Diffusion of zinc in the Cu₃Au alloy

by
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Secondary ion mass spectroscopy (SIMS) was used to measure the diffusion coefficients and isotope effects of zinc in the Cu₃Au alloy in various temperatures across L₁₂-type order-disorder transition one. The temperature dependence of diffusion coefficient is not explained by a simple activation process of Arrhenius type because of the order-disorder transition. The activation energy $Q$ and pre-exponential factor $D₀$ for diffusion were

$$Q = 126 \left(1 - 0.70S + 0.65S²\right) \text{kJ/mol}$$
$$D₀ = 1.04 \times 10^{-5} \text{cm/sec},$$

where $S$ is a long-range order parameter. The isotope effect remained about 0.5 in the disordered region, while it increased with decreasing temperature in the ordered region.

1. Introduction

Dental gold alloys exhibit age hardening characteristics, which depends on the diffusion behavior of impurity atoms in the crystal lattice. It is important to clarify the diffusion behavior of impurity atoms in the dental gold alloys.

Secondary ion mass spectroscopy (SIMS) is capable of analyzing the distribution of impurity atoms from the surface to the inside of metals. The high spatial resolution of SIMS makes it possible to determine small diffusion coefficients below ordering temperature.

In this paper, we will examine the diffusion coefficients and isotope effects of zinc in the Cu₃Au alloy by using SIMS. Atomic arrangement of the Cu₃Au alloy changes from the disordered state to the L₁₂-type ordered state at 663K. We will reveal the relation between the ordered state of the Cu₃Au alloy and the diffusion behavior of impurity atoms.

2. Experimental Procedure

The bulk of the Cu₃Au alloy was prepared by induction melting of 99.99% gold and 99.99% copper. The bulk was pre-annealed for 86ks at 873K and slowly cooled in an electric furnace in order to reduce lattice defects. The bulk was cut into the blocks of about 3 mm × 3 mm square and 1 mm thickness. After the block surfaces were polished with a buff, the surfaces were covered by a vapor deposited zinc layer of 0.01μm thickness. Subsequently, the layer was covered by a vapor deposited Cu₃Au layer of 0.05μm thickness in order to protect the zinc layer from oxidation and contamination. The blocks covered by the double layers were isothermally annealed in vacuum of $10^{-2}$ Pa at temperatures of 873K ~ 573K for 86.4ks ~ 864ks. The distributions of zinc along the depth direction were measured with a secondary ion mass spectrometric analyzer (Hitachi - 2 A), by using sputter ions of O⁺. Under the assumption of a constant sputter rate, the depth of the crater at each time was estimated from the sputter rate, where the sputter rate was calculated from a final sputter time at a final depth observed by a surface analysis instrument.

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3. Results and Discussion

The diffusion coefficients were determined on the assumption of concentration distributions in the Gauss function type as follows,

\[ C = A \exp\left(-\frac{x^2}{4Dt}\right) \]

where \( C \) is the concentration of zinc at position \( x \) along the depth direction after a diffusion interval \( t \), \( D \) is the diffusion coefficient of zinc, and \( A \) is constant. The values of \( D \) were calculated from the slope of the line of \( \ln C \) versus \( x^2 \).

Fig. 2 shows the logarithmic plots of secondary ion intensities of zinc versus \( x^2 \) in the Cu₃Au alloy annealed for 864ks at 593K and for 86.4ks at 873K. Because zinc remains near surface after diffusion-annealing, the concentration of zinc is high near \( x = 0 \). The good linearity appears at the region of large \( x^2 \). We determined the diffusion coefficients of zinc from the slopes of the lines. The temperature dependence of the diffusion coefficient of zinc in the Cu₃Au alloy is shown in Fig. 3. The temperature dependence of diffusion coefficient is not explained by a single line of the Arrhenius type because of order-disorder transition. According to the Arrhenius equation for diffusion

\[ D = D_0 \exp\left(-\frac{Q}{kT}\right), \]

the activation energies \( Q \) and pre-exponential factors \( D_0 \) were determined as follows

\[ D_0 = 1.04 \times 10^{-5}\text{cm/sec}, \quad Q = 126kJ/mol \quad \text{in the disordered state at 873K−673K}, \]
\[ D_0 = 1.93 \times 10^{-11}\text{cm/sec}, \quad Q = 41kJ/mol \quad \text{in the ordered state at 653K−573K}. \]

