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ATOMIC ENERGY AUTHORITY
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ABSTRACT

Solid state sintering behavior of cylindrical compacts, (1 cm diameter and 1 cm height), made of copper powder was studied within a range of compacting pressure of 75 up to 300 MPa., sintering temperature of 600 up to 900 ^{o}C , and sintering time of 5 up to 60 min in a reducing atmosphere composed of H_2 and N_2 gases with a volumetric ratio 3 : 1.

The green and the sintered densities were found to increase with the compacting pressure. Higher sintering temperature, and time favour increased sintered density. Probable mechanisms during the initial stage of sintering were disclosed. It was found that low pressures cause dilation of closed pores, and vice versa. At low pressures and temperatures the surface diffusion mechanism is favoured, while high tempreatures favour lattice diffusion mechanism. At high pressures, the lattice diffusion mechanism is suppressed while surface diffusion predominates. Density and hence shrinkage were also found to increase with the increase of sintering time, while its rate increases with the increase of sintering temperature.

The influence of sintering conditions on the hardness of the compacts was studied. An increase in hardness, when higher compacting pressures and higher sintering temperatures were adopted, has been obtained.

As it has been concluded from the results of this research the sintering rate steadily decrases after a certain period of time depending on the sintering temperature and the compacting pressure, hence applying sintering for longer time to obtain improved properties is impractical.

1. INTRODUCTION

Solid masses may be made from powders to a very precise composition limits, and with low and uniform impurity levels. This is due to the availability of commercial powder raw materials. Incompatible materials, such as ceramic - metallic powders, can be intimately blended together and consolidated into a dense solid mass without macrosegregation.

Cold pressing is used for producing parts of relatively limited volumes . In this method the powder is contained in all directions by the die walls which has the shape of the required part to be produced. It is then pressed from one direction, (uniaxial pressing) , two directions, (biaxial pressing),or from all directions, (cold isostatic pressing), (1). Explosive powder compaction, for metallic powders, was also used to produce thin rectangular plates (2). The influence of pressing is raising the integral contact area per unit volume, thus producing an increase in the green density, introducing elastic and plastic deformation, cracking of surface layers and inclusions of air and other gases.

The actual sintering process is not influenced by the compacting stresses, as these are eliminated too rapidly at the early stages of sintering. For copper compacts, the residual stresses are responsible for the early shrinkage from 210 °C to not less than 500 °C (3). The actual densification takes place only above 650 °C, after the stresses have been largely eliminated (4). Experiments showed that the oxide layers are cracked, not by the compacting pressure itself, but by the relative movement of the faces against each other (4).

In the case of die compacted powders, shrinkage is usually found to be different in directions parallel and normal to the direction of pressing. This is a result of the density distribution in the compact and unequal distribution of the contact areas in various directions. The ratio between the radial and the longitudinal shrinkage is dependent on compacting pressure, sintering temperature, dimensions, and the method of supporting the specimen. However, this ratio can never be predicted nor fully explained. Nowadays, it is believed that all the factors influencing the sintering process are known and some researchers are concerned with determining the effect of each parameter separately, while others are concerned with controlling the sintering mechanisms throughout the entire process. The stages of sintering, the shrinkage accompanying each stage, the driving force for sintering in each stage, as well as the sintering mechanisms were studied and are very well known now (3-14).

Theoretical studies on models dealing with pressing (1), or sintering process were the subject of research in too many investigations (4,11,15-19). The model of two spherical particles by Frenkel and Coble (4,15), or a sphere set on a plane by Kuczynski (20), or two wires by Ichinose et al. (12), for dealing with neck growth mathematically taking one mechanism only into consideration is in use successfully now. All the equations state that the neck radius raised to some power, which depends on the mechanism in question is directly proportional to the sintering time. The neck radius in the case of sphere to sphere model can be replaced by the shrinkage since X^2,

(where X is the neck radius), is directly proportional to $\Delta L / L_o$, (the relative linear shrinkage).

Copper compacts prepared by pressing and sintering copper powder have many applications. Of these we may mention self lubricated bearings, slides, sintered porous elements, filters, friction linings, mechanical parts, current collector rings, on cranes, pump connecting rod slider, and lock components.

The sintering kinetics of copper containing channels was the subject of some recent studies (21,22). The effect of additions such as lithium stearate, zinc stearate and aluminum metal powder, to copper during the hot pressing of copper compacts on the sintering response and conductivity was investigated (23,24). The additions of lithium stearate or stearic acid and, graphite or Al_2O_3 to copper compacts were found to increase the conductivity of sintered compacts (25). The liquid phase sintering and kinetics were studied for Cu-Si and Cu-Ti alloys (26).

