Article ID: 1003 - 6326(2003)05 - 1066 - 04

Synthesis and characterization of metastable Ag-B solid solutions①

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Abstract: Mechanical alloying (MA) was applied to Ag-B immiscible binary systems by ball milling elemental Ag and B powders. The microstructural characterization of the milled powders was carried out by XRD and TEM. The results show that face-centered-cubic (FCC) Ag-B solid solutions are formed and that the maximum ratio of B to Ag is 4∶1. The structure evolution of Ag-B solid solution during ball milling indicates that the formation of Ag-B solid solution may be divided into two stages, which are mainly substitutional and interstitial solutions separately. The decomposition of the as-milled granules under the irradiation of electron beam is observed by TEM, which reveals that the solid solutions are metastable.

Key words: mechanical alloying; Ag-B solid solution; metastable.

CLC number: TB 303 **Document code:** A

1 INTRODUCTION

Mechanical alloying (MA)[1] has become a widely used technique to synthesize a variety of materials, such as amorphous alloys, nanocrystalline materials, compounds, solid solutions and so forth. Especially, the formation of nonequilibrium materials composed of immiscible elements by MA has received increased attention. A number of binary systems have been investigated, including Ag-Cu[2-4], Ag-Fe[5], Fe-Cu[6], Ag-Ni[7] and others. Comparison with other synthesis methods, such as rapidly quenching, MA has advantages to synthesize supersaturated solid solutions though contaminations are inevitable. But according to our knowledge, few efforts were done to prepare metals-nonmetal solid solutions from immiscible elements.

Borides can be used as refractory compounds because of their high hardness, high-temperature stability and so on. The borides synthesized by ball milling the metal powders along with B include Co-B[8], Fe-B[9], Ni-B[10], Nb-B[11], and Ti-B[12] phases. However, these borides are all stable phases. Although silver boride will not be refractory compound since the melting point of silver is not high enough, the synthesis of silver boride, is attractive for the immiscibility between Ag and B. Synthesis and characterization of silver boride have been carried out in present investigation. The MA products by ball milling Ag and B powders are Ag-B solid solutions.

2 EXPERIMENTAL

Elemental Ag (Shanghai Chemistry Reagent Corp., China) with 99.9% purity and particle sizes of 100 μm and B (Merck Corp., Darmstadt, Germany) with 99.9% purity and particle sizes of 2 μm, were blended to give average compositions of AgB_x with $x = 2, 4, 6, 10$, which were named as specimen 2#, 4#, 6# and 10#, respectively, in the following paragraphs. The MA was performed in a planetary ball mill with stainless steel vial and balls at ambient temperature. The ball-to-powder mass ratio was about 10∶1 and the speed of rotation was 300 r/min. To avoid contaminations from atmosphere, the steel vial was sealed in dry argon atmosphere with an overpressure about 0.2 MPa. The milling process was interrupted at different milling times, and a small amount of the milled powders was removed for analysis. The powders were characterized using a Rigaku DMX/2550 X-ray diffractometer (XRD) with CuK_α radiation. The scanning step of 2θ was 0.02° and the accumulating time for every step was 3 s. The XRD peak positions were determined by non-linear least-squares profile fitting program. The lattice parameters were calculated using software Wincell. After removing instrumental contribution from the observed profiles, the average grain sizes were obtained from the broadening of (111) and (200) reflections by single line profile analysis[13]. In all the cases, the con-

① **Foundation item:** Project(G59871047) supported by the National Natural Science Foundation of China and project(G598054) supported by the Natural Science Foundation of Zhejiang Province, China

Received date: 2002 - 10 - 16; **Accepted date:** 2003 - 01 - 15

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tamination of iron due to abrasion of the milling tools, which was determined by means of energy-dispersive X-ray spectroscopy (EDX), was less than 1% in the final milled products. The as-milled powders were also examined by transmission electron microscopy (TEM) using a PHLIPS CM200 electron microscope operated at 200 kV.

3 RESULTS AND DISCUSSIONS

XRD patterns obtained from specimens $2^{\#}$, $4^{\#}$, and $6^{\#}$ milled for 40 h ($10^{\#}$ for 50 h) are shown in Fig. 1. For comparison, the XRD pattern of the simply mixed Ag and B (mole ratio of 1∶4) powders is also given. Because the scattering factor of boron is much smaller than that of silver, the intensities in the range from 5° to 30° are magnified by 15 times for clarifying the B peaks. It can be seen that no boron peaks are found in as-prepared $2^{\#}$ and $4^{\#}$ samples, but boron peaks can be found in $6^{\#}$ and $10^{\#}$. These observations demonstrate that B can be dissolved in the Ag to form a homogeneous B-rich solution and the solid solutions have the same structure as that of silver even though the B content is three times higher than that of silver. The maximum ratio of B to Ag for Ag-B solid solution is about 4∶1.

