MODELLING OF BREAKUP OF Cr FILAMENTS IN WIRE-DRAWN Cu-BASED IN SITU COMPOSITES①

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ABSTRACT The breakup kinetics of Cr filaments in Cu-3%Ag-10%Cr (mass fraction) wire drawn in situ composites ($\eta = 3.95$) was monitored by quantitative metallography. Experimental results were compared with existing models and an appropriate physical model for breakup of filaments was provided. Breakup kinetics in this composite was consistent with interfacial diffusion, and the interfacial diffusion coeffcient was found to be D_i(Cr in Cu(Ag)-Cr interface) = $47.4\exp(-137\,000/RT)$ cm^2/s between 600 and 950 ℃ by Courtney's boundary splitting model, R in J/(mol·K).

Key words Cu-based in situ composite Cr filament breakup kinetics modelling

1 INTRODUCTION

The Cu-based in situ composites, because of their excellent mechanical and physical properties[1], have been considered as a candidate for the long-pulse high-field magnets[2]. Due to suffering a certain temperature in prolonged service, it is important to consider both the mechanical and morphological stability of these composites. Previous researches[3-5] have indicated that coarsening and breakup of refractory metal filaments occurred during annealing. But the studies were only qualitative. Courtney *et al*[6,7] have investigated the instability of Fe plates in Cu-Fe in situ composites and provided mathematical models, but they have not provided experiment to test and verify their models. In the present paper, we study the morphological developments of Cr filaments in wire drawn Cu-3%Ag-10%Cr in situ composites and compare our results with the existing models and try to show the appropriate physical model for breakup kinetics of Cr filaments.

2 EXPERIMENTAL PROCEDURE

Ingots of Cu-3%Ag-10%Cr were prepared by consumable arc melting. The final ingot was approximately 18.0 mm in diameter. After consolidation, the material was swaged from 18.0 to 6.7 mm, then drawn to 2.5 mm in diameter. Deformation reduction was given in terms of logarithmic strain by $\eta = (A_0/A_f)$, where A_0 is the initial section, A_f is the final section. In this paper the deformation reduction is $\eta = 3.95$. The samples were annealed at various temperatures and times in vacuum. The microstructures of the wire drawn and annealed were examined respectively by scanning electron microscopy (SEM) and optical microscopy. Data of the breakup diameter was measured by quantitative metallography, each experimental value was the average of 50 measurments.

3 RESULTS

Previous study[8] indicated that the microstructure of Cr phase in as-drawn Cu-3%Ag-10%Cr alloy ($\eta = 3.95$) presents thin filament. On transverse section, the Cr dendrites adopt a filamentary morphology, the Cr filaments are 4.40 μm wide and 0.60 μm thick on average, the ratio of width to thickness (w/d) is 7.33. On longitudinal section, the filament thickness is

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0.87 μm, the interfacing between filaments is 3.33 μm on average. During annealing, the Cr filaments are subjected to longitudinal splitting, initial breakup, spheroidization and Oswald ripening. Fig.1 shows the SEM micrographs of wire drawn Cu-3%Ag-10%Cr alloy (η=3.95) after annealing at 1 000 ℃ for 4 h. It is obvious on the transverse section (Fig.1(a)) that the filaments have been broken up by splitting through its thickness. On longitudinal section (Fig.1(b)), longitudinal splitting, cylinderization and breakup occur.

The observation indicated that the longitudinal splitting of Cr filaments occurs at a temperature as lower as 400 ℃. This maybe result from the sufficient dislocations and subgrain boundaries. After longitudinal splitting, the cylinderization occurs. For cylinderization, Courtney[7] has given a model (interfacial diffusion is dominant):

$$t/\tau_b d = 0.0293(w/d)^{7/3} \quad (1)$$

where t is the interface thickness over which interfacial diffusion occurs; τ_b is a base time, $= d^3 KT/DC_0 \gamma_s \Omega^2$, in which C_0 is the equilibrium matrix concentration of filaments material for a flat fiber/matrix interface; d is the plate thickness; w is the plate width. Owing to splitting, $w/d \approx 1$ (Fig.1(a)), then $\tau = 0.0293\ d_4^0/B_{Cr}$. Comparing with Table 2, we can see that the time required by cylinderization are 2 to 3 orders of magnitude smaller than that by breakup, which can be neglected. Through longitudinal splitting and cylinderization, the Cr filaments gradually change into long and narrow rods, which are relatively unstable and tend to break up into a series of small spheroids. The detectable breakup occurs after annealing at 500 ℃ for 2 h. Then the breakup diameter increases with increasing annealing temperature and time. In the whole process of microstructure changes of Cr filaments the breakup stage is dominant. The schematic of the Cr filament instability is shown in Fig.2.