Sintering atmosphere is an extremely important factor in the sintering of metals. Inert or reducing gases in case of metals are must to protect the metal from oxidation. Reducing gases, such as hydrogen, mixed with inert gases, such as Argon or nitrogen, reduce the oxide layer on the surface of the green body if present and protect the compact from oxidation. The object of this study is to investigate the effect of compacting pressure on the green density of copper compacts using stearic acid as an addition. The effect of both temperature and time on the sintered density are also investigated.

2 . EXPERIMENTAL TECHNIQUES AND RAW MATERIALS

2.1. Starting Materials:

The copper powder was imported from Aldrich, U.S.A., with 99.7% purity, while the stearic acid was imported from Riedel - de Haan, Germany, with purity of 99.5%.

2.2. Determination of Density:

2.2.1. Apparent density of the powder:

The apparent density of the powder was measured by determining the volume of a certain weight of the powder by putting the powder in a graduated jar. Then the apparent density is calculated from the equation: $\rho_B = W/V$.
Where:

ρ_B : is the apparent density of the powder , **g cm^{-3}.**
W : is the weight of the powder in **g.**
V : is the bulk volume of the powder, **cm^3.**

2.2.2. Tap density of the powder:

It is measured by putting a powder sample in a graduated jar, and jolting the jar well until the height of the sample becomes constant.

The volume, (V_t) in **cm**, of the sample is now known and its weight, (**W**) in **g**, can be determined with a balance. The tap density, (ρ_t) in **g cm^{-3}**, is the ratio between the weight, (**W**), and the volume (V_t).

The tap density is widely used in industry for storage, packing or transport of commercial powders, and as a control test on mixing powders.

2.2.3. True density of the powder:

It was determined using a 50 cm^3 in volume glass pycnometer and Archimedes principle. Xylene with known density was used as the fluid. The clean dry glass bulb was weighed empty and after that full with xylene, from which the weight of xylene is calculated. After that, a weighed amount of the copper powder was introduced into the pycnometer. Then the pycnometer was introduced into a desiccator and the latter was evacuated using a water pump to drive off any adsorbed gases. The evacuation was stopped after driving off all these gases and the pycnometer was taken off and weighed . The following procedure was followed in calculating the powder true density:

W_1 = weight of empty bottle.
W_2 = weight of bottle and xylene.
W_3 = weight of powder introduced into the bottle containing xylene.
W_4 = weight of bottle containing powder and xylene.
W_5 = the weight of liquid left in the bottle.
$= W_4 - W_1 - W_3$.
V_l = the volume of the liquid.
$= W_5 / \rho_{xylene}$.
Vp = the volume of the powder.
$= V_b - V_l$.
Where V_b is the volume of the glass bulb $= (W_2-W_1) / \rho_{xylene}$.
The powder true density $(\rho_p) = W_3 / Vp$.

2.2.4. <u>Green Density</u>:

A travelling microscope, (small tool microscope type MM- 2), with accuracy $\pm$ 5 μm was used for measuring the dimensions of green pellets and hence the volume in cubic centimeters. The green density (ρ_g), in **g cm^{-3}**, is the product of division of the mass of the green body in **g** by its volume in **cm^3**.

2.2.5. Sintered Density :

The mercury hydrometer was used to determine the density of sintered bodies (ρ_s). The following equation was used in calculations:

$$\rho_s = W_1 \times \rho_{Hg} / (W_1+W_2).$$

Where :

W_1 = weight of the specimen in air.

W_2 = excess weight added to get the dipper to its original position, and

ρ_{Hg} = density of mercury.

2.3. Particle Size Analysis:

The average particle size was measured using Fisher Subsieve and Sizer model 95 (7, 27). The sieving analysis was adopted to determine the particle size distribution.

2.4. Equipment and Procedure for Sintering:

The whole set - up used for sintering is shown in Fig. (1). The main part of this equipment is the horizontal tubular furnace which is heated electrically at a heating rate of 10°C min^{-1} and the temperature is controlled by a temperature controller. The pressed pellets are put in an alumina boat inside a silica tube which is closed from both sides. From one side the thermocouple is inserted while the sintering gases pass in through the other side. These gases are nitrogen and hydrogen in the ratio 1 : 3 to provide the reducing atmosphere, which is used to prevent the oxidation that might take place during the sintering procedure of compacts if any air was present. The hydrogen to nitrogen ratio is adjusted by the pressure regulators on the gas cylinders, 8, and controlled by flowmeters, 9, Fig . (1). The furnace is evacuated and refilled by the gas mixture three times after which heating begins, while the flow of the gas continues, up to 300 °C to remove the stearic acid which was used as a binder, in the form of vapour which condenses in the cold parts of the furnace and removed after the furnace is cooled. The temperature is then raised up to the sintering temperature. The samples are kept at the sintering temperature from 5 to 60 minutes. After sintering the furnace is turned off, while keeping the gas flow, until the furnace is cooled to room temperature the gas flow is stopped and the sintered samples are taken out of the furnace for further investigations and measurements.

