

Diffusion of zinc in the Cu_3Au alloy

by

Takao MORIMURA*, Seiichiro MORI*, Takanori IDE*

Masayuki HASAKA* and Shin-ichiro KONDO*

Secondary ion mass spectroscopy (SIMS) was used to measure the diffusion coefficients and isotope effects of zinc in the Cu_3Au alloy in various temperatures across $L1_2$ -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 D_0 for diffusion were

$$Q = 126 (1 - 0.70S + 0.65 S^2) \text{ kJ/mol}$$

$$D_0 = 1.04 \times 10^{-5} \text{ cm}^2/\text{sec},$$

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^{1) - 5)}, 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)^{6) - 9)} 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^{10) - 13)}.

In this paper, we will examine the diffusion coefficients and isotope effects of zinc in the Cu_3Au alloy by using SIMS. Atomic arrangement of the Cu_3Au alloy changes from the disordered state to the $L1_2$ -type ordered state at 663K. We will reveal the relation between the ordered state of the Cu_3Au alloy and the diffusion behavior of impurity atoms.

2. Experimental Procedure

The bulk of the Cu_3Au 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 $3 \text{ mm} \times 3 \text{ mm}$ 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 $0.01 \mu\text{m}$ thickness. Subsequently, the layer was covered by a vapor deposited Cu_3Au layer of $0.05 \mu\text{m}$ thickness in order to protect the zinc layer from oxidation and contamination⁹⁾. 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 analyser (Hitachi-2A), by using sputter ions of O_2^+ . 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

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*Department of Materials Science and Engineering

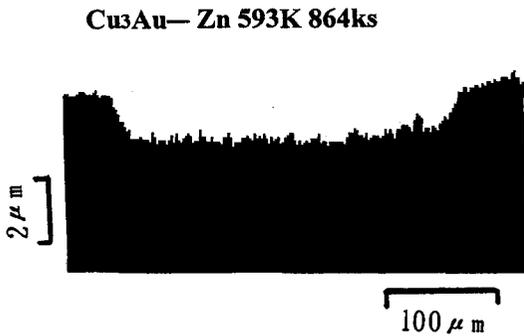


Fig.1 Crater formed by O₂⁺ sputter in the Cu₃Au alloy.

recorder, as shown in Fig.1.

3. Results and Discussion

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

$$C = A \exp(-x^2 / (4Dt)) \quad (1)$$

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 lnC versus x².

Fig.2 shows the logarithmic plots of secondary ion intensities of zinc versus x² 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 x². 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

$$D = D_0 \exp(-Q/kT), \quad (2)$$

the activation energies Q and pre-exponential factors D₀ were determined as follows

$$D_0 = 1.04 \times 10^{-5} \text{ cm}^2/\text{sec}, \quad Q = 126 \text{ kJ/mol} \quad \text{in the disordered state at 873K} - 673\text{K},$$

$$D_0 = 1.93 \times 10^{-11} \text{ cm}^2/\text{sec}, \quad Q = 41 \text{ kJ/mol} \quad \text{in the ordered state at 653K} - 573\text{K}.$$

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 alloy¹⁴.

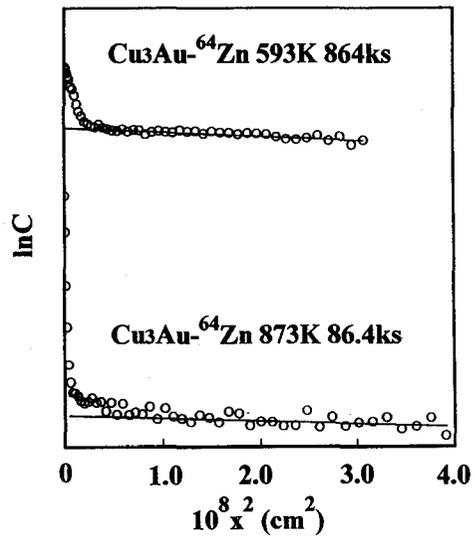


Fig.2 Diffusion profile of ⁶⁴Zn in the Cu₃Au alloy.

