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THE EFFECT OF SURFACE TENSION ON THE SINTERING
RATE OF METAL ALLOYS. ~

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MASTER

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ABSTRACT

Copper, copper-0.5% antimony and copper-1.5% antimony spherical powders with diameters of 37 to 44 microns were unidirectionally compacted to 75% to 93% theoretical density. The pure copper and high antimony alloy powders were also used for loose and tapped specimens. The surface tension of the materials decreased with increasing antimony content. Specimens were sintered at 950°C in various atmospheres and in vacuo for up to two hours. Copper specimens with densities greater than 88% theoretical and all compacted alloy specimens expanded during sintering. Expansion was attributed to air trapped in closed interparticle porosity during compaction which created an internal pressure during heating, and the formation of water vapor in the powder particles due to the reduction of internal oxides by hydrogen bearing atmospheres. The internal pressure due to air trapped in closed interparticle porosity resulted in neck rupture. Intraparticle pores were observed in the neck grain boundaries in all pressed specimens. It was concluded that these formed during pressing because surface oxides and surface roughness prevented the particles from making perfect point or planar contact. The intraparticle pores were stabilized by the presence of surface oxides and air which was trapped during compaction. It was observed that the rate at which the specimens were heated to the sintering temperature did not affect the initial expansion of copper-1.5% antimony compacts, but did affect the ultimate expansion. Using densification and neck

growth data, it was concluded that densification occurred by diffusional mechanisms, the most predominant being grain boundary diffusion, and neck growth occurred primarily by surface diffusion.

INTRODUCTION

The surface tension of materials in powder metallurgy compacts is important in determining both the thermodynamics and kinetics of sintering. When the porosity is open, the surface tension stress is the only driving force for sintering. The specimen may increase in density or undergo no density change, depending on the material transport mechanisms operating.

When the porosity is closed and sintering is done in an atmosphere, an external pressure due to the atmosphere acts in the same direction as the surface tension stress while an internal pressure due to gas trapped in the closed porosity opposes the surface tension stress and external pressure.

Most material transport mechanisms depend on vacancy concentration or vapor pressure gradients, which are functions of surface tension. If material transport is the result of a creep mechanism, the surface tension provides the stress by which dislocation motion occurs. The rate of densification is linearly dependent on the surface tension stress if diffusional or vapor transport mechanisms are operating. If a creep mechanism involving dislocation motion is operating, the shrinkage rate will be more strongly dependent on the surface tension stress.

In this work, the potential values of the thermodynamic driving forces, surface tension stress, external pressure and internal pressure have been evaluated for various cases and related to the direction of

density change of powder metallurgy compacts. Because the experimental procedure was not amenable to the determination of a stress exponent, the stress dependence approach was used qualitatively to determine if diffusional or creep mechanisms were operating during shrinkage. The measurement of the neck diameter as a function of time was also used to indicate the mechanism of material transport.

Commercially pure copper, prealloyed copper - 0.5% antimony and copper - 1.5% antimony powders were used because surface tension and diffusion data are available for these materials. These data are presented in Table 1.

Material		Cu		Cu-0.5% Sb		Cu-1.5% Sb	
Quantity							
γ	$\frac{\text{ergs}}{\text{cm}^2}$	1,770	21	980	21	905	21
D_{ov}	$\frac{\text{cm}^2}{\text{sec}}$	.621	21	.34	22	.34	22
Q_v	$\frac{\text{cal}}{\text{mol}}$	49,650	21	42,000	22	42,000	22
D_{os}	$\frac{\text{cm}^2}{\text{sec}}$	2×10^4	23	-		-	
Q_s	$\frac{\text{cal}}{\text{mol}}$	49,000	23	-		-	
D_{ob}	$\frac{\text{cm}^2}{\text{sec}}$	256	24	-		-	
Q_b	$\frac{\text{cal}}{\text{mol}}$	32,000	24	-		-	

Table 1

Surface Tension and Diffusion Data for Copper and Copper-Antimony Alloys. D_{ov} and Q_v for the Alloys are for the Diffusion of Antimony in Copper. The Surface Tension Data are for the Materials at 950°C.

Literature Survey

The sintering process has been studied since 1920. It was not until 1949, however that the process was studied in detail with great emphasis placed on the material transport mechanisms involved. Since that time, widely divergent opinions have been expressed concerning the true mechanism of sintering. Everyone seems to be in accord on only one point, that the major driving force for sintering is surface free energy.

Every substance has a certain amount of energy associated with its surface due to the presence of free atomic bonds. In liquids the energy per unit area of surface, surface free energy, can be equated to a force per unit length, surface tension. This equivalency is valid for solid metals at high temperatures.¹ It is also generally assumed that the surface tension is isotropic, which is valid when dealing with a large number of randomly oriented surfaces. The Gibbs-Thomson equation

$$\mu - \mu_0 = \gamma \Omega K$$

relates the chemical potential (μ) of atoms on a surface with curvature K to the chemical potential (μ_0) of atoms on a flat surface, as a function of surface tension (γ) and atomic volume (Ω). At equilibrium

$$\mu_{\text{surface}} = \mu_{\text{vapor}} = \mu_0$$

with P = vapor pressure. Thus,

$$P = \gamma K$$

For an isolated spherical pore of radius r , $K = 2/r$, resulting in

$$P = 2\gamma/r$$

This pressure (or surface tension stress) is effectively a compressive stress on the pore volume.² If the pore contains a gas at pressure P_{internal} and is located in a specimen which is under some external pressure, P_{external} , the pore size will be at equilibrium when

$$2\gamma/r + P_{\text{internal}} + P_{\text{external}} = 0 \quad (1)$$

The external pressure and surface tension stress, $2\gamma/r$, provide the driving force for the shrinkage of a closed spherical pore while the internal pressure is the driving force for expansion. The potential of a pore for expansion or contraction is determined by the combination of these stresses. The ability of the pore to change is determined by the means of material transport available.

It is more convenient to consider the case of open porosity in terms of a tensile stress due to surface tension acting on the inter-particle neck. From geometric considerations, Lenel, Ansell and Early³ have shown that during the early stages of sintering, when necks are well defined, the stress acting on the necks due to surface tension is

$$\sigma_{st} = \frac{4 \gamma x + 12 a \gamma \pi^2}{x^2 + 4 a \pi^2 x} \quad (2)$$

where γ = surface tension

a = particle radius

x = neck radius

This stress is the only stress acting on the metal when the porosity is open. The stress has the potential to cause neck growth and shrinkage, but the occurrence of both is again dependent on material transport. This stress does not have the potential to cause expansion.

In summary, regardless of whether the porosity is open or closed, surface tension stresses provide the driving force for the reduction of surface area by neck growth or shrinkage. If a gas is trapped in closed porosity creating an internal pressure, the surface tension stress may be negated.

The stress at the pore-particle interface is not the only consequence of surface tension. The kinetics of sintering are also dependent on surface tension. When two particles sinter together, a concave neck forms between them. The vapor pressure in the concave interparticle neck region is less than that over a flat surface of the same material², as shown quantitatively by

$$\frac{P - P_o}{P_o} = \frac{-\gamma V_o}{RT \rho} \quad (3)$$

where P = vapor pressure over a concave surface

P_o = vapor pressure over a flat surface

V_o = molar volume of the solid

γ = surface tension

ρ = radius of neck curvature

Another phenomenon is related to the concavity of the neck region. As the radius of curvature decreases, the vacancy concentration in that region increases in an effort to decrease the surface area and lower the total surface free energy². This vacancy concentration gradient is described by

$$\frac{C - C_o}{C_o} = \frac{\gamma V_o}{RT \rho} \quad (4)$$

where C = vacancy concentration under a concave surface

C_o = vacancy concentration under a flat surface

Any proposed sintering mechanism which results in neck growth and/or densification must lower the total surface free energy of the powder mass utilizing the above functions of surface tension and surface curvature; surface tension stress, vapor pressure gradient or vacancy concentration gradient.

Most sintering theories support diffusional mechanisms as the mode of material transport by which vacancies move down the vacancy

concentration gradient, away from the neck surface, resulting in material transport in the opposite direction. It has been shown that vapor transport is not plausible for most metallic systems because of their low vapor pressures⁴. The ability of diffusional and vaporization mechanisms to cause sufficient material transport for significant neck growth and/or shrinkage is questioned by some authors. Lenel and Ansell are the major proponents of the creep theory of sintering. It is their contention that the surface tension stress acting on the neck is great enough to cause dislocation motion at high temperatures. Utilizing Weertman's models for steady state creep, they maintain that the shrinkage rate should be proportional to the surface tension stress to the 4.5 power in pure metals and 3.0 power in solid solution alloys⁵. The shrinkage rate should be proportional to the shrinkage stress to the first power if shrinkage is the result of a diffusional mechanism⁵. Since the surface tension stress is a function of surface tension, the comparison of shrinkage rates of similar materials with different surface tensions should indicate the stress dependence of shrinkage. More exactly, since

$$\dot{\epsilon} = k \sigma_{st}^n \quad (5)$$

where $\dot{\epsilon}$ = shrinkage rate

k = constant

σ_{st} = surface tension stress

n = stress exponent

and $\sigma \propto \gamma$, the stress exponent can be determined from

$$n = \frac{\log \epsilon_1 / \epsilon_2}{\log \gamma_1 / \gamma_2} \quad (6)$$

where the subscripts denote values of shrinkage rate and surface tension for two materials.

It has been proposed that the exact type of diffusional mechanism operating during sintering can be identified by the determination of the neck radius as a function of time⁶. Frenkel⁷ was the first to propose an equation for the rate of neck growth. Kuczynski⁶ incorporated Frenkel's ideas into a comprehensive paper dealing with the rate of neck growth when various mechanisms were operating. His results were:

for viscous or plastic flow $x^2 \propto t$

evaporation and condensation $x^3 \propto t$

volume diffusion $x^5 \propto t$

surface diffusion $x^7 \propto t$

with x = neck radius

t = time

A short time later Kuczynski⁸ presented these results in a slightly different, and more general form

$$\frac{x^n}{a^m} = \gamma t A(T) \quad (7)$$

where a = particle radius

$A(T)$ = a function of temperature which is dependent on the type of mechanism

and for viscous flow	$m = 1$	$n = 2$
evaporation and condensation	1	3
volume diffusion	2	5
surface diffusion	3	7

This work provided the basis for all subsequent experiments in which the mechanism of sintering was determined by observing the rate of neck growth. Rather than using actual powder compacts, model experiments were performed to avoid complicating factors and facilitate neck measurement. Most of these experiments consisted of sintering spheres to spheres⁴, wires to wires¹⁰ or spheres to plates⁵. The ability of various processes to contribute to densification, as opposed to just neck growth, has been demonstrated by Coble using a two sphere model⁷. He showed that surface diffusion and evaporation and condensation may contribute to neck growth but not densification, while volume diffusion and grain boundary diffusion may contribute to both processes. Lenell and Ansell⁵ have shown that slip may also contribute to both processes.

Kuczynski's equations and model experiments have been the subjects of many papers^{11, 12, 13, 14}. The assumption of various pore

configurations and diffusion distances coupled with the uncertainty of diffusion coefficients and normal experimental error has resulted in the support of virtually all material transport mechanisms as contributing to neck growth. The major shortcoming of this approach is that only one mechanism is assumed to be operating. Wilson and Shewmon¹⁵ and Rockland¹⁸ have made analyses which indicate the predominant mechanism rather than assuming that only one material transport mechanism is acting. Both analyses are for diffusion mechanisms only and do not consider vapor transport or slip mechanisms. Surface, volume and grain boundary diffusion coefficients are available for several metals, and are listed for copper in Table 1. At all temperatures grain boundary and surface diffusion are approximately 10^5 times faster than volume diffusion. The complicating factor in comparing them as sintering mechanisms is that they act over different volume elements. Wilson and Shewmon¹⁵ solved this problem by first showing the rate of neck growth for the various cases described by Coble¹⁰. Ratios of these rates resulted in

$$\frac{\dot{x}_s}{\dot{x}_v} = \frac{2}{3} \frac{D_s \sigma_s}{D_v p} \quad (8)$$

$\dot{x}_s$ = rate of neck growth due to material transport from the particle surface to the neck surface by surface migration

$\dot{x}_v$ = rate of neck growth due to volume diffusion from grain boundary and surface sources

D_s = surface diffusion coefficient

δ_s = thickness of surface layer, usually one atomic diameter

D_v = volume diffusion coefficient

ρ = radius of neck curvature

$$= \frac{x^2}{2a}$$

x = neck radius

a = particle radius

In isothermal sintering, the only variable will be ρ , the radius of neck curvature, which can be measured. Surface diffusion dominates neck growth with volume diffusion becoming increasingly important as ρ increases. For volume diffusion to dominate the neck size would have to be much larger than is normally encountered in sintering experiments. Rockland¹⁶ arrived at a similar conclusion using the same approach but with slightly different initial equations.

