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Nanocrystalline Alloys and Nano-grain Size Stability

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Overview

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Alloys with grain size less than 100 nm are known as nanocrystaline alloys. Due to their enhanced physical and mechanical properties, there is an ever-increasing demand to employ them in various industries such as semiconductor, biosensors and aerospace.

To improve the processing and application of nanocrystalline alloys, it is necessary to develop close to 100% dense bulk materials which requires a synergistic effect of elevated temperature and pressure. By increasing the applied temperature and pressure, small grains start to grow and lose their distinguished properties. Thus, it is technologically important to reach a compromise between inter-particle bonding with minimum porosity and loss of nano-scale grain size during consolidating at elevated temperatures.

In this study we aim to eliminate oxygen from solid solution to improve the nano-grain size stability at elevated temperatures. Nano-crystalline Fe-14Cr-4Hf alloy will be synthesized in a protected environment to avoid oxide particles formation.

Principles

Grain boundaries have a relatively high Gibbs free energy. Thus, the total Gibbs free energy in nanomaterials, due to having a large volume of grain boundaries, is relatively high. High Gibbs free energy makes the material unstable, especially at elevated temperatures. By increasing the temperature, unstable grains grow easily and the materials lose their mechanical properties (e.g. strength, ductility, etc.). This means that by decreasing the grain size, the whole material goes far beyond the equilibrium condition leading to altered thermodynamic properties, which decreases the grains stability especially at elevated temperatures. In other words, each material needs to be thermodynamically stable. Using mechanical techniques to change regular materials to nanomaterials alters their thermodynamic properties. It means that they are not stable anymore and prefer to return to their original state. Increasing temperature helps this occur easier. Therefore, newly developed nanomaterials must be stabilized at high temperature.

To analyze grain size, the Scherrer equation (Equ. 1) can be used in conjunction with X-ray diffraction data. After heat treatment (at each temperature) samples will be analyzed by XRD machine to get the relevant peaks. The Scherrer equation relates the size of nano-grains to the broadening of a peak in a diffraction pattern.

$$D = K \lambda / (\beta \cos\theta)$$

where D is the nanograin size, K is shape factor (~1), β is the line broadening at the half maximum intensity (FWHM) after subtracting the instrumental line broadening, in radians. λ is the X-ray wavelength and θ is the Bragg angle in degree.

Recent studies in nano-crystalline materials reveal that segregation of alloying elements to the grain boundaries improves grain size stabilities. All ranges of segregation, from strongly segregated alloys in Ni-P system to weakly segregated in Ni-W, can develop thermodynamic stability.

In this study, a non-equilibrium stabilizer solute (Hafnium (Hf)) is introduced such that when it segregates to grain boundaries at elevated temperatures, the Gibbs free energy decreases and a metastable equilibrium state can result with nanocrystalline materials.

The thermodynamic grain size stability mechanism may improve by oxygen elimination from solid solution. Oxygen elimination prevents oxide particle formation in the material, leading to more solute remaining in the solid solution that can segregate to the grain boundaries. By increasing the amount of solute contents in the grain boundaries, it reaches a saturation value leading to grain size stability.

The free energy decrease for HfO_2 oxide formation is about an order of magnitude larger than the free energy decrease for Hf grain boundary segregation. By elimination O from the matrix (and increasing the solute segregation to the grain boundaries) the grain boundary mobility decreases relative to the high O content.

Nominally oxygen free (OF) nanocrystalline Fe14Cr4Hf alloy were produced in a glove box by mechanically filing the solid material. This alloy has been chosen because the recent regular solution models predict that Hf would facilitate thermodynamic grain size stabilization in Fe14Cr4Hf alloys at elevated temperatures.

This study is limited to alloys that have solute/stabilizer with high oxide formation enthalpy. Otherwise, oxygen elimination may have no significant influence on grain size stability.

Procedure

1. File the high purity low oxygen content bulk materials (Fe, Cr and Hf targets) in the glove box using a reciprocating mechanical filing machine in order to minimize oxygen contamination in the starting powders.

2. Load the powder mixture for a specific alloy (Fe14Cr4Hf wt.% in this study) into a stainless-steel vial along with 440C stainless steel milling balls (**Fig.** 1). The diameters of the milling balls are 6.4 and 7.9 mm and the ball powder-to-weight ratio is 10:1. The sealed vial needs to be kept under protective atmosphere in the glove box.
3. Carry out high energy ball milling for 20 hours using SPEX 8000M high energy ball mills (**Fig.** 2).
4. Anneal the ball milled Fe14Cr4Hf for 60 min at temperatures between 500 and 1200_ at steps of 100_.
5. Measure the nanograin size, using X-ray diffractometer and the Scherrer equation. Analyses should be done for as-milled and annealed samples. The grain size can be calculated assuming Lorentzian peak profiles for the four most intense peaks after subtracting the instrumental broadening. For this below steps should be followed:
    - Run XRD on the heat-treated samples.
    - Measure the width of the peaks at half maximum height.
    - Put the data in the equation 1 and calculate the grain size.
    - These steps should be repeated for all temperatures.

