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Electric resistivity anomaly and martensitic phase transformation in Cu–Al–Zn alloy

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The quenched Cu–16.5Al–14.9Zn alloy has been examined by electric resistivity and X-ray diffraction measurements. It is confirmed that electric resistivity anomaly (ERA), observed so far in the quenched Au–Cd and Au–Cu–Zn alloys, appears also in the present alloy quenched from the Heusler type β_1-phase region followed by heating. ERA is considered to be due to annihilation of quenched-in vacancies with activation energy of about 0.33 eV. The appearance of ERA modulates considerably schema of the martensitic phase transformation, especially the transformation temperature. In this paper, the reason why ERA does not appear in the case quenched from disordered β-phase region, and the quenching effect on premartensitic and other behaviours are discussed in detail.

1. Introduction

As previously reported in this journal [1], as quenched β_1-phase of Au–Cd alloys exhibits the electric resistivity anomaly (ERA), with an irreversible characteristic to thermal cycles. That is, we can observe such an ERA only once in the first heating beyond a critical temperature, T_a, after quenching and thereafter it never appears in any thermal processes. The T_a temperature depends on both the alloy compositions and the quenching temperature, T_q. The β_1-phase has the CsCl type structure before and even after ERA occurs and hence ERA is not due to any phase transformation. Based on the detailed analysis, we conclude that ERA is originated from the annihilation of the quenched-in vacancies with an activation energy of about 0.35 eV.

It must be noticed that ERA has a marked influence on the martensitic phase transformation of Au–Cd alloys, although such an ERA effect depends on the alloy compositions. In the case of the quenched Au–47.5 at % Cd alloy, for example, the electric resistivity increases during the martensitic phase transformation when the alloy is cooled immediately after quenching, while the reverse change occurs after the alloy once exhibits ERA. Furthermore, the transformation temperatures rise considerably as a consequence of the appearance of ERA; an increment of the M_s (martensite start) temperature attains about 30°. The transformation behaviour after ERA occurs is quite the same as that of the slowly cooled alloy which does not exhibit ERA. The ERA effect can be also observed in the other quenched Au–Cd alloys with various compositions.

The results mentioned above indicate clearly that ERA as a reflection of the quenching effect plays an essential role in the martensitic phase transformation in the β_1-phase of the Au–Cd alloys. At the present stage, however, ERA has been found only in Au–Cd alloys thus raising the question whether ERA is a property peculiar to Au–Cd alloys. Therefore, it is important to examine this problem in order to understand the nature of the martensitic phase transformation. From this viewpoint, we have studied the quenching effect concerning the martensitic phase transformation in the β-phase alloys and found that ERA occurs also in several alloys other than Au–Cd. A brief result on Au–Cu–Zn alloy has already been reported [2]. In the present paper, we will consider in detail the case of Cu–Al–Zn alloy.

2. Experimental procedure

In the present study, we use a β-phase alloy of Cu–Al–Zn system. The alloy was prepared by melting together the component metals copper, aluminium and zinc of 99.999% purity in an argon-filled quartz tube at 1373 K and shaking vigorously many times. It was homogenized at 1073 K for three days and then quenched into ice water. The alloy composition was determined by using an energy dispersive X-ray analyser to be Cu : 68.6, Al : 16.5 and Zn : 14.9 in atomic units. The high temperature phase of this alloy, i.e. the β-phase with the bcc structure exists stably above about 820 K. When quenched from the β-phase region, the metastable β_1-phase with a CsCl type structure appears. In this β_1-phase, an ordering reaction to the Heusler type structure occurs by heating up to about 350 K.

For the electric resistivity measurements, we prepared strips of sheet 0.2 mm thick cut from the alloy ingot with a spark cutter. Just before the measurements were taken, the strips were annealed and then quenched into ice water. The annealings in the disordered β-phase and the Heusler type β_1-phase regions were carried out respectively in argon-filled pyrex glass tubes for 300 sec and by direct immersion in heated silicone-oil bath for 600 sec. The electric resistivity was measured by a 4-terminal method, with 5 deg min^{-1}, under atmosphere of mixed gases of argon and helium. By using an X-ray diffractometer, we analysed crystal structures for powder specimens

