

Dynamics of phase transformation of Cu-Cr-Zr-Ag Alloy

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Abstract: Dynamic kinetic of phase transformation of Cu-Cr-Zr-Ag alloy has been studied according to the relationship between electrical conductivity and the volume fraction of phases during the aging. Based on above experiments, the Avrami empirical equation and electrical conductivity equation can be respectively identified at different aging treatment. S-curve of the dynamic kinetic during the aging process and C-curve of isothermal transformation for the Cu-Cr-Zr-Ag alloy are obtained.

Keywords: Cu-Cr-Zr-Ag alloy; Electrical conductivity; Microstructure; Phase transformation; Dynamic kinetic

1. Introduction

The Cu-Cr-Zr-Ag alloy has been widely used for many applications such as railway contact wire [1], lead frame and electrodes cap [2-5], because of their good mechanical properties as well as high electrical conductivity [2,6]. The fine Cr-rich and Zr-rich phases are precipitated during aging process attribute to the excellent strength[6,7], whereas the high conductivity is owe to the extremely low concentration of Cr and Zr in Cu matrix at room temperature [8-11].

In Cu-Cr-Zr-Ag quaternary alloy, the process that solute atoms Cr and Zr are precipitated from supersaturated solid solution to form new phases is a complex phase transformation process. Moreover, the volume fraction, size, morphology and distribution of precipitated phases are closely related to the properties of the alloy, and there are many factors affecting the phase transformation process. Therefore, it is almost impossible to systematically analyze the phase transformation process from the perspective of kinetics. However, in the phase transformation process of Cu-Cr-Zr-Ag alloy, the precipitation of the second phase has a great influence on the electrical conductivity [12]. So, by



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measuring the transformation of electrical conductivity of Cu-Cr-Zr-Ag alloy during aging, this chapter obtains the conversion rate of the second phase during aging, determines the Avrami equation of phase transformation kinetics, and draws the temperature-time-transformation (TTT) curve of Cu-Cr alloy, so as to provide a theoretical basis for experimental research and industrial production of the alloy.

2. Experiment

A cold rolled $\Phi 5\text{mm}$ Cu-0.74Cr-0.12Zr-0.095Ag (wt. %) bar was put under solid solution treatment at 1000°C for 1h. It was then aged at 400°C , 450°C , 500°C and 550°C for 5 min to 24 hours. The electrical conductivity of the samples after different treatments were measured by the TH2512B intelligent DC low resistance tester. The samples used for TEM observation were cut from the bar aged for different time durations and then prepared by the electro-polishing method with the mixture electrolyte of 50ml HNO_3 and 150ml CH_3OH at -30°C . Most of the thin foils for this study was studied by using acceleration voltages of 200kV in JEM 2100 LaB6 microscope.

3. Experimental results and Discussion

3.1 Calculation of volume fraction of the new phase in the aging process of Cu-Cr-Zr-Ag Alloy

In the aging process of Cu-Cr-Zr-Ag alloy, the supersaturated solid solution is precipitated and decomposed, and a great deal of solute atoms are precipitated from the matrix, forming a new phase. Even if phase equilibrium can be reached inside the alloy, not all solute atoms of Cr, Zr and Ag in the alloy can precipitate out. In this case, the volume conversion f of the new phase β can be expressed as [13]:

$$f = V^\beta / V_p^\beta \quad (1)$$

Wherein, V_p^β is the equilibrium volume of the new phase formed in unit volume, and V^β is the volume of the new phase formed in unit volume at a certain time point in the aging process. The moment aging is started, $V^\beta=0$, $f=0$, and the electrical conductivity is marked as initial electrical conductivity σ_0 ; When the alloy reaches the phase equilibrium state at this aging temperature and the electrical conductivity almost does not change any more, the electrical conductivity can be considered to have reached its maximum value σ_{\max} , i.e. $V^\beta=V_p^\beta$, $f=1.0$.

