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Experimental study of amorphous and nanocrystalline Fe-based alloy

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Abstract: The mechanical alloying of FeNiPB(Cu, Nb) mixed powders was studied by X-ray diffraction (XRD), transition electron microscope (TEM), scanning electron microscopy (SEM) and extended X-ray absorption fine structure (EXAFS). The results show that the FeNiPB(Cu, Nb) mixed powders alloy after milling for 20 h, as the milling time increases to 80 h, Fe and Ni atoms are in an amorphous environment, the morphology of FeNiPB(Cu, Nb) mixed powders appears as cotton fiber and its electron diffraction pattern shows a typically diffuse amorphous halo. So FeNiPB(Cu, Nb) mixed powders transform to amorphous state under this condition. After the FeNiPB(Cu, Nb) amorphous alloy was heated at 520 ℃ for 1 h, the nanocrystalline FeNiPB(Cu, Nb) was produced. So, the Fe-based nanocrystalline alloy can be prepared by partially crystallizing the FeNiPB(Cu, Nb) amorphous alloy.

Key words: nanocrystalline; mechanical alloying; FeNiPB(Cu, Nb) alloy

Recently a new type of materials has been synthesized, which are called nanocrystalline materials, with graining size below 100 nm. The nanocrystelline materials have attracted considerable interest because of their specific physical properties which differ from those of polycrystalline of the same chemical composition[1-3]. Nanocrystalline magnetic materials including FINEMEN alloy and NANOPERM alloy have been proved to be excellent soft magnetic materials[4, 5]. Both FINEMEN alloy and NANOPERM alloy are two-phase nanocrystalline materials obtained by partial crystallization of an amorphous alloy, which is composed of nanograins about 10 nm embedded in amorphous precursors. In the present study, we have investigated the evolution of the FeNiPB (Cu, Nb) alloy structure and phase transformations during the mechanical alloying and crystallizing process.

1 Experimental Procedure

The fine powders of the elements of Fe, Ni, P and Cu and polycrystalline pre-alloys of Fe-Nb and Fe-B were used as starting materials to make the desired composition of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$. The powder mixture was sealed in a cylindrical stainless-steel container, and a few drops of methanol were used to prevent excessive welding in the chamber, thus allowing a high degree of mixing. The mechanical alloying was performed in a planetary ball mill. The ball-to-powder weight ratio was 80∶1, and the speed of the ball mill was 240 r/min.

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The X-ray diffraction (XRD) patterns were obtained using CuK_α radiation with a graphite monochromater by a D/max-γA X-ray diffractometer. The secondary electron images were obtained by X-650 scanning electron microscope (SEM). The high-resolution secondary electron images were obtained by LEO-1550 field emission scanning electron microscope. The transition electron microscope (TEM) micrograph and electron diffraction pattern were obtained by JEOL 2000-ES transition electron microscope. The extended X-ray absorption fine structure (EXAFS) measurements were performed at HASYLAB using synchrotron radiation from the DORIS Ⅲ storage ring. A Si(111) double crystal monochromator was used. Energy calibration was made by spectra of a bulk Fe metal foil and a bulk Ni metal foil, which were measured simultaneously as a reference.

2 Results and Discussions

The structural evolution of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders during 0 to 80 h milling was followed by XRD. The XRD patterns are displayed in Fig. 1. It can be seen from Fig. 1 that after the powders were milled for 20 h, the (Fe, Ni), $(Fe, Ni)_3P$ can be seen in the XRD pattern. The powders alloyed and were polycrystalline under these conditions. With the milling time extended up to 60 h, there is a single broadened diffraction peak at the lower angle in the XRD pattern, but it is not the typical amorphous pattern. It indicates that as the milling time increased further, the crystalline alloy transformed partly to a amorphous pattern. As the milling time increases to 80 h,a halo pattern is

visible in the XRD pattern, which is a typical amorphous pattern. Thus the polycrystalline powders transformed to a fully amorphous pattern.

