Coarsening behaviour of Pb particles in a Al-5wt%Pb nanocomposite alloy produced by mechanical alloying

Wu Zhi-fang, Liu Chao, Wu Runong

Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, China

Abstract: The coarsening behavior of Pb particles in a Al-5wt%Pb nanocomposite alloy produced by mechanical alloying has been studied by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Result shows that the cube of the average particle radius of Pb phase grows proportional with the annealing time even though the size of the constituent phase was in nanometer range. The activation energy for coarsening of Pb particles closes to the activation energy of grain boundary self-diffusion of solvent matrix (Al). In the nanocomposite alloys, the solute atoms diffuse along the grain boundaries of the solvent matrix.

Keywords: Nanocomposite alloy, Mechanical alloying, Secondary phase, Coarsening

INTRODUCTION

Nanocomposite alloys, which consist of at least two phases in nanometer size, have potential application in the fields of magnetic materials [1], hydrogen storage materials [2], hard metals [3], bearing alloys [4], and so on. The unique nanocomposite structure makes those materials exhibit properties much superior to those with conventional phase size. The size of the secondary phase particles has a direct influence on the properties of nanocomposite alloys. In this case the structure stability of nanocomposite alloys is very important because their significant high fraction of grain boundary provides a strong driving force for coarsening and results in change of properties. Thus, to clarify the coarsening behaviour of secondary phase in nanocomposite alloys is of great importance.

For the conventional grain sized composite alloys with constant volume faction ratio, as it is well known, the coarsening, or called as Ostwald ripening, of the small faction component was formulated by Lifshitz, Slyozov and Wagner, and is widely referred to as the LSW theory [5, 6]. The LSW theory predicts that the cube of the average particle radius grows proportionally with the annealing time if the mass transport is governed by a diffusion mechanism. However, the LSW theory is valid only in the physically unrealistic limit of zero volume fraction of secondary phase. Effort has been made to modify LSW theory and extend to high volume fraction of dispersed phases using both analytic and numerical method. The results show that the cubic law can be used for embedded phase of high volume fraction, with the coarsening rate being dependent on volume fraction [7, 8].

For the nanocomposite alloys, the results show that the coarsening of secondary phase still follows the LSW theory and the activation energy for coarsening of secondary phase is different from that of conventional grain sized alloys [9, 10]. Actually, the LSW coarsening theory assumes zero volume fractions of secondary phases, which is obviously not suitable for the case of nanocomposite alloys due to their high volume fractions of secondary phases (26.6-50.88%). In addition, the interparticle diffusion interactions are more remarkable when the size of the constituent phase is in nanometer range. Therefore, it's necessary to take into account the effect of volume fraction to investigate the coarsening kinetics of secondary phase with nonzero volume fraction in the nanocomposite alloys.

In this study, the coarsening behavior of Pb phase with very small volume fraction has been studied. This is because of Al-Pb is a typical immiscible system and the Al-Pb nanocomposite alloys fabricated by MA exhibit super wear resistance which is very much dependent on the grain size (and/or phase size) [11]. Therefore, a study of the coarsening behavior of Pb phase with very small volume fraction in Al-Pb nanocomposite alloy is significant to both the fundamental research of nanocomposite alloys and their application in engineering.

EXPERIMENTAL

Al and Pb powders of 99.9% purity with the average particle size of 70~80 micron were used as raw materials. An alloy with composition of Al-5wt%Pb was selected, in which the volume fraction of Al and Pb phase is 99.32% and 0.68%, respectively, and Al and Pb are hence regarded as matrix phase and secondary phase with very small volume fraction, respectively. The powder mixtures were sealed in stainless steel vials together with hardened steel balls. The weight ratio of the powder to ball was 1 to 10. The handling of powders was performed inside a glove box filled with pure argon. The milling process was performed in a QM-3SP2 planetary ball mill. The milled powders were uni-axially cold pressed under a pressure of 440 MPa to get bulk samples. The as-compacted bulk samples were then heated at different temperatures for different times under the protection of pure argon atmosphere. Then the samples were characterized by X-ray diffraction (Philips X'Pert MPD with Cu-Kα radiation), scanning electron microscopy (SEM, FEI-Navo Nano SEM 400) and transmission electron microscopy (TEM, JEM-2100).

