crystallites. These property alterations in nanocrystalline materials compared to their coarse-grained counterparts include reduced density, higher diffusivity [6], enhanced solute solubility [7], increased specific heat [8], enhanced thermal expansion coefficient [9], superior soft magnetic properties [10], higher
electrical resistivity [11, 12], reduced elastic constants [13, 14], increased strength/hardness [15-17], and improved ductility/toughness [18].

2.1.1.1 Hall-Petch Relationship:

Grain size has a significant influence on the mechanical behavior of materials, particularly on the yield stress [19]. The 0.2% yield strength of Pd sample was reported to increase from 52 mN m$^{-2}$ to 250 mN m$^{-2}$ when grain size is reduced from 50 $\mu$m to 14 nm [20]. The dependence of yield stress on grain size in metals is found to follow the Hall-Petch relation [21, 22]:

$$\sigma_y = \sigma_0 + kd^{-1/2};$$

(2.1)

where $\sigma_y$ is the yield stress, $\sigma_0$ is the friction stress, $k$ is a constant and $d$ is the grain size diameter. A significant increase of hardness and strength is expected via reducing grain size to nanometer level [23-27]. The Hall-Petch plot for nanocrystalline Fe shows a four-fold rise from micronscale to nanoscale grain size [28]. Strengthening is achieved if the dislocation motion is suppressed [29]. Thus, solute atoms [30, 31] and second phase particles [32] can also strengthen materials. However, the hardness cannot increase beyond the theoretical strength limit. After some critical grain size, it has sometimes been observed that the strength decreases with a decrease in grain size, which is the inverse Hall-Petch relationship [33, 34]. In this case, a negative value $k$ takes place for the slope as shown in Eq. (2.1).
2.1.2 Non-Equilibrium Processing Methods

Several non-equilibrium processing methods have been developed to form nanocrystalline materials in a highly metastable state, such as rapid solidification from the liquid state [20, 35], mechanical alloying [36], plasma processing [37, 38] and vapor deposition [39].

2.1.2.1 Mechanical Alloying (MA):

MA has been defined as a dry, high-energy, ball milling process, resulting in alloy powders with controlled and extremely fine microstructures [40-45]. Shingu et al. first reported successful synthesis of nanostructured Al-Fe alloys [46] via mechanical attrition. The collisions between balls and powders repeat welding, fracturing and rewelding of powder particles. Nanoscaled grain size can be obtained in almost any material due to the severe plastic deformation induced. The as-milled grain size decreases with milling time and then reached a constant value for a given set of milling conditions. This indicates a balance between defect creation and recovery during the deformation process. The minimum grain size of metals with different structures such as fcc, bcc and hcp as a function of their melting temperatures are plotted in Fig. 2.2. It was observed that the minimum grain size scaling inversely with the melting temperature for fcc metals [47], while it was relatively stable for bcc and hcp metals and several intermetallic compounds.
Fig. 2.2 Minimum grain size of fcc, bcc, hcp metals and intermetallic compounds vs. their melting temperatures. Date from Ref. [41, 47-49]

Furthermore, the solute solubility in the boundary region is larger than the solute solubility in the crystal lattice [1]. In this way, MA can synthesize nanostructured alloys with immiscible components, opening a wide range of options for material design. Cu and Nb are mutually insoluble with the equilibrium solubility of Cu in Nb is less than 0.5 at.% at room temperature. Nanocrystalline Cu-Nb alloys have been formed by mechanical alloying [50] with extended solubility of almost 25 at.% Cu in Nb. MA has been applied to several other alloy systems to obtain extensive solid solubility [51-53]. However, the amount of impurity picked up from milling media and/or atmosphere is increased with milling time and some contamination is inevitable in mechanical alloying processing.
2.2 Grain Growth

As discussed by Turnbull [54], nanostructured materials are considered morphologically metastable due to high density of grain boundaries, interphase boundaries and dislocations. Therefore, nano-grains will grow to a more stable state with lower system energy via reducing boundary area [55]. The driving force/ pressure (P) for grain growth is based on the curvature of the gain boundary [56]:

\[ P = A \gamma_{gb} / r; \]  

(2.2)

A is a constant, \( \gamma_{gb} \) is the grain boundary free energy per unit area and \( r \) is the radius of curvature of a grain, which is proportional to the grain size \( d \). Nanocrystalline materials with grain size (\( d \)) in the range of nanometer scale, produce a large driving force. Thus, extensive grain growth is expected. There are two kinds of grain growth, normal and abnormal. Fig. 2.3 schematically presents the changes in the shape of the grain size distribution as a result of each grain growth mode [57]. In normal grain growth, the shape of the grain size distribution is constant as a function of time and temperature while moving to larger grain size values [58-60]. The anomalous grain growth changes the shape of the grain size distribution throughout the process, usually from unimodal to bimodal, and possibly back to unimodal distribution again in the final stage.
Fig. 2.3 Schematic representation of changes in distribution as a result of (a) normal and (b) abnormal grain growth. The frequency of a particular grain size is plotted as a function grain diameter (D) and annealing time (t). In the normal grain growth, grain size shifts to a larger value while the distribution shape remains similar. In the abnormal grain growth mode, the grain size shifts to a larger value, while the shape of distribution changes with annealing time.
2.2.1 Normal Grain Growth

The kinetics of normal grain growth under isothermal annealing conditions follow the Eq. (2.3) [57]:

\[ d^2 - d_0^2 = K t^n; \]  

(2.3)

where \( d \) is the grain size at time \( t \), \( d_0 \) is the average of initial grain size (i.e. at \( t=0 \)), \( n \) is a constant. \( K \) is associated with the activation energy (\( Q \)) for grain growth in Eq. (2.4) [61]:

\[ K = K_0 \exp \left( \frac{-Q}{RT} \right); \]  

(2.4)

Theoretically, the maximum value of \( n \) is 0.5, which can be achieved in ultra-high-purity metals at temperatures close to their melting points [62]. Experimentally, the deviation of \( n \) value from 0.5 may be caused by solute drag effect, interactions with particles or texture effect [63]. The time exponent (\( n \)) measured in isothermal grain growth of various nanocrystalline materials is shown in Fig. 2.4. The \( n \) value changes with normalized annealing temperatures and approaches the theoretical value of 0.5 in high purity systems or at high annealing temperatures.
Fig. 2.4 Time exponent (n) for isothermal grain growth of various nanocrystalline materials as a function of the normalized annealing temperature (T/Tm) [1, 64].

The activation energy and the exponent of the kinetic equation have been influenced by the addition of 5.5 mass% Ti in nanophase NbAl [65]. The activation energy is 45 kJ/mol higher than pure mechanically alloyed NbAl alloy, successfully suppressing grain growth with the smaller n value.

2.2.2 Abnormal Grain Growth

As mentioned earlier, effects such as precipitates can help retard grain size growth to some extent. When the particles or precipitates show limited stability within an alloy system, an
anomalous grain growth will occur [66, 67]. Other phenomena could also lead to the abnormal growth mode including an initial very broad grain size distribution, spatially non-uniform distributed solute, and the presence of texture [68, 69].

2.2.3 Stabilization Mechanisms

Consolidation is necessary to turn nano powders into bulk form for further application. However, to accomplish full and theoretical density requires the use of high consolidation temperatures. Besides, some applications such as structural materials in reactors require elevated temperatures. In this way, materials are in jeopardy of losing nanostructures, along with the associated superior properties. Therefore, the study of thermal stability of nanocrystalline materials is imperative for commercial processes and future applications. The velocity of a grain boundary (GB) is the product of mobility and driving force, which follows Eq. (2.5) [70, 71]:

\[
v = M \times P = M_0 \exp \left( \frac{-Q_m}{RT} \right) \frac{2Y_{gb}}{r},
\]

\(v\) is the velocity of a grain boundary, \(M\) is the mobility of grain boundaries, \(M_0\) is a pre-exponential factor, \(Q_m\) is the activation energy for GB migration [72], \(P\) is the curvature driven pressure mentioned in Eq. (2.2). In theory, the coarsening of grains can be eliminated by either zero mobility or zero driving force. This determines two approaches- kinetic and thermodynamic, to reduce or eliminate the GB movement.
2.2.3.1 Kinetic Stabilization Mechanism:

The method of retaining nanostructure kinetically is characterized by reducing GB mobility. It includes porosity pinning [16], second phase pinning [73], solute drag [74, 75], chemical ordering [76] and grain size stabilization [77].

*Solute Drag Effects:*

For the case of solute (impurity) drag, the retarding force exerted on GB migration depends on the concentration of solute atoms at GBs [74, 78] and the solute-solvent interactions. As solute concentration increases, GBs require a higher driving force to break away from the solute atmosphere, and grain growth is inhibited [75]. P. Knauth et al. [79] studied the thermal stability of pure Ni and the Ni-Si solid solution. If Si is present, the grain growth was observed at distinctly higher temperatures due to GB enrichment with solute atoms. In the Ni-Si solid solution, the moving grain boundaries incorporate solute Si, which inhibits GB motion until sufficiently high temperature assists grain growth.

*Second Phase Pinning Effects:*

It has been well documented in the literature that the presence of particles and precipitates can significantly control grain growth in various alloy systems. This result is gained by inhibiting grain boundary migration. Fig. 2.5 illustrates how the high angle grain boundary is pinned by an Al₂O₃ particle [57].
C. Zener [70, 81] first treated this stabilization mechanism and put forward the (Zener) equation:

\[ P = \frac{3}{2} \gamma_{gb} \frac{f}{r}; \]

(2.6)

\( P \) is the pinning force per unit area of grain boundary; \( f \) and \( r \) are the volume fraction and radius of the particles, respectively. \( \gamma_{gb} \) is the grain boundary energy. The pinning effect
depends on the type and amount of particles. For successful stabilization, where grain growth stops, the pinning force should be larger than the driving force shown in Eq. (2.2). When the driving force equals to the pinning force exerted by a second phase particle in Eq. (2.6), a limited grain size \( r_{\text{lim}} \) can be predicted.

\[
 r_{\text{lim}} = C r / f; 
\]

where \( C \) is a constant and measured to be 4/3 by Zener.

Nanocrystalline Fe-10 wt.%Al with grain size of 60 nm was obtained after heating above 1100 °C [82]. This nanostructure retention was attributed to the dispersion of FeAl2O4 at low annealing temperatures and AlN, Al2O3 at high annealing temperatures. Cu-Nb nanocrystalline alloy is found to be very stable, opposing coarsening up to 900-1000 °C [83]. The high thermal stability results from the microstructure of the alloy with small Nb precipitates embedded in the nanoscale matrix. Mechanical strength and other properties such as electrical conductivity strongly depend on the microstructure. For example, the presence of second phase particles in Cu-Nb alloy system hindered the dislocation motion, contributing to hardening.

Boylan et al. [73] and Mehta et al. [84] observed relatively high thermal stability in Fe-P supersaturated solid solution below 360 °C, owing to a continuous P-segregation along the grain boundaries (a metastable equilibrium state). However, above 360 °C annealing temperature, P atoms no longer lower the free energy of the system by occupying GB sites but form the equilibrium precipitates of Ni3P [85, 86]. Therefore, at higher temperatures, precipitation is more favorable compared to solute segregation. The solute segregation will be described in 2.2.3.2 in detail.
Chemical Ordering Effects:

The grain boundary mobility is found to be higher in a disordered state than a chemical ordered one [76, 87, 88]. The obstructed migration may due to the low diffusion kinetics in ordered structures.

Grain Size Stabilization Effects:

It is surprising that the growth rate found in nano-scaled grains is slower than that from their coarse grain regime [16], even in the absence of impurity concentrations [89, 90]. The nanocrystalline Ni-P sample with smaller grains showed enhanced thermal stability, requiring higher temperature and larger activation energy for grain growth [91]. This is contradictory to grain growth in conventional polycrystalline materials. The small grain size stability effect is attributed to the configuration and energetic state of the interfaces provided by nanostructured materials. Grain size affects the rate-controlling mechanism for grain growth through redistribution of excess volume localized in the boundary region. Vacancies can be produced as a result of GB area reduction [92], increasing the free energy of the system accordingly [90]. Therefore, the appearance of non-equilibrium vacancy concentration acts as an inhibiting factor to grain growth.

2.2.3.2 Thermodynamic Stabilization Mechanism:

Kinetic stabilization will eventually be overcome with sufficient thermal energy. A more promising approach is the thermodynamic stabilization effect [93]. Grain boundary segregation is a thermodynamic stabilization approach and it describes the localized concentration of solute species segregating at GBs in solids. Fig. 2.6 gives a compositional profile for a variety of solute segregants in different alloy systems. The drop of the
continuous curve reveals the decay of the segregation level from the GB to the grain interior for different segregation systems [94].

![Graph showing compositional profile](image)

Fig. 2.6 Compositional profile for a variety of segregants in different systems.

According to the Gibbs adsorption Eq. (2.8), the grain boundary energy can be modified by the solute concentration ($c_s$) [95]:

$$\frac{\partial Y_{gb}}{\partial \ln c_s} = -RT \Gamma_s;$$

(2.8)
\( \Gamma_s \) is the interfacial solute excess, \( R \) is the gas constant and \( T \) is temperature. Grain boundary segregation (where \( \Gamma_s > 0 \)) is the interaction of solute atoms with the topological defects (GBs), leading to a reduction of the GB specific energy. Large atomic misfit between solute and solvent intensifies the grain boundary segregation effect. This is because GBs provide excess free volume to accommodate large solute atoms, relieving the elastic strain of solute atoms residing in the lattice. Over-sized solutes can segregate along GBs with lowering energy than bonding with solvents in the grain interior [96, 97]. An apparent increase in activation energy for grain growth was observed in nano-RuAl with Fe impurities. The accumulation of impurities in GBs postponed the structural evolution of reordering, strain relaxation and grain growth during heat treatment [98].

Grain boundary solute coverage in PdZr was grain size-dependent. Fig. 2.7 (a) shows the solute concentration of Zr segregated at GBs (\( c_{Zr}^{GB} \)) and the average grain size as a function of annealing time at the temperature of 600 °C. The combination of \( c_{Zr}^{GB} \) and grain size plotted in (b) shows a linear increase of solute content with grain growth. This linear relationship directly confirms that the segregation results from the moving GBs capturing solute atoms during expansion instead of solutes diffusing to the GBs through the lattice [75].
Fig. 2.7 Isothermal grain growth of MA nanocrystalline Pd81Zr19. (a) The concentration of Zr segregated at GBs ($c_{Zr}^{GB}$), and the average grain size as a function of annealing time. $c_{Zr}^{GB}$ was calculated from the lattice parameter measurements. A homogeneous solute
distribution \((c_{Zr}^{\text{GB}}=19\ \text{at.\%})\) was assumed for the initial state. (b) Plot of \(c_{Zr}^{\text{GB}}\) vs. average grain size.

Weissmuller [95, 99] correlated the thermodynamic properties of a solid solution with interactions of solutes and topological defects based on the McLean model [100]:

\[
\gamma_{gb} = \gamma_0 + \Gamma_s[\Delta H_{\text{seg}} - T\Delta S_{\text{seg}}];
\]  

(2.9)

where \(\gamma_0\) is the non-segregated GB energy, \(\Delta H_{\text{seg}}\), \(\Delta S_{\text{seg}}\) are the enthalpy and entropy of segregation respectively. \(\Delta H_{\text{seg}}\) consists of two components: chemical term \(\Delta H_{\text{chem}}\) and elastic strain energy term \(\Delta H_{\text{els}}\) [101-103]. A metastable state is then reached in nanocrystalline alloys with the specific grain boundary energy to be zero or even negative if the heat of segregation is large enough [95]. Ideology and extensive derivations of \(\gamma_{gb}=0\) can be seen in references [72, 86, 99, 104, 105]. In the famous zero creep experiment of Fe-P alloys [106], the grain boundary energy \(\gamma_{gb}\) decreases and grain boundary excess \(\Gamma_s\) increases with higher P-content in the system, as shown in Fig. 2.8. At low P-concentration, \(\Gamma_s\) approaches zero and \(\gamma_{gb}\) is approaching \(\gamma_0\). Above a certain P-concentration, a linear drop of \(\gamma_{gb}\) has been observed as a function of the logarithm of phosphorus content [86] and \(\Gamma_s\) reaching its saturation value.
Fig. 2.8 Grain boundary energy and grain boundary excess vs. total phosphorous content in Fe-P alloys.

