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Influence of recovery heating rate on shape memory effect in up-quenched Cu−Al−Mn alloy

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Abstract: The effect of recovery heating rate on shape memory effect of the up-quenched Cu−8.88Al−10.27Mn (mass fraction, %) alloy was investigated by optical microscopy, electron transmission microscopy (TEM) and electrical resistivity measurement. It is found that the shape recovery rate decreases as the heating rate decreases. It can reach 75% when the heating rate is 20 °C/min, while it is only 8% when the heating rate is 1 °C/min. In situ microstructure observation indicates that the dependence of shape memory effect on recovery heating rate is caused by the stabilization of twinned martensite induced by deformation. The analysis of electrical resistivity shows that the stabilization of twinned martensite may be ascribed to formation of compound defects of vacancies and dislocations at the boundaries of twinned martensite during the slow heating. The compound defects prevent the reverse transformation of twinned martensite.

Key words: Cu−Al−Mn alloy; shape memory effect; martensitic phase transformation; twinning

1 Introduction

For Cu-based shape memory alloys (SMAs), martensitic stabilization is the big concern when they are employed in the field of engineering and medical science [1]. The martensitic stabilization refers to the phenomenon in which the reverse transformation temperature A_f is increased with increasing the aging time, and eventually the reverse transformation is suppressed by aging. This time-dependent behavior is critical to the reliability of devices using SMAs as it is desirable to have a reproducible and stable transformation temperature. Therefore, understanding the origin of martensitic stabilization is of both fundamental and practical importance and many researches have been conducted to find the proper methods to suppress it. So far, several mechanisms have been put forward to explain the origin of martensitic stabilization for Cu-based alloy, such as martensite reordering [2−4], precipitate effect [5], excess vacancy pinning behavior [6−8] and short-range order of point defects [9]. Among these researches, studies for martensitic stabilization behavior are generally conducted for alloys at a constant temperature. However, in the practical application, a non-isothermal heating process maybe need to active the Cu-based devices to function properly when they are in service, but at present there are still a few reports for this kind of cases [10,11]. In the reported studies, martensitic stabilization was most found in directly quenched Cu-based alloys, such as Cu−Zn−Al and Cu−Al−Ni alloy, after a low temperature aging, and it is well known that an up-quenching or step-quenching heat treatment can markedly suppress the martensitic stabilization in both Cu−Zn−Al and Cu−Al−Ni alloys [12−15]. However, in our study, an interesting phenomenon was observed that the shape memory effect (SME) of up-quenched Cu−8.22Al−10.27Mn alloy had a significant dependence on recovery heating rate. In other words, the martensitic stabilization still occurred in the alloy even it had been subjected to up-quenching treatment, which was not reported before.

In this work, the effects of recovery heating rate on the shape memory effect and microstructure evolutions before and after heating in the deformed up-quenched Cu−Al−Mn alloy were investigated. Based on the experimental results, the relationship between recovery heating rate and martensitic stabilization was mainly discussed.

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2 Experimental

The alloy with nominal composition of Cu−8.22Al−10.27Mn (mass fraction, %) was prepared by melting pure elements Cu (purity>99.9%), Al (purity>99.9%) and Mn (purity>99.9%) in vacuum induction furnace. After homogenization at 1093 K for 23 h, the ingot was squeezed into bars at 1073 K and finally cold drawn into wires of 1.5 mm in diameter. All samples for test were cut from the as-cold drawn wires. The as-cold drawn samples were solution treated at 1123 K for 15 min, followed by quenching in water at room temperature. The quenched samples were immediately held in boiling water for 15 min, which was the up-quenching (UQ) treatment.

The shape memory effect of the up-quenched samples was measured at room temperature by a bending test. Details of the measurement have been described elsewhere [16,17]. Different recovery heating rates were utilized to heat samples to 150 °C, and then shape recovery ratios were calculated. The transformation temperatures were determined by an electrical resistivity−temperature curve.

