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Hot-Press Sintering of Precious Metals and Glass Beads*

(Received Nov. 28, 1959)

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Abstract

In order to study the fundamental mechanism of hot-press sintering, spherical beads of platinum, gold, 30-70 Au-Ag alloy and glass of equal sizes are sintered in a small cylindrical vessel under compressive load. The relations among the diameter of bead, load, sintering time and temperature (the temperature for the beginning of sintering) are determined by the testing method deviced by the author. The values of diameters of beads tested are mainly 0.85 mm, and for investigation of particle size effect 1.35 and 0.45 mm diameters are also used.
The rate of lowering of *"the lowest sintering temperature"* with the increase of load keeping the sintering time and the radius of bead constant has a maximum value in the range of recrystallization temperature of each metal or softening point of glass.

By the theoretical formula on the adhered area of glass, it is shown that the viscous flow is the rate-determining mechanism in hot-press sintering of glass.

The activation energy to effect hot-press sintering changes with temperature and load. It becomes smaller with temperature, but has a minimum value within the range of recrystallization temperature of each metal or softening point of glass, and then it becomes larger.

It is shown by this report that the recrystallization phenomena plays a prime role in hot-press sintering.

I. Introduction

Much previous research in powder metallurgy has been performed on normal sintering, but very little information is available from the literature on powder metallurgy on hot-press sintering.1) 2) 3)

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* A part of this research (in Japanese) has been published in J. Appl. Phys. Japan ; 25, 305, 403 (1956); 26, 229, 363 (1957); 28, 60 (1959).

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1) P. Schwarzhapf, "Powder Metallurgy", Macmillan, New York (1947).

2) C. G. Goetzel, "Treatise on Powder Metallurgy", Vol. I, II, Interscience, New York (1949).

3) E. Kingston, editor, "The Physics of Powder Metalluagy", McGraw-Hill, New York, (1951). etc.

A prime and fundamental problem in hot-press sintering phenomena, as well as in *normal sintering*, is to decide in what conditions powders can be sintered or not. The conditions that powders can be sintered depend on a particle size-pressure-temperature-time relationships and the atmosphere. When the materials that are hardly oxidized in air at high temprature are used, we need not consider the effect of atmosphere to avoid the oxidization of the materials. So the relationships of particle size-pressure-temperature-time are investigated by the use of precious metals.

Soda glass, gold, platinum and 30-70 Au-Ag alloy, which are scarcely oxidized at high temperature in air, are hot-perss sintered in air. Gold and platinum were selected as typical examples of medium and high melting point metals respectively, 30-70 Au-Ag alloy as a typical example of alloys and soda glass as that in non-crystalline materials.

The spherical beads of these materials which are produced by a new method⁴⁾⁵⁾ are used instead of powder for convenicence in handling of particles.

The conditions whether these spherical beads can be "*sintered or not*" are determined by a testing method which is named "*drop method*" by the author. By this method "*the lowest temperature*" for the beginning of hot-press sintering are determined.

That these materials can be sintered at extraordinary low temperature is shown by this report.

II. Experimental Apparatus

Schematic diagram of the experimental apparatus is illustrated in Fig. 1. Beads are put in an iron cylindrical die *A*, inside diameter of which is a little larger than the diameter of a bead, and whose depth is about six times the size of a bead. A quartz die is used instead of iron at high temperature to avoid mutual reaction between iron and the precious metals. *A* is separable into two pieces, as shown at the upper corner in the figure, to make easy the placing and removing of the beads. The two pieces, however, are bound together by a wire during the experiment. Both the load *W* and the punch or pressing rod *C* transmit pressure on the beads in the die. Temperature of beads in the electric furnace *F* is measured by a thermocouple *T*.

The die in which 3 or 4 beads are ranged in a column, are brought into *F* the temperature of which is kept a little higher than the required one. After a few minutes when the temperature of the beads reach the required degree, *C* and *W* are set on the range of beads for hot-pressing. In this case, the bottom tip of *C* is preheated to the required temperature or a little above. Heating for certain minutes, the beads are taken out from the die to examine whether they are sintered or not: if

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4) M. Masima & M. Sakata, J. Appl. Phys. Japan, **20**, 57 (1950).

5) M. Masima & M. Sakata, This Proceedings, **4**, No. 12, p. 1 (1951).

all of the beads are not adhered at all, the beads, of course, *"have not been sintered"*; if at least two beads of them are adhered mutually the following test is made.

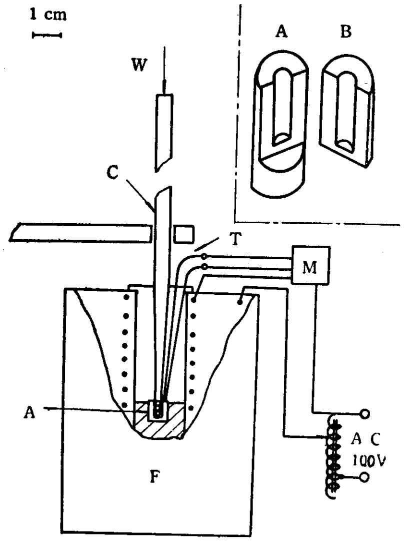


Fig. 1. Schematic diagram of the experimental apparatus.
A is cylindrical vessel;
B, divided piece of the vessel;
C, pressing rod;
F, furnace;
M, millivoltmeter with temperature control unit;
T, thermocouple; and
W, load.

III. "*Drop Method*" to measure the Degree of Progress of Sintering

Many methods may be devised to measure the degree of progress of sintering: measurment of the rate of interface growth; measurment of the strength required to separate the interface; measurment of the electrical conductivity; etc. In many cases, these measurments are more or less ambiguous and sometimes difficult. In the present experiment the following method which the author has tentatively named "*Drop Method*". This is also ambiguous and only gives a standard, but the duplication of data is good indicating their reliability, and the result of experiment is easily obtained in short time.

In this method the adhered beads are dropped many times on a glass plate from a certain height, and the degree of progress of sintering is measured by the number of drops required to separate the beads. The impact portions on the beads differ in each and the impulsive forces are not equal each time. When the beads are dropped a few times only, the experimental data flactuate irregularly because of the contingency of the impulsive forces. To avoid this, beads are dropped many times.

The more the number of drops, the more the beads are repeatedly impacted by various intensity of forces. When the numbers of drops are equal for each sample, the interface of each sample is impacted with almost simillar force in sum.

According to this idea, when beads are dropped many times, it is possible to distinguish the degree of progress of sintering by the number of times at which the beads are wholly separated. The absolute strength of the interface is not measurable by this method, but this is convenient for the comparison of the degree of sintering. (The interface strengthes of some beads are measured after the "*drop test*".)

In practice, the adhered beads are repeatedly dropped from the hight of 10 cm, and when the beads are wholly separated at 20 times or below, it is regarded as "*not sintered*" but when they are not separated at 20 times or above, it is regarded as "*sintered*".

IV. The Lowest (Hot-Press) Sintering Temperature

Under a constant particle size, constant load and constant sintering time, two beads will "*sinter*" at some higher temperature, but will "*not sinter*" at lower temperature.

This means that there is a certain temperature, above which the beads can be always sintered, and below which cannot be sintered. This borderline temperature is named "*the lowest (hot-press) sintering temperature*". In other words, this is the temperature where sintering begins in a sense of a macro measure. *The lowest sintering temperature* is determined under various load, sintering time and size of bead by the use of a few kinds of precious metal and glass.

V. Materials

Materials which have been investigated are a soda glass, cp gold, cp platinum, cp 30–70 Au–Ag alloy. These are hardly oxidized in air at high temperature. The metals were obtained from The Tanaka Precious Metal Manufacturing Company in Japan. The purity of each metal is 99.99% respectively. The spherical beads of metals have been prepared by a new method[4] of producing beads. The spherical glass beads are obtained from The Sugitoo Optical Glass Manufacturing Industry in Iapan. The composition of soda glass is SiO_2 71, Na_2O 15, CaO 8, MgO 4, Al_2O_3 1.5 (%).

The beads of metals are chemically cleaned in dilute aqua regia and subsequently washed throughly distiled water and dried by an infrared lamp. Soda glass beads are chemically cleaned in chromic-mixture and washed and dried by the same method.

VI. Results and Discussions

A. The Lowest Sintering Temperature-Load-Time Relationships, 0.85 mm Constant Diameter.

To determine *the lowest sintering temperature* T_s, under constant size of beads, the diameter is kept constant at 0.85 ± 0.05 mm to make easy handling of beads.

The relationships among T_s, load W, and sintering time t, are shown in Figs. 2, 3, 4, and 5.

In these figures each curve means: under the pressing load, value of which is written near the curve, if the beads are hot-pressed at a condition no the curve or above, beads will be "*sintered*", and this temperature on the curve is "***the lowest***

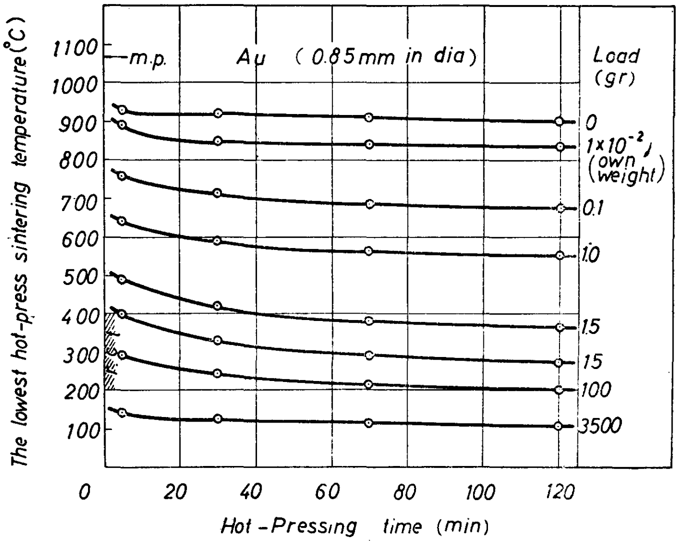


Fig. 1.

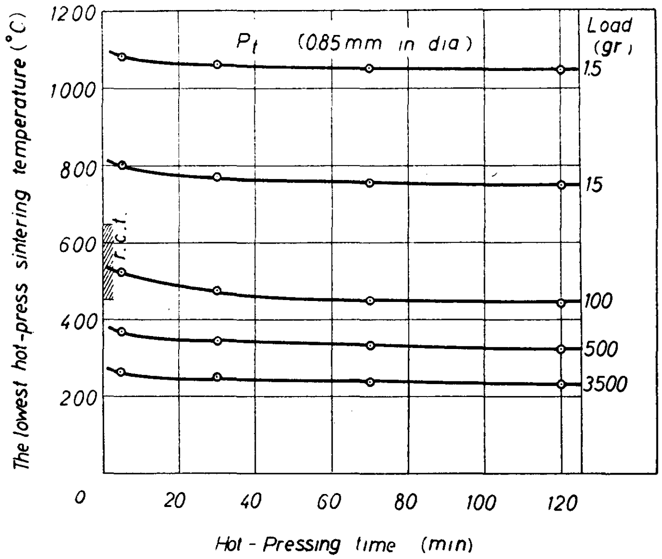


Fig. 2.