Other applications of GB segregation can be found in the Ti-Cu system [107], TiO$_2$-Ca system [108], and nanocrystalline electroplated Ni with W additions [109-112]. The Ti-Cu alloy system has a positive heat of mixing in the solid and a negative one in the liquid [113]. Cu atoms prefer occupying GB sites relative to grain interior due to the liquid –like disordered GB structure [107, 114]. GB segregation is enhanced until the intermetallic phase (CuTi$_2$) nucleates. C.D. Terwilliger et al. [108] measured Ca coverage along GBs of TiO$_2$ samples as a function of grain size, in the range of 50-750 nm. At a grain size close to 350 nm, the boundaries were saturated with solute segregation. Ultimately, GB segregation was
lost and precipitates (CaTiO$_3$) of equilibrium intermetallic phases were observed at higher annealing temperatures [86].

### 2.3 Radiation Resistant Materials

A large amount of fossil fuels are consumed each year, which influences the global climate in the meantime [115]. The utilization of nuclear energy will surely reduce the dependence on fossil fuels and global warming issues as well. An international effort initiated the Generation-IV (Gen-IV) reactor for nuclear energy system [116, 117]. The goal of Gen-IV is to produce safer, more reliable, sustainable, longer reactor life (60 years or more), higher proliferation resistant and profitable nuclear power reactors than the current ones. However, the structural materials applied in Gen-IV reactor need to endure high temperature, high neutron doses and extremely corrosive environment.

#### 2.3.1 Radiation Damage

Irradiating materials with sufficiently energetic particles such as neutrons, ions or electrons can create atomic displacements in materials, significantly changing microstructures along with physical and mechanical properties [118]. Radiation damage is measured in dpa (displacements per atom). Primary damage appears as point defects such as vacancies, interstitial atoms and Frenkel pair consisting of a vacancy and a self-interstitial atom (SIA) [119]. Subsequently, these point defects agglomerate forming cavities and dislocations. Eventually a variety of microstructural changes occurs in the irradiated materials. The
evolution of microstructural damage may cause several detrimental phenomena: radiation-induced amorphization, radiation hardening, thermal and electrical conductivity reduction, radiation-induced segregation and precipitation, dimensional instability and high temperature embrittlement.

2.3.1.1 Radiation-induced Segregation and Precipitation:
The mobile SIAs and vacancies cause solute segregation to point defect sinks. Precipitation of new phases such as MC, M₆C and M₂₃C₆ carbide occurs due to the material composition and local enrichment or depletion of solute atoms [120, 121].

2.3.1.2 Dimensional Instability:
There are three kinds of dimensional instability generated by irradiation: irradiation growth due to anisotropic nucleation and growth of dislocation loops [122-124], irradiation creep due to biased adsorption of point defects [125] and volumetric swelling due to the accumulation of vacancies [126]. Excess of 5% of volumetric swelling for structural materials is hard to accommodate via engineering design [127] while above 10% swelling, void channeling and loss of ductility could lead to embrittlement [128].

Shiori Ishino et al. monitored the microstructural evolution for various metals [129, 130] at high dose rate. Swelling in bcc materials such as ferritic/martensitic steels is reported less evident than in austenitic stainless steel with fcc structure [126, 131, 132]. The resistance to swelling in bcc materials could be explained by the lower dislocation bias for SIA adsorption, higher point defect sink strength [124] and more energy required for transformation of small helium-filled bubbles to relatively large voids. The swelling
resistance in hcp is attributed to the migration of anisotropic point defects, enhancing defect recombination and annihilation [133]. However, it can potentially form anisotropic swelling in hcp materials, inducing cracking at grain boundaries [134-136].

2.3.1.3 Irradiation Hardening:

The dislocation motion is largely suppressed in irradiated materials by the presence of a high density of defects. The study of radiation-induced defects and deformation-produced dislocations in austenitic stainless steel displayed similar net effects on strain-hardening behavior [137]. Irradiation hardening is pronounced at low temperatures (<0.3T_m) [138] and typically accompanied by reduction in tensile elongation and fracture toughness [121, 139]. At higher irradiation temperatures, coarsening of defects may diminish the hardening effect [140, 141].

A hardening model has been put forward by G.E.Lucas to predict changes in properties based on structure-property relations. The increase in yield stress (Δσ_y) is measured by the increase of stress required to move a dislocation around obstacles with strength α and interspacing of l.

\[ \Delta \sigma_y = M\alpha\mu b/l = \begin{cases} M\alpha\mu b\sqrt{Nd}, & \text{for discrete obstacles;} \\ M\alpha\mu b\sqrt{\rho_d}, & \text{for dislocations;} \end{cases} \]  \( (2.10)\)

Here, \( \mu \) is the shear modulus of the matrix, \( b \) is the Burgers vector of the moving dislocations, \( M \) is a factor in the range of \( \sqrt{3} \) and 3 [121], \( N \) and \( d \) are the number density and the average size of discrete obstacles, respectively. \( \rho_d \) is the number density of dislocations.

Table 2.1 shows the obstacle strength (\( \alpha \)) of different microstructural features based on experimental data fitting.
Table 2.1 The obstacle strength ($\alpha$) of various microstructural features from experimental data fitting.

<table>
<thead>
<tr>
<th>Relative strength</th>
<th>Barrier type</th>
<th>Obstacle strength ($\alpha$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>Orowan</td>
<td>~1</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>Voids</td>
<td>~1</td>
<td>[120, 142, 143]</td>
</tr>
<tr>
<td></td>
<td>Precipitates</td>
<td>~1</td>
<td>[142]</td>
</tr>
<tr>
<td>Intermediate</td>
<td>Dislocation loops</td>
<td>0.33-0.45</td>
<td>[120, 142, 144]</td>
</tr>
<tr>
<td></td>
<td>Small carbides</td>
<td>0.33-0.45</td>
<td>[144]</td>
</tr>
<tr>
<td>Weak</td>
<td>Small bubbles</td>
<td>0.2</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>Small loops/clusters</td>
<td>0.2</td>
<td>[145]</td>
</tr>
<tr>
<td></td>
<td>Vacancy clusters</td>
<td>&lt;0.25</td>
<td>[121]</td>
</tr>
</tbody>
</table>

This shows that voids and precipitates are comparable with the Orowan mechanism, which is assumed to be impenetrable obstacles. It should be noted that the hardening contribution from each barrier type not only depends on their obstacle strength but also their average size and the number density ($N$ or $\rho_d$), as shown in Eq. (2.10). The total yield stress is obtained by superposition of the unirradiated yield stress and the contribution of each defect type generated during hardening.
2.3.1.4 High Temperature Embrittlement:

Large quantities of He atoms are generated by the nuclear transmutation reactions in fusion reactor environments at elevated temperatures ($\geq 0.5T_m$). The growth of He bubbles along grain boundaries slows the strain rate and eventually results in failure. He embrittlement can also occur even at low temperatures. For example, intergranular fracture was observed for 304 stainless steel irradiated at 370 °C [146, 147]. Embrittlement is measured by reduction in fracture toughness and increase in the ductile to brittle transition temperature (DBTT) of bcc alloys [138]. Relatively good resistance to helium embrittlement has been observed in bcc metals such as Nb [148] compared to fcc metals such as copper [149, 150]. The factors opposing embrittlement in bcc materials are the efficient trapping of He in the grain interior, the larger critical radius needed for bubble-void transformation, and the lower matrix strength of ferritic steel compared to austenitic steel [151-153].

2.3.2 Promising Candidates

Due to the severe working environment, the development of high-performance structural materials in nuclear power reactor requires performance characteristics for Gen-IV structural materials such as excellent dimensional stability, good mechanical properties (strength, ductility, creep rupture, etc.), acceptable irradiation damage resistance (irradiation hardening, He embrittlement), and a high degree of chemical compatibility of the structural materials to the coolant and the fuel. Candidates for material systems for structural applications now include ferritic/martensitic steels (F-M), austenitic stainless steels, Ni-base superalloys, refractory alloys, ceramic, and oxide dispersion strengthened steel (ODS) [117].
2.3.2.1 Oxide Dispersion Strengthened (ODS) Steel:

ODS steel is one of the promising candidates with good irradiation damage resistance, improved creep strength and oxidation/corrosion resistance at elevated temperatures [154]. ODS steels have been developed and investigated for many years in Japan [155], Europe [156] and the United States [157, 158] etc. Several ODS steels related to this thesis are listed in Table 2.2 along with their chemical composition and microstructural features.

Table 2.2 Selected ODS steel with their chemical compositions and microstructural characteristics.

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Chemical composition</th>
<th>Microstructural characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Y1</td>
<td>Fe-12Cr-0.25Y₂O₃</td>
<td>Y₂O₃ particles with 10-40 nm</td>
<td>[159, 160]</td>
</tr>
<tr>
<td>12YWT</td>
<td>Fe-12Cr-2.5W-0.4Ti-0.25 Y₂O₃</td>
<td>Y-Ti-O nanoclusters with 2-4 nm</td>
<td>[159, 160]</td>
</tr>
<tr>
<td>14YWT</td>
<td>Fe-14Cr-3W-0.4Ti-0.3 Y₂O₃</td>
<td>Y-Ti-O nanoclusters ~2nm</td>
<td>[161]</td>
</tr>
<tr>
<td>MA956</td>
<td>Fe-20Cr-4Al-0.4Ti-0.25 Y₂O₃</td>
<td>(Y,Al)O particles with two types of sizes: 5-100 nm &amp; up to 500 nm</td>
<td>[162]</td>
</tr>
<tr>
<td>PM2000</td>
<td>Fe-20Cr-5.5Al-0.5Ti-0.5 Y₂O₃</td>
<td>(Y, Al)O particles</td>
<td>[163]</td>
</tr>
</tbody>
</table>
The addition of Ti refines the particles and forms more complex oxides [164-168]. TEM studies shown in Fig. 2.9 display very different microstructures of (a) 12Y1 and (b) 12YWT ODS steels. For 12Y1 sample, the particles observed as black dots in Fig. 2.9 (a) are identified as pure crystalline Y₂O₃ with diameters of 10-40 nm and number densities of 10²⁰-10²¹ m⁻³. By adding Ti in the 12YWT sample, the particles in (b) exhibit a much smaller particle size (3-5 nm) and a larger number density (1-2×10²³ m⁻³) compared to those found in 12Y1.

Fig.2.9 Transmission electron micrographs of microstructures of (a) 12Y1 and (b) 12YWT experimental ODS steels.

Three-dimensional atom probe tomography revealed the composition of the nanoclusters (NCs) with high number density to be Y-Ti-O enriched particles in 12YWT and 14YWT
ODS steels with those nanoclusters are called nanostructured ferritic alloys (NFA). The higher concentration of Ti in NCs compared to that of Y in NCs validates the dissolution and subsequent reformation processes [160]. The extremely small NC is a defective and non-equilibrium phase, exhibiting high thermal stability for long time exposure up to 800 °C or short time exposure around 1300 °C [169]. The resistance to coarsening of NCs suggests a slow diffusion rate in at least one element (Ti/Y/O). Oxygen is considered as a rapid diffuser in iron since it is an interstitial species, while yttrium and titanium atoms are slow diffusers due to their large atomic size compared to iron atoms. The combination of high number density and thermal stability of NCs remarkably improves the high-temperature tensile and creep strength of 12YWT at elevated temperatures (such as 700 °C) compared to 12Y1 [159, 170].

The presence of nanoclusters in ODS steels not only improves the mechanical properties but also enhances the irradiation tolerance [171, 172]. The TEM study revealed an uneven cavity distribution in the irradiated Fe-14Cr samples shown in Fig. 2.10 and a unimodal distribution in the irradiated K3-ODS (Fe-16Cr-4Al-2W-0.3Ti-0.3 Y₂O₃) sample, shown in Fig. 2.11. The distribution of helium bubbles demonstrated that bubbles preferentially nucleate heterogeneously along dislocation lines and inclusion particles [173]. The HRTEM study of the helium bubble formation in Fig. 2.11 (e) manifests a thin “shell” feature surrounding the amorphous nanocluster region. The generation of this core/shell structure is illustrated graphically in Fig. 2.11 (f), where several individual bubbles were trapped by the nano-sized clusters and then coalesced to form a bubble shell around the disordered cluster core.
Fig. 2.10 (a) Bright-field TEM image and (b) HRTEM images of the microstructure of cavities in irradiated Fe-14Cr sample. (c) The histogram of cavity size vs. frequency shows a bimodal distribution.
Fig. 2.11 TEM images of microstructure of spherical cavities mostly located (a) at the oxide/matrix interface and (c) around the nanoclusters. Microstructures of the corresponding...
(b) crystalline-oxide particles (~10 nm) and (d) nanoclusters (<2 nm) are clearly seen by changing the overfocus/defocus conditions. (e) HRTEM image of He bubbles appeared as white contrast in association with a disordered cluster domain. (f) The appearance of the nano-cluster core/bubble shell structure is a result of coalescence of small bubbles trapped by the cluster/matrix interface.

L.K. Mansur et al. reported a critical number density of $5 \times 10^{22} \text{ m}^{-3}$ for the alloy design of swelling-resistant materials [174]. Because of the helium dilution effect, swelling will never occur, or will only take place at very high dose for materials with extremely high cavity density ($>5 \times 10^{22} \text{ m}^{-3}$). The cavity number density in irradiated K3-ODS alloy is measured to be $2 \times 10^{23} \text{ m}^{-3}$, greater than the critical design value, while only $2 \times 10^{22} \text{ m}^{-3}$ of cavities were formed in irradiated Fe-14Cr samples. Consequently, the radiation-induced swelling is suppressed significantly in K3-ODS compared to the Fe-14Cr. Furthermore, the number density of crystalline-oxide particles (~10 nm) in K3-ODS alloy is measured to be only $1.0 \times 10^{22} \text{ m}^{-3}$. The much higher cavity density suggests that the helium bubbles were mostly trapped by amorphous nanoclusters (<2 nm) compared to relatively large nano-oxides. Therefore, the presence of high-density of amorphous nanoclusters may be the dominant contributor to the swelling resistance of a specific material.

2.3.2.2 Nanomaterials:
A primary reason for the improved irradiation resistance in NFAs is the large volume fraction of interfaces provided by NCs, removing irradiation-induced point defects and controlling the
nucleation and growth of helium bubbles. Nanomaterials exhibit a large portion of grain boundaries, which is expected to display a similar or even better radiation damage resistance. The fabricated nanolayer Cu-Nb composite showed a remarkable tolerance to radiation damage as a consequence of the short diffusion distance to the nearest sinks. The high flow strength (~2 GPa) is also achieved due to nanoscaled layer thickness according to the Hall-Petch law [175, 176]. Bai et al. [177] modeled the interactions between defects and grain boundaries and found the “loading-unloading” effect. The result is illustrated in Fig. 2.12(b), and compared to the defect motion in a conventional material, shown in Fig. 2.12 (a) [178].

Upon irradiation, the induced interstitials are captured by grain boundaries (“loading”), and then emitted back to annihilate with the vacancies located within a certain range (“unloading”). This “loading-unloading” process for recombination requires much lower energy than conventional vacancy diffusion to the GBs, particularly for those immobile vacancies within the annihilation range. The self-healing mechanism in nanomaterials suggests future development and investigation of improved radiation resistant alloy systems.
Fig. 2.12 (a) In a conventional material, the irradiation induced interstitial defects move to the GBs and cause swelling. The induced vacancies slowly agglomerate to form immobile voids, leading to embrittlement. (b) In a nanomaterial, the interstitial defects get trapped and then re-emitted from GBs to annihilate with vacancies, leaving a healed crystal.

2.4 References


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Chapter 3 Experimental Techniques

3.1 Sample Preparation

3.1.1 High-Energy Ball Milling

Non-equilibrium nanocrystalline powders are synthesized by high-energy ball milling using a SPEX SamplePrep 8000M Mixer/Mill, as shown in Fig. 3.1 (a). The clamp movement is 5.9 cm back-and-forth and 2.5 cm side-to-side, and the clamp speed is 1060 cycles/minute. This high rate of impact deformation increases the internal temperature during the milling process. An additional high-capacity fan was installed on the top of the mill to prevent excessive temperature rise.

Fig. 3.1 (a) The SPEX SamplePrep 8000M Mixer/Mill and (b) the hardened steel grinding vial set.
Different elemental powders and/or compounds are blended and milled together. Material transfer involved in the mechanical alloying process produces a homogeneous solid solution [1-4]. Three alloy types are prepared in this thesis: Fe-14Cr base alloy; Fe-14Cr alloy with Zr/Hf/Sc additions; ODS steel (Fe-14Cr-0.25 wt.%Y₂O₃-0.4 wt.%Ti) with Zr/Hf/Sc additions (designated as 14YT-Zr/Hf/Sc). Elemental powders of Fe, Cr, Zr, Hf, Ti (with purity of 99.9%, 99.9%, 99.95%, 99.995%, 99.5%, respectively and particle size ~325 mesh) were obtained from Alpha Aesar for ball milling. The starting Sc powders were prepared under Argon protective atmosphere via filing arc-cast pellet of pure Sc bulk from Alfa Aesar. Yttria powders with micron-size (less than 10 μm) and nano-size (25-50 nm) were used in this work to investigate the influence of the size of the starting powders on the final microstructures and properties.

