

X-RAY STUDY OF COLD-WORK AND RECOVERY IN TUNGSTEN

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ABSTRACT

X-ray line broadening in freshly cold-worked and partially annealed tungsten filings has been subjected to Fourier analysis. Values of small domain size, microstrains and dislocation densities have been estimated. Annealing for an hour at 300° C is shown to reduce the dislocation density in the filings from 3.30×10^{11} to 1.68×10^{11} cm/cm.³ The flow stresses estimated from dislocation densities at different temperatures are found to approximate to measured yield stress values for an annealed sample extrapolated to an extremely high strain rate.

INTRODUCTION

X-RAY line shape analysis of cold-worked metals is done in terms of small domain size, microstrains and stacking faults within these domains. These features are all a manifestation of the complex dislocation substructure in cold-worked metals and a categorization is made only for convenience in analysis. With modern X-ray diffractometer techniques it is now possible to separate out these causes of X-ray line broadening quantitatively with a reasonable degree of confidence.

The object of the present paper is to study the recovery of dislocation density in cold-worked tungsten on annealing at increasing temperatures. Owing to the elastic isotropy and absence of stacking faults on cold-work in tungsten, it is possible to attempt an empirical correlation of the X-ray line broadening results in terms of small domain size and lattice strain with the mechanical properties of the metal.

EXPERIMENTAL PROCEDURE

High-purity tungsten (99.99%) was deformed by filing at room temperature (30° C). The resultant filings were screened through 0.075 mm classifiers and compacted to the required briquette shape for the diffractometer holder. X-ray diffraction peaks were chart-recorded in a Philips X-ray Diffractometer with a scanning speed of 1/8° (in 2θ)/minute, using filtered CuK_α radiation. The deformed filings were annealed for one hour under high vacuum (~10⁻⁵ torr) successively at 300° C, 550° C and 800° C. The X-ray diffraction peaks were chart-recorded from hand-packed briquettes of these filings. Well-annealed tungsten powder (G.E. Standard) was used for recordings of X-ray diffraction peaks under identical conditions to correct for instrumental broadening.

To determine accurately the background level of the broadened peaks the comparison method after Sato¹ was employed. Intensity data from broadened and standard diffraction peaks were used for computation (with an IBM 7044 computer) to arrive at the values of Fourier coefficients corrected for instrumental broadening by the Stokes² method.

EXPERIMENTAL RESULTS

Tungsten is an element of high stacking fault energy and thus the contribution to the broadening of X-ray diffraction peaks by stacking faults is negligible. To separate out the effects of strain and domain size, the Warren-Averbach method³ was followed. The experimentally determined Fourier coefficients (after Stokes correction) A_L are given in this method by

$$A_L = A_L^p \cdot A_L^D \quad (1)$$

where the particle size coefficients A_L^p represent the effect of small domain size and are independent of the order of reflection, while the distortion coefficients A_L^D represent the effect of lattice strains and may be approximated by the relation

$$A_L^D = \exp. \left[\frac{-2\pi^2 L^2 \langle \epsilon_L^2 \rangle}{d^2} \right] \quad (2)$$

where $\langle \epsilon_L^2 \rangle$ is the mean square strain at a distance L normal to the diffracting planes of spacing d . Thus the intercept of a plot of $\ln A_L^p$ against $1/d^2$ for different orders of the same reflection gives A_L^p directly, while the negative initial slope is equal to $2\pi^2 L^2 \langle \epsilon_L^2 \rangle$. Since tungsten is elastically isotropic, data for all reflections can be used for obtaining a plot of $\ln A_L$ vs. $1/d^2$. Figure 1 shows the plots of A_L^p vs. L for the cold-worked and partially annealed tungsten samples. The values of domain size \bar{D} found from the intercept of the initial slope of the A_L^p curve onto L axis are