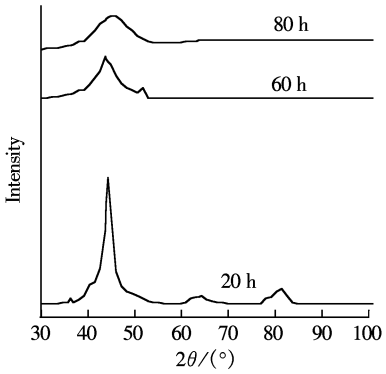

Fig.1 XRD patterns of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders milled for different times

EXAFS spectroscopy extracts structural information from a sample analyzing its X-ray absorption spectrum. EXAFS method is very suitable for local structure because it can determine the chemical environment of a special atom. In Fig. 2, the EXAFS curves for $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders after milling 80 h are compared with the EXAFS curves for Fe metal and Ni metal. The EXAFS curves for $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders have a sinusoid shape, low amplitude and steep decline. It is conformed that the Fe and Ni atoms are in an amorphous

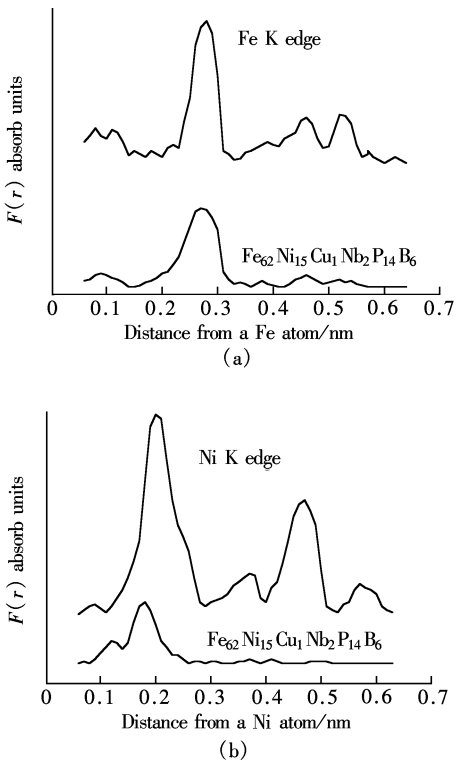

Fig.2 Radial distribution function of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders after milling 80 h. (a) Compared with Fe metal; (b) Compared with Ni metal

environment.

Parallel to the investigation by XRD and EXAFS spectroscopy, the morphology and electron diffraction of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders during milling was followed by TEM. Fig. 3 gives the TEM of powders milled for 80 h and its electron diffraction pattern. It can be seen that the morphology of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders after milling 80 h appears as cotton fiber and its electron diffraction pattern shows a circle, which is a typically diffuse halo characteristic of amorphous patterns. The electron diffraction of powder confirms the XRD and the EXAFS conclusion that the $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ amorphous alloy can be prepared by milling the mixed powders for 80 h.

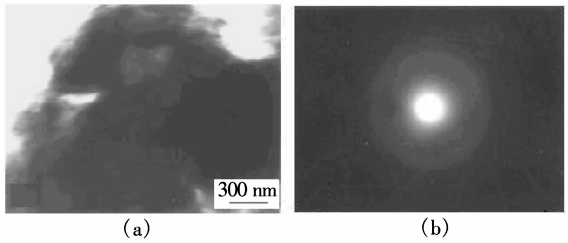

Fig.3 TEM bright-field micrograph of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ powder milled for 80 h and its electron diffracting pattern

$Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders mechanical alloying was performed in a ball mill. The metallic powder particles and pre-alloy powder particles were trapped by the colliding balls, heavily deformed and cold-welded. Finally, a true alloying took place. As the milling time increased the powder particles refined and the size of grains decreased. Thus, new particle surfaces and new grain surfaces increased. Further, the high intensity of milling introduced severe plastic deformations into powder particles, which generated many points and lattice defects (vacancies, interstitials and dislocations, etc.). The large number of defects raised the free energy. When the defect concentration reached the critical value at which the free energy of faulted intermetallics was above that of the amorphous phase, the powders amorphized.