3 . EXPERIMENTAL RESULTS AND DISCUSSION

3 .1 . Cold Pressing:

The particle size analysis for the copper powder showed that the average particle size is 94.8 μm as has been calculated from the results of sieve analysis. The average particle size from the sieving analysis corresponds to the weight mean diameter. The average particle size as obtained from Fisher Subsieve and Sizer was 32.8 μm, this value corresponds to the hydraullic mean diameter. No correlation can be interpreted

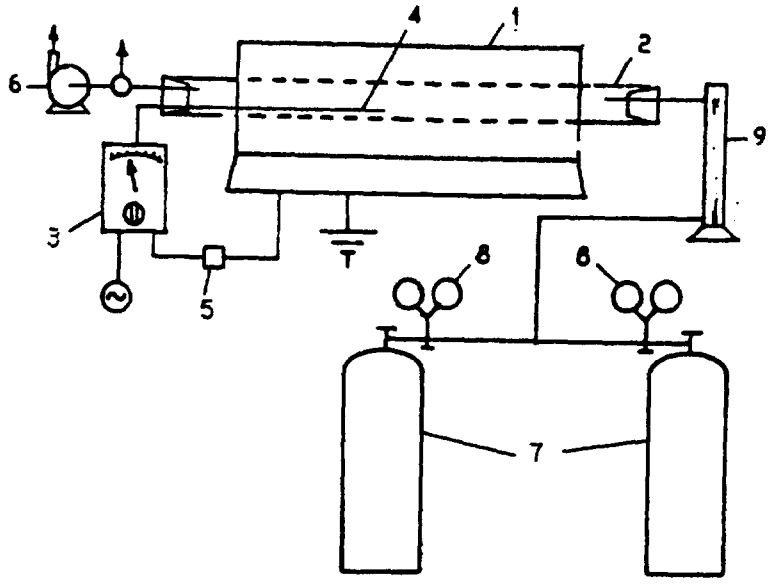

Fig . (1) A schematic drawing of the set - up used for sintering , together with its attachments .

1 . electric furnace , 2 . silica tube , 3 . temperature controller & regulator 4 . thermocouple , 5 . fuse , 6 . vacuum pump , 7 . gas cylinders , 8 . pressure regulators , 9 . gas flow meter .

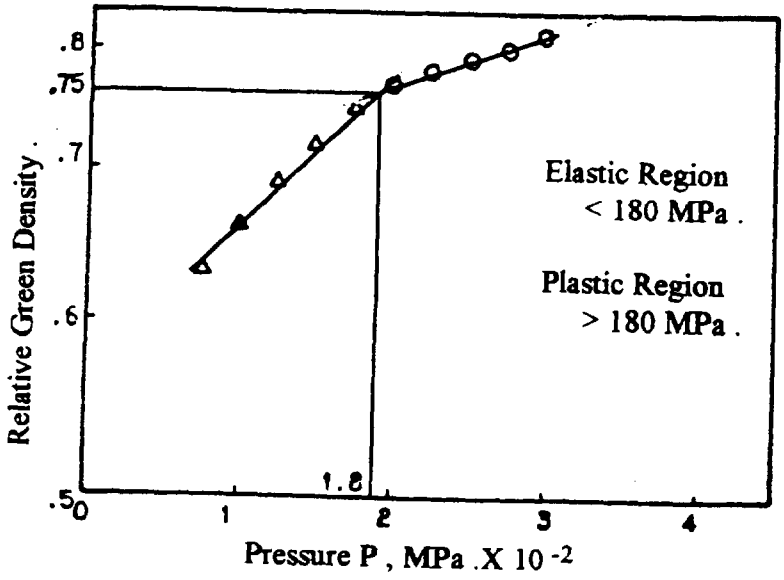

Fig . (2) Relation between compacting pressure and green density

between the two previously mentioned results since the hydraullic mean diameter corresponds to a single point analysis. The apparent density of the powder is 2.53 g cm^{-3}, the tap density is 2.84 g cm^{-3} and the true density is 8.75 g cm^{-3} as measured by the techniques described previously in the experimental. The copper powder with the previous specifications, after being mixed with stearic acid 0.5 % by weight as a binder, is pressed into cylindrical pellets of 1 cm diameter and 1 cm height using a hand, unidirectional, 25 ton capacity press from Perkin Elmer, under a compacting pressure ranging from 75 to 300 MPa. The effect of compacting pressure on the green density is investigated. The relation between the relative green density and the compacting pressure is shown graphically in Fig. (2). From this figure it is obvious that a change in the behaviour occurs at 180 MPa. This change is due to the transfer from the elastic region to the plastic region and the elastic limit is at 180 MPa. Using the least square method, the linear equations which best fit the experimental data were as follows:

$$\rho_g = (\ 5.58\ E-01\ ) + (\ 1.067\ E-09\ ) * P.$$

for the elastic region (**< 180 MPa .**).

$$\rho_g = (\ 6.868\ E-01\ ) + (\ 3.514\ E-10\ ) * P.$$

for the plastic region (**> 180 MPa .**).