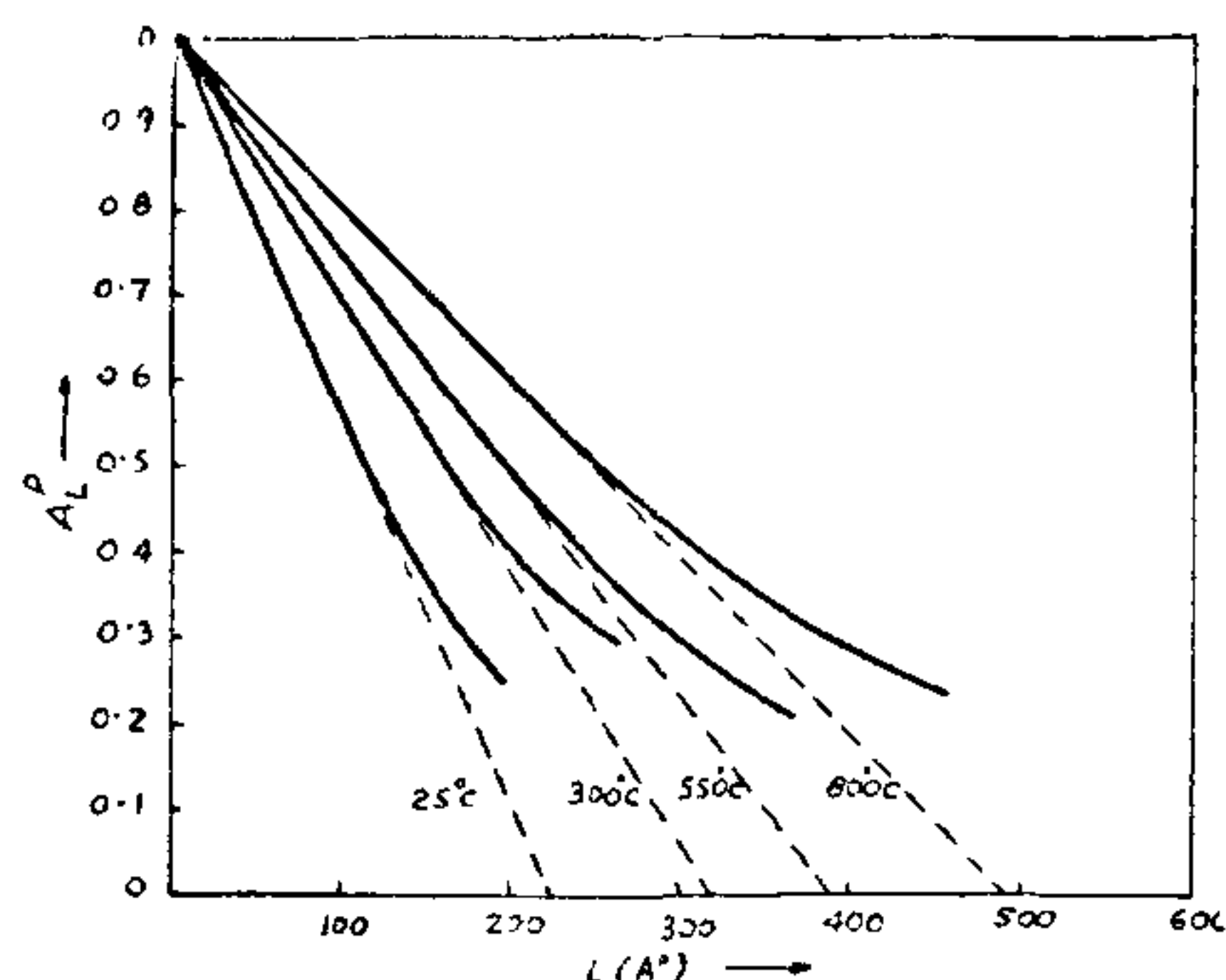


FIG. 1. Plots of particle size coefficients (A_L^P) versus distance in Angstroms (L) for cold-worked and partially annealed tungsten filings.

listed in Table I. Figure 2 shows the variation of the rms strain $(\epsilon_L^2)^{1/2}$ with L . Values of $[(\epsilon_L^2)^{1/2}]^{\bar{D}}$, averaged over the entire domain length (from $L = 20 \text{ Å}$ to \bar{D}) are also given in Table I.

TABLE I

Results of Fourier analysis of X-ray line broadening in tungsten filings

| Temperature °C | Domain size \bar{D} Å | Strain $[(\epsilon^2)^{1/2}]^{\bar{D}} \times 10^3$ | Dislocation density data | | | | Flow stress τ psi |
|----------------|-------------------------|---|--------------------------|--------------------------|-----------------|--------------------------|------------------------|
| | | | $\rho_D \times 10^{-11}$ | $\rho_E \times 10^{-11}$ | ρ_D/ρ_E | $\rho_t \times 10^{-11}$ | |
| 30 | 225 | 2.70 | 5.93 | 1.84 | 3.22 | 3.31 | 104000 |
| 300 | 320 | 1.90 | 2.93 | 0.97 | 3.02 | 1.68 | 75800 |
| 550 | 390 | 1.56 | 1.97 | 0.62 | 3.18 | 1.10 | 59160 |
| 800 | 490 | 1.21 | 1.30 | 0.39 | 3.33 | 0.69 | 46000 |

