Stabilization of Nanocrystalline Grain Size at Elevated Temperatures: Theory and Experiment

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Introduction

- Knowledge of the thermal stability of nanocrystalline materials is important for both technological and scientific reasons.
- It is well known that nanocrystalline metals are unstable to grain growth.
- Strategies for stabilization of nanocrystalline grain size have focused on either thermodynamic or kinetic mechanisms.
- This talk will summarize the theories for thermodynamic and kinetic mechanisms, as well as the recent concept of complexions.
- The experimental evidence for these stabilization mechanisms will be presented and tentative conclusions for high temperature stabilization given.

Reviews of thermal stabilization of nanocrystalline materials

- Koch, C. C., Scattergood, R.O., Saber M. et al. “High temperature stabilization of nanocrystalline grain size: thermodynamic vs. kinetic strategies” J. Mater. Res. (2013) 28: 1785-1791.

- Andrievski, R.A. “Review of thermal stability of nano-materials” J. Mater. Sci. (2014) 49: 1449-1460.

- Saber, M., Koch, C. C., Scattergood, R.O. “Thermodynamic grain size stabilization models: an overview”, Mater. Res. Lett. (2015) 3: 65-75.

- Peng, H.R.,Gong, M.M., Chen, Y.Z., Liu, F. “Thermal stability of nanocrystalline materials: thermodynamics and kinetics” Inter. Mater. Rev.(2017) 62: 303-333.

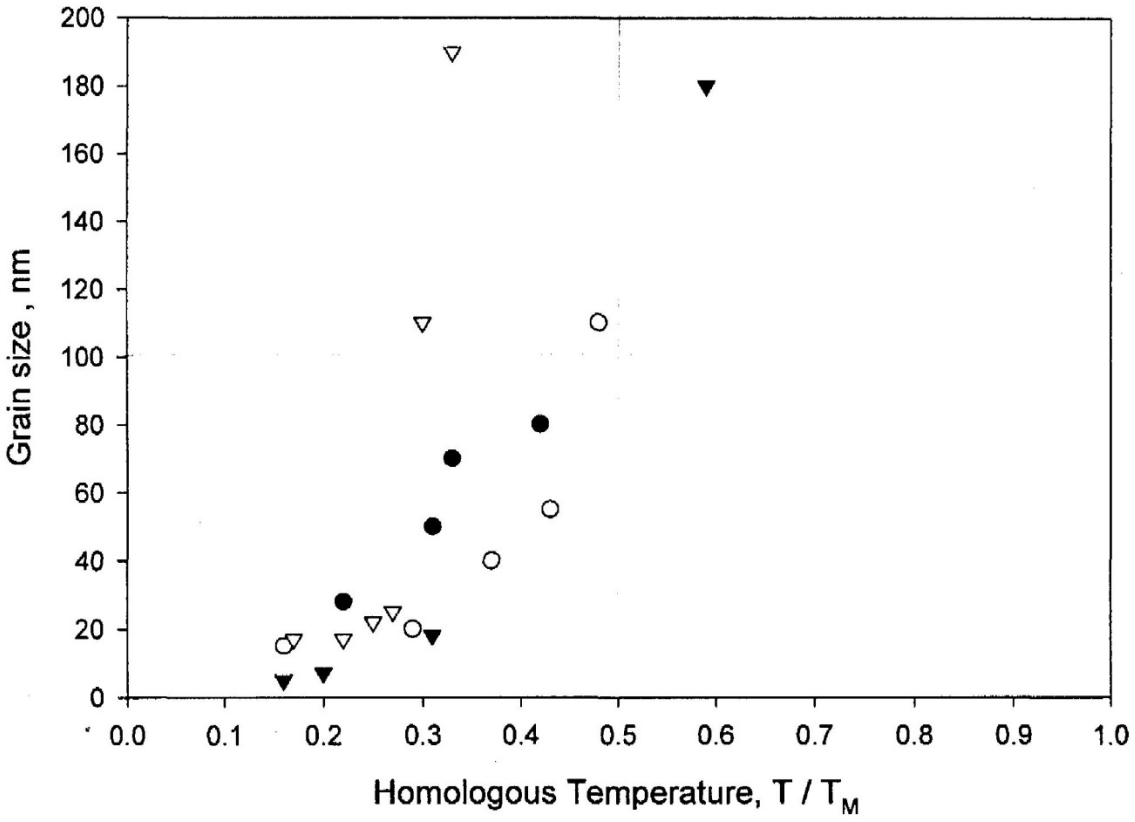
Talk Outline

- Nanocrystalline microstructures are unstable.
- Theories for kinetic stabilization.
- Theories for thermodynamic stabilization
- Grain boundary complexions
- Experimental examples of stabilization, Fe-base alloys with solute additions.
- Summary of experimental data from our laboratory and the literature and tentative conclusions on the efficacy of the stabilization mechanisms.

Grain growth in pure nanocrystalline metals

- Significant grain growth (doubling the grain size in 24 h) seen at room temperature in low melting point metals (Sn, Pb, Al, Mg).
- Abnormal grain growth seen at room temperature in pure Cu, Ag, and Pd.
- Grain growth in nominally pure elemental metals typically pushes the average grain size to above the nanoscale, that is greater than 100 nm, at annealing temperatures less than 0.5 of the melting temperature.

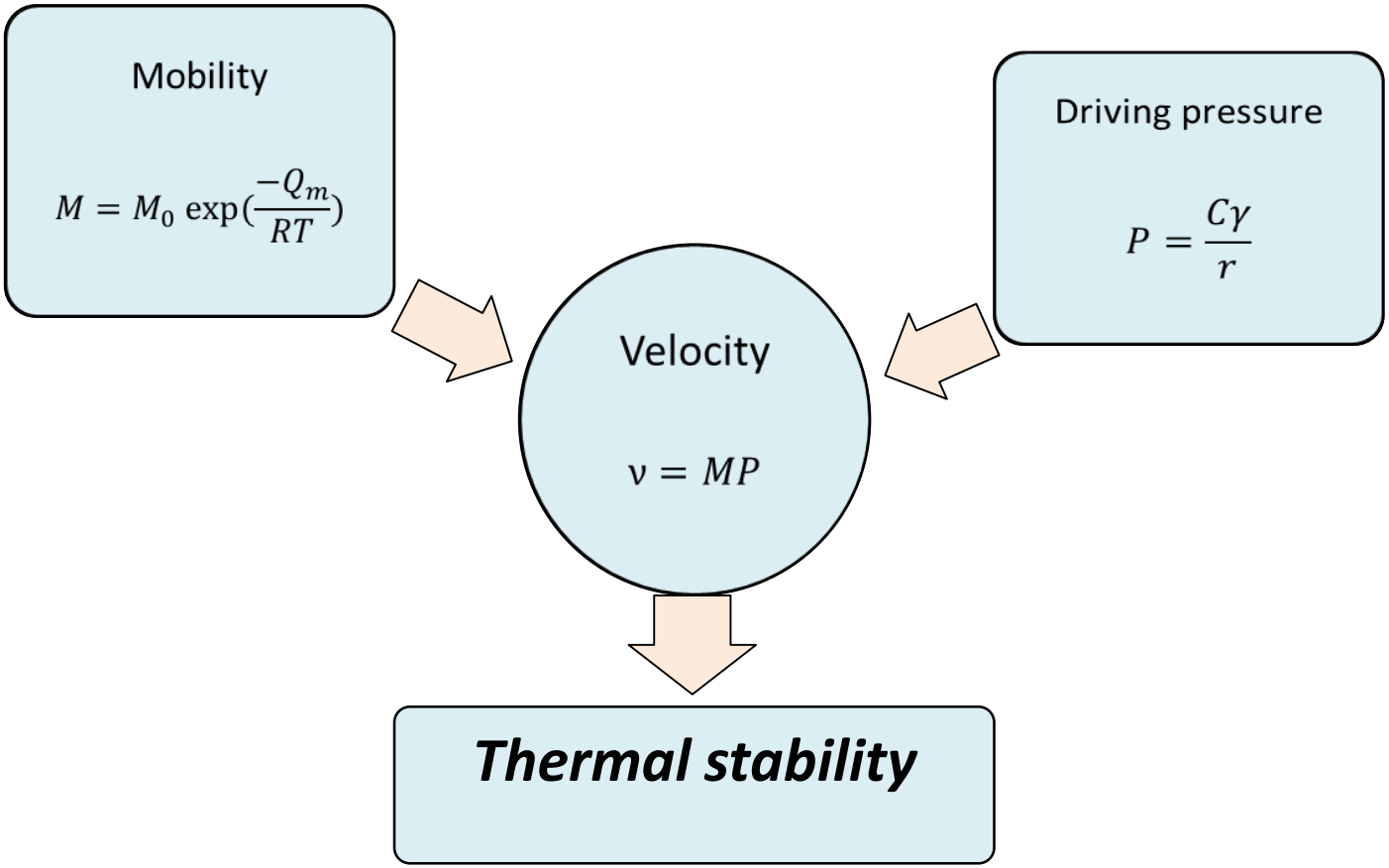
Grain size vs. T/T_M for nominally pure nanocrystalline Pd, Fe, Cu, and Ni.