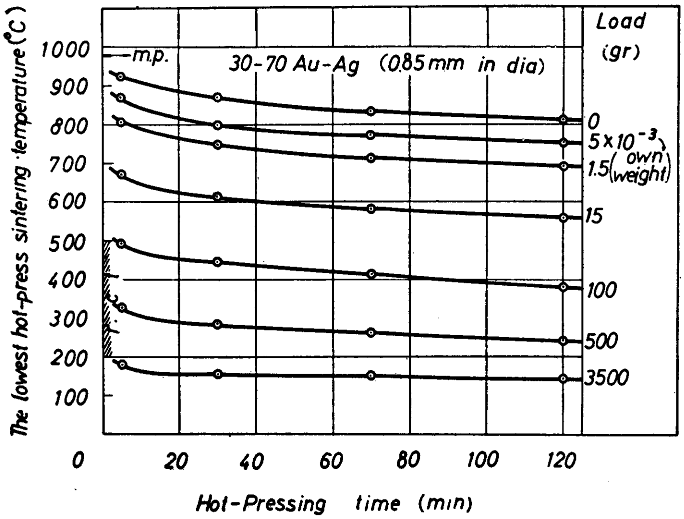


Fig. 3.

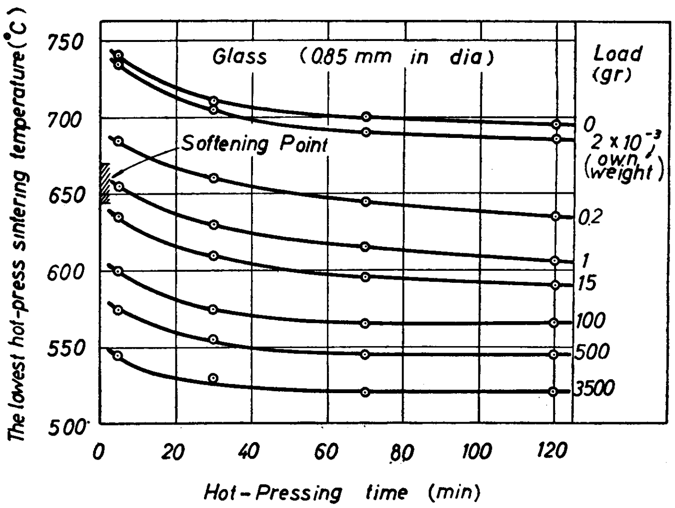


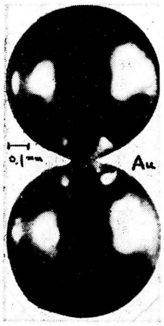
Fig. 4.

Figs. 2, 3, 4, 5. Relation among the *lowest sintering temperature*, load and time. In the upper region of each curve, the beads can be sintered.

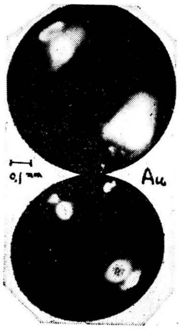
sintering temperature" T_s, at the load and the time. In other words, if T_s is measured at a sintering time t_s keeping the load constant, and when a sintering temperature is just T_s or higher keeping t_s constant beads will be *sintered*, but below T_s beads do "*not sinter*"; when sintering time is just t_s or longer keeping T_s constant beads will be *sintered*, but shorter than t_s beads do *not sinter*.

The load "zero gram" means beads are placed in contact horizontally, and "own weight" means beads are placed in the die and ranged in a column and no punch and weight are set on it.

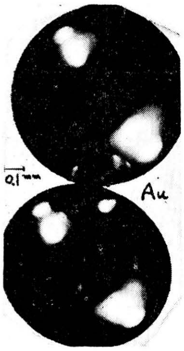
We assumed at first T_s would be nearly equal the melting point of metals at zero gram in load, but unexpectedly T_s proved to be much lower than melting point. In gold and Au-Ag alloy these are both about 9/10 of melting point in absolute temperature for 5 minutes hot-pressing time. In glass it is about 2/3 of melting point (about 1570° K), but it is about 1.1 times of the softening point which is measured by Littleton's method[6] (645°~650°C) or by Lillie's methods[7] (660°~670°C). As the hot-pressing time becomes longer, T_s becomes lower under the same load, but above 2 hours it scarcely becomes lower. With increasing of load, moreover, T_s becomes lower under the same hot-pressing time. At 3.5 kg in load, T_s are surprisingly lower, and each ratio of T_s to melting point of each material for 2 hours hot-pressing time is shown as follows: in glass, 1/2; in platinum, 1/4; in gold, 7/25; in Au-Ag, 1/3. In glass, it is 4/5 of softening point of the glass in question. If the value of load is increased more than 3.5 kg in load, T_s scarcely becomes lower. It is very interesting that these metals are sintered at such a low temperature. In gold, for example, however, above 5 kg in load at room temperature the beads can be joined mutually and it seems that beads are "*sintered*" at room temperature. Then it might be regarded as the hot-press sintering at a temperature of 300° K. At a room temperature, however, the effect of gas and moisture at the contact point between two beads, the problem of optical contact, or that of ringing and others are connected with this experiment at this load, and these problems are so apart from the aim of our experiment that the case at a room temperature is omitted. For this reason, the largest value of load is selected as 3.5 kg in this experiment. The beads which are sintered at the *lowest sintering temperature* are shown in the following photographs.



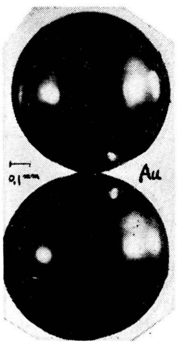
(1) 0.85mm, 0gr, 30min, 920°C.



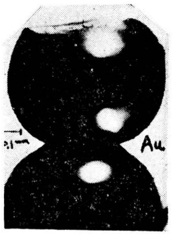
(2) 0.85mm, 0.01gr, 70min, 840°C.



(3) 0.85mm, 1gr, 70min, 565°C.



(4) 0.85mm, 100gr, 70min, 215°C.



(5) 0.85mm, 3500gr, 70min, 113°C.

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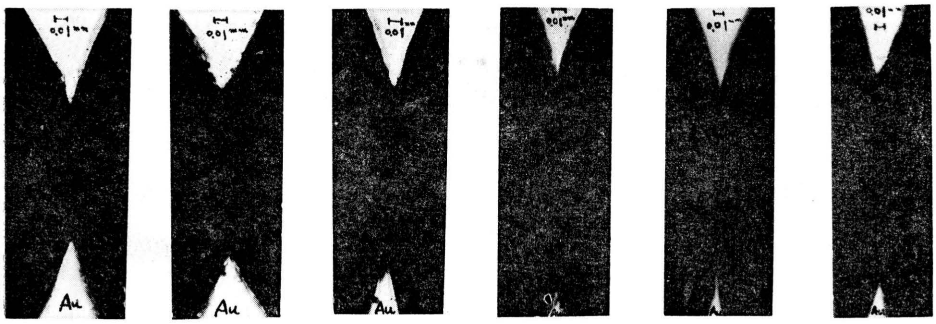
[6] J. T. Littleton, J. Am. Ceram. Soc., **10**, 259 (1927).

[7] H. R. Lillie, J. Am. Ceram. Soc., **14**, 502 (1931).



(**6**) 0.45mm, 0 gr, 5 min, 920°C.

(**7**) 0.45mm, 100gr, 5 min, 270°C.

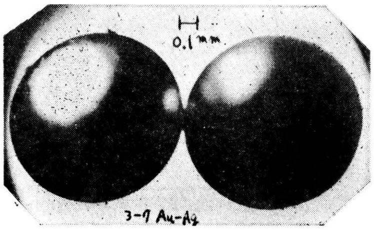
(**8**) 0.85mm, 0 gr, 5 min, 930°C.

(**9**) 0.85mm, 100gr, 5 min, 290°C.

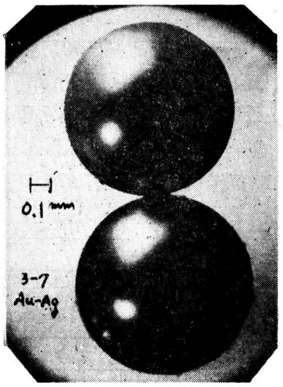
(**10**) 1.35mm, 0 gr, 5 min, 1020°C.

(**11**) 1.35mm, 100gr, 5 min, 335°C.

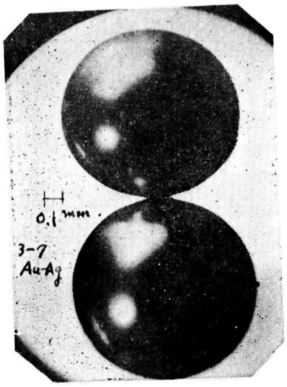
Photoes. I, (1)~(**11**). The "*neck*" of gold beads which are sintered at *the lowest sintering temperature* T_s. The sintering conditions are mentioned above, which are bead diameter, load, sintering time, and T_s in order.



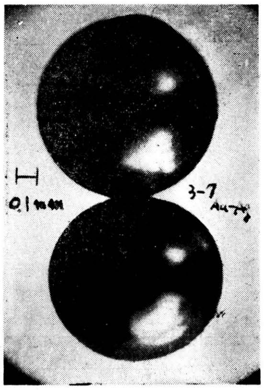
(1) 0gr, 30min, 870°C.



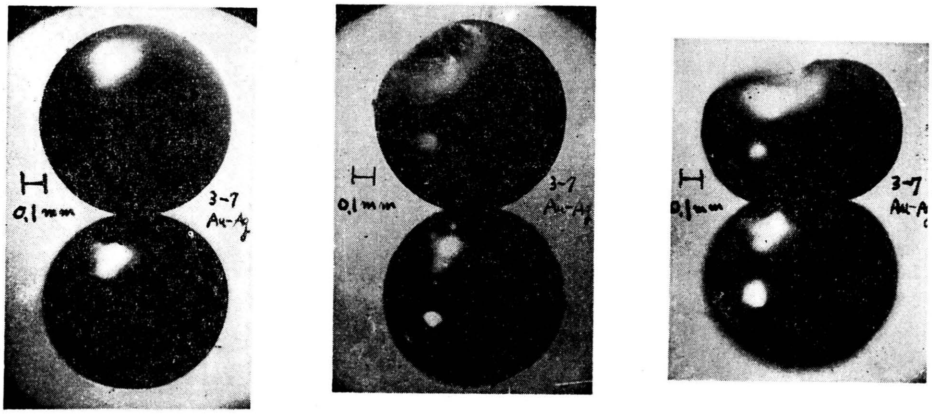
(**2**) 0.005gr, 30min, 805°C.



(**3**) 1.5gr, 30min, 745°C.

