

THE PRECIPITATION OF SECONDARY PHASE PARTICLES  
FROM SUPERSATURATED SOLID SOLUTION IN A DILUTE  
URANIUM ALLOY

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Introduction

It has been shown that the scale of precipitate dispersion is an important factor in determining the mechanical properties of heat-treated alloys. During the last few years there has been considerable interest in studying the mechanism and kinetics of the precipitation in dilute uranium alloys (1-3). The size, shape and the distribution of precipitated phases depend on the composition of the alloy and on the type of heat-treatment. A knowledge of the rate at which a second phase separates from supersaturated solid solution and of the factors affecting the particles growth is of great importance and can reveal details of the controlling physical mechanism.

The object of the present investigation was to study the kinetics of precipitation of secondary phase particles in a multicomponent uranium alloy using the technique of thin foils electron microscopy.

Experimental Procedure

An alloy containing 1300 ppm Mo, 170 ppm Si, 500 ppm Fe, 500 ppm Al and 1000 ppm C was investigated. The alloying procedure and specimen preparation for electron microscopy were described in some earlier reports (4,5).

Prior to ageing the specimens were homogenized for 24 hours at 850°C and water quenched. The specimens were aged in evacuated and sealed silica tubes at 600, 625 and 640°C.

The specimens were examined in a JEM-7 electron microscope. Average particle radii were measured on the photographs by means of micro-recorder with an accuracy of about  $\pm 0.02 \mu\text{m}$ .

## Results

Electron microscopic examination indicated that all the alloying elements were in solid solution on quenching from the  $\gamma$  phase. During subsequent ageing a marked precipitation at subgrain boundaries was observed. At lower temperatures the scale of precipitation was finer.

The change in particle size as a function of temperature and ageing time is shown in Fig. 1. It can be seen that after an initial rapid growth the growth rate at lower ageing times becomes much slower. Since the volume fraction

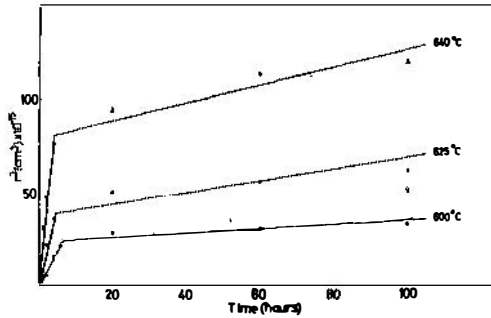


FIG. 1

Variation of particle size with ageing time

of precipitation is rising from effectively 0 to its equilibrium value it is reasonable to suppose that this stage of ageing is governed by nucleation and growth processes. However, at longer ageing times, when the equilibrium volume fraction is approached, growth can take place only by the selective coarsening process termed Ostwald ripening (6,7). That is, only when the alloy had reached the equilibrium at the ageing temperature the only subsequent change is coarsening of particles. Thus, nucleation and growth aspects can be clearly distinguished from the subsequent coarsening of particles.

In order to obtain a more complete definition of the kinetics of nucleation and growth process the approximate relationship between volume fraction of precipitated phase

f and the time t was employed:

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

where k and n are constants (8). A plot of  $\ln(1/1 - f)$  vs t for the present results gives straight lines with n values ranging from 0.86 at 640°C to 0.68 at 600°C (Fig. 2).

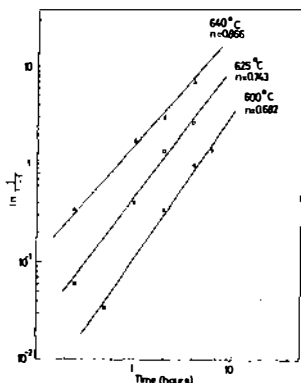


FIG. 2

Plot of  $\ln(1/1 - f)$  vs t for various temperatures

The time-dependence of growth by Ostwald ripening can be expressed by the Lifshitz-Wagner equation:

$$r^3 - r_0^3 = kt \quad (2)$$

where r is the mean particle radius at time t,  $r_0$  the mean particle radius at the onset of growth ( $t_0$ ), while k is a constant. The above relationship can be applied only when diffusion through the matrix is the rate-controlling process, i.e. in the case of "diffusion controlled" particle growth.

Grain boundaries also play an important role in particle growth, since particles may concentrate on grain boundaries by finding it easier to nucleate there. A complete statistical analysis for the case of particle growth in this situation has not yet been developed, but according to Greenwood (9) the growth will follow the law of the form:

$$r - r_0 = kt^{1/4} \quad (3)$$

Thus,  $r - r_0$  is expected to increase linearly with  $t^{1/4}$ . Since there was no departure from linearity it would be considered that coarsening of particles takes place on grain

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<sup>†</sup>It is previously assumed that the region showing slower growing rates is that associated with coarsening of particles and this assumption enabled an estimate of  $r_0$  to be determined from the point of intersection of the lines of rapid and slow growth rates.

boundaries (Fig. 3).