Because the concentration of solute atoms in Cu-Cr-Zr-Ag alloy is quite low, the resistivity of the alloy, according to Matthiessen-Fuliminge Law [14], can be expressed as:

$$\rho_s = \rho_0 + a\rho \quad (2)$$

Wherein, ρ_0 is the resistivity of pure copper, a is the atomic fraction of solute, and ρ is the variation of resistivity induced by solute atoms. Formula (2) shows that there is a linear relationship between the solid solution atomic fraction and the resistivity of copper alloys. Therefore, it can be concluded that the volume conversion f of the new phase also have linearly relation with the alloy's electrical conductivity σ , as shown in the following equation:

$$\sigma = \sigma_0 + Af \quad (3)$$

When phase transformation comes to an end, it can be confirmed that $\sigma=\sigma_{\max}$, $f=1$, and $A=\sigma_{\max}-\sigma_0$. Therefore, the volume conversion rate of the new phase can be calculated only by measuring the

alloy's electrical conductivity under a certain aging regime.

The influence of aging time at 400~550°C on the electrical conductivity of Cu-Cr-Zr-Ag alloy shows in Figure.1. Table 1 shows the relationship between the volume fraction of new phase and Cu-Cr-Zr-Ag quaternary alloy's electrical conductivity of solid solution during the aging process at 400~550°C.

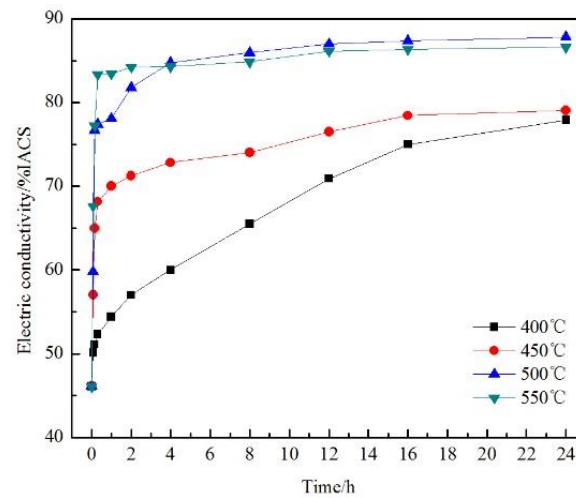


Figure. 1 Electrical conductivity curves of Cu-Cr-Zr-Ag alloy under different aging regimes

Table 1 Volume fraction of new phase and electrical conductivity of Cu-Cr-Zr-Ag alloy under different aging regimes

t/min	400°C		450°C		500°C		550°C	
	σ/IACS%	f/%	σ/IACS%	f/%	σ/IACS%	f/%	σ/IACS%	f/%
0	46.1	0	46.1	0	46.1	0	46.1	0
5	50.1	13.42	57	33.07	59.8	32.83	67.6	53.02
15	53.8	25.84	65	57.35	76.68	73.27	77.23	76.77
30	56.4	34.56	68.16	66.92	77.39	74.99	83.37	91.89
60	58	39.93	70.01	72.56	78.09	76.65	83.44	92.07
120	60.2	47.32	71.24	76.27	81.81	85.57	84.23	94.03
240	62	53.36	72.82	81.07	84.75	92.61	84.31	94.21
480	66.5	68.46	74.04	84.78	85.97	95.55	84.85	95.56
960	71	83.56	76.49	92.21	87	98.02	86.15	98.77
1440	73	90.27	78.45	98.15	87.4	98.97	86.38	99.32

3.2 Precipitation kinetics equation and electrical conductivity equation

The relationship of aging time t with the volume fraction f of Cr phase and Zr-rich phase in the aging process of Cu-Cr-Zr-Ag alloy satisfies the kinetic equation of phase transformation - Avrami empirical equation [14]:

$$f=1-\exp (-bt^n) \quad (4)$$

Wherein, b and n are constants. To calculate the two constants, Equation (4) can be converted into:

$$1-f=\exp (-bt^n) \quad (5)$$

Taking quadratic logarithm for both sides of Equation (5), we can obtain:

$$\ln(\ln(1/(1-f))) = \ln b + n \ln t \quad (6)$$

According to Equation (6), in a coordinate system where $\ln(\ln(1/(1-f)))$ is the ordinate and $\ln t$ is the abscissa, the relationship between the two should be linear, the value of n is equal to the slope of the straight line, while the intercept is $\ln b$, so constants n and b in Equation (4) can be calculated.