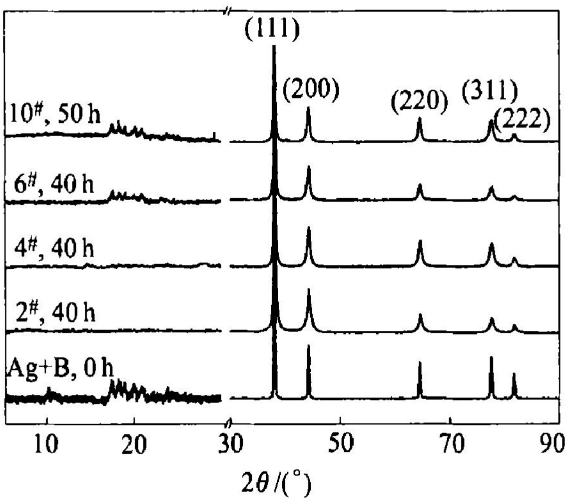

Fig. 1 XRD patterns of MA Ag-B solid solutions milled with different mole ratios for different times

Fig. 2 shows XRD patterns of specimen $2^{\#}$ at different milling times. The diffraction peaks broaden with increasing milling times, indicating the refinement of grains and introduction of microstrain. Similar structural variations were also observed in specimens $4^{\#}$, $6^{\#}$ and $10^{\#}$.

The lattice parameters and grain sizes of solid solutions change with increasing milling time. Fig. 3 shows variations of lattice parameters and grain sizes

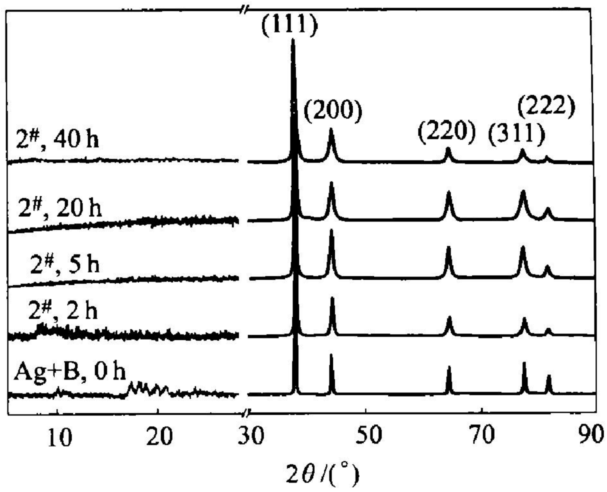

Fig. 2 XRD patterns of specimen $2^{\#}$ milled for different times

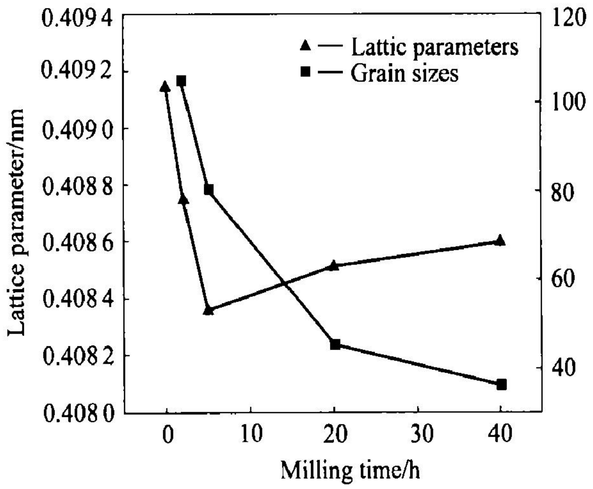

Fig. 3 Variations of lattice parameters and average grain sizes of Ag-B solid solutions in specimen $2^{\#}$ with milling time

as a function of milling time for specimen $2^{\#}$. It can be seen that the lattice parameters decrease with increasing milling time till 5 h, and then increase with increasing milling time. The grain sizes, however, continually decrease with increasing milling time. The same phenomena are also observed in other specimens. The variation of lattice parameters with milling time can be interpreted as following. The lattice parameters of solid solution are related with some factors, such as grain size, solubility and the type of the solid solution. The lattice parameters should be changed continually with decreasing (or increasing) grain size and solubility. The average grain size of the solution in the initial stage is larger than 80 nm and it has no observable effect on the lattice parameters. So that the decrease of lattice parameters in this stage is mainly caused by the formation of substitutional solid solution, in which B atoms substitute Ag atoms in the surface layers of silver particles. During further milling, the B atoms diffuse gradually into the central of Ag particles and mainly take the interstitial positions in the silver lattice, which causes the lattice parameters to increase.