The microstructure was examined by the OLYMPUS CK-40M optical microscope. To determine the local nature of microstructural changes, a focused ion beam (FIB) based technique was used to locate, isolate, and prepare cross-sectional TEM specimens from precise positions in the specific area. An in-situ lift-out technique was used to prepare the final TEM specimen. A Pt layer was first deposited to cover the region. Then, two trenches were made around this area and a membrane was milled down to 1 μm using 30 kV Ga^+ ion beam. The membrane was picked out and welded onto copper grid. Finally, the 1 μm membrane was polished down to electron transparency using 5 kV Ga^+ ion beam. TEM specimens were examined by a Tecnai F20 electron microscope at 200 kV.

3 Results and discussion

3.1 Shape memory effect

Figure 1 shows the shape recovery rate of up-quenched samples as a function of recovery heating rate when the bending deformation was 5%. From the results, it was shown that the shape recovery rate reached 75% when the recovery heating rate was 20 °C/min, while the shape recovery rate reached 8% when the recovery heating rate was 1 °C/min. The lower the recovery heating rate is, the lower the shape recovery rate is.

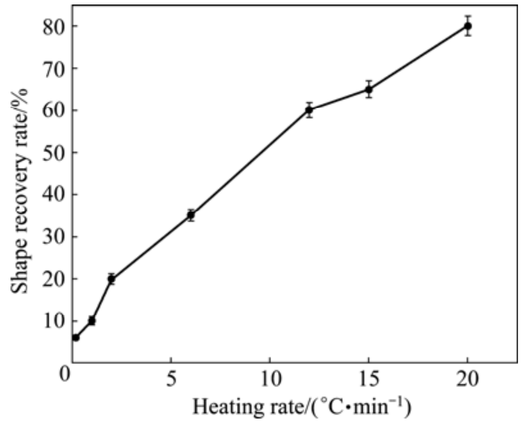

Fig. 1 Relationship between shape recovery rate and recovery heating rate in up-quenched Cu−8.22Al−10.27Mn alloy

3.2 Microstructure observation

Different areas in an up-quenched sample before and after bending deformation were selected and the optical microstructure evolutions of the same sample were observed in sequence, and the results are shown in Figs. 2(a)−(f). It was found that most of the phases consisted of martensite at room temperature before deformation (Fig. 2(a)) because the martensitic transformation temperatures T_s and T_f were 69 °C and 23 °C, respectively. After deformation, some thin parallel plates were introduced inside a block martensite, as indicated by the white arrows in Figs. 2(b) and (e). When the deformed sample was heated to 150 °C at 20 °C/min and then cooled down to room temperature, most of these introduced parallel plates disappeared (Fig. 2(f)). In contrary, most of them were still observed at room temperature when the heating rate was 1 °C/min (Fig. 2(c)).

To get further insight into the nature of these parallel plates, the above samples were studied by TEM. Here FIB technique was employed to locate the precise positions for TEM specimens preparation where several parallel plates existed, as shown in the square area in Fig. 3(a). Several positions were selected randomly at different parallel plate areas for each sample. Selected-area electron diffraction (SAED) patterns acquired at the single plate were indexed as M18R martensite. More interestingly, most of these parallel M18R martensites formed A/D boundaries with twin plane $(20\bar{2}0)_{18R}$ (Fig. 3(c)) [18,19]. This result shows that the thin parallel plates are twinned deformation martensite. Furthermore, these twinned deformation martensites will be stabilized when the recovery heating rate is rather low.

3.3 Electrical-resistivity behavior

Figure 4 shows the change of electrical resistivity ($\rho-\rho_0$) during the heating process at different heating

