MASTER

PORE SHRINKAGE AND OSTWALD
RIPENING IN METALLIC SYSTEMS

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ABSTRACT

The new theory of Ostwald ripening phenomena is gradually unfolding.

Based on the principle of minimum rate of entropy production, the general method including the mathematical formalisms of variational calculus, is now understood and has been applied to the case of annealing of void structures, a situation somewhat simpler to model than is particle coarsening. The resultant void distribution function is compared with that expected from the LSW theory and with experiments.

Developments in the experimental program in three areas are described:

- (a) generation and annealing of voids in HVEM,
- (b) distribution of Ni_3Al in Ni-Al alloys, and
- (c) production of reproducible pore structures in nickel powder compacts.

INTRODUCTION

Coarsening phenomena are central to a variety of technological bottlenecks, including the elimination of porosity in powdered metal and ceramic products, the preservation of large catalyst surface area and the retention of dispersion strengthening effects of alloys in high temperature service.

A considerable body of experimental data exists which documents several such coarsening phenomena. The theoretical rationale for these has been the theory (called the LSW theory) developed originally by Lifshitz and Slyozov (1) and by Wagner (2) and subsequently modified by others (3-6). In most instances this classical theory adequately predicts the time dependence of average particle sizes but fails in practically every case to accurately predict particle size distributions. The purpose of this project is (1) to develop a more comprehensive theory for such coarsening phenomena and (2) to test both theories against several coarsening phenomena, for which limited but statistically highly reliable data can be accumulated.

THE NEW THEORY

Revised
In Appendix A, a preliminary manuscript is included, a paper to be presented in June at the Fifth International Conference on Sintering and Related Phenomena which will be convened at Notre Dame. This paper outlines the general methods involved and illustrates their application to the void distribution problem which is summarized here.

During the evolution of a system of dispersed spherical pores in time, entropy is produced both by changes in configuration resulting from small pores shrinking, large pores growing and by "fluctuations" of vacancy concentration which may be visualized as trapped near the pores. The calculation of the

configurational entropy increase rate has been performed for a random pore distribution. In this case for N_v pores per unit volume

$$\Delta S_1 = - N_v k \int_0^{\infty} p \ln p dr \quad (1)$$

where the distribution function $p(r,t) dr$ represents the fraction of pores of radius between r and $r + dr$ at time t . Ultimately, it can be shown that

$$\frac{d\Delta S_2}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \ln p dr \quad (2)$$

where $u(r,t) = v(r,t) p(r,t)$, where $v(r,t) = \frac{dr}{dt}$.

Starting with the expression for the increment of Helmholtz free energy ΔF , of the cloud of vacancies with excess concentration ΔC around a single spherical pore

$$\Delta F_1 = \frac{4\pi}{\Omega} \int_r^L [\Delta f + K \left(\frac{d\Delta C}{dx}\right)^2] x^2 dx \quad (3)$$

where Ω is atomic volume, K the coefficient measuring the response of the system to gradients of concentration (see J. W. Cahn and J. E. Hilliard, J. Chem. Phys. 31, 688 (1958)) and Δf the increase of free energy per atom due to the increment of vacancy concentration. L is a distance from the center of the pore to the point where ΔC vanishes. One can minimize function (3) with the auxiliary condition of steady state:

$$\nabla^2(\Delta C) = 0 \quad (4)$$

and obtain the total change of free energy ΔF of N_v pores

$$\Delta F = \frac{4\pi N_v}{\Omega} \int_0^{\infty} [-n \ln \left(\frac{r}{L}\right) + Kr\Delta C(r)^2] p dr \quad (5)$$

where n is a constant. From the deDonder theorem

$$\frac{d\Delta S}{dt} = -\frac{1}{T} \frac{d\Delta F}{dt} \quad (6)$$

one obtains the rate of entropy increase ΔS_2 due to vacancy fluctuations

$$\frac{d\Delta S_2}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \left[-n \ln \left(\frac{r}{L} \right) + 4\pi K r \Delta C(r)^2 \right] p dr \quad (7)$$