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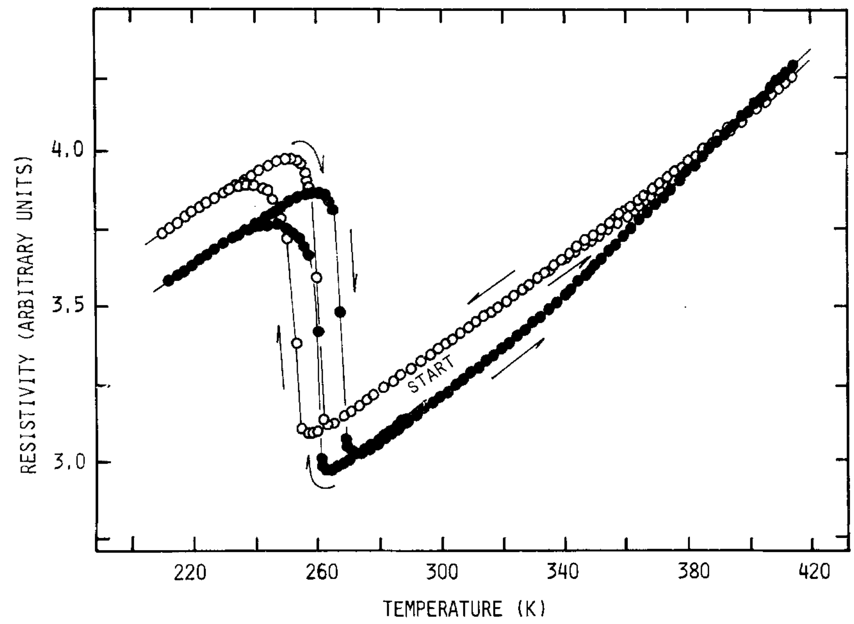

Figure 1 Electric resistivity against temperature curves of the specimen quenched from 923 K. Solid and open circles correspond to the first and second thermal cycles, respectively.

prepared from filings of part of the alloy ingot and heat-treated in argon-filled pyrex glass tubes.

3. Results

Fig. 1 shows a result of the specimen quenched from 923 K. The series of solid circles shows the martensitic phase transformation to occur by cooling at about 265 K. Successive heating causes the reverse transformation at about 260 K with small hysteresis. Such a schema of the resistivity changes is repeated every thermal cycle so far as the heating does not increase beyond about 350 K. Once heated over this limit, however, the gradient of the heating curve begins to increase slightly, and then the subsequent behaviour changes so that the transformation temperatures fall downward by about 5° accompanied by an increase in the resistivity values, as the series of open circles shows. All the specimens quenched from the β-phase region exhibit similar resistivity phenomena.

When the specimens with the Heusler type structure are quenched, on the other hand, the resistivity curves exhibit ERA as shown in Fig. 2. In this case, the specimen is first quenched from 923 K and then annealed at 513 K for 600 sec, followed by quenching into ice water. During such an annealing, the ordering to the Heusler type structure is completed. The series of solid circles corresponding to the first thermal cycle indicates that the martensitic and reverse transformations occur respectively at about 245 and 230 K. By successive heating, the resistivity increases in a linear fashion up to about 355 K, and then the temperature gradient of the resistivity begins to decrease, i.e. ERA appears. When cooled in the second thermal cycle shown by the series of open circles, the resistivity decreases monotonically and the martensitic phase transformation occurs at about 256 K. This is about 10 K higher than that in the first thermal cycle. It must be noticed that ERA does not appear in the second heating process. Such resistivity behaviour is repeated in the following thermal cycles.

ERA also appears in the other specimens quenched from various temperatures in the Heusler type β_1-phase region. Analysis of the results lead to the conclusion that the resistivity drop due to ERA depends on the quenching temperature. Fig. 3 shows that the logarithm of $\Delta\varrho/\varrho_0$ at ERA-state temperature, T_a, changes linearly against the reciprocal quenching temperature, $1/T_q$; $\Delta\varrho$ is the magnitude of the resistivity drop and ϱ_0 the resistivity on cooling. Clearly the Arrhenius relation is satisfied. That is, ERA

