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MC simulation in microstructure evolution and grain growth during desorption−recombination processing of NdFeB alloy

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Abstract: Based on the mechanism of grain growth during desorption−recombination process of NdFeB alloy, Monte Carlo (MC) physical model was introduced to simulate microstructure evolution during grain growth process of $Nd_2Fe_{14}B$ phase at various processing temperatures. Furthermore, the grain growth kinetics was studied. The analysis shows that the grain growth can be well simulated, and the average growth exponent $n\approx0.8$ for the entire time domain by fitting the experimental data with the theoretical model, higher than the normal value of 0.5.

Key words: Monte Carlo simulation; grain growth; NdFeB alloy; desorption-recombination processing

1 Introduction

Nanocrystalline NdFeB-type magnetic materials have attracted considerable attention in recent years [1−2]. Due to the exchange coupling across the grain boundaries and the fact that the grain size is well below the threshold for a single domain, such materials have been shown to manifest enhanced remanence ($M_r/M_s>0.5$) and coercivity, which leads to higher energy products as compared with the conventional microcrystalline counterparts [3−4].

The process of hydrogenation, disproportionation, desorption, and recombination (HDDR) has been reported as a promising technique to produce highly coercive NdFeB alloy powders with submicron $Nd_2Fe_{14}B$ grains [5−6]. By the conventional HDDR processing, however, it is not feasible to obtain nanocrystalline $Nd_2Fe_{14}B$ grains. To produce nanocrystalline NdFeB-type magnets by utilizing HDDR reactions, we have recently developed a new process which incorporates mechanical milling with HDDR processing [7]. The process consists of two separate steps: (1) mechanically activated disproportionation of NdFeB-type alloy by room-temperature ball milling in hydrogen to obtain nano-structured as-disproportionated precursory microstructure; (2) isothermal desorption−recombination processing of the as-milled disproportionated alloy powders to form nanocrystalline $Nd_2Fe_{14}B$ grains.

In our previous work, the disproportionation and microstructure evolution of some NdFeB alloys during ball milling in hydrogen was investigated [8−9]. This work investigates the microstructure change of disproportionated NdFeB alloy, and the grain growth kinetics during grain growth process of $Nd_2Fe_{14}B$ phase at various processing temperatures is investigated during desorption−recombination by using MC method, to better understand and optimize this process.

2 Model and simulation procedure

2.1 Monte Carlo algorithm

MC simulation is performed by mapping the microstructure onto a discrete lattice. Each lattice element contains a random allocated number Q representing its phase and crystallographic orientation. The grain nucleation and growth are simulated by appropriately switching and reorientation attempts involving the lattice elements. In particular, the application of the lowest energy principle ensures the minimization of the total energy of system for microstructure evolution, thus, the atomic jumps should always be directed towards one of the nearest neighbors only, which reveals a typical physical meaning of transition rule. To simulate the closed, complete system or large-area material, the neighbors for the edges are

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obtained by applying periodic boundary conditions. Thus, MC model can extend to the multi-phase application successfully despite taking into account both grain growth and diffusion process.

2.2 Model parameters and simulation procedure

When exposed to hydrogen environment, the NdFeB-based alloys can be hydrogenated or disproportionated into α-Fe, NdH_x, and Fe_2B phases. These matrix phases would desorb hydrogen and recombine to the original $Nd_2Fe_{14}B$ phase by vacuum annealing at above 680 °C. The reaction of DR process can be represented as follows.

Desorption:

$$2\,NdH_{2\pm x} \longrightarrow 2\,Nd + (2\pm x)\,H_2 \quad (1)$$

Recombination:

$$2\,Nd + 12\,Fe + Fe_2B \longrightarrow Nd_2Fe_{14}B \quad (2)$$

Due to the small diameter of hydrogen atom that diffuse easily, the desorption rate is much higher than the recombination process. Namely, desorption is not the control step. Thus, research on the microstructure evolution and grain growth kinetics disproportionated NdFeB alloy are of significant importance for process control and optimization. According to Eqns. (1) and (2), there are three phases: Nd, Fe and $Nd_2Fe_{14}B$ in the system and the microstructure transformation between the same phase or different phases can be simulated by the following model.

