

Research Progresses on Thermal Stabilization of Metal Nanocrystalline Alloys



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Abstract: In nano-structured metals, due to grain size decreasing, grain boundary volume fraction increases markedly, which leads to a high driving force for grain growth. So nanocrystalline metals are always remaining at an unstable state upon heating, or even at room temperature, resulting in obstacles in the aspects of their fabrication and application. In this paper, the research progresses on thermal stability of binary nanocrystalline alloys at present stage are introduced from the view of thermodynamics and kinetics. Main theoretical models such as Trelewicz/Schuh (TS) model, Wynblatt/Ku (WK) model, and strategy adopted by Koch et al in thermodynamics stabilization, and basic theory in kinetics stabilization are reviewed and compared.

Key words: binary nanocrystalline alloy; thermodynamics stabilization; kinetics stabilization; grain boundary segregation

Nanocrystalline materials are always the focus of material research because of their unique and superior mechanical properties. For a long time in the past, the problem of acquiring ultra-high strength and appropriate ductility at the same time has been always facing a challenge. With research work going deep, some progresses have been made in these years, and many reports confirmed the acquiring of nanocrystalline materials with elongation up to 10%^[1-3]. In fabricating process of nanocrystalline materials, such as sintering in powder metallurgy and annealing after severe plastic deformation, it's inevitable to involve heating. On the other hand, the thermal influence of employment environment is also inevitable. However, the intrinsic thermal instability of nanocrystalline materials and the tendency of easy coarsening of nano-scaled grains during heating will lead to the loss of mechanical properties, which restricts the fabrication and application of the nanocrystalline materials.

As grain size decreasing, grain boundary volume fraction increases significantly, and it can be estimated by following equation^[4]:

$$f_{ig} = 1 - \left(\frac{d-t}{d}\right)^D \quad (1)$$

where f_{ig} is grain boundary volume fraction, d and t are grain size and average grain boundary thickness, respectively, and D is grain dimensionality. According to Eq.1, when grain size is below 10 nm, grain boundary volume fraction is more than 14%. Thus, high grain boundary energy becomes a great driving force for grain growing, and makes thermal stability of nanocrystalline metal and alloy decrease upon heating or even at room temperature.

There are two basic ways to enhance thermal stability of nanocrystalline metals and alloys, i.e. thermodynamics stabilization and kinetics stabilization. Thermodynamics stabilization is achieved by reducing grain boundary energy through solute atoms segregating at grain boundary, so driving force for grain growth is reduced (or even eliminated). While for kinetics stabilization, grain boundary migration is impeded by solute atom dragging and the second phase pinning, then grain boundary mobility decreases and grain growth is suppressed.

1 Thermodynamics Stabilization

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The concept of thermodynamics stabilization is first developed by Weissmuller^[5,6]. When solute atoms segregate at grain boundaries, the surface energy of grain boundary decreases because of interaction between atoms of solute and solvent and releasing of elastic strain energy, then the driving force for grain growth is reduced or even eliminated (Millet et al indicated explicitly that grain boundary energy can indeed be reduced to zero under the specific conditions^[7]). Considering on the whole mixing system, Gibbs free energy also decreases with solute atoms segregating at grain boundaries and thermodynamics stabilization is achieved. Weissmuller deduced grain boundary energy γ from Gibbs adsorption equation:

$$\gamma = \gamma_0 - N_B^{\text{sat}} (\Delta H_{\text{seg}} + RT \ln \frac{N_B^{\text{M}}}{N^{\text{M}}}) \quad (2)$$

where γ_0 is grain boundary energy of ideal solid solution, N_B^{sat} is solute excess at grain boundary, ΔH_{seg} is segregation enthalpy and $R \ln(N_B^{\text{M}}/N^{\text{M}})$ is segregation entropy.

Usually, the solute with great atomic size misfits to solvent and low solubility in solvent is easy to segregate at grain boundary, which is one of the primary criteria for solute element selection.

