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One new method for preparing nanocrystalline metal

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ABSTRACT

In this work, we explore the new method for synthesizing the nanocrystalline metals. Without resorting to the initial nano-metallic powders, for the metals with anomalous melting line, we first put forward a totally new one-step method to prepare the nanocrystalline metal by means of dynamic decompression technique. The experimental results indicate that the nanocrystalline metal may be prepared successfully and the grains mainly range from 30 to 50 nm. This proposed one-step method may pave a new way for the synthesis of nanocrystalline metal and alloys with anomalous melting line.

1. Introduction

Due to the outstanding properties and the wide potential applications in the fields of mechanics, physics, materials, defense, etc, the nanocrystalline metals (nc-metals) have attracted much attention in recent years. And their remarkable performance and the special microstructure provide a new way to tune the material properties by controlling the microstructure. For instance, the nc-metals can exhibit both higher strength and better ductility than conventional metal [1,2]. Also, the nc-metals present the conspicuous radiation-tolerance behaviors [3], because they contain much more interfaces which can attract, absorb and annihilate point and line defects.

Up to date, for the preparation of nc-metals, two main approaches have been proposed and utilized, i.e., two-step method and one-step method. For the two-step method, the nano-metallic powers are synthesized first, then through the solidification techniques, such as shock wave consolidation technique [1,4], in situ thermal compression, thermal equal-compression techniques [5] and so on, the metallic powers are solidified into nc-metals. For the one-step method, the bulk nc-metals are synthesized directly by means of external actions, among which the most important one is the severe plastic deformation [6,7]. In all, these methods have been utilized to prepare the nc-metals successfully. However, some restrictions still exist. For example, regarding the two-step method, the grain sizes of prepared nc-metals are always larger than the initial nano-powder sizes and the porosity usually exists; for the one-step method, the large residual stress may be retained and the grain size distribution may be relatively broad. These restrictions may sacrifice the outstanding macroscopic properties of nc-metals, and need to be overcomed.

In this paper, to overcome the conventional restrictions, we proposed a totally new one-step method for the fabrication of nc-metals by using the dynamic decompression technique. Further, we carried out the experiments for the metal bismuth and performed the diagnostics. The experimental results show that the nano-metallic bismuth may be prepared successfully and the grain sizes mainly range from 30 to 50 nm.

2. Experimental results and discussion

In shocking processes, the compression strain rate and the temperature increment is very rapid for the materials. After the shocking processes, the rarefaction waves are reflected from the free surfaces and penetrate into the materials, leading to the dynamic decompression processes afterwards. Consequently, both the stress and temperature decreases quickly. According to isentropic decompression assumption, when the rarefaction waves arrive, the decompression rate for the stress and temperature is very high [8] and may reach $10^5 – 10^9$ GPa/s and $10^7 – 10^9$ K/s. They are much higher than the cooling rate 10^6 K/s, almost the highest value achieved in conventional laboratories. These unique characters of the dynamic decompression processes might enable the fabrication of unique samples, e.g., nc-metals.

First, let us examine the pressure effects on the melting temperature (MT) of metals. For most of the metals, the MT usually increases with the increase of the pressure, and this pressure dependence of MT could be called the normal melting line (NML). But for other metals, inversely, the MT decreases with the increase

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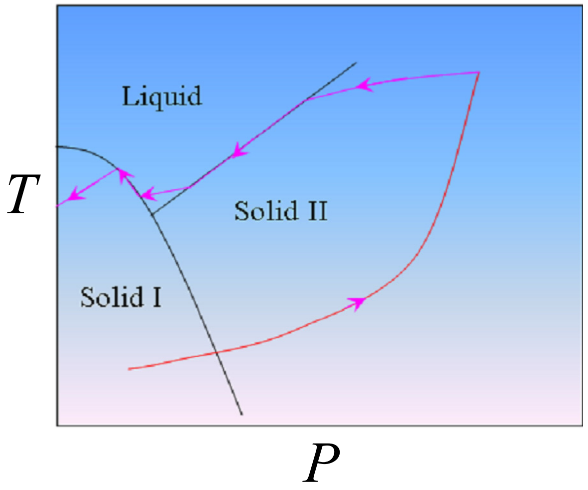

Fig. 1. Schematic simplified $T-P$ phase diagram of bismuth and the designed thermodynamic path for the fabrication of nano-crystalline metal: the black lines denote the phase boundaries; the red, pink lines denote the experienced thermodynamic path for bismuth in the shock compression and dynamical decompression processes. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