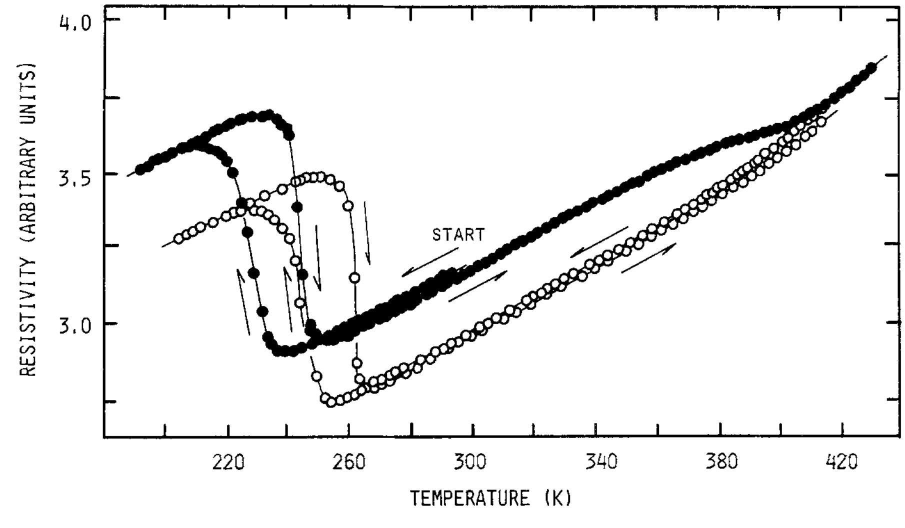

Figure 2 Electric resistivity against temperature curves of the specimen quenched from 513 K. Solid and open circles correspond to the first and second thermal cycles, respectively.

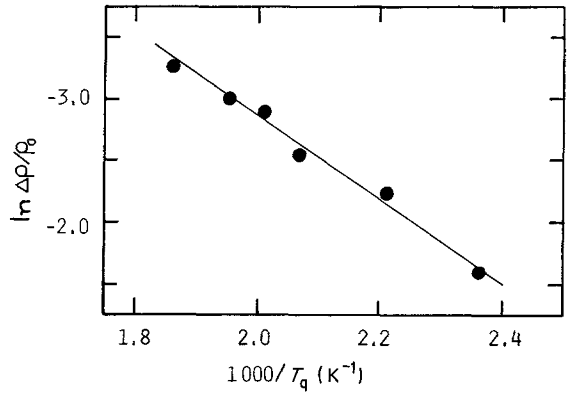

Figure 3 Relation between logarithm of the magnitude of ERA and reciprocal quenching temperatures T_q.

corresponds to a thermally activated process such as the annihilation of the quenched-in vacancies. The activation energy is estimated to be about 0.33 eV.

The M_s (martensite-start) temperature is one of the most important factors concerning the phase stability in the martensitic phase transformation. In the present case, increasing the quenching temperature T_q in the Heusler type β_1-phase region produces a decrease of the M_s point on the first cooling curve. Once ERA occurs, however, the M_s point shifts to about 256 K irrespective of T_q, as shown in Fig. 4. It is clear that the appearance of ERA means a complete annihilation of the quenching effect, which is so amplified with elevating T_q that it depresses the martensitic phase transformation. It is also noticed that the M_s point after ERA appears is nearly the same as that of the second cooling process in Fig. 1.

Finally, we show briefly that ERA is not concerned with any structural change. Fig. 5 is a part of the X-ray measurements. The superlattice reflections 1 1 1 and 2 0 0, which are the Heusler type indices, can be used as a measure to determine the superlattice structure of the β_1-phase. Pattern (a) proves that the specimen quenched from 923 K has a CsCl type structure; here 2 0 0 must be substituted as 1 0 0 in the CsCl type indices. Once heated over about 350 K, an ordering reaction to the Heusler type structure occurs. This specimen, however, does not exhibit ERA. The specimen quenched from 513 K, on the other hand, gives patterns (b) and (c), which correspond to the states before and after ERA appears, respectively. Hence the specimen has the Heusler type structure regardless of ERA. In these patterns no detectable intensity change can be observed. Consequently, we conclude that neither phase transformation nor change of the degree of order is responsible to ERA.

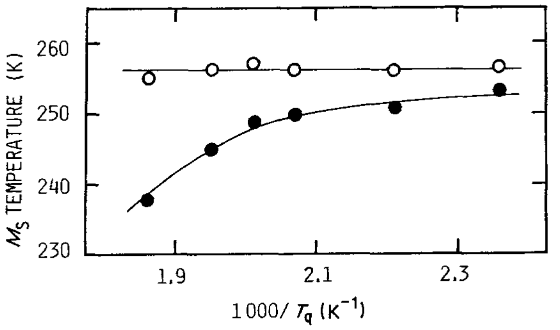

Figure 4 Relation between the M_s temperatures and reciprocal quenching temperatures T_q. Solid and open circles correspond to the M_s temperatures before and after ERA appears, respectively.

