



On the Experimental Assessment of Thermodynamic Stability of Nanostructured Solid Solutions

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Abstract

Thermal stability in nanocrystalline alloys has been extensively explored using both experimental and theoretical approaches. However, there is rarely any direct evidence of the specific stabilization mechanisms. Therefore, whether the stability is achieved by kinetic barriers or by reaching an equilibrium thermodynamic state remains an open question. Indeed, although kinetic and thermodynamic stabilities are intrinsically different from the conceptual point of view, their experimental assessment, identification, and results interpretation present several difficulties. In this regard, a general agreement about the experimental findings required to ascertain the thermodynamic stability is also still missing. In this work, a thorough discussion on the experimental assessment of thermodynamic stability of nanostructured solid solutions is presented and experimental conditions sine qua non able to, at least, identify the possibility of thermodynamic stability occurrence is proposed.

Keywords: Nanocrystalline alloys; Thermodynamic stability

Opinion

Grain growth in polycrystalline materials stems from the inherent energetic penalty that drives the material to eliminate grain boundary (GB) toward a thermodynamically favored single crystal [1]. This concept is illustrated in Figure 1 where the Gibbs free energy, G , of the system as a function of grain size at constant material composition, temperature and pressure is reported. Curve a (black line) represents the classical condition where G monotonically decreases as the grain size increases up to reach its minimum when the single crystal structure is approached (point S with grain size $\rightarrow\infty$). Therefore, whatever the grain size of the as-produced material (point A and A' in Figure 1), grain growth takes place in order to minimize the Gibbs free energy of the system.

However, non-conventional thermodynamic effects induced by grain boundary segregation in alloyed materials lead to consider different grain size evolution. Specifically, the idea of segregation-induced thermodynamic stability in nanocrystalline solids considers the change in the Gibbs free energy of a polycrystals upon alloying. Indeed, GB segregation in a multi-component material may lower the system Gibbs free energy, thus opening the possibility that, at a given temperature, pressure, and composition, the thermodynamic stable state of the system may correspond to a polycrystalline

material with a finite grain size rather than the single crystal condition [2]. This completely different scenario, represented in Figure 1 by curve b (red line), appears when a minimum of the Gibbs free energy with respect to the grain size exists. Indeed, starting from a material with a grain size given by point B, grain growth will occur to make the system lowering its value of G . On the other hand, grain growth stops once the minimum of the Gibbs free energy (equilibrium grain size E) is reached. Interestingly, identical thermodynamic considerations may be invoked when the as-produced material has the grain size given by point B'.

The existence (profile b) or non-existence (profile a) of thermodynamic stable states other than the single crystal strongly depends upon the alloy, its composition as well as temperature and pressure conditions. It worth bearing in mind that, even if such a state exists, the value of the equilibrium grain size may vary as a function of the same variables just mentioned. Of course, the grain size of point E should be less than 100 nm in order to have a thermodynamically stable nanostructure. On the other hand, the thermodynamic analysis is not affected by the exact position of point E, provided that the corresponding grain size has a finite value. Therefore, hereafter, we will refer to a polycrystalline structure for the sake of generality [3].

Regardless the specific mechanisms taking place and according to the picture depicted in Figure 1, materials structures can reach their thermodynamically stable state following two different paths, i.e., “from below” or “from above” [4]. According to the former one, stable grain size is commonly obtained fabricating by some non-equilibrium processing method (e.g., mechanical alloying, rapid solidification, etc.) a materials whose grain size is usually finer (cf. points A, A', and B in Figure 1) than the final size to which the system grows (cf. points E and S, in Figure 1). Alternatively, stable grain

size can be approached “from above”, i.e., occurring by natural grain refinement starting from a grain size that is coarser (cf. point B' in Figure 1) than the stable one (cf. point E in Figure 1). Theoretically, in alloyed materials involving grain boundary segregation there is support for such grain shrinkage. Indeed, in the case of the grain boundary solute enrichment is energetically favored, finer grained structure can accommodate higher number of segregated atoms thus presenting a lower value of Gibbs free energy than the starting coarser structure [5].