The difference in initial rate equations also makes little difference in the results in the two papers for the comparison of the roles of volume and grain boundary diffusion in densification. Rockland used two separate equations for volume diffusion contributing only to adhesion (neck growth) and densification. Shewmon used the same equation for both cases. Shewmon's comparison of shrinkage rates

due to grain boundary and volume diffusion is

$$\frac{\dot{\gamma}_b}{\dot{\gamma}_v} = \frac{D_b \delta_b}{2D_v X} \quad (9)$$

Rockland's equation is (using Shewmon's notation)

$$\frac{\dot{\gamma}_b}{\dot{\gamma}_v} = \frac{\delta_b D_b}{\pi \rho D_v} \quad (10)$$

where $\dot{\gamma}_b$ = linear shrinkage rate due to grain boundary diffusion

$\dot{\gamma}_v$ = linear shrinkage rate due to volume diffusion

δ_b = grain boundary width

D_b = coefficient of grain boundary diffusion

Although the equations are quite similar, Rockland concludes that volume diffusion controls densification and Shewmon concludes that grain boundary diffusion dominates. The difference in conclusions is due to the values of diffusion coefficients used. Rockland did not use published values of D_b , but rather approximated it. Substituting the same values into each equation leads to similar results. At low temperatures grain boundary diffusion will definitely dominate. At higher temperatures and small values of X , grain boundary diffusion will also dominate.

Model experiment have been useful in developing an understanding of the ability of various material transport mechanisms to cause neck

growth and shrinkage. Their applicability to powder compacts is in question, however. Irregular powders and pore arrangements make it difficult, and at this time impossible, to predict densification as a function of green density, sintering time and temperature on the basis of material transport mechanisms.

The use of dilatometers to study the linear shrinkage rate of pressure compacted specimens represents a more realistic approach to the study of sintering. Hirschhorn and Berglund¹⁷ did a dilatometric study of the sintering of silver compacts in atmospheres with varying oxygen contents. The surface tension of the material decreased as the oxygen partial pressure increased while the surface diffusion coefficient increased. It was found that, especially at low green densities, the shrinkage rate increased as the oxygen partial pressure increased, indicating a low stress dependence and a diffusional mechanism. Since the coefficient of surface diffusion was increasing at the same time it was concluded that at low densities and high temperatures surface diffusion was the sintering rate controlling mechanism. They concluded that grain boundary diffusion was the rate controlling mechanism at higher densities.

Dilatometric studies have one major drawback, only the length change of a powder compact can be measured during sintering. Hausner, et al.¹⁸ have shown that the ratio of the radial shrinkage to axial

shrinkage is a function of sintering temperature and specimen compaction pressure. In general, as the compaction pressure increases, the radial to axial shrinkage ratio increases, so the sintering of compacts would be more accurately described by changes in volume and density. This approach has been taken by several authors, although some precision is sacrificed with the loss of the dilatometer.

Studies of the densification of compacts bring the development of sintering theories closer to reality, but are also plagued by many more problems than model experiments. Rhines, Birchenall and Hughes¹⁹ did one of the early experiments with compacts, showing the effect of the sintering atmosphere. They sintered electrolytic copper powder compacts in a vacuum, hydrogen and argon. It was found that after long sintering times the specimens in argon began expanding, while those in hydrogen and vacuum continued shrinking. They concluded that as sintering progressed and the porosity closed, the atmospheres were trapped in the porosity. Hydrogen is fairly soluble in copper at high temperatures and diffuses rapidly so that it could escape the porosity more easily than argon. The entrapped argon had the effect of increasing the pressure in the pores until the pores started growing.

Pines, Sirenko and Sukhinin²⁰ studied the sintering of electrolytic copper and mixtures of copper and low melting point powders in hydrogen and a vacuum. It was found that pure copper pressed specimens expanded during sintering if they had less than 14% porosity. It was found

that compacted specimens composed of binary combinations of copper with antimony, tin, lead, cadmium and zinc expanded while copper specimens with the same initial density contracted. With loose powder aggregates however, the mixtures contracted more than the pure copper powders.

The work of Rhines¹⁹ and Pines²⁰ serves to emphasize that the sintering of powder compacts is too complicated to be explained by any simple models. Johnson²⁵ has recently proposed a model for the sintering of uncompacted spherical powders which brings sintering theory closer to reality. Utilizing this model, the relative importance of diffusional mechanisms in controlling neck growth and shrinkage can be identified even when several mechanisms are operating at once. Grain boundary and volume diffusion coefficients can be found directly from the model and experimentally determined shrinkage, shrinkage rate and neck growth data. The coefficient of surface diffusion can be estimated through the computer synthesis of sintering curves.

Experimental Procedure

Powder

The powders used in this investigation were atomized copper and two copper-antimony alloys with the following chemical analyses:

<u>Copper</u>	<u>Antimony</u>	<u>Balance Impurities</u>
99.83%	None	0.17%
99.42%	0.50%	0.08%
98.62%	1.30%	0.08%

All powders were spherical with a wide size range. Only the 37 to 44 size range was used. The 44 and smaller fraction of powder was initially separated from the larger fractions using U.S. Standard 140, 270 and 325 mesh sieves placed on a Ro-Tap Shaker for thirty minutes. The fraction collected in the pan was then placed on a U.S. Standard 400 mesh sieve, five grams at a time, in an Allen-Bradley Sonic Sifter for three minutes. The fraction retained on the sieve was collected and rerun two more times.

It was felt that the major impurity in the powders was oxygen. The ideal method for purification would have been annealing in hydrogen. An adequate procedure was developed for the pure copper powder, but it was not feasible for the alloy powders. Even at low temperatures antimony vaporized from the alloy powders causing them to

agglomerate during the anneal. The alternative procedure used for all powders was acid reduction. The inherent disadvantage of this was that only surface oxides could be reduced. The powders were placed in a 50% solution of hydrochloric acid for one minute. The acid was decanted and replaced by a fresh acid solution which was allowed to stand for five minutes. The acid solution was again decanted and the powder was rinsed three times with acetone. The powder was then left in acetone for five minutes. This was decanted, followed by rinsing the powder once more in acetone and placing it in a tube through which argon was flowing for five hours to dry.

Separate experiments with copper oxides showed that they were eliminated by hydrochloric acid, forming copper chloride and water. Powders which were ready for pressing were tested to see if any copper chloride remained. The qualitative test consisted of dissolving the treated powder in nitric acid and adding a saturated solution of silver nitrate in water. Any chloride ions present would have resulted in the precipitation of silver chloride. None was observed, so the rinsing procedure was effective.

Specimen Preparation

All powders behaved similarly when pressed. Their spherical shape was not amenable to making low density specimens. There was little difficulty in making specimens in the range from 85% to 95%

theoretical density. Specimens were pressed to densities as low as 75% theoretical density but were very fragile and had to be handled with great care.

If there are any density variations in a specimen sintering will not progress homogeneously throughout the specimen. Two precautions were taken against local density variations; a low specimen length to diameter ratio was used and the specimens were double compacted. The specimen diameter was fixed by the die which had a slightly elliptical cross section varying from 0.4790 centimeter to 0.4800 centimeter. On the average, the specimens were 0.60 centimeter long. Double compaction was achieved by two pressing operations. The die and punches were first lubricated with a solution of sterotex in acetone. The powder and punches were then placed in the die and pressed to the desired pressure. The die was then turned over and the compact was repressed to the same pressure. This procedure was successful since, after sintering, the maximum taper noted over the length of the specimen was 0.0002 centimeter, the limit of accuracy of the micrometer.

Specimens were also made which were not pressed. Several methods were tried for making uncompacted specimens, none of which was entirely satisfactory. One was finally chosen that was best for specimens which would be tapped. Quartz tubing 0.370 centimeter

in diameter was cut to lengths of approximately 1.5 centimeters. One end was sealed in a carbon arc so they were essentially small test tubes. They were filled to the top with powder just before sintering. Where required, the samples were tapped 1000 times on a Numinco Tap-Pak Volumeter to obtain higher densities.

Density Measurements

It was felt that the greatest accuracy could be achieved if the measurements of green and sintered densities would be made by the same method. This was possible for the pressed specimens but could not be done for the loose and tapped specimens. All density determinations were made at room temperature.

The pressed specimens were first weighed to 0.0001 gram. It was noted that after sintering the radial dimensional changes at the widest and narrowest points on the elliptical cross section were equal fractions of the green dimension. The edges of low density pressed specimens would sometimes chip when placed in the furnace tube, leaving powder in the furnace tube which could sinter to the surface of the specimen. In several cases this made it difficult to determine the widest point of the cross section, so the narrowest point was used for diameter measurements on all pressed specimens. These measurements were made with a metric micrometer to 0.0002 centimeter. The length was not measured with a micrometer because

the high density specimens had burrs on the ends and the low density specimens were too fragile. Instead, the length was measured optically with the equipment provided with a Tukon microhardness tester. The specimen was placed in a steel fixture on the stage and viewed through a microscope equipped with a Filar eyepiece. One end of the specimen was lined up with the cross hair in the eyepiece. The stage was then moved until the other end of the specimen lined up with the cross hair. Measurements could be made to within 0.0005 centimeter. Tests of the reproducibility of the measurements showed that they varied by ± 0.0005 centimeter. From the data the green and sintered densities of the pressed specimens could be calculated.

Because the tubes which contained the uncompacted specimens were closed at one end, accurate length measurements could not be made. Instead, direct density measurements were used. The green density was measured by filling a quartz tube ten centimeters long with powder and finding the weight of the powder. The tube was then filled with water and weighed, the volume being calculated from this. When the procedure was worked out so that consistent measurements could be made, the average of five such determinations was used to calculate the green density. To determine the tap density of the powders, a small piece of quartz tubing was cut with parallel ends and fit into graphite blocks. It was filled to overflowing with powder and tapped 1000 times.

The excess powder was removed and the powder in the tube was weighed. The average weight of powder in the tube was determined from five weighings. From tube length and diameter measurements and the powder weight, the tapped density was calculated.

The sintered densities of the loose and tapped specimens were measured by a jolly balance technique, according to ASTM standard B 328-60. The following data is needed:

- A = weight in air of oil free specimen in grams
- B = weight in air of oil-impregnated specimen
- C = weight of the oil-impregnated specimen
immersed in water

From this, the density, D , of the specimen can be calculated using

$$D = \frac{A}{B-C}$$

Determination of the Fraction Closed Porosity

The open porosity (P) can be determined in volume per cent using the specific gravity of the impregnant (S) in addition to the data used in determining the density form

$$P = \frac{B-A}{(B-C) S} 100$$

The total porosity volume is equal to 100 minus the specimen density expressed in per cent theoretical density. The open porosity volume divided by the total porosity volume, both expressed as per cent, yields the fraction open porosity. One minus the fraction open porosity equals the fraction closed porosity.

Sintering

The following procedure was used for all runs except the one in vacuum and the one in argon-5% hydrogen used to obtain data for Figure 8. The runs in argon, hydrogen and argon-5% hydrogen, with the one exception mentioned, were identical.

For each material six specimens were made at a given density. Each specimen was sintered continuously for one of the following times; 7.5, 15, 30, 45, 60, or 120 minutes. Each data point represents a separate specimen sintered isothermally for the time noted.

There was great concern that the alloy composition would decrease in antimony content during sintering. The sintering procedure was designed to try and maintain a constant alloy composition and to avoid a long heating time before isothermal sintering could take place.

All sintering was done in a Lindberg Hevi-Duty resistance furnace with an off-on type controller. The heat zone was four inches long and was lined with additional refractory to obtain a uniform temperature profile. Sintering was done in a region three inches long at the center of the heat zone where the temperature as a function of position varied from 951°C to 948°C. The temperature did not vary with time.

Each alloy was sintered in separate quartz tubes which had one end sealed. The atmosphere passed by oil bubble jars before reaching the furnace tube, as shown in Figure 1. In this way, the gas

Figure 1 - A Schematic Representation of the Sintering Apparatus.

pressure in the tube was always maintained at atmospheric pressure and the atmosphere in the tube was fairly stagnant, so vaporized metal would not be swept away.

The specimens were placed in the quartz tube with an equal weight of powder of the same material at the ends of the heat zone. This was done to help provide an atmosphere which would inhibit the preferential evaporation of antimony from the specimens. The tube was then evacuated and purged with the sintering atmosphere five times. After purging, the tube was placed in the furnace, which was at 950°C , and sintering proceeded under the same atmosphere which was used for purging. The procedure of putting the specimens in the furnace at the sintering temperature was used for all but one specimen and will be referred to here after as a heat quench.

