TEM observation of oxidation of CuZnAlMnNi shape memory alloy

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Abstract **The atmospheric oxidation of a quenched CuZnAlMnNi alloy after ion-polishing was examined by transmission electron microscopy (TEM). It was found that a lot of oxide grains with various sizes yield homogeneously on the surface of the alloy after exposure at room temperature for 90 d. The grains mainly form along the planes of stacking fault, meanwhile, they can also be observed at the stacking fault tetrahedrals or around the dislocation lines. The formation of the oxides gives rise to the reduction of the stacking faults, and even complete disappearance in some zones, which is partly responsible for the decrement of shape memory effect (SME) of the alloy quenched during long-term holding at room temperature.**

Keywords: shape memory alloy, oxidation, stacking fault tetrahedral, dislocation line.

As an important functional material, shape memory alloys (SMA) have attracted much interest. The SME of the alloy is associated closely with the forward and reverse martensite transformation during cooling and heating. The stable microstructure amount taking part in the transformation is the basis for achieving the stable SME, on the contrary, the alteration of microstructure always brings about the change of SME[1,2], which is particularly true for Cu-based SMAs, in which the SME of the alloys is extremely susceptible to the microstructral alterations. For example, the segregation of precipitate[3—5], the formation of bainite[6,7], and so on, may lead to the decrease of SME of the alloys. During long duration of application, the surface of SMA actuators contacts with atmosphere and inevitably oxidizes, resulting in the variation of surface microstructure and finally the reduction of SME. So the decrement of SME during long-term holding at ambient temperature after solution treatment of Cu-based SMAs, depends not only upon the martensite stabilization[8,9], but also upon the oxidation to some extent. However, few reports are available concerning the oxidation of Cu-based SMAs. Because the oxidation rate of the alloys is comparatively slow in ambient atmosphere, it is difficult to obtain the information of surface oxidation by normal measurement methods. In this work, the specimen of the quenched CuZnAlMnNi alloy was ion-polished, exposed in atmosphere for 90 d, and examined by TEM, thus we obtained the micro-information related to the surface oxidation of the alloy.

1 Experimental

The material investigated was a polycrystalline Cu-23.6Zn-4.47Al-0.23Mn-0.17Ni (weight percentage) alloy, whose preparation is the same as that in literature[10]. The sample was spark machined into the dimension of 150 mm × 4 mm × 1 mm, solution treated at 840℃ for 20 min, quenched into the boiling water for 30 min, and then cooled to ambient temperature. The transformation temperatures of the alloy measured by DSC-41 differential scanning calorimeter are as follows: M_s=39℃, M_f=22℃, A_s=45℃ and A_f=63℃.

A small specimen cut from the alloy quenched was ground to 30 μm or so, ion-polished by a GL-69D type of polisher to punch a hole locally, and then examined using an H800 transmission electron microscope. The specimen ion-polished was held for 90 d at room temperature in atmosphere and re-examined by TEM.

2 Results and discussion

Fig. 1 shows the TEM microstructure and the corresponding diffraction pattern immediately after quenching. It can be seen that the substructures in the martensite quenched are stacking faults, which play an important role in the SME of Cu-based SMAs[11—13]. From the diffraction pattern, it can be determined that the structure of the martensite quenched is M18R type. Fig. 2 exhibits the TEM microstructure and the corresponding diffraction pattern when the same ion-polished specimen was held 90 d at ambient temperature in atmosphere. It is obvious that a lot of grains with various sizes yield homogeneously in the specimen. From the diffraction pattern in fig. 2, there appear a series of close rings around the center spot besides the normal spots resulted from the M18R martensite. Thus it can be seen that the grains are oxides due to the reaction between the alloy and the oxygen in atmosphere. Note that the diffraction rings generated by oxides almost fall onto the diffraction spots of martensite, indicating that the interplanar spacings of the oxides are approximately identical to those of martensite, and the oxides form along the martensite planes and grow up gradually. From a careful observation on the oxide grains in fig. 2, it can be found that the grains form along the stacking fault planes. The generation of oxides gives rise to the decrement of the substructure of stacking faults, and even to the complete disappearance in local zones. The microstructural change inevitably impairs the SME of the alloy.

In addition, it can still be observed from fig. 2 that the oxidation takes place at the stacking fault tetrahedrals as marked by A and B. Because the CuZnAlMnNi alloy has low fault energy (approximately 4×10^{-6} J/cm^2), the stacking fault tetrahedrals easily form during quenching, whose existence increases the energy of the system, and thus leads susceptibly to oxidation at the tetrahedrals. After oxidation, the stacking faults in the tetrahedrals are difficult to be distinguished.