An extreme example of unstable grain growth in a nanocrystalline metal

- Ames et al. (Acta Mater. 2008) observed the grain growth at room temperature of nanocrystalline pure Pd.
- The high purity Pd sample was prepared by the inert gas condensation method and had a grain size of 10 nm.
- The grain size of this sample increased first by abnormal grain growth, but with time this transient stage changed to self-similar normal grain growth.
- After about two months at room temperature the grain size had increased to greater than 10 μm – more than 3 orders of magnitude, although Pd has a high melting temperature of 1552^{o}C.

Grain Growth Velocity a Function of Mobility and Driving Pressure



Kinetic Stabilization Theories

- There are a number of possible mechanism that have been proposed that may limit the mobility of nanocrystalline grain boundaries.

- These include porosity drag, solute drag, second phase (Zener) drag, chemical ordering, and grain size stabilization.

- The most general applicability to a variety of systems and most important of these mechanisms are solute drag and second phase (Zener) drag.

Solute Drag Mechanism

- The Cahn-Lucke-Stuwe (CLS) models provide good semi-quantitative account of the effects of solute on grain boundary mobility.
- According to these models, at low velocities the velocity is inversely proportional to solute concentration.
- At higher driving forces or lower solute concentrations, there is a transition to a high velocity regime where the velocity is independent of solute content.
- The effect of solute is less at higher temperatures. The solute atmosphere becomes much weaker.
- Solute drag has been used to explain experimental results of stabilization of a number of nanocrystalline materials, e. g. Ni-1 at.% Si, Pd-19 at.%Zr

Second Phase (Zener) Drag

- The second phase may be a precipitate or dispersoid (e. g. oxide).
- This pinning effect is less sensitive to temperature than solute drag, especially if a dispersoid is resistant to coarsening.
- Particle size and distribution play a key role in the effect.
- The expression for the pinning pressure exerted on the grain boundary by small particles is , in the original Zener formulation, $P = 3f\gamma/2r$ where f is the volume fraction of particles randomly distributed of spherical radius r, and γ is the specific grain boundary energy.
- A refinement of this model (Doherty, 2012) gives: $D = 0.17\ d/f$ for low volume fractions, where D is the critical grain size, d the particle size, and f the volume fraction.
- A large number of experiments on stabilization of nanocrystalline grain sizes have been explained using Zener drag (e.g. Fe-10Al with dispersoids)

Other Kinetic Pinning Mechanisms

- Other mechanisms for decreasing grain boundary mobility include porosity drag, chemical ordering, and grain size effect.

- Porosity can reduce grain boundary mobility. This was demonstrated in the grain growth of ceramic TiO_2 prepared by the inert gas condensation method (Hofler and Averback, 1990)

- Reduced grain growth has been observed for ordered nanocrystalline intermetallic compounds. For example Fe_3Si (Gao and Fultz, 1993).

- Grain size stabilization has been predicted by theoretical models and observed experimentally. It is suggested that the decrease in free volume which occurs on grain growth is offset by the non-equilibrium vacancy concentration increases in the matrix as the excess free volume is released on grain growth.

Thermodynamic Stabilization Theories:Background

- The reduction of excess interface Gibbs free energy G with increasing solute content can be described by the Gibbs adsorption isotherm:

  $d\gamma = -\Gamma\, d\mu$ where μ is the chemical potential of the solute atom dissolved in a matrix of solvent atoms.

- Γ is the excess amount of solute atoms segregated to the boundary.

- Plots of γ = dG/dA vs. global solute content (Hondros and Seah) show a reduction of γ with increasing solute content.

- Large solute atoms intensify this and could reduce the excess grain boundary free energy with possible grain boundary stabilization at $\gamma = 0$.

- γ is not to be confused with grain boundary cohesive energy

- Weissmuller was the first to apply these ideas to stabilization of nanocrystalline grain size.

Weissmuller Model of Thermodynamic Stabilization

- The model was based on a dilute solution limit. The equation has the form:
- $\gamma = \gamma_o - \Gamma_{sat} [\Delta H_{seg} + RT \ln(x_c)]$ where γ_o is the grain boundary energy of the pure metal, Γ_{sat} is the solute excess for fully saturated grain boundary interface , ΔH_{seg} is the segregation enthalpy and $RT\ln(x_c)$ represents the ideal mixing entropy for bulk solute concentration x_c.
- This equation implies that the grain size at stabilization decreases as the solute content increases at a fixed temperature.
- The analysis of Weissmuller was extended by Kirchheim to include the temperature dependence of grain size for a metastable equilibrium state.

Trelewicz and Schuh (TS) Model of Thermodynamic Stabilization

- The regular solution model of Trelewicz and Schuh eliminates many of the approximations in the previous models, e. g. fully saturated grain boundaries or dilute solution approximations.

- This model has grain boundary regions and bulk regions with variable volume fractions and solute concentrations separated by transitional bonds.

- δG_{mix} is obtained from the difference in the nearest neighbor bond energy and mixing entropy of this system relative to equivalent volumes of unmixed pure A and pure B with no grain boundary.

- The equilibrium state is obtained by simultaneous minimization of δG_{mix} with respect to variations of the solute concentraation and the grain boundary volume fraction, subject to conservation of solute.

- Elastic size misfit enthalpy was not included in this model.

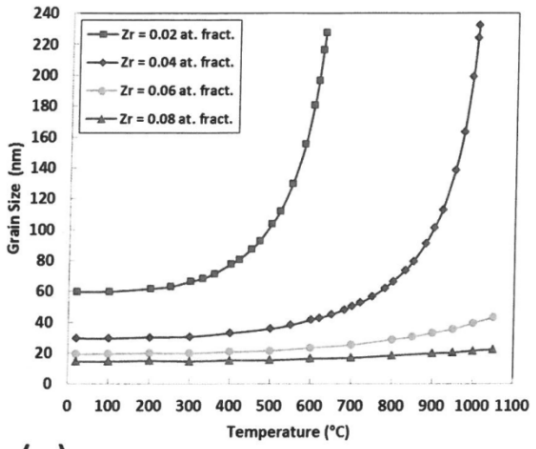
Modified TS Model Proposed by Saber et al.

- A regular solution model for thermodynamic stabilization was proposed using a Wynblatt-Ku approximation to incorporate both chemical and elastic enthalpy.
- The equilibrium condition is defined by minimization of the total Gibbs mixing free energy with respect to simultaneous variations in the solute contents and volume fractions with the constraint of overall mass balance.
- The Lagrange multiplier technique was used to obtain an explicit solution to the constrained equations in a form easily solved using standard numerical software packages.
- Results for Fe-Zr alloys are given in the next slide.

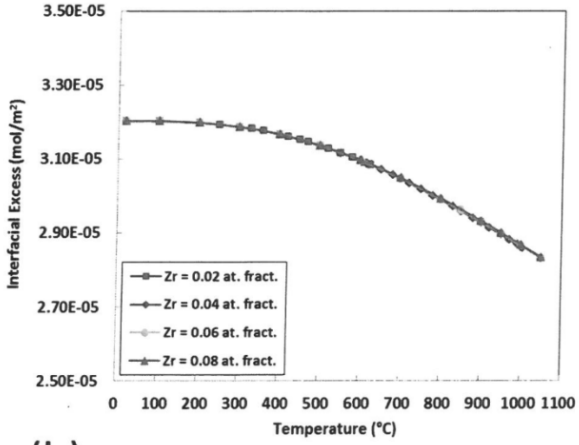
Saber et al. Model Predictions

Model predictions of a) grain size and

b) Interfacial solute excess fro Fe-Zr alloys as a function of temperature



(a)



