

Phase formation in mechanically alloyed Nb-Sn powders

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기계적합금화 방법에 의한 Nb-Sn 상형성

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Abstract The microstructure evolution during mechanical alloying (MA) of Nb and Sn powder; of average composition Nb_3Sn , has been investigated by X-ray diffraction (XRD). The structural development with milling time depends on the ball size for a given powder/ball ratio. Using a larger ball of 9.5 mm diameter, the elemental powders initially alloy mechanically to form an A15 structure phase, and then amorphized with continued milling. However, in case of milling with a smaller ball of 3.968 mm diameter, an amorphous phase is first formed. These results can be understood by considering the dependence of the milling energy on the ball size. The homogeneous stoichiometric Nb_3Sn phase could be easily obtained by heat treatment of supersaturated solid solution produced by MA. Heat treatment of an amorphous phase formed by MA resulted in the mixture of the Nb_3Sn and Nb_6Sn_5 phases.

요 약 조성이 Nb_3Sn 인 Nb와 Sn 혼합분말에 대해 기계적 합금화 과정중의 미세구조 변화를 X선회절실험으로 관찰하였다. 분쇄시간에 따른 결정구조 변화는 볼/분말비와 볼의 크기에 따라 변화하였다. 지름이 9.5 mm인 볼을 사용한 경우, 각 분말들이 초기에는 기계적으로 합금되어 A15구조를 갖는 상을 형성하였고, 그 이후에는 비정질화가 이루어졌다. 지름이 작은 3.968 mm인 볼을 사용한 경우 초기에 비정질화하였다. 이들 결과들은 볼크기에 따라 분쇄에너지 효과가 다르기 때문이라고 생각될 수 있다. 순수한 Nb_3Sn 화학양론조성의 상이 기계적 합금화 방법으로 제조된 과포화 고용체를 열처리하여 쉽게 얻어졌다. 기계적 합금화로 비정질화된 분말을 열처리한 경우, Nb_3Sn 과 Nb_6Sn_5 상의 혼합물이 얻어졌다.

1. Introduction

High energy ball-milling is widely used to mechanically alloy metallic powders. Such mechanical alloying can result in the formation of equilibrium [1] or metastable [2-5] phases, the latter being amorphous or crystalline, which depends on the alloy system. The study of synthesis of metastable (or nonequilibrium) phases using nonequilibrium processing routes such as mechanical alloying is a subject of great interest not only from the scientific point of view, but also from the technical point of view.

In this work, we choose to ball-mill mixtures of Nb and Sn crystalline powders because the

structural development with milling time during mechanical alloying of these elements is not clear. Kim and Koch [6] reported that mechanical alloying of the elemental Nb and Sn powders of average composition 75 at.%Nb-25 at.%Sn, first produced the crystalline A15 (Nb_3Sn) compound, which, after continued milling, transforms to the amorphous structure. Previously White [7] had reported the possible formation of amorphous Nb_3Sn by a similar technique.

From the Nb-Sn phase diagram [8] in which other intermetallics separate the A15 phase from the lower melting temperature constituent, an equilibrium reaction of the elements at low temperature should at some time produce each of the

intermetallics that exist in this system. The overall composition of the mixture will, of course, determine the phase/phases that eventually are produced. For kinetics reasons, the establishment of this equilibrium phase can take such a long time. i.e. other metastable products can be the result of such a reaction. It has been reported that the mixture of Nb and Sn powders of the overall composition Nb_3Sn formed a metastable mixture of Nb and $NbSn_2$ by a heat treatment at $750^\circ C$ [7]. Hence, it is required that special techniques be used to produce the desired Nb_3Sn phase which has engineering importance as superconducting material. To get more information on these problems we have investigated the phase formation in mechanically alloyed Nb-25%Sn powder.

2. Experimental

Nominally pure Nb (99.9%) and Sn (99.9%) elemental powders were mixed to give the desired average composition of Nb_3Sn (at.%) and mechanically treated in a SPEX mixer/mill model 8000 with a ball-to-powder weight ratio of 6:1. The vial and balls were made of stainless steel. Balls used were 9.5 mm and 3.97 mm diameter. The Ball-milling was interrupted for 10 min every 10 min milled. A fan was used during the milling to cool the vial. At selected milling times some amounts of the ball-milled powder were removed for analysis. The samples were characterized by X-ray diffraction with Cu $K\alpha$ radiation. Differential scanning calorimetry (DSC) was used to verify the presence of a crystallization peak.

