RECOVERY OF COLD DEFORMED HIGH PURE SILVER①

Ning Yuantao, Wen Fei, Zhao Huaizhi, Deng Deguo
Institute of Precious Metals, Kunming 650221

ABSTRACT The changes of mechanical and electrical properties as well as lattice distortion of cold deformed silver with high purity of 99.999% were studied in its recovery processes at 23 and 50 ℃ temperatures. The high pure silver showed a low recrystallization temperature of 70 ℃ and obvious natural recovery softening effect. The recovery process was quickened with increasing cold deformation degree and rising age temperature, obeying an isothermal recovery rate equation: $\ln(x_0/x) = Kt$. The recovery activation energy of the high pure silver was found to be $E = 20$ kJ/mol, and the recovery process was mainly controlled by point defect recovering mechanism.

Key words silver recovery recrystallization

1 INTRODUCTION

It was found long ago in the production that the mechanical properties of cold deformed highly pure silver were not stable, and would decrease to a certain extent during storage, which was called "a natural age softening phenomenon." Although this phenomenon was studied by several authors in literatures[1-5], it was still short of thorough investigation on the substance of the phenomenon as well as the changes of structure and kinetics.

In order to understand the substance of the phenomenon, the changes of properties and structure as well as the kinetics in the ageing process were studied for the cold deformed silver with high purity in present paper.

2 EXPERIMENTAL PROCEDURE

The silver ingot with purity of 99.999% was processed into wire and sheet by cold deformation. The quantitative spectral analysis for 14 impurities in the silver materials indicated that the individual content was less than 0.0005% for Au, Fe, Ir, Ni, Pb, Pt, Rh, Sb, and Sn, less than 0.0004% and 0.0003% for Mg and Cu respectively, and less than 0.00002% for Al, Bi and Pd. The sheet samples with compressibility $\varepsilon = 75\%$ and 90% and wire samples with section shrinkage $\Phi = 98\%$ were aged isothermally at 23 and 50 ℃. The changes of hardness, tensile strength, elongation, electrical resistivity and lattice distortion, etc. were measured in the isothermal ageing process.

3 RECOVERY AND RECRYSTALLIZATION OF HIGHLY PURE SILVER

3.1 *Recrystallization Temperature of Highly Pure Silver*

The recrystallization temperature of metal is related to its purity and cold deformation degree. In present work, the wire samples with $\Phi = 98\%$ were annealed at different temperatures for 0.5 h. The dependence of the measured tensile strength on annealing temperature is shown in Fig. 1. The recrystallization temperature of highly pure Ag can be determined to be 70 ℃, which is in accord with the value of 64 ℃ reported in literature [3] for Ag with the same purity and cold deformation degree.

① Supported by the National Natural Science Foundation of China Received Mar. 8, 1995; accepted Jun. 9, 1995

3.2 *Changes of Properties of* Ag *in Recovery Process*

3.2.1 Strength Properties

Fig. 2 shows the changes of hardness of sheet samples with $\varepsilon = 75\%$ and that of tensile strength of wire samples with $\Phi = 98\%$ for pure Ag. With prolonged age process, the strength and hardness decrease rapidly, showing an obvious age softening. The relative decrements of the strength and hardness of Ag aged for 70 d are listed in Table 1. It can be seen from Table 1 that, the higher the cold deformation degree and the age temperature, the larger the decrements of the strength and hardness. On the other hand, the tensile strength values of Ag aged at 23 ℃ for 30 d and aged at 50 ℃ for 20 d have reached a stable value of about 200 MPa. Compared with the corresponding data reported in Ref. [3] for two pure silver samples with purities of 99.999% and 99.95% and with cold deformation degree $\varepsilon = 90\%$, the stable strength value got in present work is comparative, but the recovery time for reaching the stable strength value is between those of the two pure silver samples in Ref. [3]. Seeing that the purity and the cold deformation degree of Ag in present work are 99.999% and 98%, respectively, the above comparison indicates that the higher the purity of Ag, the faster the recovery process when the cold deformation degree is the same; and that the higher the cold deformation degree, the faster the recovery process when the purity of Ag is the same.

Fig. 1 Tensile strength σ_b vs annealing temperature for cold deformed Ag
($\Phi = 90$, purity of Ag= 99.999%)

Table 1 Relative decrement of strength and hardness of Ag on the 70th day in recovery process

Age treatment		Hv/ %	σ_b / %
$\varepsilon = 75\%$	23 ℃	25	–
	50 ℃	45	–
$\Phi = 98\%$	23 ℃	–	40
	50 ℃	–	50

The elongation changes of pure Ag wire samples with cold deformation degree $\Phi = 98\%$ in recovery process are shown in Fig. 3. The elongation of cold deformed Ag was about 1%. In 23 ℃ recovery process, the elongation increased gradually and reached 25% on the 70th day; in 50 ℃ ageing process, the elongation increased rapidly during early days and then reached a stable value of about 28% after 30 d.