3 . 2 . Sintering of Copper Compacts:

The effect of temperature, compacting pressure, sintering time on the final relative density of the copper pellets prepared as mentioned before in 3.1., were investigated and the results are reported in this section. The compacting pressures used in this investigation were 75, 100, 125, 150, 175, 200, 225, 250, 275, and 300 MPa. The sintering temperatures were 600, 700, 800, and 900 °C. The sintering time ranged from 5 min up to 60 min.The sintering atmosphere was a reducing atmosphere (H_2 and N_2 gas mixture with a volumetric ratio 3 : 1), as it was described before in section 2 . 4.

The relation between the relative sintered density and sintering time, sintering shrinkage and sintering time for the compacts pressed at 75 and 300 MPa., is shown graphically in Figures 3 and 4. The results at the other compacting pressures show the same trend as those shown in Figures 3 and 4.

It is clear from these figures that the sintering shrinkage and the relative sintered density for the samples sintered at 600 °C and 700 °C are small in comparison with those sintered at 800 °C or 900 °C provided that the same sintering time is adopted. It is also obvious that the sintering shrinkage and hence the sintered density increase as the sintering time increases at 800 and 900 °C, i.e. reduction of closed pores takes place, while the rate of shrinkage increases with the increase of sintering temperature. At low pressures the peaks appearing in the curves indicate the dilation of closed pores. As the compacting pressure increases, the peaks decrease due to the decrease of initial porosity obtained when high initial compacting pressure was used.

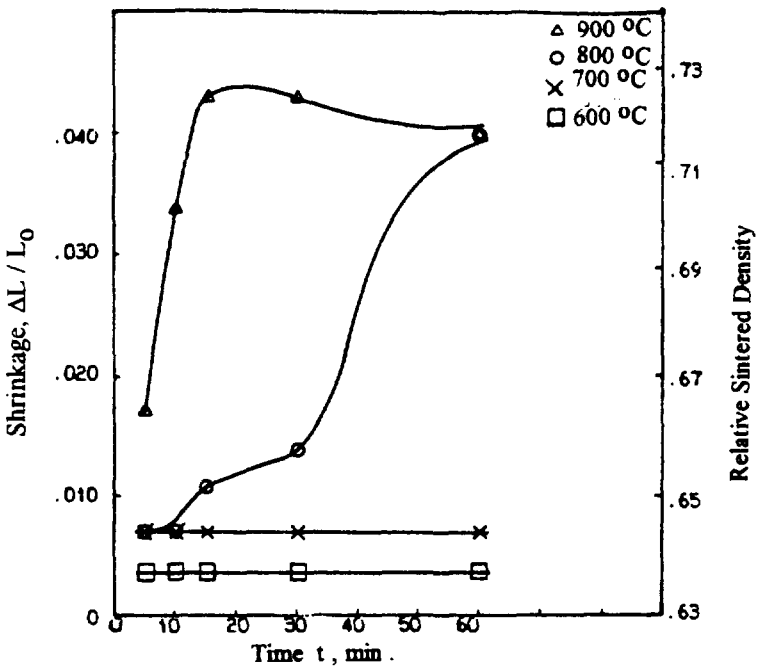

Fig . (3) Relation between shrinkage and time along a 600 - 900 °C temperature range ; P = 75 MPa .

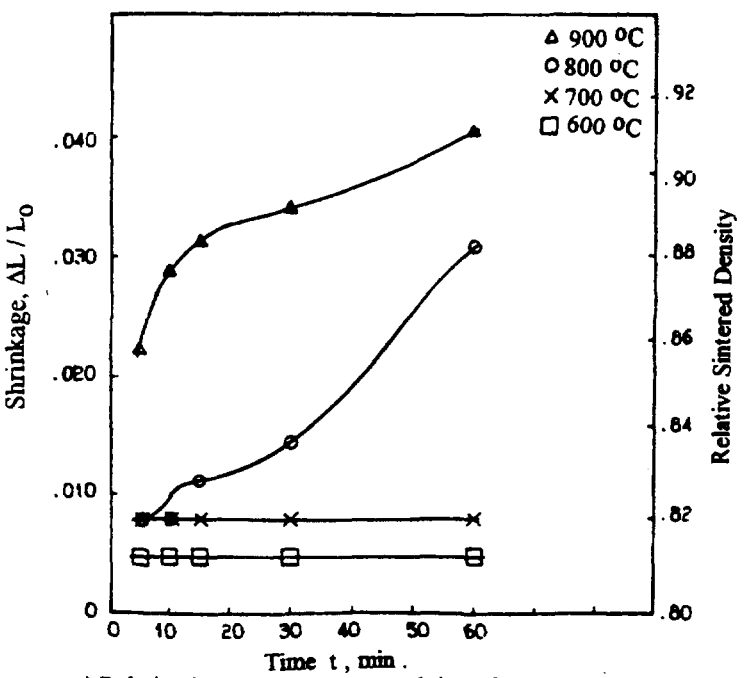

Fig . (4) Relation between shrinkage and time along a 600 - 900 °C temperature range ; P = 300 MPa .