After having been milled for 40 h (specimen 10# for 50 h), the relationship of lattice parameters and grain sizes of Ag-B solid solutions with compositions are summarized in Fig. 4. Notice that the lattice parameter does not continue to increase evidently with increasing B content in the specimens. It also indicates that the maximum ratio of B to Ag is about 4∶1 in the solid solutions.

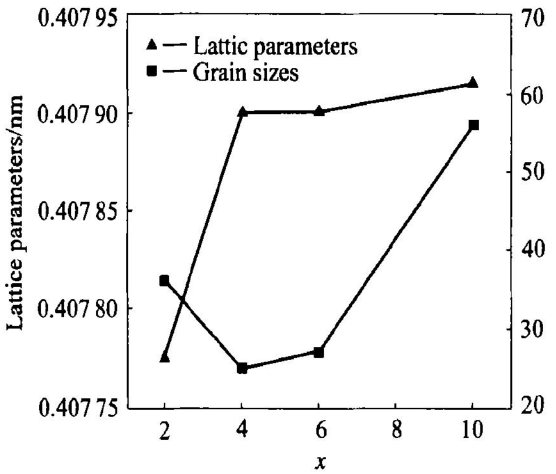

Fig. 4 Relationship of lattice parameters and grain sizes of solid solutions with compositions of AgB_x

Although the grain sizes of the milled specimens are nanocrystalline, the granules sizes are too large to be observed their microstructure by TEM. During the TEM observation, some of the granules decomposed under the irritation of electron beam within a fraction of a second, while small Ag and B crystals were formed. The same phenomena have been observed in MA $Ag_{37}Cu_{63}$ alloys[3]. Fig. 5 shows the shape variation and decomposing of a granule during electron irratiation for AgB_2 solid solution milled for 40 h. An electron diffraction pattern for the sample after irradiation is also given in Fig. 5(c). Two diffraction spots located symmetrically between central bright spot and Ag (111) diffraction loop and the spots can been indexed as (024) spots of B by arrows in Fig. 5(c). The temperature of the specimen under electron irritation is below 156 ℃[3], which is much lower than the melting points of elemental Ag and B. The decomposing of the Ag-B solid solution under electron irritation reveals that the solid solution is a non-equilibrium phase and has reserved a higher energy in the course of the ball milling, i. e. the MA solid solutions are metastable.

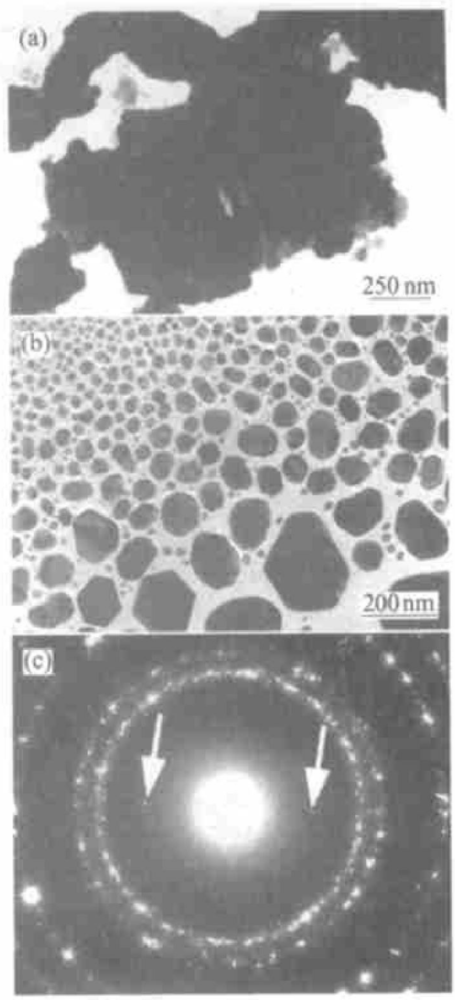

Fig. 5 Shape and structure variations for specimen 2# during TEM observation
(a) —Initial shape; (b) —After irradiation;
(c) —Diffraction pattern taken from (b)

4 CONCLUSIONS

1) MA has been employed to synthesize FCC Ag-B solid solutions, and the maximum ration of B to Ag in the Ag-B solid solution is about 4∶1.

2) Detailed studies from XRD data of the prepared samples demonstrate the course of the formation of the solid solution.

3) The solid solutions are mainly substitutional solution in the initial stage of milling, and the interstitial mechanism is dominated during prolonged milling.

4) Some granules of the solid solution decompose into small Ag and B crystals under irradiation of electron beam in the process of TEM observation, which indicate that the Ag-B solid solutions are metastable.

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(Edited by HE Xue-feng)