RESULTS AND DISCUSSION

The X-ray diffractograms of Al-5wt%Pb powders after milling for different times are presented in Fig. 1. It can be observed that there are only diffraction peaks of Al and Pb phase and they have no obvious shift. That means that only pure Al and Pb phase existed in the milled powder and no supersaturated solid solution formed. It is obvious that the diffraction peaks of both Al and Pb phases broaden gradually with increased of milling time, which reveals the remarkable grain refinement of Al and Pb phases after ball milling. The grain size of Al and Pb phase were estimated from broadening of different peak using the Vogit method [12], and the results are shown in Fig. 2. It shows that the grain sizes of Al and Pb reduce sharply in the initial stage (1-10 h) and then tend to level off with increase of milling time, and they reach 77 and 7 nm, respectively after 30 h of milling.
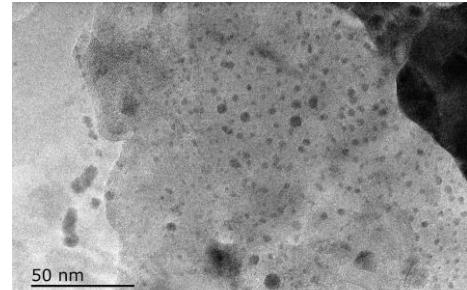
Figure 3 shows a bright field image of Al-5wt%Pb sample milled for 30 h. It can be seen that Pb particles with nanometer sizes are single crystal particles. Therefore, it is assumed that the Pb particles embedded in Al matrix are generally single crystal and the grain size of Pb phase estimated from XRD analysis represents the size of Pb particles. The average grain size is about 10 nm, which is in good agreement with the XRD result.
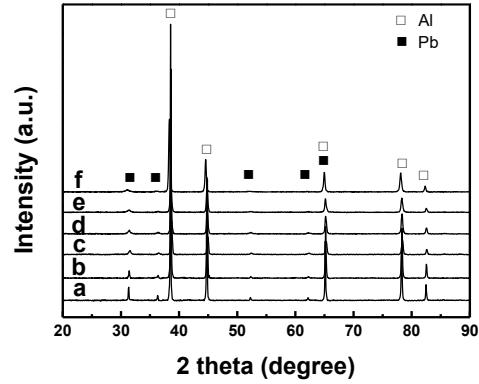
Fig. 1. X-ray diffractograms of Al-5wt%Pb alloy powder after milling for different times: (a) 1 h; (b) 2 h; (c) 5 h; (d) 10 h; (e) 20 h; and (f) 30 h.
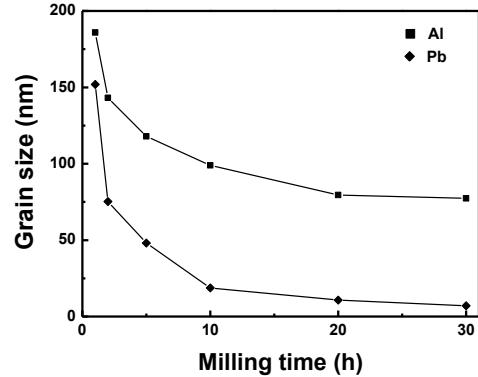
Fig. 2. Dependence of grain sizes of Al and Pb in Al-5wt%Pb powders on milling time.


Fig. 3. TEM bright field image of Al-5wt%Pb alloy powder milled for 30 h.

Fig. 4 gives the XRD patterns of Al-5wt%Pb samples after 30 h milling and then heating for 1 h at different temperatures (573, 623, 673 and 723 K). It is obvious that diffraction peaks of Al and Pb phase become sharper with increase of heating temperature which indicates that Al and Pb phases grew gradually during heating. As shown in Fig. 5, the grain size of Pb phase increases with the increasing of heating temperature.

Fig. 6 shows SEM images of Al-5wt%Pb alloy compacted from the milled powder and heated at different temperatures for 1 h. For the as-compacted Al-5wt%Pb alloy, as shown in Fig. 6(a), the bright Pb particles are very fine and uniformly distributed in the dark Al matrix. It is obvious that the size of Pb particles increase with increase of

heating temperature and the particles of Pb phase are also homogeneously distributed in the Al matrix of as-heated Al-Pb sample.
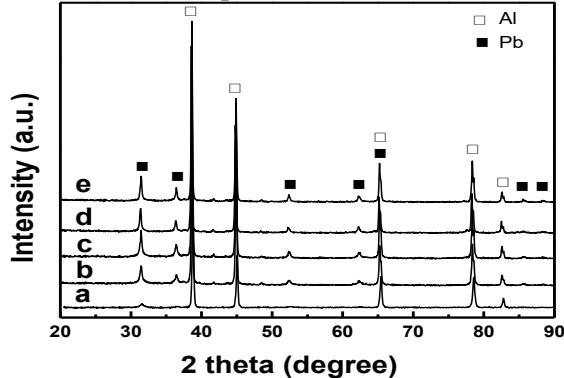

