Effect of Aging and Stress on Stability of β Phase in Au-Cd-Ag

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\textbf{Abstract}

Au\textsubscript{52.5},Cd\textsubscript{47.5}Ag, is a well-known martensitic alloy.\textsuperscript{1-4)} The β phase of this alloy exists as a single phase over a wide composition range. Although it shows a complex composition dependence, the martensitic transformation temperature \(T_0\) decreases as the Ag concentration changes: as the Ag content increases, the atomic order of the \(\beta\) phase changes from \(B2\) (CsCl) to \(L2_1\) (Heusler) to \(B2\). The \(\beta\) phase transforms to \(M2H\) martensite.\textsuperscript{5) We have studied the atomic order and stability of the \(\beta\) phase, which exists in the range of \(x \leq 41\), of this noble metal alloy.\textsuperscript{4)} Furthermore, \(T_0\) for the \(M2H\) transformation decreases and shows a complicated Ag composition dependence; the temperature range gradually narrows as the Ag content increases. It is supposed that the \(\beta\) phase has good stability at room temperature because \(T_0\) is lower than 240 K in the region of 15 \(\leq x \leq 41\).

For \(x \geq 43\), the \(\alpha\) phase coexists with the \(\beta\) phase, and the temperature range of the coexistence phase extends to room temperature or below.\textsuperscript{5,6)}

For \(x \geq 47\), another phase appears in which the \(\beta, \alpha,\) and \(\zeta\) coexist, and in this region, \(T_0\) increases.\textsuperscript{7)} There is some kind of relationship between the phase stability and the single phase/triple phase.

It is well known that aging stabilizes the \(\beta\) phase of the Ag-Cd alloy, and so it is expected to destabilize the coexisting phases.

In this work, we studied the effects of aging and stress on the stability of the \(\beta\) phase and other phases that are observed in the region of \(\beta\) single phase to define the phase diagram of Au\textsubscript{52.5},Cd\textsubscript{47.5}Ag.

\textbf{1. Introduction}

Au\textsubscript{52.5},Cd\textsubscript{47.5}Ag\textsubscript{4} is a well-known martensitic alloy.\textsuperscript{1-4)}

The \(\beta\) phase of this alloy exists as a single phase over a wide composition range. Although it shows a complex composition dependence, the martensitic transformation temperature \(T_0\) decreases as the Ag concentration changes: as the Ag content increases, the atomic order of the \(\beta\) phase changes from \(B2\) (CsCl) to \(L2_1\) (Heusler) to \(B2\). The \(\beta\) phase transforms to \(M2H\) martensite.\textsuperscript{5)} We have studied the atomic order and stability of the \(\beta\) phase, which exists in the range of \(x \leq 41\), of this noble metal alloy.\textsuperscript{4)} Furthermore, \(T_0\) for the \(M2H\) transformation decreases and shows a complicated Ag composition dependence; the temperature range gradually narrows as the Ag content increases. It is supposed that the \(\beta\) phase has good stability at room temperature because \(T_0\) is lower than 240 K in the region of 15 \(\leq x \leq 41\).

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\section{2. Experimental}

Samples with 6 different compositions were prepared. The sample alloys were prepared by melting the component elements in evacuated quartz tubes. After homogenizing at temperature or lower.\textsuperscript{5,6)}

\section{3. Results}

Profiles of the X-ray diffraction patterns of the a), b), and c) samples are shown in Fig. 1, 2, and 3, respectively. Coexistence of the \(\beta\) and the \(\alpha\) phases was observed for all compositions for samples a) and c). All three phases \((\alpha,\beta,\delta)\) were observed for all compositions of sample b). The experimental values of the lattice parameter, atomic order, and atomic site of the \(\beta\) phase in the heat-treated powder samples obtained from the Rietan analysis were consistent with the former re-
The crystal structure of the α phase was A2. The atomic order and lattice parameters of the α phase were also consistent with the former report. The crystal structure of the ζ phase was hcp. The atomic order of the ζ phase in the non-heat-treated samples was not determined because the peak of the ζ phase was widened by the stress, and a good enough value of R factor could not be obtained. The ζ phase of the near equi-atomic Ag-Cd alloy is A3. The ζ phase observed in Au52.5-xCd47.5Agx is estimated to be on the same atomic order as near equi-atomic Ag-Cd.9) The obtained lattice parameters of the ζ phase are shown in Fig. 4.