Now the problem is reduced to minimizing the integral

$$\frac{d\Delta S_1}{dt} + \frac{d\Delta S_2}{dt} = N_v k \int_0^{\infty} \frac{\partial u}{\partial r} \left[\ln p - n \ln \left(\frac{r}{L} \right) + \frac{r}{r_c} \right] dr \quad (8)$$

subject to two auxiliary conditions

$$1. \quad \int_0^{\infty} p \, dr = 1 \quad (9)$$

2. Total volume of pores and excess vacancies is constant. In the first approximation the contribution of vacancies can be neglected and this condition reduces to the conservation of pore volume

$$\frac{d}{dt} \int_0^{\infty} r^3 p \, dr = 0 \quad (10)$$

Using Lagrange multipliers λ and μ and usual procedures of the calculus of variations, one obtains two Euler's equations which yield

$$p(r,t) = \exp(\phi(t)) \left(\frac{r}{L} \right)^n \exp\left(-\lambda r^3 - \frac{r}{r_c}\right) \quad (11)$$

$$u(r,t) = - \int_0^r \left(\mu + \lambda \frac{d \ln N_v}{dt} r^3 \right) p \, dr + \psi(t) \quad (12)$$

where $\phi(t)$ and $\psi(t)$ are functions of time only. These expressions contain two constants λ and μ , two functions $\phi(t)$ and $\psi(t)$ to be determined, from the two auxiliary conditions (9) and (10) and two additional conditions, namely that

$$u(0,t) = \frac{d \ln N_v}{dt} = \psi(t) \quad \text{and} \quad (13)$$

$$u(\infty,t) = 0$$

because the rate of growth of larger pores should approach zero as $r \rightarrow \infty$. They allow in principle a determination of all constants and time dependent functions. From (12), $v(r,t)$ can be obtained in the form

$$v(r,t) = \frac{u(r,t)}{p} \quad (14)$$

which, it can be shown, reduces to

$$v(r,t) = \frac{\mu}{p} \left[\frac{1 - \lambda \int_0^r r^3 p dr}{1 - \lambda \bar{r}^3} - \int_0^r p dr \right] \quad (15)$$

where $\bar{r}^3 = \int_0^\infty r^3 p dr$.

The shape of $p(r,t)$ is similar to that obtained by Wagner (Z. Electrochemie 65, 581 (1961)) at least for small values of r . For large values, however, it differs drastically from that of Wagner because while the latter has a sharp cut off at large r , (never observed experimentally) the one given by equation (11) displays a well defined tail.

Also the expression for $v(r,t)$ at first glance is similar to that obtained by Wagner, $v \sim 1/r^n$, as can be seen from (14) or (15). However, there is a very fundamental difference. In Wagner's theory the exponent n characterizes the rate controlling process ($n = 1$ for interface reaction and $n = 2$ for diffusion control). In the present theory the characterization of the process is expressed by the function L which for interface reaction should be proportional to $N_v^{-1/3}$ and for diffusion, to $r + \sqrt{Dt}$. Wagner's expression for $v(r,t)$ was obtained by application of the mean field approximation which assumes the average solute vacancy concentration exists throughout the whole matrix. In the present derivation the application of this approximation was apparently eliminated. However it returns in a different form in estimation of the shapes of L for various processes.

VOID DISTRIBUTIONS

A proposal was submitted to the HVEM/Tandem Steering Committee of Argonne National Laboratory in April 1978, following submission of the current year's DOE renewal proposal, asking for time on the 1.2 MeV Kratos microscope under installation at the time. It was proposed to generate void distributions in rather thick nickel foils by in situ electron bombardment and then follow subsequent void distribution changes on annealing. At that time it seemed possible that this could be undertaken during Summer 1978, however, a variety of problems with the instrument delayed this until February 1, 1979.

As of the end of March, we have had two one-day sessions, primarily for learning the alignment and operation of the microscope and one two-day period in which the first serious experiments were undertaken. First attempts to create voids in nickel by electron bombardment failed, so that temporarily at least, it was necessary to employ samples with preexistent void structure, heavy ion bombarded nickel which contained rather high dislocation densities as well. These samples were useful principally in establishing the temperature range in which convenient void annealing rates could be observed. The generation of voids in the HVEM is intimately related to material factors such as gas content; for nickel, it is recommended to ensure the sample is well charged with hydrogen initially (7), which will be tried shortly. The microscopy technique includes routine stereoscopy, which ensures that the region of sample being analyzed is sufficiently thick and that voids near the free surfaces can be excluded from measurement. In relation to the theoretical analysis, it is possible to create a number of unusual experimental situations for challenging the theory such as the creation of a bimodal void distribution by irradiating at two different temperatures or superimposing some final point defect generation rate on the otherwise static annealing process.