3. Result and Discussion

The change in the X-ray diffraction pattern of the mixed powders mechanically alloyed using balls of 9.5 mm diameter in argon for times from 0 to 50 h is shown in Fig. 1. After mechanical alloying (MA) for 2 h all the diffraction peaks for Nb and Sn are still apparent, although broadened. MA for 10 h totally removed the β -Sn peaks and further broadened the Nb peaks owing to the refinement of crystallite size and to the introduction of mechanical strain. After 20 h of MA no Nb peaks are visible and only peaks of the A15 are seen.

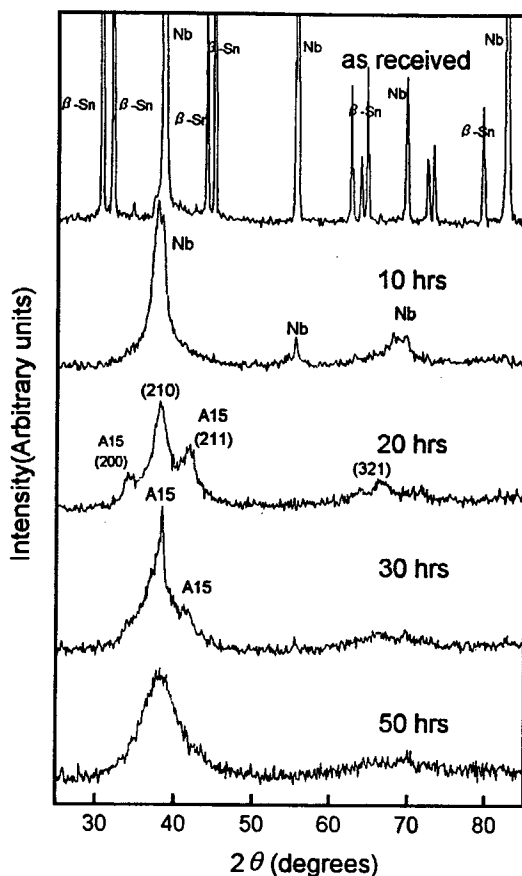


Fig. 1. X-ray-Diffraction patterns of a mixture of Nb and Sn powders during the ball milling process using stainless steel balls of 9.5 mm diameter in argon.

Continued milling produces further structural changes and after 30 h of MA small remnants of the A15 peaks are visible above the broad diffraction maximum typical of an amorphous structure. After 50 h of milling only a diffuse diffraction maximum could be observed, indicating the transformation of the A15 phase into an amorphous phase. These phase formation with milling time is consistent with that of Kim and Koch [6].

It is well known that the kinetics of the structural development during milling depends on the milling condition such as the milling media, the ball-to-powder ratio and vial atmosphere. It has been reported recently that for the SPEX mill system used in the present work the average energy involved for collision of the balls increases with ball diameter at a given ball-to-powder ratio [8]. Figure 2 shows the X-ray patterns of the powder mixture as a function of the milling time, in

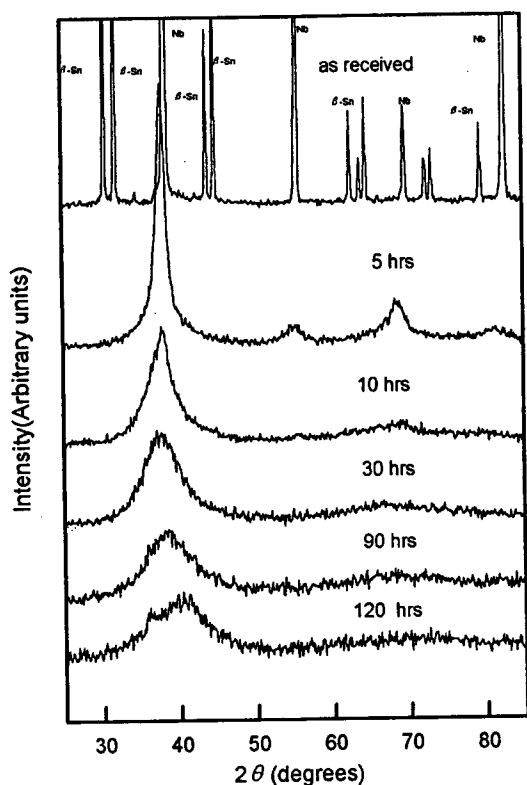


Fig. 2. X-ray diffraction patterns of a mixture of Nb and Sn powders during the ball milling process using stainless steel balls of 3.968 mm diameter in argon.

which mechanical alloying was conducted using balls of 3.97 mm diameter in argon. At the beginning of the MA process, the X-ray diffraction peaks from Sn crystalline powders drastically diminish compared with those of Nb crystalline powders, which is similar to the result shown in Fig. 1. However, contrary to the case of MA using the balls of 9.5 mm diameter (Fig. 1), an amorphous phase is directly synthesized from Nb and Sn crystalline powders without intermediate formation of any compounds (e.g. A15 phases). Further milling up to 120 h appeared to produce partially crystallized powders as inferred from small peak shoulder visible in Fig. 2. This seems to indicate that the amorphous alloy can be transformed into a crystalline phase.