The mole fraction of the three phases obtained by the present analysis are listed in Table 2 and shown in Fig. 5.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Without heat treatment (No stress released)</th>
<th>With heat treatment (Stress released)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16Ag</td>
<td>β:α:ζ = 53:30:24</td>
<td>β:α = 97:3</td>
</tr>
<tr>
<td>18Ag</td>
<td>β:α:ζ = 85:6:9</td>
<td>β (L2₁), α‴</td>
</tr>
<tr>
<td>23Ag</td>
<td>β:α:ζ = 86:6:8</td>
<td>β (L2₁), α‴</td>
</tr>
<tr>
<td>26Ag</td>
<td>β:α:ζ = 75:13:13</td>
<td>β (L2₁), α‴</td>
</tr>
<tr>
<td>38Ag</td>
<td>β:α:ζ = 54:25:21</td>
<td>β (B2)</td>
</tr>
<tr>
<td>41Ag</td>
<td>β:α:ζ = 39:33:28</td>
<td>β:α = 85:15</td>
</tr>
</tbody>
</table>

* in these cases, the amount is too small to allow estimation of the mole fraction

Fig. 1 Profiles of the X-ray diffraction patterns of the aged bulk samples. The peak indicated by the solid circle is from the sample holder.

Fig. 2 Profiles of the X-ray powder diffraction patterns of the aged samples. These samples were not heat treated after filing.

Fig. 3 Profiles of the X-ray powder diffraction patterns of the aged samples. These samples were heat treated for stress release after filing.

Fig. 4 Lattice constants of the ζ phase of the non-heat-treated powder samples.

Fig. 5 Mole fraction of the β, α, and ζ phases in the non-heat-treated and heat-treated powder samples.
4. Discussion

Both the \(\alpha\) and \(\zeta\) phases were observed in the aged Au-Cd-Ag alloys in the composition range that has been regarded as the \(\beta\)-single-phase (Table 1). These two phases do not exist as the thermal equilibrium state in the composition range of \(x \leq 41.7\). The atomic order of the \(\beta\) phase in the aged samples was the same as that before aging as shown in Table 1 for all compositions. The \(\beta\) phase of the 18Ag, 23Ag, and 26Ag samples has a highly ordered \(L_2_1\) structure. Considering the results in Table 2 and Fig. 5, it is estimated that the higher atomic order makes the \(\beta\) phase more stable against aging and stress. The ratio of Au to Ag is close to 1:1 in the 26Ag sample compared with that in the 18Ag and 23Ag samples. Therefore, the 26Ag sample has the highest ordered structure of all the alloy samples. The stability of the \(\beta\) phase is sensitive to the Au - Ag equality; compositional differences between Au and Ag make the phase transition easier and recovery to the \(\beta\) phase harder.

In all compositions of the aged powder samples without heat treatment after filing, three phases were observed. The mole fraction of the \(\alpha\) phase, which was estimated from the main peak intensity (\(\alpha_{111}\)), is different from that of the bulk samples. The \(\zeta\) phase appears in the powder samples. Stress induces the phase transition from the \(\beta\) phase to the \(\alpha\) or \(\zeta\) phase.

In the case of the heat-treated aged powder samples, the \(\alpha\) phase was observed. The peak intensities of the \(\alpha\) phase in the 18Ag, 23Ag, and 26Ag samples are too weak to allow estimation of its mole fraction. The \(\zeta\) phase was not observed in the samples prepared under these conditions. The \(\zeta\) phase is easily induced by stress and easily reduced by heating. Therefore, this phase is unstable in the range of \(x \leq 41\). The \(\alpha\) phase is more stable than the \(\zeta\) phase after heat treatment at 773 K. The \(\zeta\) phase exists in the thermal equilibrium state in the composition range of \(x \geq 47\), which is further from the composition of the equivalent Au-Ag ratio than that in the range over which the coexisting phase of the \(\beta\) and the \(\alpha\) exists (41 < \(x\) < 47).

A similar stress-induced phase transition from the \(\beta\) phase to the \(\zeta\) phase has also been observed in Ag-Zn alloy.\(^{10,11}\) Therefore, Ag is supposed to play an important role in determining the transition phase induced by stress.

5. Conclusions

The \(\alpha\) phase coexists with the \(\beta\) phase in aged \(\text{Au}_{52.5-\text{x}}\text{Cu}_{47.5}\text{Ag}_x\) alloys for \(x \leq 41\) as the thermal equilibrium state. The \(\alpha\) and \(\zeta\) phases appear on adding stress. The mole fractions of these two phases increase with an increase in the deviation from equivalent Au and Ag. The \(\zeta\) phase disappears when stress is released, while the \(\alpha\) phase remains. The \(\zeta\) phase was unstable in the range of \(x \leq 41\). On the other hand, the \(\alpha\) phase is stable in this region. It is speculated that Ag plays an important role in the different phase transition processes in the case of heating or stress addition because a similar phenomenon was also observed in Ag-Zn.

REFERENCES