The changing trend of the strength properties and elongation indicated that highly pure silver showed a self-softening phenomenon in the

Fig. 2 Dependence of hardness and tensile strength of Ag on recovery time
($\varepsilon = 75\%$, $\Phi = 98\%$)
1—23 ℃; 2—50 ℃

Fig. 3 Dependence of elongation of Ag on recovery time
1—50 ℃; 2—23 ℃

natural ageing process. Obviously, the self-softening effect is because that, under low recrystallization temperature of highly pure silver (about 70 ℃), the recovery process can go on spontaneously at ambient temperature. So, the self-softening of highly pure Ag is just its recovery softening.

3.2.2 Electrical Resistivity

The electrical resistivity of pure Ag is 1.59 μΩ·cm. It increased with the cold deformation degree and reached 1.71 μΩ·cm when ϕ = 98% (Fig. 4(a)). In the recovery process followed, the resistivity decreased from the value of 1.71 to 1.64 μΩ·cm at 23 ℃ ageing and 1.61 μΩ·cm at 50 ℃ ageing for 50 d (Fig. 4 (b)). According to the relationship between the resistivity and the cold deformation degree, the remnant deformation in the recovery process could be derived to be 45% and 25% at 23 and 50 ℃ ageing for 50 d, respectively.

3.2.3 Crystal Lattice Distortion

The changes of (420) X-ray diffraction peaks of Ag in both states of cold deformation with ε = 90% and ageing at 23 ℃ for different times are shown in Fig. 5. Because of the lattice distortion and crystal grain smashing, the diffraction peaks of cold deformed silver are diffusing and broadening, just like the 1 day's peak in Fig. 5. During the natural ageing (at 23 ℃) process, the full width at half-maximum (FWHM) of the diffraction peak reduced gradually (Table 2); the two peaks of $K_{\alpha 1}$ and $K_{\alpha 2}$

Fig. 4 Electrical resistivity (a, b) and remnant deformation (c) in cold deformation and recovery processes
1—23 ℃; 2—50 ℃

Fig. 5 Changes of (420) diffraction peak of cold deformed(ε = 90%) Ag in 23 ℃ recovery process
1—32 d; 2—20 d; 3—11 d; 4—7 d; 5—3 d; 6—1 d

were separated on the 7th day and then became sharper and sharper. It is clear that the cold deformed silver has a tendance of gradually reducing its lattice distortion at ambient temperature. The process was quickened as the age temperature rising. The separated pesks, $K_{\alpha 1}$ and $K_{\alpha 2}$, became sharper at 50 ℃ ageing for 32 d. The diffraction peaks separated completely at 80 ℃ ageing(Fig. 6); in other words, pure Ag has recrystallized, and the lattice distortion caused by cold deformation has disappeared.

Fig. 6 The (420) diffraction peak of Ag aged at 80 ℃
1—7 d; 2—3 d; 3—1 d

Table 2 Changes of FWHM of (420) peak of cold deformed Ag in 23 ℃ recovery process

Time/d	2θ/(°)	FWHM
1	114.938	0.754
3	114.958	0.707
7	114.936	0.426
11	114.916	0.238
20	114.834	0.191
32	114.912	0.180

It is well known that both crystal grain smashing and lattice distortion would cause the diffraction peak broadening (except that caused by instrument). According to the theory of diffraction peak broadening of deformed metal, the broadening caused by crystal grain smashing can be expressed by Scherrer formula:

$$\beta(2\theta) = K\lambda/L \cdot \cos\theta \quad (1)$$

and the broadening caused by lattice distortion can be expressed as:

$$\beta(2\theta) = 4\delta d/d \cdot \tan\theta \quad (2)$$

Under the cold deformation condition, both broadenings exist simultaneously, so:

$$\beta(2\theta) = K\lambda/L \cdot \cos\theta + 4\delta d/d \cdot \tan\theta \quad (3)$$

where $\beta(2\theta)$ is the width of 2θ diffraction peak; λ is the length of diffraction wave; L is the size of crystal grain or subgrain due to crystal smashing; $\delta d/d$ is lattice distortion. The broadening expressed by formula (3) can be approximative using Cauchy or Gauss functions; and based on the approximation, a special analytical program for grain size and lattice distortion can be drawn up. In present work, after introducing the width values of (311), (331), (420) and (422) peaks to the program, the lattice distortions and sizes of subgrains were found for Ag in both states of the cold deformation with $\varepsilon = 90\%$ and the recovery. Their changes in the recovery process are shown in Fig. 7.

The subgrain size of Ag was about 40 nm in cold deformed state and grew up to about 110 nm in aged state at 23 ℃ for 32 d. The lattice distortion caused by cold deformation reduced gradually in the natural recovery process. Obviously, the evolution tendence of the lattice distortion is the same as that of the strength

Fig. 7 Changes of lattice distortion(a) and subgrain size(b) of cold deformed Ag in natural recovery

properties of Ag, indicating that it is the relaxation and reduction of lattice distortion that lead to the decrease of the strength and hardness of Ag, namely the recovery softening.