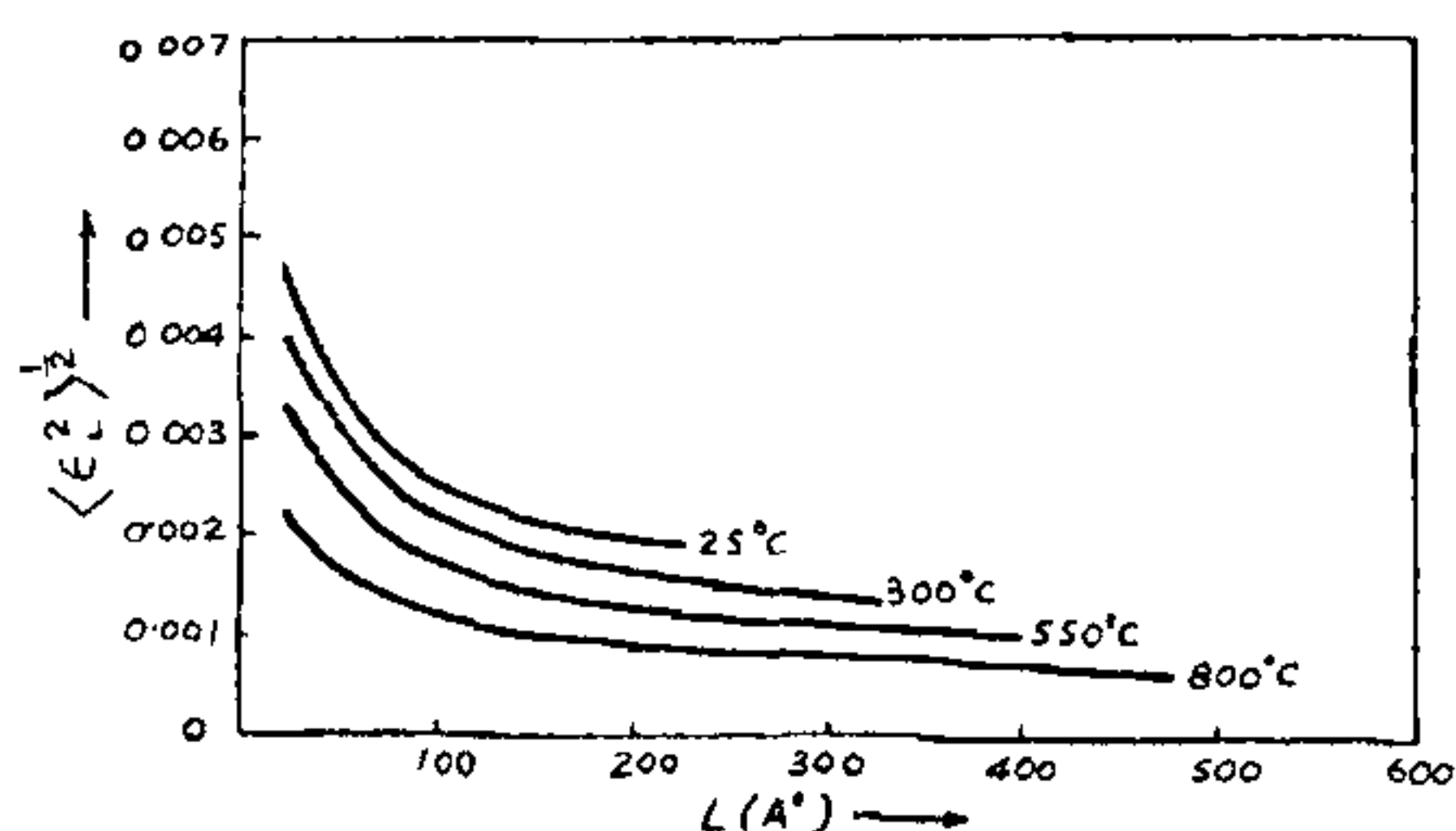


FIG. 2. Plots of rms strain $(\epsilon_L^2)^{1/2}$ versus distance in Angstroms (L) for cold-worked and partially annealed tungsten filings.

DISCUSSION

Williamson and Smallman⁴ have shown that it is possible to obtain two estimates of dislocation density from X-ray line broadening measurements. The contribution to dislocation density ρ_D by domain size is given by

$$\rho_D = \frac{3}{\bar{D}^2} \quad (3)$$

The dislocation density can also be computed from the rms strain using the following relationship

$$\rho_E = \frac{k [(\epsilon_L^2)^{1/2}]^{\bar{D}}}{b^2} \quad (4)$$

where b is the Burgers vector and k is a parameter of the order of 20. The true dislocation density is generally evaluated as

$$\rho_t = [\rho_D \rho_E]^{1/2} \quad (5)$$

Values of ρ_D , ρ_E , ρ_D/ρ_E and ρ_t are also listed in Table I.