Based on the data provided in Table 1, the curves of relationship between $\ln(\ln(1/(1-f)))$ and $\ln t$ are drawn, as shown in Figure. 2, where the former is the ordinate and the latter is the abscissa. It can be seen from Figure. 2 that after linear regression, the curve becomes a straight line.

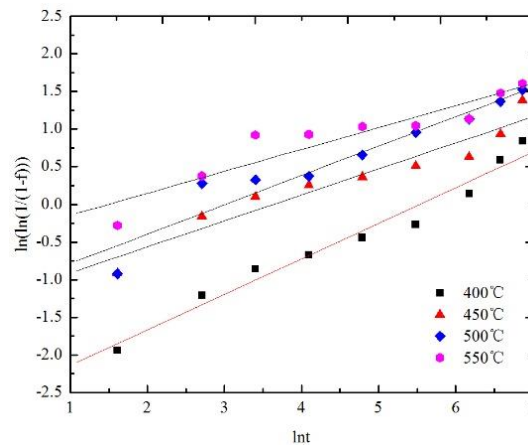


Figure. 2 Relationship between volume fraction and transition time under different aging regimes of Cu-Cr-Zr-Ag alloy

From Equation (6) and Figure.3, we can know the slope and intercept of the straight line, thus obtaining the values of n and b in the equation. These values and the corresponding equations (4) of quaternary alloy at different aging temperatures are shown in Table 2.

Table 2 Equation Coefficients A , n , B and the equations of phase transformation obtained under different aging regimes of Cu-Cr-Zr-Ag alloy

Temperature	Cu-Cr-Zr-Ag			Phase transformation equation
	A	n	b	
400°C	29.8	0.47	0.08	$f=1-\exp(-0.07t^{0.47})$
450°C	32.9	0.34	0.29	$f=1-\exp(-0.29t^{0.34})$
500°C	41.7	0.39	0.31	$f=1-\exp(-0.31t^{0.39})$
550°C	40.6	0.29	0.65	$f=1-\exp(-0.65t^{0.29})$

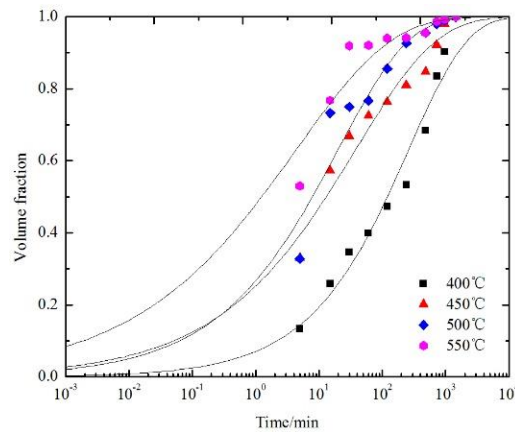


Figure.3 Kinetic curves of phase transformation and transition time of the quaternary alloy under different aging regimes

According to the equations listed in Table 2, we can draw the TTT curves of the precipitate of the alloy aged at 400~550°C. Using Equations (3) and (4) in combination, we can obtain the electrical conductivity equations of Cu-Cr-Zr-Ag alloy isothermally aged at 400~550°C, as shown in Table 3.