In separate experiments with a thermocouple in the tube, it was noted that the inside of the tube reached 550°C after one minute and 950°C within four minutes. The sintering time was started as soon as the tube entered the furnace and was stopped as the tube was removed from the furnace. By sliding the specimens down to the end of the tube which had protruded from the furnace, they were cooled to room temperature in the sintering atmosphere within five minutes.

The specimens sintered in vacuum varied from the standard procedure, explained above, only in the purging procedure and atmosphere

control. The furnace tube was evacuated for a minute and argon was let into the tube. The tube was then evacuated for five minutes and placed in the furnace with the vacuum pump still running, so that the runs were made in a dynamic vacuum. The vacuum was provided by a Cenco Hyvac 2 pump and was less than 10^{-4} .

Only two specimens were used for Figure 8. Sintering and heating were carried out in argon-5% hydrogen. The method of providing and controlling the atmosphere was the same as in all the other runs using atmospheres. The only difference was in the heating rate and cycle. One specimen was heated to 950°C from room temperature in steps by increasing the furnace temperature every half hour. The average heating rate was 250°C per hour. When 950°C was reached the tube was removed from the furnace and the specimen was measured and weighed. This was plotted as zero sintering time. A green specimen was then placed in the tube with the other specimen and they were heat quenched to 950°C for the following cycles:

<u>Time of Each Cycle at 950°C</u>	<u>Total Time at 950°C</u>
7.5 minutes	7.5 minutes
7.5	15
15	30
15	45
15	60
60	120

The tube was purged with argon-5% hydrogen before each cycle and the specimens were measured after each cycle. Each curve in Figure 8 represents one specimen rather than each data point representing a separate specimen as in all other figures. The only difference between the two specimens is that one underwent a slow heating up cycle before it was heat quenched for the isothermal cycles.

Metallography

Sintered specimens were cut in half with a diamond saw and mounted in bakelite. This was followed by grinding on wet 240, 320, 400 and 600 grit paper. The first polishing step was carried out on canvas duck cloth using coarse alumina suspended in water as an abrasive. After this step all scratches from grinding were removed and the specimen surface was planar. Individual particles could be readily distinguished, but there was a considerable amount of metal forced into the porosity. This metal was removed by polishing on a billiard cloth with 0.05 μ alumina suspended in water. Water was supplied copiously during this operation to prevent the metal from flowing and to keep the cloth's nap from becoming matted. It was felt that the nap facilitated the removal of metal from the porosity.

When the metal had been removed from the porosity, final polishing was done on a velvet cloth using a very dilute suspension of chrome oxide in water as an abrasive. In this step, the specimens were

polished until the particle edges were no longer rounded, a result of polishing with a billiard cloth, and the surface was scratch free when examined under a microscope at 100X. There were some fine scratches which could not be removed by mechanical polishing.

A polish-etch technique was used on specimens which were used to show grain structure, with the polishing being done on a stationary velvet lap. Two etchants were used. Potassium dichromate was used on the pure copper specimens and $1\text{H}_2\text{O} : 1\text{NH}_4\text{OH} : 2\text{H}_2\text{O}_2$ (3%) on copper-1.5% antimony specimens. The reason for this was that the dichromate etch had less tendency to cause pore enlargement than any other etch, but it stained the alloy severely.

The data for intraparticle pores per particle were obtained by photographing the specimens at 50X and enlarging the prints for an effective magnification of 100X with one exception. The data for the alloy specimens sintered in vacuo were obtained by projecting the image of the specimen on a glass screen. The particle and pore counts were made directly from the screen rather than from a photograph. This technique was faster and better than taking photomicrographs because various areas of the specimen can be sharply focused. This procedure was carried out at 100X. The number of intraparticle pores per particle was the average for 100 to 125 particles, as determined by either the photographic or projection technique. Neck size

determinations were made with a microscope, equipped with a calibrated eyepiece, at 400X. The average value was determined from the measurement of 50 particles and 25 necks.

Results

Specimen and Powder Chemistry

The procedure used to maintain constant composition was not completely effective but did provide adequate control. Chemical analyses were made of specimens of all compositions with various densities sintered in argon-5% hydrogen for a variety of sintering times. The composition ranges are shown below:

<u>Copper</u>	<u>Antimony</u>	<u>Balance Impurities</u>
99.77 - 99.90%	None	0.23 - 0.10%
99.38 - 99.40%	0.50% - 0.55%	0.11 - 0.05%
98.40 - 98.70%	1.25% - 1.50%	0.20 - 0.05%

These variations have little effect on surface tension²¹.

Copper and copper-1.5% antimony powders and one sintered specimen of each were analyzed for oxygen content. The copper powder contained 0.063% oxygen and the alloy powder contained 0.031% oxygen. After sintering in argon-5% hydrogen for 15 minutes the oxygen content of an 85% dense copper specimen was reduced to 0.014%. The oxygen content of an 86% dense copper-1.5% antimony specimen sintered for 30 minutes in argon-5% hydrogen was reduced to 0.0093%.

All specimens sintered in all atmospheres lost weight during sintering. In general, low density specimens lost more weight than higher density specimens of the same material and copper specimens

lost more weight than the alloy specimens. The maximum weight loss was about 1% while most specimens decreased in weight by approximately 0.5%. The weight losses could not be correlated to changes in composition or density.

Dimensional and Density Changes

An example of the linear changes which specimens undergo during sintering is shown in Figure 2 for a pure copper compact. It can be readily seen that changes in radial and axial dimensions can differ in magnitude and direction. Figure 2 demonstrates the well known and interesting fact that the diameter may decrease while the length increases, but the opposite behavior is rarely seen. This was the case for all specimens in this study.

The progress of sintering is described more accurately by changes in density than by changes in linear dimensions. A unitless densification parameter was chosen in which the sintered density minus the green density was divided by the theoretical density minus the green density. A negative densification parameter indicates that the specimen density decreased during sintering while, a positive densification parameter indicates an increase in density.

The curves in Figures 3-7 showing the densification parameter as a function of isothermal sintering time in argon-5% hydrogen all

exhibit minima. For pressure compacted copper specimens, the minima occur at longer sintering times as the green density decreases. The loose and tapped copper specimens have minima at 15 minutes. The pressure compacted copper-0.5% antimony specimens have only one minimum, which occurs at 45 minutes. The pressure compacted copper-1.5% antimony specimens behave similarly with the minima at 30 minutes and a second minimum at 60 minutes for the highest density specimens. The tapped specimens of this material have a minimum at 15 minutes; while the loose specimens exhibit minima at sintering times of 15 and 60 minutes.

Figure 8 demonstrates the effect of heating rate on the densification of two copper-1.5% antimony compacts which subsequently underwent identical sintering cycles. The specimen which was heated slowly to the sintering temperature underwent little change during sintering, while the specimen which was initially heat quenched decreased in density for the first 45 minutes of total sintering time and then showed little change in density.

The effect of sintering atmosphere on pure copper is shown in Figure 9. Specimens sintered in pure hydrogen undergo considerable initial expansion, exhibiting a pronounced minimum after 7.5 minutes of sintering. The specimens of the same density sintered in argon-5% hydrogen show a net densification and exhibit only slight minima at 15 and 45 minutes.

Figure 10 relates the densification parameter and time for a series of copper-1.5% antimony specimens which were sintered in vacuum, pure hydrogen, pure argon and argon-5% hydrogen. The specimens sintered in hydrogen and argon-5% hydrogen show one minimum at 30 minutes, while the specimens sintered in argon reach a minimum at about 60 minutes.

It is clear in Figure 3-7 that the densification parameter is strongly dependent on the green density of the compacts. The three alloys are most readily compared by plotting the densification parameter against green density (expressed as per cent theoretical density) at constant isothermal sintering times in argon-5% hydrogen, as is done in Figures 11-16. In general, the materials at all times show a decrease in densification parameter (or a decrease in density) as the green density increases. When the green density is greater than 90% theoretical, the values of densification parameter decrease precipitously to large negative values, indicating considerable expansion of the specimens. In general, for a given density and time, copper has the greatest densification parameter, copper-0.5% antimony the next and copper-1.5% antimony the least. The most notable exceptions are the high values of densification parameter for low density copper-1.5% antimony alloys after 30, 60 and 120 minutes of sintering. In all cases, the green density at which the densification parameter becomes negative is

lower for the high antimony alloys than for the pure copper specimens.

Porosity and Microstructure

Although the densification parameter gives an accurate picture of the variations of density with sintering time and green density, it gives no information about the nature of the porosity. In Figures 17-20 the fraction closed porosity is shown as a function of sintering time for copper and copper-1.5% antimony compacts. The lack of data for some curves is due to the fact that some specimens were used for metallography before the determination of the fraction closed porosity was considered and some were used for chemical analyses.

For pure copper loose and tapped specimens (47.6% and 51.6% theoretical density) the fraction closed porosity reaches a minimum value at 45 minutes. The curves for copper specimens with densities of 77.5%, 86.9% and 90.7% have maxima at 45, 15 and 15 minutes, respectively, followed by minima. The 85.7% dense copper specimen sintered in hydrogen reaches a maximum value of fraction closed porosity at 15 minutes and remains fairly constant thereafter.

The fraction closed porosity for all pressed copper-1.5% antimony specimens (densities of 75.9% theoretical or greater) reaches a maximum at 30 minutes of sintering. After 30 minutes, specimens which were sintered in atmospheres containing hydrogen and had densities of 85.6% theoretical or greater reached a minimum. The other pressed

specimens underwent a steady decrease in fraction closed porosity after the maximum was reached. The loose and tapped copper-1.5% antimony specimens (55% and 59% theoretical density) exhibit maxima at 15 minutes followed by minima, another maximum and finally another decrease in the fraction closed porosity.

Some metallographic work was done to investigate the nature of the porosity and the microstructures of the powder and compacts. Figures 21 and 22 show polished and etched copper and copper-1.5% antimony powder particles in the as received condition. About 25% of the copper particles had dendritic structure, the remainder being cellular. The powder morphology seemed to be independent of particle size. The phase between the dendrites and in the grain boundaries was blue and generally formed small globules. In some cases the interdendritic structure appeared to be lamellar, although it was difficult to resolve. This is thought to be the Cu_2O -Cu eutectic. The as received copper-1.5% antimony particle shown in Figure 22 is typical of all particles for that alloy, having a cellular structure. Again the grain boundaries were blue, indicating the presence of the Cu_2O -Cu eutectic. Some porosity was noted in all powders.

A tapped copper-1.5% antimony specimen is shown in Figure 23 after 7.5 minutes of sintering in argon-5% hydrogen at 950°C.

Comparison of Figures 22 and 23 indicates that recrystallization and grain growth has occurred and the Cu_2O is no longer evident. There were many small spots within the particles but it could not be discerned if they were pores or another phase. All specimens examined had undergone recrystallization and grain growth during the first 7.5 minutes of sintering. All appeared to be single phase. The microstructures of the alloys and the pure copper appeared to be identical, although the porosity differed. Figure 24 shows the same tapped copper-1.5% antimony specimen unetched. Figures 25 and 26 show copper-1.5% antimony specimens which had green densities of approximately 82.5% theoretical and expanded after 7.5 and 120 minutes of sintering in argon-5% hydrogen. The normal interparticle porosity is seen in all three compacts. The pressure compacted specimens have small pores located in the necks, termed "intraparticle porosity," in addition to the normal interparticle porosity. This intraparticle porosity was most prevalent in the pressure compacted copper-1.5% antimony specimens and was present to a lesser degree in pressure compacted copper specimens, as shown in Figures 35-44 presented in the appendix. It was not present in loose or tapped type compacts of copper or copper-1.5% antimony (none being made for copper-0.5% antimony) sintered for up to two hours. Figures 27 and 28 show that the intraparticle pores still exist in copper-1.5% antimony specimens after

sintering for an hour and two hours in vacuo. These figures also show that the original grain boundaries usually remain in the neck region.

Some semiquantitative metallography was done to relate the intraparticle porosity to green density and sintering time. This was done as an exploratory survey rather than an extensive investigation and the results should be regarded as such. The data was reproducible to within 10%, but a wider range of densities should be investigated. Figure 29 shows that the number of intraparticle pores per particle undergoes little change as sintering progresses. Trends can be seen for each material, density and atmosphere; however the changes are slight and there is some question as to whether they are true or due to statistical scatter. Figure 30 indicates that the number of intraparticle pores per particle increases as the green density increases.

The ratio of neck diameter to particle diameter was measured for tapped copper and tapped copper-1.5% antimony specimens sintered in argon-5% hydrogen for 7.5 minutes. The copper specimen had a ratio of 0.329 and the copper-1.5% antimony specimen had a ratio of 0.410.

Figure 2.. The fractional linear changes as a function of sintering time for copper compacts with a nominal green density of 86.9% sintered in argon-5% hydrogen.

