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The prediction of upper limit of copper content in CoBCu glass-forming alloys

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ABSTRACT

The soft magnetic properties of ferromagnetic nanocrystalline alloys can be enhanced considerably by addition of copper until the upper limit of Cu content which is unknown at present. This study explored the upper limit of Cu content in the $Co_{81-X}B_{19}Cu_X$ (X = 2, 3 and 5) alloy system using *ab initio* molecular dynamics simulations and experiments. It was found that when the Cu content rose above 2 at%, the first-nearest-neighbor peaks of partial pair distribution function for Cu-Cu pair became stronger steadily with the decreasing temperature, demonstrating that Cu clusters were formed during the quenching processes from initial melt. As to the Cu content was less than or equal to 2 at%, the trace of such clusters was difficult to find. So the maximal Cu content in $Co_{81-X}B_{19}Cu_X$ alloys in as-quenched amorphous state was predicted to be less than 2 at%. $Co_{81-X}B_{19}Cu_X$ ribbons were prepared using the melt-spinning technique with as large cooling ability as possible. Structure analysis results from X-ray diffraction patterns of the three as-quenched alloys supported the above theoretical predictions. These results would provide a theoretical reference for the design of ferromagnetic nanocrystalline alloys.

1. Introduction

The excellent soft magnetic properties of Fe-based nanocrystalline alloys have generated great interest since the development of Finemet type FeCuNbSiB alloys in 1988 by Yoshizawa [1]. Finemet alloys have extensive applications in high-frequency electricity transformation, electronic information and other fields, and has become one of the key functional materials specially required for energy savings and carbon emission reduction. A nanocrystalline FeSiBPCu alloy with a high saturation flux density (B_s) of 1.97 T is newly reported by Markino and attracted great attention due to the elimination of the high-cost element Nb [2,3]. The existence of Cu element elevated the alloy's B_s value.

The most important development in these alloy systems was the addition of Cu to ferromagnetic amorphous alloys, which when combined with an appropriate heat treatment formed a double-phase structure of nano-sized crystals embedded in an amorphous matrix that improved the soft magnetic properties [2–8]. The Cu was uniformly distributed in the as-quenched amorphous melt-spun specimens initially [4,8]. After a proper heat treatment of the amorphous precursor, the Cu clusters (or also named Cu-rich clusters) were precipitated from the amorphous matrix [4,8]. Cu clusters acting as high-density nucleation centers played the role as nucleation stimulator of the nano-sized crystals [4,8]. Annealing at temperature below the crystallization temperature of Finemet alloy systems, the Cu clusters were the amorphous in nature. In the very early stages of the crystallization process [4,7,8], the onset of the formation of Cu clusters shifted to lower temperatures with increasing Cu content [4,7,8]. Moreover, Cu was an active element in the field of metallic glasses. Cu-Zr based alloys usually demonstrated perfect glass-forming ability (GFA) [9]. Cu-Cu atom pairs presented a strong sensitivity to atomic concentrations [10]. The liquid-liquid phase would be separated in Co-Cu binary alloys with high Cu content above 16 at% [11], and the icosahedra clusters in the rapid cooling process contributed to the glass formation of the Cu-Ag alloy [12].

The Cu content in widely studied ferromagnetic nanocrystalline alloy systems, including FeBCu, FeSiBCu, FeSiBNbCu, FePCCu and FeSiBPCu, was less than 1.5 at% [2–5,13–15]. Recently, the preset-crystal nucleus technique by two-step annealing was found to be an effective method to improve the magnetic properties of FeBCuM (M = C, Si, P) systems [16,17]. In both the Finemet one-step crystallization process and the preset-crystal two-step crystallization process of high B_s nanocrystalline alloys, the first step is the precipitation of Cu

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clusters from the amorphous matrix. The Cu cluster density and resulting nucleation density were almost proportional to the Cu content [2,5,14]. The highest Cu content at which amorphous precursor of nanocrystalline alloy could be obtained by melt-spinning technique was defined as the upper limit. Too higher Cu content would decrease the GFA of alloy system. So the closer Cu content approaches to the upper limit, the better the soft magnetic properties. But the upper limit of Cu content in ferromagnetic nanocrystalline alloys is currently unknown.