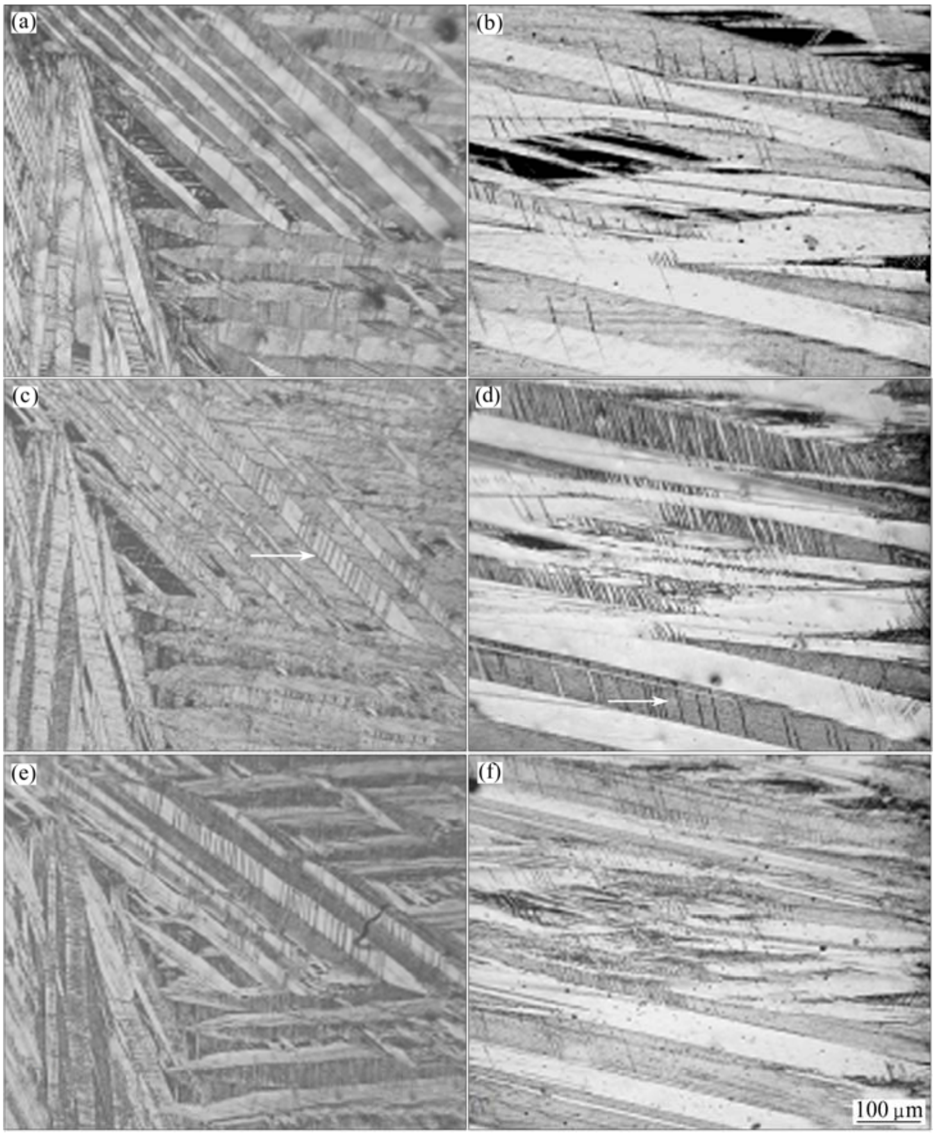

Fig. 2 In-situ optical micrographs of up-quenched Cu−8.22Al−10.27Mn alloy under different conditions: (a,b) Initial heat treatment without deformation for two different areas; (c,d) After 5% bending deformation for two different areas; (e,f) After being heated at 1 °C/min and 20 °C/min for two different areas, respectively

rates for up-quenched samples after 5% bending deformation. The electrical resistivity started to decrease slowly by heating due to the reverse martensitic transformation. When the heating rate was 1 °C/min, it decreased till 120 °C, which implied the finish of the transformation. However, the transformation completed over 120 °C when heating rate was either 10 °C/min or 20 °C/min. In addition, the higher the heating rate was, the greater the change of electrical resistivity was. This result revealed that the higher the heating rate was, the more martensite reverted to parent phase β. Specially note that the change of electrical resistivity behaved differently during the process of holding after the samples were heated to 140 °C with different heating rates. The electrical resistivity almost remained constant after the sample was heated with heating rate of 1 °C/min. However, it kept on decreasing slowly after samples were heated with heating rates of 10 °C/min and 20 °C/min.