Figure 3. The densification parameter as a function of sintering time for pressed copper compacts with various green densities sintered in argon-5% hydrogen.

Figure 4. The densification parameter as a function of sintering time for loose and tapped copper specimens with nominal green densities of 47.6% and 51.6% sintered in argon-5% hydrogen.

Figure 5. The densification parameter as a function of sintering time for pressed copper-0.5% antimony compacts with various green densities sintered in argon-5% hydrogen. Note: Compacts with densification parameters of less than -0.7 are plotted as -0.7 in Figures 14 and 16.

Figure 6. The densification parameter as a function of sintering time for pressed copper-1.5% antimony compacts with various green densities sintered in argon-5% hydrogen.

Figure 7.

Figure 7. The densification parameter as a function of time for loose and tapped copper-1.5% antimony specimens with green densities of 55% and 59% sintered in argon-5% hydrogen.

Figure 8. The densification parameter as a function of sintering time for two pressed copper-1.5% antimony compacts with green densities of 85.2% and 85.0% heated to the sintering temperature, 950°C., by slow heating and heat quenching.

Figure 9. The densification parameter as a function of sintering time for copper compacts with green densities of 86.9% and 85.7% sintered in argon-5% hydrogen and pure hydrogen.

Figure 10. The densification parameter as a function of sintering time for copper-1.5% antimony compacts with green densities of approximately 86% sintered in various atmospheres.

Figure 11. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 7.5 minutes.

Figure 12. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 15 minutes.

Figure 13. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 30 minutes.

Figure 14. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 45 minutes.

Figure 15. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 60 minutes.

Figure 16. The densification parameter as a function of green density for specimens sintered in argon-5% hydrogen for 120 minutes.

Figure 17. The fraction closed porosity as a function of sintering time for copper compacts with various green densities sintered in argon-5% hydrogen.

Figure 18. The fraction closed porosity as a function of sintering time for copper compacts with green densities of 85.7% and 86.9% sintered in hydrogen and argon-5% hydrogen.

Figure 19. The fraction closed porosity as a function of sintering time for copper-1.5% antimony compacts with various green densities sintered in argon-5% hydrogen.

Figure 20. The fraction closed porosity as a function of sintering time for copper-1.5% antimony compacts with green densities of approximately 85% sintered in various atmospheres.

Figure 21. Copper powder, as received, 500X. Etchant: $1\text{NH}_4\text{OH}:1\text{H}_2\text{O}:2\text{H}_2\text{O}_2$ (3%).

Figure 22. Copper-1.5% antimony powder, as received, 500X. Etchant: $1\text{NH}_4\text{OH}:\text{H}_2\text{O}:2\text{H}_2\text{O}_2$ (3%).

Figure 23. Tapped copper-1.5% antimony sintered 7.5 minutes in argon-5% hydrogen, 500X. Etchant: $1\text{NH}_4\text{OH} : 1\text{H}_2\text{O} : 2\text{H}_2\text{O}_2$ (3%).

Figure 24. Tapped copper-1.5% antimony sintered 7.5 minutes in argon-5% hydrogen, 500X. Unetched.

Figure 25. Copper-1.5% antimony compact with a green density of 82.5% sintered for 7.5 minutes in argon-5% hydrogen, 500X. Unetched.

Figure 26. Copper-1.5% antimony compact with a green density of 82.5% sintered for 120 minutes in argon-5% hydrogen, 500X. Unetched.

Figure 27. Copper-1.5% antimony compact with a green density of 85% sintered for 60 minutes in a vacuum, 500X. Etchant: $1\text{NH}_4\text{OH}:$
 $1\text{H}_2\text{O}:2\text{H}_2\text{O}_2$ (3%).

Figure 28. Copper-1.5% antimony compact with a green density of 85% sintered for 120 minutes in a vacuum, 500X. Etchant: $1\text{NH}_4\text{OH}:$
 $1\text{H}_2\text{O}:2\text{H}_2\text{O}_2$ (3%).

Figure 29. Intraparticle pores per particle as a function of sintering time for copper specimens with green densities of □ 82.3%, ○ 93.4%, copper-1.5% antimony specimens with green densities of x 82.5% all sintered in argon-5% hydrogen and copper-1.5% antimony specimens with green densities of Δ 85% sintered in a vacuum.

Figure 30. Intraparticle pores per particle as a function of green density for copper and copper-1.5% antimony specimens sintered for 7.5 minutes in argon-5% hydrogen.

Discussion of Results

The Origin and Effect of Stresses

The curves in the previous section result from the interaction of different stresses in a compact during sintering. The fact that a compact may be shrinking at one time and growing at another indicates that the magnitude and direction of stresses and material transport are changing as sintering proceeds. By first dealing with each stress separately and then combining them, the sintering curves can be explained.

Equation 2 in the literature survey describes the surface tension stress acting on the interparticle necks. This surface tension stress is the only stress acting on the metal when the porosity is interdonnected and it can cause neck growth. The stress has the potential to cause shrinkage, but this does not necessarily result. Because of the X^2 term in the denominator, the sintering stress decreases as the neck radius increases. This is, in part, the reason the rate of shrinkage decreases steadily with time in experiments where σ_{st} is the only stress acting.

The sintering curves provided by model experiments and some experiments with low density compacts provide a starting point for the study of expansion. Figures 25 and 26 indicate that necks grow and porosity becomes rounded in an effort to reduce surface area even

when specimens expand. This indicates that some other effect is superimposed on the sintering behavior. It was noted in the literature survey that the conditions for a pore to be in thermodynamic equilibrium are

$$\frac{2\gamma}{r} + P_{\text{internal}} + P_{\text{external}} = 0$$

If the porosity is open, the internal pressure equals the external pressure, so the only stress acting is the compressive stress, $\frac{2\gamma}{r}$, exerted by the metal surface on the pore. If

$$P_{\text{internal}} > \frac{2\gamma}{r} + P_{\text{external}}$$

the pore will expand. For this inequality to exist, there is a tacit assumption that there is a gas trapped in isolated, spherical porosity which causes the expansion. In this work, the internal pressure could result from any or all of the following factors:

1. metal vapor pressure
2. any gas trapped in existing pores at room temperature, air being the most likely, and heated to the sintering temperature
3. any gas trapped during heating to the sintering temperature, the sintering atmosphere being most likely, and heated to the sintering temperature.
4. any gas trapped during isothermal sintering, the sintering atmosphere being most likely.
5. the solid state reaction of hydrogen in solution in the metal and oxide particles or oxygen in solution in the metal to form water vapor in closed pores.

Possible causes of all stresses on closed pores in this work and their potential values are listed in Table 2. Further explanations of the causes of stresses and the derivations of their values are in Appendix 1.

<u>Stress</u>	<u>Origin</u>	<u>Approximate Magnitude (ATM.)</u>		
		<u>Cu</u>	<u>Cu-0.5% Sb</u>	<u>Cu-1.5% Sb</u>
$\frac{2\gamma}{r}$ = Shrinkage stress ($r = 1 \times 10^{-3}$ cm)	surface energy & curvature	3.6	2.5	1.8
P_I = Internal pressure	total metal vapor pressure	10^{-8}	3.25×10^{-4}	9.75×10^{-4}
	gas trapped at room temperature	4.08	4.08	4.08
	gas trapped at 537°C	1.51	1.51	1.51
	internal water vapor formation	9,700	9,700	9,700
P_E = External pressure	atmosphere	1	1	1
	vacuum	0	0	0

Table 2

The potential stresses on a pore 1×10^{-3} cm in radius. A closed pore of this size is likely to be of the interparticle type. The pressure exerted by a gas trapped in an existing pore at some temperature (third and fourth entries) is strictly a mechanical effect.

It should be emphasized that the stresses listed in Table 2 are exerted on or by the pore. Using these stresses, a free body diagram of a pore can be drawn, as in Figure 31. The ability of these stresses to cause growth or shrinkage of a pore can be determined by finding the equilibrium pore size and pressure and comparing them to the actual pore size and pressure. This process is carried out in detail in Appendix 2. The results of calculations of this type are summarized in Table 3 for pore with radii of 1.0×10^{-3} cm, which should be quite common in compacts composed of particles with radii of 2.0×10^{-3} cm. Case (2) is especially interesting, since if the pores were 0.5×10^{-3} cm larger they would grow in all materials and if they were 0.5×10^{-3} cm smaller they would shrink in all materials. It can be seen from Table 3 that internal water vapor formation is the most potent source of expansion. The closure of pores during isothermal sintering is the least likely cause of expansion. Its main effect is that it prevents the pore from disappearing since any pore containing a gas will have an equilibrium size.

A closed pore should shrink or grow until it reaches its equilibrium size. The fact that the fraction closed porosity may steadily increase with sintering time and then suddenly decrease, as shown in Figures 17-20, indicates that the closed porosity is being opened before it reaches its equilibrium size. The pressures due to trapped gases, may be great enough to cause expansion and neck rupture. If closed porosity,

<u>Stresses</u>	<u>Origin of P_I</u>	<u>Pore Behavior</u>		
		<u>Cu</u>	<u>Cu-0.5%Sb</u>	<u>Cu-1.5%Sb</u>
$2 \gamma / r$	-	Shrinks	Shrinks	Shrinks
$2 \gamma / r - P_I$	1) Total Metal Vapor Pressure	Shrinks	Shrinks	Shrinks
$2 \gamma / r - P_I + P_E$	2) (1) + Inert Gas Trapped at Room Temperature	Shrinks	Grows	Grows
$2 \gamma / r - P_I + P_E$	3) (1) + Gas Trapped at 537°C	Shrinks	Shrinks	Shrinks
$2 \gamma / r - P_I + P_E$	4) (1) + Internal H_2O Vapor Formation	Grow	Grows	Grows

Table 3

The effects of various stresses on a pore with a radius of 1×10^{-3} cm are shown. In cases 2, 3 and 4 an external pressure of one atmosphere is also present.

which was initially expanding, was suddenly opened so that the internal pressure was relieved, the porosity would be free to shrink, since the net stress acting on it would be the surface tension stress. This is borne out well by comparison of Figures 6 and 7 with Figure 19. At times of less than 60 minutes, minimum values of the densification parameter occur with maximum values of fraction closed porosity. The subsequent increases in densification parameter occur with decreases in the fraction closed porosity, which result from neck rupturing. The correlation is not as strong at 60 and 120 minutes because the porosity which closes as a result of normal sintering at advanced sintering time does not contain gases at high pressures, so it contributes to densification rather than expansion.

The fraction closed porosity in copper specimens is either decreasing or reaches a maximum followed by a minimum at sintering times of 45 minutes or less. The pressed copper-1.5% antimony specimens consistently reach a maximum value of fraction closed porosity at a sintering time of 30 minutes. The maximum is then followed by an abrupt decrease in fraction closed porosity. This indicates that neck rupturing occurs more readily in pure copper than in the alloy. This could be related to the amount of pressure built up or the mechanical strength of the necks. The pure copper powder contained more oxygen than the alloy, so there was more chance of water vapor formation

in pure copper, when sintering in an atmosphere containing hydrogen.

The Cu_2O is also probably reduced more rapidly in pure copper than in the alloy because pure copper should have higher solubility for hydrogen, according to solubility theories put forth by Wagner²⁶. There is no experimental proof of this in the copper-antimony system, however.

Hopkin²⁷ has shown that at 600°C Cu-1.7%Sb has a yield strength of 4 KG/mm^2 while pure copper's is half that value.

The analysis of the origin and effects of stresses can be used to explain all sintering curves and is summarized below.

1. The sintering stress due to surface tension and curvature, σ_{ST} , causes neck growth and decreases steadily regardless of whether the specimen is shrinking or growing.
2. Closed porosity can shrink until the internal gas pressure, which is increasing, matches the shrinkage stress which is increasing more slowly. At this time the pore is in equilibrium and will undergo no further changes.
3. Growth of closed pores occurs until the internal pressure, which is decreasing, matches the shrinkage stress, which is decreasing more slowly, or the pressure is relieved by neck rupturing.

These concepts can now be applied to the experimental results.

Linear Dimensional Changes

The ability of a compact to shrink radially while it grows axially as in Figure 2 can be attributed to the directionality of the porosity²⁸.

Unidirectional pressing results in a pore with an elliptical cross section, with the short axis parallel to the pressing direction. The internal

Figure 31. A free body diagram of a spherical pore containing a gas which exerts an internal pressure, P_i , and opposes the external pressure, P_e , and shrinkage stress, $2\gamma/r$.

Figure 32. A free body diagram of a pore with an elliptical cross section which has the radii of curvature $r_2 > r_1$, resulting in a lower shrinkage stress parallel to the pressing direction.

pressure exerted by entrapped gases on the metal surface is constant at all points on the surface. However, the shrinkage stress, $2\gamma/r$, will vary with the radius of curvature. The smallest radius of curvature is in the radial direction, so the shrinkage is more likely to occur in this direction. One part of the pore may be in equilibrium while another part is still changing. The pore geometry and stresses are shown in Figure 32.