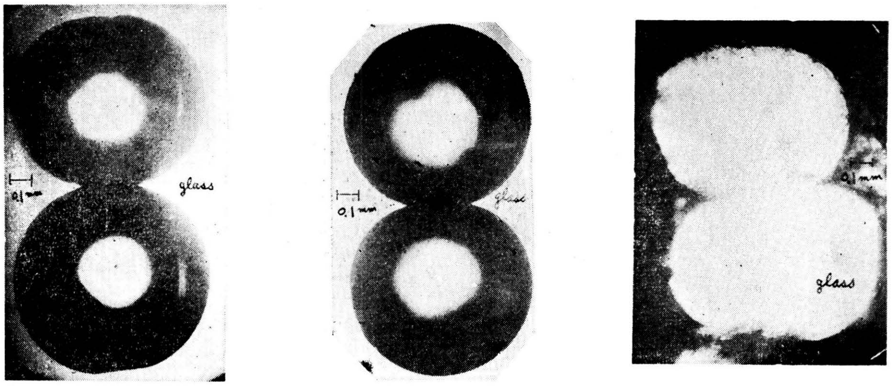


(**4**) 15gr, 30min, 615°C.



(5) 100gr, 30min, 445°C. (6) 500gr, 30min, 285°C. (7) 3500gr, 30min, 155°C.

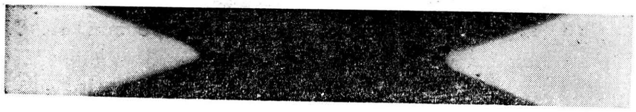
Photoes. II, (1)~(7). The "*neck*" of 30-70 Au-Ag alloy beads which are sintered at *the lowest sintering temperature* T_s. The sintering conditions are mentioned above, which are load, sintering time, and T_s in order. Beads diameters are all 0.85 mm.



(1) 100gr, 30min, 575°C. (2) 500gr, 5min, 575°C. (3) 500gr, 5min, 585°C. 585° =(T_s+10°)

Photoes. III, (1)~(3). The "*neck*" of glass beads sintered at *the lowest sintering temperature* T_s. The beads in (3) were sintered at 10°C higher than T_s, moreover, it showes the cross sectional area containing the center line between two beads. Beads diameters are all 0.85 mm and the conditions are mentioned above and they are load, sintering time and T_s in order.

(1) 30-70 Au-Ag, 0.85mm, 0gr, 120min, 810°C, (580X).



(2) glass, 1.30mm, 0gr, 120min, 710°C, (120X).

Photoes. IV, (1), (2). The "*neck*" of Au-Ag alloy and glass are enlarged. The radious of curvature on the "*neck*" between two beads of glass is compared with that of metals. (Au-Ag alloy beads are shown as a example of metals used.)

The radious of curvature on the "*neck*" between the two beads of glass sintered, namely the both ends of the "*neck*" in Photoes. IV, is larger than that of metals. That of glass becomes larger with T_s. We learn that the rate of viscous flow of glass is much larger than that of metals from these photographs.

The lowest sintering temperature T_s, is plotted *versus* $\log_{10} W$ in Figs. 6, 7, 8 and 9 under various constant sintering times.

The T_s in metals are much lowered with the increase in load, but T_s in glass is not so much lowered as in metals, then it is obvicus that the effect of changing of the load upon the lowering of T_s is greater in metals than in glass. In hot-press sintering the strain energy is very useful as in *normal sintering,* and as glass can store little strain energy in comparison with metals, the T_s in glass does not becomes lower with load as that in metals do. If the load W becomes $W+dW$, T_s becomes T_s-dT_s, so the rate of lowering of the lowest sintering temperature with the increase in load ξ under the same sintering time t and the same radius of bead r is defined as follows,

$$\xi=[-(dT_s/T_s)/(dW/W)] \qquad (1)$$

$$\xi=\left[\frac{-d\log T_s}{d\log W}\right] \qquad (2)$$

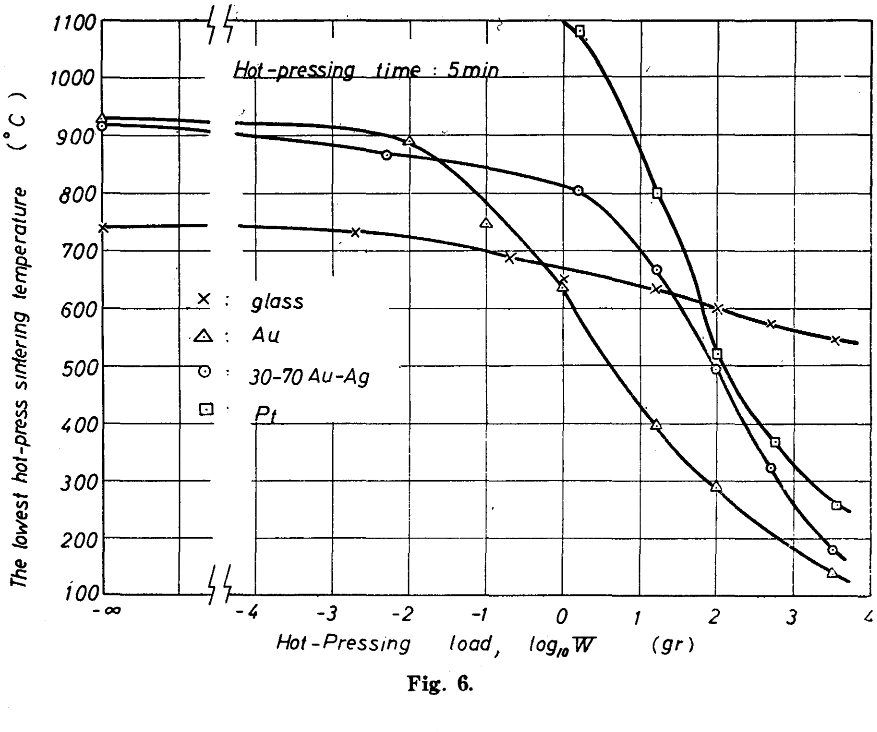


Fig. 6.

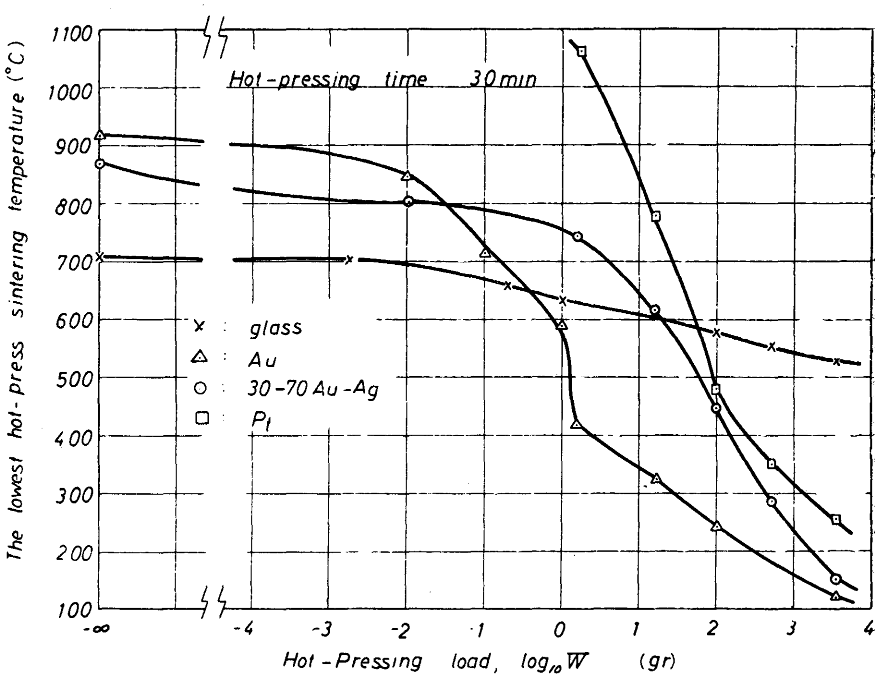

Hot-pressing time 30 min
The lowest hot-press sintering temperature (°C)
1100
1000
900
800
700
600
500
400
300
200
100
-∞
-4
-3
-2
-1
0
1
2
3
4
Hot-Pressing load, $\log_{10}W$ (gr)
× : glass
△ : Au
○ : 30-70 Au-Ag
□ : Pt

Fig. 7.

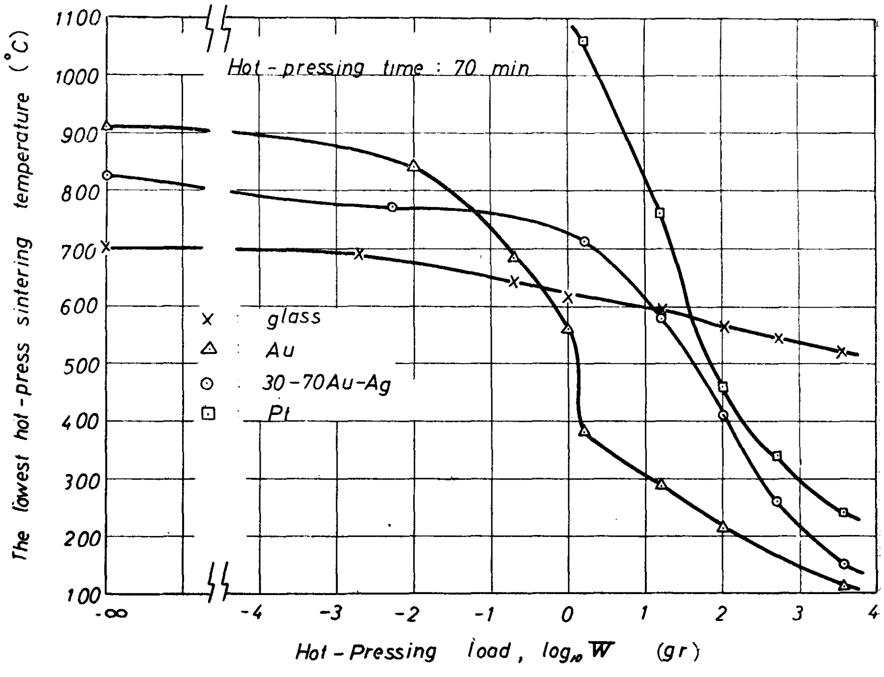

Hot-pressing time : 70 min
The lowest hot-press sintering temperature (°C)
1100
1000
900
800
700
600
500
400
300
200
100
-∞
-4
-3
-2
-1
0
1
2
3
4
Hot-Pressing load, $\log_{10}W$ (gr)
× : glass
△ : Au
○ : 30-70Au-Ag
□ : Pt

Fig. 8.

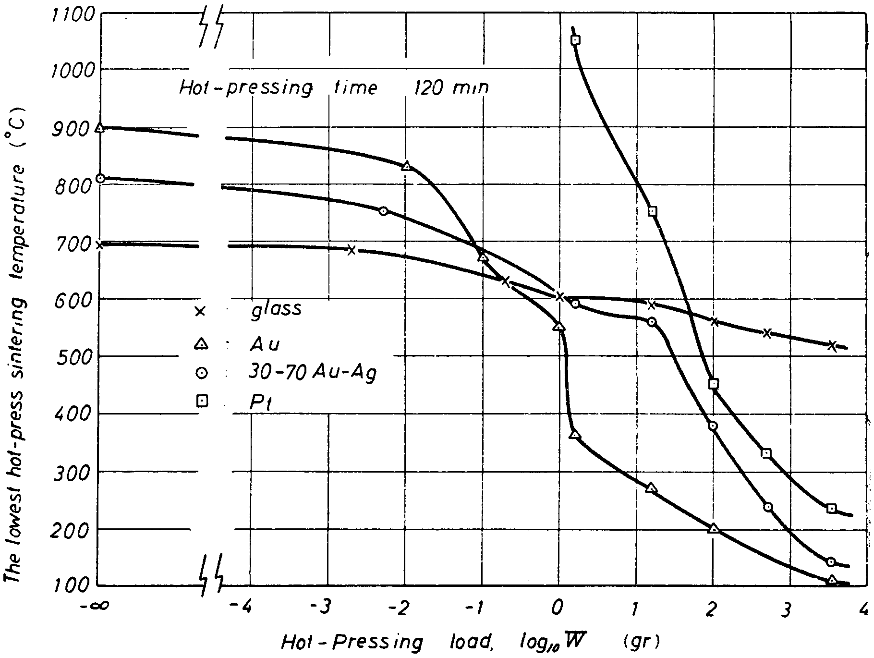


Fig. 9.