3 . 2 . 1 . Effect of Temperature on Sintering Mechanisms:

The log - log relation between the linear sintering shrinkage ($\Delta L / L_0$) and the sintering time is shown graphically in Figures 5 and 6, for the pellets pressed at 75 and 300 MPa pressure range and sintered at 600 up to 900 °C temperature range. The slope of each straight line in these figures is studied in relation with temperature to determine the mechanism governing the sintering process. The slope of the resulting lines (0.4 or less), corresponds to surface diffusion mechanism at low temperatures (600 and 700°C). At higher temperatures, 800 and 900°C, lattice diffusion mechanism prevails. These resuls are supported by the work of Ichinose et al. and Moon et al. (12,13). The pellets pressed at the other pressures and sintered under the same conditions show the same trend.

3 . 2 . 2 . Effect of Green Density on Sintered Density:

The effect of green density on the sintered density at 700, 800, 900 °C after 1 hr sintering time is shown graphically in Fig. 7. It is clear from this figure that the relative sintered density increases as the green density and/or the sintering temperature increases. This could be attributed to the increase of surface contact area between adjacent particles, and hence increasing the driving force for sintering.

3 . 2 . 3 . Effect of Sintering Temperature on Sintered Density:

The relation between the relative density and sintering temperature after 1 hr sintering time is shown graphically in Fig.8 for compacts pressed unidirectionally at compacting pressures ranging from 75 to 300 MPa. From this figure it is clear that the increase in sintering temperature is accompanied by an increase in the sintered density due to the increase in atom mobility and hence material transport.

3 . 2 . 4 . Effect of Sintering Time on Sintered Density:

The relation between the sintering time and the relative sintered density is shown graphically in Fig. 9 for compacts pressed at 150 MPa. and sintered at 700, 800, and 900 °C. From this figure it is obvious that the relative sintered density increases with the sintering time as the sintering time proceeds at 800 and 900 °C. On the other hand, the sintering rate decreases after a certain time characteristic for each temperature which is attributed to the decrease in the driving force for sintering and approaching the system equilibrium state, i.e. approaching the limiting final density due to the formation of small pores isolated from grain boundaries which makes their annihilation by diffusion more difficult.

3 . 2 . 5 . Hardness Measurement:

The hardness for some copper pellets, which are cold pressed at compacting pressures ranging from 75 to 175 MPa. and sintered at 800 °C for 1 h was measured using a microhardness tester type M, Shimadzu, and the results are shown graphically in Fig. 10. It is obvious that the hardness increases with the increase in the compacting

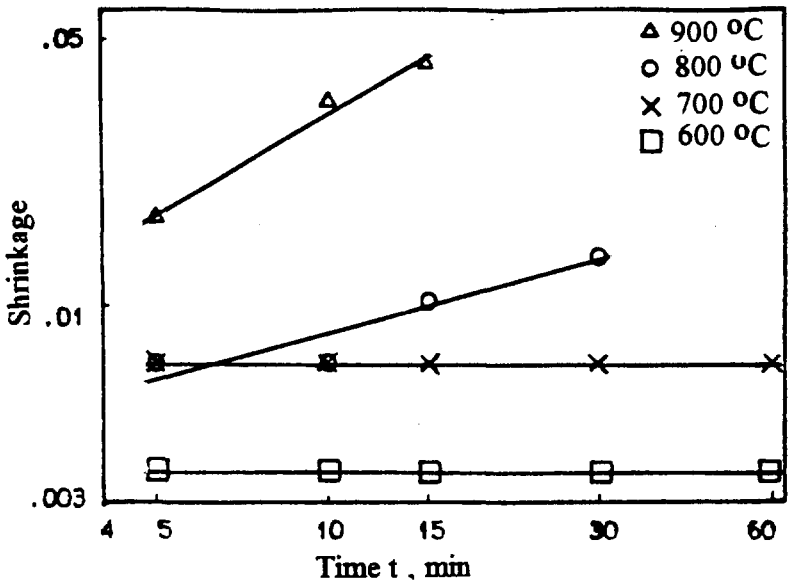

Fig . (5) Logarithmic relation between shrinkage and time along a 600 - 900 °C temperature range ; P = 75 MPa .