The Effect of Sintering Atmosphere on Intraparticle Porosity

The runs involving different atmospheres, the results of which are shown in Figures 9 and 10, enable the effects of the sintering atmosphere on densification and intraparticle porosity to be determined. The formation of intraparticle pores will be dealt with first. Two questions arise concerning these pores: first, how do they form and second, why haven't they been noted more frequently in the literature. Both questions can be resolved by the process of elimination. Mechanisms which have the potential to cause pore formation at grain boundaries are listed below.

1. Antimony could have been preferentially vaporized during sintering, causing an excess vacancy concentration in the neck region and resulting in the precipitation of pores in the grain boundaries. This would be analogous to the dezincification experiments by Baluffi and Seigle²⁹ in brass.
2. Creep experiments indicate that voids with circular or elliptical cross sections may form at the grain boundaries

in copper and many of its alloys as the result of grain boundary sliding³⁰.

3. If oxide particles had been present at the grain boundaries, hydrogen could have reacted with them to form water vapor in the volume previously occupied by the oxide.
4. The intraparticle voids may have been formed during pressing. If the powder particles were not in intimate contact some areas of the neck would sinter while others would not.

The first possibility is negated by the fact that the voids were present in copper specimens and were not present in the loose and tapped copper-1.5% antimony specimens.

Grain boundary sliding may also be ruled out as a source of intraparticle pores because they were not present in all specimens. In addition, Hopkin³¹ has shown that during creep grain boundary voids do not form in copper-antimony alloys. Voids will form, however in copper-antimony-zinc alloys if the zinc vaporizes, causing a supersaturation of vacancies near the grain boundaries. There is also some question as to whether the stresses present in the neck region are great enough and of the proper orientation to cause grain boundary sliding.

The third potential mechanism of intraparticle pore formation, internal water vapor formation, is eliminated by the fact that the pores formed in all atmospheres, including argon and vacuum.

This leaves only the fourth possibility, that the intraparticle pores were formed during pressing. No intraparticle porosity was seen in

loose and tapped specimens because the particles were essentially in contact only at a point. During sintering, the necks could grow by some form of material transport (to be discussed later) forming an uninterrupted grain boundary. In pressed specimens, the initial contact between particles is planar. Although the particles were spherical, their surfaces were not completely smooth. In the absence of considerable plastic deformation it is quite reasonable that the initial plane of contact was a somewhat imperfect mating of the surfaces. This is further borne out by Figure 30, showing the green density and material dependence of the number of intraparticle pores per particle. At higher compaction pressures, and specimen density, the particles deform more so that the contact plane is larger and there is a greater possibility of surface disparities. The greater number of intraparticle pores in the copper-1.5% antimony alloys is a result of this material's greater strength²⁷ and brittleness^{21,22}. One other factor may influence the ability of particles to be in intimate contact. If the surfaces of the particles were initially covered with an oxide coating, the oxide would be abraded during pressing, resulting in a planar contact area between particles which consisted of regions of metal-metal, metal-oxide, and oxide-oxide interfaces. Incomplete sintering and void formation could be associated with the oxides. The surface oxides would remain in tact in regions where the particles did not make contact. Any of the

intraparticle pore formation mechanisms listed above could be effective under a given set of circumstances, however the ability of the particles to make good contact during pressing is the most general of all possibilities and is best supported by the data.

The dearth of information about intraparticle pores in the literature is also supported by the concept of imperfect surface mating. In model experiments only point contacts are made initially. Little metallographic work has been done on powder metallurgy specimens which were pressure compacted. The quantitative metallography done by Rhines, De Hoff, et al.^{32,33} has been focused on loose powder aggregates. Earlier work on pressed specimens utilized electrolytic and other irregular powders in which it is impossible to ascertain what is intraparticle porosity and what is interparticle porosity. Even when spherical powders are used, it is difficult to distinguish the two types of porosity in high density compacts and compacts which have been sintered for long times. The formation of intraparticle pores at the grain boundary between metal particles was noted previously only by Simonsen³⁴. Using a hot stage microscope, he observed the vacuum sintering of pressure formed compacts of spherical copper powder. The intraparticle pores were difficult to see during sintering, but they were clearly evident when the specimens were repolished after sintering for up to 30 hours. The pores seemed to have a retarding effect on sintering, in that the microstructures

after 3 and 30 hours were identical. Simonsen also carried out several sintering experiments in hydrogen. Intraparticle pores were still present but there were fewer and less than when sintering was carried out in vacuum. He attributed the pores to the lack of good contact between particles and the presence of surface oxides.

The intraparticle pores present in the green compacts are undoubtedly quite irregular compared to those shown in Figure 25 after 7.5 minutes of sintering. The pore can assume an equilibrium shape quite rapidly by any material transport mechanism. The shape of the pore is determined by the relation of the surface energy to the grain boundary energy. The fundamentals of sintering theory should apply to these pores. The intraparticle pore shape can come to equilibrium before the pore size does. If, when sintering in vacuum, it is assumed that the intraparticle pores are evacuated, the only stress acting is the surface tension stress so there is a strong driving force for sintering. Since the pores are in grain boundaries, material transport should occur rapidly. Using the equation of Hull and Rimmer³⁵ (detailed in Appendix 4) for the shrinkage of a void in a grain boundary, a pore one micron in radius will take less than a second to disappear by grain boundary diffusion. Figures 27, 28 and 29 indicate that although some intraparticle pores have been eliminated, the majority remain in copper-1.5% antimony compacts sintered in vacuum. The stability of the small intraparticle pores is

quite intriguing. Their stability could result from any or all of the following factors:

1. The assumption that the pores are evacuated is incorrect and there is an internal pressure counteracting the surface tension stress.
2. An oxide coating on the surface of the pore is retarding sintering.
3. A material transport mechanism is working against the normal sintering mechanisms.

If a gas were present in the intraparticle porosity it would have to be air which was sealed in during pressing. Oxidation would have resulted, but it is difficult to say if enough oxide would be present to observe metallographically. If the air exerted an internal pressure of one atmosphere at room temperature, the pressure would increase to approximately four atmospheres at 950°C . There would be no external pressure acting on the specimen, since sintering was done in a vacuum. Figure 20 indicates that neck rupturing occurs adding credence to the theory that air is present. In this figure it is shown also that the fraction closed porosity does not increase after neck rupture occurs, and in Figure 10 it is shown that the density undergoes little change until sintering has proceeded for 120 minutes, by which time the density has decreased. This supports the second theory that there was an oxide film on the powder inhibiting sintering. Some of the oxide undoubtedly formed when the powders were weighed and pressed. Further

oxidation would have occurred in the intraparticle porosity during sintering if air had been present in these pores. So the combination of the first two possibilities explains the behavior of the vacuum sintered specimens reasonably well. Air would have been present in the intraparticle pores in all specimens, regardless of sintering atmosphere, so the combination of the two theories should also apply to specimens sintered in various atmospheres. Figures 10 and 20 demonstrate a distinct difference between sintering atmospheres which contain hydrogen and which are hydrogen free. It can be seen that copper-1.5% antimony specimens sintered in hydrogen bearing atmospheres start increasing in density after 30 minutes of sintering and reach a minimum value of fraction closed porosity at 45 minutes followed by an increase in fraction closed porosity. This indicates that once neck rupture occurs, the surface oxides are reduced by hydrogen and densification proceeds. The continued presence of intraparticle voids in copper-1.5% antimony compacts after 45 minutes of sintering does not negate this theory since neck rupture does not occur at all necks. Another factor which may invalidate this theory is that the results of theoretical calculations presented earlier in this section indicate that pores with diameters on the order of one micron, such as intraparticle pores, should shrink in all materials if the internal pressure is due to a gas trapped at room temperature and heated to 950°C. It should be remembered however, that these

calculations utilize surface tension values for clean surfaces, so they do not apply to the closed intraparticle porosity when it is assumed that surface oxides may be present. Also, the intraparticle pore radii may have decreased to their equilibrium size while the larger closed interparticle pores increased in size and caused neck rupture, as is indicated in the next section. So, although there are complicating factors which can't be resolved as supporting or negating the theory, the hypothesis that air trapped in intraparticle porosity and surface oxides may stabilize the intraparticle porosity is supported by this work. The entire theory does not support the work of Simonsen³⁴. Since he used hot stage microscopy to observe sintering, the specimens were polished before sintering. The intraparticle pores which he observed intersected the polished surface, so they could not contain gases which would exert an internal pressure and inhibit sintering. There may still have been an oxide coating, as he believed, which retarded sintering.

Another possibility is that, as stated earlier, a material transport mechanism may be operating which is counteracting the normal sintering mechanisms. A material transport mechanism will now be proposed which could explain the stabilization of pores which do not contain any gases. Proof of this mechanism lies only in the theoretical base established by model experiments.

Stability of pores can be maintained by dynamic conditions in

which competing processes are operating at equal rates, producing no net change in the system. In Coble's early analysis of sintering mechanism¹⁰, he assumed that surfaces and grain boundaries were equally effective as vacancy sinks, with equal chemical potentials. This analysis has been accepted and used in most subsequent analyses of sintering. As shown in the literature survey, the equilibrium concentration of vacancies is inversely proportional to the radius of neck curvature¹⁰, so that as the radius of curvature increases the equilibrium concentration of vacancies decreases. The radius of curvature can increase rapidly if surface diffusion is operative in neck growth so that the region below the neck surface becomes supersaturated with vacancies. Normally, the excess vacancies would move to the particle surface, resulting in no densification, or to the grain boundaries which, acting as sinks, would cause densification¹⁰. If voids are located in the grain boundaries and the voids are equal to grain boundaries in their effectiveness as sinks, the vacancies can move to the voids as well as the grain boundaries and particle surfaces.

The Effect of Sintering Atmospheres on Density Changes

When considering changes in density, four types of porosity should be distinguished and treated separately; the usual open and closed interparticle porosity, intraparticle porosity in the neck which is formed during pressing, and intraparticle porosity in the particle interior. If

the sintering atmosphere does not react chemically with the powder particles, it should have no effect on the sintering of open porosity. In other words, particles which are surrounded by open porosity should have the same neck growth and density changes in various inert atmospheres. If the powders initially had slight oxide coatings on their surfaces the presence of a reducing agent, such as hydrogen, in the atmosphere would enhance sintering. The water vapor formed when hydrogen is used as a reducing agent would have no deleterious effects on sintering³⁶ since it could leave the open porosity by convection. If the interparticle porosity became closed after sintering for some time it would contain the sintering atmosphere at a pressure equal to that of the external sintering atmosphere, so the net stress acting on the pore would be solely due to surface tension. If the pore continued shrinking, the internal pressure would increase until it matched the sum of the external pressure and surface tension stress. If the sintering atmosphere was soluble in the metal, the internal pressure could be relieved by the gas going into solution in the metal, and densification could continue. According to a recent analysis by Greenwood³⁷, the solubility would be proportional to the internal pressure. When sintering in an inert gas, this would not be possible since inert gases are insoluble in metals³⁸. If an oxide persisted on the metal surface when the porosity closed and sintering was being done in hydrogen, the

oxide could be reduced. The formation of water vapor would not cause an increase in pressure in the closed interparticle porosity, since one hydrogen molecule would be replaced by one water molecule. The only harmful effect would be that water vapor can not go into solution in the metal so it would act like an inert gas in limiting the pore size to some equilibrium value. If the interparticle porosity was closed during pressing and contained air, the trapped air would cause an internal pressure when heated to the sintering temperature. As shown earlier in the discussion the pressure caused by a gas when heated from room temperature to 950°C is $4.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$. When sintering in an atmosphere, this pressure would be partially counteracted by the external pressure. The oxygen would cause oxidation while, in copper, the nitrogen would behave as an inert gas. If hydrogen was present in the sintering atmosphere and it diffused into the closed interparticle pore, no increase in pressure would result from water vapor formation. Densification may be enhanced by the reduction of surface oxides, but the minimum pore size would be limited to the equilibrium value resulting from the interplay of internal pressure, external pressure and surface tension stress.

Assuming that intraparticle porosity in the neck region is formed during pressing, contains air, and has an oxide coating on its surface, its behavior will be identical to that of interparticle porosity closed

during pressing, as discussed above. The intraparticle porosity in the interior of particles may have been formed when the powder was produced or by the internal formation of water vapor. As shown earlier in the discussion, this can result in a pressure on the order of 10,000 atmospheres.