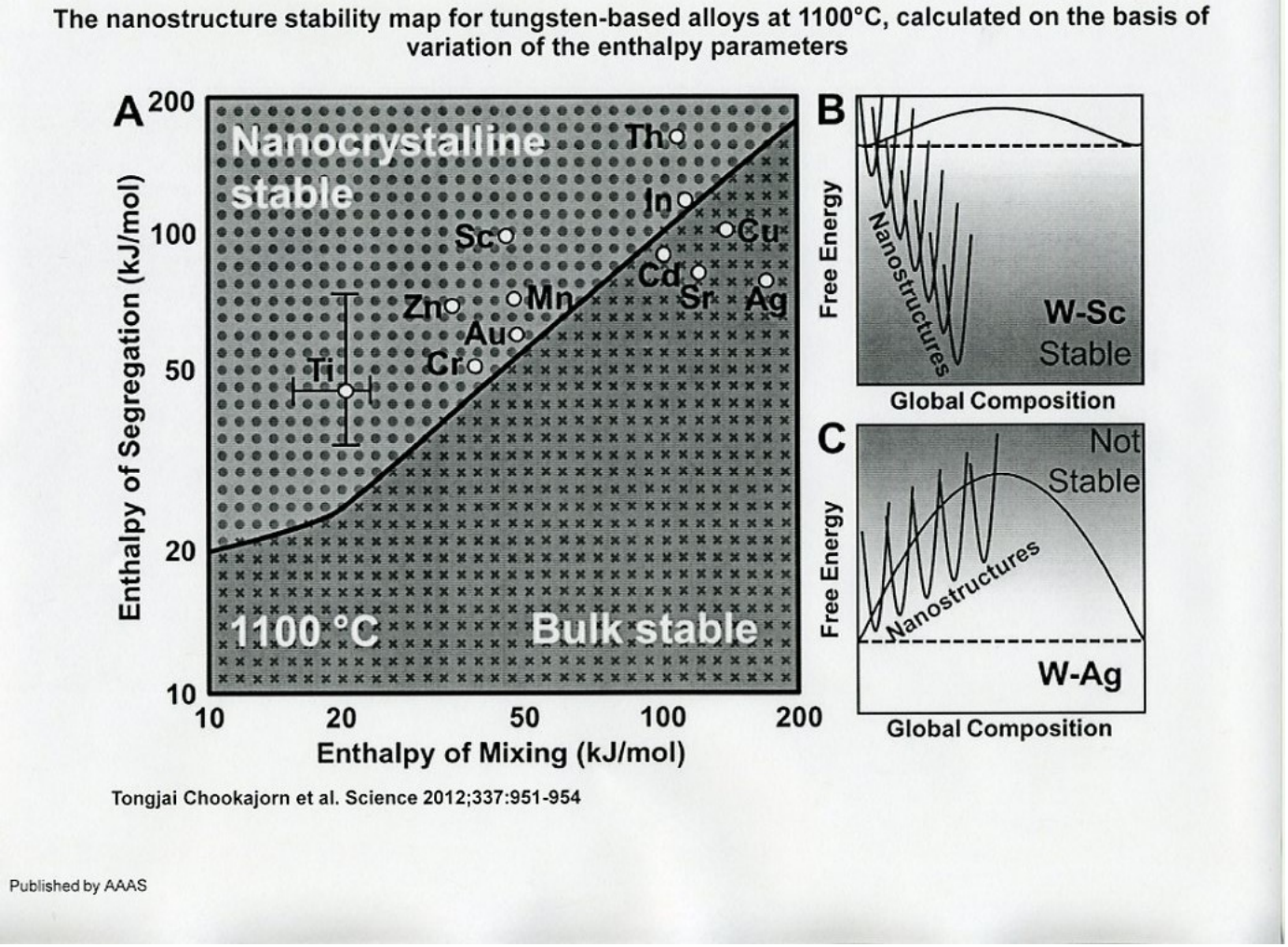
(b)

Model predictions of (a) grain size and (b) interfacial solute excess for Fe-Zr alloys.

Recent Models on Stabilization vs. Both Grain Growth and Phase Separation

- The previous models did not consider the competition with precipitation of second phases or phase separation.
- Murdoch et al. addressed this problem using an analytical approach based on the TS model. They simplified the problem by considering only alloys with positive enthalpies of mixing.
- Stability maps of enthalpy of segregation vs. enthalpy of mixing were constructed for several elements. One for W is shown in the next slide.
- Subsequently, Schuh and co-workers have extended the range of alloys and details of the grain boundary structure by using Monte Carlo simulations to construct stability maps with 6 different regions of nanocrystalline stability including duplex nanostructures.

Nanostructure Stability Map for W-based Alloys at 1100°C (Chookajorn et al. Science, vol. 337 (2012) 951)



Examples of Recent Results from Schuh's Group on Thermal Stabilization

- Chookajorn et al. (J. Mater . Res. 30 (2015) 151) studied a duplex nanocrystalline alloy, W – 15 at.% Cr. Heating the ball-milled alloy to 950^{o}C formed a nanoscale Cr-rich phase at the grain boundaries. These precipiates mostly dissolved in the W-rich grains leaving Cr-enriched grain boundaries and nanoprecipitates at 1400^{o}C. The microstructure observed was in agreement with Monte Carlo simulations. Nanocrystalline grains were stabilized up to 1400^{o}C ($T/T_m = 0.47$).

- Clark et al. (JOM, 68 (2016) 1625) used the predictions of Murdoch et al. to compare the thermal stability of a predicted stable nanocrystalline alloy, Fe-10 at.% Mg with a predicted unstable alloy, Fe-10 at.% Cu. The predictions were verified experimentally, with the Fe-Mg alloy remaining nanocrystalline at 763^{o}C ($T/T_m = 0.57$) while Fe-Cu grains grew to > 100 nm. Fe-Mg showed grain boundary segregation, Fe-Cu exhibited phase separation.

Simulation of nanocrystalline configurations in ternary and multicomponent alloys from Schuh's group

- Schuh's group used their lattice Monte Carlo approach to examine a case of ternary alloys where one solute stabilizes the grain boundaries and the second forms nanoscale precipitates (Xing et al. Scripta Mater. 127 (2017) 136).

- Selection of different bond orders (bond energies for components in grain boundaries or in grains, 12 for a ternary alloy) due to different mixing enthalpies gave several complex microstructures with or without a "core-shell" grain structure.

- This simulation suggests the myriad complex microstructures that can be formed in ternary or multicomponent alloys and the large range of multinary nanostructures.

A Thermokinetic Model of Nanocrystalline Grain Growth

- Chen et al. (Acta Mater. 60 (2012) 4833-4844) have presented a thermokinetic model for grain growth in nanocrystalline metals containing solute elements

- This model was developed incorporating the effects of activation energy and grain boundary energy.

- The equation they derive contains the $D^2 - D_o^2$ term of a similar form to the power law of Burke and Turnbull, but the rest of the equation's terms stem from the interaction between the kinetic and thermodynamic aspects of grain growth.

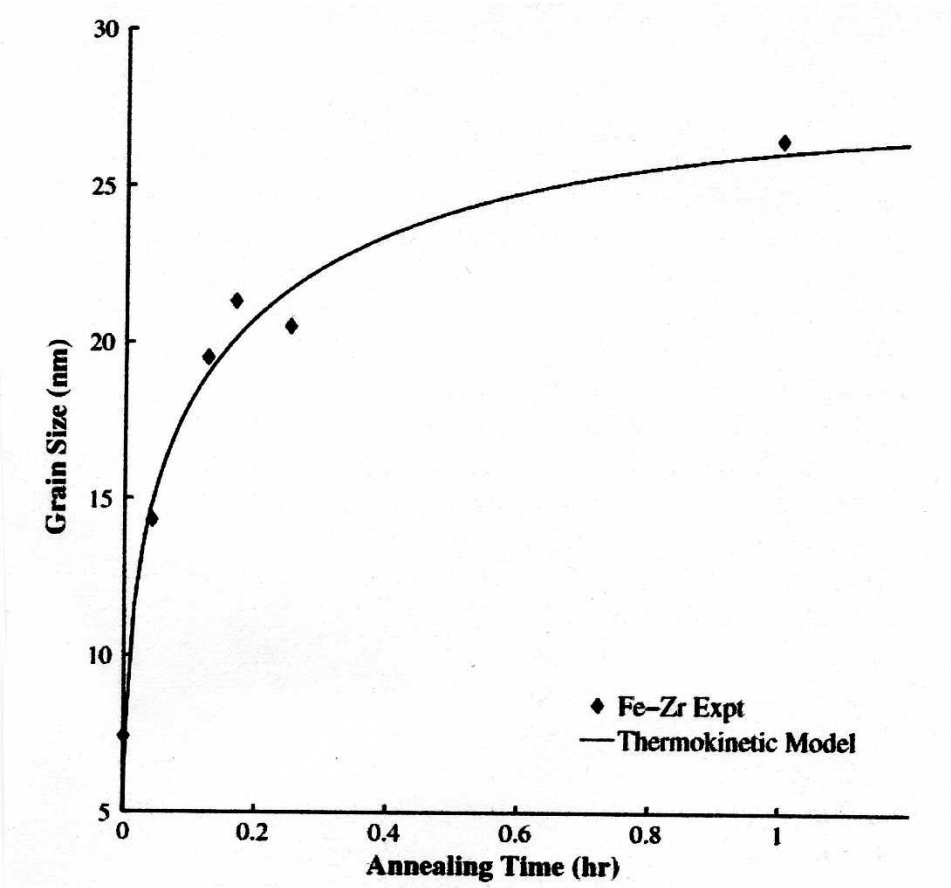
- Their model predicts that activation energy increases and grain boundary energy decreases with grain growth due to solute segregation.

Tschopp et al. Computational Mater. Sci. 131 (2017) 250-263

Tschopp et al. compared the results of grain size measurements with Chen et al.'s thermokinetic model.

They extended the model by incorporating the effect of temperature and the initial grain size distribution.

Grain size measured by XRD line broadening for nanocrystalline Fe – 4 at.% Zr gave good agreement with the model.



Evolution of the average grain size as a function of annealing time for nanocrystalline Fe–4% Zr alloy annealed at 800 °C.

Tang et al. Model for Solute Segregation and Thermal Stability of Nanocrystalline Solid Solution Systems

- Tang et al. (Nanoscale 11 (2019) 1813-1826) presented a model coupling first principles and thermodynamics to describe the thermal stability of nanocrystalline solid solution alloys.

- The proposed model coupling first principles and thermodynamics can evaluate thermal stability of the nanocrystalline solid solutions based on the deduced grain-boundary formation energy and change of the total Gibbs free energy as deterministic functions of solute concentration, grain size, and temperature.