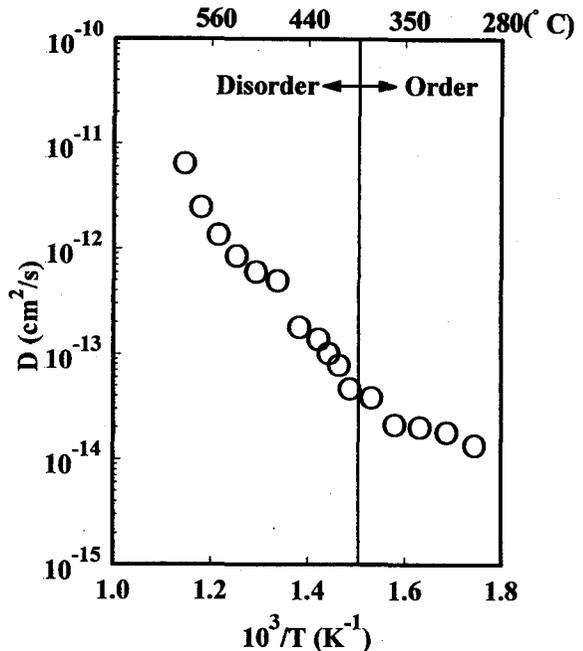


Fig.3 Temperature dependence of diffusion coefficient of ⁶⁴Zn in the Cu₃Au alloy.

We will discuss the dependence of the activation energy on the ordered state of the Cu_3Au alloy. The occupation probabilities of copper atoms on α and β sublattices of L_{12} are defined as $(3+S)/4$ and $3(1-S)/4$, 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

$$S = (3/16) (T/T_0) \ln((3+S)(1+3S)/3(1-S)^2) \quad (3)$$

where T_0 is order-disorder transition temperature. The activation energy of the diffusion is approximately represented as

$$Q = Q_0 (1 + aS + bS^2) \quad (4)$$

where Q_0 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

$$H \equiv (-RT/Q_0) \ln(D/D_0) - 1/S = a + bS \quad (5)$$

is derived, where R is gas constant, and D_0 is the pre-exponential factor in disordered state. After substituting the values of D , D_0 and Q_0 , 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 $a = 0$, $b = 0.156^{15)}$ and $a = 0$, $b = 0.23^{16)}$ for the self-diffusion and 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,

$$E = (1 - D_\alpha/D_\beta) / (1 - (m_\beta/m_\alpha)^{1/2}) \quad (6)$$

where m is the mass number, the subscripts α and β indicate isotope. For zinc m_α and m_β are 64 and 66

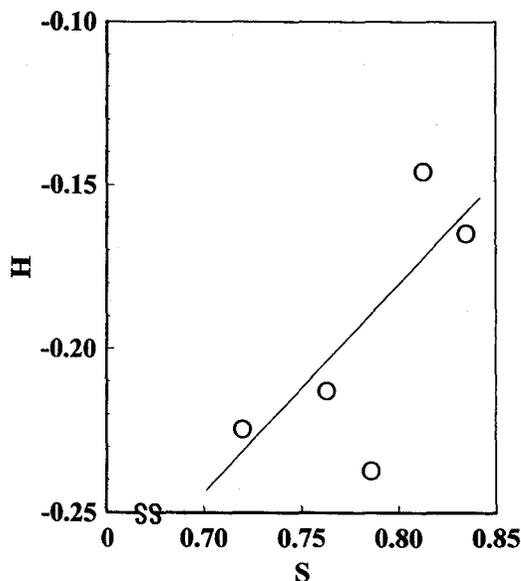


Fig.4 Relationship between H in Eq. (5) and longrange order parameter S .

