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Ordering transitions in quenched $Au_7Cu_5Al_4$ alloy and effect of order on martensitic transformation

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ABSTRACT

A metastable phase of DO_3 ordering was observed between 171.6 °C and 281.3 °C in quenched $Au_7Cu_5Al_4$ alloy followed by heating at 2 °C/min. With further increasing of temperature, B2 → A2 order–disorder transition happened above 495.3 °C and finished at 616.5 °C. The evolution of metastable DO_3 ordering at 200 °C was also studied. Martensitic transformations of corresponding ordering structures were investigated by DSC. It is found that both the DO_3 and B2 ordering suppressed the martensitic transformation start (M_S) temperature dramatically, contrary to the $L2_1$ ordering which favors martensitic transformation. The effect of order on martensitic transformation in quenched $Au_7Cu_5Al_4$ alloy was also discussed.

1. Introduction

The β phase in the ternary $Au_7Cu_5Al_4$ alloy is known to give a displacive transformation and forms an interesting surface texture, which results in a new family of gold alloys known as 'Spangold' [1,2]. Shape memory effect was also investigated in $Au_7Cu_5Al_4$ alloy with many excellent properties, including good castability and good resistance to corrosion [3,4]. Little precipitate or decomposition has been observed in $Au_7Cu_5Al_4$ alloy [5], which is beneficial to the reliability of shape memory effect. Moreover, it could be considered as a good candidate for biomedical implant applications because gold is biocompatible and is radio-opaque due to its high atomic number. All of above functionalities are associated with martensitic transformation in $Au_7Cu_5Al_4$ alloys. It was also known that the martensitic transformations are always closely related to the ordering state in the β phase noble alloys [5,6].

Cortie and Levey [2,5,6] found that $Au_7Cu_5Al_4$ alloy underwent A2 → B2 → $L2_1$ ordering transitions during slow cooling process. T_C temperatures of ordering transitions were also investigated with the combination of thermal analysis, electrical resistivity method and internal friction and the results were shown in Table 1 [7].

Previous work [6] focused on the martensitic transformation occurred at about 20 °C in the $L2_1$ ordering structure which was obtained by slow cooling or appropriate aging between 80 and 250 °C after water quenched from above 600 °C. The latter result indicated that the ordering transition in $Au_7Cu_5Al_4$ alloy could be interrupted by quenching and reactivated by heating. In actual production, the samples were always heat treated in the way of quenching and aging. But this process and underlying mechanism is still unclear.

Generally, ordering structure and the degree of order had a noticeable impact on the martensitic transformation in β phase alloys such as CuZnAl [8], CuAlNi [9], AgZnAl [10] and AuCd [11] alloys. Optimization of ordering state is crucial for the martensitic transformation and associated properties. However, there were only a few studies focused on such area because the ordering state is difficult to manipulate for those alloys. $Au_7Cu_5Al_4$ alloys seemed appropriate for such a research because its ordering structure can be easily controlled by quenching and following aging.

In the present research, the ordering transitions in quenched $Au_7Cu_5Al_4$ alloy were characterized by electrical resistivity method. The martensitic transformation corresponding to different ordering state was measured by DSC. The mechanism about the effect of order on martensitic transformation in $Au_7Cu_5Al_4$ alloy was also discussed.

2. Material and methods

Samples were prepared by arc melting pure elements (at least 99.9 pct) in argon atmosphere. Composition of ingots was tested by EDX: $Au_{7.01}Cu_{5.15}Al_{3.77}$ (mole fraction). The ingots were hot rolled at 680 °C and followed by a homogenization treatment under an argon atmosphere at 680 °C for 8 h and slow-cooled in furnace. Then the ingot was cut into a variety of shapes for electrical resistivity and DSC experiments.

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Table 1
Comparison of T_C[a] temperatures of ordering transitions determined by different methods [7].

	T_C[a] temperature of A2–B2 ordering transition (°C)	T_C[a] temperature of B2–$L2_1$ ordering transition (°C)	Finish temperature of ordering transition (°C)
Thermal analysis	638(DSC)/ 623(TE)	388	290
Electrical resistivity	630	–	270
Internal friction	630	380	270

[a] T_C is the critical temperature of ordering transitions.

The ordering transitions of the samples were characterized by electrical resistivity method. Electrical resistivity measurement (ER) was experimented by four probe technique equipped with a KEITHLEY 2182 nanovoltmeter. The samples for ER were cut into plate with the size of $1 \times 2 \times 20$ mm^3. Martensitic transformations were monitored by differential scanning calorimetry (Perkin–Elmer Diamond DSC). The weight of the samples for DSC was between 5 and 10 mg.