1.1 Trelewicz/Schuh (TS) model^[8,9]

Trelewicz and Schuh divided the full volume of A (solvent)-B (solute) binary alloying system into two separate regions: the bulk (i.e. grain) region and the intergranular (i.e. grain boundary) region, and introduced the concept of “transitional” bonding to capture bonds bridging these two regions, as shown in Fig.1.

For the given global composition X , solute content of bulk and intergranular regions are defined as X_b and X_{ig} , respectively with mass conservation condition:

$$X = (1 - f_{ig})X_b + f_{ig}X_{ig} \quad (3)$$

where f_{ig} is determined by Eq.1, the bonding probability in different regions is determined by X_b and X_{ig} . Combining with bonding energies of solute and solvent atoms E^{AA} , E^{BB} and

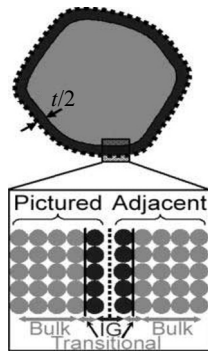


Fig.1 Schematic of the atomic configuration (“Bulk” and “IG” indicate bulk and intergranular regions, respectively; “Transitional” captures bonds that bridge between these two regions^[8])

E^{AB} , the change of Gibbs free energy in bulk and intergranular regions can be calculated:

$$\Delta G_{\text{mix}}^b = zX_b(1 - X_b)\varpi_b + KT[X_b \ln X_b + (1 - X_b)\ln(1 - X_b)] \quad (4)$$

$$\Delta G_{\text{mix}}^{ig} = zX_{ig}(1 - X_{ig})\varpi_{ig} + \frac{\Omega}{t}(1 - X_{ig})\gamma_A + \frac{\Omega}{t}X_{ig}\gamma_B + KT[X_{ig} \ln X_{ig} + (1 - X_{ig})\ln(1 - X_{ig})] \quad (5)$$

where z and Ω are coordination number and atomic volume of solvent, respectively, K is Boltzmann’s constant, T is temperature, ω_b and ω_{ig} are interaction parameters in bulk and intergranular regions, respectively, and shown as follows:

$$\varpi_b = \left(E_b^{AB} - \frac{E_b^{AA} + E_b^{BB}}{2} \right) \quad (6)$$

$$\varpi_{ig} = \left(E_{ig}^{AB} - \frac{E_{ig}^{AA} + E_{ig}^{BB}}{2} \right) \quad (7)$$

subscript “b” and “ig” represent bulk and intergranular regions, respectively. Then Gibbs free energy of the whole mixing system is given:

$$\Delta G_{\text{mix}} = (1 - f_{ig})\Delta G_{\text{mix}}^b + f_{ig}\Delta G_{\text{mix}}^{ig} + z\nu f_{ig} \left\{ \left[X_{ig}(X_{ig} - X_b) - (1 - X_{ig})(X_{ig} - X_b) \right] \varpi_{ig} - \frac{\Omega}{zt}(X_{ig} - X_b)(\gamma_B - \gamma_A) \right\} \quad (8)$$

where ν ($\nu=1/2$) is transitional bonding fraction, and the last term indicates energy contribution from transitional region to the whole system.

According to Eq.8, the global composition X is held as constant at given temperature T , a three-dimensional free energy surface can be constructed as the function of grain size d and grain boundary concentration X_{ig} . If this free energy surface has a minimum (as shown in Fig.2), it can be concluded that nanocrystalline grain is thermodynamically stable at the given global composition X and temperature T . Accordingly, there exists a grain boundary concentration X_{ig} that makes free energy the lowest for the specific grain size (Fig.3).

From equilibrium condition of Eq.8:

$$\frac{\partial \Delta G_{\text{mix}}}{\partial X_{ig}} = 0 \quad (9)$$

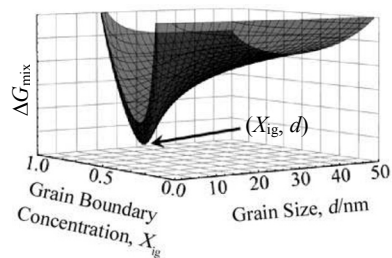


Fig.2 Schematic of free energy surface as a function of grain size d and grain boundary concentration X_{ig} ^[9]

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