The diameters of Cr filaments, which have just broken up after annealing at various processes, are plotted in the form of lg d vs lg τ in Fig.3. We can know that the data exhibit some scatter, which perhaps mainly comes from the heterogeneity in initial microstructure state and experimental error. From Fig.3 we can also see that the experimental values give the reasonable straight line plots. The slopes of the line are approximately the same as that of line n=4.

We measure the ratios of the wavelength to the diameter of the breakup filaments. At 600 to 1 000 ℃, the average values of ratios vary between 3.30 and 4.40, the range of values observed varies between a minimum of 1.41 and a maximum of 7.79. The distributions of ratio are

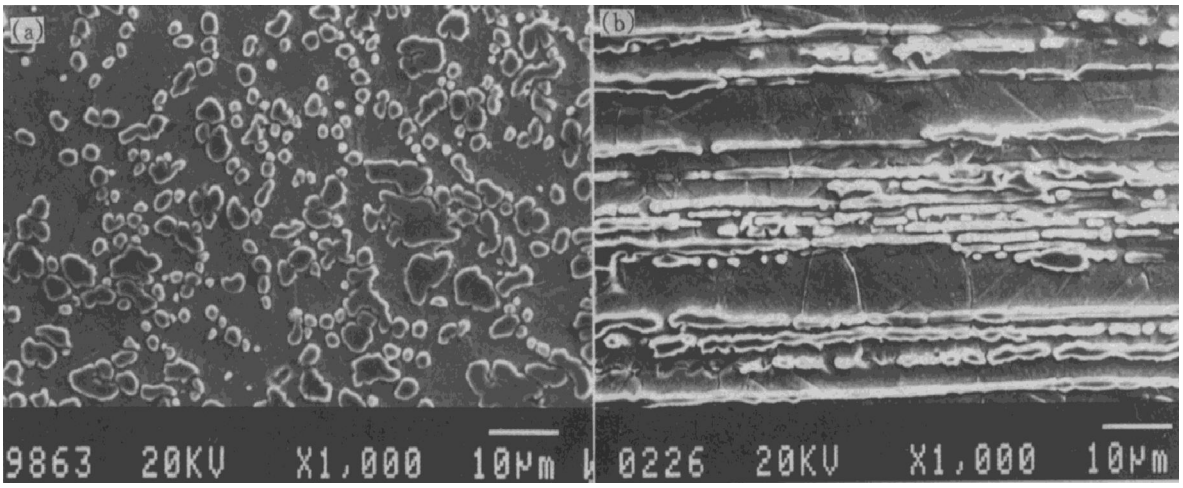

Fig.1 SEM micrographs of shape changes of Cr filament of (a) transverse and (b) longitudinal sections in Cu-3%Ag-10%Cr wire drawn in situ composites(η=3.95) after 1 000 ℃ for 4 h annealing

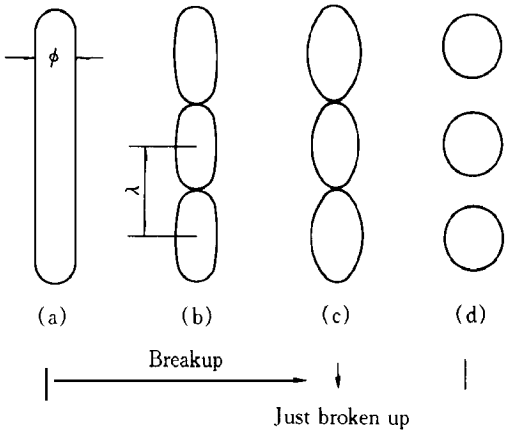

Fig.2 Schematic of Cr filaments instability in wire drawn Cu-Ag-Cr (η=3.95) composite