The mixed powders were loaded into a hardened steel vial along with the grinding media of 440C martensitic stainless steel balls. The loading process was operated in a glove box under argon atmosphere with O₂< 1 ppm. The ball to powder ratio (BPR) is 10:1 with 16 balls of 1/4 inch, 17 balls of 5/16 inch in diameter and a total of 5.1 g mixed powders. The hardened steel grinding vial set is shown in Fig. 3.1(b). The mix was then milled for 20 hours till reaching a steady state when the composition of every powder particle is the same as the portion of the elements in the starting powder mix.

### 3.1.2 Isothermal Heat Treatment

The as-milled powder was annealed isochronally at different temperatures from 400 °C to 1200 °C for 1 hour. Long time stability of 14YT-4Sc was studied by annealing as-milled
powders at 1000 °C from 1 hour to 60 hours. The heat treatment process was conducted in a Lindberg tube furnace with a quartz tube and a thermocouple for more accurate temperature measurements. Powders were placed in a ceramic boat covered by a piece of Zr foil, so as to avoid reaction with excess oxygen at elevated temperatures. The furnace tube was filled with Ar-2% H₂ gas with positive pressure up to 2-5 psi during the whole annealing process. Temperature fluctuation observed at each annealing temperature was in the acceptable range of ±5 °C. Subsequent cooling was conducted at room temperature with cooling rate of 3-5 °C/s.

3.1.3 Powder Mounting & Uniaxial Pressing

As-milled powders or annealed powders (~0.2 g) were dispersed on glass slides with a proper ratio of Buehler EpoThin Epoxy resin and hardener. This EpoThin Epoxy system is a room temperature curable resin with cure time of ~9 hours and peak temperature of less than 30 °C. After the mixture is fully cured, further polishing was conducted by using silicon carbide sandpapers from 400 to 600, then 800 and 1200 grits, followed by a mechanical polisher with 1 μm alumina suspension for final polishing. The polished dispersed specimens were used for Vickers microhardness tests.

The compacted disk-shaped specimens were prepared through uniaxial hydraulic pressing for FIB channeling contrast imaging and TEM sample preparation. An appropriate amount of powders were mounted in the die and punch set made from tungsten carbide and then subjected to a 2.5 GPa uniaxial pressure at room temperature. The dimensions of disks after
compaction were 1 mm in thickness and 3 mm in diameter. To prepare the samples for He irradiation and further nanoindentation tests, the annealed powders were cold compressed into discs and mechanically polished with an Allied Multiprep system.

3.1.4 FIB “Lift-Out” Technique

Since the Fe based alloys exhibit ferromagnetic properties, high hardness and weak particle bonding, several common TEM sample preparation methods such as jet polishing are not applicable in this work. Hence, the focused ion beam (FIB) in-situ “lift-out” technique [5] was done in a FEI Quanta 3D FEG DualBeam instrument used for TEM/HRTEM sample preparation. A Pt metal line was deposited over the area of interest as a protection layer with a thickness of ~3 μm. Stair-step FIB trenches are cut on each side of the area of interest [6] with 30-50 nA beam currents of Ga⁺ ions accelerated to 30 keV. A thin machined-out membrane was then lifted out of the bulk sample by an OmniProbe micromanipulator and positioned onto a copper grid. The membrane was thinned to electron transparency through the applications of 1 nA to 300 pA, 30keV Ga⁺ ions with the milling angle of 52 ± 2.5° followed by a final polishing using 27 pA, 2 keV Ga⁺ ions with milling angle of 52 ± 6°.

3.1.5 Irradiation Conditions

Ion irradiation process was performed at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. He ions were accelerated to 200 keV with a fluence of $6.5 \times 10^{20}$ ions/m² and a flux of $2.2 \times 10^{17}$ ions/m² for irradiation. Samples during irradiation were
subjected to a temperature of 400 °C/500 °C under a pressure of $8 \times 10^{-5}$ Pa. The simulated peak irradiation damage of Fe-14Cr alloy is 5 dpa at the depth of 500 nm, and the estimated peak He concentration of 4 atom% at the depth of 550 nm was obtained using the SIRM (Stopping and Range of Ions in Matter) program [7].

### 3.2 Sample Characterization

#### 3.2.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a convenient method for phase identification and mean crystallite size estimation. XRD analyses in this work were performed on a Rigaku DMax/A X-ray diffractometer using CuKα radiation. The reduction of crystallite size will broaden the displayed peaks in the XRD profile. The stored strain in a material and the instrumental broadening also affect the width of diffraction peaks [8]. The instrumental broadening was measured to be $\approx 0.1^\circ$ using a single crystal Al$_2$O$_3$ standard. After subtracting the instrumental effect, the grain sizes of as-milled or annealed samples were evaluated using the Scherrer equation [9, 10].

$$d = \frac{K \lambda}{B \cos \theta};$$  \hspace{1cm} (3.1)

$d$ is the crystallite size, $K$ is a crystallite-shape factor, usually approximated to be 0.9 [11], $\lambda$ is the wavelength of the incident radiation (0.1542 nm), and $B$ is the full width of half-maximum of the XRD peak at the Bragg angle $\theta$ after subtracting the instrumental broadening.
Since the Eq. (3.1) does not separate strain broadening from B, the estimated value is smaller than the true grain size. Therefore, the Williamson-Hall method was applied to calculate a more accurate grain size along with the microstrain within the matrix [12, 13]. The approximate formulae for size broadening \((B_s)\) and strain broadening \((B_e)\) with respect to Bragg angle \(\theta\) are given as:

\[
\begin{align*}
B_s &= \frac{k\lambda}{d \cos \theta}; \\
B_e &= C \varepsilon \tan \theta;
\end{align*}
\]  

(3.2)

C is a constant depending on the strain, typically \(\approx 4\) or \(5\). \(\varepsilon\) is the stored strain within alloy systems. The contributions from each factor should be convoluted to get the total broadening B. The assumption of the Williamson-Hall method is a sum of \(B_s\) and \(B_e\). Then multiplying both sides by \(\cos \theta\), we get:

\[
B \cos \theta = C \varepsilon \sin \theta + \frac{k\lambda}{d};
\]

(3.3)

By plotting \(B \cos \theta\) vs. \(\sin \theta\), as illustrated in Fig. 3.2, the strain component of each system can be obtained from the slope \((C \varepsilon)\) and the grain size can be calculated from the intercept \((\frac{k\lambda}{d})\). Although the absolute values of grain size and strain calculated by XRD patterns are not as accurate as those characterized from TEM, their relative values give some useful information, which can reveal trends in grain size/strain evolution upon annealing. In general, grain sizes greater than about 40 nm do not contribute to broadening and are not included in the XRD results.
Fig. 3.2 A Williamson-Hall plot. The slope determines the strain and the intercept is related to grain size.

The Cohen’s method was combined with the least-square method to measure the lattice parameter of each sample [8, 14]. For cubic systems, the Bragg law can be written as [15]:

\[
\sin^2 \theta_{tr} = \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2);
\]  

where \( \theta_{tr} \) is the true angular position where no sources of errors present; \( a_0 \) is the lattice constant, and \( h,k,l \) are the reflection indices. A correction term \( DF(\theta_{ob}) \) was introduced when taking all the other systematic errors into consideration. Based on the analytical treatment proposed by Cohen [16], \( D \) is the drift constant and \( F \) is a correction term as a function of observed Bragg angle \( \theta_{ob} \) with the relation of \( F(\theta_{ob}) = \sin^2(2\theta_{ob}) \); then:
\[
\sin^2 \theta_{ob} = \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2) + D \sin^2 (2\theta_{ob}); \quad (3.5)
\]

Rewrite Eq. (3.5) in a more simplified form:

\[
\sin^2 \theta_{ob} = A\alpha + D\delta; \quad (3.6)
\]

where \( A = \frac{\lambda^2}{4a_0^2} \) is related to the lattice constant \( a_0 \), \( \alpha = h^2 + k^2 + l^2 \) and \( \delta = \sin^2 (2\theta_{ob}) \).

\( \sin^2 \theta_{ob}, \alpha \) and \( \delta \) are known from indexing the diffraction pattern. The least square method is combined with Eq. (3.6) to minimize random observational errors for the lattice constant calculation.

\[
\sum (\text{Error})^2 = \sum (A\alpha + D\delta - \sin^2 \theta_{ob})^2; \quad (3.7)
\]

The best value of coefficients \( A \) and \( D \) can be obtained by solving the following equations:

\[
\begin{align*}
\sum \alpha \sin^2 \theta &= A \sum \alpha^2 + D \sum \alpha \delta, \\
\sum \delta \sin^2 \theta &= A \sum \alpha \delta + D \sum \delta^2;
\end{align*}
\quad (3.8)
\]

In this way, a more accurate lattice parameter is acquired from the coefficient \( A \).

### 3.2.2 Microhardness Indentation & Nanoindentation Tests

The measurement of the resistance to localized plastic deformation gives an overview of the strength of materials. To avoid the influence of the plastic zone with particle boundaries, the dispersed powders were mounted on glass slides with the particle diameter/indent depth ratio around 10:1. Vickers microhardness tests were then performed on individual particles using a Buehler MicroMet II machine with a load of 50 grams and an automated dwell time of 12 seconds. Eight data points were collected for each sample to obtain an average microhardness.
value with a standard deviation. “Out of range” values were probably caused by indenting near the edges of particles and ignored during the data collection.

The change of hardness caused by irradiation-induced defects occurred within a narrow range from the irradiated surface due to the shallow irradiation affected depth. Therefore, the nanoindentation technique was utilized to study irradiated samples and their unirradiated counterparts. Nanoindentation testing was implemented on a Hysitron Ubi-1 quasistatic Nanoindenter with high displacement sensitivity and a low thermal drift derived from the design of its three-plate capacitive transducer. A NorthStar cube corner indentation tip with radius < 40 nm was used since this allows greater indentation depth compared to the Berkovitch indenter at the same load. The maximum load of this Nanoindenter was 10,000 $\mu$N. In situ scanning probe microscopy (SPM) attached to the nanoindenter was used to image sample surfaces before and after indentation. A stand-alone Hysitron nanoindenter is shown in Fig. 3.3.
3.2.3 FIB Channeling Contrast Imaging (FIB-CCI)

FIB-CCI was done using the FEI Quanta 200 3D FEG DualBeam FIB system. This allowed analyzing the microstructure of materials in a relatively large area compared to TEM investigations. The area of interest was illuminated by a 10 pA Ga\(^+\) ion beam at 30 keV to generate secondary electrons for channeling. The image contrast results from the alteration in the ion channeling efficiency [17], which reflects the changes in the grain orientations.
3.2.4 Scanning/Transmission Electron Microscopy (S/TEM)

A JEM-2010F microscope operating at 200 keV was used for Transmission Electron Microscopy (TEM) investigation to precisely characterize the mean grain size, the distribution and the microstructure of grains, and the size of precipitates. The image analyses were carried out using Image J software.

Images using STEM high-angle annular dark-field (HAADF-STEM) were acquired on an aberration-corrected FEI Titan G2 microscope operated at 200 keV. The image contrast in HAADF is determined by the atomic number (Z), the material density and the sample thickness [18]. Thereby different phases could be detected.

Energy-dispersive X-ray spectroscopy (EDS) characterization was done in the STEM mode at 200 keV. The SuperX EDS system with four Bruker Silicon Drift Detectors (SDD) collects X-Ray signal at high counts per second, which enables the detection of solute elements even at low concentration [19].

3.3 References


4.1 Abstract

The influence of 1 to 4 at.% Hf additions on the thermal stability of mechanically alloyed nanocrystalline Fe-14Cr alloys was studied in this work. XRD-calculated grain size and microhardness results were reported versus isochronal annealing treatments up to 1100 °C. Microstructural evolution was investigated using channeling contrast FIB imaging and TEM. Grain size of samples with 4 at.% Hf was found to be maintained in the nanoscale range at temperatures up to 1000 °C. Zener pinning was considered as a major source of high temperature grain size stabilization. By comparing the Orowan strengthening contribution to the total hardness, the deviation of grain size predictions from the actual grain size in Fe-14Cr-4Hf suggests the presence of thermodynamic stabilization by the solute segregation to grain boundaries (GBs). A predictive thermodynamic model indicates that the thermodynamic stabilization can be expected.

Keywords: Mechanical alloying; Nanocrystalline Fe-Cr alloys; Grain growth; Thermal stability
4.2 Introduction

Nanocrystalline materials possess exceptional physical and mechanical properties due to their nano-scale grains [1]. However, they are usually thermally unstable at high temperatures because of a large driving force for grain growth due to high grain boundary area per unit volume [2]. Kinetic stabilization by solute drag, second-phase particle pinning (Zener pinning) [3], chemical ordering, or porosity can reduce the mobility of grain boundaries (GBs) at high temperatures. The second important mechanism to retain nanocrystalline grain size at high temperatures is thermodynamic stabilization, where a non-equilibrium solute segregates to grain boundaries to reduce the grain boundary energy [4].

Kinetic stabilization occurs, when a moving grain boundary encounters second phase particles. There is a pinning pressure $P_z$ exerting on the grain boundary [5], which reduces mobility. In Zener pinning, $P_z = \frac{3F\gamma}{2r}$, where $F$, $\gamma$ and $r$ are the volume fraction, specific GB energy and the radius of the precipitates, respectively. $P_z$ is the pinning pressure on unit area of the boundary. Therefore, stronger pinning effect is obtained with a larger volume fraction of smaller precipitates.

In thermodynamic stabilization, the Gibbs interface analysis gives: $\gamma = \gamma_0 + \Gamma_s [\Delta H_{seg} - T\Delta S_{seg}]$ where $\gamma_0$ is the non-segregated (intrinsic) grain boundary Gibbs free energy; $\Gamma_s$ is the solute excess of the grain boundary and $[\Delta H_{seg} - T\Delta S_{seg}]$ is the Gibbs free energy change associated with segregation of the solute atoms into GBs [6, 7]. $\gamma$ can decrease and reach a metastable equilibrium state with non-equilibrium solute segregating to GBs [6, 8]. In this mechanism, grain growth can be controlled and the nano-scale grain size will be retained at elevated
temperatures. The change of grain size versus annealing temperatures was reported by Darling et al. [9] for various solute additions in Fe. The effect of zirconium additions on grain size stability of mechanically alloyed nanocrystalline Fe-Cr alloys was first reported by Saber et al. [10] and followed by Xu et al.[11]. Hafnium has been used as an addition to titanium, tungsten and iron alloys to improve materials strength at high temperatures, due to second-phase formation [12]. The enthalpy of formation of hafnium oxide is more negative than that of ZrO$_2$, indicating that the second-phase formation leading to Zener pinning effect might be enhanced in Fe-14Cr-Hf alloy system compared to Fe-14Cr-Zr alloy system [13, 14]. On the basis of our recent models [15, 16], which incorporate elastic strain energies due to atomic size misfits along with chemical contributions for both the primary (base) and secondary solutes, we can evaluate the possible thermodynamic grain size stabilization for nanocrystalline Fe-Cr-Hf alloys.

The objectives of this study were to investigate the effect of hafnium additions on the thermal stability of grain size, and to compare the hafnium additions with zirconium additions with respect to the stabilization mechanisms.

4.3 Experimental

Non-equilibrium solid solutions of Fe-14Cr-Hf/Zr containing 0, 2, 4 atomic percent (at. %) of Hf/Zr were synthesized using mechanical alloying in a SPEX SamplePrep 8000M Mixer/Mill. The Fe-14Cr alloy system has no bcc to fcc phase transformation upon annealing treatment which avoids the effect of $\alpha\rightarrow\gamma$ phase transformation on the grain size evolution in
this system [17, 18]. Starting materials of pure Fe, Cr, Hf and Zr powders (with 99.9%, 99.9%, 99.995% and 99.95%, respectively) were obtained from Alpha Aesar for ball milling. These starting powders were sealed into a hardened steel vial along with stainless steel balls under argon atmosphere. The ball to powder mass ratio was 10:1. After 20 hours milling, the as-milled powder was annealed isochronally at different temperatures (from 400°C to 1100°C) for 1 hour under Ar-2%H₂ atmosphere.