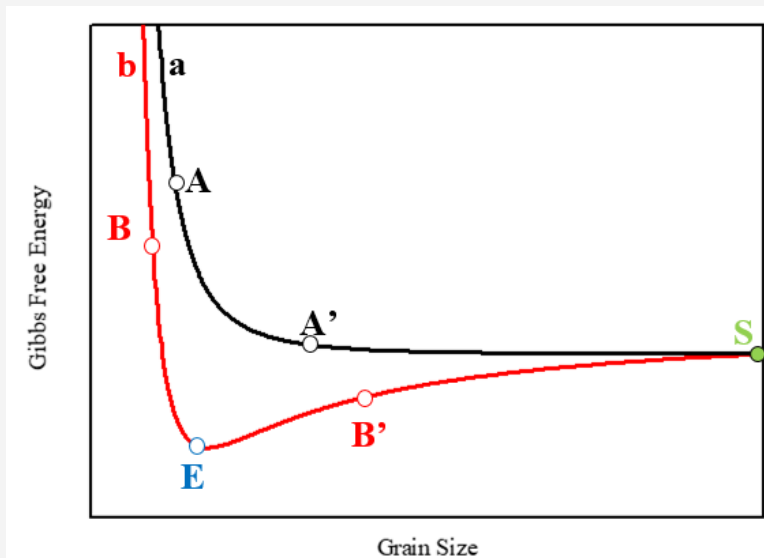


Figure 1: Gibbs free energy as a function of grain size for a) conventional polycrystalline materials (black curve), and b) thermodynamically stable polycrystalline alloy (red curve). Points A, A', B, and B' represent as-produced materials. Points S and E are the single crystal condition (grain size $\rightarrow \infty$) and the finite-grain size equilibrium structure, respectively.

However, the spontaneous grain refinement representing the “from above” approach would require interface-generating mechanisms whose experimental evidences, at the best of Author’s knowledge, are still lacking. This may due to very high activation energies for these phenomena to take place, thus introducing a kinetic impediment to the thermodynamics-guided evolution of the system toward its stable state. On the other hand, and regardless the system behavior is depicted by curve a or curve b in Figure 1, kinetic barriers may dramatically affect also the “from below” approach to the material thermodynamically stable grain size (Points E and S). A clear evidence of this may be gained recalling that real materials under normal conditions are typically characterized by a polycrystalline structure. Indeed, even when a thermodynamically stable finite grain size does not exist, materials are hindered to reach the thermodynamic goal of GBs total removal because of the arrest of grain growth once grains have reached a certain size. Similarly, a finer structure than the thermodynamically stable one can result apparently stable because of kinetic obstacles.

Such apparently stable grain size can be understood again by considering grain growth as the product of the grain-boundary mobility M and the driving force P . Latter quantity, which embed the thermodynamic constraints, is proportional to the grain boundary area that decreases as the material average grain size increases.

Quantity M is instead related to thermally-activated phenomena so that grain growth naturally increases as thermal exposure (temperature and/or time) increases. It is then inferred that coarse microstructure at low temperatures may appear as the material stable state in place of the single crystal one. Moreover, materials where grain boundary mobility is characterized by high activation energies may show coarsening resistance, which is typically understood and identified as thermal stability due to the thermal-activated character of phenomena contributing to grain growth. It is then obvious that, from a thermodynamic perspective, the (apparent) kinetic stability just described is a transient state whose (apparent) stationarity is a consequence of adopted observation time scales shorter than the system evolution characteristic time. Indeed, latter one can be extremely long at low temperature because of the slow diffusion phenomena or in the case of drag forces exerted on grain boundaries, which can dramatically reduce GB mobility so that to virtually immobilize them.

According to the descriptions reported above, kinetic and thermodynamic stabilities are intrinsically different from the conceptual point of view. However, their experimental assessment, identification, and results interpretation present several difficulties. Moreover, the interplay between thermodynamic and kinetic stabilization mechanisms has not so far been explored in

detail, so that conditions under which each mechanism dominates and whether the two acts together or compete are yet to identify. At first glance, high temperatures and long treatment times can help in discriminate between kinetic and thermodynamic effects. Clearly, application of high temperatures may overcome kinetic barriers while longer times allow materials to reach their preferred states. It stems also out that thermodynamic and kinetic stability are practically indistinguishable when materials are exposed at too low temperatures for too short times. On the other hand, too high temperature treatments are not free of drawbacks. Indeed, increasing the temperature to make the kinetics-related mechanisms influence substantial may lead to the underestimation of thermodynamic effects when the results are interpreted in terms of materials structure stability. In fact, as mentioned before, although in less degree than kinetic mechanisms, the thermodynamic stable state is temperature dependent. Therefore, an increase of the grain size as the temperature is increased may be due to the overcome of kinetic barriers as well as to the change of thermodynamic stable state. In this sense, long-run experiments may potentially give rise to less contradictory results. Indeed, at least in principle, whatever the temperature level and given the system enough time, it will be end up single crystal (no stability of polycrystalline structure) or finite-grain-size structure (thermodynamic stability). However, prolonged experiments may result resource-consuming, and for the case of too low temperature treatment, lacking practical sense due to the extremely long time needed.