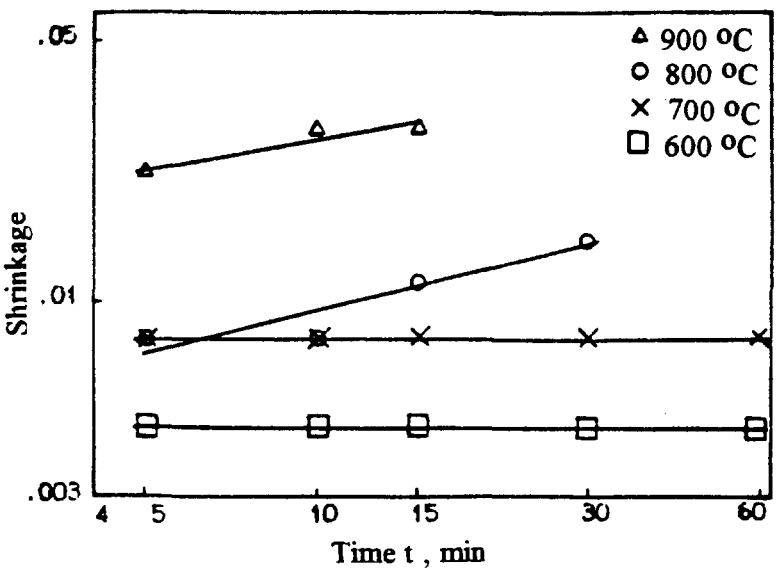

Fig . (6) Logarithmic relation between shrinkage and time along a 600 - 900 °C temperature range ; P = 300 MPa .

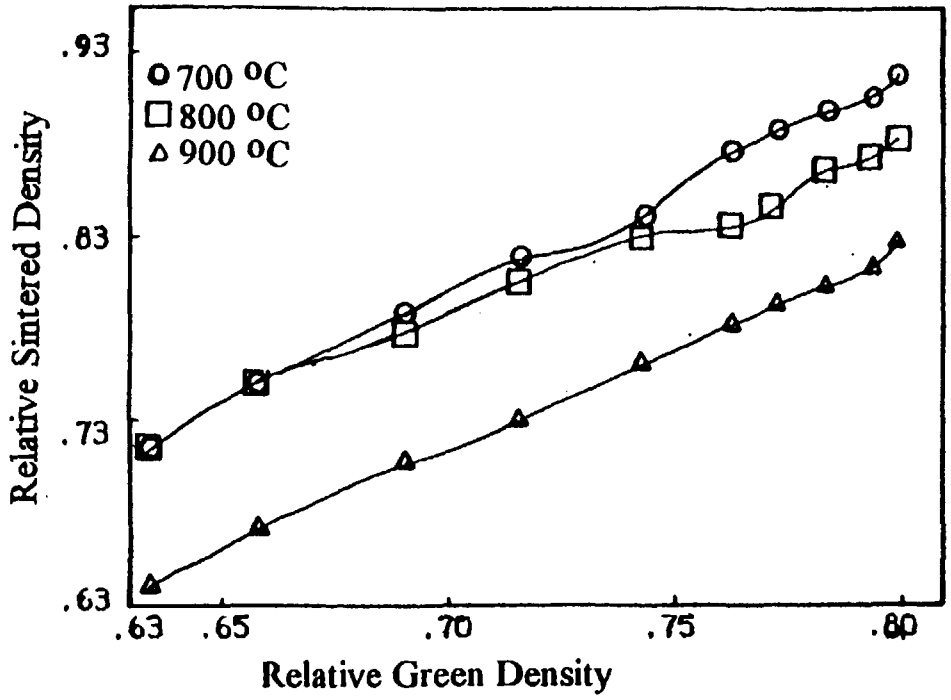

Fig . (7) Relation between green and sintered densities as a percentage of copper theoritical density after 1 hr sintering time .