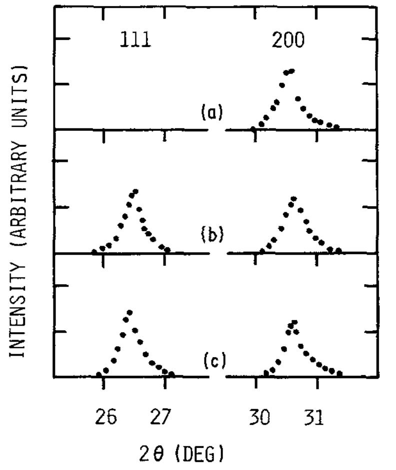

Figure 5 X-ray diffraction profiles of the superlattice reflections 1 1 1 and 2 0 0. (a) Specimen quenched from 923 K, (b) and (c), corresponding to the states before and after ERA appears, respectively, specimens quenched from 513 K.

4. Discussion

In the present study, we find ERA also occurs in Cu–Al–Zn alloy. The obtained results suggest strongly that ERA, observed so far in Au–Cd and Au–Cu–Zn alloys [1, 2], is not a property unique to such alloys but might appear in the other quenched β-phase alloys. As frequently mentioned, schema of the martensitic phase transformation are remarkably influenced by the appearance of ERA. Consequently, it is very important to examine the nature of ERA to understand the martensitic transformation mechanism. From this viewpoint, we will consider several problems concerning ERA in the following summary of results.

1. The specimen quenched from the β-phase region has the CsCl type structure and does not exhibit ERA. By heating above about 350 K, an ordering reaction to the Heusler type structure occurs, and then the M_s point falls to about 255 K with subsequent cooling.
2. The specimen quenched from the β_1-phase region shows ERA. Before and after ERA appears, the Heusler type structure remains unchanged; also no change of the degree of order can be detected.
3. The resistivity drop due to ERA so depends on T_q that the Arrhenius relation is satisfied, and hence a thermally activated process with the activation energy of 0.33 eV is responsible to ERA.
4. Increasing T_q in the Heusler type β_1-phase region lowers the M_s point. Once ERA appears, however, the M_s point of all the specimens with various T_q converges at 256 K, which is nearly the same as that of the case quenched from the β-phase region and then heated over about 350 K.

Based on the above results, we will first consider the nature of ERA. Evidently ERA has no relation to any structural change but it corresponds to the disappearance of the quenching effect due to heating. As is well accepted, a typical role of the quenching is to introduce excess vacancies into the quenched specimen, the present case being no exception. For example, Ghilarducci and Ahlers [3, 4] have observed several kinds of internal friction peaks associated with excess vacancies quenched into Cu–Al–Zn alloys from temperatures ranged in the Heusler type β_1-phase region. We must also emphasise that the magnitude of ERA satisfies the Arrhenius linearity against $1/T_q$. If we take these facts into consideration, it is quite reasonable to conclude that ERA is originated from the annihilation of the quenched-in vacancies, as in the cases of Au–Cd and Au–Cu–Zn alloys [1, 2]. These circumstances may suggest that ERA is not due to a peculiar property of only the few alloys so far examined but so with many other β-aphase alloys.

Now we consider the problems concerning quenching from the disordered β-phase region. T_q of this case is much higher than that of the quenching from the β_1-phase region. Therefore, it is natural to suppose that the quenched specimen of this case will include so many quenched-in vacancies when compared to the latter case. It is also likely that ERA will appear more markedly than that of the latter case, if ERA is due to quenched-in vacancies. Nevertheless ERA is not observed in this case as shown in Fig. 1. The reason why ERA does not appear is not clear at the present stage but the following interpretation is probable.