The final target of exploring nanocrystalline alloy is the formation of double-phase nano-sized structure responsible for the excellent magnetic properties. Obtaining a uniform distribution of high-density Cu clusters in amorphous alloys before crystallization is an overarching goal. Raising the Cu content above 1.5 at% may be a practical way to obtain as many Cu clusters as possible in melt-spun ribbons.

This study focused on finding the upper limit for Cu content in the CoBCu glass-forming system by modeling the quenching process with *ab initio* molecular dynamics (AIMD) and melt-spinning experiments. It was found that Cu clusters were formed during the quenching processes and stimulated the precipitation of crystalline phases.

2. Methods

Raw materials—Co (99.99 mass%), B (99.5 mass%), Cu (99.99 mass %)— were melted into ingots with nominal compositions of $Co_{81-X}B_{19}Cu_X$ (X = 2, 3 and 5) using an electric arc furnace with a purified argon atmosphere. As-quenched ribbons were prepared using single-roller melt-spinning technique under an Ar atmosphere.

To attain as large cooling rate as possible, the melt-spinning parameters were optimized: a water-cooled oxygen-free copper wheel sized φ300 × 60 mm, a wheel speed of 40 m/s, a small spinning pressure difference of 10 kPa, and the smallest circular hole sized 0.3 mm in diameter on top of the quartz tube. The ribbons were 18 μm thick and 1.5 mm wide. All of the ribbons were excellent in surface quality. The structure of the as-quenched ribbons was examined by X-ray diffraction (XRD) using Cu-K_α radiation. The melting point of as-quenched $Co_{81-X}B_{19}Cu_X$ alloys were determined by differential scanning calorimetry (DSC, NETZCH 404C) at a heating rate of 10 °C/min. The obtained melting points of these alloys are around 1400 K.

AIMD is often used to calculate the static liquid and amorphous structure of materials and to deduce general trends by systematically comparing a number of amorphous alloy systems with different chemical compositions, and it reliably reproduced experimental observations [18–24]. In our simulations, a cubic cell containing 100 atoms with periodic boundary conditions was used to simulate the $Co_{81-X}B_{19}Cu_X$ alloy system, whose composition is actually (81 − X)% Fe, 19% B and X% Cu. The system was equilibrated and relaxed at T = 1873 K for 12 ps with 3000 configurations from the last 9 ps period. Then, the last configuration was quenched at a cooling rate of 3.33×10^{14} K/s towards the target temperatures, 1473, 1073 and 300 K, respectively. The number of motion steps was adjusted to ensure the same cooling rate for the different quenching temperature ranges. Following this quenching, the three last configurations obtained were equilibrated at 1473, 1073, 300 K for 9 ps again to provide 3000 configurations collected for structural analysis, respectively. Once the total energy of the cell was fluctuated around an average value rather than monotonously increased or decreased after hundreds or thousands of motion steps, the system reached its equilibrated state. Usually, 3000 steps were enough to ensure this.

All the dynamical simulations were carried out in the canonical ensemble (*nvt*) through a Noséthermostat to control temperature [25]. The model cell was continuously optimized by adjusting the cell size to ensure the external pressure was located in ± 5.00 kbar and the optimal cell size of $Co_{81-X}B_{19}Cu_X$ (X = 2, 3 and 5) alloys are 10.02, 10.04 and 10.05 Å, respectively. Typical topological structure, atomic configuration and pair distribution function (PDF) were deduced from the statistical analysis of the 3000 configurations. Automatic k-point mesh of 1 × 1 × 1 containing Gamma was used for geometry optimization. The convergence criteria used in the electronic self-consistent and ionic relaxation was set to 10^{-4} eV per cell. For more details, please refer to [20,26].