X-ray diffraction analyses of the as-milled and annealed samples were carried out using a Rigaku DMax/A X-ray diffractometer using CuKα radiation with a nominal instrumental broadening of 0.1 °. The grain size was calculated by the Scherrer equation from peak broadening [19] after the subtraction of instrumental broadening, assuming the peaks have the Gaussian profile. The lattice parameter was calculated by Cohen’s method combined with the least-square method to minimize error [19, 20]. Vickers hardness was tested for both as-milled and heat-treated powders using a Buehler MicroMet II machine. Powders were mounted on glass slides with Buehler Epothin epoxy. After mechanical polishing, hardness tests were done on individual particles with a load of 50 grams.

Focused ion beam channeling contrast imaging (FIB-CCI) was done on individual particles of Fe-14Cr-4Hf alloys using a FEI Quanta 3D FEG dual-beam FIB system. FIB-CCI images were used to analyze microstructures of the samples in a relatively large area. The transmission electron microscope (TEM) was used to obtain higher resolution images of microstructure for the Fe-14Cr-4Hf alloys annealed at 900 °C. TEM samples were prepared by the FIB “lift-out” technique. TEM images were acquired by a JEM-2010F microscope operating at 200 kV and subsequent image analysis was done using Image J software.
4.4 Results and Discussions

Fig. 4.1a shows the X-ray diffraction patterns of various as-milled Fe-14Cr alloys containing 0-4 at.% Hf/Zr solute additions. The grain size and lattice parameter are also indicated for each composition. As shown in Fig. 4.1a, there is a peak position shifting toward smaller angles by adding the solute elements Hf/Zr. This indicates an increase in the lattice constant of Fe-Cr-Hf/Zr alloys. This also shows that a grain size of less than 10 nm is achieved after mechanical alloying via ball milling. Since internal strain exists in the microstructure due to the severe plastic deformation, the calculated grain size from peak broadening can be smaller than the actual grain size. Fig. 4.1b indicates the changes of the lattice parameters of the bcc alloys versus annealing temperatures. By adding ternary solute elements, lattice parameters of as-milled samples are increased with respect to the reference point (Fe-14Cr). This deviation is attributed to the formation of non-equilibrium solid solution of Fe-Cr alloys with large atomic size misfit caused by- Hf or Zr additions. The higher content of solute added, the more deviation from the reference point occurs. It is evident that excess solute is dissolved into the solid solution of as-milled samples. The trend in Fig. 4.1b is similar for different alloy compositions: lattice parameters decrease as T is increased. This indicates that excess solute atoms and vacancies gradually come out of solid solution. Above 700 °C, all the lattice parameters converge to the same value, within experimental error. The similar lattice parameters of samples annealed at higher temperatures implies that excess solute atoms are no longer present within the bcc matrix.
Fig. 4.1: a) XRD patterns of different alloys under the as-milled condition. D represents diameter of grains, a represents lattice parameter. b) Lattice parameters of each alloy in relation to different annealing temperature.
Fig. 4.2: a) XRD-calculated grain sizes as a function of annealing temperature and b) Vickers hardness as a function of annealing temperature for different alloy compositions.

Fig. 4.2a and 4.2b show the XRD grain size and Vickers hardness, respectively, of various alloys as a function of annealing temperatures. Since lattice strain broadening caused by the presence of second phases is not included in the Scherrer’s method, the actual grain size of
annealed samples can be significantly larger than the value calculated from the XRD pattern [10]. Based on prior experiences, we assume alloys to be nanocrystalline only if the XRD value is less than 40 nm. It is necessary to confirm the grain size by the use of FIB channeling contrast or TEM images.

At lower annealing temperatures (0 to 400 °C), the Vickers hardness of each alloy is high (≥ 8 GPa) due to the defects introduced during the ball milling [21] and the nanocrystalline grain size. The hardness slightly increased up to 400 °C while there is no significant increase in the grain size. The unrelaxed atomic structure and high dislocation density, introduces excess enthalpy into the as-milled microstructure [22]. At low temperature annealing, the excess enthalpy is released through relaxation of large angle grain boundaries without significant grain growth. The grain boundaries reconstruct to a more continuous and ordered state [23] with grain boundary dislocations regularly spaced, enhancing the mechanical properties. Excess vacancies generated during ball milling also facilitate solute atom diffusion to the dislocations [24, 25], and contribute to dislocation pinning. This leads to a hardness increase at low temperature annealing up to 400 °C. In this range of temperature, there is no difference in the effect of Hf and Zr additions on the microstructural evolution and hardness change. Since the diffusion rate of Hf/Zr is very slow in this temperature range, the solute drag mechanism would be the most effective mechanism to mitigate grain growth [2, 26-28].

At intermediate annealing temperatures (400 °C to 800 °C), the XRD grain size of Fe-14Cr base alloy is increased beyond the nano-scale range (Fig. 4.2a). This is consistent with the hardness evolution, which sharply drops with increasing annealing temperatures (Fig. 4.2b).
By adding solute atoms of Hf/Zr, the grain size remains in the nano-scale range up to 800 °C (Fig. 4.2a), and the hardness decreases more gradually compared to the alloy with no Hf/Zr additions (Fig. 4.2b). In this range of temperature, the XRD results show only bcc peaks and no extra peaks corresponding to precipitates are observed. Based on the phase diagrams of Fe-Zr and Fe-Hf alloys [29], the solubility limit for Hf or Zr in Fe is very small, indicating that the fraction of excess solute atoms segregated into GBs could provide thermodynamic stabilization [30], in addition to the solute drag mechanism. The effect of Hf additions on the grain growth and mechanical behavior are similar with Zr additions in this temperature range. Grain size and hardness at high annealing temperatures (>800 °C) are influenced by both the atomic fraction and the type of the solute additions of Hf/Zr. As shown in Fig. 4.2a and 4.2b, increasing the solute content (from 0 to 4 at.%) leads to greater grain size stabilization effect. Both 4 at.% Hf and 4 at.% Zr can stabilize nanocrystalline alloys up to 1000 °C. These alloys still maintain Vickers hardness of 5.2 GPa, which can be useful for high temperature applications. Adding the same content of Hf or Zr addition, the alloy with Hf additions provides better grain size stabilization effect compared to Zr. Hf additions also provide higher hardness than Zr additions up to higher temperature. This is illustrated in Fig. 4.2b where the hardness of Fe-14Cr-4Hf is higher than that of Fe-14Cr-4Zr after 1000 °C heat treatment.

Fig. 4.3 shows XRD patterns of four alloys of Fe-14Cr-Hf/Zr annealed at 900 °C. Black dots (*) indicate extra peaks, which are associated with precipitates. No extra peaks are resolved in the 900 °C annealed Fe-14Cr-2Zr sample. The intensity and the number of extra peaks in Fe-14Cr-4Hf sample are greater than those of Fe-14Cr-4Zr alloy. Additionally, the alloy
systems with higher contents of solute addition have more extra peaks than those with lower solute addition. This suggests that Hf additions introduce more precipitates as well as greater stability compared to equivalent amount of Zr. Therefore, the stability of Fe-14Cr-4Hf extends to higher temperatures, compared to the Fe-14Cr-4Zr alloys.

![XRD patterns](image)

**Fig. 4.3:** XRD patterns for Fe-14Cr-Hf/Zr alloys annealed at 900 °C. Dots (*) point out extra peaks besides four BCC peaks.

The channeling contrast images of Fe-14Cr-4Hf alloy annealed at 900 °C, 1000 °C, and 1100 °C are shown in Figs. 4.4a, b, and c, respectively. Grain size distribution is uniform for each annealing temperature and no abnormal grain growth is observed. The grain size is in the nanoscale range at 900 °C. At 1100 °C, the grains maintained a size of around 200 nm,
thus showing excellent high temperature stabilization by Hf solute additions. Fig. 4.4 also shows that, at annealing temperatures higher than 900 °C, the calculated values for the grain size from XRD results are no longer reliable because the contribution of precipitation-induced strain to the peak broadening can be significant.

![Channeling contrast FIB image of Fe-14Cr-4Hf alloy annealing at different temperatures. a) 900 °C, b) 1000 °C, c) 1100 °C.](image)

Bright and dark field images and the diffraction pattern are shown in Fig. 4.5a to c for Fe-14Cr-4Hf annealed at 900 °C. The grain size distribution obtained is in the nano-scale range.
The diffraction pattern in Fig. 4.5c shows numerous small spots in-between bcc rings of the matrix, corresponding to the presence of precipitates formed during the annealing treatment. The number average grain size for the distribution (Fig. 4.5e) is 52 nm, calculated from more than 200 grains measured using the DF images. Moreover, as illustrated in Fig. 4.5d, the arrows in the enlarged area indicate nanosized precipitates, uniformly distributed throughout the grains. The presence of precipitates is consistent with the extra peaks found in the x-ray diffraction patterns in Fig. 4.3. Therefore, it is likely that Zener pinning contributes to stabilization of Fe-14Cr-4Hf alloy at high temperatures.
Fig. 4.5: TEM image of Fe-14Cr-4Hf annealed at 900 °C. a) bright field image, b) dark field image, c) diffraction pattern, d) bright field image with higher magnification. The insert image is the enlarged area as plotted in d) of dashed square. e) histogram of number fraction of grain size
There are several mechanisms contributing to the total hardness of alloys. Grain size refinement can be inferred by the Hall-Petch equation; \( \sigma_y = \sigma_0 + K_y D^{-1/2} \); where \( \sigma_y \) is the yield stress, \( K_y \) is a constant determined by the slope of the Hall-Petch line, and \( D \) is the grain diameter. Since Vickers hardness is related to the yield stress by the relation of \( H/\sigma \approx 3 \), the Hall-Petch equation can also be given in terms of the hardness [31]: \( H_y = H_0 + K_H D^{-1/2} \). The TEM results obtained for mean grain size were 52 nm, 143 nm, and 173 nm for alloys annealed at 900 °C, 1000 °C, and 1100 °C, respectively. The corresponding Hall-Petch plot is shown in Fig. 4.6. The line plotted includes the base Fe-Cr alloy from ref. [10] and Fe-14Cr-4Hf alloy annealed at 700 °C and 1100 °C. We assume that 700 °C annealed sample does not form precipitate at this temperature, and also all excess solute Hf atom are segregated to GBs. Therefore, precipitation and solid solution hardening can be negligible for this sample. At 1100 °C, according to Fig. 4.4c, grain size increased three times compared to 700 °C. The Orowan strengthening can also be neglected at this point due to coarsening of nano-scale precipitates. Thus, the Orowan strengthening is only considered for the 900 °C and 1000 °C annealed samples. The trend line shown gives \( H_0 = 2.31 \) GPa and \( K_H = 22.35 \) GPa nm\(^{1/2} \). \( \Delta H \) (Orowan hardening) is calculated through subtraction of the total hardness from the grain size hardening for 900 °C annealed sample. Accordingly, \( \Delta H = 1.26 \) GPa is taken to be the Orowan strengthening contribution \( (H_{oro}) \) [32]:

\[
\Delta H = H_{oro} = 3\sqrt{3} \left( \frac{\ln(d/r_0)}{\ln(L/r_0)} \right)^{3/2} \frac{Gb \ln(L/r_0)}{L} \frac{1}{2\pi},
\]

where \( d \) is the precipitate size, \( L \) is the interparticle spacing, \( G \) is the shear modulus (85.3 GPa), \( b \) is the Burgers vector (0.248 nm) and \( r_0 \) is the dislocation core radius, assumed to be
four times the Burgers vector. Substituting the values of $d=23$ nm obtained from the TEM images (not shown here) into the Orowan strengthening equation, the interparticle spacing $L$ is obtained as 41 nm. $L$ is related to the volume fraction, $f$, of spherical particles by:

$$L = d \left[ \left( \frac{\pi}{4f} \right)^{\frac{1}{2}} - 1 \right];$$  \hspace{1cm} (4.2)

This predicts that the volume fraction of precipitates is 0.107. According to the Zener pinning model [33]:

$$\frac{d}{d} = \frac{Z}{f^{m}};$$  \hspace{1cm} (4.3)

For Fe-based alloys, $Z$ is 1.635 and $m=0.5$ when $f>0.05$ [33] and equation (3) gives a grain size of $D=115$ nm. The deviation of the Zener pinning predictions (115 nm) and the actual grain size (52 nm) suggests that in addition to kinetic stabilization, there is a possible contribution from thermodynamic stabilization of the nano-grains in Fe-14Cr-4Hf alloy at 900 °C.
To provide insight into the possible thermodynamic contribution, the thermodynamic model by Saber et al. [16] is used to assess the effect of Hf additions on the grain size stability via solute segregation to GBs. Using thermodynamic parameters available in the literature [34-38], the grain size predictions versus the temperature for Hf additions to Fe-14Cr are shown in Fig. 4.7a. The plot indicates that 4 at.% Hf addition can stabilize the nano-scale grain size up to 1000 °C by the thermodynamic mechanism. However, it should be emphasized that these predictions only consider thermodynamic stabilization in the absence of other
contributions. The formation of precipitates can influence the magnitude of solute segregation to GBs, and consequently, the grain size at each annealing temperature would be greater than the value that is predicted by the thermodynamic model. Fig. 4.7b shows the excess amount of Hf content that would remain in the solid solution at each temperature after segregation to GBs. This indicates that at 900 °C, the Hf content left in the bcc matrix would be sufficient (1.5 at.%) to initiate precipitation, given that the equilibrium Hf solubility in Fe is <1 at.% at 900 °C. Therefore, within this range of temperature, the Zener pinning stabilization would compete with thermodynamic stabilization. HRTEM and EDS-STEM studies are required to establish the contribution of each mechanism to stabilizing nano-scale grain size for this range of temperatures. The characterization of the nanocluster precipitates including crystal structure, chemistry and the orientation relationship to the bcc matrix will be discussed in a forthcoming paper.
Fig. 4.7: Model predictions for Fe-14Cr-xHf alloys. a) grain size b) excess of Hf.
4.5 Conclusions

This investigation has shown that additions of Hf up to x=4 at.% in ball milled Fe-14Cr-xHf can give effective grain size stabilization in the nano-scale range up to 1000 °C. The hardness of nearly 5.2 GPa is maintained in Fe-14Cr-4Hf at 1000 °C. This offers a possible route for maintaining high strength, thermally stabled nanocrystalline ferritic alloys. Employing the Hall-Petch grain size strengthening and Orowan particle strengthening equations for Fe-14Cr-4 at% Hf annealed at 900 °C, the deviation of grain size predictions from the actual grain size suggests the possibility of a thermodynamic stabilization mechanism contribution due to solute segregation to GBs. The use of a thermodynamic model shows that thermodynamic stabilization can be a viable additional mechanism in conjunction with Zener pinning for stabilizing the nano-grains in Fe-14Cr-4Hf at 900 °C.

4.6 Acknowledgements

Support for this study by the Department of Energy, Grant DE-NE0000538, is gratefully acknowledged. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

4.7 References


Chapter 5 Influence of Scandium Addition on the High-Temperature Grain Size

Stabilization of Oxide-Dispersion-Strengthened (ODS) Ferritic Alloy

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5.1 Abstract

The influence of 1 to 4 at.% Sc addition on the thermal stability of mechanically alloyed ODS ferritic alloy was studied in this work. Sc addition was found to significantly stabilize grain size and microhardness at high temperatures. Grain sizes of samples with 1 and 4 at.% Sc was found maintained in the nanoscale range at temperatures up to 1000 °C with hardness maintained at 5.6 and 6.7 GPa, respectively. The detailed microstructure was also investigated from EDS elemental mapping, where nanofeatures [ScTiO] were observed, while nanosized [YTiO] particles were rarely seen. This is probably due to the concentration difference between Sc and Y, leading to the formation of [ScTiO] favoring that of [YTiO]. Precipitation was considered as the major source for the observed high temperature stabilization. In addition, 14YT-Sc alloys without large second phases such as Ti-oxide can exhibit better performance compared to conventional ODS materials.

*Keywords: Mechanical alloying; Oxide-dispersion-strengthened alloy; Thermal stability; Sc stabilization*
5.2 Introduction

Oxide-dispersion-strengthened (ODS) ferritic steels possess high temperature stability, high creep strength, and high-dose irradiation tolerance, which make them promising for structural applications in nuclear power reactors [1]. Extensive experiments have been done to develop and optimize ferritic ODS alloys for structural application in nuclear environments. 14YWT, which is Fe-14Cr-3W-0.25 wt.%Y₂O₃-0.4 wt.%Ti [2], was found to have a more refined microstructure with superior properties. Yttria (Y₂O₃) is selected for standard ODS alloys due to its extremely high temperature stability. (Tₘ Fe=1538 °C, Tₘ Y₂O₃ =2425 °C). 14% Cr is chosen because Fe-14Cr composition lies outside of the α→γ transformation area in the Fe-Cr phase diagram. Relatively high Cr content also provides good corrosion/oxidation resistance.