Microstructures are mapped onto a quadratic lattice with 4/8 nearest neighbours (NN) and periodic boundary conditions. Each lattice point represents a Monte Carlo unit (MCU), which has assigned an integer value representing the orientation Q of the lattice point. The system of MCUs is set as 200×200 field in the present 2D simulations. The edge length of quadratic site is 1nm in simulation domain, so the area of each site is 1 nm^2, and the corresponding actual grain diameter is 10 nm. Then 400 grains can be calculated. We assigned the orientation number Q from 1 to 400 based on the initial volume ratio of Nd and Fe being 0.28:0.72, Q from 1 to 112 is assigned to Nd phase lattice sites, Q from 113 to 400 is assigned to Fe phase, and $Nd_2Fe_{14}B$ phase is embedded with Q from 401 to 400+N. The simulation time is expressed as the number of Monte Carlo Steps (MCS).

In all, the general routine of microstructure simulation during phase transformation or grain growth is as follows: building lattice, generating initial microstructure, assigning energy value to all nodes of system, simulating microstructure evolvement, emulating with visual images and statistically calculating of microstructure characteristic values.

3 Results and discussion

3.1 Microstructural evolution

The microstructure evolution results using the MC simulation model are illustrated in Fig. 1. As a whole, for the transition will occur if only the energy change is minus, and that the exact value of the driving force represented by the Gibbs free energy reduction is excluded from the transition probability, so the grain boundaries in the MC model are generally straighter and smoother than those in other modes [10].

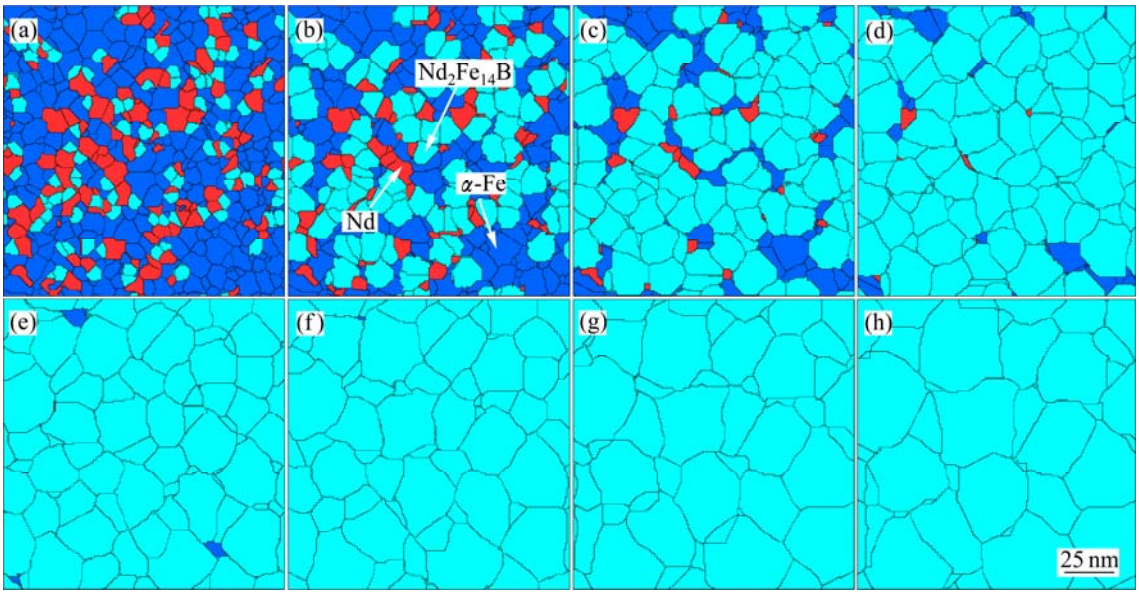

Fig. 1 Simulated microstructures of grains at 800 °C after different MCSs: (a) 10 min, 2%; (b) 15 min, 17%; (c) 25 min, 50%; (d) 35 min, 80%; (e) 45 min, 95%; (f) 57 min, 99%; (g) Extended growth 70 min, 100%; (h) Extended growth 85 min, 100%

