

Composition dependence of structure in $\text{Au}_{52.5-x}\text{-Cd}_{47.5}\text{-Ag}_x$ shape memory alloys

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The β -phase of $\text{Au}_{52.5-x}\text{-Cd}_{47.5}\text{-Ag}_x$ alloys undergoes a martensitic transformation on cooling. The Ag substitution for Au affects martensitic transformation temperatures, crystal structures, and the orthorhombic distortion although it is expected that the substitution has no changes in atomic size, electron concentration.

In this work, X-ray powder diffraction measurements and Rietveld analysis were performed for both the β -phase and the martensite phase in $\text{Au}_{52.5-x}\text{-Cd}_{47.5}\text{-Ag}_x$, $x = 17, 20, 23, 26, 29, 32, 35, 38$ and 41 at.%, alloys to investigate the composition dependence of crystal structures and atomic positions. The lattice constants of β -phase have a minimum value around $x = 26$. In the martensite phase, the lattice constants also have the bounds of increasing / decreasing around $x = 26$. The volumes have a minimum around $x = 26$ in both phases.

Based on the present results we discuss briefly the relation between the transformation temperature and the structural parameters such as the lattice constants, the orthorhombic distortion and the atomic positions.

Key words: Martensitic transformation, Rietveld analysis, crystal structure, orthorhombic distortion, composition dependence

1. INTRODUCTION

The β -phase of Au-47.5at.%Cd-Ag alloys undergoes a martensitic transformation on cooling. The structure of the martensite is M2H for entire Ag concentrations although the transformation temperatures exhibit a minimum at the Ag concentration around 26 at.%(1) As already known, the β -phase of the alloys with Ag concentration around 26 at.% exhibits the L2₁-type ordered structure, while the β -phase with lower and higher Ag concentrations is the B2-type ordered structure.(2)(3) Thus, it has been considered that the difference of the ordered structures in the β -phase results in such a composition dependence of the transformation temperature.

The lattice constants and the atom positions in both the β -phase and the martensite phase are important for understanding the martensitic transformation, especially in considering the relative stability between the β -phase and the martensite phase. It is expected that the lattice constants and the atom positions depend on both the composition and the ordered state. (4)

Therefore, in this work, we measured X-ray powder diffractions of the β -phase and the martensite phase of Au-47.5at.%Cd-Ag alloys with various Ag concentrations, and using a Rietveld method, determined the structural parameters such as the lattice constants and the atom positions in both the β -phase and the martensite phase. Based on the present results, we discuss the characteristics of the transformation temperatures in the β -phase of Au-47.5at.%Cd-Ag alloys in terms of the structural parameters.

2. EXPERIMENTAL PROCEDURES

$\text{Au}_{52.5-x}\text{-Cd}_{47.5}\text{-Ag}_x$: $x = 17, 20, 23, 26, 29, 32, 35, 38$ and 41, alloys were prepared by melting the component elements in evacuated quartz tubes. The alloys were homogenized at 823 K for 72 h in evacuated Pyrex tubes and cooled to room temperature. Powdered samples were made by filing and then sieved less than 53 μm in size. Before measuring, the powder samples were annealed at 823 K for 1200 s in evacuated Pyrex tube to get relief from stress and then slow cooled to room temperature. X-ray powder diffraction measurements were performed for all samples at room temperature (β -phase) and $T = 80$ K (martensite phase), from 20° to 110° in 2θ space with a step width of 0.02°.

Rietveld analysis was performed to precisely determine the lattice constants and the positions of atoms by using RIETAN-2000(5).

3. RESULT AND DISCUSSION

3.1 Lattice constants and orthorhombic distortion

The lattice constants refined by the Rietveld analysis were shown in Figure 1, (a) β -phase and (b) martensite phase. In the β -phase, the lattice constant has a minimum around the composition $x = 26$ where the composition is close to the stoichiometric composition Au-Ag-Cd₂. In the martensite, the lattice constants of a - and b -axis have a minimum / maximum around $x = 26$, on the other hand, that of c -axis has a tendency of linear increase as Ag at.% increases.