A variety of precipitates with different sizes, morphologies, compositions and structures were observed and analyzed by M. C. Brandes et.al [3]. Ti (O,N,C), with size in the range of 20-50 nm, mostly were found to locate along the grain boundaries (GBs). Near stoichiometric complex oxides Y₂Ti₂O₇ and Y₂TiO₅ precipitates with sizes in the range of 5-10 nm were observed at grain boundaries and grain interiors [4]. Much smaller Y-Ti-O particles with sizes around 1-4 nm with high lattice coherency with the bcc ferritic matrix are termed nanoclusters (NCs). The presence of these NCs was first discovered by Larson et al. [5] through atom probe tomography (APT), and then later confirmed [6, 7]. These studies found Y-Ti-O nanoclusters with new crystal structures, which might be sub-oxide or even coherent GP zone-type structures [2]. The smallest Y-Ti-O nanoclusters are the key microstructural features in impeding grain growth and dislocation motion at elevated temperatures [8-11].
Recently, Brandes et al. [9] have demonstrated that NCs pin gliding dislocations. In addition, the large surface area of nanoclusters provides sites to trap He atoms into fine-scale bubbles, reducing He embrittlement caused by irradiation [12].

The nature of precipitate in ODS alloys depends on the processing time and temperature [13-15]. Also, the alloy composition influences the precipitation formation. Ukai et al. first observed the benefit of Ti addition in refining oxide dispersoid (Y₂O₃) sizes, and increasing nanoparticle densities and volume fraction, through changing their chemical composition. Since then various TEM studies have investigated the structures of those refined Y₂Ti₂O₇/Y₂TiO₅ oxides [16-21]. However, it is reported that high O: Ti ratio results in the formation of coarser TiO₂ particles instead of the finer Y-Ti-O NCs [1]. Y-Ti-O nanoclusters resist coarsening and chemistry changes at elevated temperatures [13, 22, 23]. The high temperature stability of NCs may result from vacancy-oxygen pairs, as predicted by Fu et al. based on ab initio calculations [24], and also the presence of Ti [25]. The high affinity of NCs for vacancies would slow the diffusion rate of solute atoms from matrix to NCs [7].

In our previous studies of Fe-14Cr alloy with Zr/ Hf addition [26-28], it is found that both Zr and Hf provide good grain size stabilization at elevated temperatures. This observation is consistent with the thermodynamic ternary model proposed by Saber et al.[29, 30]. The model also predicts that Sc can serve as a good stabilizer, even more effective than Zr and Hf. Scandium behaves mechanically and physically similar to Y [31], Zr and Hf [32-34]. It was first used in Al and Al alloys in 1971 [35, 36]. Subsequently, it has been found that Sc-doped nickel and steels exhibit better resistance to radiation swelling and embrittlement [37]. There are several patents for Fe and Ni based alloys containing Sc [38-40]. Sc addition in
01Kh18T steel (Fe-18%Cr) made the ferrite grains smaller and slowed grain growth during heating processes [41]. However, at the present time, Sc containing alloys have not been widely used due to the high cost for producing Sc and incorporating Sc into the matrix [41]. Mechanical alloying such as high-energy ball milling can produce nanocrystalline materials with grain size less than 100 nm. Nano-grains can still be maintained after a subsequent high temperature annealing. Fe, Y₂O₃ and Sc are essentially immiscible. One of the possible approaches for synthesis is high-energy ball milling. In this way, yttria (Y₂O₃) and Sc can be introduced into the Fe matrix by the combination of fragmentation and severe plastic deformation, leading to the formation of a highly supersaturated solid solution [42]. Y reacts readily with oxygen and so does Sc [35]. Hence, the competition between Sc and Y atoms to form oxide nanoclusters will be investigated in this study, where both Sc and Y are added into the Fe-based alloy system.

Recent advances in nanocrystalline materials with outstanding properties require high-temperature stability, particularly in future fission reactors. In this study, we report a new alloy system based on conventional ODS (14YT) with Sc addition to provide better high temperature stability and strength.

5.3 Experimental

The samples used in this study were prepared by mechanical alloying of component elemental and oxide powders in a SPEX SamplePrep 8000M Mixer/Mill (clamp movement is 5.9cm back-and forth and 2.5cm side-to-side; clamp speed is 1060 cycles/minute). An additional high-capacity fan was installed on the top of the mill to prevent excessive
temperature rise during the milling process. Starting powders (Fe, Cr, Y_2O_3, Ti) and bulk pure Sc (arc-cast pellet) were obtained from Alfa Aesar, and Sc powders for ball milling were prepared by filing bulk pure Sc under a protective atmosphere. The base alloy is Fe-14Cr-0.25 wt.%Y_2O_3-0.4 wt.%Ti, which hereafter designated as 14YT for simplicity. Sc addition influence is studied by preparing solid solutions of 14YT containing 1, 2, and 4 atomic percent (at.%) Sc, denoted as 14YT-1Sc, 14YT-2Sc, and 14YT-4Sc, respectively. These mixed powders of 5.1g along with stainless steel balls (16 of 1/4 inch and 17 of 5/16 inch in diameter) were sealed into a hardened steel vial with ball to powder mass ratio of 10:1. To reduce the contamination of excess oxygen and carbon, the preparation processes of filing, weighing and sealing process are performed in an argon-filled glove box with less than 1 ppm oxygen. 20 hours milling results in nanostructured ferritic alloy (NFA) of the as-milled powders. These powders were annealed isochronally at different temperatures (from room temperature to 1100 °C) for 1 hour under Ar-2% H_2 environment.

X-ray diffraction was conducted using Cu Kα radiation in a Rigaku Smartlab X-ray diffractometer. XRD analyses were used to calculate the grain size and microstrain within the matrix of each sample using the Williamson-Hall method [43]. Vickers hardness is used to measure the material’s resistance to localized plastic deformation. Powders of both as-milled samples and thermally treated samples were mounted on glass slides with Buehler Epothin epoxy. Hardness measurements were carried out with a load of 50 grams on individual particles after mechanical polishing.

Various characterization techniques were used to analyze the microstructural change with different alloy composition and processing history. Focused ion beam channeling contrast
imaging (FIB-CCI) was used to study the grain size distribution within an individual particle in a relatively large area, employing a FEI Quanta 200 3D FEG dual-beam focused ion beam instrument. Transmission electron microscopy (TEM) is particularly useful for characterizing nanometer-scale features at higher resolution. TEM analyses were done on a JEM-2010F microscope operated at 200keV. HAADF-STEM images were taken in an aberration-corrected FEI Titan G2 microscope operated at 200keV. The TEM/STEM specimens were prepared by FIB milling and the “lift-out” method. Energy-dispersive X-ray spectroscopy (EDS) characterization was done in the STEM mode at 200 keV, to obtain EDS elemental mapping.

5.4 Results and Discussions

The grain size evolution and corresponding hardness changes as a function of annealing temperature are shown in Figs. 5.1a) and b). The grain sizes of the Fe-14Cr are beyond the nano-scale range after 600 °C. The base ODS alloy (14YT) with Y₂O₃ and Ti addition shows stabilization with respect to hardness up to around 700 °C. After that, the hardness data for Fe-14Cr and 14YT are similar when error bars are considered. Notably, Sc additions from 1at.% to 4 at.% significantly stabilized and maintained nano grains and high hardness to higher annealing temperatures. 14YT alloys with 1 at.% and 2 at.% Sc additions show nearly overlapping curves for both grain size and hardness data. This indicates that small increase of Sc stabilizer did not lead to higher stabilization. However, with increasing the Sc content up to 4 at.%, hardness data in Fig. 5.1b) displays a significant rise compared to other alloys.
Continue increasing the annealing temperature to 1200 °C causes all the grains to grow to micron size and to produce similar hardness values.

![Graph showing grain size and hardness vs. annealing temperature](image)

Fig. 5.1 a) XRD-calculated grain sizes as a function of annealing temperature and b) Vickers hardness as a function of annealing temperature for different alloy compositions.

The high hardness for 14YT-Sc alloys after 1000 °C annealing indicates the existence of effective strengthening mechanisms. Hall-Petch grain size strengthening and Orowan nanoparticle size strengthening are expected to make the dominant contributions. However, hardness is reduced at higher annealing temperatures or at longer time due to grain growth and/or precipitate coarsening. The smallest oxide nanoclusters found in ODS alloys can serve as stable obstacles to dislocation motion. They are the main reason for high strength and irradiation resistance [44].
Figs. 5.2a) and b) show the XRD patterns of 14YT alloys with 0 to 4 at.% Sc addition in as-milled condition and after being annealed at 1000 °C for 1 hour, respectively. In Fig. 5.2a), only four major BCC peaks are observed in all of the alloys, which confirm a complete solid solution after ball milling. In the base alloy without Sc addition, Alinger et al. has confirmed a supersaturated solid solution obtained via dissolving Y and O by mechanical alloying (MA) [2]. Hence, high external energy can result in the dissolution of Sc into the ferrite matrix in the same way. The radius of Sc (0.163 nm) and Y (0.180 nm) atoms significantly differ from that of the Fe (0.126 nm). Furthermore, a high dislocation density is obtained after ball milling. Thus, peaks shown in the XRD patterns in Fig. 5.2a) are broadened. Calculated grain sizes are similar for different alloy compositions. However, peak positions shift as indicated by the purple arrows and yellow dash lines with increasing addition of Sc, accompanied by the internal strain increase. This is caused by the lattice constant change to accommodate more Sc in the non-equilibrium solid solution state. After annealing at 1000 °C for 1 hour, the base 14YT alloy has experienced recovery with nearly zero internal strain, as shown in Fig. 5.2b). The other three alloys containing Sc show a decrease in internal strain compared to those of their as-milled counterparts; however, higher Sc addition yields larger microstructural strain. It should be pointed out that no extra peaks can be resolved in the XRD patterns, suggesting that a metastable solid solution is preserved during high temperature annealing or the size/and volume fraction of precipitates is too small to be resolved by the XRD technique.
Fig. 5.2 XRD patterns of 14YT alloys with 0, 1, 2 and 4 at.% Sc addition. a) under as-milled condition and b) annealed at 1000 °C for 1 hour. Internal strain of each alloy is indicated above each pattern. The yellow dash lines and purple arrows represent peak positions of the 14YT base alloy and 14YT-4Sc alloy, respectively, to show the peak position shifting.
The microstructure of the 14YT-1Sc sample after 1000 °C annealing was obtained by FIB ion channeling contrast imaging at low magnification, as shown in Fig. 5.3a). A bimodal distribution is evident in this large area. However, the fraction of nano-scaled grains (<100 nm) is larger than that of micron-scale grains. TEM was used to further analyze the stabilized nano-grain area after 1000 °C annealing. Figs. 5.3b), c) and d) are the TEM bright field images at different magnifications. Precipitates are observed in Fig. 5.3d) and can be seen as small black spherical regions embedded in the matrix. The distribution of precipitates is relatively homogeneous from grain to grain, while the size of precipitates varies within a very small range. Precipitates grow faster at locations of high defect densities such as grain boundaries or triple junctions. However, even after 1000 °C annealing (0.65\(T_m\)), the largest precipitate size is still very small (<10 nm), and can exert a high pinning pressure on the grain boundary. Histograms showing the distribution of grain size and precipitate size are given in Figs. 5.3e) and f), respectively. It is shown that a few grains underwent coarsening while the major fraction of grains remained nano scale with an average grain size of 50.8 nm. This result is in good agreement with the representative images presented in Fig. 5.3a). Thus, even at 1000 °C annealing temperature, 1at.% Sc addition exerted a significant stabilization effect on 14YT alloys. Data in Fig. 5.3f) indicates no appreciable growth of the precipitates. The average precipitate size is determined to be 3 nm. These extremely small precipitates can play a key role in impeding grain growth at high temperatures. For precipitates nucleated along the grain boundaries, their sizes can be larger than those nucleated within the matrix due to faster diffusion along grain boundaries. This size variation is shown in Fig. 5.3d).
Fig. 5.3 Microstructures of the 14YT-1Sc alloy annealed at 1000 °C for 1 hour. a) Ion channeling contrast image with high magnification; b), c) d) Bright-filed TEM images with increasing magnification. e) and f) are histograms of number fraction of grain sizes and precipitate sizes.
precipitation sizes, respectively. The average size of grains (51 nm) and precipitates (3 nm) are calculated.

Fig. 5.4a) is the ion channeling contrast image of the 14YT-4Sc sample after being annealed at 1000 °C for an hour. Unlike the 14YT-1Sc sample treated under the same condition, the microstructure shows no bimodal distribution. Nano sized grains are further confirmed by the TEM images shown in Figs. 5.4b), c) and d) with increasing magnification. Fig. 5.4d) shows the precipitate size and distribution in 14YT-4Sc alloys. The grain boundary is a favorable location for precipitate nucleation and growth, where the size and number density of precipitates are larger than those in the matrix. This is indicated by the white arrows in Fig. 5.4d). Figs. 5.4e) and f) show the distribution of grain sizes and precipitate sizes in the 14YT-4Sc alloys annealed at 1000 °C, respectively. With more Sc addition, the grain size distribution becomes narrower with a mean diameter of around 32 nm. The better grain size stabilization with increasing Sc concentration is consistent with grain size trend in Fig. 5.1a). The distribution in Fig. 5.4f) gives a mean precipitate size of 3.6 nm, which is slightly larger than that in the 14YT-1Sc sample in Fig. 5.3f). The majority of precipitates are still in the range of 2.5~3 nm, while nanoclusters along the grain boundaries grew relatively larger to 5-6 nm. This might be produced by the segregation of excess Sc atoms to grain boundaries, which provides more solute atoms for nanoclusters to agglomerate.
Fig. 5.4 Microstructures of the 14YT-4Sc alloy annealed at 1000 °C for 1 hour. a) Ion channeling contrast image with large magnification; b), c) Bright-filed TEM images with increasing magnification. White arrows show larger precipitates along grain boundary compared to those within the matrix. e) and f) are histograms of number fraction of grain
sizes and precipitation sizes, respectively. The average size of grains (32 nm) and precipitates (4 nm) are calculated.

In order to further clarify the effect of Sc on grain size stabilization, EDS mapping in Figs. 5.5 and 5.6 was used to reveal element distributions in the 14YT-1Sc and 14YT-4Sc alloys after 1000 °C annealing, respectively. The HAADF image presented in Fig. 5.5a) shows precipitates as black dots. Based on the remaining images in Fig. 5.5, the black dots both along GBs and within the matrix can be identified as [ScTiO] nanoclusters. YO aggregation was detected by EDS in Fig. 5.5, but is not as obvious as the [ScTiO] NCs. Fe is clearly depleted in those precipitates while Cr concentration is quite low. The [ScTiO] NCs are also observed by EDS for 14YT-4Sc alloys in Fig. 5.6. However, YO is not detected in this figure, which suggests that Y₂O₃ may be dissolved in the matrix, or all the oxygen atoms are combined with Sc. Precipitates pin the GBs (shown as yellow dashed line in Fig. 5.6a) and are coarsened to some extent at the triple junction positions.

Sc and Y elements are chemically similar [45]. The kinetics of nanoparticle nucleation depends on various factors such as the solute atom concentrations, diffusion rate of the nanoparticle-forming elements, volume free energy change and interfacial energy change associated with their formation. The latter two energies determine the nucleation energy barrier [46]. The formation energy of Sc₂O₃ is -1537 KJ/mol, and that of Y₂O₃ is -1548 KJ/mol at 1000 °C [47]. The similar affinity for oxygen leads to nano-oxide formation competition between Sc and Y atoms. However, when adding 4 at.% Sc into base 14YT alloy system, the concentration difference between Sc and Y elements is significant. Nearly all the
oxygen atoms are consumed by Sc, instead of forming [YO]. Ti atoms are also found in nanoparticles as seen in the EDS mapping. The similar particle size to that observed in conventional ODS steel suggests that Ti atoms help refining the precipitate size, increasing the particle number density, and changing the chemical composition from Sc$_2$O$_3$ to [ScTiO].