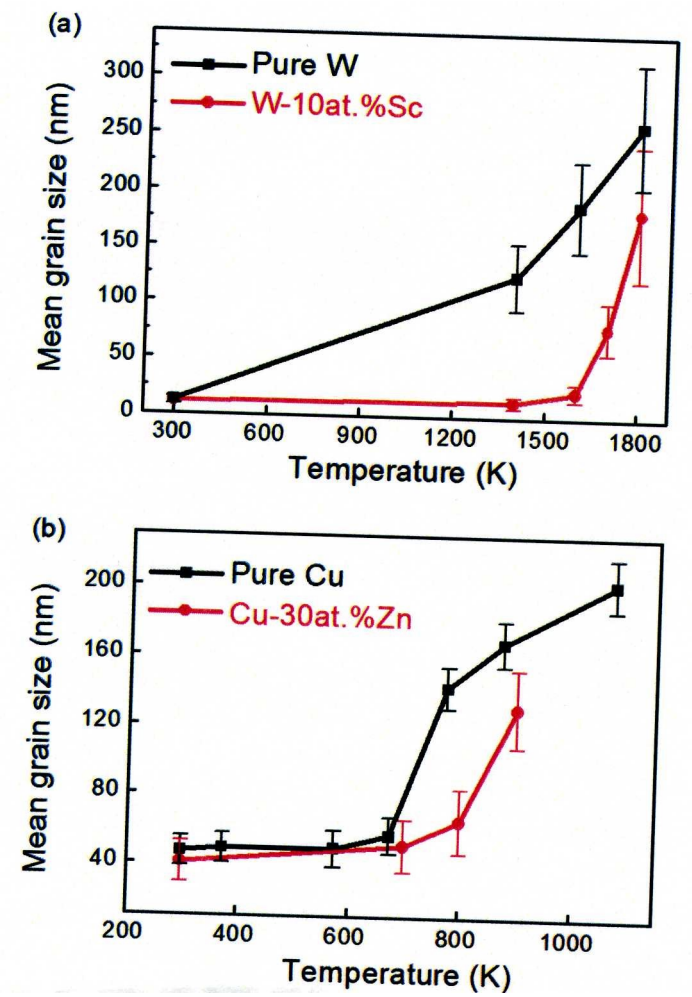
- The combined impacts of the solute concentration, initial grain size, and temperature on the grain structure stability differ for strongly and weakly solute-segregating systems.

Experimental verification for model of Tang et al.

Stabilization of the nanocrystalline grain sizes in the solid solutions with respect to the solvent metals

a) W – Sc as a strongly solute-segregating system

b) Cu – Zn as a weakly solute-segregating system.



Phase Field, Diffuse Interface Model of Foiles and Co-workers

- Abdeljawad and Foiles (Acta Mater. 101 (2015) 159-171) have developed a phase field, diffuse interface model for the stabilization of nanocrystalline alloys by grain boundary segregation.

- Abdeljawad et al. (Acta Mater. 126 (2017) 528-539) applied this method to immiscible nanocrystalline alloys to address the competing roles of grain boundary segregation and bulk alloy phase separation. Grain boundary segregation exhibited a dominant role as the heat of segregation increases in comparison with the bulk heat of mixing.

Simulation and Experimental Study of Segregation of Au in a Pt – 10 at. % Au Alloy

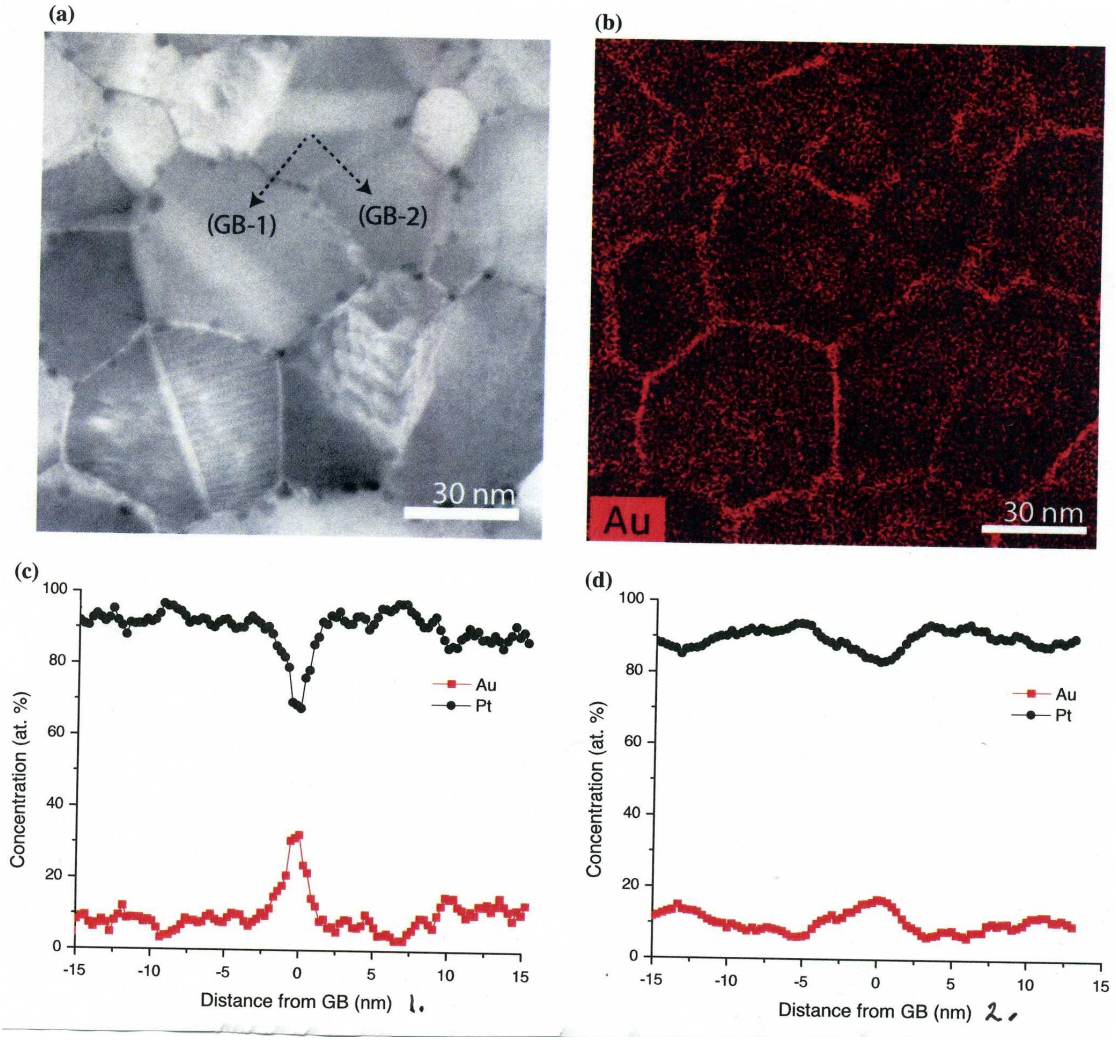
- O'Brian et al. (J. Mater. Sci. 53 (2018) 2911-2927) used a combination of Monte Carlo (MC) and molecular dynamics (MD) methods to study grain boundary segregation in Pt -10 at. % Au.

- Both approaches alternated between MD simulations at temperature to equilibrate the structural aspects, and MC simulations to equilibrate the compositional degrees of freedom. Both approaches used the embedded atom method potential for PtAu.

- The modeling studies indicated that the segregation to grain boundaries is highly non-uniform and sensitive to boundary character.

- Experimental results on Pt – 10 at.% Au thin films corroborated the simulations showing different degrees of segregation at different boundaries using electron microscopy and HAADF and STEM-EDS Au intensity maps.