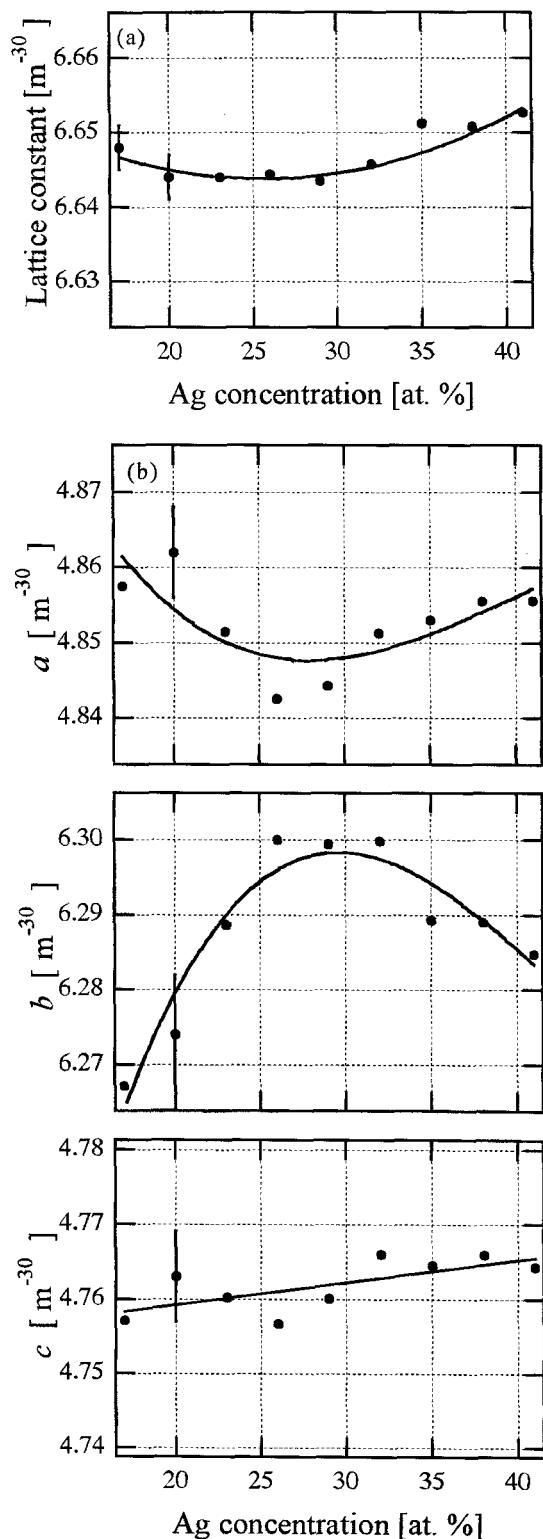


Figure 1. Ag composition dependence of lattice constants of (a) β -phase, (b) martensite, respectively. The lattice constants of the β -phase and a -axis of the martensite have a minimum, and b -axis of the martensite has a maximum around $x = 26$. The lattice constant of c -axis, on the other hand, increases as Ag atomic percent increases.

The volumes of β -phase and martensite are shown in Figure 2. The β -phase has a minimum volume around $x = 26$. The martensite also has a minimum volume around $x = 26$ in the x region where the $L2_1$ ordered structure exist. (3)

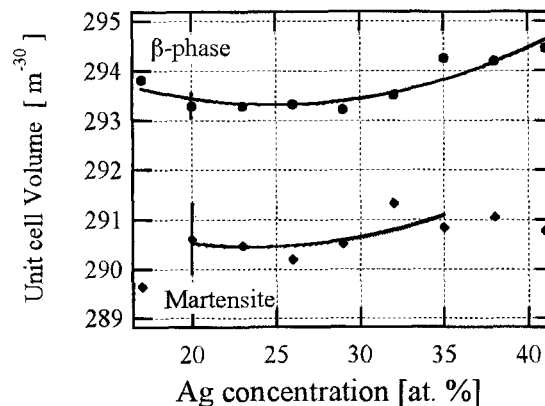


Figure 2. Ag composition dependence of unit cell volume of β -phase (●) and martensite (◆). The volume of β -phase has a minimum around $x = 26$. The martensite also has a minimum volume around $x = 26$ in the x region where the $L2_1$ ordered structure exist.