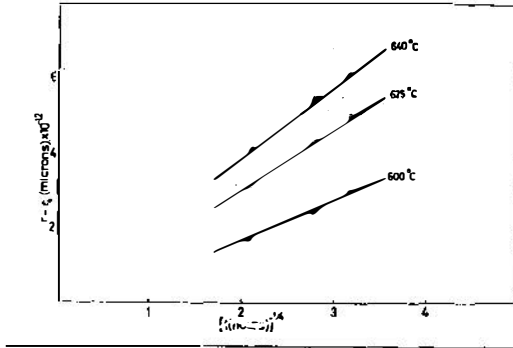


FIG. 3

The linear variation of  $r - r_0$  with  $t^{1/4}$

To calculate the activation energy for the process of nucleation and growth the Arrhenius equation was employed and times for  $f=0.5$  were plotted vs reciprocal absolute temperature (curve a, Fig. 4). The slope of the straight line

corresponds to the activation energy of 1.84 eV. The activation energy for the coarsening of particles calculated for  $r - r_0 = 0.04 \mu\text{m}$  is 4.4 eV (curve b, Fig. 4).

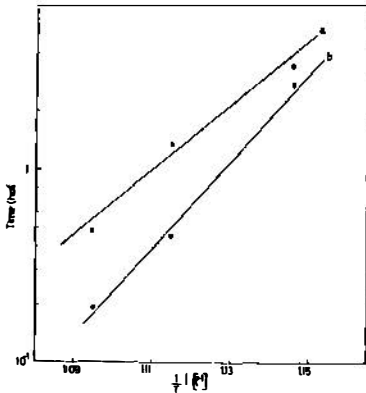


FIG. 4

Arrhenius plot of time to reach  $f=0.5$

#### Discussion

The average value for the exponent  $n$  from the equation (1) was 0.76. This value is similar to that obtained by previous workers; for example, Smith (10) obtained  $n=0.68$  studying the precipitation

from supersaturated solid solution in "adjusted" uranium. James and Fern (11) found that  $n$  was 0.77 for the precipitation of  $\text{UAl}_2$  in a dilute uranium-iron-aluminium alloy over the temperature range from 500 to 640°C, which is in excellent agreement with the present result.

The value of  $n$  has been shown theoretically to vary with the mechanism of nucleation and precipitate shape. For homogeneous nucleation this value ranges between 1 and 2.5 (12,13). For heterogeneous nucleation on individual dislocations or on grain boundaries, theoretical values from 0.5 to 1 have been reported (14). In the present work electron microscopical evidence for the precipitation on subgrain boundaries has been unequivocally observed. These observations together with  $n$  values lead to the conclusion that heterogeneous nucleation occurred.

The calculated values for activation energies of nucleation and growth and subsequent coarsening of particles are somewhat higher than that obtained in "adjusted" uranium (3,12).

#### References

1. P.L. Ryder and J. Nutting, *J. Inst. Metals* 93, 178, (1964-65)
2. D.I. Marsh et al., *ibid*, 93, 471, (1964-65)
3. A.F. Smith, *J. Less-Common Metals*, 9, 233, (1965)
4. Đ. Drobnjak and M. Jovanović, *Bull. Boris Kidrič Inst. Nucl. Sci.*, 19, 1, (1968)
5. M. Jovanović, *Bull. Soc. Chim.*, 32, No. 8-9-10, 505, (1967)
6. C. Wagner, *Z. Elektrochem.*, 65, 581, (1961)
7. J.M. Lifshitz and V.V. Slyozov, *J. Phys. Chem. Solids*, 19, 35, (1961)
8. W. A. Johnson and R.F. Mehl, *Trans. Met. Soc. AIME*, 135, 416, (1939)
9. G.W. Greenwood, *The mechanism of phase transformations in crystalline solids*, *Inst. of Metals (London)*, 1, (1968)
10. A.F. Smith, *J. Nucl. Mat.*, 27, 194, (1968)
11. P.F. James and F.H. Fern, *op. cit.* 10.
12. J. Burke, *Phil. Mag.*, 6, 1439, (1961)
13. C.A. Wert and C. Zener, *J. Appl. Phys.*, 21, 5, (1950)
14. R. Bullough and R.C. Newman, *Phil. Mag.*, 6, 403, (1961)

## DISCUSSION

R.D. Doherty : Did you attempt to compare your experimental values of  $k$  in the  $r - r_0 = kt^{1/4}$  relationship with the theoretical values?

M. Jovanović : No.