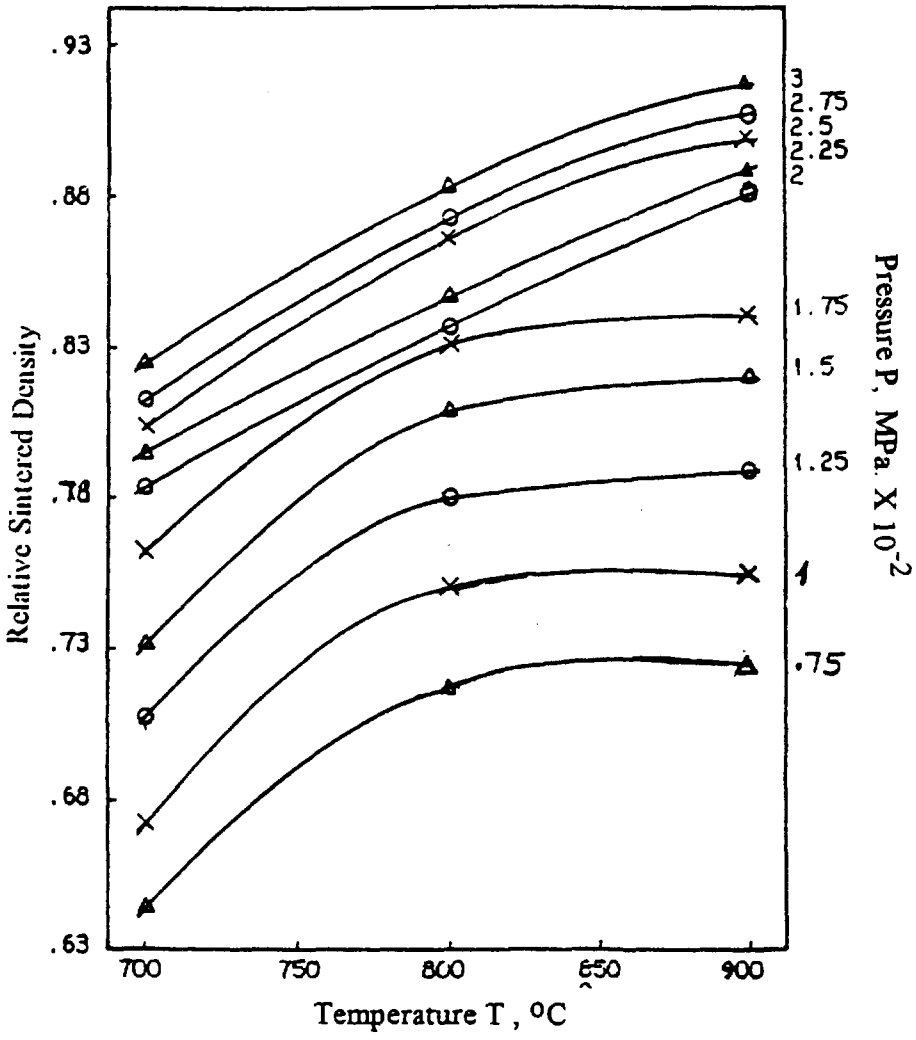

Fig . (8) Relation between sintering temperature and relative sintered density of copper compacts pressed in the pressure range ; P = 75 - 300 MPa after 1 hr sintering time .

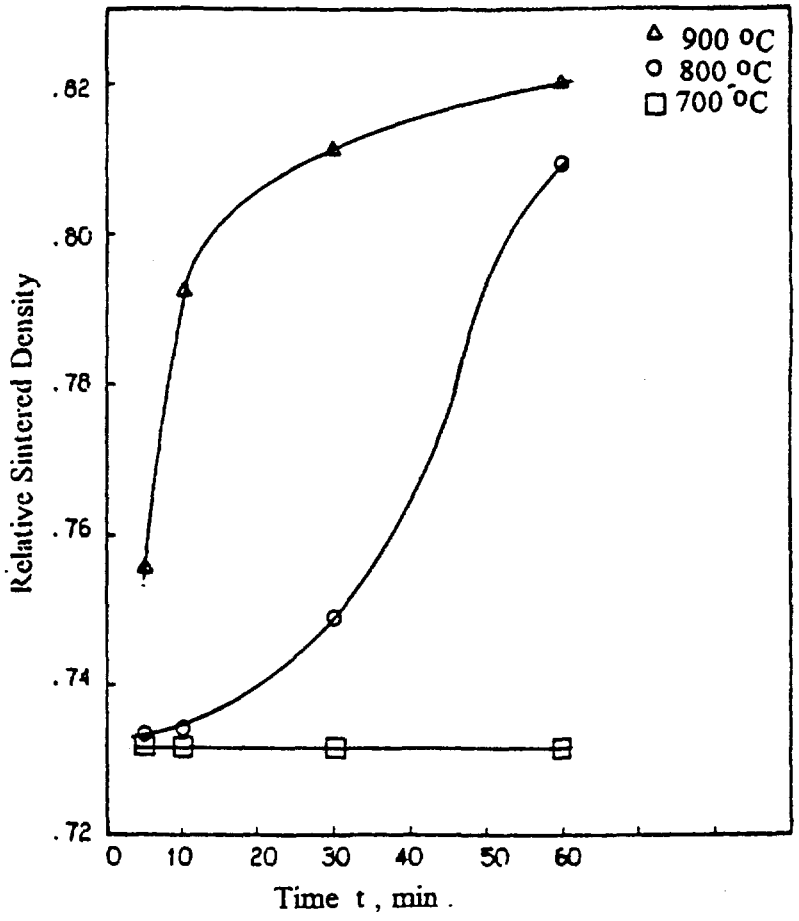

Fig . (9) Relation between the sintering time and the relative sintered density of copper compacts pressed at a pressure P = 150 MPa .