The orthorhombic distortion was calculated by using the lattice constants a and b of the martensite phase. The Ag composition dependence of the orthorhombic distortion is shown in Figure 3. The orthorhombic distortion increases to $x \sim 26$, turn to decreases to $x \sim 35$, and then slightly decreases as Ag at.% increase. These two bounding points are consistent with the bounds of the martensitic transformation temperature. (3)

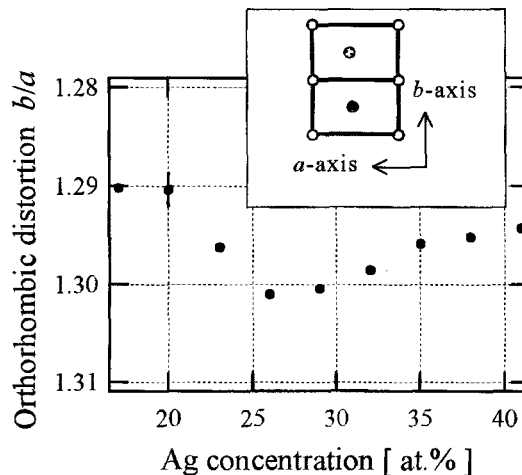


Figure 3. Ag composition dependence of orthorhombic distortion. The orthorhombic distortion has a maximum at $x \sim 26$.

3.2 Atomic position

Atomic position parameters $x(Au1)$, $x(Ag1)$, $x(Au2)$, $x(Ag2)$ and $x(Cd)$ were precisely determined by Rietveld analysis. For Rietveld analysis of the martensite phase, the space group $Pmmn$ for $x = 20, 23, 26, 29, 32$ and $Pmma$ for $x = 17, 35, 38, 41$ were adopted. The coordinate parameters of atomic positions are shown in

Table I.

Table I The coordination parameters of atomic positions. (Aun) or (Agn) : $n = 1, 2$, means that Au or Ag atom is dominant at the site.

Atom	x	y	z
Au	$x(\text{Au}1)$	1/4	0
	$x(\text{Au}2)$	3/4	1/2
Ag	$x(\text{Ag}1)$	3/4	0
	$x(\text{Ag}2)$	1/4	1/2
Cd	$x(\text{Cd})$	0	1/2

The Ag composition dependence of coordination parameters is shown in Figure 4. In $z = 0$ plane, Cd position is fixed at the origin. The atomic positions $x(\text{Au}1)$ and $x(\text{Ag}1)$ shift to the direction that the displacement increases as Ag concentration increases. The $x(\text{Au}1)$ site disappears at $x > 35$ because of low concentration of Au at.%. The displacement of $x(\text{Ag}1)$ has a maximum at $x \sim 35$ and then the displacement decreases as Ag concentration increases. In $z = 1/2$ plane, $x(\text{Au}2)$, $x(\text{Ag}2)$ and $x(\text{Cd})$ shift to the displacement increasing direction and then $x(\text{Ag}2)$ and $x(\text{Cd})$ turn to shift to the displacement decreasing direction at $x \sim 35$.

To compare the displacements of atomic positions in $z = 0$ plane and $z = 1/2$ plane, we show the distances between $x(\text{Au}2)-x(\text{Cd})$ and $x(\text{Ag}2)-x(\text{Cd})$ in the a -axis direction as $l(\text{Au}-\text{Cd})$ and $l(\text{Ag}-\text{Cd})$, respectively in Figure 5. These distances l correspond to the distances between $x(\text{Au}1)-x(\text{Cd})$ at origin) and $x(\text{Ag}1)-x(\text{Cd})$ at origin) in $z = 0$ plane. The $l(\text{Au}-\text{Cd})$ and the $l(\text{Ag}-\text{Cd})$ decrease as Ag concentration increases. The $l(\text{Au}-\text{Cd})$ disappears at $x > 35$ because of same reason as $x(\text{Au}1)$. The $l(\text{Ag}-\text{Cd})$ has a maximum at $x \sim 35$ and then turn to increase.