4 KINETICS OF RECOVERY OF COLD DEFORMED Ag

Suppose x is the instantaneous value of a certain property at the time t, then, the decaying rate of x in the isothermal ageing process depends on x[7], that is:

$$dx/dt = -\alpha x \quad (4)$$

and

$$\alpha = A\exp(-E/kT) \quad (5)$$

where E is the activation energy; k is Boltzmann constant; A is a constant; T is kelvin temperature.

Substitute formula (5) into formula (4) and integrate it:

$$\ln(x_0/x) = -K'\exp(-E/kT)t \quad (6)$$

Suppose E is independent of x, and

$$K = -K'\exp(-E/kT) \quad (7)$$

Then formula (6) can be rewritten as:

$$\ln(x_0/x) = Kt \quad (8)$$

Eq. (8) is the isothermal recovery rate equation, where K is the recovery rate constant. In present work, taking the tensile strength σ_b as x in formula (8), the plot of $\ln(x_0/x)$ vs t was obtained and shown in Fig. 8. The isothermal recovery rate constants of Ag were found to be $1.17\times10^{-3}\ h^{-1}$ at 23 ℃ and $2.27\times10^{-3}\ h^{-1}$ at 50 ℃, respectively.

The recovery activation energy (E) calculated from formula (7) was 20 kJ/mol, lower than the recrystallization activation energy (88 kJ/mol)[3] of Ag with 99.995% purity and 98% cold deformation degree. Because the temperature of recovery is much lower than that of recrystallization, and the purity of Ag used in present work is higher, the lower recovery activation energy measured should be reasonable.

5 DISCUSSION

That the resistivity of Ag increased in cold deformation process is attributed to the increase of the concentration of point defect and the dislocation density. The concentration (C) of point defect is related to the plastic deformation degree ε[6]:

$$C \approx 10^{-4}\varepsilon \quad (9)$$

Fig. 8 Recovery rate equation of cold deformed Ag

($\ln(x_0/x) = Kt$, $x = \sigma_b$, $\Phi = 98\%$)

1—50 ℃; 2—23 ℃

In recovery process, both the resistivity and remnant deformation of Ag decreased (Fig. 4 (b), (c)). The remnant deformation was about 45% at 23 ℃ ageing for 50 d, and about 25% at 50 ℃ ageing for the same time, meaning that the concentration of point defects reduced also. On the other hand, the diffusion of vacancies and movement of dislocations led to a series of changes of microstructure, such as the dislocation loops disappearing, the dislocation dipoles annihilating, the remnant dislocation rearranging, polygonization, subgrain growth and so on, by means of which the storage energy of cold deformation was freed out. So, the recovery process of cold deformed Ag deals with a comprehensive recovery mechanism of point, line and plane defects. Based on the low recovery activation energy, the recovery mechanism is controlled, fundamentally speaking, mainly by the recovery mechanism of point defects. Since the driving force, namely the barrier potential needed to be overcome, for recovery of point defect is small, the lattice distortion would reduce, in

other words, the distorted lattice would become relaxation, and subgrains would grow up even at ambient temperature.

So, the parameter x in formula (4) can be considered as the intensity of point defects causing changes of properties of cold deformed metal, and α represents the probability of disappearance of point defect in a unit of time[6]. The recovery process of high pure Ag just reflects this characteristic.

6 CONCLUSIONS

(1) The recrystallization temperature of Ag with purity of 99.999% and cold deformation degree of 98% was determined to be 70 ℃. At ambient temperature, the cold deformed highly pure Ag showed a feature of natural recovery softening, and its hardness, tensile strength, resistivity and lattice distortion, etc. decreased, whereas the elongation increased and subgrain sizes grew up. The recovery softening process was quickened with the increase of cold deformation degree and the rise of ageing temperature.

(2) The recovery process of cold deformed highly pure Ag obeyed the isothermal recovery rate equation: $\ln(x_0/x) = Kt$. The calculated K values of highly pure Ag with cold deformation degree $\Phi = 98\%$ were $1.17 \times 10^{-3}\ h^{-1}$ at 23 ℃ ageing and $2.27 \times 10^{-3}\ h^{-1}$ at 50 ℃ ageing. The recovery activation energy was found to be $E = 20\ kJ/mol$. The recovery process of cold deformed highly pure Ag was controlled mainly by the recovery mechanism of point defects. In this sense, the parameter x in formula (4) could be considered as the intensity of point defects causing changes of properties of cold deformed metal, and α represented the probability of disappearance of point defects in a unit of time.

REFERENCES

1 Osswald E. Z Metallkd, 1935, 27: 101.
2 Althaus B. Metall, 1963, 17: 708.
3 Harmsen U, Saeger E K. Metall, 1974, 28: 683.
4 Liu Zeguang, Liu Qing, Yang Futao, Li Xienong. Precious Metals, (in Chinese), 1991, 12: 12.
5 Yang Futao, Liu Zeguang, Tang Min. Precious metals, (in Chinese), 1992, 13: 22.
6 Martin J W, Doherty R D. Stability of Microstructure in Metallic System. London: Cambridge University Press, 1976.

(Edited by Li Jun)