Experimental Results Showing Differences in Grain Boundary Segregation for two Boundaries in Pt-10 at.% Au

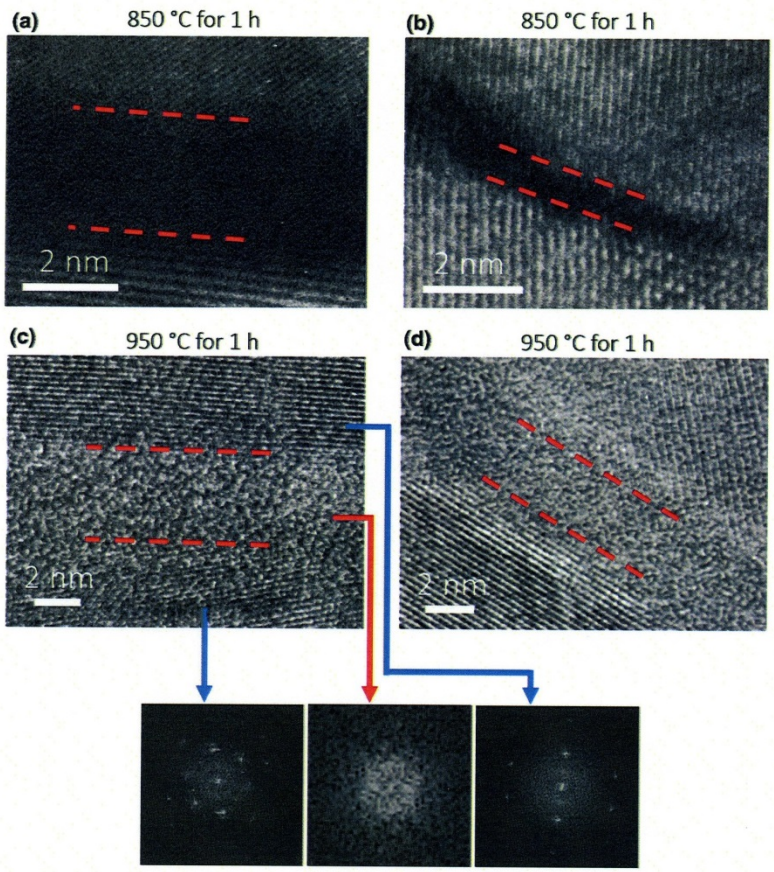


Complexions as Possible Sources of Nanocrystalline Grain Size Stabilization

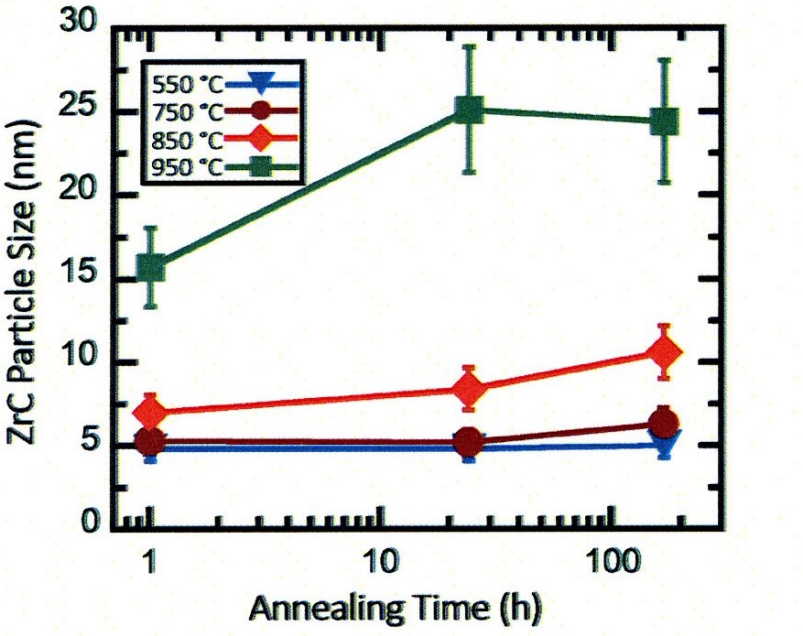
- Interface “complexions” are grain boundary “phases” in thermodynamic equilibrium that have stable, finite thicknesses.
- Dillon, Harmer, and co-workers have created a categorization scheme based on studies of Al_2O_3 doped with calcia, silica, magnesia, or neodymia.
- Six Dillon-Harmer complexions were identified using high resolution TEM images of the boundaries.
- Rupert has recently reviewed the role of complexions in metallic nanocrystalline materials with regard to thermal stability and deformation. (Current Opinion in Solid State and Materials Science,2016)
- Khalajhedayati and Rupert (JOM,2015)reported remarkable thermal stability in nanocrystalline Cu – 3at.% Zr with a nanoscale (54nm) grain size remaining after heating for a week at 950^{o}C (98% of the solidus temperature). They attributed this stability to segregation at the grain boundary forming amorphous intergranular films (complexions) and to Zener pinning by ZrC nano-particles.

High Resolution TEM of the Grain Boundary Complexion in Cu -3 at.% Zr – an Amorphous Grain Boundary Layer

- HRTEM a



Nanoscale ZrC particles were also observed in the Cu - 3 at.% Zr alloy, so kinetic pinning must also be important



ZrC particle growth vs. annealing time

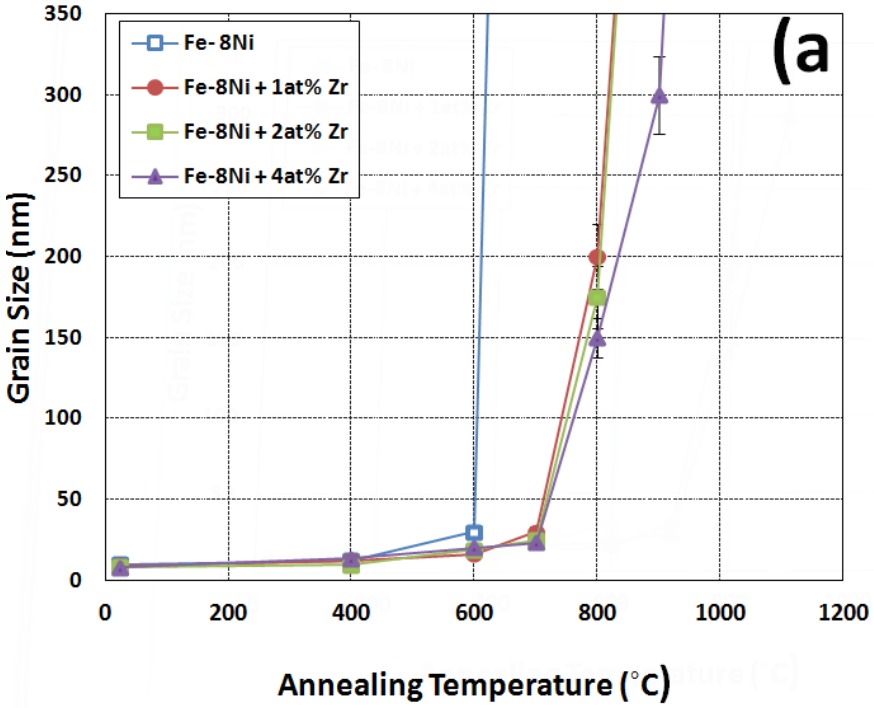
Experimental Evidence for Thermal Stability of Nanocrystalline Alloys

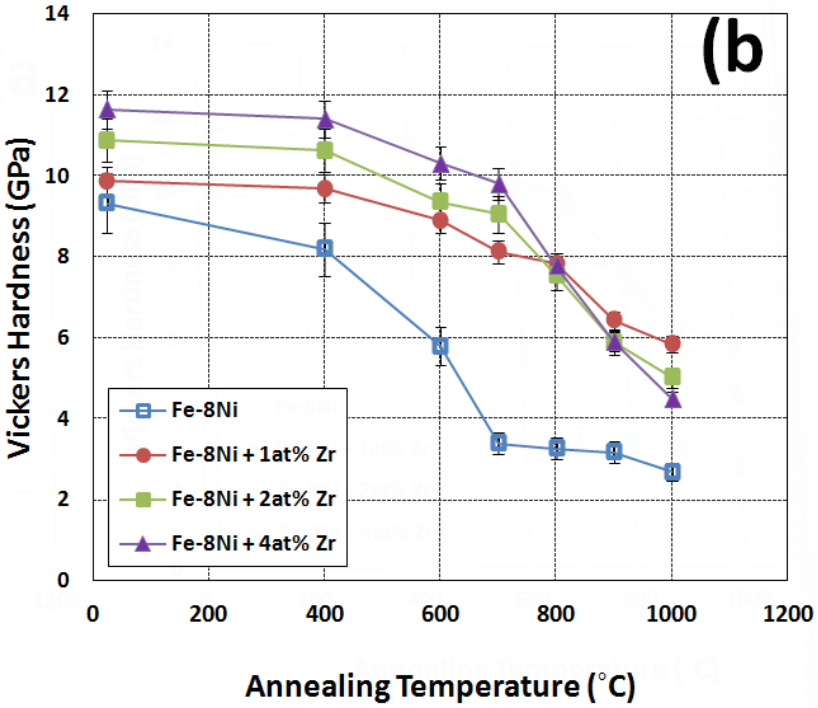
- The remainder of the talk will present experimental evidence for thermal stabilization of nanocrystalline alloys.
- Experimental studies from our group at North Carolina State University will be given as examples of attempts to use thermodynamic stabilization and its competition with kinetic stabilization. Fe- Ni and Fe-Cr nanocrystalline alloys with selected dopants will be discussed.
- Finally, a comparison will be made using the available data from the literature and our group of thermodynamic, kinetic, combinations of the two, and complexions for stabilization of nanocrystalline alloys as a function of homologous temperature.

Grain Growth in Nanocrystalline Fe-Ni alloys with Zr Additions

- Grain growth in Fe-8at.% Ni-1at.%Zr was studied by XRD, FIB microscopy, and TEM in samples made by MA.
- The rate of grain growth for samples containing Zr was much less than that for pure Fe or Fe-8at.% Ni.
- The grain growth of the alloy containing Zr at high annealing temperatures was coupled with precipitation of Fe_2Zr.
- The fine nano-scale precipitate dispersion added to the hardness and thermal stability of the alloy.
- Grain growth accelerated dramatically above the α to γ phase transformation at about 700^{o}C.