During quenching from the β-phase region, the specimen undergoes two kinds of processes, the ordering to the CsCl type structure and the freezing of non-equilibrium excess vacancies. For any ordering reaction, vacancies play in general an essential role, and hence the above processes cannot proceed independently, but occur in close correlation. Therefore, characteristics of the quenched specimen on the present subject seem to be quite different from those of a specimen quenched from the Heusler type β_1-phase region without any ordering reaction. When the specimen is heated above ~ 350 K, it undergoes the second ordering reaction to the Heusler type structure as proved by the X-ray study. This process proceeds in association with a very complicated behaviour of vacancies, because the temperature range in the region of 350 K at which the ordering occurs corresponds to T_a, the annihilation temperature of the quenched-in vacancies, as observed in Fig. 2. It is also taken into account that, if the ordering to the Heusler type structure and the annihilation of the quenched-in vacancies are independent phenomena, they act commonly to decrease the electric resistivity. However, here this is not so. Thus the reason why ERA does not appear might be attributed to the two kinds of ordering reactions occurring, respectively, in complicated correlation with excess vacancies. Nevertheless it may be possible to observe ERA even in an alloy quenched from the β-phase region, provided that the alloy has a different composition from that of the present case and undergoes the ordering to the Heusler type structure at a higher temperature than T_a.

In addition, Fig. 1 shows that the M_s temperature decreases once heated above about 350 K. Since this heating causes the ordering to the Heusler type structure accompanied by the annihilation of excess vacancies, such a depression of the M_s temperature means that the CsCl type lattice including quenched-in vacancies is unstable as compared with the Heusler type one without excess vacancies. As shown in Fig. 4, on the other hand, heating above T_a raises the M_s temperatures of the specimens quenched from various T_q in the Heusler type β_1-phase region. This means that the annihilation of the quenched-in vacancies stimulates unstability of the Heusler type lattice, i.e. excess vacancies stabilize the Heusler type lattice while the reverse occurs in the CsCl type lattice. These situations indicate clearly that the role of excess vacancies depends strongly on the schema of the atomic arrangements in the crystal lattice. The degree of off-stoichiometry in alloys would influence greatly the lattice-vacancy correlations as observed in Au–Cd and Au–Cu–Zn alloys [1, 2].

Fig. 4 also shows that the M_s temperature varies very sensitively with vacancy concentrations. Therefore, if excess vacancies in the specimen are mobile even at a lower temperature than T_a, the ageing effect such as time dependent change of the M_s temperatures in the quenched specimen is also expected to appear. In fact, there is evidence for the high mobility of vacancies, the ageing effect on the transformation temperatures and other effects in several kinds of Cu–Al–Zn alloys [5–7]. These very complicated phenomena in the quenched Cu–Al–Zn alloys, however, can be removed by heating just above T_a and, after such a treatment, the martensitic and reverse transformations occur stably and reproducibly for repeated thermal cycles.

We now mention briefly the effect of quenched-in vacancies on the preceding phenomena of the martensitic phase transformation. Since the M_s temperatures vary distinctly after the appearance of ERA, the premartensitic anomalies so far observed must be strongly modulated by the quenched-in vacancies. The elastic behaviour in Au–Ag–Cd alloys, as reported previously [8], is evidence of such a situation. In the case of Au–35.0Ag–47.5Cd alloy, for example, the M_s temperatures of both the specimens quenched and slowly cooled from about 570 K are about 120 and 280 K, respectively. The elastic softenings in the quenched specimen are more remarkable than those in the slowly cooled one and, in addition, the magnitude of the elastic constants in the former is about ten times smaller than that in the latter. These phenomena are explained as follows. The quenched-in vacancies introduced into the specimen by quenching stabilize the β_1-phase and hence prevent the martensitic transformation occurring. Therefore, in order to cause the phase change under such a barrier, the elastic constants as the resistance to the lattice shears must become considerably softer than the slowly cooled case. Concerning the elastic anomalies, the results of Cu–Zn–Al alloys obtained by Planes *et al.* [7] are also of interest. Here, the elastic constant C' corresponding to the $(1\,1\,0)[1\,\bar{1}\,0]$ shear exhibits rapid decrease at the initial stage of ageing near room temperature. They have explained this phenomenon as being due to the decrease in vacancy concentration during ageing. This situation is quite similar to the cases of Au–Ag–Cd alloys. Besides the elastic anomalies mentioned here, diffraction anomalies as the premartensitic phenomena are also markedly influenced by the quenched-in excess vacancies [9, 10].

Concerning the martensitic transformation, the nucleation mechanism is one of the most important subjects to be examined. As frequently proposed [11–15], lattice defects such as vacancies are expected to be available as nucleation centres. Thus localized and anisotropic stress fields around the lattice defects will enhance favourable anharmonicity for the lattice shears to form the martensites. Therefore, it is of interest to examine the effect of the quenched-in vacancies on the anharmonic behaviours in the premartensitic state.

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