6. Run multiple annealing treatment and X-ray analysis at each of the annealing temperatures of interest in order to establish an accurate grain size and ensure the reproducibility.
7. Employ a 5 mm die and punch with hydraulic press (3 tons) to press the powder for microscopic analysis.
8. Load sample in the Transmission Electron Microscope (TEM) to see the grain size and nanoparticles formations.
9. Compare the grain sizes, resulted from TEM microscope and X-ray diffraction with similar powder with oxygen contamination.

Figure 1: Stainless steel vial with two different sizes of balls.

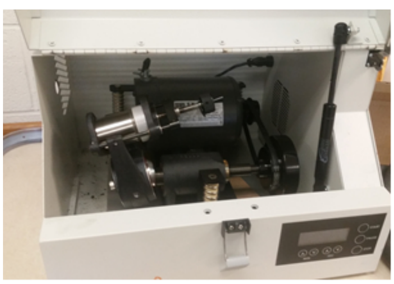

Figure 2: High energy SPEX 8000M Ball milling.

Results

Fig. 3 shows the XRD data for ball-milled OF-Fe14Cr4Hf annealed for one hour at temperatures ranging from 500 to 1200 . There is sharpening of the peaks along with slight peak shifts, due to relaxation of lattice strain as the annealing temperature rises. When the annealing temperature rises, several small peaks are revealed between the four major BCC peaks. These would indicate the formation of secondary phases. However, comparing the 900 scan in Fig.3 with same temperature scan for the high O content Fe14Cr4Hf alloy (Fig. 1) there are many more small peaks appearing in the latter.
Fig. 4a-c shows TEM images and diffraction pattern for OF-Fe14Cr4Hf annealed for 1 hour at 900 . Nanoscale particles in a size range up to about 20nm are present.

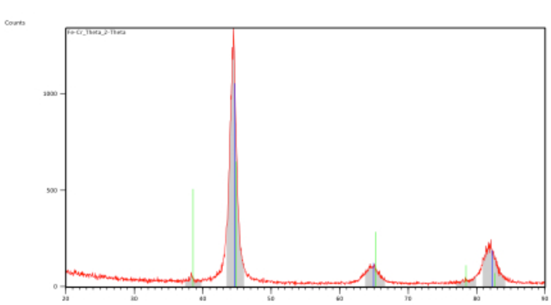

Figure 3: XRD patterns for as-milled OF-Fe14Cr4Hf and annealed for 60 min at temperatures from 500 to 1200°C.

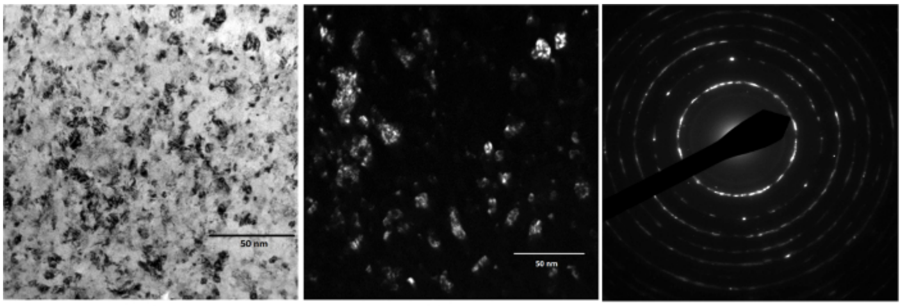

Figure 4: TEM images and diffraction pattern for OF-Fe14Cr4Hf annealed at 900 for 60 min.

Applications and Summary

The experiment demonstrates how the nano-grain size stability of the nominally oxygen free nanocrystalline materials may improves compare to the alloys with significant amount of oxygen. In this study the OF powders synthesized in a protected atmosphere to minimize the interaction between oxygen and solid solution leads to increase the segregation of alloying elements to the grain boundaries and improve the thermodynamic grain size stability. TEM microscope introduced itself as a cost-effective, time-saving and powerful tools to characterize the grain boundaries and nanoparticles.

Fatigue strength and creep resistance are the key properties required for aircraft components that may have a direct influence on aircraft life time. To increase the life of aircraft it is critically important to employ materials with elevated fatigue/creep strength/resistance, achievable mainly due to a reduction in the grain sizes. High-temperature stable nanomaterials, with grain size in the order of less than 10-7 m, may provide fatigue life three times more than conventional materials. Furthermore, this new generation of nanocrystalline materials is stronger and able to operate at relatively high temperatures leading to a significant increase in aircrafts speed and fuel efficiency.

The high temperature stable nanocrystalline materials are perfect candidates for space crafts as well. Various parts of the space crafts (e.g. rocket engines, thrusters and vectoring nozzles) are working at higher temperatures compared to aircrafts.

Satellites, with dual applications of civilian and defense, are also a reasonable target for high temperature stable nanomaterials. Thruster rockets using in the satellite to change their orbits, need nanomaterials that could tolerate elevated temperatures. On board ignitors, developed from conventional materials, may wear out quickly and lose their efficiency, whereas proposed nanomaterials last longer.