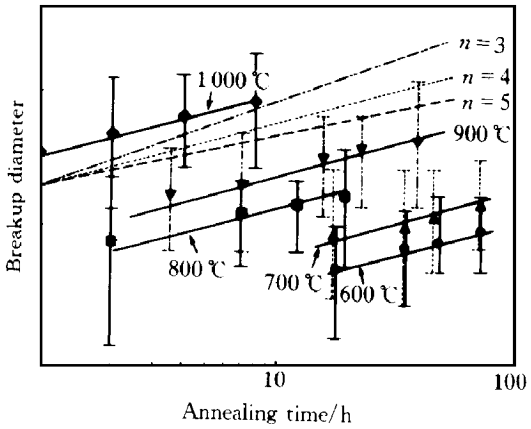

Fig.3 Plot of lg d vs lg τ at 600, 700, 800, 900 and 1 000 ℃ (Three straight lines n(1/slope) = 3, n = 4 and n = 5 are referential lines)

listed in Table 1.

4 DISCUSSION

4.1 Breakup models

The mechanisms which induce changes in rod- or plate-shaped structures upon elevated temperature exposure are driven by capillary forces. Nichols and Mullins delineated the basic physics and developed the fundamental mathematics necessary for understanding the shape changes due to capillarity-induced surface diffusion. The starting point for their description is the Gibbs-Thomson relation:

$$\Delta\mu = \Omega K \gamma_s \quad (2)$$

where $\Delta\mu$ is the difference in chemical potential of an atom on a curved surface relative to one on a flat surface; Ω is the volume of diffusing atoms; K the is surface curvature difference between surfaces; γ_s is the surface energy. The driving force is the chemical potential gradient.

4.1.1 Perturbation model (Model 1)

The growth of a shape perturbation on liquid cylinder was analysed a century ago by Rayleigh. Then, Nichols and Mullins, Cline and Weatherly extended Rayleigh's perturbation assumption to a solid cylinder and platelet. The quantitative model was drawn from Eq.(2). Their analyses[9-11] predict that if the interfacial diffusion controls the perturbation process, then the rate of growth of a sinusoidal perturbation in an infinite cylinder will be given by

$$d\delta/d\tau = \delta B \omega^2 (1/r_0^2 - \omega^2) \quad (3)$$

where δ is the perturbation amplitude; τ is the annealing time; $\omega = 2\pi/\lambda$ is the spatial frequency of the perturbation; λ is the wavelength of perturbation; r_0 is the initial radius; $B = D_I \gamma_I v \Omega^2 / KT$, in which D_I is the interfacial diffusion coefficient, γ_I is the interfacial energy, v is the number of diffusing atoms per unit area, and $v = \Omega^{-2/3}$, Ω is the volume of diffusing atoms, k is the Boltzmann's constant, T is the absolute temperature.

After mathematical dealing the time required for the filaments of radius r_0 to breakup will be given by

$$\tau = \ln(r_0/\delta_0)/[B(T) \cdot C(r_0, \lambda] \quad (4)$$

Table 1 Data on breakup

Annealing process	Wavelength-to-breakup diameter ratio Average value (minimum and maximum observed)	Average breakup diameter (/μm)
600 ℃, 2 h	4.26 (2.62 to 7.13)	0.39 ±0.07
700 ℃, 2 h	3.47 (1.70 to 6.31)	0.51 ±0.09
800 ℃, 2 h	4.40 (2.20 to 6.10)	0.60 ±0.20
900 ℃, 2 h	3.67 (1.41 to 5.57)	0.84 ±0.17
1 000 ℃, 2 h	3.33 (1.41 to 7.79)	1.60 ±0.45

where $C(r_0, \lambda) = \omega^2(1/r_0^2 - \omega^2)$; δ_0 is the initial sinusoidal perturbations(It can be taken to be of the order of Burgers vector[5]).