The experimental results in Figure 10 show the effects of sintering atmospheres on pressed copper-1.5% antimony compacts with green densities of approximately 86% theoretical density. It is reasonable to believe that since the specimens all had similar green densities they were essentially identical before sintering. As a starting point, the specimens sintered in a vacuum will be considered. There is no external pressure on these specimens, any internal pressure is due to air trapped during pressing, and the surface tension stress is present. If there was an oxide coating on the powder prior to sintering it would probably not be completely removed during sintering. CuO is unstable at 950°C but Cu_2O is still stable³⁹. The oxide formed during sintering as a result of entrapped air would be Cu_2O . Figure 20 indicates that after 7.5 minutes of sintering about 9% of the porosity is closed. This is probably composed of both intraparticle and interparticle porosity. Because of the oxidation which undoubtedly occurs in pores containing air it is difficult to determine the equilibrium size of closed pores. However, any closed pore larger than 9.5μ which contained air

would grow when heated from room temperature to 950°C . Regardless of the surface condition, it seems unlikely that the internal pressure in intraparticle pores would be great enough to cause pore growth. Geometry adjustments during the first 7.5 minutes of sintering could result in specimen growth while the individual pore volumes remained constant. If the intraparticle pores were long and flat after pressing, the specimen would grow axially when they changed to a more spherical cross section and shrink radially, as shown in Figure 33. This could occur in all specimens, regardless of sintering atmosphere. Any other growth which occurs is due to closed interparticle porosity containing air. The neck rupture which occurs is also due to closed interparticle porosity containing air. The presence of intraparticle pores in the neck region would decrease the strength of the necks and facilitate rupture. By comparing Figures 10 and 20 it can be seen that increases in the fraction closed porosity for vacuum sintered specimens are not associated with decreases in a density, as is generally the case for specimens sintered in atmospheres. This is because porosity which closes during vacuum sintering contains no gas and consequently there is no internal pressure to retard sintering. Closed interparticle pores which were initially growing and did not have the internal pressure relieved by neck rupture were apparently still growing after two hours of sintering, resulting in a large decrease in density. This decrease

Figure 33. This is a schematic representation of intraparticle pores after pressing, Case A, and after sintering, Cases B and C. Each pore is in a separate neck aligned axially in the specimen and all pores have equal volumes. Case B shows the axial change which results when the pore change occurs by volume diffusion, grain boundary diffusion or plastic flow. The axial increase is accompanied by a radial decrease. Case C shows the slight length increase which occurs when the pore shape change occurs by surface diffusion or vapor transport.

does not occur earlier because at shorter sintering times the surface tension stress is still quite large.

The curve for the densification of specimens sintered in argon in Figure 10 demonstrates the mechanical effects of the presence of an atmosphere during sintering. It can be seen by comparing Figures 10 and 20 that during the first 30 minutes of sintering decreases in density are associated with increases in the fraction closed porosity. Neck rupturing occurs between 30 and 60 minutes of sintering. This is followed by a slight increase in density but no further change in the fraction closed porosity. The lack of more significant densification after neck rupturing is due to the fact the metal surfaces are coated by oxides. It should be noted that no gross oxidation was seen. The specimens sintered in argon and vacuum appeared slightly less reflecting than those sintered in hydrogen bearing atmospheres. The neck rupture of specimens sintered in argon was probably due to air trapped in closed porosity during pressing. The greater decreases in density seen when sintering in argon are the result of argon being trapped in porosity during sintering, creating an internal pressure and limiting the shrinkage of newly closed pores.

The curve for the densification parameter as a function of sintering time for copper-1.5% antimony specimens sintered in pure hydrogen demonstrates that hydrogen can cause tremendous expansion. All of

the mechanical effects of argon and entrapped air are present when sintering in hydrogen, except that hydrogen is soluble in copper and its alloys so that it can diffuse out of closed pores. The great expansion shown in Figure 10 is due to the chemical effect of hydrogen reacting with internal oxides and oxygen in solid solution to form voids containing water vapor. Although there is no data for a sintering time of 45 minutes, the data in Figure 20 for 60 minutes indicates that the decrease in fraction closed porosity after the maximum value is reached at 30 minutes is close to the decrease for specimens sintered in vacuum and argon. This indicates that internal water vapor formation may not be active in causing neck rupture. The great decrease in density results from particles swelling, while neck rupture results from air trapped in closed interparticle porosity during pressing. The increase in density following neck rupture occurs because the hydrogen can enter the pores which were formerly closed and reduce the surface oxides so that sintering may take place more readily.

Copper-1.5% antimony specimens sintered in argon-5% hydrogen undergo density changes almost identical to those for specimens sintered in pure hydrogen except that the magnitude of the expansion is not as great, as shown in Figure 10. If the curves for sintering in pure hydrogen and pure argon were averaged a curve for densification parameter as a function of sintering time would result which had exactly

the same shape as the curve for specimens sintered in argon-5% hydrogen. The lower percentage of hydrogen limits the amount of internal water formation and therefore the ultimate expansion while it supplies enough hydrogen to clean the surfaces of ruptured pores and allow greater densification than pure argon.

The effect of pure hydrogen on copper specimens is even more drastic than hydrogen's effect on copper-1.5% antimony compacts. Copper specimens with green densities of approximately 87% theoretical increased in density when sintered in argon-5% hydrogen but expanded when sintered in pure hydrogen, as shown in Figure 9. This large and sudden expansion can be attributed to the three ways in which copper differs from copper-1.5% antimony alloys. As shown by chemical analysis, the copper had a greater oxygen content than the alloys, copper is not as strong as the alloys²⁷, and hydrogen is probably more soluble in pure copper than in the alloy²⁶. Figure 18 demonstrates that the fraction closed porosity resulting from sintering in the two atmospheres is not as consistent as the fraction for the alloys. The great expansion of copper particles coupled with the internal pressure in closed interparticle porosity may have resulted in neck rupture during the first 7.5 minutes of sintering in pure hydrogen.

The majority of the specimens of all materials were sintered in argon-5% hydrogen. The curves relating the densification parameter

and fraction closed porosity to sintering time can be analyzed in the same manner as the curves described in this section.

The Effect of Heating Rate and Sintering Cycle

Figure 8 shows the effect of the initial heating rate to the sintering temperature on two copper-1.5% antimony specimens which subsequently underwent identical sintering cycles. One specimen was heated to 950°C from room temperature in argon-5% hydrogen. At the rate of 250°C per hour and withdrawn from the furnace and measured. The densification parameter was measured and plotted at zero sintering time. This specimen and another copper-1.5% antimony specimen which was green were then heat quenched and quench cooled to make measurements at the total sintering times shown in Figure 8. The rate at which the specimens were heated the first time to 950°C had little effect on their initial expansion. The ultimate densities which the specimens attain is markedly effected by the initial heating rate, however. The specimen which was initially heated to the sintering temperature slowly underwent no change in density during the following cycles. The specimen which was initially heat quenched decreased in density during the sintering cycles until a total sintering time of 45 minutes, after which there was little change in density. The fact that the initial expansion is independent of the initial heating rate indicates that it

is a function of temperature in copper-1.5% antimony alloys rather than time. This adds credence to the theory that air is trapped in closed interparticle porosity during pressing and, upon heating to the sintering temperature, the attempt of the gas to undergo thermal expansion results in an internal pressure which ultimately causes expansion of the compact.

The lack of density changes during sintering in the specimens which was initially heated slowly to 950°C can be attributed to neck rounding during heating. If, by the time the sintering temperature was reached, the radius of curvature of the necks was large, there would be little driving force for sintering and pore closure. The specimen which was heated rapidly to the sintering temperature underwent density changes similar to those of copper-1.5% antimony specimens sintered isothermally in argon. The initial rapid heating rate raised the specimen to the sintering temperature before excessive neck rounding could occur. The surface tension stress would remain great enough to cause the closure of open pores, entrapping the sintering atmosphere. The presence of this atmosphere would inhibit the shrinkage of the newly closed pores while the surface tension stress on the necks in open porosity decreased and the air trapped during pressing continued to cause pore growth. The net effect of these factors was the continued expansion of the specimen up to a total sintering time of 45 minutes,

after which time there was little change in density. The slight increase in density at 120 minutes may have resulted from neck rupture due to air trapped during pressing.

The Effect of Green Density and Surface Tension on Densification

Figures 11 through 16 illustrate the strong density dependence of sintering and to some extent, the stress dependence. The expansion noted in the high density specimens is not due to high density per se but rather to the large fraction of closed porosity. In high density specimens the porosity should have a smaller radius of curvature than in low density specimens so initially there should be a higher sintering stress. The photomicrographs presented in the results section show that necks form and become rounded very rapidly, so this driving force diminishes rapidly. Assuming that the initial pore configurations in specimens of all materials of equal densities are identical, excluding intraparticle pores, the only variable is surface tension due to differences in composition. At high and intermediate densities the densification parameters of copper specimens is consistently higher than those for copper-0.5% antimony and copper-1.5% antimony specimens, while at lower densities the behavior is not as consistent. This indicates that the dependence of densification on surface tension increases as the density increases and the total surface area decreases. If the total change in

surface energy of a compact is thought of as

$$\Delta \text{ total surface energy} = \Delta \gamma' (\text{surface area})$$

it is clear that a high density (low surface area) material will be more sensitive to a change in specific surface tension than a lower density material.

This approach and Equation 1 can be applied to the experimental data. In open porosity the surface tension is the driving force for the reduction of surface area. In closed porosity the combination of net pressure and sintering stress determine not only whether the pore will grow or shrink but also the ultimate pore size. Since the specimens were sintered under identical conditions, the initial net pressures should be similar. Because the surface tension of copper is about twice that of copper-1.5% antimony the net pressure required to cause growth in closed pores of similar configuration in copper and the alloys is twice as great for copper as for the alloys. Because of this, there are as many or more closed pores growing in the alloys than in the pure copper and the pores in the alloys will have a greater equilibrium size than those in copper. As density increases, the closed porosity constitutes a larger fraction of the porosity, increasing the effect of closed porosity and the dependence on surface tension.

In loose and tapped specimens closed porosity constitutes

a small fraction of the total porosity and densification appears to proceed independently of surface tension. At shorter times the copper densifies to a greater degree than the alloy because the water vapor reaction is occurring, negating most of the shrinkage which occurs in the alloys. When the pores containing water vapor reach their equilibrium sizes densification can proceed. At longer times, when the water vapor reaction is no longer occurring, the alloy specimens attain a higher density than the pure copper specimens. This would not be the case if the sintering rate were dependent on the surface tension to the fourth power as predicted by models supporting creep theories of sintering. Since the copper-1.5% antimony specimens attain a higher density than the pure copper low density specimens the sintering rate must depend on the surface tension to the first power as predicted by models supporting diffusion controlled sintering. Since antimony segregates to the surface and its diffusion rate in copper is faster than the self diffusion of copper^{21,22}, the densification of these compacts is best explained by a diffusion mechanism.

The Rate of Neck Growth

The ratio of neck diameter to particle diameter was determined for tapped copper and copper-1.5% antimony specimens after 7.5 minutes of sintering in argon-5% hydrogen. The ratio for the alloy was greater than that for the pure copper specimens, indicating a

small dependence on surface tension and a diffusional mechanism of neck growth. Using the equations of Wilson and Shewmon¹⁵, and Rockland¹⁶, this data can be used to determine the mechanism of sintering for pure copper specimens. There is insufficient diffusion data for this method to be applied to the alloys. The equations and data used are shown in Appendix 3. The results are shown in Table 4. Table 4 shows that the best agreement between experimental and theoretical data results when the mechanisms are neck growth by surface diffusion and shrinkage by grain boundary diffusion. The ratios shown in Table 5 are based on theoretical equations for the rate of neck growth by volume or surface diffusion and the rate of shrinkage by grain boundary or volume diffusion. The ratios in Table 5 reaffirm the dominance of surface diffusion in neck growth and grain boundary diffusion in shrinkage. The equations used in determining the ratios are presented in Appendix 3.

<u>Mechanism</u>	<u>Quantity</u>	<u>Experimental Value</u>	<u>Theoretical Value</u>
Neck Growth by Surface Diffusion	x^7/a^3	$4.45 \times 10^{-15} \text{ cm}^4$	$3.7 \times 10^{-15} \text{ cm}^4$
Neck Growth by Volume Diffusion	x^5/a^2	$2.04 \times 10^{-11} \text{ cm}^3$	$0.15 \times 10^{-11} \text{ cm}^3$
Shrinkage by Volume Diffusion	x^4/a	$9.5 \times 10^{-11} \text{ cm}^3$	$0.121 \times 10^{-11} \text{ cm}^3$
Shrinkage by Grain Boundary Diffusion	x^6/a^2	$1.3 \times 10^{-14} \text{ cm}^4$	$2.11 \times 10^{-14} \text{ cm}^4$

Table 4

The experimental and theoretical values of $\frac{x^m}{a^n}$ are shown for neck growth and shrinkage by various mechanisms for a tapped copper specimen sintered in argon-5% hydrogen for 7.5 minutes. All equations were from Rockland¹⁶.