Figs. 6, 7, 8, 9. The relationship between T_s and $\log_{10} W$. The sintering time is different in each figure.

and its value is shown in Table I. That the value of ξ is larger shows the effect of load to lower the sintering temperature is larger.

The values of ξ with metals take almost equal value at same range of load, and are larger than that with glass. The value of ξ has the maximum within the range of the recrystallization temperature or a little higher in each metal, or within the range of softening temperature with glass. It is interesting that the effect of load to lower the lowest sintering temperature is largest at the recrystallization temperature or at the softening temperature.

The experimental formula between T_s (°K) and W (gr) for metals are as follows:

with Au

$$\log_{10} T_s = T_0(t) - \xi \log_{10} W \tag{3}$$

$$T_0(t) = 2.96 \sim 2.92 \quad \text{at } W = 0.01 \sim 1 \text{ gr}$$

$$T_0(t) = 2.91 \sim 2.81 \quad \text{at } W = 1.5 \sim 3500 \text{ gr}$$

(where the sign $\sim$ shows the variable range by the change of sintering time t),

with 30-70 Au-Ag alloy

$$\log\left(\frac{1000}{T_s} - \frac{1000}{T_{s0}}\right) = A + B \log_{10} W \tag{4}$$

$$\frac{1000}{T_{s0}} = 0.792+6.15\times10^{-2}\log_{10} t$$

$$A = -1.06+8.78\times10^{-4}\,t$$

$$B = 0.35$$

(where t (min) is the sintering time).

with Pt

$$\frac{1000}{T_s} = 0.628+0.353\log_{10} W \tag{5}$$

(at the sintering time $t = 30$ min: The values of the constants change a little with the sintering time).

These formulas and (8), which is shown in next section, may be classified in two typical types as;

Table I.

$\xi\times100$, $\xi = \left[\frac{-d\log T_s}{d\log W}\right]_{r,t=\text{const}}$ ($2r = 0.85$ mm)

Materials	Range of lord (gr)	Hot-pressing time			
		5 (min)	30(min)	70(min)	120(min)
Glass	0.002~0.2	2.2	2.0	2.1	2.3
	0.2 ~ 1.0	0.83	0.85	0.86	0.90
	1.0 ~ 15	0.80	0.82	0.84	0.64
	15 ~ 100	2.1	2.1	1.9	1.8
	100 ~ 500	1.8	1.5	1.5	1.4
	500 ~ 3500	1.8	1.6	1.6	1.6
Au	0.01 ~ 0.1	5.2	5.5	6.5	6.4
	0.1 ~ 1.0	5.3	5.9	5.8	6.2
	1.0 ~ 1.5	44	54	60	63
	1.5 ~ 15	5.5	6.1	6.7	6.9
	15 ~ 100	9.3	8.0	7.6	7.3
	100 ~ 3500	8.7	7.4	6.5	6.2
30-70 Au-Ag alloy	0.005~1.5	0.95	1.0	0.95	1.1
	1.5 ~ 15	5.8	5.9	6.4	6.3
	15 ~ 100	11	11	11	13
	100 ~ 500	16	16	15	15
	500 ~ 3500	14	14	12	11
Pt	1.5 ~ 15	10	10	11	11
	15 ~ 100	15	18	18	18
	100 ~ 500	13	12	11	11
	500 ~ 3500	9.6	8.5	9.2	9.2

with Au and 30-70 Au-Ag

$$\log\frac{1}{T_s} \propto \log_{10} W + \text{const} \tag{6}$$

with Pt and glass

$$\frac{1}{T_s} \propto \log_{10} W + \text{const} \tag{7}$$

B. Diameter of "*neck*"

Sintering may occur by material filling in between the spheres or by the centers of the spheres approaching. Then the "*neck*", the interface between adhered spheres, grows to a diameter d_n at T_s.

If the temperature is higher than the T_s, it becomes larger than d_n.

The diameter of "*neck*" is shown in Fig. 10.

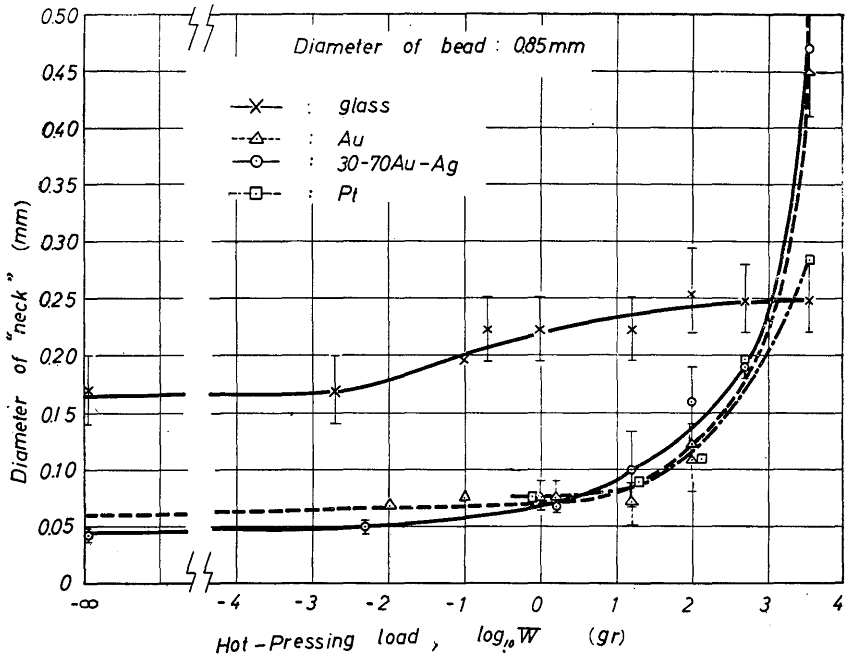


Fig. 10. The diameter of "*neck*" between adhered spheres, which are sintered at *the lowest sintering temperature* at each load. The values change with the sintering time, so the mean values and its maximum and minimum are shown.

The diameter of "*neck*" takes almost equal value at a few grams in load or below in each metal, and its value is about 7×10^{-2} mm, and this value is 8% of bead diameter. But in glass, its value is about 2×10^{-1} mm and 23% of bead diameter. At small load, the lowest sintering temperature of glass is higher than the softening temperature, so the glass flows viscously (as shown in Photo IV (2)) and the "*neck*" diameter becomes larger than metals'. However, the T_s of each metal is far lower than each melting point, so the "*neck*" diameter does not become large as that of glass.

Above a few grams in load, the "*neck*" of each metal becomes larger abruptly with load because of the plastic flow owing to the larger pressure of load in spite of lower T_s, In glass, the "*neck*" becomes larger gradually with load, but it ceases at certain load because of the poor malleability of glass at low temperature and its value is smaller than the metals.

The ultimate bending or shear strength of "*neck*" τ_{mb} is measured by the apparatus shown in Fig. 11 using many beads sintered at various conditions.

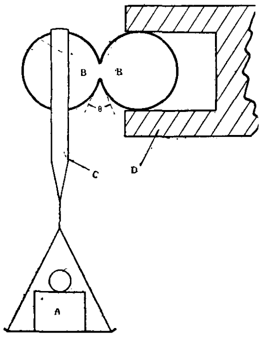


Fig. 11. The schematic diagram of the apparatus to measure the ultimate bending or shear strength of "*neck*",
A : weights,
B : beads sintered at T_s,
C : belt to suspend the weights,
D : rigid yoke,
θ : notch angle.

The τ_{mb} of the "*neck*" is very much smaller than the ultimate shear strength of its own material τ_{mm} and the ratio τ_{mm}/τ_{mb} is 4~6 as shown in Table II. It is supposed that this is because of the so called "*notch effect*", so we examined it with Neuber's theroy for three dimensional deep notch.[9] That is, the values of stress

Table II.

Materials	Au	30-70 Au-Ag	Pt	Glass
τ_{mb} (10^8 dyne/cm^2)	1.9±0.6	2±1	3±0.6	0.5±0.2
τ_{mm} (10^8 dyne/cm^2)	10 [8]	9 *	17 [8]	2.3 *
τ_{mm}/τ_{mb} ≈	5.3	4.5	5.6	4.6
α_{kb}	5.6	5.4	5.9	4.4
α_{ks}	4.5	4.3	4.8	3.5

τ_{mb} : the ultimate bending or shear strength of "*neck*".
τ_{mm} : the ultimate shear strength of material ≈ ½ (the ultimate tensile strength).[8]
α_{kb}, α_{ks} : the stress concentration factors of circlar shaft with deep V-notch in bending and shear.[9]
* : measured value by authors.

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8) Astronomical Observatory in Tokyo, "Physical Annual Table", Maruzen, Tokyo, p. Phys-21 (1959)

9) H. Neuber, "Kerbspannugslehre", Springer, Berlin, p. 83, p. 87 (1937).

concentration factors of circular shaft with deep V-notch in bending and shear, the shape of which is simillar to that of the sintered beads in Fig. 11, were calculated in accordance with Neuber's method and shown in Table II also. In this calculation, however, we used the values 0.25 and 0.4 for Poisson's ratio of glass and other metals. Moreover we ignored the variety of the notch angle θ shown in Fig. 11, the value of which is in the range of 30° to 50°, but its effect on the calculation will be small.10) In Table II the results are summarized, and a comparison is made for all the values of the stress concentration factors α_{kb} and α_{ks} which are calculated theoretically and τ_{mm}/τ_{mb} which are measured experimentally. The theoretical values and experimental values are both of the same order of magnitude. This shows that the apparent strength of the "*neck*" of beads is reduced by the "*V-notch effect*" and moreover that the beads are cohered with each other with the strength equal to the material's natural strength.

The *normal sintering* mechanism for glass is determined as *viscous flow phenomena*,11)12) but at hot-press sintering its mechanism is not yet determined. The adhered area $A \approx d_n x^2/4$ becomes larger with load, time and temperature. The viscosity of glass becomes smaller with temperature, so A must be the function of Wt/η by dimensional analysis and we can write:

$$\frac{A}{t} = C_1 \frac{W}{\eta} \tag{8}$$

where

t = sintering time (sec)

W = gravitational force of load (gr·cm/sec^2)

η = coefficient of viscosity (gr/(cm·sec))

C_1 = proportionality coefficient $=4\times10^{-2}$

The coefficient of viscosity of this glass is measured by Lillie's method (to measure the rate of elongation of glass fiber heated at high temperature under various loads) using glass fiber of the same kind as the glass beads, and its value is shown in Fig. 12.