4.1.2 Thermal groove model (Model 2)

If an array of internal boundaries or sub-boundaries is introduced into a plate structure, an initial local equilibrium of surface tension will be established at each of the triple point junctions and form a grain boundary groove. This introduces curvature into the plate interface and a chemical potential gradient. Diffusion of atoms leaving the curved groove in response to the chemical potential gradient will force the groove to grow and finally cause a plate to break up. Mullins and co-workers have described the physics of thermal grooving. The growth model of depth and width of grain boundary thermal groove has been drawn based on derivation and solution of Eq.(2). If the interfacial diffusion is dominant, the depth of the thermal groove is given by[12-13]

$$r = 0.974\, m(Bt)^{1/4} \tag{5}$$

where t is the annealing time; m is the slope of the interface at the groove root, $\approx \gamma_b/2\gamma_s$ (see ref.[12]); B has been defined previously.

The time for the thermal groove at either end to meet can be estimated from eq.(4) and given by

$$\tau = (r_0/0.974\, m)^4/B \tag{6}$$

4.1.3 Boundary splitting model (Model 3)

Courtney *et al*[7] have drawn another model for shape instabilities of Fe plates in Cu-Fe in situ composites due to thermal groove. This model is based on a simple averaging of Fick's first law over the process. The instantaneous rate of diffusional volume transport (dV/dt) is obtained by multiplying the atomic flux (J) by the atomic volume (Ω) and diffusion area (A), thus

$$dV/dt = J\Omega A \tag{7}$$

and using Fick's first law Eq.(6) was changed into

$$dV/dt = D\Omega A(dc/dx) \tag{8}$$

The time for completion of each process by manipulation of Eq.(7) is

$$\tau = \delta V/[D\Omega(A\delta c/\delta x)] \tag{9}$$

Then the calculations are approximate ones involving geometrical estimations on volume transport, diffusion area and length, and curvature. Eq.(9) can be given by

$$\tau/\tau_b d = \{[\cos\phi/(1-\sin\phi)^2]\cdot [1-\sin\phi/2-(\pi/2-\phi)/2\cos\phi]\}(\pi/2-\phi)/64(1-\sin\phi)^2 \tag{10}$$

where t is the interface thickness over which interfacial diffusion occurs; d is the plate thickness; $\phi = \cos^{-1}(\gamma_b/2\gamma_s)$; τ_b is a base time, $= d^3KT/DC_0\gamma_s\Omega^2$ in which C_0 is the equilibrium matrix concentration of filament material for a flat fiber/matrix interface. Other parameters have been defined previously.

To model our results, we use some physical constants to calculate the predicted values. The appropriate data for the diffusion of Cr at a Cu(Ag)-Cr interface are not commonly found, we use the surface diffusion coefficient $D_s = 1.1\exp(-52000/1.987\,T)\,cm^2/s$[14], surface energy $\gamma_s = 2.3\times10^{-4}$ J/cm^2[15], grain boundary energy $\gamma_b = 0.98\times10^{-4}$ J/cm^2[15], slope of interface at the groove root $m = 0.213$ (calculated), atomic volume $\Omega = 0.8158\times10^{-23}$ cm^3 (calculated), and initial sinusoidal perturbations $\delta_0 = 0.001\, r_0$ (assumption[5]). Therefore, we can use the above-mentioned three models to analyse the behaviour of breakup. For Cr filaments, the simplified forms are listed in Table 2. It is clear that the main form is identical, only the coeffcients are not the same for three models.

Table 2 Comparison of breakup models for Cr filaments

Model 1	Model 2	Model 3
$\tau = 1.73\, d_0^4/B_{Cr}$ ①	$\tau = 33.74\, d_0^4/B_{Cr}$	$\tau = 18.72\, d_0^4/B_{Cr}$ ②

① assume maximum growth rate $\lambda/d = \sqrt{2}\pi$[16]

② used $tC_0 = v$[13]

4.2 **Modelling**

Mclean[9] indicated that n(1/slope) gives the mechanisms controlling the kinetics of the breakup process: $n = 1$ for viscous or plastic flow, $n = 2$ for interfacial control, $n = 3$ for volume diffusion in all phases, $n = 4$ for interfacial diffusion, and $n = 5$ for pipe diffusion. Here

$n \approx 4$. Ma[10] has indicated that the process of breakup of cylinder is dominated by interface diffusion. Nichols and Mullins[16] have also indicated that when the diffusional distance is $\leq 5\ \mu m$, the surface diffusion is dominant; the dominance of volume diffusion requires diffusion distance $\approx$ 500 μm; in the intermediate range, both processes are important. From Table 1 we can see that in this case the diffusion distance is less than 5 μm. Thus, the breakup process of Cr filaments is dominated by interface diffusion.