The UQ treatment at 100 °C for 15 min is usually enough to suppress the stabilization of thermal martesnite in Cu−Zn−Al alloys because of the extinction of most of quenched-in vacancies and the increase of ordering of parent phase [14]. However, in our studies, the stabilization of twinned deformation martensites occurred in the Cu−8.22Al−10.27Mn alloy that had been subjected to UQ treatment when the recovery heating rate was rather low.

After deformation, some defects, such as dislocation, will be introduced especially at the boundaries of the

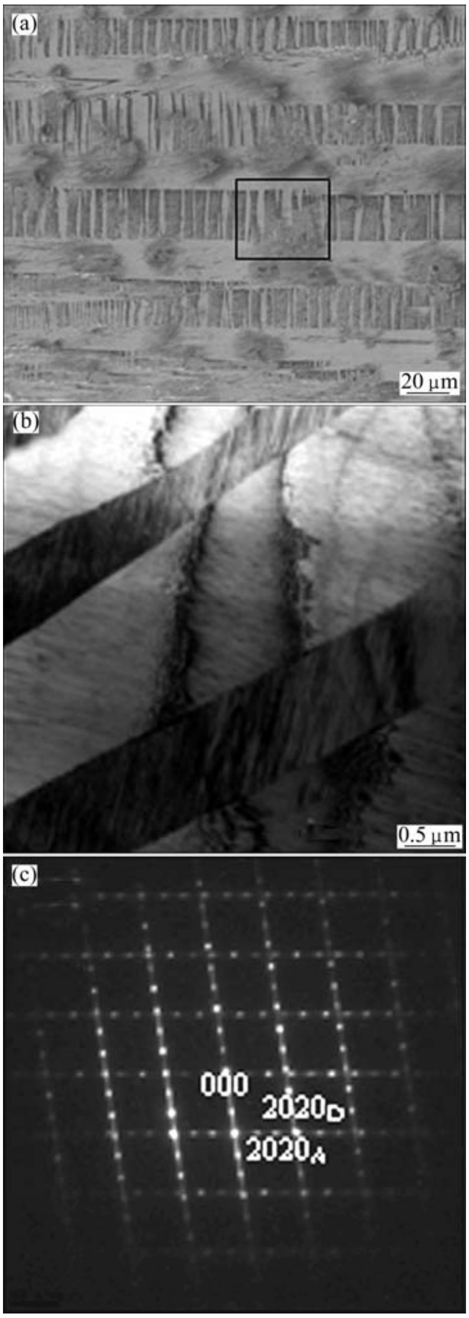

Fig. 3 Micrographs of up-quenched Cu−8.22Al−10.27Mn alloy after 5% deformation: (a) SEM image of parallel plates; (b) TEM bright field image of parallel plates in area designated by rectangle in (a); (c) Selected-area electron diffraction pattern of parallel plates showing A/D twin boundary

twinned deformation martensite [19,20]. During the process of heating, the vacancy will be attracted and trapped by these dislocations because they can combine and form a compound defect with lower energy. Considering the vacancy motion is a diffusive process, the interaction between dislocations and vacancies would behave differently at different heating rates. When the heating rate is rather low, there will be enough time for the formation of the compound defect. The stable

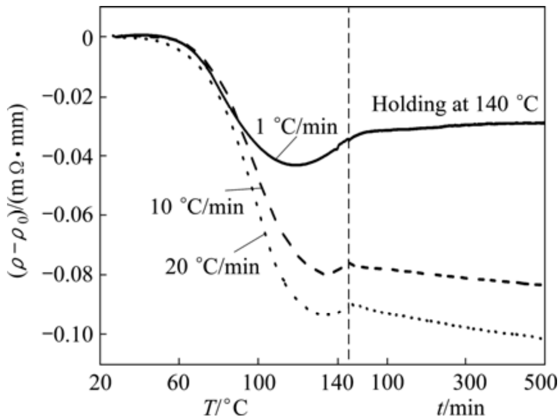

Fig. 4 Change of electrical resistivity during process of heating at different rates and then holding at 140 °C for up-quenched Cu−8.22Al−10.27Mn alloy after 5% deformation