The influence of the milling condition (that is, ball diameter) on the reaction product of ball milling could be explained as follows. During the early stages, ball milling produces powder particles with a characteristically layered microstructure due to cold welding and repeated mechanical deformation

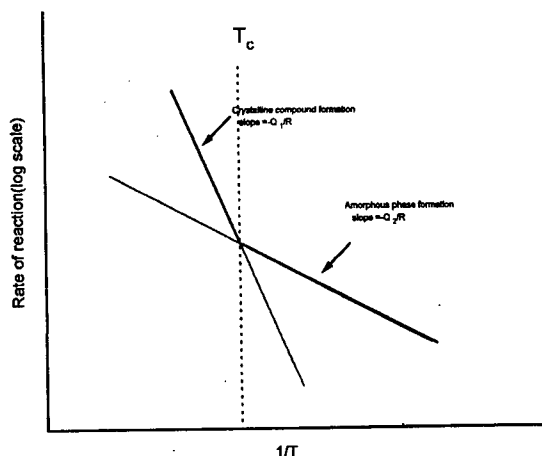


Fig. 3. Possible kinetic regimes in a nucleation reaction occurring during mechanical alloying.

[3, 4]. It has been shown that ball milling leads to an ultrafine layered microstructure and amorphization by MA is closely related to the solid-state interdiffusion in thin film multilayers [3, 9, 11]. A true alloying by a solid-state interdiffusion reaction may lead to an amorphous alloy or the competing crystalline intermetallic phase. From the fact that the temperature to form a crystalline compound is higher than that to form the corresponding amorphous alloy, it can be assumed that the activation energy barrier of nucleating the stable phase is larger than that of the metastable amorphous phase [11, 12], i.e. no nucleation of the stable phase is attributed to a high activation barrier.

In the case of mechanical alloying, the intense deformation generates large defect densities and increases the free energies of both pure components with respect to the product of amorphous or crystalline compound phase, which leads to intrinsic instability of ultrafine layered structure formed by MA. In general one would expect that the lower activation energy barrier of nucleating the amorphous phase gives the greater nucleation rate of the metastable phase. However, since kinetics dominates the reaction, for two probable nucleating phases of amorphous and crystalline compound the reaction would depend on the temperature as shown in Fig. 3, where the temperature dependence of the reaction rate is given by the Arrhenius rate equation of

$$\text{rate} \propto \exp(-Q/RT)$$

that is, at low temperatures the process having a

lower activation energy (Q_2) is dominant and at high temperatures above TC the reaction follows the higher activation (Q_1) process. Weeber and Bakker [13] have shown that the amorphization reaction path depends on the local temperature after a hit with a ball and not on the average temperature during the milling. Thus, the reaction during MA may depend on the local temperature after an impact during the milling, which is a function of ball diameter in this work. Based on the above picture, the reaction favors the metastable state of an amorphous phase when the milling is performed in a low energy state, as shown in Fig. 2. If the milling energy input (i.e. the local temperature) is large enough to form crystalline nuclei of an intermetallic phase, the reaction follows the crystalline compound formation as shown in Fig. 1. It is suggested that there is a critical energy input for a solid-state amorphization by MA of elemental crystalline powders, which would depend on the alloy system.

It is very important from the technical point of view that we develop the technique to obtain the homogeneous stoichiometric Nb_3Sn compound by heat treatment because heat treatments of the mixture of Nb and Sn powders of the overall composition Nb_3Sn result in the formation of other compounds [7]. Figure 4 shows the DSC scans at