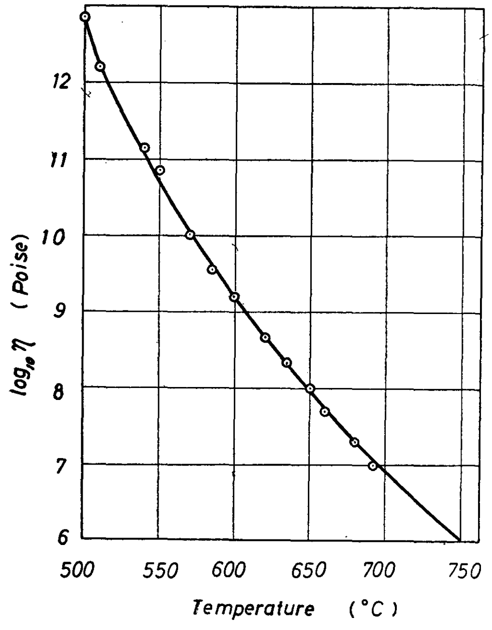

Fig. 12. The coefficient of viscosity of soda glass at various temperature.

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10) R. E. Peterson, "Stress Concentration Design Factors", John Wiley & Sons, New York, p. 45 (1953)

11) G. C. Kuczynski, J. Appl. Phys. **20**, 1160 (1949)

12) W. D. Kingery and M. Berg, J. Appl. Phys. **26**, 1205 (1955)

When the load is larger than about 1gr, the formula (8) is verified in agreement with the measured value of the experimental result. But when the load is smaller than about 1gr, Frenkel's term[11)13)] must be added to it, that is:

$$\frac{A}{t} = C_1 \frac{W}{\eta} + C_2 \frac{3\pi\sigma r}{2\eta} \tag{9}$$

where

σ = surface energy (erg/cm^2)
r = radius of bead (cm)
C_2 = proportionality coefficient = 1×10^{-2}.

The coefficient C_2 is decided from the data in the case of $W=0$ (taking $\sigma = 300$ erg/cm^2), and C_1 is decided from the inclination of line in Fig. 13. From this figure, we see that the formula (9) is in agreement with the experimental result. This shows that the mechanism of hot-press sintering of glass is also the *viscous flow process*.

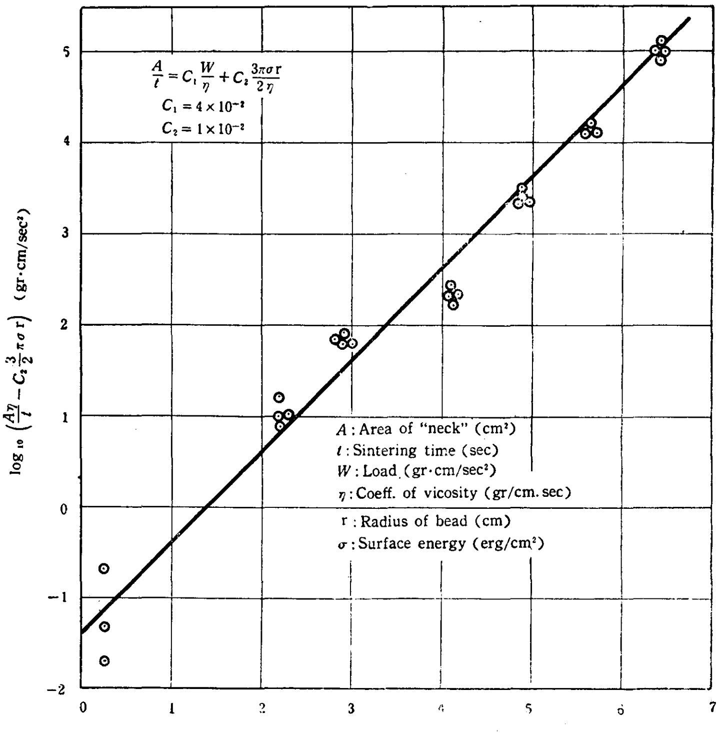

Fig. 13. The dots is the experimental data, and the line represents the formula (9). The coefficient C_1 is determined by this inclination of line.

The coefficient of viscosity calculated from Frenkel's equation ($\eta = 3\pi\sigma rt/2A$) and from the formula (9) ($\eta = 10^{-2} \cdot 3\pi\sigma rt/2A$) at 710°C which is the T_s at no load for 30 min

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13) J. Frenkel, J. Phys. (U. S. S. R.) **9** (5), 385 (1945)

are 4.6×10^8 and 4.6×10^6 respectively, and the measured value is 5.0×10^6. In this case, the equation (9) is in better agreement with the measured value than Frenkel's formula.

C. Activation Energy for Hot-Press Sintering

Many theories on "*normal sintering*" have been proposed, but we now propose in first rough approximation, that "*hot-press sintering*" is a first order reaction. The theory of the first order reaction is often used to elucidate the recrystallization phenomena.14)15)16)17)

The beads are hot-pressed under constant load W and constant temperature T_s. After an incubation period, "*seeds of sintering*" start to grow from a number sites which are in the contacted points in the area of "*neck*", the number of sites increases with time, and the seeds grow to "*islands*", then "*islands*" grow until they impinge each neighboring ones.

Let the diameter of the impinged "*island*" be unity and x the fraction sintered in time t sec. It is assumed that the rate of sintering is proportional to the fraction $(1-x)$ that had not yet sintered. That is,

$$dx/dt=k(1-x) \tag{10}$$

where k is the linear rate of growth of "*seed and island*".

Integrating this formula with the condition $x=0$ at $t=0$, one obtains

$$\log(1-x)=-kt \tag{11}$$

or

$$x=1-\exp(-kt) \tag{12}$$

Let the diameter of an impinged ith island be δ_i, and the diameter of the total "*true sintered*" area d_t in the area of "*neck*" at time t, in general d_t is equal with or less than the diameter of "*neck*" d_n, then

$$d_t=\sum_i x_i\delta_i=\sum_i[1-\exp(-k_it)]\delta_i \tag{13}$$

where x_i is the fraction sintered in the i th island. and k_i is its linear rate of growth.

$$d_t=\sum_i\delta_i-\sum_i\delta_i\exp(-k_it) \tag{14}$$

If k_i is substitued with its mean value k_m, and the apparent (or measured) diameter of "*neck*" d_n is substitued with $\sum_i\delta_i$, one obtains

$$d_t=d_n[1-\exp(-k_mt)] \tag{15}$$

$$\log(1-d_t/d_n)=-k_mt \tag{16}$$

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14) M. Balicki, ibid. W. E. Kingston, editor, p. 58 (1951).

15) I. I. Betcherman, "Progress in Metal Physics", Vol. 2, B. Chalmers, editor, Pergamon Press, London, p. 83 (1950).

16) A. Krupkwski, ibid. B. Chalmers, editor, Vol. 3, p. 227 (1952).

17) A. Krupkwski & M. Balicki, Ann. Akad. Tech. Varsovie, 4, 270 (1937).

$$1/t = k_m[-\log(1-d_t/d_n)]^{-1} \tag{17}$$

Arrhenius' theory of rate processes postulates the following relationship, that is

$$k = k_0 \exp(-E/RT) \tag{18}$$

where k_0 is the constant or the function of T; E is the energy of activation; and R is the gas constant. In this experiment, however, E is the activation energy to effect hot-press sintering, T is the T_s, and k_0 is the function of load and temperature. By substituting k in (18) for k_m into the formula (17), one obtains

$$1/t = k_0 \exp(-E/RT_s)[-\log(1-d_t/d_n)]^{-1} \tag{19}$$

$$1/t = a(W, T_s)\exp(-E/RT_s)$$

where

$$a(W, T_s) = k_0(W, T_s)/-\log(1-d_t/d_n) \tag{20}$$

or

$$\log_{10} 1/t = \log_{10} a - 0.4343E/RT_s \tag{21}$$

The relation between the logarithm of the reciprocal of the hot-pressing time and the reciprocal of the absolute lowest sintering temperature is represented by a straight line in Figs. 14, 15, 16 and 17 the slope of which is proportional to the energy of activation and its value is calculated from the formula (19), and also $a(W, T_s)$ is calculated.

The activation energy for hot-press sintering changes with the temperature, which is shown in Figs. 18, 19, 20 and 21.

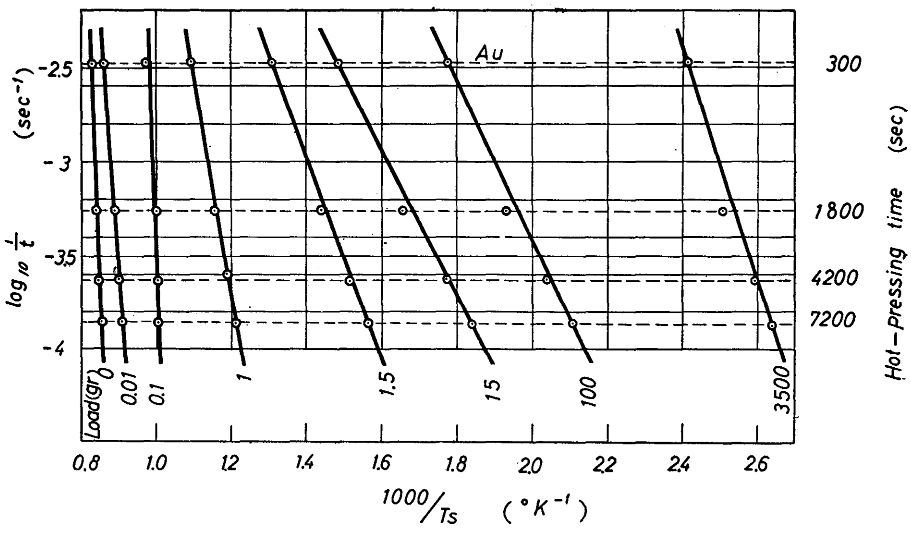


Fig. 14.

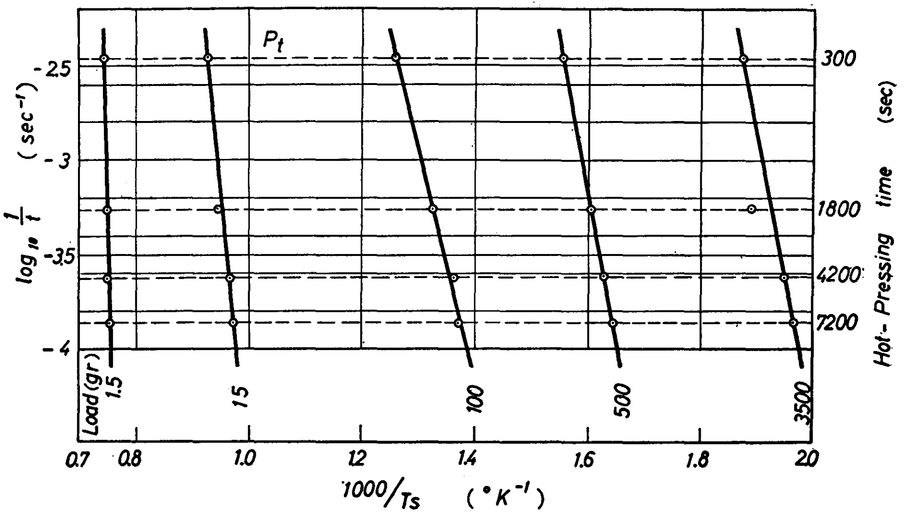

Pt
-2.5
-3
-3.5
-4
log₁₀ 1/t (sec⁻¹)
300
1800
4200
7200
Hot-Pressing time (sec)
Load(gr)
1.5
15
100
500
3500
0.7
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/Ts (°K⁻¹)

Fig. 15.