Experimental process was designed as following:

1. All of the $Au_7Cu_5Al_4$ alloy samples were water quenched from 680 °C and called as-quenched sample in the paper.
2. Ordering transition in heating and martensitic transformation for different ordering states: Ordering transitions of as-quenched $Au_7Cu_5Al_4$ alloy in heating process were characterized by the changing of electrical resistivity as a function of temperature with rate of 2 °C/min from RT to 680 °C. Some as-quenched $Au_7Cu_5Al_4$ alloy plates were heated in same rate to different temperatures between RT and 680 °C and water quenched followed by testing their martensitic temperatures in DSC from 100 °C to −50 °C.
3. Evolution of a metastable ordering in aging and its martensitic transformation: The as-quenched sample was heated to 200 °C with the rate of 100 °C/min and then the changing of electrical resistivity as a function of aging time at 200 °C was characterized for clarifying the evolution of a metastable ordering. The temperature of 200 °C was determined by the former results. Martensitic transformations of the aged samples with different aging time were also monitored by DSC from 100 °C to −50 °C.

In order to investigate the nature of ordering structures of the β-phase, powder X-ray diffraction (XRD) measurements were also carried out. The $Au_7Cu_5Al_4$ alloy powder was firstly prepared by filing and purified with magnet followed by annealed at 650 °C for 8 h in the protection of argon gas. And then they were heat treated according to the characteristic temperatures in ER results.

3. Results

3.1. Ordering transitions in a quenched $Au_7Cu_5Al_4$ alloy

Fig. 1 shows the electrical resistivity as a function of temperature in a quenched $Au_7Cu_5Al_4$ sample slowly heated from room temperature up to 680 °C at a rate of 2 °C/min. At the low temperature stage, a couple of distinct resistivity changes can be seen between 171.6 °C and 281.3 °C. It implied that structural changes might occur during such heat treatment in the as-quenched sample and the details will be discussed later. Then the resistivity increased linearly with temperature until the temperature was up to 495.3 °C. Another distinct resistivity change occurred between 495.3 °C and 616.5 °C, which is in a good agreement with the B2–A2 order–disorder transition [7,12]. Finally,

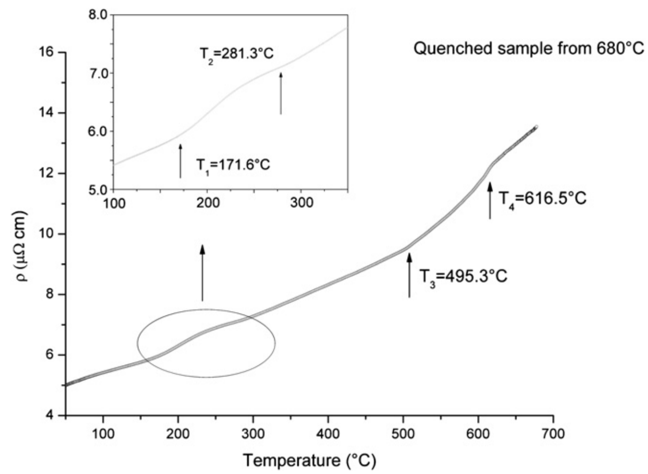

Fig. 1. Electrical resistivity as function of temperature heated from room temperature to 680 °C in a quenched $Au_7Cu_5Al_4$ sample.

the $Au_7Cu_5Al_4$ alloy returned to A2 disorder structure above 616.5 °C, which is accordance with the previous work [7,12].

3.2. Martensitic transformation of different ordering structures

The ordering structures at high temperature could be retained at room temperature because the ordering transitions could be interrupted by rapidly quenching. Therefore, martensitic transformations in different ordering structures can be investigated by water quenched from different temperatures corresponding to such ordering structures followed by DSC method. The quenched $Au_7Cu_5Al_4$ alloy plates were heated from room temperature to 680 °C with rate of 2 °C/min. In this progress, the samples were quenched into water from different temperatures.

Fig. 2 shows the M_S temperature as a function of quenching temperature in heating process for the quenched $Au_7Cu_5Al_4$ alloy samples. The M_S temperatures were determined by the onset points of heat flow peak in the DSC patterns as Fig. 2(a). The change of M_S temperature with different quenching temperature can be divided into 5 stages as Fig. 2, corresponding with the Fig. 1. Stage 1 (RT–180 °C): Martensitic transformation occurred around 0 °C, where the M_S temperature was very sensitive to quenching process. Stage 2 (180–280 °C): M_S temperature decreased dramatically in the temperature range, which agrees with the structural transition characterized by electrical resistivity in Fig. 1. The details of the structural transition and its effect of martensitic transformation will be shown in the next section. Stage 3 (280–480 °C): No obvious changing of M_S temperature was observed in this stage and values of M_S temperature were near 0 °C. It is possibly because that the parent structure in this stage is close to the as-quenched sample. Stage 4 (480–610 °C): in the range of quenching temperature, M_S temperature decreased again. This temperature range is very in accordance with the B2–A2 order–disorder transition in previous work [7]. Therefore, it can be considered that B2 ordering suppressed martensitic transformation. Stage 5 (610–680 °C): the sample quenched from A2 disorder structure and its M_S temperature was in accordance with stage 1, where the samples were also quenched from A2 structure.

3.3. Ordering structures studied by XRD

The powder X-ray diffraction (XRD) measurement was applied to clarify the structural transition occurred in quenched $Au_7Cu_5Al_4$ alloy as shown before. According to the states of atomic