Fig. 5.5 EDS elemental mapping of 14YT-1Sc alloy after being annealed at 1000 °C for 1 hour. a) HAADF-STEM image shows the selected area near the grain boundary. Elemental mapping of b) Fe, c) Cr, d) Sc, e) Ti, f) Y, g) C and h) O.
Fig. 5.6 EDS elemental mapping of 14YT-4Sc alloy after being annealed at 1000 °C for 1 hour. a) HAADF-STEM image. The dashed yellow lines show grain boundaries of a selected grain. Elemental mapping of b) Fe, c) Cr, d) Sc, e) Ti, f) Y, g) C and h) O. Red arrows indicate that precipitates, which are enriched in Sc, along the grain boundary are smaller than those located at triple junctions.

It must be emphasized here that the significant microstructural difference between 14YT-Sc alloy and the conventional ODS steel is the lack of large precipitates such as TiO$_2$ and intermetallic compounds. The formation energy of TiO$_2$ at 1000 °C is -931 KJ/mol [48]. It is therefore apparent that oxygen interaction with Sc and Y atoms is favored over that for Ti atoms. No excess oxygen content was left to form large Ti-oxides. For the intermetallic compounds, heats of formation energy are either positive or slightly negative for compounds such as ScCr, ScTi, ScY and FeSc [49]. This makes the intermetallics less likely to form.
Hirata et al. [50] proposed that a defective rock-salt crystal structure can be fully coherent to the bcc matrix of 14YWT-ODS alloy. Due to the high chemical variability, this NaCl-type structure allows the formation of non-stoichiometric nanoparticles with a broad compositional range. In addition, high radiation damage tolerance of the nonstoichiometric nanoparticles is improved by the defective structure [13]. Moreover, the structural coherence with the matrix, along with the low solubility of solutes in $\alpha$-Fe, effectively prevent nanoparticles from coarsening [51]. Therefore, nanoclusters in base ODS alloys exhibit remarkable stability at high temperatures. The 14YT-Sc alloy system investigated here shows better high temperature stability and hardness than conventional ODS steel. Different alloying compositions have also been evaluated. 1 at.% Sc addition is sufficient to keep both the grain size and mechanical properties stable at lower temperatures, whereas for high temperature application, up to 4 at.% Sc addition needs to be used.

5.5 Conclusions
Sc was added into base ODS alloy (14YT) to study the evolution of grain size and hardness. A small grain size of 32 nm and high hardness of 6.7 GPa are maintained in 14YT-4Sc after 1000 °C heat treatment for 1 hour. The dominant stabilization mechanism at this high temperature is precipitation, where [ScTiO] nanofeatures were observed in EDS elemental mapping. With Sc content increasing, the nano sized [YTiO] particles were not observed, indicating O and Ti atoms prefer combining with Sc than Y in 14YT-Sc alloy system. These nanoparticles exhibit excellent thermal stability and high-temperature performance. 14YT-Sc alloys with a large number of nanoclusters exhibit negligible second phase growth under
thermal treatments. In addition, 14YT-Sc alloys without large second phases could exhibit better performance compared to conventional ODS materials.

5.6 Acknowledgements

Support for this study by the Department of Energy, Grant DE-NE0000538, is gratefully acknowledged. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

5.7 References


Chapter 6 Long-Term Stability of 14YT-4Sc Alloy at High Temperature

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6.1 Abstract

14YT alloy (Fe-14Cr-0.25wt.%Y_2O_3-0.4wt.%Ti) with 4 at.% Sc addition was previously reported to exhibit a nanoscale microstructure and high strength when annealed at temperatures up to 1000 °C (0.65T_m) for 1 hour. Here we report that the microstructure and mechanical behavior of 14YT-4Sc alloy after long-term annealing for up to 60 hours at 1000 °C. FIB analysis shows abnormal grain growth with annealing time, while a large fraction of the matrix still consists of nanoscale grains. TEM images reveal a slight growth of nano grains, with estimated grain growth exponent, n, to be 0.29. Sc-Ti-Y-O enriched nano oxide particles (<10 nm) were observed in EDS mapping of the 14YT-4Sc-60h sample. The nanostructure retention at the high temperature of 1000 °C for 60 hours is attributed to these complex nano oxides.

*Keywords:* Nanocrystalline ODS ferritic alloys; Grain growth; Sc stabilization; long-term stability

6.2 Introduction

ODS ferritic steels, with excellent creep strength [1, 2] and high resistance to irradiation, have been the focus of extensive research for possible structural applications in generation IV fission and fusion reactors [3, 4]. A major requirement for this class of steels is to have high
microstructural stability in order to withstand a very hostile environment such as high neutron fluxes and elevated temperatures [5].

Grain growth falls into two categories: normal grain growth, where grains grow almost uniformly [6]; and abnormal grain growth, where “abnormally large grains” may nucleate and grow at the expense of a relatively fine matrix [7]. This abnormal grain growth may be caused by a local low pinning force [8, 9], resulting in a large growth rate. It appears that an abnormal grain can develop from a matrix where normal grain growth took place, indicating that no initial size advantage is needed [10]. It is suggested that normal grain growth should ideally follow a parabolic relationship [6, 11]:

\[ D^2 - D_0^2 = Kt \]  

(6.1)

where \( D \) is the mean grain size at time \( t \), \( D_0 \) is the initial mean grain size and \( K \) is a temperature dependent rate constant. However, in practice, the experimental data for isothermal grain growth has been fit to a power-law incorporating the time exponent \( n (\leq 0.5) \) [12]:

\[ D^{1/n} - D_0^{1/n} = Kt \]  

(6.2)

The parameter \( n \) depends on the grain growth mechanisms [6, 13, 14], which may be influenced by residual strain, grain boundary energy and pinning force as a result of second phase particles or solute drag [15]. Research and theories suggest that the growth rate of nanomaterials can be retarded by the solute drag effect and vacancy generation model [16]. The kinetics of grain growth in pure ball-milled Fe has been reported to show good agreement with the excess-volume model, with linear growth at small grain sizes and transferring to nonlinear kinetics when the grain size >150 nm [17].
Previous researches have investigated the addition of Zr [18, 19] and Hf [20, 21] elements to the ball milled Fe-14Cr base alloy in context with the thermodynamic stabilization ternary model [22, 23]. It is found that Zr/Hf additions help to stabilize a nano microstructure at up to 900 °C and 1000 °C, respectively. Sc is also predicted to be a strong stabilizer to the Fe-Cr alloy based on the model [22, 23] and 14YT (Fe-14Cr-0.25wt.%Y₂O₃-0.4wt.%Ti) ODS alloy with Sc addition was reported to have good microstructural and mechanical stability after high temperature annealing [24]. The high temperature stabilization is mainly attributed to the presence of a dispersion of [ScTiO] nanoclusters. These nanoclusters exert pinning forces on grain boundaries, thereby inhibiting grain coarsening. The grain growth may occur, when second phase particles coarsen [25] caused by Ostwald ripening [26] or when chemical modifications of the matrix result in less solute drag [5, 27]. At high temperatures, the solute drag effect is negligible. Therefore, the size distribution of second phase nanoclusters is one of the key stabilizers of the 14YT-4Sc alloy in this work. However, there are very few reports on the grain growth behavior of ODS ferritic alloys in the literature, especially no detailed study regarding the effects of long-term thermal exposure on the 14YT-4Sc alloy.

In this work, an isothermal annealing at 1000 °C (0.65Tₘ) was carried out on 14YT-4Sc samples from 1 hour to 60 hours. The subsequent evolution of microstructure and mechanical property (hardness) was investigated. The study of grain growth behavior of nanocrystalline 14YT-4Sc alloy can facilitate hot compaction of mechanically alloyed powders into fully dense nanostructured compacts [15]. High pressures/temperatures are needed for consolidating and sintering such high hardness alloys [28]. While the temperature studied in
this work (1000 °C) is higher than expected under service conditions in reactors [29], it is relevant to study the long-term thermal stability of 14YT-4Sc alloy.

6.3 Experimental

The alloy studied in this work, Fe-14Cr-4Sc-0.25wt.%Y₂O₃-0.4wt.%Ti, will be referred to as 14YT-4Sc hereafter. Powders used for the long term annealing study were mechanically alloyed using a SPEX SamplePrep 8000M Mixer/Mill [24]. After 20 hours milling, the as-milled powders were subjected to isothermal annealing at 1000 °C for 1h, 10h, 15h, 24h, and 60h under Ar-2%H₂ environment, and these will be designated as 14YT-4Sc-Xh (X=1, 10, 15, 24, 60). The annealing was done in a Lindberg tube furnace with a thermocouple to monitor the temperature. Powders were covered with a piece of Zr foil, so as to avoid reaction with excess oxygen during the annealing procedure, and placed into a quartz tube. Subsequent cooling was conducted at room temperature by moving the tube away from the furnace. X-ray diffraction was done for both as-milled and annealed samples using a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation. The Williamson-Hall method [30] was applied to estimate grain size and microstrain from the XRD data. Micro-hardness was measured with a 50g load. The variation of grain size with annealing time was determined by both focused ion beam channeling contrast imaging (FIB-CCI) and TEM. The FEI Quanta 200 3D FEG dual-beam FIB system measures a relatively large area to show grain size distribution and abnormal grain growth. Image contrast was resulted from the changes in the grain orientations, leading to variations in ion channeling efficiency [31]. TEM images were obtained using a JEM-2010F microscope to more precisely characterize the average nano
grain sizes and their distribution. More detailed EDS elemental mapping and HAADF-STEM images were obtained using an aberration-corrected FEI Titan G2 microscope at 200 kV [32].

6.4 Results and Discussions

The grain size and microstrain obtained from XRD and the corresponding Vickers microhardness as a function of annealing time are shown in Fig. 6.1(a) and (b), respectively. For the as-milled condition, the average grain size is about 25 ± 5 nm with the highest microstrain of 0.67%. The grain size in Fig. 6.1(a) increases with longer annealing and nanograins were maintained for up to 20h. In the first hour of annealing, the grain growth occurs very fast, which can be attributed to subgrain incorporation [33]. Coincident with the initial rapid grain growth, the microstrain decreases sharply at the beginning of annealing due to the annihilation of dislocations [34], and then drops slowly with annealing time. Krill et al. [17] suggested that the decrease of dislocation density annealing gives rise to high grain growth rate. In Fig. 6.1(b), the change in micro-hardness is consistent with the trend of microstrain in Fig. 6.1(a), which decreases significantly at first and then exhibits remarkable stability after long term annealing. Only a 1.64 ± 0.58 GPa drop in hardness is observed from the 14YT-4Sc-1h sample to the 14YT-4Sc-60h sample. This indicates that the 14YT-4Sc alloy possesses high thermal stability.

To further study the microstructural evolution during annealing, large-area FIB ion contrast imaging was used. Fig. 6.2 (a) to (e) shows the grain size distribution of 14YT-4Sc with increasing annealing time from 1h to 60h, respectively. The 14YT-4Sc-1h sample in Fig.
6.2(a), displays a uniform grain size throughout the entire region, while after 10h annealing Fig. 6.2(b) shows large grains in some regions marked by red arrows, indicating abnormal grain growth. The size distribution of grains above the nanoscale (>100nm) is plotted in Fig. 6.2(g). As the grains grew larger upon annealing, the size distribution range above the nanoscale becomes broader. An average grain size in this range for 10h, 15h, 24h, and 60h annealing times were estimated from Fig. 6.2(g) to be 0.4, 0.52, 0.63 and 1.18 µm, respectively. Apart from those grains, a large fraction of nanoscale grains can still be observed even after 60h annealing. These nanoscale grain sizes provide for a primary contribution to the mechanical properties after high temperature annealing. The area fraction of micron grains and nano grains at different annealing times were measured using FIB images, and are plotted in Fig. 6.2(f). The area fraction of micron grains (blue column) increases with annealing times. Nevertheless, the nano grains (red column) dominate, illustrating the remarkable stability of the 14YT-4Sc alloy.
Fig. 6.1 (a) XRD-calculated grain sizes, micro strain, and (b) Vickers hardness as a function of annealing time at temperature of 1000 °C for 14YT-4Sc alloy.
Fig. 6.2(a)-(e) FIB-CCI images showing microstructures of 14YT-4Sc alloy annealed at 1h, 10h, 15h and 24, respectively; Red arrows marked in (b) indicate large grains observed in
14YT-4Sc after 10 h annealing; (f) shows variation of the area fraction of micron grains and nano grains with annealing times; (g) histogram of number fraction of micron grains.

Figs. 6.3(a) to (d) are TEM bright field images of 14YT-4Sc annealed at 1h, 15h, 24h and 60h, respectively, taken from the nanocrystalline region. Grain size in this region increases slightly with increasing annealing time. Numerous small dispersoids are observed. Nano grain size and dispersoid size were estimated by statistical counting of more than 200 examples for each sample using TEM dark field images. The statistical histograms of nano grain size and dispersoid size distributions are shown in Fig. 6.4(a) and (b), respectively. The mean grain/particle size shifts to larger values and their distribution becomes broader with annealing. For the 14YT-4Sc-15h sample, the average nano grains grow from 32 nm to 47 nm compared to the 14YT-4Sc-1h sample, while the dispersoid size shows limited coarsening from 4 nm to 6 nm. Although the dispersoids exhibit growth, these are still extremely small and can exert strong pinning pressure on grain boundaries to mitigate grain growth. The stability is also reflected in the small hardness drop of 0.57 ± 0.26 GPa from the 14YT-4Sc-1h to the 14YT-4Sc-15h samples. The average nano grain size of 14YT-4Sc-24h and 60h are estimated to be 70 nm and 76 nm with dispersoid size of 6.8, and 9.7 nm, respectively. The small nanoclusters (<10 nm) maintain a relatively high resistance to particle growth at high temperatures. The stability of the dispersoids after long-term thermal annealing is beneficial for the stability of both microstructures and mechanical properties of the 14YT-4Sc alloy.
Fig. 6.3(a)-(d) Bright-field TEM images focusing on nanocrystalline region of 14YT-4Sc alloy annealed at 1h, 15, 24h and 60h, respectively.

Fig. 6.4(a) and (b) are histograms of number fraction of nano grains and dispersoids, respectively. The average size for each sample is estimated.
The average micrometer grain size and nanometer grain size for different annealing times of 14YT-4Sc samples are plotted separately in Fig. 6.5(a). Nanoscale grains grow slightly, while micronscale grain size becomes significantly larger, indicating that the growth rate of nano grains is much slower. Beck et al. [12] proposed the grain growth equation (6.2) including the empirical time exponent $n$ to allow for the description of isothermal grain growth. Equation (6.2) can be rewritten as:

$$\log\left(\frac{dD}{dt}\right) = \log(K) + \log(n) + \left(1 - \frac{1}{n}\right)\log(D) \quad (6.3)$$

The constant $n$ for each alloy system can be obtained from the slope of the curve of log(dD/dt) vs. log(D). Equation (6.3) predicts that the rate of grain growth is related to the instantaneous grain size $D$ i.e., grain size dependent growth. The data for nanograins in Fig. 6.5(a) was used to plot the log(dD/dt) term as a function of log(D), as shown in Fig. 6.5(b). The $n$ value is 0.29, calculated from the slope of the straight line. This deviates from the theoretical value of 0.5 for ideal grain growth [15]. Malow and Koch [15] reported an $n$ value for nanocrystalline Fe prepared by mechanical attrition that increased to 0.33 at a temperature of $0.45T_m$, and then increased to 0.5 when $T > 0.45T_m$. Here, 14YT with 4 at.% Sc addition manifests a much lower $n$ value in a very high temperature of $0.65T_m$, demonstrating greater resistance to grain growth with time. The mechanisms for the inhibited grain boundary migration rate can be residual strains [35], anisotropic grain boundary energy [36], solute drag effect [37] and pinning forces exerted by second phase particles. In this work, the second phase particles are the likely major source for maintaining $n$ constant.
Fig. 6.5(a) Micron grain size and nano grain size for 14YT-4Sc alloy annealed at different times calculated from Fig. 4(a) and (b) are plotted as a function of annealing time; (b) nano grain size data is used to plot log(dD/dt) vs. log(dD) to estimate the grain growth rate for nanocrystalline region. The n constant calculated from the straight line is 0.29.
Fig. 6.6 Total hardness data and the calculated grain refinement strengthening data from Hall-Petch equation are plotted with annealing times. The deviation between those two curves is considered to be Orowan strengthening effect.