Grain Size and Hardness vs. Annealing Temperature for Fe-8at.%Ni, Fe-8at.%Ni + 1,2, or 4 at.%Zr





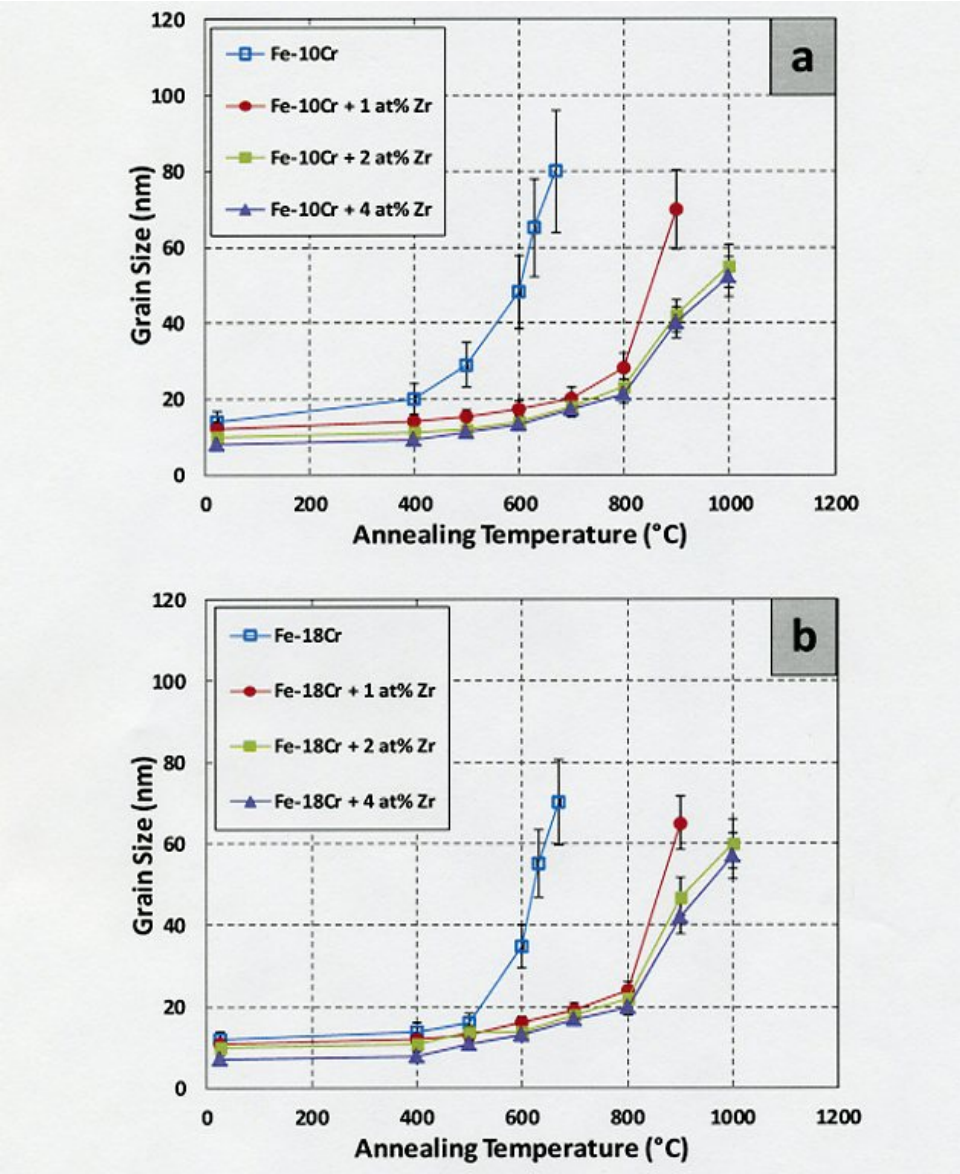
Thermal Stability of Nanocrystalline Fe-Cr Alloys with Zr Additions

- The influence of 1 to 4 at% Zr additions to Fe-10 and 18 at.%Cr alloys on the thermal stability of the nanocrystalline microstructure was studied.
- Grain sizes were determined by XRD, channeling contrast FIB imaging, and TEM for isochronal annealing treatments up to 1000^{o}C.
- Grain size stabilization in the nanoscale range was maintained up to 900^{o}C by adding 2 at.% Zr.
- Kinetic pinning by nanoscale intermetallic particles was identified as one source of high temperature grain size stabilization.
- The analysis of hardness, XRD data and measured values from the TEM image for Fe-10 at.%Cr + 2 at.% Zr suggested that both thermodynamic and kinetic mechanisms would contribute to grain size stabilization.
- There was no significant difference in the results for the 10 and 18at.% Cr alloys, which indicates that the $\alpha \rightarrow \gamma$ transformation does not influence the grain size stabilization.

Grain Size vs. Annealing Temperature

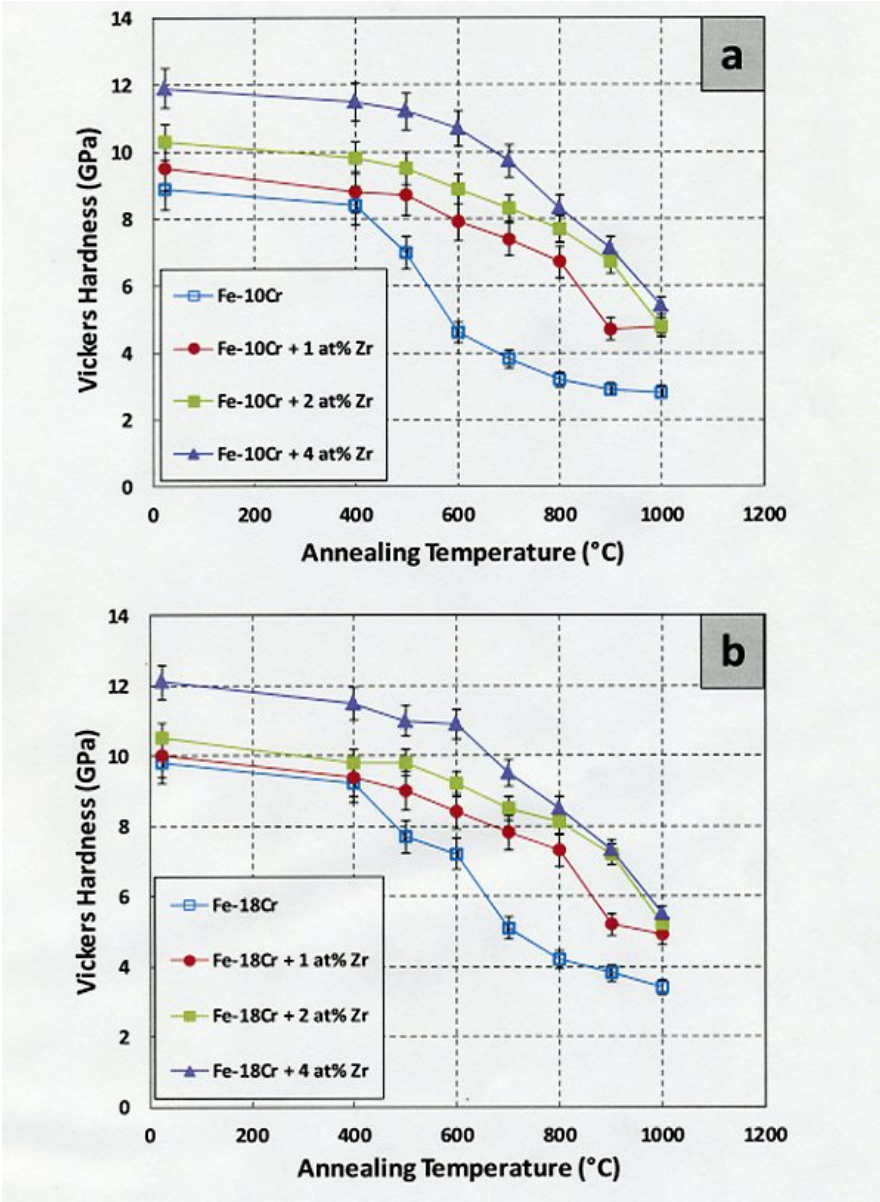
Estimated from XRD line broadening analysis.

Data for grain sizes greater than about 40 nm is suspect.

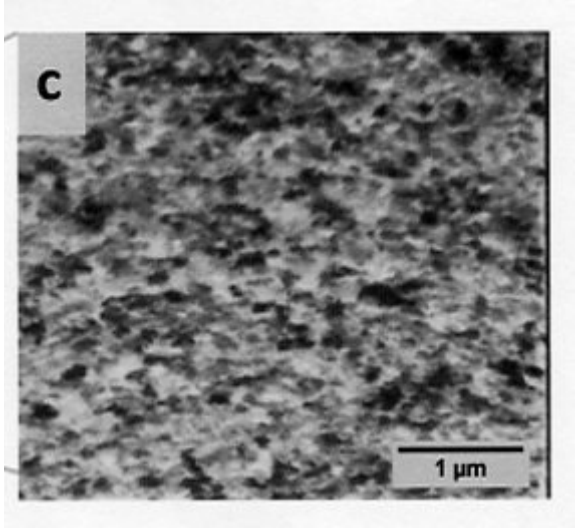


Hardness vs. Annealing Temperatures

Note drop in hardness for Fe-Cr with 1 at.% Zr at 900°C which suggests the grain size from XRD is not valid here.