The $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ amorphous alloy was heated at 520 ℃ for 1 h, and the nanocrystalline $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ was produced by heat treatment from amorphous $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$. Fig. 4 is the high-resolution morphology of the nanocrystalline $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ taken by field emission SEM. It can be seen that the small grain size (about 25 nm) and random orientation of crystallines embedded in the amorphous matrix in $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ nanocrystalline alloy. The formation of this $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ nanostalline alloy could be

attributed to the Cu and Nb atoms. It was the Nb atoms that promoted body centered cubic iron precipitation and suppressed Fe-B compound formation because they were insoluble in Fe, Cu and formed face centered cubic clusters in amorphous. So the nanograins embedded in an amorphous precursors were formed in $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$.

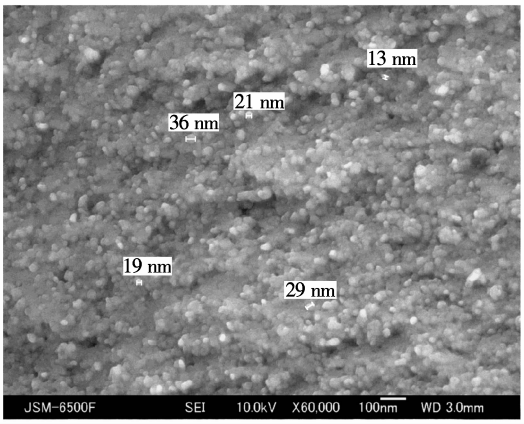

Fig.4 High-resolution morphology of the nanocrystalline $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$

3 Conclusion

The result of the XRD is that the FeNiPB(Cu, Nb) mixed powders alloy after milling for 20 h and as the milling time increases to 80 h, the polycrystalline powders transform to a fully amorphous state. The result of the EXAFS is that Fe and Ni atoms are in an amorphous environment, so the FeNiPB (Cu, Nb) mixed powders transform to an amorphous state after milling for 80 h. The results of the TEM are that the morphology of $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ mixed powders after milling 80 h appears as cotton fiber and its electron diffraction pattern shows a circle, which is a typically diffuse halo characteristic for amorphous alloy. The result of the SEM is that after the FeNiPB(Cu, Nb) amorphous alloy was heated at 520 ℃ for 1 h, the nanocrystalline $Fe_{62}Ni_{15}Cu_1Nb_2P_{14}B_6$ was produced. Therefore the conclusions of experimental studies are that the FeNiPB (Cu, Nb) mixed powders are mechanically alloyed after milling 20 h, and the FeNiPB(Cu, Nb) alloy transformed from crystalline phase to amorphous phase after milling 80 h. So, the Fe-based nanocrystalline alloy can be prepared by partially crystallizing the FeNiPB(Cu, Nb) amorphous alloy.

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非晶、纳米晶铁基合金的实验研究

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摘要: 用 X 射线衍射分析仪(XRD), 透射电子显微镜(TEM), 扫描电子显微镜(SEM)和 X 射线吸收精细结构分析仪(EXAFS)对机械合金化后的 FeNiPB(Cu, Nb)混合粉末进行了分析研究. 研究结果表明: FeNiPB(Cu, Nb)混合粉末球磨 20 h 后合金化, 球磨 80 h 后 FeNiPB(Cu, Nb)混合粉末中的 Fe, Ni 原子处于非晶环境中, 粉末的形态为棉絮状, 电子衍射为典型的非晶环. XRD, EXAFS, TEM 的分析结果表明在该条件下, FeNiPB(Cu, Nb)混合粉末完全转变成了非晶. FeNiPB(Cu, Nb)非晶合金在 520 ℃加热 1 h 后产生纳米晶, 所以纳米晶铁基合金可通过 FeNiPB(Cu, Nb)非晶合金部分晶化获得.

关键词: 纳米晶; 机械合金化; FeNiPB(Cu, Nb)合金

中图分类号: TG132.2⁺71; TG139⁺.8