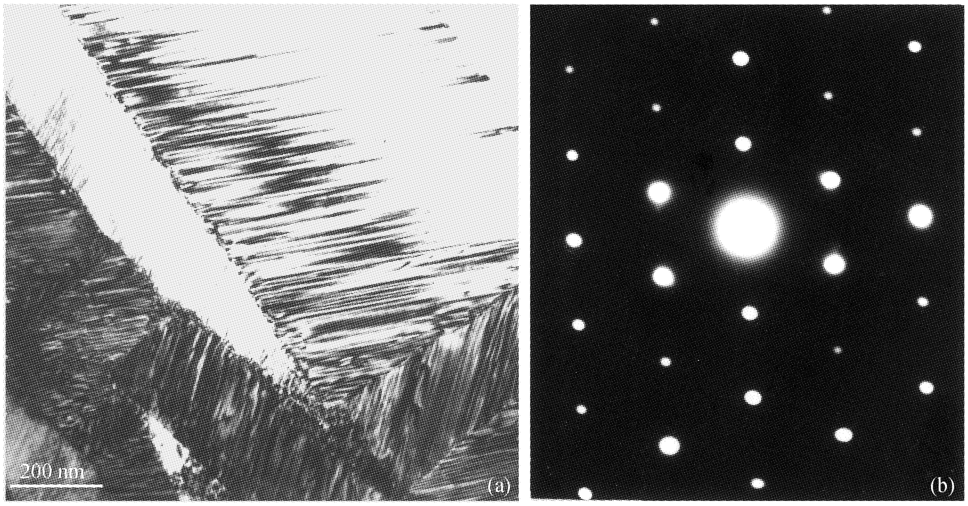

Fig. 1. TEM microstructure of the quenched CuZnAlMnNi alloy (a) and the corresponding diffraction pattern (b).

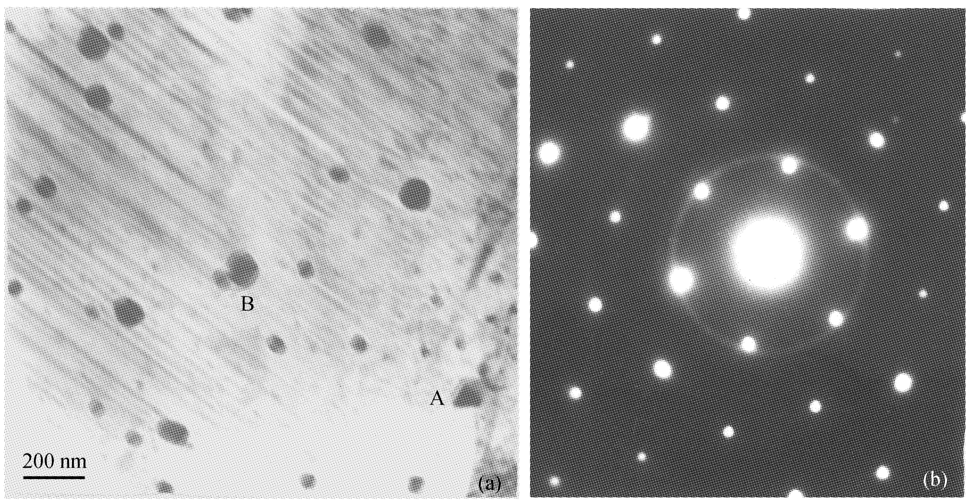

Fig. 2. TEM microstructure of the same ion-polished specimen after exposure of 90 d in atmosphere (a) and the corresponding diffraction pattern (b).

The oxide grain A in fig. 3 forms around dislocation lines. It is apparent that the grain around dislocation lines is bigger than any others in the selected zone, because dislocations have much higher energy than stacking faults, they are unstable and liable to reaction with the surrounding media. Owing to the severe oxidation around dislocation lines, the stacking faults nearby almost disappear thoroughly.

The above experimental result further demonstrates that even at room temperature, due to the long-term contact with atmosphere and a large number of defects on the surface, Cu-based SMAs oxidize certainly. The formation of oxides not only changes the surface microstructure and lowers the SME of the alloys, but it also produces unfavorable effect on SME and suppresses the shape recovery as a result of the high strength, high hardness and high brittleness of the oxides. This, of course, results in the reduction of actuation reliability of the SMA actuators

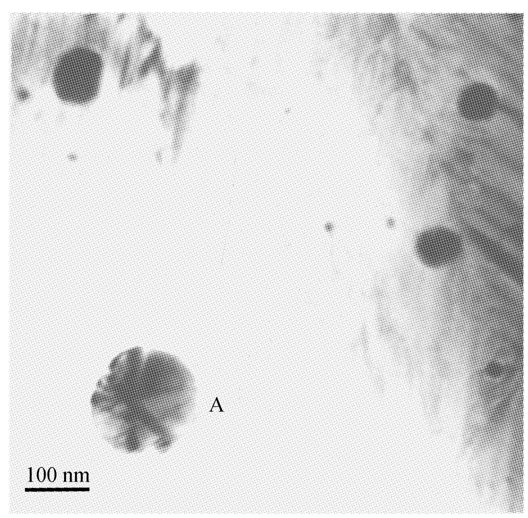

Fig. 3. The oxide grain formed around dislocation lines.

during practical application. The fact that the oxidation happens on the surface of Cu-based SMA at room temperature in ambient atmosphere indicates that it is necessary to take certain measures to protect the surface of Cu-based SMA actuators so as to lessen or put an end to oxidation. These measures are helpful for the actuators to give full play to their shape memory property and ensure the stability and reliability of the working actuators.

3 Conclusion

Compared with the microstructure of the quenched CuZnAlMnNi alloy, when the ion-polished specimen was exposed 90 d at room temperature in atmosphere, the oxide grains form along the planes of stacking faults in martensite plates, at the stacking fault tetrahedrals or around the dislocation lines, which leads to the decrease of the stacking faults, and even to a locally complete disappearance. The alteration of the microstructure gives rise to the reduction of SME of the CuZnAlMnNi alloy. So it is necessary to take some measures to protect the surface of the SMA actuators.

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