After high temperature annealing for long times, the grain size and the second phase particles would be the primary contributions to the strengthening. The hardness data is plotted in Fig.6.6 as a function of annealing time. The grain size effect can be evaluated using the Hall-Petch equation (6.4) from the base alloy Fe-14Cr [20]:

\[
H = H_0 + kD^{-1/2}
\]  

(6.4)

D is the average grain size, \(H_0=2.31\) GPa and \(k=22.35\) GPa nm\(^{1/2}\). The grain size strengthening effect is calculated by combining the nano grain size and micron grain size contributions to hardness, based on the ratio of their area fractions. Orowan strengthening can also contribute to the total hardness. This can be evaluated using the Zener pinning...
model to estimate the volume fraction of nanoparticles. According to the Zener pinning model [38]:

\[
\frac{D}{d} = \frac{Z}{f m}
\]  

(6.5)

By inputting the nanograin size \( D \) and nanoparticle size \( d \) in equation (6.5), we estimate the volume fraction \( f \) of particles needed to maintain \( D \). For Fe-based alloys, \( Z \) is 0.17 and \( m = 1 \) if \( f < 0.05 \) [38]. The Orowan strengthening contribution is:

\[
H_{oro} = 3\sqrt{3} \left( \frac{\ln(d/r_0)}{\ln(L/r_0)} \right)^{3/2} \frac{Gb \ln(L/r_0)}{L} \frac{2\pi}{2\pi}
\]  

(6.6)

\( H_{oro} \) depends on both particle size \( d \) and interparticle spacing \( L \), where \( L \) depends on the volume fraction \( f \):

\[
L = d \left[ \left( \frac{\pi}{4f} \right)^{1/2} - 1 \right]
\]  

(6.7)

The Orowan strengthening effect is then obtained for each annealing time, and is plotted in Fig. 6.6. It can be seen that Orowan strengthening makes a small and nominally constant contribution to the hardness for all annealing times.

Nano dispersoids are further characterized in the HAADF-STEM images shown in Fig. 6.7. Increasing the annealing time from 1h shown in Fig. 6.7(a) to 60h shown in Fig. 6.7(b) led to subsequent matrix and dispersoid coarsening. The majority of nanoclusters are observed along the grain boundaries of nanograins, both in the 14YT-4Sc-1h and 14YT-4Sc-60h samples. In the 14YT-4Sc-1h sample, several small second phase particles can be observed within the matrix. At the longer the annealing time, a cleaner region within the matrix is observed, implying that nanoparticle phases prefer to reside along grain boundaries. The high resolution image shown in Fig. 6.7(b) confirms that almost all nanoparticles help reduce
nanograin growth. Furthermore, a locally inhomogeneous distribution of dispersoids appeared in the 14YT-4Sc-60h sample marked by red arrows in Fig. 6.7(b). Grain boundary migration caused by the absence of pinning sites, which results from the inhomogeneous distribution of nanoparticles (nanoclusters) indicated in Fig. 6.7(b). This nonuniform distribution could arise in two ways. First is the “statistical effect” [10] wherein variation occurs from region to region. Even if the microstructure is uniform initially, particular grains can find a growth advantage with locally a lower than average pinning force. Second is the “true” microstructural heterogeneity. Since no strong crystallographic texture is achieved after high-energy ball milling and no stress is applied during heat treatment, the inhomogeneous distribution of nanoclusters evolves the first way. Anomalously large grains can appear once an initial small grain grows beyond a critical size and it can continue to grow at the expense of neighboring small grains.
Fig. 6.7 HAADF-STEM images of 14YT-4Sc alloy annealed at 1000 °C for (a) 1h and (b) 60h. Red arrows indicate the inhomogeneous distribution of nanoclusters after long term thermal treatment.

EDS mapping of each element in the 14YT-4Sc-60h sample is shown in Fig. 6.8 to reveal the composition of the nanoclusters. The composition of these nanoclusters is [ScTiYO], depleted of Fe and Cr. For the long-time annealed alloy (60h), Sc atoms are observed mainly in the nanoclusters while Y atoms only show slight segregation tendency to nanoclusters. This preference is also seen in the short term annealed sample [24], which could be explained by the large difference of the element content (Sc/Y) added and the strong affinity between Sc and O. In addition, after 60h annealing, no intermetallics were observed, suggesting the possibility of good mechanical proprieties.
Fig. 6.8 HAADF-STEM image and EDS elemental mapping of 14YT-4Sc-60h sample, showing the distribution of Fe, Cr, Sc, Ti, Y, and O atoms.

Hayashi et al. [1] have observed nanoclusters segregating at the grain boundaries and forming a chain-like structure which inhibits grain growth at $T > 0.6T_m$. The chain-like features are also observed here in the 1h annealed sample, prior to anomalous grain growth, and this becomes clearer in the nanoscale region for the 60h annealed sample. It suggests that the enhanced nucleation at and diffusion along the grain boundaries aid in nanoclusters forming preferentially on grain boundaries [39]. Therefore, a three-dimensional chain-like network can be formed during annealing. In this way, nano-structures during long term annealing are strongly pinned and stabilized by the nanoclusters’ network. Even though abnormal grain growth has occurred, those nanoclusters provide a strong interaction with boundaries. Thus, there is no dramatic difference in nano grain size for short-term annealed and long-term annealed samples (both of them on the order of 100 nm). The stability of nano grain size is due to the high thermal stability of nanoclusters to resist growth upon annealing.
In 14YT-4Sc-1h sample [24], the Y element is not observed in [ScTiO] nanoclusters, thus most yttrium atoms must be either in solid solution or in the form of very small clusters that were not resolved by EDS elemental mapping. In the long-term thermal annealing, Y diffused to the dispersoids, forming more complex nanoclusters, as indicated in Fig. 6.8. The segregated Y atoms may also help stabilize initial nanoclusters by forming complex ternary oxides. Further investigation will be needed to evaluate long-term irradiation performance of 14YT ODS ferritic alloys with Sc addition for fusion reactors application.

6.5 Conclusions

The microstructural and mechanical long-term stability of 14YT-4Sc has been studied. Abnormal grain growth was observed with increasing annealing time. However, a stabilized nanoscale grain region is found to dominate the matrix with limited grain growth. n is constant for this stabilized region and is estimated to be 0.29, at 0.65 T_m, lower than the value expected from the literature. Additionally, the stabilized microstructure leads to subsequent high hardness, such that only a 24.51% drop in hardness from 1h annealed sample to 60h one is occurred. The high hardness of 14YT-4Sc-1h alloy can be explained by the formation of fine complex oxides of [ScTiO] due to the Sc addition. After 60 hours annealing, EDS mapping indicates that Y atoms gradually segregate to nanoclusters, forming more complex oxides [ScTiYO] with extremely small size (<10 nm).
6.6 Acknowledgements

We are grateful for the financial support from the Department of Energy, Grant DE-NE0000538. The authors also acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

6.7 References


Chapter 7 Evolution of Nano-Hardness of Ferritic Alloys after Helium Implantation

Lulu Li, Weizong Xu, Mostafa Saber, Yuntian Zhu, Carl C. Koch, Ronald O. Scattergood

To be submitted

7.1 Abstract

This paper is an experimental investigation of irradiation-induced hardness evolution of Fe based alloys. Irradiation experiments were performed using He implantation up to 5 dpa at temperature of 500 °C and the estimated peak He concentration is 4 atom% at the depth of 550 nm. Nano-indentation measurements were used to evaluate the irradiation hardening effect and probable bubble distribution.

7.2 Introduction

There are several techniques to simulate the helium production in ferrous alloys during irradiation. One of them is “dual-beam” ion irradiation with self-ions and helium ions simultaneously irradiating the sample [1]. This technique can produce fusion-relevant high-energy cascades at any desired helium production ratio (He/dpa) [2, 3]. However, the range of displacement damage is often limited within less than 1 micron from the irradiation surface [1]. In order to evaluate the mechanical property of ion-irradiated materials, the nano-indentation technique has been applied to the very thin subsurface layer (i.e. irradiation effected zone) [4-6].
For a “classical” hardness measurement, a single indent with one complete cycle of loading and loading is made [7], where the unloading curve is regarded as purely elastic while the loading curve is attributed to the combination of elastic and plastic deformation. Oliver, Hutchings and Pethica suggested the determination of hardness from the indenter shape function, which is the cross-sectional area of the indenter as a function of the distance from its tip [8, 9]. Fig. 7.1 shows a complete loading-unloading cycle with yielded values of peak load $P_{max}$, displacement $h_{max}$ at the peak load, the final residual depth $h_f$ after unloading, and the initial unloading stiffness $S$.

Fig. 7.1 A schematic representation of load, $P$ vs. indenter displacement, $h$. 

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The derived hardness $H$ for samples with constant elastic modulus is according to Eq. (7.1):

$$H = \frac{P}{A_c};$$  \hspace{1cm} (7.1)

where $P$ is the load and $A_c$ is the projected area of contact between the indenter and the specimen. The traditional indentation data analysis was based on the Oliver-Pharr method [10, 11] and further developed by Doerner and Nix [12]. Their approach is based on the elastic behavior of the indentation contact at the start of unloading, which is similar to that of a flat cylindrical punch. This is confirmed from the experimental observations in model materials such that the initial portion of the unloading curve is linear as expected for the flat-punch geometry. The contact stiffness $S$ is experimentally measured from the upper portion of the unloading data and is [13-15]:

$$S = \frac{dP}{dh} = 2E \sqrt{\frac{A_c}{\pi}};$$  \hspace{1cm} (7.2)

Eq. 7.2 was originally derived for a conical indenter. Buylchev, Pharr, Oliver, Brotzen et al. confirmed that this relationship could be applied to other geometries such as spherical and cylindrical indenters [14, 16, 17]. Sneddon et al. derived a general relationship among load, displacement, and contact area for many simple punch geometries [18, 19]:

$$P = \alpha h_e^m;$$  \hspace{1cm} (7.3)

where $h_e$ represents the elastic displacement of the indenter, $\alpha$ and $m$ are constants. However, it becomes more complicated when the indentation contact includes plasticity. In this case, the nonlinear constitutive equations and the knowledge of other materials parameters such as yield strength, work hardening coefficient [20] should be thoroughly examined. Tabor et al. observed that only the depth of the impression is recovered after
unloading, while the diameter of the contact impression in the surface is not. They also found that the load-displacement behavior was not repeatable if performed on only one complete cycle. It was suggested that several loading and unloading cycles be conducted to achieve a perfectly reversible P-h profile \([21, 22]\).

To study the depth and size dependence of the hardness, impressions at different loads need to be performed. In this way, the lateral sample hardness effect is introduced into the investigation \([23]\). The continuous stiffness measurement (CSM) was developed with a small force oscillation during penetration and the depth response related to the force modulation is recorded \([24]\). A multicycling indentation test was developed here for conventional nanoindentation equipment without CSM facilities \([25]\). A series of single cycles of loading-partial unloading is performed with stepwise increasing of the maximum applied load. Typically, the partial unloading is around 10-20\% of the applied load so as to maintain the contact between the impression and the tip of indenter. Each cycle yields a set of values including maximum load \(F_i\), total penetration \(h_i\), contact depth \(h_{ci}\), contact area \(A_{ci}\), and stiffness \(S_i\) at the beginning of unloading, which is \(dP/\text{dh}\). Therefore, the hardness \(H_i\) and indentation modulus \(E_i\) for the cycle are:

\[
\begin{align*}
H_i &= \frac{F_i}{A_{ci}}, \\
E_i &= \frac{S_i}{2\sqrt{A_{ci}/\pi}};
\end{align*}
\]

However, a drift effect occurs in the long-term multicycling test and is a major source of error, which will largely influence the calculated data. The multicycling method gives discrete data, whereas some mechanical properties require the knowledge of a continuous
function with the depth. What’s more, indentation creep is significant in soft materials with small stress exponent n. The persisting creep during partial unloading and reloading results in the discordance of those two curves. Therefore, the multicycling method cannot apply to every system.

For the irradiated specimen, the contributions from different microstructural features in different depths complicated the hardness profile. The surface effect and the displacement effect dominate the surface layer while the irradiated layers are influenced by He-ion damage. Below this, the layer is free of irradiation damage and is related to the intrinsic hardening mechanisms [26]. The loading curve contains a lot of information, but it is not easily accessible for data analysis. The continuous hardness profile for irradiation specimens is best calculated from the unloading curve intersected with every peak point of the loading curve rather than directly measured from single/multicycling indentation. 

\[ A_c \text{ depends on } h_c \text{ with the relationship of } A_c = f(h_c). \] Normally, the experimental contact areas from the calibration procedure are fitted to a function of

\[ f(h_c) = C_0 h_c^2 + C_1 h_c^1 + C_2 h_c^{1/2} + C_3 h_c^{1/4} + \cdots; \quad (7.5) \]

The unloading process in P-h curve is determined by (a) the effective elastic modulus of the materials, (b) the contact depth \( h_c \) and (c) the projected area of contact \( A_c \). If the changes in elastic properties are negligible after irradiation, then, the unloading P-h curve for a certain materials using the same indenter can be expressed by \( h_c \) alone, i.e. \( P = f_{\text{unloading}}(h_c) \). It was confirmed that the unloading P-h curves obtained from irradiated specimens did not significantly deviate from the \( f_{\text{unloading}}(h_c) \) obtained from their unirradiated counterparts.
using fitting to a polynomial function. Therefore, the continuous nano-hardness profile is given as follows:

\[ H(h_c) = \frac{P^*}{A(h_c)}; \tag{7.6} \]

where \( P^* \) is the intersection value of the loading curve \( f_{loading} \) and the calibrated unloading curve \( f_{unloading} \), as illustrated in Fig. 7.2 [26].

Fig. 7.2 Schematic illustration of continuous nano-hardness profiling method.
7.3 Experimental

7.3.1 Selected Materials

The materials used in this study were produced via high-energy ball milling up to 20 hours, followed by heat treatment with specified temperature and time. The heat-treated powders were then cold compressed into discs under 2.5 GPa and mechanically polished before irradiation. The alloy compositions and the corresponding annealing histories of temperature-time and their average grain sizes evaluated by TEM studies are listed in Table. 7.1.

Table. 7.1 List of designations, compositions, heat treatment parameters and evaluated average grain size for all the alloy systems studied in this work

<table>
<thead>
<tr>
<th>Designations</th>
<th>Alloy compositions</th>
<th>Heat treatment (temperature-time)</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCr-large grain</td>
<td>Fe-14Cr</td>
<td>900 °C-1h</td>
<td>~8100</td>
</tr>
<tr>
<td>FeCr-large nano grain</td>
<td>Fe-14Cr</td>
<td>500 °C-26h</td>
<td>~63</td>
</tr>
<tr>
<td>FeCr-nano grain</td>
<td>Fe-14Cr</td>
<td>500 °C-1h</td>
<td>~17</td>
</tr>
<tr>
<td>FeCr-1.5Zr</td>
<td>Fe-14Cr-1.5Zr</td>
<td>900 °C-1h</td>
<td>~95</td>
</tr>
</tbody>
</table>

7.3.2 Ion Irradiations

Ion irradiation process was performed at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. He ions were accelerated to 200 keV with a fluence of $6.5 \times 10^{20}$ ions/m² and a flux of $2.2 \times 10^{17}$ ions/m² for irradiation. Samples during irradiation were subjected to a temperature of 500 °C under the pressure of $8 \times 10^{-5}$ Pa. The simulated peak
irradiation damage of Fe-14Cr alloy of 5 dpa at the depth of 500 nm, and the estimated peak He concentration of 4 atom% at the depth of 550 nm by the SIRM (Stopping and Range of Ions in Matter) program [27] are shown in Fig. 7.3. The unirradiated counterparts were treated under the same condition (temperature, time, etc.) for comparison. The surface of samples was mirror-mechanically polished prior to irradiation.

Fig. 7.3 Implantation profile. Ion damage is given by left-hand vertical axis (displacement per atom). He atom concentration is given by right-hand vertical axis (atomic %)
7.3.3 Nanoindentation

A Hysitron Ubi-1 nanoindenter was used for the study. A NorthStar cube corner indentation tip with radius < 40 nm was used for depths < 700 nm. In situ scanning probe microscopy (SPM) was used to image sample surfaces before and after indentation. A constant loading and unloading rate of ±100 μN/s was selected. Fig. 7.4 illustrates the load-time regime of a multi-indent used for all the unirradiated specimens. The initial sequence was 3 times of loading and unloading at a constant rate, where loading to the peak of 9500 μN and unloading to 10% of the peak maintains full contact. After the third unloading, a fully contact between tip and sample surface was held for 100 s with a small load and the corresponding displacement was monitored for thermal expansion correction [10]. Here, the displacement measured in the low load period was considered caused by thermal drift, which is assumed to be constant throughout the whole test. After the holding period, a final load was performed and another 100 s holding time was conducted at peak load. In this way, the time dependent plastic effect was mitigated. Finally, the specimen was fully unloaded.
Fig. 7.4 The sequence of load-time profile with peak load of 9500 $\mu N$ and partial unloading to 950 $\mu N$. Two 100 s hold periods are inserted following the successive loading-partial unloading process.