It is obvious from the data in Table I that the dislocation density (ρ_t) in tungsten filings is reduced on annealing at 300°C to nearly half the value at 30°C. Although Koo⁵ and Schultz⁶ attributed the recovery of electrical resistivity at annealing temperatures below 400°C to annealing out of single vacancies with an activation energy of 1.7 eV and above 400°C to the annihilation and rearrangement of dislocations, the present X-ray findings show without doubt that annihilation and rearrangement of dislocations take place to a considerable extent even at as low a temperature as 300°C in this metal with the highest melting point (3,410°C). Rearrangement of dislocations at 400°C has been observed⁷ by electron microscopy and X-ray topography, which supports our present findings. Our X-ray results are also consistent with the fact that in tungsten dislocations along (110) planes are not extended, so that the screw dislocations can glide out of their original slip planes for annihilation and rearrangement without requiring a high activation energy. Similarly, the climb of edge dislocations is also expected to occur readily in tungsten.

The ratio ρ_D/ρ_E remains nearly the same for cold-worked and partially annealed samples (Table I), thus suggesting that with increase in temperature the dislocation density (ρ_t) decreases, but the distribution of dislocations remains perhaps the same as in the fresh filings at room temperature, since small domain size and strain are a manifestation of the number

and distribution of dislocations in a deformed metal.

We have recently found⁸ in case of deformed filings of several HCP metals that the flow stress values calculated from dislocation densities obtained by similar X-ray analysis are approximately equal to the yield strengths of the well-annealed metals. The values of flow stress (τ) in cold-worked and partially annealed filings of tungsten calculated in the same way from the relation

$$\tau = 0.3 bG (\rho_L)^{1/2} \quad (6)$$

(where G is the shear modulus) are listed in Table I. The top curve of Fig. 3 shows the variation of τ with temperature.

The yield stress (YS) in tungsten has been found to be markedly sensitive to the strain rate. For example, increase in strain rate from about 10^{-5}sec^{-1} to about 10^{-2}sec^{-1} raises the YS by a factor of 3 (Betchold⁹). When extrapolated to a strain rate of 10^{-1}sec^{-1} the YS is approximately 80,000 psi at 250° C, which is in good agreement with our extrapolated value of τ at 250° C (Fig. 3). Thus, it may be concluded that the flow stress in drastically deformed tungsten (filings) calculated from equation (6) is approximately equal to its yield strength measured with a very high strain rate ($\sim 10^{-1}\text{sec}^{-1}$).

Also shown in Fig. 3 are the values of flow stress for tungsten as a function of temperature for different strains at a constant rate of extension ($2.8 \times 10^{-4}\text{sec}^{-1}$) from the data of Betchold and Shewman.¹⁰ Filing is a drastic form of deformation both in terms of strain and strain rate, thus τ (for filings) can be considered to represent the flow stress for an extremely high strain value. This is supported by the results shown in Fig. 3, since

the plot of τ vs. temperature as per our X-ray data lies above the curve for flow stress vs. temperature at the highest strain ($\delta = 0.05$). If we plot the flow stress values against natural strain (δ) from Fig. 3, our values are found to approximate to flow stress values extrapolated for $\delta = 0.1$.