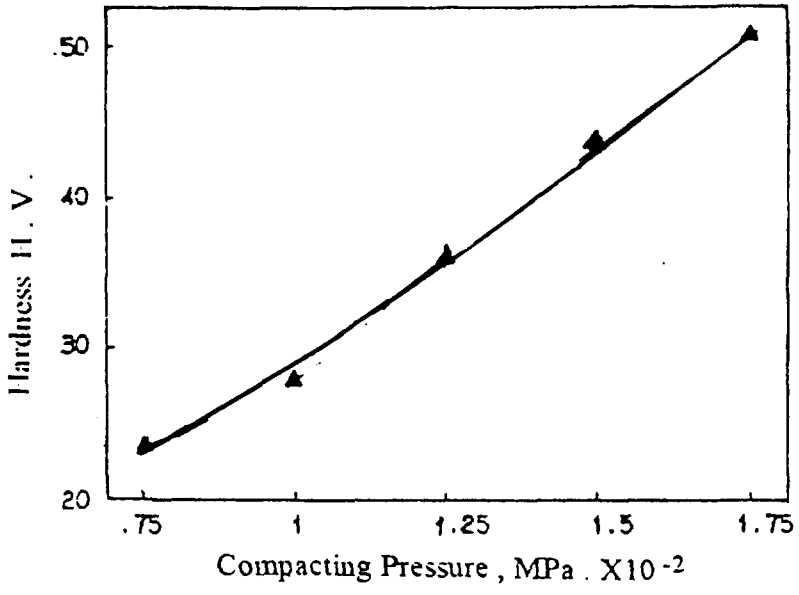

Fig . (10) Relation between the compacting pressure and the hardness of the sintered compacts , T = 800 °C , t = 60 min .

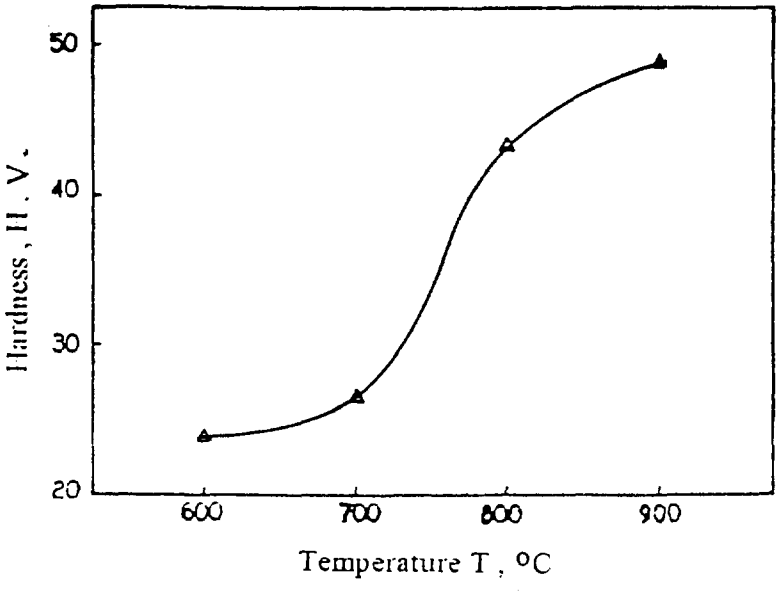

Fig . (11) Relation between sintering temperature and the hardness of the sintered copper compacts .

pressure provided that all the other parameters are the same. This may be attributed to the increase in the final relative density after sintering as the compacting pressure increases. The relation between the hardness and sintering temperature is shown graphically in Fig. 11, for the pellets which are compacted at 150 MPa. and sintered in a reducing atmosphere, as it was described before, at 600, 700, 800, and 900 °C for 1 h. From this figure it is clear that the Vickers hardness increases by increasing the sintering temperature, which is due to the increase in the relative sintered density of the sintered copper compacts.

4 . CONCLUSIONS

According to the results of this work, the following conclusions may be drawn:

1 . The green density increases with the compacting pressure.
2 . The sintered density increases with the compacting pressure, sintering temperature, and time.
3 . The sintering rate decreases after a certain time characteristic for each temperature, hence applying sintering for longer periods of time to obtain improved properties is economically impractical.
4 . low compacting pressures cause dilation of closed porosity.
5 . Shrinkage (reduction of closed porosity), increases with the increase of sintering time, while its rate increases with the increase of sintering temperature.
6 . At low compacting pressure , low temperatures favour the surface diffusion
mechanism, while high temperatures favour the lattice diffusion mechanism.
7 . Hardness of sintered copper increases with the compacting pressure and sintering temperature.

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