It is then clear that, given that present state-of-art of this field, an analysis of experimental results aimed to ascribe them to kinetic or thermodynamic stability could probably prove to be ineffective. Nonetheless, it is Author's opinion that a sort of experimental

condition sine qua non able to, at least, identify the possibility of thermodynamic stability occurrence can be given. In order to clarify this important issue, let us assume to investigate experimentally the structure evolution of materials subjected to thermal treatment, and to exemplify materials features by grain size only for the sake of convenience. Grain size time-evolution may be complex and temperature-dependent. However, a schematic illustration of conceivable evolutions as a function of thermal exposure time at a given temperature may be gained by Figure 2. For the sake of clarity, let us first illustrate these behaviors, while postponing successively the corresponding interpretation in terms of kinetic or thermodynamic stability. Specifically, starting from point (state) O, representing the as-produced material structure, several distinct behaviors can be identified according to the obtained experimental temporal profile of the grain size. Curve a (red) represents the conventional growth where material grain size continuously increases without reaching a stationary value. Alternatively, grain size time-profile can follow curve b (green), thus initially increasing up to reach a steady state value (point B). Curve c (blue) exemplify the situation where thermal exposure does not appreciably change the materials grain size. For the sake of completeness, two hypothetical experimental behaviors representing the "from above" approach are also reported. In particular, the steady state D, whose grain size value is lower than the initial one, can be reached according to curve d (cyan), which depicted an initial decrease followed by a grain size-invariant period. Finally, it is worth noting that, theoretically speaking, the steady state B can be reached also according to curve b' (magenta line) starting from a coarser grain size (point O') in addition to the "from below" approach given by curve b.

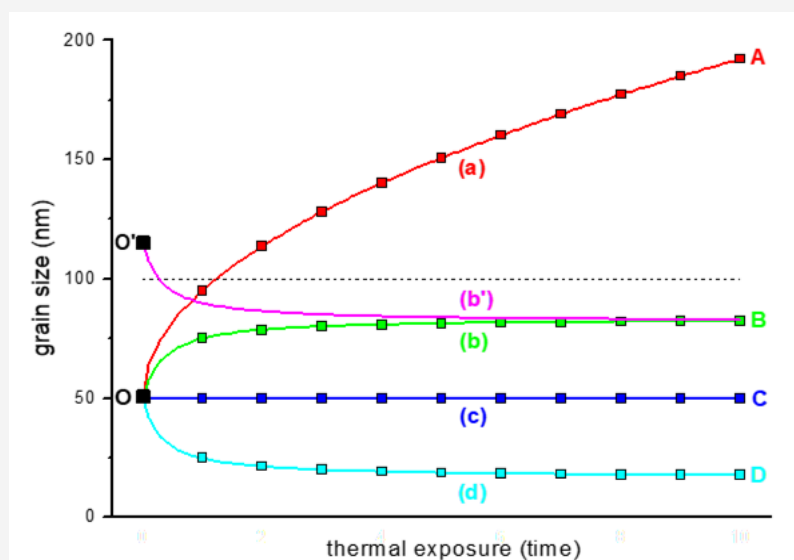


Figure 2: Conceivable grain size temporal evolution of polycrystalline materials undergoing thermal treatment. Points (state) O and O' represent the as-produced material structure. Curve a (red) depicts the conventional growth where material grain size continuously increases without reaching a stationary value. Curve b (green) exemplifies a time-profile according to which grain size initially increases up to reach a steady state value (point B). Curve c (blue) illustrates the situation where thermal exposure does not appreciably change the materials grain size. Two hypothetical experimental behaviors representing the "from above" approach is also reported. The steady state D, whose grain size value is lower than the initial one, can be reached according to curve d (cyan), which shows an initial decrease followed by a steady-state period. Finally, theoretically speaking, the steady state B can be reached also according to curve b' (magenta line) starting from a coarser grain size (point O') in addition to the "from below" approach given by curve b.