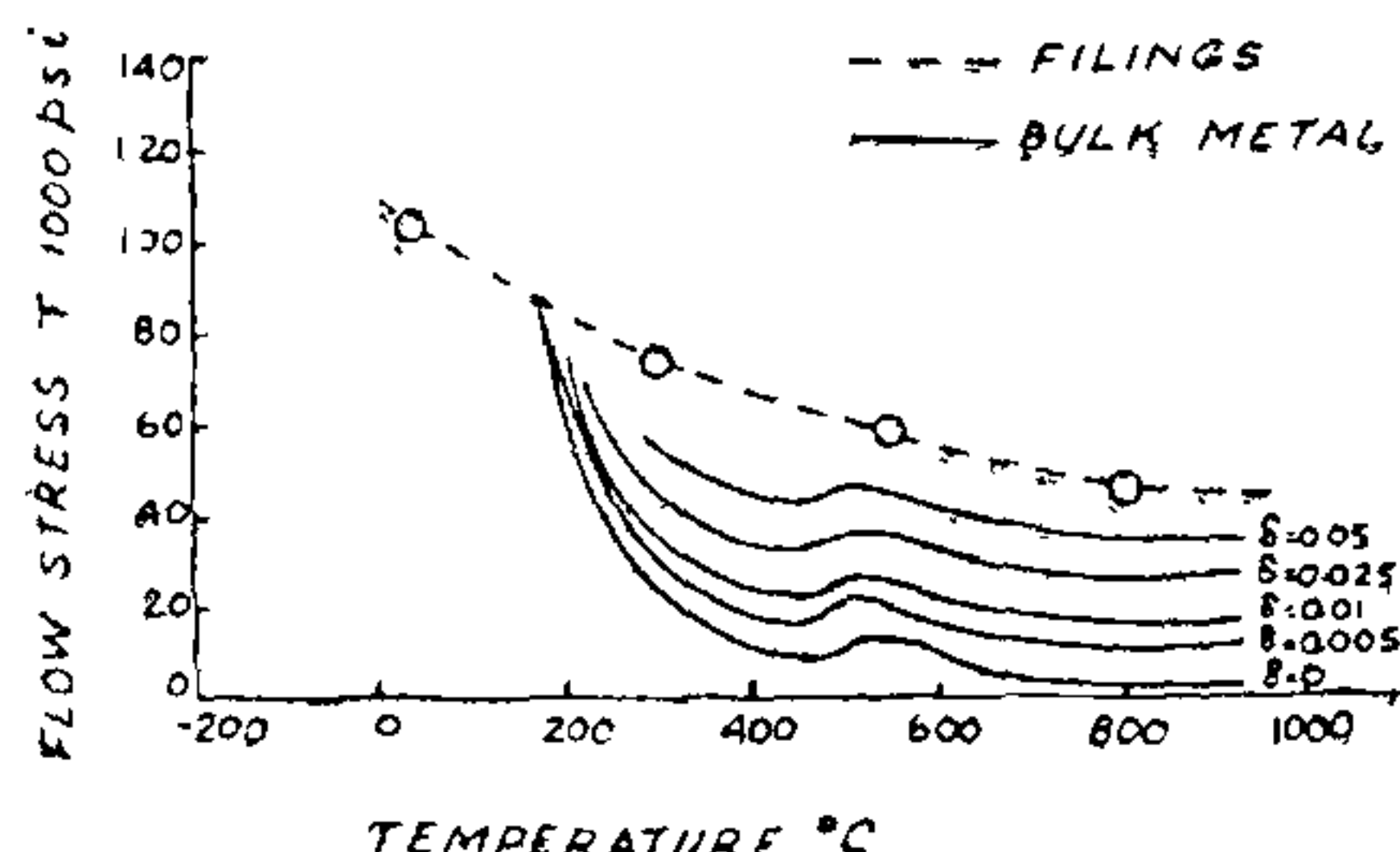


FIG. 3. Effect of temperature on flow stress of (a) cold worked and partially annealed tungsten filings (present work) and (b) annealed tungsten with different strain at the constant extension rate of $2.8 \times 10^{-4}\text{sec}^{-1}$ (from the data of Betchold and Shewman).

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1. Sato, S., *Japan J. Appl. Phys.*, 1962, **23**, 805.
2. Stokes, A. R., *Proc. Phys. Soc.*, 1948, **61**, 382.
3. Warren, B. E., *Progr. Metal Phys.*, 1959, **8**, 147.
4. Williamson, G. K. and Smallman, R. E., *Phil. Mag.*, 1956, **1**, 39.
5. Koo, R. C., *Reactive Metals* (edited by Clough, R. W.), Interscience Publishers, New York, 1959, p. 265.
6. Schultz, H., *Z. Naturforsch.*, 1959, **14**, 361.
7. Koo, R. C., *J. Less-Common Metals*, 1961, **3**, 412.
8. Gupta, R. K. and Anantharaman, T. R., Communicated to *J. Less-Common Metals*.
9. Betchold, J. H., *Trans. TMS-AIME*, 1956, **206**, 142.
10. — and Shewman, P. G., *ASM Trans.*, 1954, **46**, 397.

E.S.R. STUDIES ON GLYCINE COMPLEXES OF MANGANESE CHLORIDE AND MANGANESE BROMIDE

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DIGLYCINE Manganese Chloride dihydrate $(\text{NH}_2\text{CH}_2\text{COOH})_2 \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (hereafter referred to as G_2MCD), is one of the very few paramagnetic substances showing ferroelectric nature at room temperature. Pepinsky et al.¹ studied the dielectric properties of this crystal

from 345° K to 77° K. Beyond 328° K, it loses its water of hydration. In the above range of temperature, they could not find the Curie temperature, θ . E.S.R. studies on this compound have been taken up by us with a view to estimate the Curie temperature and the