compound defect will inevitably pin the boundaries of the twinned deformation martensite, leading to its stabilization. When the heating rate is high, there will not be enough time for the formation of the compound defect. Consequently, the twinned deformation martensite can revert to parent phase. Our present electrical resistivity measurements in the deformed up-quenched Cu−8.22Al−10.27Mn confirmed this. During slow heating of 1°C/min, the vacancies had been trapped by the dislocations. As a result, it is difficult for them to disappear during the process of holding at 140 °C because the compound defect formed by vacancies and dislocations is more energetically stable. Thus the electrical resistivity almost remained constant when holding at 140 °C. On the contrary, more vacancies still remained when the sample was heated with the heating rates of 10 °C/min and 20 °C/min because there was not enough time for the formation of the compound defect. Consequently, the vacancies would further disappear to reach equilibrium when holding at 140 °C, leading to the decrease of the electrical resistivity.

Although most of the quenched-in vacancies become extinct after UQ treatment, these results indicate that the remained vacancies play an important role in the reverse transformation of the twinned deformation martensite although they have little effect on that of thermal martensite. It can be expected that further decreasing the concentration of vacancies will suppress the occurrence of the stabilization of twinned deformation martensite and it sheds light on our next work to study how to suppress this recovery heating rate phenomenon.

4 Conclusions

1) Shape memory effect shows strongly dependence on recovery heating rate in Cu−8.22Al−10.27Mn alloy

subjected to up-quenching treatment. The shape recovery rate decreases from 75% to 8% as the heating rate decreases from 20 °C/min to 1 °C/min.

2) In-situ microstructure observation indicates that the dependence of shape memory effect on recovery heating rate is related to the stabilization of twinned martensite induced by deformation. When the recovery heating rate is low, most of these twinned martensites still maintain after heating.

3) Electrical resistivity measurement shows that the remained excess vacancy after up-quenching treatment plays an important role in the stabilization of the twinned deformation martensites. When the recovery heating rate is slow, the vacancy will be trapped easily by the dislocations at boundaries of twinned martensite because they can combine and form a compound defect with lower energy. The compound defect pins the boundaries of twinned martensite and thus results in the stabilization of twinned martensite.

References

[1] MADDEN J D. Artificial muscle begins to breathe [J]. Science, 2006, 311: 1559−1560.

[2] CIATTO G, SOLARI P L, de PANFILIS S, FIORINI A L , AMADORI S, PASQUINI L, BONETTI E. Atomic ordering in CuZnAl shape memory alloys investigated via X-ray absorption and diffraction [J]. Appl Phys Lett, 2008, 92: 241903−241905.

[3] SAULE F, AHLERST M. Stability, stabilization and lattice parameters in Cu−Zn−Al martensites [J]. Acta Metall Mater, 1995, 43: 2373−2384.

[4] LI Zhou, XIAO Zhu, BAO Ji-qing, XU Gen-ying, ZHENG Feng. Atom exchange of martensite in Cu−13Zn−15Al alloy during non-isothermal aging [J]. Transactions of Nonferrous Metals Society of China, 2006, 16(5): 1064−1068.

[5] ASANOVIC V, DELIJIC K, LEKA Z. Aging effects in Cu−Zn−Al shape memory alloy [J]. Mater Sci Forum, 2004, 187: 453−454.

[6] SURESH N, RAMAMURTY U. Aging response and its effect on the functional properties of Cu−Al−Ni shape memory alloys [J]. J Alloys Compd, 2008, 449: 113−118.

[7] KUSTOV S, PONS J, CESARI E, van HUMBEECK J. Pining induced stabilization of martensite, Part II: Kinetic stabilization in Cu−Zn−Al alloy due to pinning of moving interfaces [J]. Acta Mater, 2004, 52: 3083−3096.