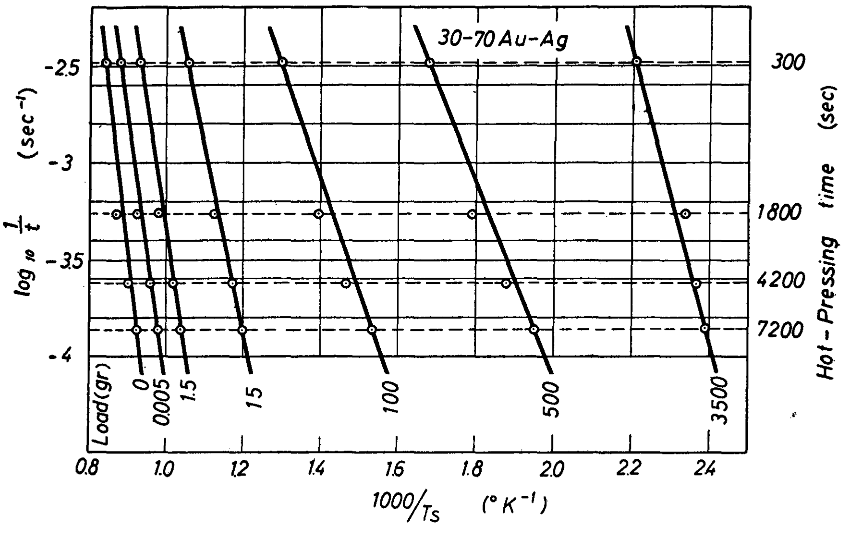

30-70Au-Ag
-2.5
-3
-3.5
-4
log₁₀ 1/t (sec⁻¹)
300
1800
4200
7200
Hot-Pressing time (sec)
Load(gr)
0
0.005
1.5
15
100
500
3500
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
1000/Ts (°K⁻¹)

Fig. 16.

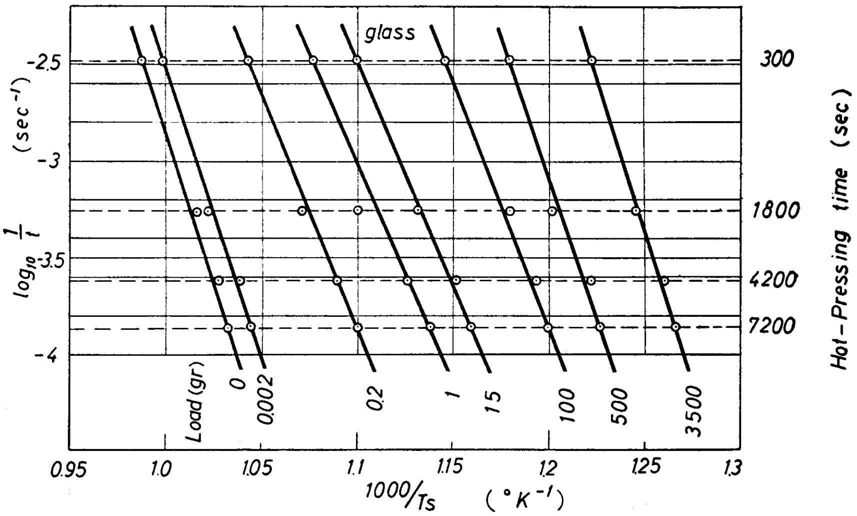


Fig. 17.

Figs. 14, 15, 16, 17. Relation between $\log_{10} t$ and $10^3/T_s$, where t is the sintering time and T_s the lowest sintering temperature.

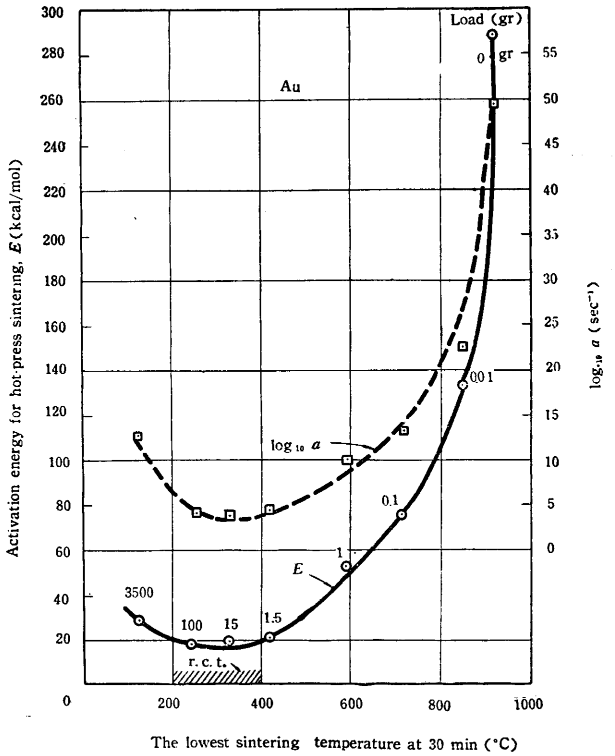


Fig. 18.

Fig. 19.

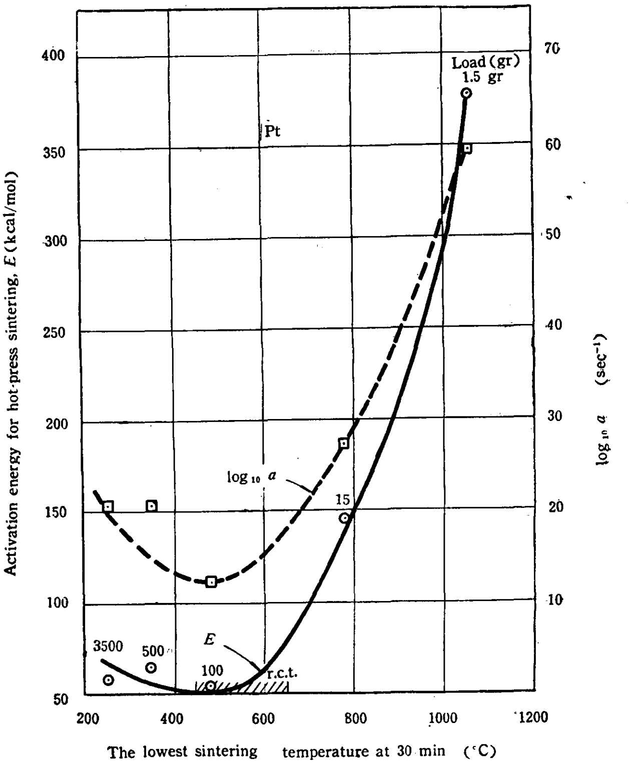
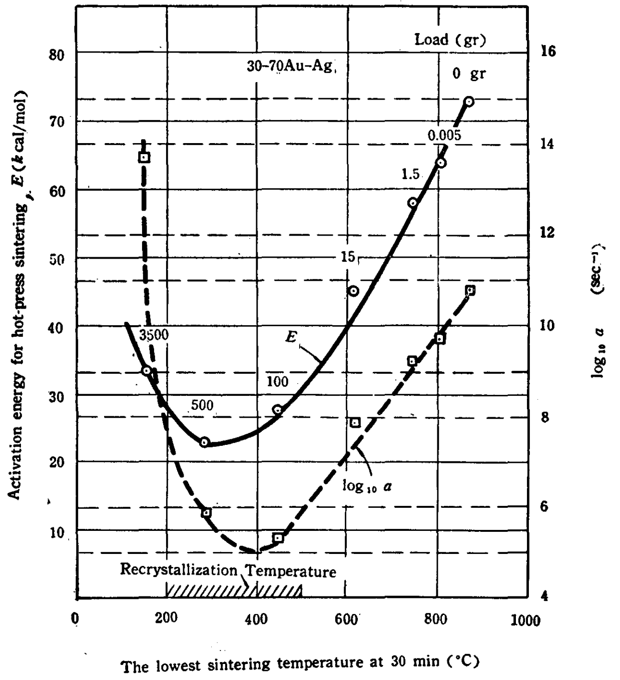

Activation energy for hot-press sintering, E (kcal/mol)
400
350
300
250
200
150
100
50
70
60
50
40
30
20
10
log₁₀ a (sec⁻¹)
Pt
Load (gr)
1.5 gr
15
log₁₀ a
E
3500
500
100
r.c.t.
200
400
600
800
1000
1200
The lowest sintering temperature at 30 min (°C)

Fig. 20.


Activation energy for hot-press sintering, E (k cal/mol)
80
70
60
50
40
30
20
10
16
14
12
10
8
6
4
log₁₀ a (sec⁻¹)
30-70Au-Ag
Load (gr)
0 gr
0.005
1.5
15
E
3500
500
100
log₁₀ a
Recrystallization Temperature
0
200
400
600
800
1000
The lowest sintering temperature at 30 min (°C)

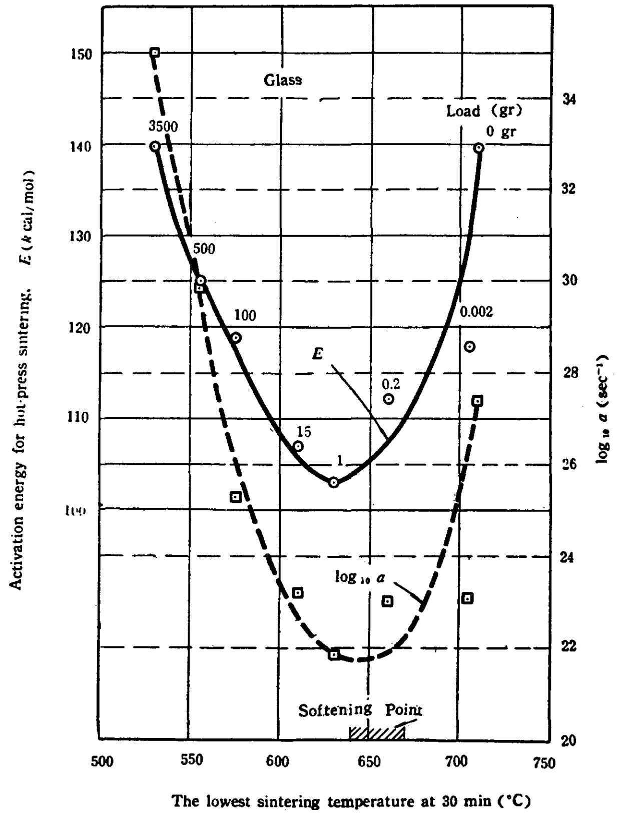


Fig. 21.

Figs. 18, 19, 20, 21. Relation belween activation ehergy or $\log_{10} a(W, T_s)$ and temperature.

In these figures the lowest sintering temperature for 30 min is taken as the abscissa, because its temperature is about the mean value between 5 and 120 min sintering time.