Morphologically, various microstructural features appear during grain growth, such as homogeneously distributed grains having tetragonal or polygonal shape, with average side of 6, 120° angles at most grain corners, and equiaxed grains appearing in the recombination transformation conform to observations in 2D MC simulations performed by Exxon group [11]. Dynamically, the shrinkage of some grains and the contemporaneous growth of other grains are driven by grain boundary migration and the jump of atoms in the desorption-recombination process. Generally, large grains grow up while small grains shrink. As to this reaction transformation, Fe and Nd phase constantly transform to $Nd_2Fe_{14}B$ phase, at the same time, new $Nd_2Fe_{14}B$ phases devour some of the second phases (Fe and Nd phase) to grow up, and then the newly generated phases are incorporated within the matrix grains or still situated at the boundaries or junctions of grains, so they merge together to accomplish the transformation finally.

To check shapes of grain's dependence on time, further analysis continues. Considering the growth of grains with different grain sides, the relationship between the growth and the sides evolution is demonstrated in Fig. 2.

During the grain growth, the topological change of neighboring grains is caused by the disappearance of the grains with few sides. Specifically, the grains with $3<n<6$ (n denotes grain side) must transform to three-sided grains by neighbor switching before they vanish and the grains with the shortest side is most likely to disappear [12]. Figs. 2(a) and (b) show this transformation type during grain growth. As can be seen from Fig. 2(a), the grain labeled as 'A' transforms from the original six-sided microstructure to four-sided and then to three-sided grain gradually and vanishes in the system at last. However, researches [13−15] reported that the four-sided and five-sided grains maintain their shapes invariant until they disappear completely. So far, few reports are available concerning two-sided grains and their consumption phenomenon. As can be observed from the present simulation, some grains with two or more sides transform to two-sided grains before vanishing. Fig. 2(b) illustrates the disappearance of four-sided grains. The grain labeled 'B' directly shrinks to a quadric junction without pre-transformation to a three-sided grain, which contributes to the "neighboring grains" growth. Then, the unsteady junction transforms rapidly to a new edge. Consequently, the topological characteristics of both the surrounding grains change along with the junction variation respectively and the other two grains maintain the original topological classes.

3.2 Kinetics of grain growth

In the present simulation, the kinetics of grain growth of polycrystalline domain embedded in an infinite matrix follows the classical power law form:

$$D^m - D_0^m = Bt \tag{3}$$

where D is the mean grain size, t is the time, and D_0, m and B are the fitting parameters. The grain growth exponent is defined as $n=1/m$. If $D^m >> D_0^m$ holds, thus the time dependence on the grain growth can be expressed as:

$$D = Bt^{1/m} = Bt^n \tag{4}$$

The temporal evolution of mean grain size (D) as a function of simulation time (MCS) is plotted in Fig. 3, exhibiting power-law behavior for all cases. As can be seen from Fig. 3, grains of the material processing under higher temperature grow fast, and the grain growth

