MASTER

PORE SHRINKAGE AND OSTWALD
RIPENING IN METALLIC SYSTEMS

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PROGRESS REPORT

"STUDY OF PORE SHRINKAGE AND OSTWALD RIPENING IN METALLIC SYSTEMS"

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ABSTRACT

A new theory of Ostwald ripening (the coarsening of particles in a matrix or on a substrate) is being developed, which is based on the principle of minimum entropy production. This theory yields particle size distribution functions whose general shape is in much closer agreement with existing observations than is that of well established theories.

Progress is reported both in the theoretical development and in several areas of experiment. The goal of the experimental program is the determination of actual distributions from very large numbers of size measurements, in order to provide statistically more significant basis for comparison with the various theories than has previously characterized such measurements. The report describes the status of experiments involving

- (1) pore shrinkage in powder compacts,
- (2) coarsening of Ni_3Al in a Ni-Al alloy,
- (3) coarsening of Pt particles on a single crystal Al_2O_3 substrate and
- (4) the development of a Au-20 at pct Fe alloy for study.

INTRODUCTION

From a practical point of view coarsening phenomena of various sorts are important in solid materials, because they normally are responsible for a degradation of physical properties of interest. For example, the growth of platinum particles on alumina as substrate produces a marked decrease in catalytic activity of the system as the total catalyst surface decreases. And the coarsening of dispersed second phase particles causes the degradation of mechanical strength in dispersion and precipitation strengthened alloys.

A considerable body of experimental data already 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 somewhat by others (3-6). In most instances this classical theory adequately predicts the time dependence of average particle sizes but fails to accurately match particle size distributions. The purpose of this project is (1) to develop a more comprehensive theory for such coarsening phenomena which is free of the restrictive assumptions of the LSW theory and (2) to test both theories against several coarsening phenomena, for which limited but statistically highly reliable data can be accumulated.

THEORY

The present state of this new theory, which is based on the principle of minimum entropy production, has been summarized recently for the case of particles in a matrix phase (7): a copy of this reference accompanies this Progress Report. The results of this theory to date, in relation to those of the LSW theory are

- (a) the total volume fraction of precipitate increases with average particle size, consistent with experimental fact (the LSW theory assumes constant volume fraction).

- (b) The functional form of the particle distribution curve predicts an exponential tail for larger sizes, consistent with what is almost always observed (the LSW theory gives a rather sharp cut-off in the distribution at about 1.4 times the average particle size).
- (c) For particle sizes approaching the lower limit for identification of a cluster as a physical particle, the distribution falls off quite sharply as $\exp[-H/r^n]$ where $H = H(t)$ and $2 \leq n \leq 4$ depending on rate controlling mechanism. (The LSW theory yields a more gentle variation, r^n , for small r). Neither theory fits the few experimental data (8) available for the range of sizes in which one would expect the most critical test (a few nanometers). However, in the case of residual pore shrinkage in copper (9) a consistently sharp change in the size distribution has been found for pores of radius less than approximately four-tenths the average. Fig. 8 of Ref. (9), reproduced here as Fig. 1, illustrates this behavior. In contrast, the data for a Ni + 6.35 w/o Al alloy, showing coarsening of Ni_3Al at 625°C , are assembled in Fig. 2 for results in Ref. (10).

Fig. 1. Fig. 8 from Watanabe, Tada and Masuda (9), normalized size distribution for residual pores in copper compacts. Dashed curves represent LSW master curve.

Fig. 2. After Ardell and Nicholson (10). Distributions of Ni_3Al particle sizes in $\text{Ni} + 6.35 \text{ wt pct Al}$ alloy aged at 625°C for 24, 48, 72, 96 and 146 hr. in relation to the master curve of the LSW quasi-stationary distribution theory.