Channeling Contrast Image of Fe-18at%Cr + 4 at.% Zr Annealed at 900^{oC}



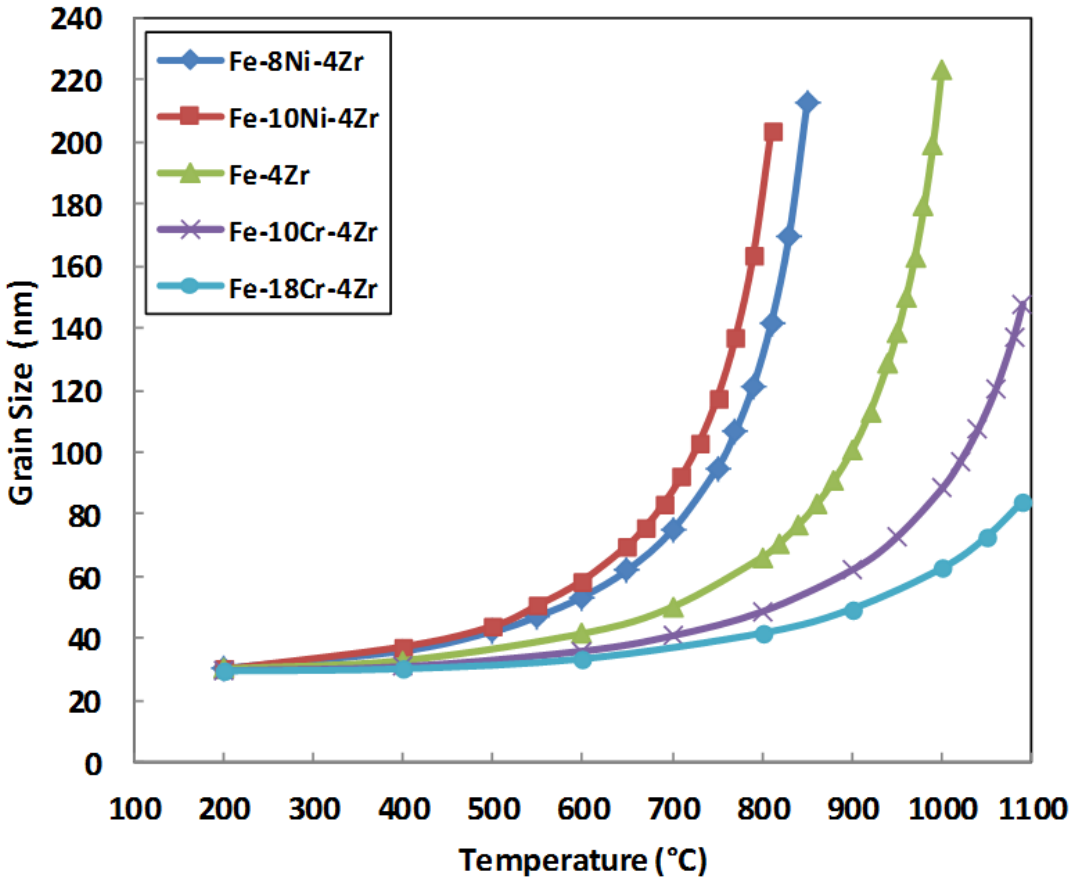
Summary of Study of Thermal Stability of Fe-Cr Alloys with Zr Additions

- Additions of 2, 4 at.% Zr provided effective thermal stabilization in the nanocrystalline range up to temperatures of 900^{o}C.
- The high temperature stabilization is presumed to be due to Zener pinning by Zr (Fe_xCr_{1-x}) intermetallic precipitates (kinetic mechanism) or segregation of Zr to grain boundaries (thermodynamic mechanism).
- Analysis based on the Hall-Petch strengthening and Orowan strengthening for Fe-10Cr-2at.% Zr annealed at 900^{o}C was used to extract the volume fraction of intermetallic particles having a mean size of 20 nm. The stabilized average grain size was 82 nm whereas the Zener pinning size model predicts a grain size of 168 nm. The additional stabilization is attributed to the thermodynamic mechanism.

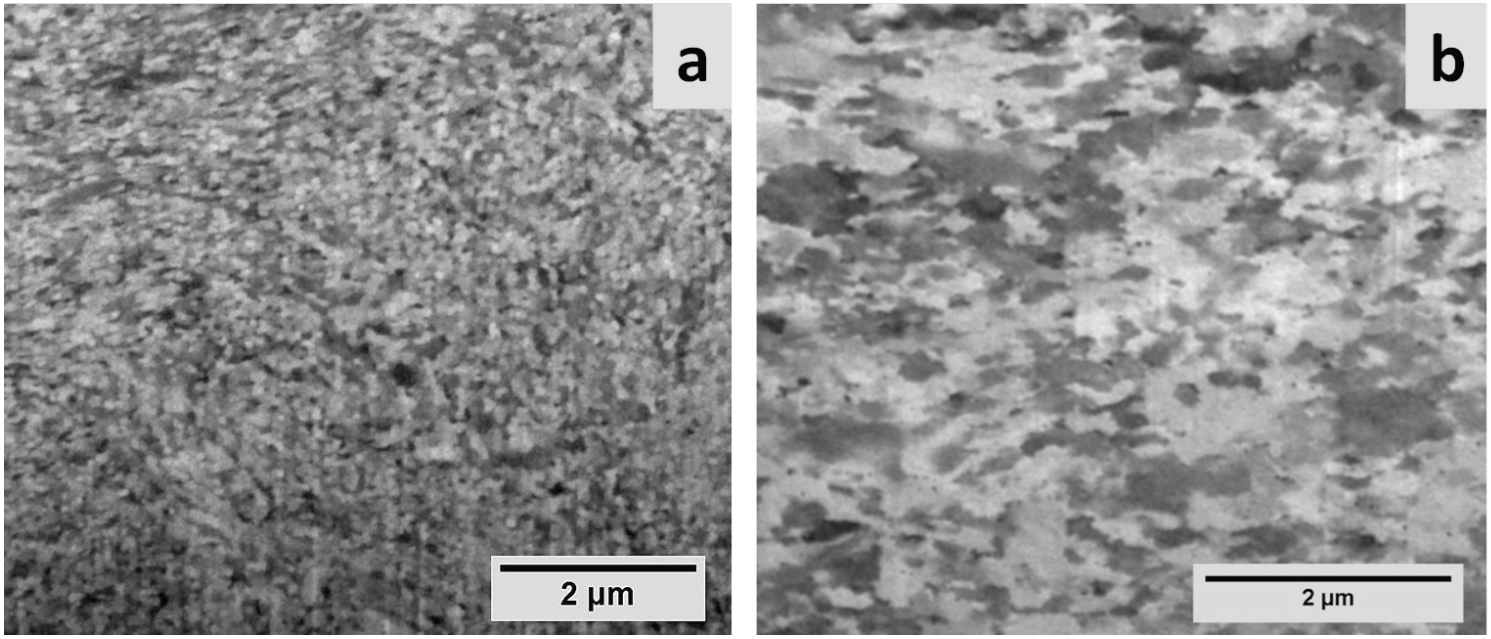
Predictions from the thermodynamic model of Saber et al. for the Fe-Ni and Fe-Cr alloys with Zr additions

- Saber et al. extended their thermodynamic model for binary alloys to ternary systems.
- Their predictions for additions of Zr to either Fe – Ni or Fe – Cr alloys is presented in the next slide.
- The following slide shows the experimental evidence that supports this prediction.

The prediction model for Fe-8Ni-4Zr, Fe-10Ni-4Zr, Fe-4Zr, Fe-10Cr-4Zr, and Fe-18Cr-4Zr alloys.