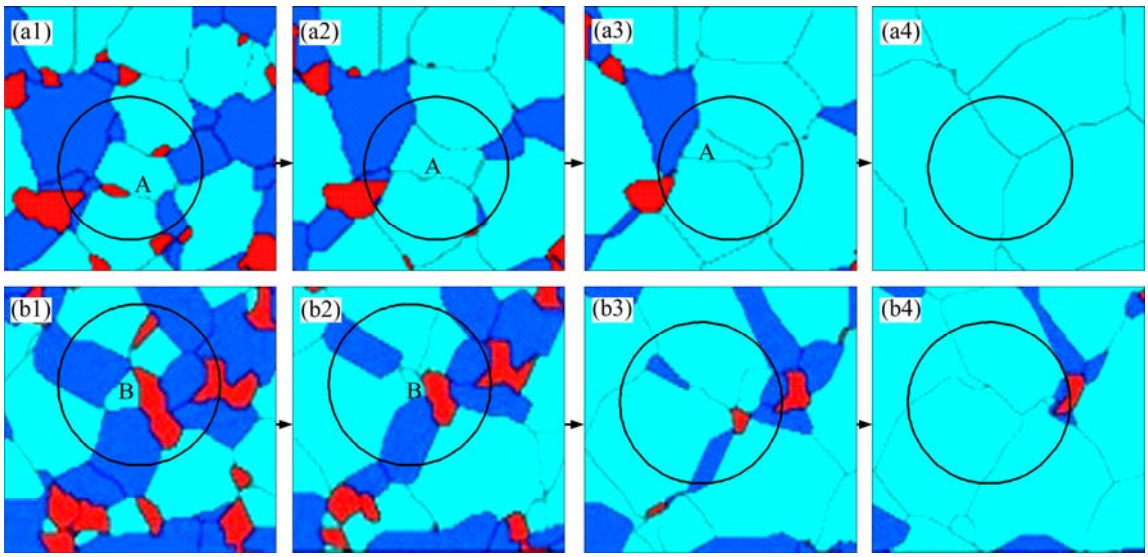

Fig. 2 Grain growth process: (a) Indirect vanishing process of six-sided grain; (b) Direct vanishing of four-sided grain

hasn't been approached or attained a steady state in the simulated time interval. Figure 4 shows the near liner relationship of log-log plot by Eq. (4). The regression analysis results indicate the grain growth exponents (n) ranging between 0.78 and 0.91 (Fig. 4), that is, the mean value of n≈0.8, which is obviously larger than 0.5 for normal grain growth regardless of purities [16−17]. The larger mean value indicates that kinetics of the grain growth in DR process is modified, which is different from the way described in the conventional theory, without attaining the steady state within simulating time, but phase transformation can be completed within short time. Factors like thermally activated atomic jumps across a boundary may influence the grain growth kinetics, and the impetus for atomic jumps is thermal activation determined by processing temperature.

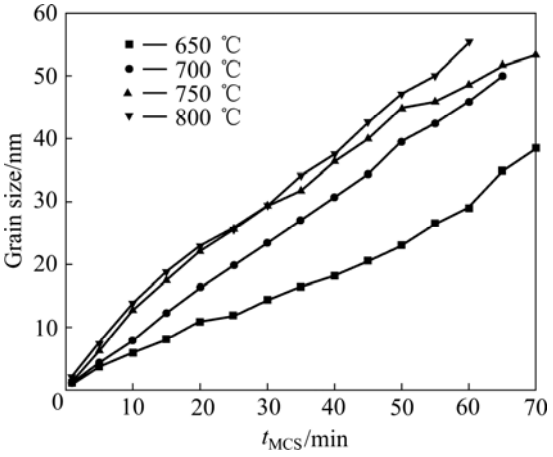

Fig. 3 Changes of grain size with simulated time

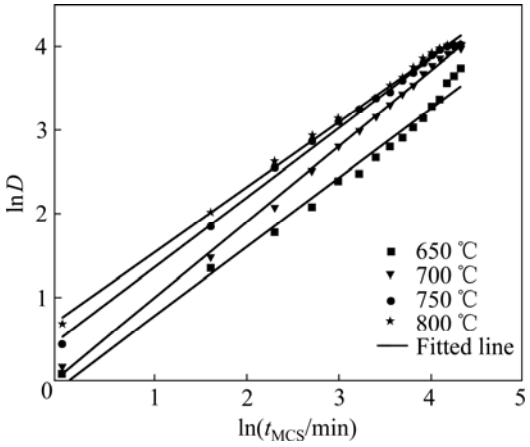

Fig. 4 Plot of ln D as function of ln t_{MCS} for experimental and simulated data, and fit based on Eq. (4)

Specifically, as illustrated in Fig. 5, the value of n shows an upward trend from 650 to 750 °C, and then drops off, but n is slightly higher at 800 °C than at 700 °C. Namely, the growth exponent, in general, increases with the rising of temperature. However, n peaks at 0.91 at 750 °C, suggesting that grain growth as well as solid- state phase transformation is the fastest under this optimal temperature, in accordance with the previous work [18]. In fact, nuclei grow more quickly at a higher processing temperature due to the widening energy-level disparity between atoms and activation-energy barrier during the solid-state phase transformation.