EXPERIMENTAL PROGRAM

The experimental emphasis during the first year has been devoted to the following:

1. Preliminary development of porous sintered copper compacts for pore shrinkage studies. The goal was to establish a well defined spherical pore structure which is initially finer than has been reported (9). The pore structure however did not pass from interconnected to discrete until the average size exceeded several μm , as found by others (9). Attempts to modify this substantially by blending of predetermined particle sizes were remarkably unsuccessful. Copper was chosen for this because it has served in powder metallurgy for decades as a model pure metal, readily available in a variety of starting powder size distributions and particle shapes and requiring easily achieved sintering temperatures. While not all possibilities have been exhausted for fabrication of a fine system of pores in this material, attention is turning to alternative candidate materials. Pure metals certainly are to be preferred because of the relatively simple processes involved in volume diffusion (vacancy mechanism involving a single diffusing atom-type). In any event the quantitative metallography of porous systems is at best difficult due to material smearing into the pores and subsequent etching, distorting the actual pore microstructure.
2. The coarsening of Ni_3Al in Ni-Al alloys has been extensively studied previously (10-16) for the purpose of understanding the detailed mechanisms of the solid state coarsening phenomenon. As illustrated in Fig. 2 which is typical of these results, there is rather large scatter in the experimental results when plotted on the normalized scales of the LSW distribution master graph. This arises in part at least from errors in measure-

ment. However, this may reflect as well 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 factors, no single distribution curve can be said to have been intensively established. The size intervals are fairly large and their number consequently fairly small so that a few hundred measurements could yield acceptable statistical difference. The goal of this aspect of the present research is to determine a few such distributions with great care, particularly for distributions with rather small average size (6-9 nanometers, say). A variety of aging treatments have been done with Ni + 6.35 w/o Al, initially solution treated at 1200°C, and CTEM performed. The bottleneck has been in the analysis of these distributions for which a Zeiss Particle Size Analyzer (TGZ-3) was ordered at the initiation of this contract in July 1977. This equipment was delivered in December but proved to be optically defective and unuseable. We are still awaiting its replacement. In the meantime this work continues in the effort to produce those few electron micrographs with unusual resolution from regions of good thickness, which are necessary to successfully achieve the goal of this portion of the experimental program.

3. Also during this period some attention has been turned to the relationship between the new theory and the growing body of information on the distribution of particles on substrate surfaces, which model catalytic systems (8,17-19). Work has begun to recast the theory into this two dimensional context, recognizing the additional complication that very fine particles may rather easily migrate en masse by Brownian motion. The theory developed by Chakraverty (3) is based on the surface diffusion

mechanism. Several attempts have been made to duplicate the experiments of Huang and Li (19) with Pt on single crystal Al_2O_3 surfaces, mostly before the literature was adequately searched on the matter, but difficulties in chemical polishing the surfaces of the single crystals (boiling phosphoric acid at $> 400^\circ\text{C}$) in order to ensure a smooth substrate, interfered with the deposition of fine and regular Pt particles.

4. An alternative system to the Ni-Al system was sought because of the impossibility of eliminating fine aluminum oxide particles from that material. It is not unusual for Ni_3Al particles to exhibit a hole-in-the-middle appearance in a superlattice dark field image (20) which is evidently indicative of the presence of oxide onto which the Ni_3Al has nucleated. A Au+20 w/o Fe alloy was prepared by arc melting, thin sheet of which was subjected to several precipitation treatments following solution treating. CTEM samples were prepared with some difficulty because of the very different electrochemical behavior of the Fe rich precipitate and the Au rich matrix. In any event the precipitates were cigar shaped and rather large. In addition, because the precipitates are ferromagnetic and enjoy several habits, correction of resulting astigmatism proved impossible.

Au-Fe alloys in this composition range have been observed to decompose by discontinuous precipitation (21) as well as possibly by spinodal decomposition (22) and normal nucleation and growth (23, 24). It is a valuable system, however, in that the presence of internal oxidation can be conveniently controlled including eliminated, by adjusting the atmosphere in which such alloys are annealed. One of the experiments suggested in the original proposal requires this capability, it is believed, the objective being to create athermal initial precipitate distributions by

gamma radiation damage which could subsequently evolve by thermal ripening.

In summary good progress has been made in the development of the theory, the initial results appearing to correspond much more closely to published experimental observations than does the LSW theory or its modifications. The analysis of data in the experimental program has been severely hampered by the optically defective Zeiss Particle Size Analyzer, the replacement of which we are still awaiting (replacement is scheduled for March 15). There is a considerable back log of micrographs to be analyzed.

PERSONNEL

During the first year of the project, the principal investigators have been G. C. Kuzynski and C. W. Allen, Professors, Department of Metallurgical Engineering and Materials Science. The research assistant has been C. T. Hu. In addition, during Summer 1977, T. R. Rehm, a graduate student in this department, as is Mr. Hu, served as a research assistant. Mr. Rehm initiated the porosity studies and Mr. Hu has been engaged in various parts of the remainder of the experimental program.

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