<u>From Equations Of</u>	<u>Ratio</u>	<u>Value</u>
Rockland ¹⁶	$\dot{x}_s/\dot{x}_v$	7.9
Wilson & Shewmon ¹⁵	$\dot{x}_s/\dot{x}_v$	7.65
Rockland ¹⁶	$\dot{y}_b/\dot{y}_v$	53
Wilson & Shewmon ¹⁵	$\dot{y}_b/\dot{y}_v$	13.7

Table 5

Ratios of Rockland's¹⁶ rate equations for shrinkage and neck growth are compared to those of Wilson and Shewmon¹⁵. These are entirely theoretically based.

Conclusions

1. Intraparticle pores form in the neck region during pressing because of the lack of intimate contact between particles. The lack of contact results from the presence of surface oxides, surface roughness and strong, brittle materials which do not plastically deform to a great extent during pressing. The number of intraparticle pores per particle increases with green density and the strength of the material. Intraparticle pores are not seen in loose and trapped specimens because the powders make essentially point contacts initially, with the neck developing during sintering. The stability of intraparticle pores may be due to the presence of surface oxides and/or air trapped in them during pressing.
2. The surface tension stress at growing necks decreases as sintering proceeds, regardless of whether the compact is growing or shrinking. When sintering in an atmosphere, the external pressure on the specimens due to the atmosphere aids sintering. Any gas trapped in a closed pore before the sintering temperature is reached will exert an internal pressure because of its attempt to undergo thermal expansion. There may be additional chemical effects such as oxidation or reduction of the metal surface which will change the surface tension of the material. If a solid state reaction occurs

between hydrogen and oxygen, water vapor at a high pressure in pores results. The mechanical effect of the internal pressure is to retard the shrinkage of closed pores and sometimes cause pore growth.

3. Pressed copper - 1.5% antimony compacts expanded during sintering. The greatest expansion occurred when sintering in pure hydrogen, indicating that internal water vapor formation is the greatest cause of expansion. All of these specimens exhibited a decrease in fraction closed porosity between 30 and 45 minutes sintering time in all sintering atmospheres. This was the result of internal gas pressure causing neck rupture. Since the decrease in fraction closed porosity was seen in vacuum sintered copper - 1.5% antimony compacts as well as those sintered in atmospheres, it can be concluded that air trapped in closed porosity during pressing was the cause of the internal pressure which resulted in neck rupture. Closed interparticle porosity containing air is more likely to have resulted in neck rupture than closed intraparticle porosity because even with an oxide on the pore surface, the shrinkage stress in the intraparticle porosity would be much greater than that in the closed interparticle porosity.

Pure copper specimens exhibited growth when sintered in pure hydrogen; specimens of similar densities shrank when sintered in

argon-5% hydrogen. The great expansion can again be attributed to water vapor formation. Although water vapor formation causes great expansion, the presence of some hydrogen in the atmosphere is beneficial. Once the pores containing air rupture, the hydrogen can reduce the surface oxides and densification can proceed.

4. The rate at which specimens are heated to the sintering temperature has little effect on the initial expansion. The ultimate density changes did depend on the initial heating rate. The specimen which was slowly heated to the sintering temperature underwent no density changes during subsequent sintering cycles. The specimen which was heated to the sintering temperature rapidly continued expanding until 60 minutes of total sintering time had elapsed, after which time little density change occurred. These results indicate that closed porosity containing air, isolated during compaction, causes compact expansion initially due to gas expansion, and closing of porosity trapping the sintering atmosphere during rapid heating leads to further compact expansion during sintering.
5. High density compacts show a greater dependence on specific surface energy during sintering than low density compacts because the total surface energy, which is a function of specific surface energy and total surface area, is decreased by a greater percentage when the former is altered.

6. Because copper-1.5% antimony loose and tapped specimens undergo more densification after long sintering times than comparable copper specimens, it has been concluded that densification occurs by a diffusional mechanism. Ratios of the neck radius to particle radius indicate that neck growth also proceeds by a diffusional mechanism, since the ratio for the alloy is greater than that for pure copper. Comparison of the theoretical and experimental values of neck radius to particle radius for a tapped copper specimen sintered 7.5 minutes in argon-5% hydrogen indicates that surface diffusion is primarily responsible for neck growth and grain boundary diffusion is primarily responsible for shrinkage in this specimen.

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Appendix 1

The Determination of Potential Values of Stresses on Closed Pores

The values in Table 2 are obtained entirely from theoretical considerations. The compressive stress exerted by the metal surface on a closed spherical $2\gamma/r$, where γ is the surface tension and r is the pore radius. The values of surface tension determined by Inman, McLean, and Tipler²¹ have been rounded off to $1800 \frac{\text{dynes}}{\text{cm}}$ for pure copper and $900 \frac{\text{dynes}}{\text{cm}}$ for copper-1.5% antimony to calculate the shrinkage stress for various pore radii, as shown below.

<u>Pore Radius</u>	<u>$2\gamma/r$ for Cu</u>	<u>$2\gamma/r$ for Cu-1.5% Sb</u>
$.1 \times 10^{-4} \text{ cm}$	$36.0 \times 10^7 \frac{\text{dynes}}{\text{cm}^2}$	$18.0 \times 10^7 \frac{\text{dynes}}{\text{cm}^2}$
1.0×10^{-4}	3.6×10^7	1.8×10^7
5.0×10^{-4}	$.72 \times 10^7$	$.36 \times 10^7$
10.0×10^{-4}	$.36 \times 10^7$	$.18 \times 10^7$
15.0×10^{-4}	$.24 \times 10^7$	$.12 \times 10^7$
20.0×10^{-4}	$.18 \times 10^7$	$.09 \times 10^7$

The internal pressure due to metal vapor pressure is a function of temperature and composition. The vapor pressure of pure substances can be found from the following equation and data from Smithell's⁴⁰.

$$\log P^O = \frac{-A}{T} + B + C \log T + DT$$

where P^O = vapor pressure in mm. mercury

T = temperature in $^{\circ}\text{K}$

$A, B, C \text{ \& } D$ = constants for a given material

copper	17,870	10.63	-.236	-.16
antimony	11,560	22.40	-3.52	-

For dilute alloys, such as the copper-antimony alloys used,

$$P_{\text{Cu-Sb}} = X_{\text{Cu}} P_{\text{Cu}}^{\circ} + X_{\text{Sb}} P_{\text{Sb}}^{\circ}$$

where $P_{\text{Cu-Sb}}$ = total vapor pressure

$P_{\text{Cu or Sb}}^{\circ}$ = vapor pressure of the pure material

$X_{\text{Cu or Sb}}$ = mole fraction

the approximate values of vapor pressure of the materials used at 950°C are:

$$P_{\text{Cu}} = 10^{-8} \text{ atmosphere}$$

$$P_{\text{Cu-0.5\% Sb}} = 3.25 \times 10^{-4} \text{ atmosphere}$$

$$P_{\text{Cu-1.5\% Sb}} = 9.75 \times 10^{-4} \text{ atmosphere}$$

When a gas is heated, it will undergo expansion. If the gas is trapped in a closed pore and no expansion occurs, the internal pressure, at constant volume, will increase with temperature according to

$$P_i = P_o \times \frac{T_i}{T_o}$$

where P_i = final internal pressure
 P_o = initial internal pressure
 T_o = initial temperature, $^{\circ}\text{K}$
 T_i = final temperature, $^{\circ}\text{K}$

If the gas in the closed pore at room temperature is under an initial pressure of one atmosphere, $1 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$, and is heated to 950°C the final internal pressure will be

$$P_i = 1 \times 10^6 \times \frac{1223}{300} = 4.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

If the external pressure is maintained at one atmosphere, the net pressure on the pore will be

$$P_i - P_e = 3.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

The presence of oxides in the metal may add to the internal pressure when sintering in hydrogen. The surface oxide on copper may be CuO or Cu_2O . The internal oxide is generally Cu_2O . If the surface oxides in open porosity are reduced by hydrogen, the only effect is that a pure copper surface is left and the water vapor goes into the atmosphere. If the surface oxide in closed porosity is reduced by hydrogen, a clean copper surface is left, but the water vapor remains trapped in the closed porosity³⁶. If the reaction occurs isothermally, the internal gas pressure will not change since one volume of hydrogen is replaced by one volume of water vapor. If the Cu_2O is inside the copper as discrete particles it will be reduced by hydrogen diffusing to it. One mole of Cu_2O occupies

23.8 cm³ and two moles of Cu occupy 14.3 cm³. When Cu₂O is reduced to Cu, the remaining volume, 9.5 cm³, will be filled with one mole of water vapor. At room temperature, a mole of gas will occupy 24,000 cm³. At 950°C it will occupy 92,000 cm³ if unrestricted. If the volume formerly occupied by Cu₂O and now filled with Cu and H₂O vapor remains constant, the pressure exerted by the water vapor trapped in the 9.5 cm³ will be

$$P_i = P_o \frac{V_o}{V_i} \frac{T_2}{T_1} = 1 \cdot \frac{92,000}{9.5} = 9,700 \text{ atmospheres.}^{41}$$

Appendix 2

The Determination of the Equilibrium Pressure and Pore Size

If the size of a pore is known the equilibrium net pressure can be determined from

$$\frac{2\gamma}{r} = P_i - P_e = P_{eq}$$

If the actual net pressure is greater than P_{eq} , the pore will grow.

If the actual net pressure is less than P_{eq} , the pore will shrink.

This equilibrium pressure is only a first approximation, however. As the pore size changes the equilibrium pressure changes. A series of calculations must be made to find the final equilibrium pressure and pore size. Consider the case in which the gas is heated from 300°K to 1250°K in a closed pore in copper with a radius of 1.54×10^{-3} cm and no expansion occurs during heating. The initial pressure is again given by

$$P_i = P_o \frac{T_1}{T_o} = 1 \times 10^6 \times \frac{1250}{300} = 4.16 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

The net pressure when sintering in an atmosphere which exerts an external pressure of $1 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$ is

$$P_i - P_e = P_1 - P_o = 3.16 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

The first equilibrium pressure is

$$P_{leq} = \frac{2\gamma}{r_1} = \frac{3.6 \times 10^3}{1.54 \times 10^{-3}} = 2.34 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

The pore will expand until P_{leq} is reached and the pore size is

$$V_2 = \frac{P_1 V_1}{P_{leq}} \quad \text{or} \quad r_2^3 = \frac{P_1 r_1^3}{P_{leq}}$$

The new equilibrium pressure can be calculated from

$$P_{2eq} = \frac{2\gamma}{r_2}$$

The procedure is repeated until the equilibrium pore size and pressure are reached. The calculations for the example are summarized below.

Net Pressure	$\frac{2\gamma}{r_1}$	r_1	r_2
$3.16 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$	$2.34 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$	$1.54 \times 10^{-3} \text{ cm}$	$1.70 \times 10^{-3} \text{ cm}$
2.34×10^6	2.12×10^6	1.70×10^{-3}	1.76×10^{-3}
2.12×10^6	2.045×10^6	1.76×10^{-3}	1.78×10^{-3}
2.045×10^6	2.021×10^6	1.78×10^{-3}	1.786×10^{-3}

It can be seen in the r_2 column that using this iterative process results in a change of less than 5% after four calculations of the equilibrium pore size. The first calculation is adequate to determine the magnitude of the change which the pores must undergo to reach equilibrium. A graphical solution to the determination of the equilibrium pore size and

pressure is more general and easier than the iterative process. It is again necessary to assume an initial pore size and net pressure. A change in pore size will change the shrinkage stress and the internal pressure. The pore will be in equilibrium when these two quantities are equal. The shrinkage stress, $\frac{2\gamma}{r}$, can be readily plotted as a function of pore radius. Using the assumed initial pore radius and net pressure, the instantaneous pressure can be calculated and plotted as a function of r , the instantaneous radius, using the following relationships.

$$P_i - P_e = P_o$$

$$P_o V_o = PV$$

$$P = \frac{P_o V_o}{V} = \frac{P_o r_o^3}{r^3}$$

The intersection of the plots of $\frac{2\gamma}{r}$ and $\frac{P_o r_o^3}{r^3}$ will be the equilibrium pressure and pore radius, for pores with initial net pressures of P_o and initial radii of r_o . The graphical solution can be made more general by plotting the instantaneous pressure as a function of pore radius on an overlay. To facilitate the use of the overlay a horizontal line can be drawn on it. The chart is used as follows. The horizontal line A on the overlay is aligned with a horizontal line on the log-log sheet. The intersection of lines A and B (instantaneous pressure) is placed at the initial net pressure and

(A)

(B)

Figure 34. (A) may be traced and used as an overlay on (B) to determine the equilibrium pore size and pressure from the initial pore size and pressure.

pore radius on the log-log paper. Line B is then followed until it intersects the line on the log-log paper (C or D, shrinkage stress) which is appropriate to the material being used. The intersection of B and C or D is the equilibrium pressure, read at the left, and the equilibrium pore size, read at the bottom. If the original pore size and pressure fall between lines C and D, the pore in copper will shrink and the pore in copper-1.5% antimony will grow.