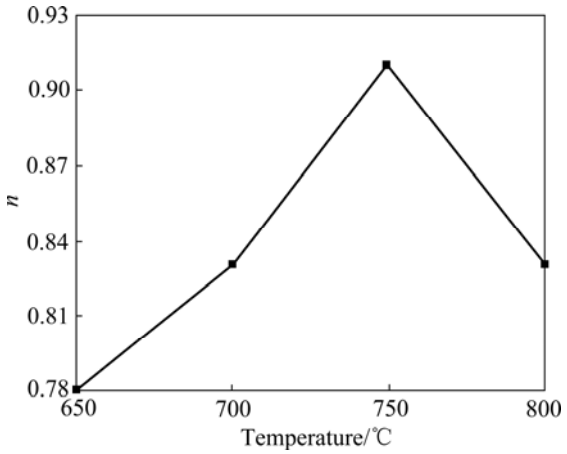

Fig. 5 Grain growth exponent for various simulation temperatures

Grain growth process is driven by the reduction of the interfacial energy related to shrinkage of grain boundaries, while the reaction is motivated by the drop of reaction free energy to minimal level connected with the mobility of the atoms, thus deviation between reaction rate and growth rate determines the average grain size. More exactly, if the reaction rate surpasses grain growth rate, relatively fine grain size can be obtained, and otherwise, relatively coarse grains appear. Based on the above mentioned work, it is essential to locate the grain size at a critical point of completion of the phase transformation at a certain temperature. The results provide the guidance for the optimal selection of technological parameters.

4 Conclusions

The microstructure evolution and grain growth kinetics during desorption and recombination process of $Nd_2Fe_{14}B$ phase at various processing temperatures is investigated. The physical model presented in this work, based on MC method and the mechanism of grain growth, provides an effective way for simulating the grain growth during phase transformation. The following conclusions are drawn from this work:

1) Driven by grain boundary migration and the jump of atoms in the desorption−recombination process, grain grows by devouring smaller neighbouring grains until reaching a steady state, generally with grain-side of four, five or six and equiaxed shape.

2) The parabolic curves of grain growth kinetics are

obtained for the entire 2D domain, and the average grain growth exponent n equals about 0.8, higher than the normal value of 0.5, which indicates the stronger reaction kinetics of the DR process. Besides, n peaks at 0.91 at optimal temperature of 750 °C.

3) The effect of reaction rate and grain growth rate on the grain size is contradictory. If the reaction rate outstrips grain growth rate, relatively fine grains can be obtained.

The advanced model has better physical basis to provide a convenient tool for studying phase-change evolution during sintering. However, we are faced with an important challenge in the concise verification of the model for the lack of quantitative experimental data, thus paying attention to future relevant research.

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NdFeB 合金粉末脱氢−再结合过程组织演变和晶粒生长的 Monte Carlo 模拟

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摘 要：基于歧化态 NdFeB 合金粉末脱氢−再结合相变过程中晶粒长大的机理，建立 MC 物理模型，实现了在不同脱氢−再结合处理温度下，再结合 $Nd_2Fe_{14}B$ 相的晶粒生长过程结构演化的计算机模拟，以及晶粒生长动力学的研究。分析表明：该模型能较好地模拟脱氢−再结合过程的晶粒生长过程，并且在模拟时间区间内，平均晶粒生长指数 n≈0.8，高于标准值 0.5。

关键词：蒙特卡洛模拟；晶粒生长；NdFeB 合金；脱氢−再结合处理

(Edited by CHEN Ai-hua)