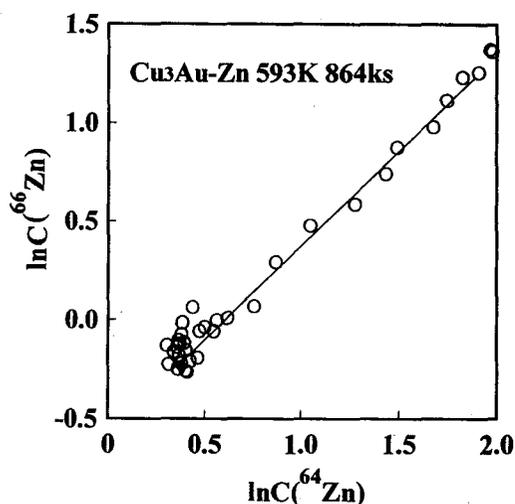


Fig.5 Plot of $\ln C_\beta$ versus $\ln C_\alpha$ in the Cu_3Au alloy annealed for 864Ks at 593K.

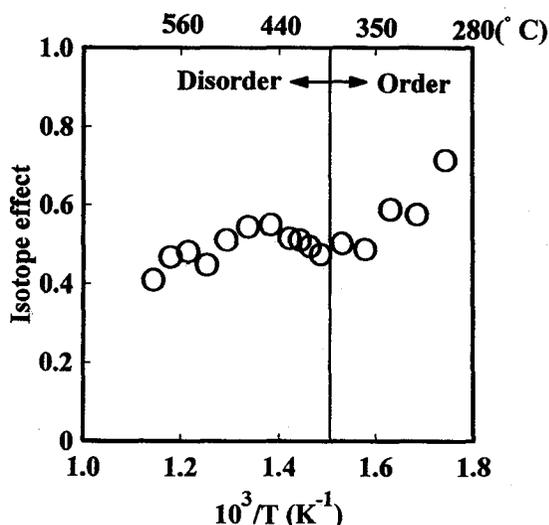


Fig.6 Temperature dependence of isotope effect of Zn in the Cu_3Au alloy.

respectively. Isotope effect E is determined by substituting the values of D_α/D_β in Eq. (6). The D_α/D_β is decided by the slope of the line of $\ln C_\beta$ versus $\ln C_\alpha$, where C_α and C_β are the concentrations of isotopes α and β measured by means of SIMS. Fig. 5 shows good linearity in the plot of $\ln C_\beta$ versus $\ln C_\alpha$.

Fig. 6 shows the temperature dependence of isotope effect. The values of isotope effects are about 0.5 in the disordered region, while the value increases with ordering.

For the diffusion of impurity atoms in the pure metal, the isotope effect is indicated as follows,

$$E = f \cdot \Delta K \quad (7)$$

where f is the correlation factor for diffusion and ΔK is the kinetic factor. The correlation factor in face-centered cubic lattice for the diffusion through the vacancy mechanism is estimated to be about 0.78¹⁷⁾. The decrease of correlation factor is expected in more complicated mechanism for diffusion. The kinetic factor is reported to be nearly 1 or less than 1. The constant isotope effect in the disordered region of the Cu₃Au alloy suggests that the diffusion mechanism remains same throughout the region. The increase of isotope effect with ordering may corresponds to the increase of correlation factor or kinetic factor. Thus, the diffusion mechanism may changes to be lowly 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 1 Diffusion parameters of Zn in the Cu₃Au alloy.

Temperature (K)	Annealing time(sec)	Diffusion coefficient(cm ² /sec)	Isotope effect
873	86400	6.202E-12	0.405
848	86400	2.377E-12	0.463
823	86400	1.302E-12	0.478
798	86400	8.179E-13	0.445
773	86400	5.777E-13	0.507
748	86400	4.785E-13	0.541
723	172800	1.727E-13	0.546
703	345600	1.329E-13	0.511
693	345600	9.760E-14	0.507
683	345600	7.540E-14	0.491
673	345600	4.496E-14	0.470
653	345600	3.702E-14	0.498
633	345600	2.045E-14	0.483
613	604800	1.929E-14	0.585
593	864000	1.726E-14	0.572
573	864000	1.299E-14	0.711

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