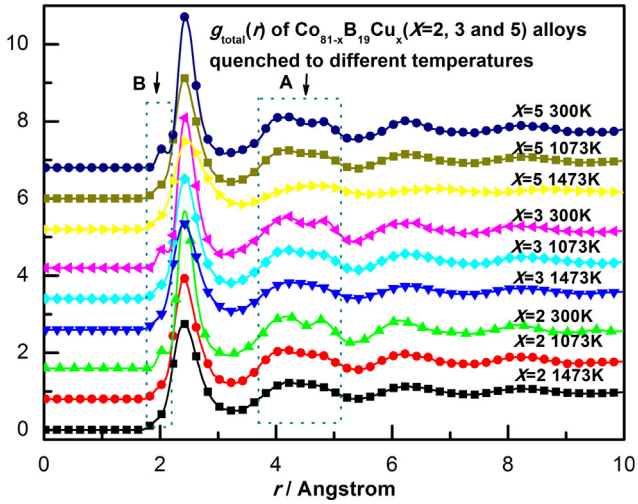

Fig. 1. Total pair distribution functions of the $Co_{81-X}B_{19}Cu_X$ (X = 2, 3 and 5) alloys during quenching.

3. Results and discussion

The total PDFs of the $Co_{81-X}B_{19}Cu_X$ (X = 2, 3 and 5) alloys during quenching are shown in Fig. 1. For all three alloys, the second peak at around 0.45 nm of the total PDFs (designated by arrow A) was smooth at 1473 K, became slightly split at 1073 K and more clearly split when quenched to 300 K. The second peak splitting into two subpeaks at 300 K was indicated the typical amorphous structure characteristic. Notably, the PDFs at 300 K even exhibited a small pre-peak around 0.2 nm (designated by arrow B).

To understand the contributions of the six atomic pairs to the total PDFs and pre-peaks of CoBCu alloy system, six partial PDFs of the $Co_{78}B_{19}Cu_3$ alloy quenched to 300 K were plotted as shown in Fig. 2. The total PDFs, i.e., $g_{total}(r)$, is composed of $g_{CoCo}(r)$, $g_{CoB}(r)$, $g_{CoCu}(r)$, $g_{BB}(r)$, $g_{BCu}(r)$ and $g_{CuCu}(r)$ functions. The B and Cu atoms demonstrated strong first-nearest-neighbor interactions with Co as evidenced by the strong first peak in the $g_{CoB}(r)$ and $g_{CoCu}(r)$ curves. The value in x-axis

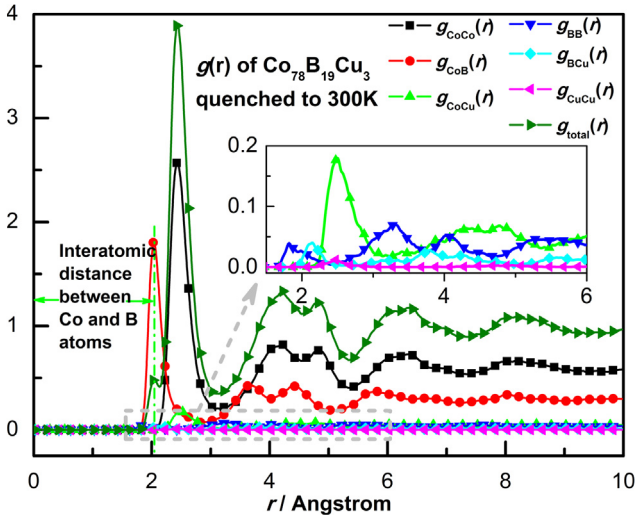

Fig. 2. Total and partial pair distribution functions for the $Co_{78}B_{19}Cu_3$ alloy quenched to 300 K.