PRECIPITATE DISTRIBUTIONS

The coarsening of Ni_3Al in Ni-Al alloys has been extensively studied previously (8-14) for the purpose of establishing the mechanisms of the solid state coarsening phenomenon. Typically, there is rather large discrepancy in the experimental results when they are compared with the LSW distributions. This arises in part at least from errors in measurement. However, it also reflects the non-stationary character of real distributions in relation to the quasi-stationary distribution of the LSW theory. Because these studies were performed for a purpose requiring comprehensive data for a variety of environmental and alloy conditions, no single distribution curve can be said to have been intensively established. In fact typically a given distribution is based on a few hundred particles counted. The goal of this aspect of the present research is to determine a few such distributions with considerable care, including those with small average sizes (5-9 nanometers, say). A variety of aging treatments have been pursued with Ni + 6.35 w/o Al, following solution treatment at 1200°C, and CTEM then performed.

It has become clear, with the smallest size regions particularly, a number of problems are exaggerated in the determination of these distributions (15). Errors enter from three non-mathematical sources: (a) image contrast of the particles themselves which is diffraction and thus depth dependent, (b) photographic contrast on the recording negative and photographic print and (c) subjective bias.

The imaging of precipitates such as Ni_3Al in its Ni-rich solid solution depends in large part on dynamical effects, particularly where the particles are very small. It is helpful to choose a matrix orientation for which dynamical conditions are realized, especially along a row of matrix reflections. The effect may be understood qualitatively in simple geometrical terms: in addition to the

primary electron beam, each of the strong matrix reflections can scatter into the ordered precipitate reflections; only those precipitate reflections which coincide with matrix reflections in the diffraction pattern can rescatter into other matrix reflection positions. The isolated superlattice reflections from which dark field precipitate images are formed in effect can only exchange energy with one another, for small volume fractions of precipitate, this is not likely. Any depth dependence of the dark field image of the precipitates arises from the depth dependence of scattering within the matrix itself. Such depth dependence is very pronounced for 120 KeV incident electrons.

The inherently marginal contrast from small particles is compounded by the additional contrast effects associated with the image photography and printing process. A study of this has been conducted, the results of which are typified by those shown in Fig. 1. In this case only the speeds of the photographic enlarging papers are different, the times being adjusted to give comparable background darkening. For the higher contrast printing condition (Fig. 1b) 7 pct more particles are countable within a given area and the distribution is noticeably broader, the standard deviation from the average increasing about 20 pct. The average in this case is the same, however, as are the qualitative features in relation to the LSW prediction (the dashed curves); namely, the peaks of the empirical distribution fall to the left of the average value (in the LSW theory the peak is to the right) and there is an obvious tail at larger sizes (in contrast to the LSW prediction of a sharp cut off).

In this photographic study, a wide range of variables were examined for a single, average quality negative. The inherent differences in image contrast associated with small and large particles are simply unavoidable, but the effects can be minimized in a more or less standard manner where more accurate distributions are required. This involves analysis of several micrographs from a given negative, one printed to underplay the smaller particles to prevent photo-

Fig. 1. Normalized Ni_3Al particle distribution. (a) Photographic enlargement: F2 @ 5 sec. (moderately low contrast print). (b) Photographic enlargement: F4 @ 20 sec. (moderately high contrast print).

graphic flaring of the larger ones; another to maximize the size of the smaller particles whose sizes will almost always be underestimated anyway if the matrix contributes at all to the image. The resultant distributions generally fit near the average size which is relatively insensitive to the printing conditions.

The third effect, that of subjective bias, was examined with four persons analyzing each of ten prints over a five week period. Substantial differences were obvious. No method for calibrating out this factor has been devised.

In order to decrease overlap problems in images of dense particle distributions characteristic of small values of average size, three new Ni-Al alloys, containing 6.0, 6.1 and 6.2 w/o Al have been prepared. The Ni + 6 Al alloy aged at 625°C for 24 hours indeed contains much less Ni_3Al but the precipitates exhibit more than twice the average size of that in Ni + 6.35 Al alloy used previously. The other alloys have not been examined yet.

In the Ni + 6.35 Al samples aged at 590°C for 24 hrs, it appears that the Ni_3Al precipitate particles are highly imperfect and initially less regular than those formed at 625°C in the same time.