7.4 Results and Discussions

To obtain hardness information from the loading curve, precise knowledge of the load $P$ as a function of $h_c$ is required. This is obtained by performing a repeated loading-unloading test to make sure that the unloading process is dominated by elastic deformation. Since the multiple cycling takes more time, drift correction is mandatory. Fig. 7.5 (a-d) shows the load-displacement curves of FeCr-large grain, FeCr-large nano grain, FeCr-nano grain and FeCr-1.5Zr in non-irradiated condition, respectively. The differences in hardness are apparent from
the large differences in depth attained at the maximum load. The softest alloy system is Fe-14Cr with large grain size, where the penetration depth at the maximum load is beyond 600 nm. The hardest alloy is Fe-14Cr with grain size in nanoscale, where the total displacement is only about 300 nm. The Hall-Petch relation can explain this hardness difference in unirradiated samples. The degree of elastic recovery varied in each alloy system, reflecting in the shape of final unloading curves. Additionally, nearly perfectly overlapped unloading and reloading curves can be observed in the FeCr-nano grain sample, which demonstrates that the deformation in this alloy system is almost purely elastic after the first loading. For FeCr-1.5Zr alloy, the material plastically deformed in the successive cycles after initial loading (i.e. reversible plasticity) and in the hold period (i.e. time dependent plasticity). However, the hysteresis loops degenerates with cycling, suggesting more elastic behavior achieved after multiple cycling indentations.
Fig. 7.5 The resulting load-displacement curve from multicyclying test for (a) FeCr-large grain, (b) FeCr-large nano grain, (c) FeCr-nano grain and (d) FeCr-1.5Zr, respectively.

The shapes of the final unloading curve for each alloy system are plotted together for better comparison in Fig. 7.6. The displacements have been shifted laterally by their corresponding $h_f$ (i.e., $h - h_f$) to ensure all the curves pass through a common origin $(0,0)$. $(h - h_f)$ represents the elastic displacement. The unloading curve of each sample can be described by the power law relation:

$$P = a(h - h_f)^m;$$  \hspace{1cm} (7.7)
Only 80 percent of the final unloading curve is used in the fitting for the determination of constants $\alpha$ and $m$. The experimentally evaluated power law exponents along with the correlation coefficients for the fit are given in Table. 7.2. The multicycling test was done several times on non-irradiated samples with different alloy compositions and the resulting constants for each alloy system fall within small deviations.

Fig. 7.6 80% of the final unloading segment of the load-indenter displacement ($P-h$) data from the highest peak load for all four materials. The displacement has been shifted according to their $h_f$ so that the curves pass through a common origin.
Table 7.2. Parameters describing power law fits of unloading segments in Fig. 7.6

<table>
<thead>
<tr>
<th>Alloy systems</th>
<th>$\alpha (\mu N/\text{nm}^m)$</th>
<th>m</th>
<th>Correlation coefficient (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCr-large grain</td>
<td>214.5</td>
<td>1.0056</td>
<td>0.9955</td>
</tr>
<tr>
<td>FeCr-large nano grain</td>
<td>43.2</td>
<td>1.3114</td>
<td>0.9991</td>
</tr>
<tr>
<td>FeCr-nano grain</td>
<td>115.77</td>
<td>1.0092</td>
<td>0.9983</td>
</tr>
<tr>
<td>FeCr-1.5Zr</td>
<td>124.72</td>
<td>1.126</td>
<td>0.9985</td>
</tr>
</tbody>
</table>

According to the Oliver-Pharr algorithm and Sneddon’s equation [10, 11, 19],

$$h_c = h - \varepsilon \frac{P}{S};$$  \hspace{1cm} (7.8)

$\varepsilon$ is an indenter geometric constant with value of 0.75 for the paraboloid indenter, 1 for the flat punch, and 0.72 for the conical indenter. The projected area depends on the geometry of the indenter and the depth of contact $h_c$. The function $f$ is established experimentally on standard fused quartz sample associated with Eq. (7.5). Thus, the single hardness value from the peak load can be obtained through the combination of $P_{max}$ and $A_c(h_c)$.

Every point in the loading curve is assigned to a hardness data. To get a continuous hardness profile for irradiated samples with layered features, the fitted unloading curve in the form of Eq. (7.7) is inserted in the loading profile as a function of displacement. Therefore, a continuous calculated hardness profile can be achieved as a function of contact depth. Fig. 7.7 (a-d) display the computed $H$ with error bars (in black) versus $h_c$ for both irradiated and unirradiated samples of FeCr-large grain, FeCr-large nano grain, FeCr-nano grain and FeCr-
1.5Zr, respectively. An increase in hardness ($\Delta H$) is found in all the alloy systems after irradiation. The values of $\Delta H$ are similar in FeCr base alloys with different grain size; however, the irradiation-induced hardening effect is not apparent in FeCr alloys with 1.5 at% Zr addition. This could be explained by the presence of second phase nano-oxides, ZrO$_2$, in the matrix, which could provide large volume fraction of interfacial area to mitigate irradiation damage, similar to the [YTiO] nanoclusters in the typical ODS steels.

Fig. 7.7 The continuous nano-hardness profiles of irradiated and unirradiated samples calculated from the combination of loading curve and unloading function in the form of Eq.
(7.7) for materials of (a) FeCr-large grain, (b) FeCr-large nano grain, (c) FeCr-nano grain and (d) FeCr-1.5Zr, respectively.

7.5 Conclusions
Careful examination of the unloading curve for each alloy system has been done via multicycling tests followed with two holding periods. The final unloading curve can be described by the power law relation with constants $\alpha$ and $m$. The fitted $m$ value varies from 1 to 1.3, suggesting that the flat punch analysis method cannot be applied to all the materials. Irradiation-induced hardening has been observed in all the alloy systems. The FeCr with Zr addition shows the best irradiation hardening resistance. This can be inferred from nanoclusters [YTiO] presented in ODS steels. The formation of nanosized ZrO$_2$ during annealing provides extra interfacial area in addition to grain boundaries in the system. Thus, the irradiation-induced defects such as self-interstitial atoms and helium bubbles are trapped along those boundaries, reducing the irradiation damage. The detailed microstructure investigations such as the size, distribution, number density of the helium bubbles and the evolution of grain size after irradiation are needed to be done in the future study through high resolution TEM.

7.6 Acknowledgements
Support for this study by the Department of Energy, Grant DE-NE0000538, is gratefully acknowledged. The authors acknowledge the use of the Analytical Instrumentation Facility
(AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

7.7 References


Chapter 8 Co-Authored Publications

Full papers are not included in the thesis

8.1 Nano ZrO$_2$ Particles in Nanocrystalline Fe–14Cr–1.5Zr Alloy Powders

Weizong Xu, Lulu Li, Mostafa Saber, Carl C. Koch, Yuntian Zhu, Ronald O. Scattergood


8.1.1 Abstract

Here we report on the formation of nano ZrO$_2$ particles in Fe–14Cr–1.5Zr alloy powders synthesized by mechanical alloying. The nano ZrO$_2$ particles were found uniformly dispersed in the ferritic matrix powders with an average size of about 3.7 nm, which rendered the alloy powders so stable that it retained nanocrystalline structure after annealing at 900 °C for 1 h. The ZrO$_2$ nanoparticles have a tetragonal crystal structure and the following orientation relationship with the matrix: (002) ZrO$_2$/|(002) Matrix and [010] ZrO$_2$/|[120] Matrix. The size and dispersion of the ZrO$_2$ particles are comparable to those of Y–Ti–O enriched oxides reported in irradiation-resistant ODS alloys. This suggests a potential application of the new alloy powders for nuclear energy applications.
8.2 Size Effect of Primary Y₂O₃ Additions on the Characteristics of the Nanostructured Ferritic ODS Alloys: Comparing As-milled and As-milled/Annealed Alloys using S/TEM

Mostafa Saber, Weizong Xu, Lulu Li, Yuntian Zhu, Carl C. Koch, Ronald O. Scattergood


8.2.1 Abstract

The need for providing S/TEM evidence to clarify the mechanisms of nano-scale precipitate formation was the motivation of this investigation. In this study, an Fe–14Cr–0.4Ti alloy was ball-milled with different amounts of Y₂O₃ content up to 10 wt.%, and then annealed at temperatures up to 1100 °C. Micron-size Y₂O₃ particles were substituted for the nano-size counterpart to elucidate the mechanism of oxide precipitate formation. The S/TEM studies revealed that the microstructure of the alloy with 10 wt.% yttria contained amorphous undissolved Y₂O₃ after ball milling, while a small part of the initial oxide particles were dissolved into the solid solution. Consequently, when the amount of yttria was reduced to 1 wt.%, the amorphous phase of the yttria vanished and the whole content of Y₂O₃ was dissolved into the BCC solid solution. Defect analysis of precipitates on the annealed samples via S/TEM and micro-hardness studies revealed that the use of micron-size primary oxide particles can produce nano-size precipitates, stable up to temperatures as high as 1100 °C, and uniformly distributed throughout the microstructure. This study indicates that the use of high energy ball milling along with micron-size primary oxide particles can lead to nanostructured ferritic ODS alloys without the use of nano-size primary oxide additions.
8.3 Microstructures and Stabilization Mechanisms of Nanocrystalline Iron-Chromium Alloys with Hafnium Addition

Weizong Xu, Lulu Li, Mostafa Saber, Carl C. Koch, Yuntian Zhu, Ronald O. Scattergood


8.3.1 Abstract

The low thermal stability of nanocrystalline metals severely limits their applications at high temperatures. In this study, we investigate the nanocrystalline stabilization mechanisms for Fe-14Cr alloys with 1, 2, and 4 at. pct Hf addition at 1173 K (900 °C). Microstructural characterizations using aberration-corrected scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy reveal high density of HfO₂ nanoparticles with sizes of ~ 4 nm dispersed throughout the ferritic matrix. This indicates that kinetic stabilization by HfO₂ nanoparticle pinning is primarily responsible for the observed high thermal stability. In addition, some Hf and Cr segregation on grain boundaries is observed in the Fe-14Cr-4Hf, suggesting the existence of thermodynamic stabilization at high Hf content. Second-phase precipitations such as hafnium carbide, M₂₃C₆, and Fe-Cr-Hf intermetallic phase are also found in the Fe-14Cr-4Hf, but their large sizes and inter-spacing suggest that their contribution to stabilization is minimal.
8.4 Effect of Nano-Oxide Size on Radiation Resistance of Iron-Chromium Alloys

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*Journal of Nuclear Materials, accepted 2015.*

8.4.1 Abstract

Radiation resistance of Fe-14Cr alloys under 200kV He irradiation was systematically investigated with varying sizes of nano oxide Zr, Hf and Cr particles. It is found that these nano oxide particles acted as effective sites for He bubble formation. Oxide particles with sizes less than 3.5-4 nm are found most effective for enhancing radiation resistance. By statistically analyzing over 700-1500 He bubbles at the depth of 200-700 nm from a series of HRTEM images, we established the variation of average He bubble size, He bubble density, and swelling percentage along the depth, and found them to be consistent with the He concentration profile calculated from the SIRM program.
Chapter 9 Summary and Suggestions for Future Works

9.1 Summary

This thesis research led to increasing the thermal stability of nanocrystalline ferritic alloys at high temperatures and long annealing times through solute additions. Kinetic stabilization mechanism such as formation of second phases and thermodynamic stabilization mechanism such as segregation of oversized solutes were both observed in the nanocrystalline ferritic alloy systems directly and/or indirectly. A new type of ODS steel with nanoscaled matrix has been developed via high-energy ball milling in this work. The interfacial area provided by both nanometer oxides and grain boundaries improved the irradiation resistance and maintained high strength, which can be expected as the potential candidate for structural materials in advanced nuclear energy systems.

In Chapter 4, the addition of Zr and Hf into Fe-14Cr ferritic alloys has been investigated and up to 4 at.% Hf addition can give effective grain size stabilization at temperature of 1000 °C. Hardness of Fe-14Cr-4Hf alloys at such high temperature can be maintained as 5.2 GPa. The Hall-Petch equation and Orowan strengthening relationship has been employed to predict possible grain size for Fe-14Cr-4Hf sample annealed at 900 °C. A deviation between predicted grain size from those two equations and the actual grain size observed from TEM study suggests the presence of thermodynamic stabilization. The ternary thermodynamic model also reflects that Hf could be a segregating solute in ferritic alloy systems.
In Chapter 5, Sc, suggested as a strong segregator by the thermodynamic model, was added into 14YT to increase the thermal stability of nanocrystalline ODS steel at high temperatures. Grain size evolution and corresponding hardness change were thoroughly studied as a function of temperature and solute content. With only 1 at.% Sc addition, nano-scaled grain size can be maintained at high temperatures. Increasing the solute content in the system further improved its thermal stability. A small grain size of 32 nm and high hardness of 6.7 GPa are maintained in 14YT-4Sc after 1000 °C heat treatment for 1 hour. The presence of nanofeatures of [ScTiO] was observed in EDS elemental mapping after heat treatment, which is considered as the dominant contributor to the high temperature stabilization. [YTiO], which is typically found in conventional ODS steel was not observed in 14YT-Sc alloy systems. This could be explained that nearly all the O atoms were consumed by the Sc solutes due to much higher concentration of Sc than that of Y in the system. In addition, Ti was found to refine nanoclusters of [ScTiO], as in conventional ODS steel with [YTiO]. More importantly, no large second phases such as TiO$_2$ and intermetallics were found in 14YT-Sc alloys, which indicates better performance compared to conventional ODS steels.

In Chapter 6, the microstructural and mechanical long-term stability of 14YT-4Sc has been studied. The nanoparticles show excellent thermal stability under thermal treatments. Abnormal grain growth was observed with increasing annealing time. However, the majority of the matrix was still made up of nano-grains with limited growth. The growth rate calculated for this stabilized region is 0.29 after annealing at 0.65 $T_m$ for 60 hours. In addition, only a 25% drop of hardness occurred in 14YT-4Sc annealed from 1 hour to 60 hours at 1000 °C. The exhibited high strengths after high temperature and long time
annealing result from the stabilized nano-grains and the extremely small oxides (<10 nm). Comparing the short time and long time annealing samples, the EDS elemental mapping showed that Y atoms gradually segregated to those nanoclusters, resulting in a more complex oxide [SiTiYO].

In Chapter 7, continuous nano-hardness evolution of irradiated ferritic alloys has been studied. Firstly, the final unloading curves of non-irradiated samples were fitted into the power law relation. Then, the fitted unloading curves for each alloy systems were inserted into the loading P-h profile for their irradiated counterparts. The intersections of loading and unloading functions give a series of data set \((P^*, h_c)\). Finally, the continuous hardness profile can be obtained as a function of contact depth. The irradiation-induced hardening was found in the alloy systems studied, while Fe-14Cr with Zr addition shows good irradiation hardening resistance compared to other systems without third solute addition. This can be inferred from nanoclusters [YTiO] presented in ODS steels. The formation of nanosized ZrO\(_2\) during annealing in the Fe-14Cr-Zr alloy provides extra interfacial area besides grain boundaries. Thus, the irradiation-induced defects such as self-interstitial atoms, helium bubbles are trapped along those boundaries, reducing the irradiation damage.

9.2 Suggestions for Future Works

According to the results obtained in this work, further studies are suggested as following:

(1) Investigation of other mechanical properties such as shear stress/tensile stress with selected solute type and solute content in nanocrystalline ferritic alloys. In this way, a more
comprehensive understanding of the strength of selected materials can be obtained. To achieve other mechanical properties, a bulk sample with stable microstructure and high density after consolidation process is mandatory.

(2) The initial elemental powders for ball milling can absorb oxygen easily due to their large area/volume ratio. Therefore, the oxygen contamination level in the resulted solid solution is relatively high. An “oxygen-free” sample is needed to study the thermodynamic stabilization mechanism. Thus, producing the starting powders via filing the bulk elements under protective environment is expected to reduce the oxygen contamination.

(3) This work suggests that the nanocrystalline ODS steel is a possible candidate for the structural materials in advanced nuclear energy system. Further investigations of 14YT-Sc alloys under ion irradiation are required. The studies include the stability of grain size, nanofeature size; the distribution, number density, and size of irradiation-induced defects such as helium bubbles; the evolution of irradiation-induced hardening, and other possible benchmarks.