Appendix 3

The Determination of Sintering Mechanisms

Log-log plots of the ratio of neck radius to particle radius $\left(\frac{x}{a}\right)$ against time are frequently used to determine the mechanism of sintering in model experiments, after Kuczyski's analysis. The slope of the line gives the time exponent, which has a unique value for each mechanism. The difference in slopes is slight however, and experimental data will often result in a slope close to those for several mechanisms. Rather than using rate equations, their integrals at a given time can be used to determine the absolute value of $\frac{x}{a}$. This is done below for a tapped copper specimen after 7.5 minutes of sintering, using the equations of various authors. The equations and substitutions are listed below. All substitutions are for pure copper, since values of D_s and D_b aren't available for the alloys.

<u>Author</u>	<u>Mechanism</u>	<u>Equation</u>
Rockland ¹⁶	neck growth by surface diffusion	$\frac{x^7}{a^3} = \frac{34 \sigma D_s \delta^4}{k T} t$
Rockland ¹⁶	neck growth by volume diffusion	$\frac{x^5}{a^2} = \frac{20 D_v \sigma \delta^3}{k T} t$
Rockland ¹⁶	shrinkage by volume diffusion	$\frac{x^4}{a} = \frac{16 D_v \sigma \delta^3}{k T} t$
Rockland ¹⁶	shrinkage by grain boundary diffusion	$\frac{x^6}{a^2} = \frac{48 D_b \sigma \delta^4}{k T} t$

Rockland¹⁶

$$\frac{\text{rate of neck growth by surface diffusion}}{\text{rate of neck growth by surface diffusion}}$$

$$\frac{\dot{x}_s}{\dot{x}_v} = \frac{\sigma_s D_s}{1.05 \cdot x^{1/2} \pi \rho D_v}$$

Rockland¹⁶

$$\frac{\text{rate of shrinkage by grain boundary diffusion}}{\text{rate of shrinkage by volume diffusion}}$$

$$\frac{\dot{y}_b}{\dot{y}_v} = \frac{\sigma_b D_b}{\pi \rho D_v}$$

Wilson & Shewmon¹⁵

$$\frac{\text{rate of neck growth by surface diffusion}}{\text{rate of neck growth by volume diffusion}}$$

$$\frac{\dot{x}_s}{\dot{x}_v} = \frac{2/3 D_s \sigma_s}{D_v \rho}$$

Wilson & Shewmon¹⁵

$$\frac{\text{rate of shrinkage by grain boundary diffusion}}{\text{rate of shrinkage by volume diffusion}}$$

$$\frac{\dot{y}_b}{\dot{y}_r} = \frac{D_b \sigma_b}{2 D_v x}$$

The symbols and substitutions used in the equations are listed below:

$$x = \text{neck radius} = 6.6 \times 10^{-4} \text{ cm}$$

$$a = \text{particle radius} = 20.0 \times 10^{-4} \text{ cm}$$

$$\rho = \text{radius of neck curvature}$$

$$= \frac{x^2}{2a} = 1.09 \times 10^{-4} \text{ cm}$$

- γ = surface tension = $1800 \frac{\text{dynes}}{\text{cm}}$
 δ = lattice parameter = $3.61 \times 10^{-8} \text{ cm}$
 D_s = coefficient of surface diffusion = $4.12 \times 10^{-5} \frac{\text{cm}^2}{\text{sec}}$
 D_r = coefficient of volume diffusion = $1.04 \times 10^{-9} \frac{\text{cm}^2}{\text{sec}}$
 D_b = coefficient of grain boundary diffusion = $5.22 \times 10^{-4} \frac{\text{cm}^2}{\text{sec}}$
 k = Boltzman constant = $1.38 \times 10^{-16} \frac{\text{ergs}}{^\circ\text{K}}$
 T = temperature = 1223° K
 t = time = 450 sec.

<u>mechanism</u>	<u>experimental value</u>	<u>theoretical value</u>
neck growth by surface diffusion ¹⁶	4.45×10^{-15}	3.7×10^{-15}
neck growth by volume diffusion ¹⁶	2.04×10^{-11}	$.15 \times 10^{-11}$
shrinkage by volume diffusion ¹⁶	9.5×10^{-11}	$.121 \times 10^{-11}$
shrinkage by grain boundary diffusion ¹⁶	1.34×10^{-14}	2.11×10^{-14}

<u>Author</u>	<u>Ratio</u>	<u>Value</u>
Rockland ¹⁶	$\dot{x}_s / \dot{x}_y$	7.9
Wilson and Shewmon ¹⁵	$\dot{x}_s / \dot{x}_y$	7.65
Rockland ¹⁶	$\dot{y}_b / \dot{y}_v$	53
Wilson and Shewmon ¹⁵	$\dot{y}_b / \dot{y}_v$	13.7

Appendix 4

The Determination of the Time Required for a Pore to Shrink

Hull and Rimmer³⁵ have suggested the following equation for the rate of radius change of pores on a grain boundary when grain boundary diffusion is the only mechanism acting.

$$\frac{dr}{dt} = \frac{2\pi\Omega D_g \delta Z (P_I - P_E - \frac{2\gamma}{r})}{kT \times r}$$

where dr = change in radius

dt = change in time

r = atomic volume = $1.2 \times 10^{-23} \text{ cm}^3$

$*D_g$ = coefficient of grain boundary diffusion = $5.22 \times 10^{-4} \frac{\text{cm}^2}{\text{sec}}$

δZ = grain boundary width = 10^{-7} cm

*Note: D_g is for pure copper.

P_I = internal gas pressure (substituted for their σ)

P_E = external gas pressure (substituted for their P_H)

γ = surface tension $900 \frac{\text{dynes}}{\text{cm}}$ (for Cu - 1.5% Sb)

k = gas constant = $1.38 \times 10^{-16} \frac{\text{ergs}}{^\circ\text{K}}$

T = absolute temperature = 1223° K

x = distance of the pores apart = $3 \times 10^{-4} \text{ cm}$

$r = R$ = initial radius = 10^{-4} cm

When sintering in a vacuum, $P_i = P_e = 0$, so

$$\frac{dr}{dt} \approx \frac{2\pi\Omega D_g \delta Z \frac{2\gamma}{r}}{kT \times r}$$

Integrating from radius R to 0 yields

$$t = \frac{kT \times R^3}{12 D_g} = .2 \text{ sec.}$$

for a pore 2μ in diameter on a grain boundary in copper-1.5 antimony to disappear. This verifies that a pore of this size should shrink if there is no internal pressure acting.

If there are internal and external pressures acting they must be taken into account in the calculation of the ultimate pore size and the time required to attain that size. Assuming an initial pore radius of 10^{-4} cm and an initial net pressure of $3.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$ the equilibrium pore radius and pressure are found to be 0.43×10^{-4} cm and $42 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$ using Figure 34. With this information the time required for the pore in copper-1.5% antimony can be calculated, using the initial general equation of Hull and Rimmer³⁵

$$\frac{dr}{dt} \approx \frac{2\pi\Omega D_g \delta Z \left(P_i - P_e - \frac{2\gamma}{r} \right)}{kT \times r}$$

$$P_i - P_e = P = \frac{P_o V_o}{V} = \frac{P_o \frac{4}{3}\pi r_o^3}{\frac{4}{3}\pi r^3} = \frac{P_o r_o^3}{r^3}$$

$$\text{Setting } K = \frac{2\pi\Omega D_g \delta^2}{kT x}$$

$$\frac{dr}{dt} \approx K \frac{\frac{P_{OO} r^3}{r} - \frac{2\delta^2}{r}}{r}$$

$$K dt = \frac{r dr}{\frac{P_{OO} r^3}{r^3} - \frac{2\delta^2}{r}}$$

$$K dt = \frac{r dr}{\frac{P_{OO} r^3}{r^3} - \frac{2\delta^2}{r}} \cdot \frac{r^3}{r^3} = \frac{r^4 dr}{P_{OO} r^3 - 2\delta^2 r^2}$$

$$\text{Setting } a = P_{OO} r^3$$

$$b = -2\delta^2$$

$$x = r$$

$$\text{Results in } K dt = \frac{x^4 dx}{a + b x^2} \quad (a)$$

For which there is the general solution

$$\int \frac{x^m dx}{(a + bx^n)^{p+1}} = \frac{1}{b} \int \frac{x^{m-n} dx}{(a + bx^n)^p} - \frac{a}{b} \int \frac{x^{m-n} dx}{(a + bx^n)^{p+1}} \quad (b)$$

Referring to equation (a), the following substitutions can be made in equation (b):

$$m = 4$$

$$n = 2$$

$$p = 0$$

Using these substitutions, the following equations result.

$$\begin{aligned} \int \frac{x^4 dx}{(a + bx^2)^1} &= \frac{1}{b} \int x^2 dx - \frac{a}{b} \int \frac{x^2 dx}{a + bx^2} \\ &= \frac{x^3}{3b} - \frac{a}{b} \left[\frac{x}{b} - \frac{a}{b} \int \frac{dx}{a + bx^2} \right] \\ &= \frac{x^3}{3b} - \frac{a}{b} \left[\frac{x}{b} - \frac{a}{b} \left(\frac{1}{2\sqrt{-ab}} \ln \frac{a + x\sqrt{-ab}}{a - x\sqrt{-ab}} \right) \right] \end{aligned}$$

Substituting the original variables yields

$$Kt = \frac{r^3}{-6\gamma} + \frac{P_o r_o^3}{2\gamma} \left[\frac{r}{-2\gamma} + \frac{P_o r_o^3}{2\gamma} \left(\frac{1}{2\sqrt{2\gamma P_o r_o^3}} \ln \frac{P_o r_o^3 + r\sqrt{2\gamma P_o r_o^3}}{P_o r_o^3 - r\sqrt{2\gamma P_o r_o^3}} \right) \right] + C$$

Using the values under Hull and Rimmer's original equation

$$K = \frac{2\pi\Omega D_g \sigma^2}{kT x} = 7.8 \times 10^{-17} \frac{\text{cm}^5}{\text{erg. sec}}$$

Setting the initial conditions of $t = 0$, $r = r_o = 10^{-4}$ cm and $P_o = 3.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$, yields the constant of integration $C = 2.96 \times 10^{-16} \frac{\text{cm}^5}{\text{erg. sec.}}$

Substituting $r = 0.43 \times 10^{-4}$ cm yields the time required for a pore

with a radius of 1μ containing a gas at an initial pressure of $3.08 \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$

to shrink to its equilibrium size, 0.43×10^{-4} cm. The time is 2.1 seconds,

roughly ten times longer than the time required for a pore of the same

initial size to disappear when it contains no gas.

With the equation derived, the time required for a pore to grow to its equilibrium size is negative. The three possible cases are listed below:

$$r = r_o , \quad t = 0$$

$$r < r_o , \quad t > 0$$

$$r > r_o , \quad t < 0$$

Appendix 5

Enlargements of Figures 35-44 were used to determine the number of intraparticle pores per particle. Figures 45 and 46 are photomicrographs of the same specimens in Figures 27 and 28, respectively, but at lower magnification.

Figure 35. Sintered 7.5 minutes

Figure 36. Sintered 15 minutes

Figure 37. Sintered 30 minutes

Copper - 1.5 antimony specimens with nominal green densities of 82.5% sintered in argon-5% hydrogen at 950°C. (50x) Unetched.

Figure 38. Sintered 60 minutes

Figure 39. Sintered 120 minutes

Copper - 1.5% antimony specimens with nominal green densities of 82.5% sintered in argon-5% hydrogen at 950°C. (50x) Unetched.

Figure 40. Sintered for 7.5 minutes

Figure 41. Sintered for 30 minutes

Copper specimens with nominal green densities of 82.3% sintered in argon-5% hydrogen at 950°C.
(50x) Unetched.

Figure 42. Sintered for 7.5 minutes

Figure 43. Sintered for 30 minutes

Figure 44. Sintered for 60 minutes

Copper specimens with nominal green densities of 93.4% sintered in argon-5% hydrogen at 950°C.
(50x) Etchant: Potassium bichromate.

Figure 45. Sintered for 60 minutes

Figure 46. Sintered for 120 minutes

Copper - 1.5% antimony specimens with nominal green densities of 84.8% sintered in a vacuum at 950°C. (250x)
Etchant: $1\text{NH}_4\text{OH}:1\text{H}_2\text{O}:2\text{H}_2\text{O}_2$ (3%).