Because of the similarity in the final microstructures, it is difficult to identify unambiguously the model of breakup. The analysis by Nichols and Mullins[16] shows that a cylinder will be stable against any perturbation that has a wavelength $\lambda \leq \pi d$ (d is diameter of filaments). Any instability with a longer wavelength can increase its amplitude and lead to breakup. An instability with a wavelength $\lambda = \sqrt{2}\pi d$ has the maximum growth rate and leads to break up most rapidly. According to this analysis, from Table 1 we can conclude that the Cr filaments break up not only by perturbation model, for the ratios $\leq \pi$, they should be by other models.

Comparison of the predicted and experimental values of breakup diameter at 756 ℃ and 835 ℃ is plotted in Fig.4. It is shown that the experimental points exhibit straight line and the slopes are the same as predicted. This further suggests that the controlling mechanism of the kinetics of breakup processes for Cr filaments agrees with the models, i.e., interfacial diffusion. The experimental values are much larger than the predicted values. These large discrepancies cannot be explained by errors in the models or by differences between the existing experimental conditions and the ideal situation under which the models are derived, but maybe come from the inappropriate diffusion coefficients.

There are four possible diffusion paths that could contribute to breakup of the filaments[13]: (a) interface diffusion; (b) volume diffusion through Cu matrix; (c) volume diffusion through Cr filaments; (d) subgrain boundary diffusion. Because the interface diffusion coefficient is much larger than other diffusion coefficients[7], this difference between predicted and experimental values cannot come from other diffusion mechanisms. The research on the stability of lamellar structure during or after deformation indicated that the deformation accelerates the spheroidization of carbides[17]. The theories proposed to explain the rapid rate of spheroidization emphasize the role of strain enhanced diffusivity, either by short-circuit diffusion paths introduced during deformation, e.g. single dislocation or subgrain boundaries, or by solute atom/vacancy complexes. Krotz *et al*[3] also indicated that increased deformation is expected to enhance diffu-

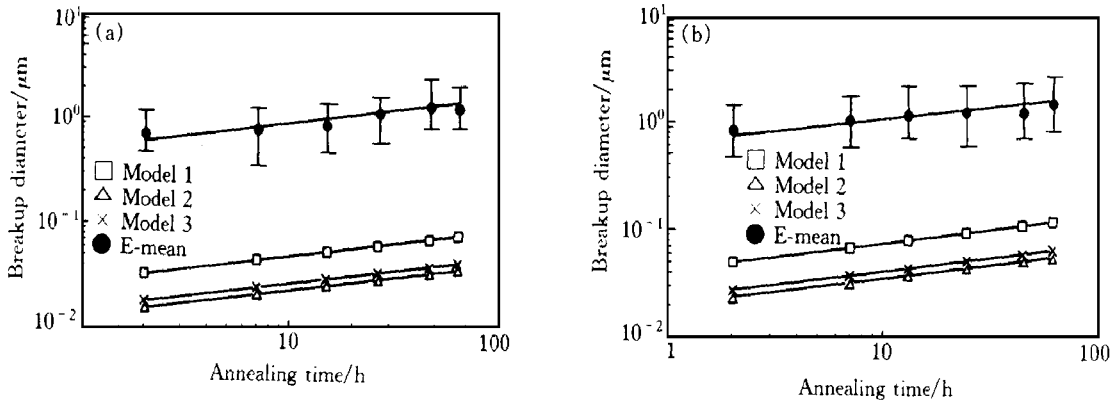

Fig.4 Comparison of predicted and experimental breakup diameters at (a) 756 ℃ and (b) 835 ℃ annealed for Cr filaments in Cu-3%Ag-10%Cr alloy wire drawn to $\eta = 3.95$
(The predicted values are calculated by surface diffusion coefficient $D_s = 1.1\exp(-52000/1.987T)\ cm^2/s$[15].)

sivity which would also contribute to microstructure change. The study on microstructural characterization of Cu-based in situ composites[18] indicated that during deformation the refractory metal filaments act as barries to the motion of matrix dislocations and the maximum dislocation density in the boundaries. Because the interface diffusion is dominant and the activation energy for diffusion along the filament-matrix interface of high density of dislocation is significantly lower than common diffusion, the high diffusivity of Cr atoms along the Cu(Ag)-Cr interface is responsible for the larger experimental values.