Channeling contrast images via FIB for Fe-10Cr-4Zr (a) and Fe-8Ni-4Zr (b) nanocrystalline alloys annealed at 900°C

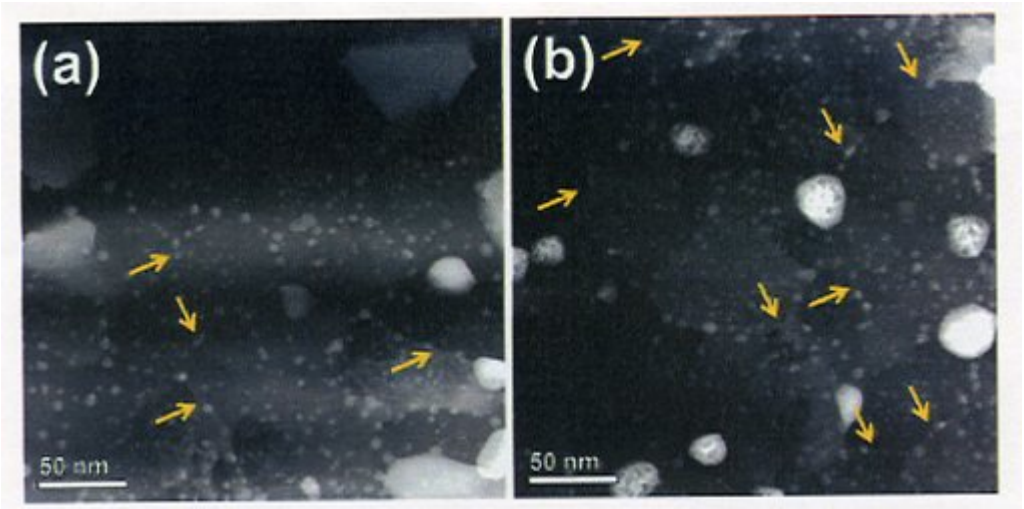


High Temperature Grain Size Stabilization of Nanocrystalline Fe-Cr Alloys with Hf Additions

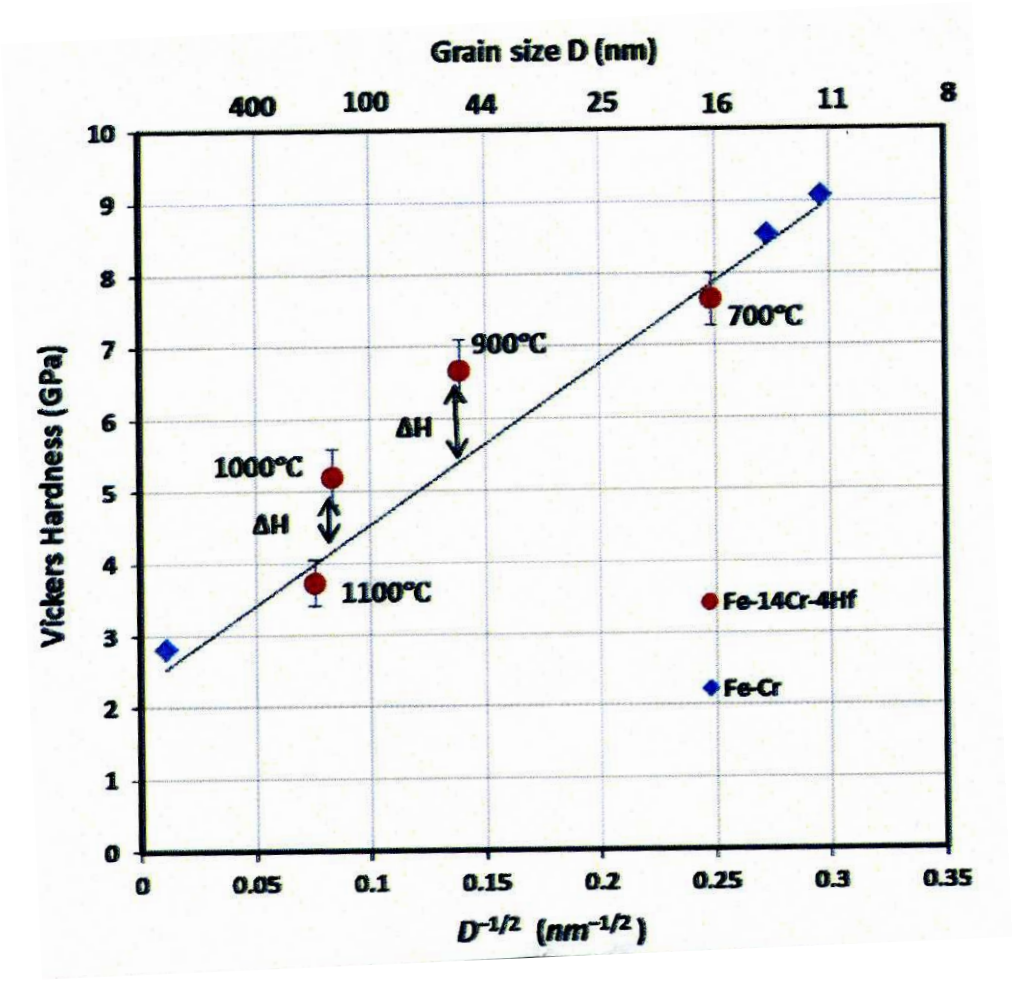
- The influence of 1 to 4 at.% Hf additions on the thermal stability of nanocrystalline Fe-14Cr alloys was studied.
- XRD, high resolution TEM, chanelling contrast FIB imaging, and microhardness were obtained for isochronal annealing temperatures up to 1100^{o}C.
- The grain size of samples with 4 at.% Hf was found to be maintained in the nanoscale range at temperatures up to 1000^{o}C.
- Zener pinning by nanoscale HfO_2 precipitates was determined to be a major source of kinetic stabilization.
- However, 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 solute segregation to grain boundaries, as predicted by the thermodynamic model of Saber et al. This is supported by HAADF-STEM and Super-X^{TM} EDS

HAADF-STEM Images of the Fe-14Cr-4Hf Alloy

- Hf and Cr grain boundary segregation is shown as bright line features pointed out by the yellow arrows in
- a) a typical region and
- b) relatively rich region



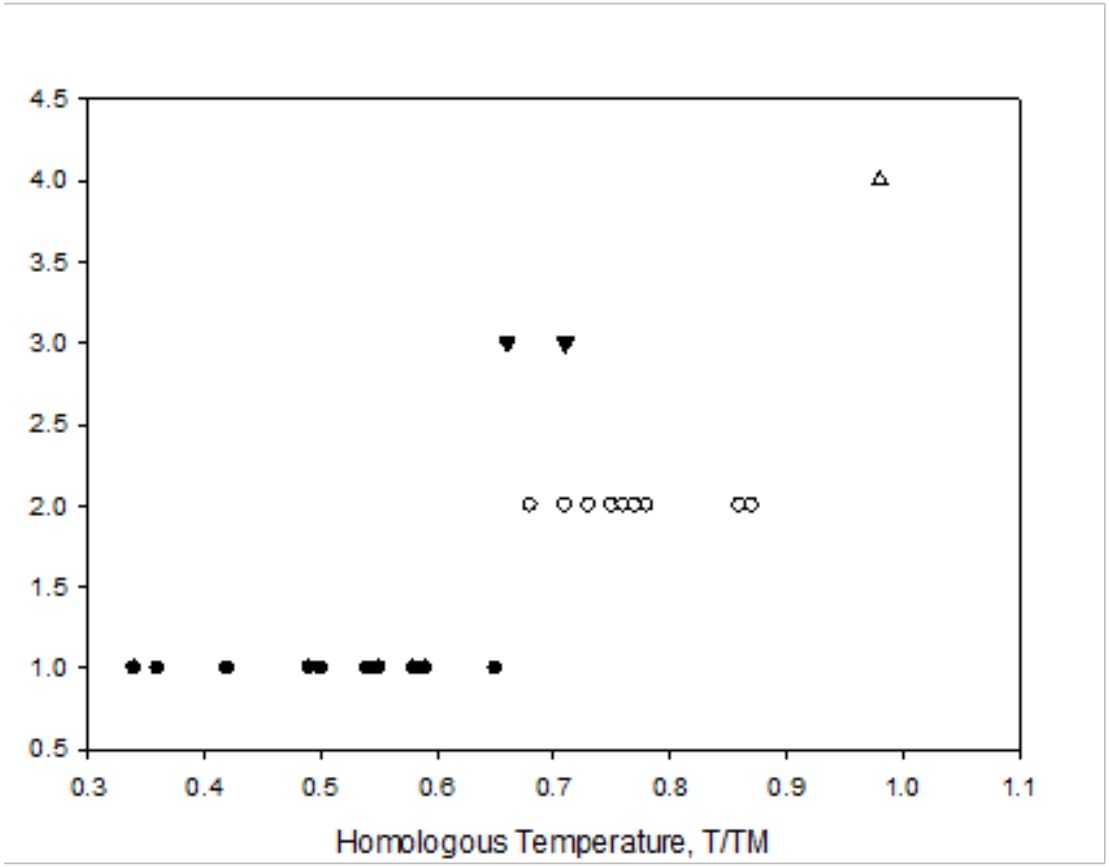
Hall-Petch Plot of Fe-14Cr-4Hf Alloy along with the Base Fe-14Cr Alloy



Comparison of Experimental Data for Thermal Stabilization by the Various Mechanisms

- In the following graph, we plot the homologous temperature at which the nanocrystalline grain size (< 100 nm) is still maintained for:
- Thermodynamic stabilization: ●
- Kinetic stabilization : ○
- Kinetic and thermodynamic stabilization : ▼
- Kinetic and complexion stabilization : Δ

Graph of Data for Thermal Stabilization Mechanisms



Summary

- From the experimental data shown in the previous slide, it would suggest that the most effective mechanisms for thermal stabilization of nanocrystalline grain size at high homologous temperatures are kinetic (Zener pinning by nanoscale particles) or a combination of this and thermodynamic stabilization by solute segregation to grain boundaries.

- The one data point for Cu-3 at.% Zr where Zener pinning is combined with the complexion (an amorphous grain boundary layer) that gives thermal stabilization almost to the melting temperature, points to a possible fertile research field to improve the properties of nanocrystalline alloys.

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