Fig. 4. X-ray diffractograms of Al-5wt%Pb alloy samples after 30 h milling and then heating at different temperatures for 1 h: (a) as-milled; (b) 573 K; (c) 623 K; (d) 673 K; and (e) 723 K.
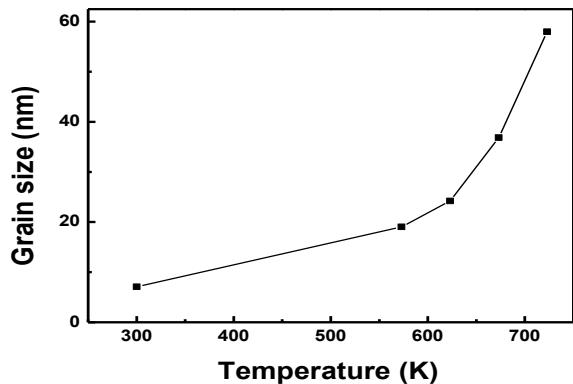
Fig. 5. Temperature dependence of the size of Pb phase in MA Al-5wt%Pb (dwelling time: 1 hour)

In order to clarify the coarsening kinetics of Pb phase, the dependence of Pb particle size, which was deduced from X-ray diffraction analysis, on heating dwelling time was determined and illustrated in Fig. 7. It is clear that there exists an excellent linear correlation between the cubic of particle size (r) and dwelling time (t) in the particle size range in this work. Here, r_0 is the average radius of the phase in the as-milled condition. This suggests that the coarsening of Pb phase follows the standard cube kinetics of diffusion-controlled particle growth. The excellent linear relationship between the cubic of r and t means the coarsening of Pb phase in Al-5wt%Pb nanocomposite alloys is controlled by diffusion even though the size of the constituent phase is in the nanometer range. The slope of each line in Fig. 7 is the particle coarsening rate constant $K(\phi)$.
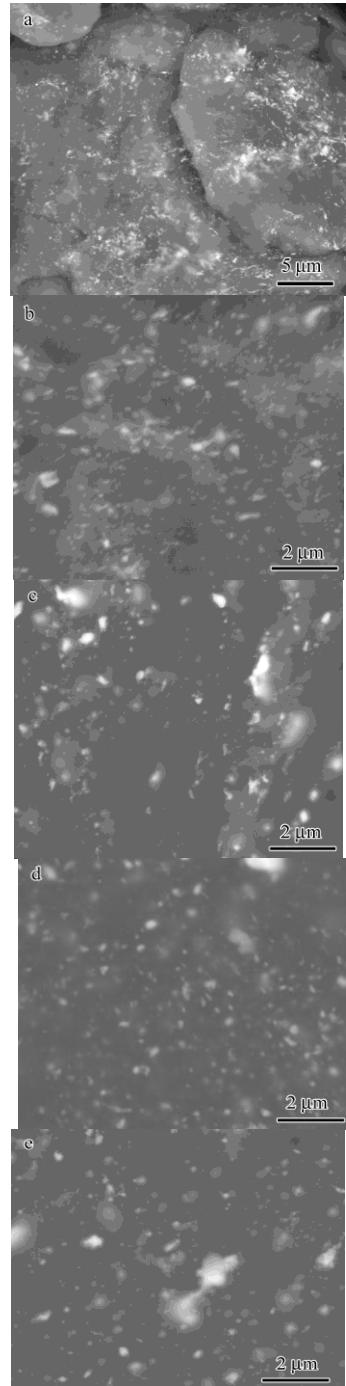
Fig. 6. SEM images of MA Al-5wt%Pb alloys: (a) as-compacted, heated at (b) 623 K, (c) 673 K, (d) 723 K and (e) 773 K for 1 h. The bright phase is Pb and the dark matrix is Al.

According to the modern Ostwald ripening theories, the coarsening rate constant $K(\phi)$ determined by $K(\phi) = \dfrac{A(\phi) C_e \Omega^2 \gamma D}{RT}$. When the diffusion coefficient D is given by $D = D_0 \exp(-\dfrac{Q}{RT})$, the constant $K(\phi)$ can be formulated as follows:

$$K(\phi) = \frac{A(\phi)\, C_e \Omega^2 \gamma D_0}{RT} e^{-\frac{Q}{RT}}, \qquad (1)$$

where $A(\phi)$ is a dimensionless constant depending on the volume fraction (ϕ) of secondary phase and $A(0) = 8/9$; thus, the theories reduce to the LSW theory in the limit of zero volume fraction. C_e is the equilibrium solute content of the matrix, Ω is the molar volume of the particle, γ is the particles-matrix interfacial energy per unit area, D_0 is a frequency factor, R is the universal gas constant (8.31 J/mol/K) and T is the absolute temperature, Q is the activation energy for Pb particles coarsening. The relationship (1) is reformulated as follows:

$$\ln\left[\frac{K(\phi)T}{C_e}\right] = constant - \frac{Q}{RT} \qquad (2)$$

In order to estimate the Q in the Al-5wt%Pb nanocomposite alloy, we calculated the solubility of Pb in Al solid-solution at different temperatures (573, 623, 673 and 723 K) according to the Ref. [13]. Therefore, the coarsening activation energy can be determined from the slope of the plot of $\ln[\frac{K(\phi)T}{C_e}] \sim \frac{1}{T}$. The coarsening rate constants $K(\phi)$ at different heating temperatures are shown as the plot of $\ln[\frac{K(\phi)T}{C_e}]$ versus $\frac{1}{T}$ in Fig. 8. The activation energy Q for Pb particles coarsening is determined to be 79.64 kJ/mol. For comparison, the diffusion activation energy of Pb in Al of different diffusion mechanisms is given in Table 1. It shows that the value obtained in this work is much smaller than that of lattice diffusion mechanism of Pb in Al and lattice self-diffusion of Al but very close to that of boundary self-diffusion of Al. This indicates that the coarsening mechanism in the nanocomposite alloys is different from that in conventional grain sized composite alloys. The observation of the cubic law for the coarsening of secondary phase in nanocomposite alloys reveals that the coarsening process is controlled by the three-dimensional long distance diffusion of solute atoms. However, the agreement of the activation energy to that of grain boundary self-diffusion of matrix indicates that the diffusion mechanism in the nanocomposite alloys is basically grain boundary diffusion. This is because the grain sizes of matrix phase and secondary phase are in nanometer range. Thus, the solute atoms should diffuse more easily along nanograin

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boundary than in conventional grain sized composite alloys.
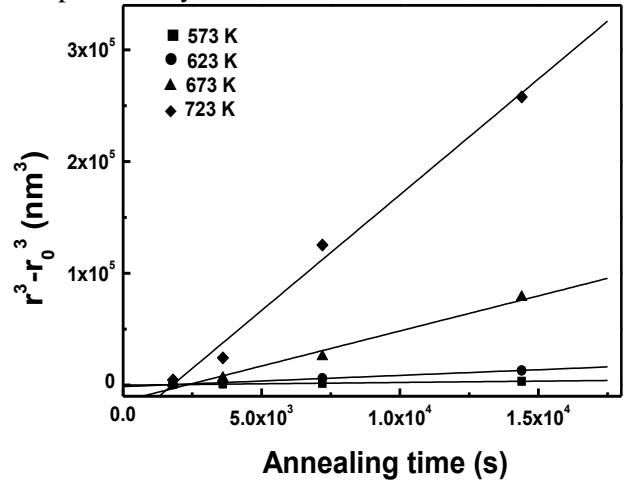
Fig. 7. Dependence of the cubic of Pb particle radius on heating time for Al-5wt%Pb alloy heated at different temperatures (573, 623, 673 and 723 K) after 30 h of milling.
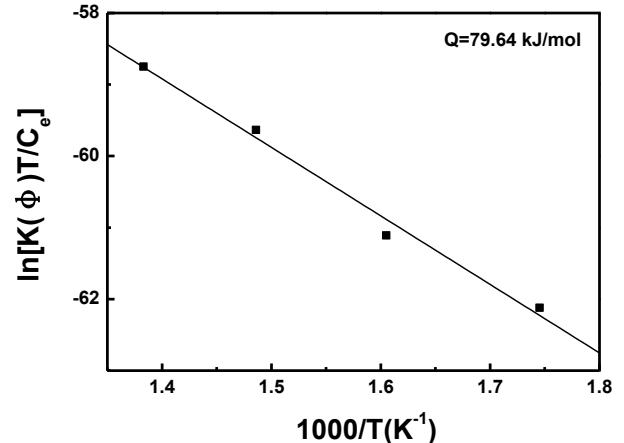
Fig. 8. Determination of the activation energy (Q) for coarsening of Pb phase in a Al-5wt%Pb nanocomposite alloy.

CONCLUSIONS

In the present work, the coarsening behaviour of Pb particles in a Al-5wt%Pb nanocomposite alloy prepared by mechanical alloying has been investigated. The main conclusions obtained from the present work are as follows:

(1) The cube of the average particle radius of Pb phase grows proportional with the annealing time even though the size of the constituent phase was in nanometer range.

(2) The activation energy for coarsening of Pb particles closes to the activation energy of grain boundary self-diffusion of solvent matrix (Al). In the nanocomposite alloys, the solute atoms diffuse along the grain boundaries of the solvent matrix.

Table 1. Activation energy in kJ/mol of experiment and theory in Al-Pb system

Activation energy of our result	Activation energy of lattice diffusion [14]	Activation energy of lattice (self-) diffusion [14]	Activation energy of grain boundary (self-) diffusion [14]
79.64	Pb in Al: 145.6(777-876 K)	Pb: 107.4 (473-596 K) Al: 142.4 (723-923 K) 144.4 (573-923 K) 123.5 (298-581 K) 126.4 (358-482 K)	Pb: 66 (487-533 K) Al: 90 (623-753 K)

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