Table 3: Electrical conductivity equations of Cu-Cr-Zr-Ag alloy at 400~550°C

Temperature	Cu-Cr-Zr-Ag
400°C	$\sigma=46.1+29.8 (1-\exp(-0.07t^{0.47}))$
450°C	$\sigma=46.1+32.9(1-\exp(-0.29t^{0.34}))$
500°C	$\sigma=46.1+41.7 (1-\exp(-0.31t^{0.39}))$
550°C	$\sigma=46.1+40.6(1-\exp(-0.65t^{0.29}))$

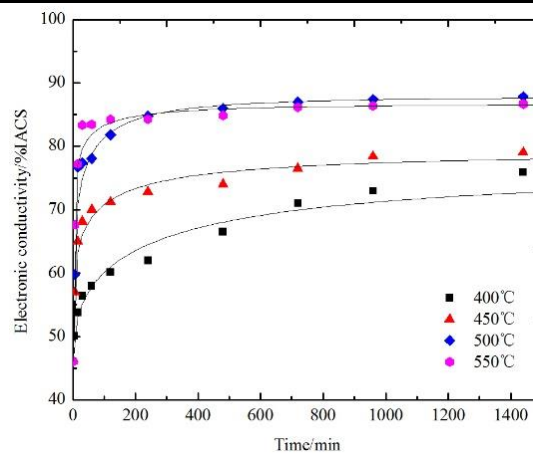


Figure.4 Electrical conductivity curves of Cu-Cr-Zr-Ag alloy under different aging regimes

Based on the equations given in Table 3 and experimental data, the alloy's electrical conductivity curves under different aging regimes are plotted, as shown in Figure. 4. The figure clearly shows the difference between the actual measured value of the alloy's electrical conductivity and the calculated result of the equation under each aging regime. Comparing calculated value (curve, CC) and the measured value (point, TC) of the electrical conductivity of Cu-Cr-Zr-Ag alloy at the aging temperature of 450°C, we see that the difference between the two values is basically controlled within 5%, which shows that the conductivity equation can satisfactorily reflect the change of conductivity.

Table 4 Comparisons between the values calculated from the conductivity equation and the actual measured values of electrical conductivity of quaternary alloy at the aging temperature of 450°C

t/min	Cu-Cr-Zr-Ag	
	TC /IACS%	CC /IACS%
0	46.10	46.10
5	57.00	59.07
15	65.00	63.12
30	68.16	65.91
60	70.01	68.76
120	71.24	71.49
240	72.82	73.93
480	74.04	75.91
720	76.49	76.82
960	78.45	77.35
1440	79.06	77.94

3.3 Temperature-time-transformation (TTT) curve

In this paper, the isothermal aging of Cu-Cr-Zr-Ag inly carried out in the range of 400°C~550°C. According to formula (7), the time that precipitation transformation start and end at each aging temperature can be obtained based on Equation (7). In this paper, the time when 10% of the new phase has appeared is defined as the starting time of precipitation reaction, and the time when 90% of the new phase has been formed is defined as the ending time [15]. According to this definition, the starting time and ending time of the alloy at 400°C~550°C can be obtained, as shown in Table 6.

$$t = \exp\left\{\frac{1}{n} \ln\left[-\frac{\ln(1-f)}{b}\right]\right\} \quad (7)$$

Table 5 Calculated precipitation time (min) of Cu-Cr alloy

Alloy	Temperature/°C	400	450	500	550
Cu-Cr-Zr-Ag	t _{start}	2.196	0.053	0.064	0.002
	t _{end}	1544	459	174	78

The TTT curve of Cu-Cr-Zr-Ag alloy plotted based on the data in Table 6 is shown in Figure. 5.

