

Effect of Interface Structures on Densification and Grain Growth during Sintering

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Abstract

Both densification and grain growth are driven by the reduction of the interfacial area, kinetics of which depends strongly on the interface structure. Abnormal grain coarsening in the system of singular solid/liquid interface such as WC-Co alloys was explained by the growth mechanism of 2-dimensional nucleation. Based on this concept, the marked inhibition of coarsening of WC grains by VC addition can be approached by the increase in the step free energy, which increases the barrier of 2-dimensional nucleation. The activated sintering in tungsten powders can be approached by the interface structure change induced by the addition of a small amount of nickel.

Keywords: sintering, densification, grain growth, abnormal grain growth, activated sintering

1. Introduction

Densification and grain growth during sintering are driven by the reduction of the interfacial free energy. Their kinetics depends strongly on the interface structure. Full densification is relatively easily achieved in some systems whereas it is hardly achieved in other systems within practical length of sintering time. Solid grains dispersed in liquid in some systems undergo normal grain growth or coarsening whereas they undergo abnormal grain growth. Such drastically different microstructural evolution is a problem of kinetics and related with the interface structure to an extent. In this paper, the effect of the interface structure on densification and grain growth behavior will be analyzed. Since the effect of the interface structure on the growth or coarsening behavior of grains dispersed in liquid is relatively a simple concept, it will be treated first and then the effect on densification will be followed.

2. Effect of Interface Structure on Grain Growth

The surface structure is classified as being rough and singular. The step free energy of a rough surface is zero; there is no excess free energy for an atom on the surface. The equilibrium shape of a crystal with a rough surface is spherical. In this case, there is no kinetic barrier for atomic attachment to or detachment from the surface. The coarsening kinetics of spherical grains dispersed in liquid becomes diffusion-controlled in the liquid phase. The process of diffusion-controlled coarsening is understood relatively well with its mathematical formulation and solution being described in the LSW theory [1,2].

The LSW theory shows that the distribution of grain size normalized by the average size does not change with time in diffusion-controlled coarsening, i.e. stationary. Such

coarsening behavior is called normal grain growth (NGG) and characterized by the unimodal size distribution in comparison with the bimodal size distribution characteristic of abnormal grain growth, which will be explained later. Experimentally, spherical grains dispersed in liquid undergo normal coarsening, which has no exception to our knowledge. Since the spherical grains would have a spherical equilibrium shape and a rough surface, the coarsening kinetics would be diffusion-controlled. Therefore, the experimental coarsening behavior as well as the theoretical analysis of the LSW theory agrees well with the kinetics expected from the rough surface structure of spherical grains.

The step free energy for a singular surface varies widely from near zero to the surface free energy, depending on the temperature or the composition. The singular interface consists typically of terrace, ledge and kink. As the step free energy increases, the excess free energy for an atom on the terrace increases. The reversible transfer of atoms takes place only at the kink.

The equilibrium shape of a crystal of a singular surface tends to be angular with faceted surfaces. In this case, there is an appreciable kinetic barrier for atomic attachment or detachment from the terrace. Therefore, the ledge-generating source such screw dislocation or two-dimensional nucleus is needed for atomic attachment. The analysis showed that the coarsening controlled by screw dislocation kinetics did not lead to abnormal grain growth (AGG) but the coarsening controlled by 2-dimensional nucleation led to typical AGG with a bimodal distribution of grain size at a proper choice value of step free energy [3].

When the step free energy is sufficiently small, the kinetic roughening is dominant and the coarsening kinetics tends to be diffusion-controlled, resulting in more or less normal growth behavior. When the step free energy is high, the barrier for 2-dimensional nucleation becomes high and

the step spacing of screw dislocations becomes wide, resulting in remarkable grain growth inhibition. The WC grains in Co liquid of WC-Co alloys, whose shape are angular and which have a singular solid/liquid interface, undergo AGG [4]. The WC grains have a shape of a truncated prism. When a small amount of VC is added, the shape of WC grains is changed to a prism without truncation and the grain growth kinetics is markedly reduced. The shape change from a prism with truncation to that without truncation indicates the increase in step free energy. Therefore, the grain growth inhibition effect of VC would come from the increase of step free energy. If the abnormality of grain growth is defined as the size ratio of the largest grain to the average, it increases with increasing step free energy. This abnormality was shown to be much larger in WC-Co alloys with VC addition than those without VC addition [5].

3. Effect of Interface Structure on Densification

In the final stage of solid-state sintering, the grain boundary diffusion plays an important role in densification. For example, when the isolated pores are located at a grain boundary, they can be removed relatively easily; however, when they are located inside a grain, they can be hardly removed. The grain boundary is known to undergo a transition between entropy-dominant disordered and enthalpy-dominant ordered structure. The facet and defacet transition was studied most clearly, where the former represents an ordered and compact structure and the latter a disordered and open structure [6]. Therefore, the grain boundary diffusivity would be much higher along defaceted grain boundaries than along faceted ones.

In the activated sintering of some refractory metals, the addition of a small amount of transition metals such as Ni drastically increases the densification rate. The enhanced densification has not been attributed to the formation of a liquid phase. The addition of Ni to W was suggested to induce a transition from an ordered to a disordered grain boundary structure, enhancing the grain boundary diffusivity and thereby the densification [7].

Once isolated pores are separated from the grain boundary and trapped inside the grain, they hardly shrink

because of low bulk diffusivity. Full densification of MgO-doped alumina is attributed to the inhibition of pore-boundary separation. The important factor in the pore-boundary separation is the dihedral angle and the mobility ratio of pore to boundary [8]. In such an analysis, the pore-boundary separation was treated mainly in the absence of liquid film along the grain boundary. However, in most cases where AGG of alumina occurs, the liquid film is known to exist. In the presence of liquid film, it seems that the pore-boundary separation is drastically enhanced [9]. We suggest that the pores entrapped inside the abnormally-growing grains are formed by the liquid film migration.

4. Summaries

The interfacial structure plays an important role in sintering kinetics of densification and grain growth. The rough solid-vapor interface free of a liquid film is desirable for densification. The grains with a singular solid-liquid interface structure tend to undergo abnormal grain growth and the grain growth can be inhibited if the step free energy is increased by adding suitable impurities.

5. References

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