These results means that Au (Ag) dominant sites displace in the opposite direction in $z = 0$ plane and $z = 1/2$ plane. The displacements of Ag dominant sites are larger than those of Au dominant sites.

4. SUMMARY

Ag composition dependence of crystal structure in $\text{Au}_{52.5-x}\text{Cd}_{47.5-x}\text{Ag}_x$, $x = 17, 20, 23, 26, 29, 32, 35, 38$ and 41 at.%, alloys is investigated by using the Rietveld analysis method. The lattice constants in both β -phase and martensite are refined. The orthorhombic distortion was calculated by using the lattice constants a and b of martensite phase. It was shown that the orthorhombic distortion has correlation with the martensitic transformation temperature.

Atomic position displacements increase as Ag at.% increases to $x \sim 35$, and then, Au dominant site disappear and the displacements of atomic position of Au dominant sites and Cd dominant site turn to decrease.

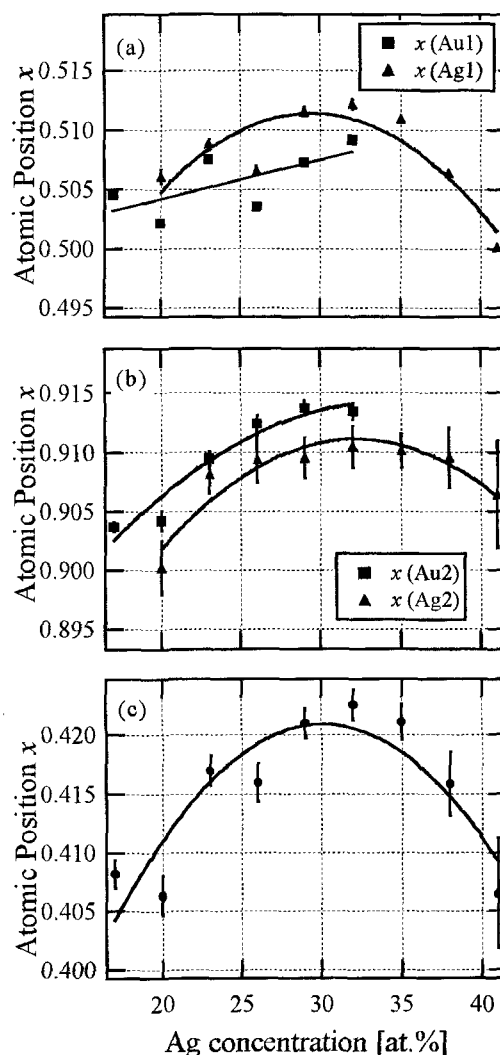


Figure 4. Atomic positions of Au and Ag dominant sites in (a) $z = 0$ plane, (b) $z = 1/2$ plane. (c) Atomic position of the Cd dominant site in $z = 1/2$ plane.

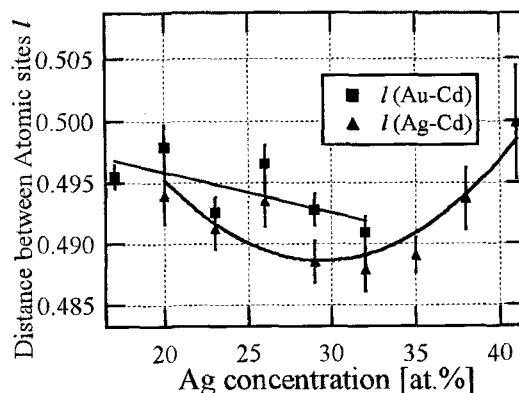


Figure 5. $l(\text{Au}-\text{Cd})$ and $l(\text{Ag}-\text{Cd})$, which are the distances between $x(\text{Au}2)-x(\text{Cd})$ and $x(\text{Ag}2)-x(\text{Cd})$ in the a -axis direction, respectively.

5. REFERENCE

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