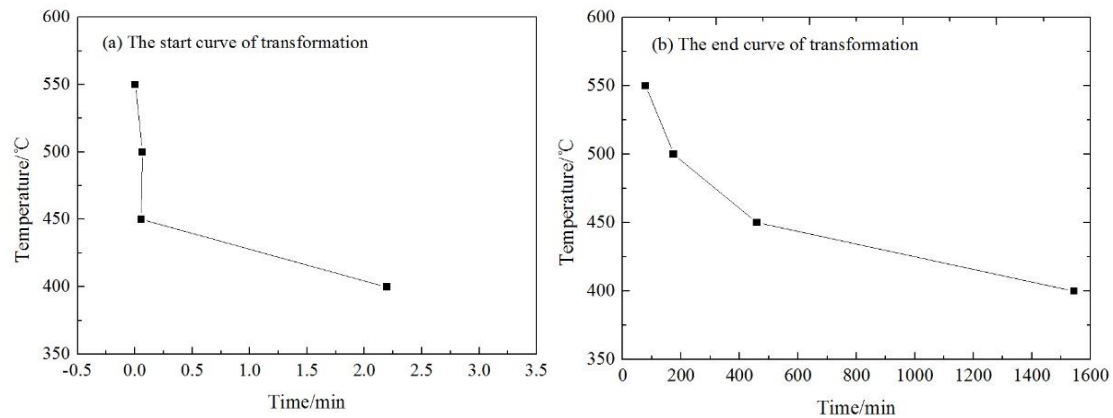


Figure.5 TTT curve of Cu-Cr-Zr-Ag alloy

As shown in Figure. 5, the two TTT curves of the quaternary alloy are both C-shaped, and the starting time of precipitation of the new phase becomes shorter as the aging temperature rises.

3.4 Microstructure observation

Figure.6 shows the Microstructure TEM patterns of Cu-Cr-Zr-Ag alloy aged at 450°C for different aging duration. When the Cu-Cr-Zr-Ag alloy aged at 450°C for 5 min, G.P zones can be found in the matrix (Figure. 6(a)), which leads to the increase of electrical conductivity at the early stage of aging. When the alloy is aged for 4 h, a great deal of Cr phases are found in Cu matrix (Figure. 6(b)). With the extension of aging time, the G.P zones transform to the Cr precipitates gradually and a large number of solute atoms precipitate out from the matrix at the same time, which decreases the contents of the solute atom in the matrix and as a result of a continuous increase in conductivity during the aging treatment. Aged for 24 h, due to the size of Cr precipitates grow larger (Figure. 6(c)) and solute atoms cannot precipitate out any more from Cu matrix, the electrical conductivity becomes stable at the later stage of aging.

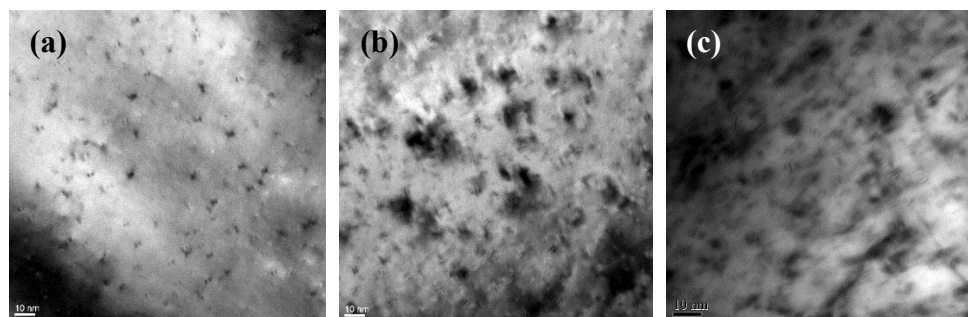


Figure. 6 Microstructure of Cu-Cr-Zr-Ag alloy aged at 450°C (a) aged for 5 min
(b) aged for 4 h (c) aged for 24 h

4. Conclusions

- (1) Under different aging regimes, the curve of relationship between the electrical conductivity and aging time of Cu-Cr-Zr-Ag alloy rises rapidly at first, then rises slowly, and finally tends to be flat.
- (2) The Avrami kinetic equation of phase transformation and electrical conductivity equation of Cu-Cr-Zr-Ag alloy at different aging temperatures are deduced and calculated.

(3) The starting time and ending time of transformation of the second phase are calculated, the TTT curve of Cu-Cr-Zr-Ag alloy is drawn, and the curve is C-shaped.

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5. References

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