The activation energy becomes smaller with the temperature and has a minimum value within the range of recrystallization temperature of each metal or softening point of glass and then it becomes larger. This is very interesting. In general, activation energy for viscosity or electrical resistance of glass becomes larger with the temperature and has a maximum value within the range of softening temperature and then it becomes smaller. It is shown in Fig. 22.⁽¹⁸⁾

The activation energy for hot-press sintering is compared with that of diffusion and heat of fusion in Table III.

From this Table we learn that the value of activation energy for hot-press sintering is much larger compared with self-diffusion or heat of fusion, and moreover

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18) I. Sawai; "Chemistry and Engineering of Glass", Tokyo, Shu-Kyoosha, p. 345 (1949).

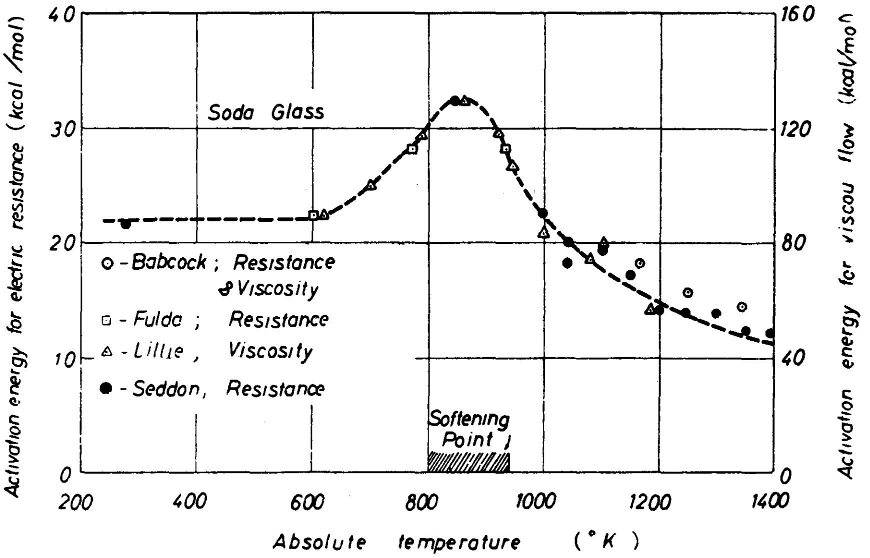

Fig. 22. The activation energy for viscosity or electrical resistance of $Na_2O-CaO-SiO_2$ glass (after Sawai).

Table III.

Materials	Activation energy of diffusion (kcal/mol)	(Act. energy of hot-press) / (Act. energy of self-diffusion)	(Act. energy of hot-press) / (Heat of fusion)
Au	53.0 19)	1/3 ~ 6	6 ~ 100
30-70 Au-Ag alloy	Au 44.1 19) Ag 44.7 (in 50-50 Au-Ag alloy)	1/2 ~ 6.5	7 ~ 25
Pt			10 ~ 80
Glass	Na_2O 20 20) CaO 78 SiO_2 65 (in soda glass)	5 ~ 7 1.5~1.8 2 ~ 2.2	

it changes in wide range. The relation between the activation energy or $\log_{10} a$ (W, T_s) and load are shown in Figs. 23 and 24.

The energy of activtion for hot-press sintering E is assumed to involve any energies such as the activation energy of the recovery process E_R; that of plastic or viscous flow E_F; that of the nucleation E_N; and that of grain growth E_G. The E_R or

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19) G. J. Dienes; J. Appl. Phys. **21**, 1189, (1950).

20) R. Kamel; J. Appl. Phys. **24**, 1308 (1953).

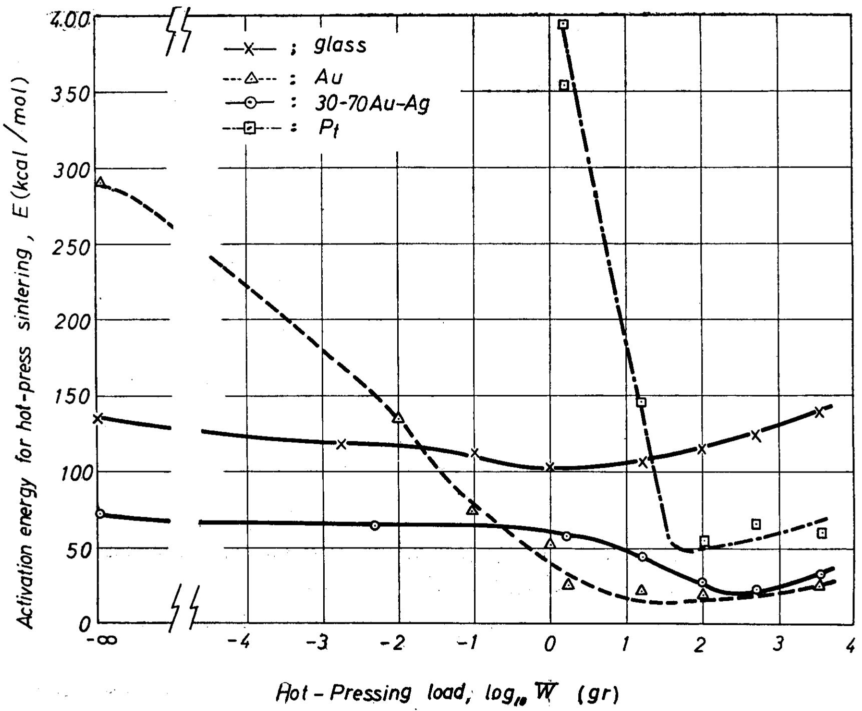

Fig. 23. Relation between the activation energy and load.

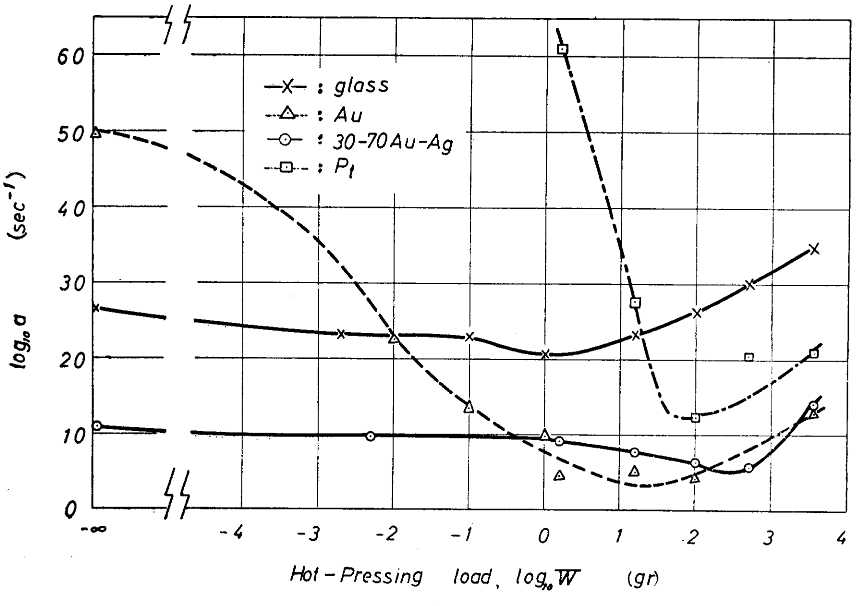

Fig. 24. Relation between $\log_{10} a$ (W, T_s) and load.

E_F has magnitude in the order of $(U_F - 4W\lambda^3/\pi d_t^2)$[21] or much larger, where λ is the interatomic spacing and U_F is a constant. Some of them are not necessary and some of them are combined into one energy under each condition.

At high temperature and small load, qualitativelly speaking, E_F, E_N and E_G[22] are large because of the small applied force in spite of high temperature and E becomes larger, but at medium temperature and medium load E_F, E_N and E_G[22] are small because of the medium appplied force and E becomes smaller. However at below recrystallization temperature and large load, the migration of atom is not easy compared with at the recrystallization temperature and medium load. And then E becomes larger, so the activation energy has minimum point in the range of the recrystallization temperature.

The example of activation energy like this is obtained in the experiment of grain growth of rock salt[22] in which the activation energy for grain growth at high temperature and small stress is larger and at low temperature and large stress it is smaller as shown in Table IV.*

The constant $a(W, T_s)$ is also plotted in the figures of activation energy. It has minimum value within the range of recrystallization temperature too. If the sintering time is constant, one obtains

$$\log_{10} a \propto E/RT_s \tag{22}$$

moreover from Fig. 18 etc., one obtains

$$\left|\frac{\partial E}{\partial (RT_s)}\right| \gg 1 \tag{23}$$

so the curve of $\log_{10} a$ resembles closely with the curve of activation energy.

D. Effect of Particle Size on The Lowest Sintering Temperature.

The effects of varying the particle size on the lowest sintering temperature are important in practice in powder metallurgy. In this experiment beads of equal sizes are hot-press sintered in a suitable die inside diameter of which is as large as the diameter of the bead tested. The sizes of beads are 1.35, 0.85, and 0.45mm in

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[21] A. H. Cottrell, "Dislocations and Plastic Flow in Crystals", Oxford, Clarendon Press, p. 187, p. 198 (1963).

[22] J. E. Burke & D. Turnbull, ibid, B. Chalmers. editor, Vol. 3, p. 249 (1952).

***Table IV.**

The activation energy for grain growth of rock salt.[22]

Stress (kg/mm²)	Temp. range (°C)	E_G (kcal/gm atom)
1	770 - 650	59.0
4	520 - 400	32.0
4	400 - 320	14.5

diameter in each metal, but in glass 1.30 mm is used instead of 1.35 mm. The lowest hot-press sintering temperatures for various diameters of gold beads are shown in Fig. 25 for example.

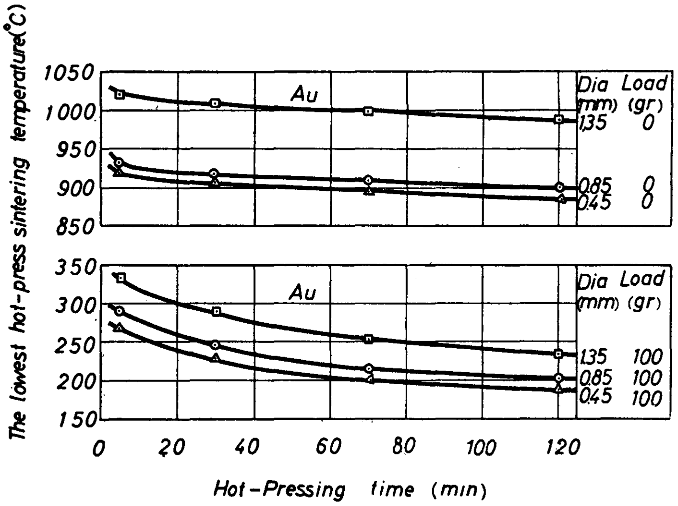


Fig. 25. Relation between *the lowest sintering temperature*, load, time and the diameter of bead. In the upper region of each curve, the beads are sintered.

The data summarized for metals and glass are shown in Figs. 26, 27, 28 and 29. The diameter of the "*neck*", average pressure (=load/area of "*neck*"), the ratio of "*neck*" diameter to that of bead and the ratio of "*neck*" area to the cross sectional area of bead etc. are shown in Table V.