PORES IN POWDER COMPACTS

The initial attempts to produce fine reproducible pore structures in powder compacts which had been pressed and sintered were based on copper. Difficulties with this system have been discussed previously (DOE Progress Report C00/4385-2). Attention was shifted to nickel with much more satisfactory results. The aim is to obtain a sample with rounded, interconnected pores. In order to have interconnected pores, porosity should not exceed 0.1. Low temperature sintering should accomplish this, but metallographic sections of such compacts usually reveal non-rounded, irregularly shaped pores.

Much time was wasted during the first year on Cu compacts, which in addition to the difficulties mentioned above, presented another, namely mechanical smearing of the metal during the polishing operation. Subsequent etching, both chemical and electrolytic, resulted in non-reproducible microstructures. Although copper displays a number of advantages for such research, it was abandoned in favor of a harder metal which would not smear during polishing. Thus, Ni was chosen. The variables which have to be controlled in preparation of the compacts with desired porosity and pore shape are compacting pressure and the temperature and time of sintering. Carbonyl Ni powder manufactured by International Nickel Co. of average particle size about 10 μm was chosen. This powder was compacted in a press resulting in green compacts 3.5 cm in diameter and 0.9 cm high. The compacting pressures ranged from 8 to 35 tons/in². The compacts were subsequently sintered in a mixed atmosphere of $3\text{N}_2 + \text{H}_2$ at temperatures ranging from 800° to 1300°C. High temperature sintering (1000 - 1300°C) resulted in rounded pores but low porosities (0.08 - 0.16). Low temperatures 800° - 950°C displayed high porosities (0.3 - 0.4) but very irregularly shaped pores. Compacts pressed at 8-12 tons/in² and subsequently sintered at 950°C for 3-5 hrs yield specimens of desired properties: rounded pores and porosities about 0.2. Reproducibility of these results was excellent. Etching of sections of these compacts with dilute nitric acid revealed that the time of etching has no measurable effect on measurements of the average pore size, provided it has not exceeded 1 minute.

The trial sintering experiments of these specimens at 1000°C for up to 8 hrs revealed a uniform increase of average pore size with porosities decreasing to 0.15 after 8 hrs of sintering. The distribution of pore sizes are determined using a Zeiss Particle Size Analyzer. Measurements of permeability are being planned.

THE PROJECT IN PERSPECTIVE

The development of the theory and the acquisition of data each represents in its own way a thorny problem. The most fundamental barrier to the development of the theory was the mathematics of variational calculus, and the problem of correctly sorting out the mathematically independent variables. In this regard the absolutely indispensable assistance of several mathematicians at Ohio State University, chiefly Prof. Drobot, a specialist in variational methods, must be acknowledge. The subsequent solution of the void (pore) distribution problem, even with its somewhat restraining assumption, is an important step forward. The result is physically appealing, behaving somewhat like the LSW distribution for small sizes, along with an exponential tail for large sizes which is consistently seen experimentally. The appearance of the K-factor of solute (or vacancy) fluctuation theory is an unavoidable additional material property, but fortunately it appears, at least in the final result of the void distribution problem, in such a way that its precise value has little influence.

Analytical solutions to the problems of distribution of particles in a matrix and on a substrate surface are now being sought.

The void annealing experiments are now progressing smoothly, although they were unavoidably delayed six months or more. The determination of size distributions of Ni_3Al precipitates should be essentially complete in Summer 1979 and most of the bugs of the porous compact study have now been worked out so that aspect of the project should proceed well in the coming year. A brief examination of the depth dependence of precipitate images as a function of incident electron energy from 100-12,00 KeV in the HVEM at Argonne National Laboratory will be performed. In short, while the publication record of the project is poor at this point, progress in this direction is very positive. Two research-in-progress presentations were made at the Fall meeting of the TMS/AIME in St. Louis, abstracts of which

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appear in Appendix II. The paper which forms Appendix I will appear in the Proceedings of the Fifth International Conference on Sintering and Related Phenomena (1979).

PERSONNEL

The principal investigators are George C. Kuczynski and Charles W. Allen, Professors, Department of Metallurgical Engineering and Materials Science, University of Notre Dame. The research assistants in this period have been Chen-Ti Hu, a doctoral candidate in the same department, who has been pursuing the various aspects of the precipitate and void experiments and John Comisky, a masters candidate who will be completing his work this May. In addition, a graduate assistant funded by the University, Anil Bansal, has performed the developmental work on the nickel powder compacts for the porosity study. Three undergraduate students in the department participated last fall in the particle size analysis study, Mark Angelini, Richard Miller and Robert Pokrzywa.

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