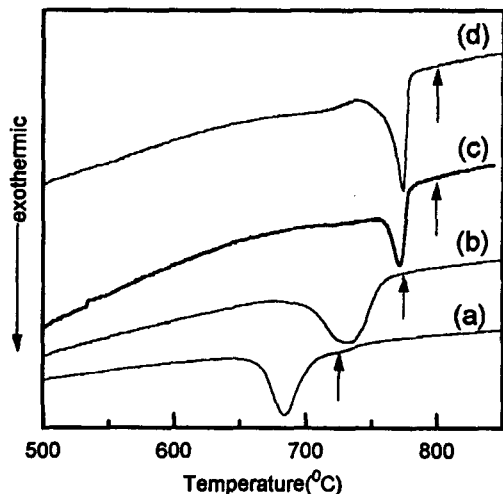


Fig. 4. Differential scanning calorimetric curves of the mixed powders with a composition Nb_3Sn prepared by mechanical alloying using balls of 3.968 mm diameter in argon atmosphere for 5 h (a), 10 h (b), 20 h (c) and 30 h (d). The heating rate was $10^\circ C/min$.

$10^\circ C/min$ for the powders after various milling times in which the milling condition was the same as used to obtain the results shown in Fig. 2. The exothermic peaks shown in Fig. 4 are associated with the formation of a Nb-Sn compound as shown in Fig. 5. The position of exothermic peaks for the samples milled for 20 and 30 hours appears to be same, indicating that the specimens are completely amorphous and chemically homogeneous. In the case of the sample milled for 10 hours, the exothermic peak occurs at lower temperature, and therefore it is assumed that the sample has been partially amorphized by milling. The DSC peak for a supersaturated solid solution (as inferred from the XRD results of expanded lattice parameters and disappearance of Sn peaks) is observed at the lowest temperature.

Figure 5 shows the XRD profiles of samples heated to the temperature, indicated with arrows in Fig. 4, and then cooled quickly to room temperature. Crystallization of samples amorphized by MA resulted in the mixture of Nb_3Sn and Nb_6Sn_5 .

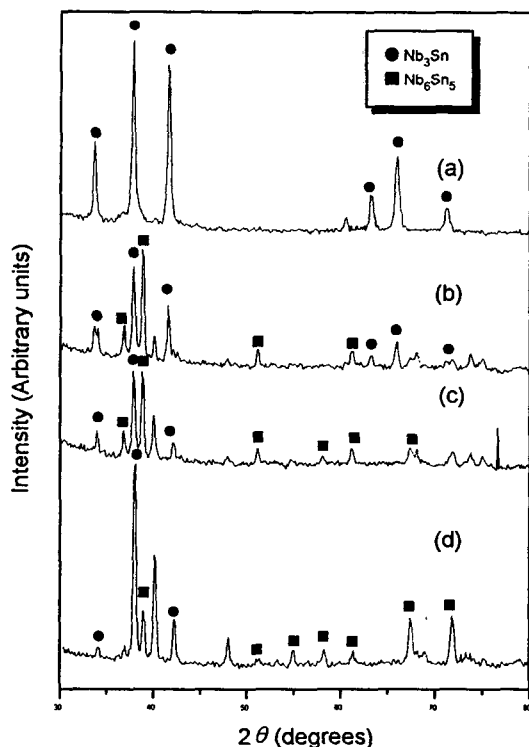


Fig. 5. X-ray diffraction patterns taken from samples heated up to temperature marked by arrow in Fig. 4 after milling for 5 h (a), 10 h (b), 20 h (c) and 30 h (d).

However, a supersaturated solid solution obtained by MA for 5 hours was transformed completely to Nb₃Sn.

From the Nb-Sn phase diagram [14], the Nb₃Sn and Nb₆Sn₅ phases are stable above 750°C. Since the Nb₃Sn phase is produced by MA as shown in Fig. 1, it is assumed that the kinetics for formation of the Nb₃Sn phase is more rapid than for the formation of the competing phase. For the sample milled for 5 h, the exothermic peak in the DSC scan appears below 750°C and, therefore, the single phase of Nb₃Sn is obtained. On the other hand, in the case of samples milled for longer milling time than 10 h, the exothermic peaks occur above 750°C at which the formation of the Nb₃Sn and Nb₆Sn₅ phases would be equally probable.

4. Conclusions

The structural development with milling time depends on the ball size (or weight) for a given powder/ball ratio. Using larger balls of 9.5 mm diameter, the elemental powders initially alloy mechanically to form an A15 structure phase, and then amorphised with continued milling. However, in case of milling with a smaller ball of 3.968 mm diameter, an amorphous phase is first formed.

The homogeneous stoichiometric Nb₃Sn phase could be easily obtained by heat treatment of a supersaturated solid solution produced by MA. Heat treatment of an amorphous phase formed by MA resulted in the mixture of the Nb₃Sn and Nb₆Sn₅ phases.

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