The ratio of the "*neck*" to the diameter of the bead is found to take almost the same value in each metals and glass under conditions in Table V. Now can discuss the effect of particle size on the sintering temperature as follows.

The *lowest sintering temperature* becomes lower with the decrease in diameter of beads. However in most cases the difference of temperature between 0.45 mm and 0.85 mm is very small, but in Au-Ag alloy the same is not true.

Activation enery and $\log_{10} a$ take almost the same value in all particle sizes under the condition in Table V as shown, but in Platinum the same is not true.

VII. Conclusion

Small spherical beads of a few precious metals and glass are hot-press sintered. The *lowest temperature* for the beginning of hot-press sintering are determined by the "*drop method*", by which method the ultimate shear or bending strength of the "*neck*" is kept constant in each material under various sintering conditions.

The larger the load, the longer the sintering time or the smaller the particle size, the lower the *lowest sintering temperature* becomes. At large load and long time

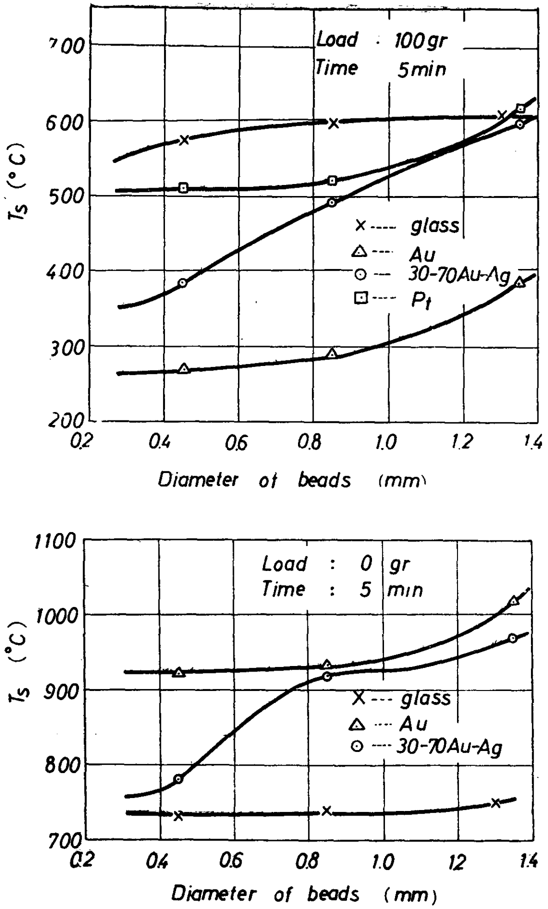

Load · 100gr
Time 5min
x---- glass
△--- Au
⊙ — 30-70Au-Ag
⊡---- Pt
T_s (°C)
700
600
500
400
300
200
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Diameter of beads (mm)
Load : 0 gr
Time : 5 min
X--- glass
△ --- Au
⊙ --- 30-70Au-Ag
T_s (°C)
1100
1000
900
800
700
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Diameter of beads (mm)

Fig. 26.

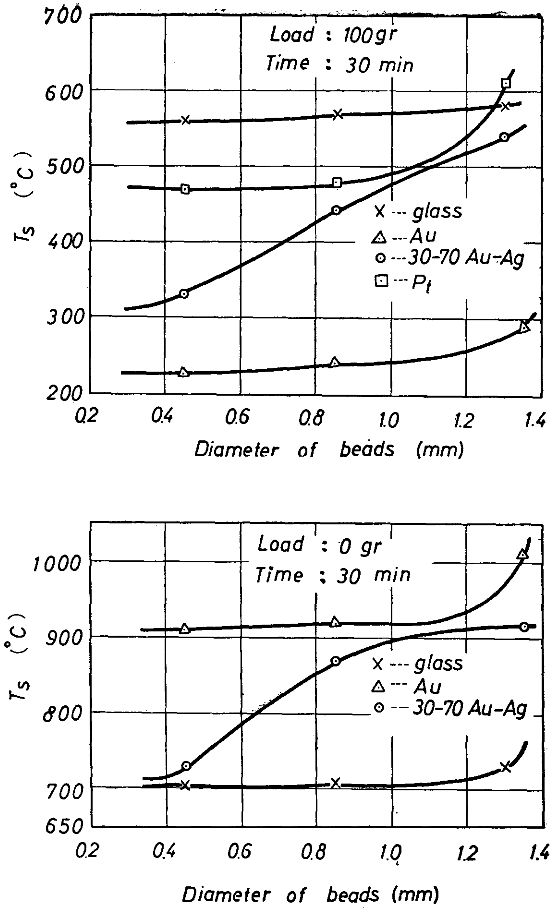
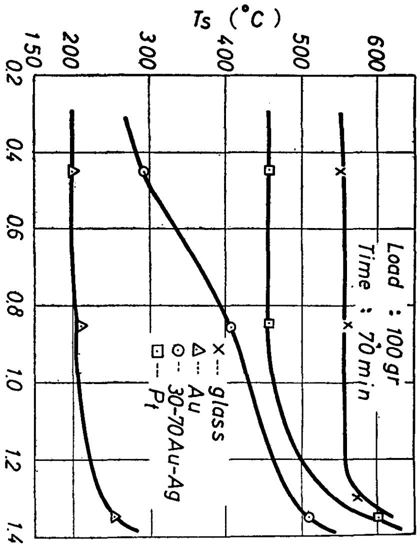
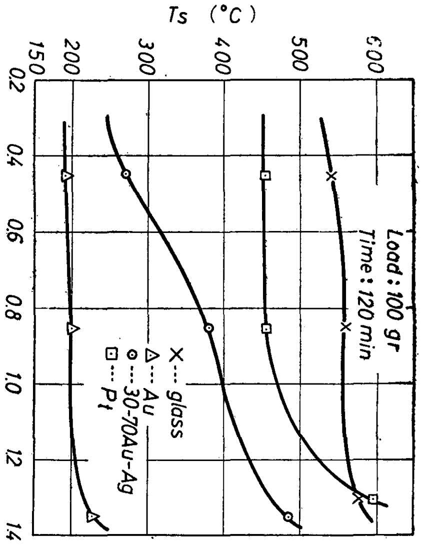

Load : 100gr
Time : 30 min
x --- glass
△ --- Au
⊙ ---30-70 Au-Ag
⊡ --- Pt
T_s (°C)
700
600
500
400
300
200
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Diameter of beads (mm)
Load : 0 gr
Time : 30 min
x --- glass
△ --- Au
⊙ --- 30-70 Au-Ag
T_s (°C)
1000
900
800
700
650
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Diameter of beads (mm)

Fig. 27.





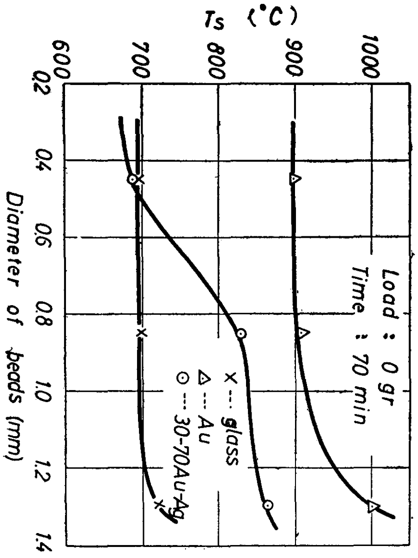


Fig. 28.

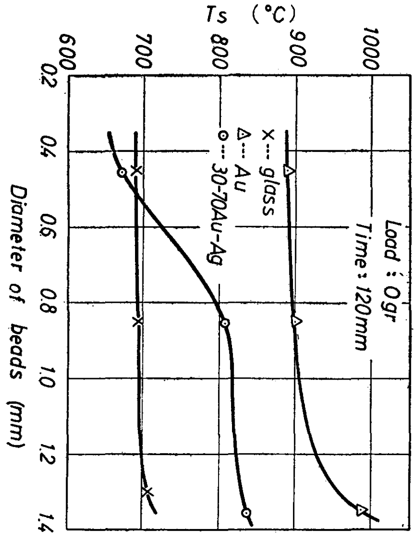


Fig. 29.

Figs. 26, 27, 28, 29. Relation between *the lowest sintering temperature* T_s and the diameters of beads for various metals and glass.

Table V.

Materials	Dia. of bead (mm)	Load (gr)	Dia. of neck (10^{-2} mm)	Area of neck (10^{-3} mm^2)	Average pressure ($\frac{kg}{mm^2}$)	$\left(\frac{\text{Dia.of neck}}{\text{Dia.of bead}}\right)$ (%)	$\left(\frac{\text{Area of neck}}{\text{Cross section of bead}}\right)$ (%)	Activation energy. E ($\frac{kcal}{mol}$)	$\text{Log}_{10}\, a$, $a = t \exp\cdot(E/RT_s)$ (sic^{-1})
Glass	1.30	0	27	57	0	21	4.3	160	32
	0.85	0	17	23	0	20	4.0	140	27
	0.45	0	9.0	6.5	0	20	4.1	160	33
	1.30	100	38	110	0.9	29	8.3	130	28
	0.85	100	25	49	2.0	29	8.6	120	25
	0.45	100	13	13	7.7	29	8.2	130	30
Au	1.35	0	9.7	7.4	0	7.2	0.52	290	45
	0.85	0	5.8	2.6	0	6.8	0.46	290	50
	0.45	0	3.3	0.85	0	7.3	0.53	290	51
	1.35	100	20	31	3.2	15	2.2	18	3.9
	0.85	100	12	11	9.1	14	1.9	19	4.6
	0.45	100	10	7.8	13	22	4.9	19	5.2
30-70 Au-Ag	1.35	0	7.1	4.0	0	5.3	0.28	63	8.5
	0.85	0	4.5	1.6	0	5.3	0.30	73	11
	0.45	0	2.6	0.53	0	5.8	0.33	56	9.1
	1.35	100	20	31	3.2	15	2.2	37	6.7
	0.85	100	16	20	5.0	19	3.5	28	5.3
	0.45	100	9.7	7.4	13	22	4.6	19	3.9
Pt	1.35	100	23	41	2.4	17	2.9	120	26
	0.85	100	11	10	10	13	1.7	54	12
	0.45	100	10	7.8	13	22	4.9	62	15

the beads are sintered at very low temperature.

The rate of lowering of the *lowest sintering temperature* with the increase of load $(-d \log T_s/d \log W)_{r,t=const}$ has a maximum value within the range of the recrystallization temperature of each metal or softening point of glass.

The ratio of the diameter of adhered area of a "*neck*" between two beads to that of the bead is found to take a constant value independent of the dimension of the bead for each metal or glass when the load is constant, but it becomes larger with the load.

It is shown that the *viscous flow* is the rate-determing mechanism in hot-press sintering of glass by our theoretical formula for its adhered area.

The activation energy of effect hot-press sintering and $\log_{10} a$ becomes smaller with tne temperature, but has a minimum value within the range of recrystallization temperature of each metal or softening point of glass and then it becomes larger. If the load is kept constant, in spite of varying of the particle size, the activation energy takes the same order of magnitude in each metal and glass respectivelly.

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