The activation energy in the ordered state is smaller than that in the disordered state, although the activation energy for self-diffusion was reported to increase with ordering in the CuZn alloy\(^{14}\).
We will discuss the dependence of the activation energy on the ordered state of the Cu₃Au alloy. The occupation probabilities of copper atoms on α and β sublattices of L₁₂ are defined as \((3 + S)/4\) and \((1 - S)/4\), and those of gold atoms on α and β sublattices \((1 - S)/4\), and \((1 + 3S)/4\), where S is a long-range order parameter. The value of S in equilibrium is obtained by the equilibrium condition of nearest neighbour pair approximation

\[ S = \left( \frac{3}{16} \right) \left( \frac{T}{T_o} \right) \ln \left( \frac{(3 + S)(1 + 3S)}{3(1 - S)^2} \right) \]

where \(T_o\) is order-disorder transition temperature. The activation energy of the diffusion is approximately represented as

\[ Q = Q_o \left( 1 + aS + bS^2 \right) \]

where \(Q_o\) is the activation energy for the diffusion in the disordered state, a and b are constants. By substituting Eq. (4) in Eq. (2), the equation

\[ H = \left( -\frac{RT}{Q_o} \ln \left( \frac{D}{D_o} \right) - 1 \right) / S = a + bS \] (5)

is derived, where R is gas constant, and \(D_o\) is the pre-exponential factor in disordered state. After substituting the values of \(D\), \(D_o\) and \(Q_o\), and S in Eq. (5), the relationship between \(H\) and S is revealed as shown in Fig. 4. The relationship results in \(a = -0.70\) and \(b = 0.65\). The values of a, b are \(a = 0\), \(b = 0.156\) for the self-diffusion and \(a = 0\), \(b = 0.23\) for cobalt diffusion in α-iron. The difference of the values of a, b between the alloys may be attributed to the diffusion mechanism peculiar to the each alloy.

Isotope effects E, which depends on diffusion mechanism, is indicated as follows,

\[ E = \left( 1 - \frac{D_a}{D_p} \right) / \left( 1 - \left( \frac{m_p}{m_a} \right)^{1/2} \right) \]

where m is the mass number, the subscripts a and b indicate isotope. For zinc \(m_a\) and \(m_p\) are 64 and 66.

\[ \text{Fig. 5} \quad \text{Plot of } \ln C_o \text{ versus } \ln C_i \text{ in the Cu₃Au alloy annealed for 864Ks at 593K.} \]

\[ \text{Fig. 6} \quad \text{Temperature dependence of isotope effect of Zn in the Cu₃Au alloy.} \]
where \( f \) is the correlation factor for diffusion in cubic lattice for the diffusion through the vacancy mechanism is estimated to be about slightly correlated one if the kinetic factor changes only slightly. The increase of correlation factor or kinetic factor.

Thus, the diffusion mechanism may change to be slightly. The constant isotope effect in the disordered region of the disordered region, while it increases with ordering.

Thus, the diffusion mechanism may change to be slightly correlated one if the kinetic factor changes only slightly.

4. Conclusion

The diffusion coefficients and the isotope effects of zinc in the Cu₃Au alloy were determined by SIMS. Table 1 shows the various diffusion parameters obtained in this work. The temperature dependence of diffusion coefficient is not explained by a simple activation process of Arrhenius type because of order-disorder transition. The activation energy of diffusion is lower in the ordered region than in the disordered region. The isotope effect is about 0.5 in the disordered region, while it increases with ordering.

<table>
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<th>Temperature (K)</th>
<th>Annealing time (sec)</th>
<th>Diffusion coefficient (cm²/sec)</th>
<th>Isotope effect</th>
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<td>1.299E-14</td>
<td>0.711</td>
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</table>

Table 1 Diffusion parameters of Zn in the Cu₃Au alloy.

References

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7) D. Mathiot and G. Fédin : Phil. Mag., A41 (1980), 447