There are some indefinite parameters in Model 1 and Model 2, so we adopt Model 3 to calculate the interface diffusion coefficient. Fig. 5 shows the relationship curve of $\lg D_I$ vs $1/T$. Ignoring the point at 1 000 ℃, the results are described by D_I(Cr in Cu(Ag)-Cr interface) = $47.4\exp(-137\,000/RT)$ cm^2/s, R in J/(mol·K).

We have finally determined whether the interface diffusion coefficient can be used to predict the breakup of the Cr diameter during annealing. We used the above-determined interface diffusion coefficient to calculate the breakup diameters for 2 h and 7 h annealing at varous temperatures, and compared them with the experimental data, as shown in Fig. 6. The agreement between prediction and measurement is good.

5 CONCLUSIONS

The Cr filaments are subjected to longitudinal splitting, cylinderization and breakup during annealing, and the breakup stage is dominant. The breakup kinetics is consistent with interface diffusion, and the interface diffusion coeffcient is found to be D_I(Cr in Cu(Ag)-Cr interface) = $47.4\exp(-137\,000/RT)$ cm^2/s between 600 and 950 ℃ by Courtney's boundary splitting model, R in J/(mol·K).

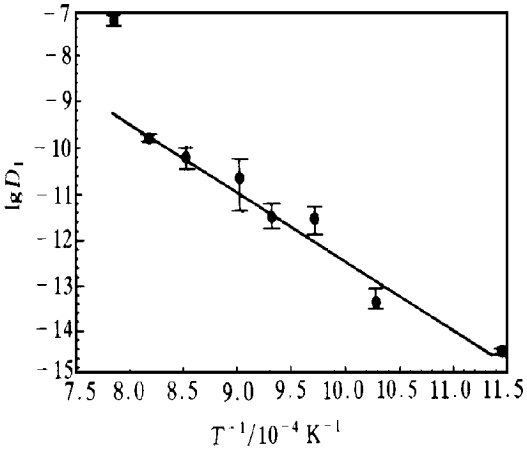

Fig.5 Logarithm of D_I, cm^2/s, vs $1/T$ for Cr in wire drawn Cu-Ag-Cr (η=3.95) composite (D_I was calculated by Courtney's boundary splitting model.)

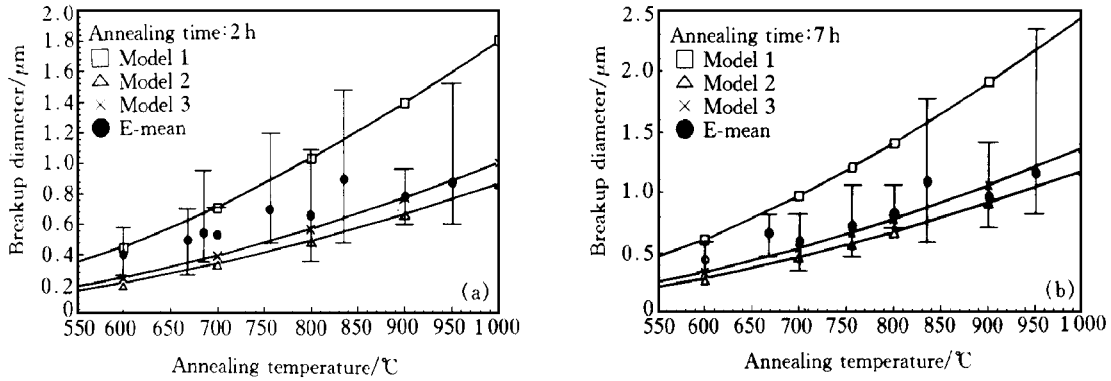

Fig.6 Comparison between experimental and simulated values of breakup diameters of Cr filaments in wire drawn Cu-Ag-Cr (η=3.95) composite (Simulated by $D_I = 47.4\exp(-137\,000/RT)$ cm^2/s, R in J/(mol·K).)

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