[8] CHEN Shu-chuan, XU Zu-yao, YANG Fan, ZHANG Ji-hua. Stabilization of martensite and parent phase ordering in a Cu−Zn−Al alloy [J]. Acta Metallurgica Sinica, 1992, 5(1): 1−6. (in Chinese)

[9] REN X B, OTSUKA K. Origin of rubber-like behaviour in metal alloys [J]. Nature, 1997, 389: 579−582.

[10] STICE J D, WAYMAN C M. Observations of aging effects in a Cu−Sn shape memory alloy [J]. Metall Trans A, 1982, 13: 1687−1697.

[11] KUSTOV S, GOLVANDIN S, SAPOZHNIKOV K, CESARI E, van HUMBEECK J, de BATIST R. Influence of martensite stabilization on the low-temperature non-linear anelasticity in Cu−Zn−Al shape memory alloys [J]. Acta Mater, 2002, 50: 3023−3044.

[12] MIELCZAREK A, KOPP N, RIEHEMANN W. Ageing effects after heat treatment in Cu−Al−Mn shape memory alloys [J]. Mater Sci Eng A, 2009, 521−522: 182−185.

[13] OBRADÓ E, MAÑOSA L, PLANES A, ROMERO R, SOMOZA A. Quenching effects in Cu−Al−Mn shape memory alloy [J]. Mater Sci Eng A, 1999, 273−275: 586−589.

[14] SCARSBROOK G, COOK J M, STOOBBS W M. The stabilization of martensite in Cu−Zn−Al shape memory alloys [J]. Metall Trans A, 1984, 15: 1977−1986.

[15] van HUMBEECK J, JANSSEN J, MWAMBA N, DELAEY L. The stabilisation of step-quenched copper-zinc-aluminum martensite, Part I: The reverse transformation temperatures [J]. Scripta Metall, 1984, 18: 893−898.

[16] JIAO Y Q, WEN Y H, LI N, HE J Q, TENG J. Effect of solution treatment on damping capacity and shape memory effect of a CuAlMn alloy [J]. J Alloys Compd, 2010, 491: 627−630.

[17] JIAO Yu-qin, LI Ning, WEN Yu-hua, HE Jia-qiang. Ageing effect on martensite transformation temperature and shape memory properties of Cu−17Al−10Mn alloy [J]. The Chinese Journal of Nonferrous Metals, 2009, 19(1): 96−100. (in Chinese)

[18] ZHANG J X, ZHENG Y F, HUANG B M, CAI W, ZHAO L C, Characteristics of the AD type twin boundary in 18R martensite in a Cu−Zn−Al alloy [J]. Mater Sci Eng A, 1998, 251: 150−156.

[19] WANG R, GUI J, CHEN X M, TAN S S. EBSD and TEM study of self-accommodating martensites in Cu75.7Al15.4Mn8.9 shape memory alloy [J]. Acta Mater, 2002, 50: 1835−1847.

[20] STOIBER J, GOTTHARDT R. Changes in stacking fault sequences during the martensitic phase transformation in Cu−Zn−Al shape memory alloys [J]. Mater Sci Eng A, 1993, 164: 443−448.

回复加热速度对上淬 Cu−Al−Mn 合金的形状记忆效应的影响

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摘 要：采用光学显微镜、透射电子显微镜和电阻率测量技术，研究回复加热速度对上淬后 Cu−8.8Al−10.27Mn 合金的形状记忆效应的影响。结果表明：材料形状回复率随回复加热速度的减小而减小。当回复加热速度为 20 °C/min 时，形状回复率可达 75%；而当回复加热速度为 1 °C/min 时，其形状回复率仅为 8%。原位金相观察表明：材料的形状记忆效应是由马氏体逆转变后的残余孪晶形变马氏体的稳定性引起的。电阻率分析结果表明：残余孪晶形变马氏体的稳定性与其界面处空位与位错在慢速加热时形成的复合缺陷相关。而复合缺陷的形成会阻碍孪晶形变马氏体的逆转变。

关键词：Cu−Al−Mn 合金；形状记忆效应；马氏体转变；孪晶

(Edited by Chao WANG)