of pressure, and this type of melting line is usually named as the anomalous melting line (AML). Based on the famous Clausius–clapeyron relation, the difference in the two types of melting lines arises from the distinction in volume variations in the solid–liquid phase transition. During this transition, if the metal volume expands and the density decreases, the metal exhibits the NML. On the contrary, the metal will present the AML. Stimulated by the interesting work upon the preparation of amorphous sulfur [9], nano-crystalline bulk selenium [10], metal glass [11,12] in terms of the dynamic compression method [13], one may conceive that for the metal with NML, if it is heated to the liquid state and then compressed rapidly by shock waves, the metal may experience the liquid–solid transition quickly and enter the solid state of nc-metals. However, the real obstacle lies in the fact that the high pressure state is always going to be relieved by the following rarefaction waves. To tackle the problem, the metal with AML are selected out. And the designed thermodynamic path and the basic principle is illustrated in Fig. 1. According to Fig. 1, the metal is first shocked to the state at the pressure P and temperature T. The temperature T should not exceed the MT under the pressure P. On the other hand, it must be relatively high and ensure that when decompressed, the metal enters the liquid state. Subsequently, the metal is dynamically decompressed and starts to crosses the AML. Because of the ultrashort time in the liquid–solid transition, there may be not enough time for the grain growth. Therefore, the grains of the recovered metal may be nanometer-sized. However, this is not sufficient, because the remnant temperature is usually still high enough to produce the annealing effect, causing the inevitable grain growth, which means that the timely water-quenching method is needed.

Based on all these considerations, the chemical detonation setup [15] and the water-quenching method are adopted. The dinitrotoluene and the aluminium box are used as the explosives and the sample container, respectively. The bismuth foil of high purity is used as the initial sample. The bismuth foil sample is a rounded sheet, and the size is D13 ×1 mm. The 3 mm thick copper flyer plate is used. For the experimental setup, the determination of shock parameters is important. But they are difficult to determine because of phase transitions in the $T-P$ phase diagram [14]. Thus accomplishing the required thermodynamic path completely is hard. To treat this problem, the shock velocity of flyer plate need to be reduced a little, insuring a part of the sample will experience the required thermodynamic path. Here the parameters at room temperature and pressure, the latent heat for fusion 10.48 KJ/mole, specific heat capacity 25.52 $\mathrm{J/(mol{\cdot}}K)$, are employed. So, the shocked temperature should be higher than the melting temperature 544.4 K and lower than 955 K $(544.4 + 10.48 \times 10^3/25.52\ \mathrm{K})$. In the experiments, the impedance matching method [15] and the shock parameters for the dense bismuth at room conditions are used.

To do the comparison and examine whether the nc-metal is formed or not, we cut the original and recovered samples, and visualize the cross-section morphology in terms of the SEM shown in Fig. 2(a) and (b). For the original sample, of noted is the absence of nano-grains. But for the recovered sample, just as expected, a large number of nanometer-sized grains indeed exist as shown in Fig. 2(b). And the grains mainly range from 30 to 50 nm as shown in Fig. 2(c), suggesting that the successful preparation of nc-metal by means of this one-step method.

Last but not the least, the unique characters of this method should be examined and commented. First, the method could only be applied for the metal with AML such as bismuth, antimony and so on. Second, by controlling the thickness of flyer plate, the shock resistance of sample container and the cooling rate, the grain sizes of the recovered sample is expected to be tuned. Third, in contrast to the severe plastic deformation method [6], the grain sizes are much smaller and the size distribution is relatively narrow. Moreover, owing to the liquid–solid transition in the decompression processes, to be anticipated, the remnant stress might be slight. However, for this method, it is still difficult to synthesize the total volume of nc-metal due to the absence of shock parameters and some uncontrollability in the experiments.

3. Conclusions

In summary, for the synthesis of nanocrystalline metals, we put forward a new one-step method, the dynamic decompression

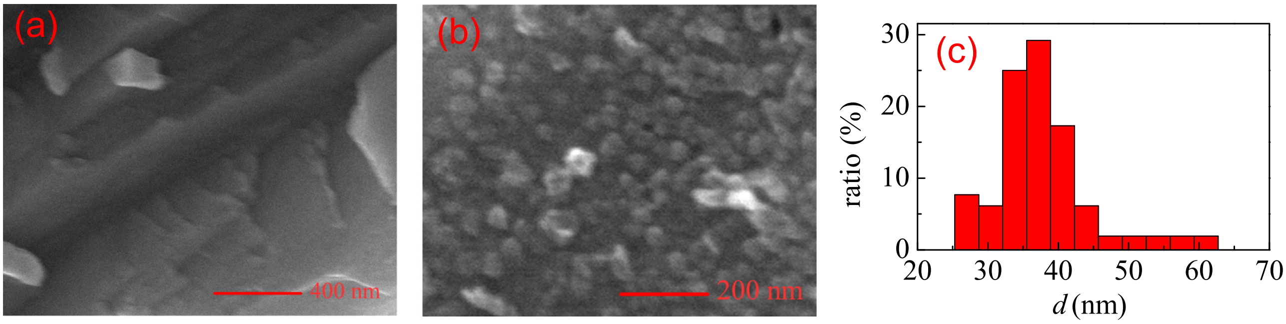

Fig. 2. Scanning electron morphology (SEM) of the cross-sections for the original and recovered shocked bismuth samples. (a) original sample; (b) recovered sample; (c) grain size distribution for the recovered sample.

technique, and carried out the experiment. The experimental results demonstrate that the nanocrystalline metal may be prepared successfully and the grain sizes mainly range from 30 to 50 nm. It may offer one new route for the preparation of nanocrystalline metals or nanocrystalline alloys in the future.

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