As mentioned before, the plausible experimental profiles reported in Figure 2 can be interpreted differently depending on which perspective stability is viewed from. Profile a shows a continuous growth so that stability, either kinetic or thermodynamic one, can be excluded. It should be however mentioned that this conclusion might be changed by the appearing of a steady state condition for prolonged treatments. Indeed, at least in principle, the existence of a finite-grain size stable state can be ruled out only in the case of the system reaches the single crystal state or when thermal treatment lasts for infinite time. On the other hand, by limiting our analysis to nanocrystalline materials, which are defined as having an average grain size less than 100 nm, stable states coarser than this bound lose any importance. Therefore, stability of nanostructures can be excluded once grain growth above 100 nm is experimentally observed. Profile b shows instead the appearance of stationary state in the nanometer range, which could be understood in terms of thermodynamic stability. Indeed, in this case, temperature level is high enough to activate grain boundary mobility, as testified by the initial grain growth. However, the latter slows down as a plausible effect of the reducing driving force, which, in turn, could be an indication that the system is approaching a minimum of its Gibbs free energy. Trivially, also hypothetical experimental profiles b' and d could be interpreted as a clue of the existence of thermodynamic stability. Vice versa, in order to explain profile c, let us assume it proves thermodynamic stability. This would imply that the grain size of the starting as-produced materials is the same of the thermodynamic stable state. Although this coincidence cannot be excluded a priori, it is hard not to consider it a very fortuitous case. More likely, in this case applied temperature is too low to activate grain boundary mobility, such that profile c is easier related to kinetic stability.

The discussion presented above has been aimed to highlight the significant difficulties for the experimental assessment of the thermodynamic stability of nanocrystalline solid solutions. In addition, two importance conditions an experimental investigation should satisfy are worth to be stressed. First, as already mentioned, the starting as-produced materials should have a structure as fine as possible. This condition would make possible the "from below" approach to the thermodynamic stable state. In fact, it is well known that grain growth-limiting phenomena (kinetic barriers) become less effective as the grain size decreases. Thus, "creating" the conditions to facilitate coarsening may help in excluding kinetics-related effects when grain growth is not experimentally observed. Furthermore, let us assume that the situation to deal with is represented by curve b in Figure 1. The existence of a stable state with finite grain size would then imply that both "from below" and "from above" approaches are available. However, since the "from above" approach is not likely to take place, starting from a coarser grain size (point B') than the one corresponding to the thermodynamic stable state (point E) could result in an apparent stability, which is the consequence of the combination between a not thermodynamically favorable grain growth and a kinetically

hindered grain refinement. Second requirement is related to the fact that an experimental temporal evolution of grain size close to profile b of Figure 2 should be obtained in order to, at least, speculate the existence of thermodynamic stability. This means that thermal treatment for different times and, possibly, at different temperatures should be performed. For instance, a very thorough exploration following this line was reported for the case of nanocrystalline RuAl intermetallics [6].

Clearly, suppression of grain growth is an important criterion for assessing the stability of nanostructured solid solutions. However, a potentially equally important stability is that with respect to phase separation or ordered (intermetallics) phases formation. Indeed, even if a nanocrystalline solution with grain boundary segregation is relatively more stable than a coarse-grained alloy of the same global composition, the nanocrystalline structure may still be less thermodynamically favored than the bulk phases separated state or the intermetallic one. Again, the "from below" approach, i.e., starting from a homogeneous nanocrystalline solid solution, seems the most suitable strategy to verify the thermodynamic stability against phase separation or intermetallics formation. Of course, there are no thermodynamic constraints to start with a multiphase system, i.e., a sort of "from above" path. Indeed, if the nanocrystalline single solid solution state is the stable one, materials should naturally tend to it also in this case. However, characteristic times of homogenization or phase dissolution phenomena may result comparable or even higher than the grain growth one, thus complicating the correct interpretation of the obtained experimental results.

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Conflict of Interest

The authors declare that they have no conflict of interest.

References

1. Sutton AP, Baluffi JW (2006) Interfaces in crystalline materials. Oxford University Press, UK.
2. Weissmüller J (1993) Alloy effect in nanostructures. *Nanostructured Materials* 3(1-6): 261-272.
3. Kirchheim R (2002) Grain coarsening inhibited by solute segregation. *Acta Materialia* 50(2): 413-419.
4. Amram D, Schuh CA (2018) Higher temperature yield smaller grains in a thermally stable phase-transforming nanocrystalline alloy. *Phys Rev Lett* 121: 145503.
5. Chookajorn T, Schuh CA (2014) Thermodynamics of stable nanocrystalline alloys: A Monte Carlo analysis. *Physical Review B - Condensed Matter and Materials Physics* 89: 064102.
6. Liu KW, Mücklich F (2001) Thermal stability of nano-RuAl produced by ball milling. *Acta Materialia* 49(3): 395-403.