ACTIVATED SINTERING OF ALUMINIUM BRONZE

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(PHYSICAL METALLURGY)

By

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CERTIFICATE

Certified that the dissertation entitled, ACTIVATED SINTERING OF ALUMINIUM-BRONZE, which is being submitted by Shri S. [illegible]. Singh in partial fulfilment for the award of the Degree of MASTER OF ENGINEERING in Metallurgical Engineering (Physical Metallurgy) of the University of Roorkee, Roorkee (India), is a record of his own work carried out by him under our supervision and guidance from 2nd January 1978 to August 8, 1978.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

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ABSTRACT

In the present investigation activated sintering of 7% aluminium bronze was carried out by boron (0.05% by weight) addition both in the solid and the liquid phase. Compacting pressures of 3.82, 5.09 and 6.36 tonne/sq.cm. were selected. Sintering was carried out at 550° C for 10 hrs. durations and at 700° C for 2.5 hrs. respectively under dynamic vacuum of the order of 5 microns.

During sintering in solid state as well as in liquid phase, the products of poorer density were obtained than the green compacts as a consequence of occurrence of net volume expansion. As far as homogenisation is concerned liquid phase sintering in general was found more successful than solid state sintering.

Liquid phase sintering produced best overall hardness in the simple aluminium bronze whereas poorest in the boron added aluminium bronze.

Improved hardness values in general were obtained by increasing the compacting pressure.

Microhardness measurements and microstructural studies gave ample evidence that the boron addition has definitely activated the rate of alloying by enhancing the rates of interdiffusion of both the components viz. copper and aluminium.

One undesirable characteristic was observed that the boron develops a non-wetting property in the liquid phase with respect to the solid phase in the present system.

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CHAPTER - I

INTRODUCTION

Sintering is the process by which solid bodies are bonded by atomic forces through the application of pressure and/or heat. It involves the basic concept of adhesion of particles by the action of surface cohesive forces. Sintering consists of three simultaneously occurring phenomena viz., bonding particles at the contact points, changes in pore geometry normally resulting in shrinkage of a compact, and grain growth. Various definitions of sintering have been proposed in the last fifty years. In putting forward any reasonable definition of sintering, the following factors must be taken into consideration.

(a) A liquid phase is present only to the extent that it leaves a solid skeleton behind.

(b) A decrease in free enthalpy of the system, which represents the driving force of the sintering process, results from,

(i) Diminution in the specific surface area due to initiation and/or growth of contacts (necks);

(ii) Decrease in pore volume and/or the surface area of the pores;

(iii) Elimination of non-equlibrium states in the lattice;

(iv) Important properties approximate to those of the compact, porosity-free material.

Based on these considerations, the following definition was proposed by Thummler & Thomma(1) :-

" By sintering is understood the heat-treatment of a system of individual particles of of a porous body, with or without the application of external pressure, in which some or all of the properties of the system are changed with the reduction of the free enthalpy in the direction of those of the porosity-free system. In this connection, at least enough solid phases remain to ensure shape stability. "

The sintering process has a unique position in the field of powder metallurgy, ceramics and the agglomeration of ore fines. This is one of the technological field where the practical performance is almost perfectly mastered inspite of the fact that the actual mechanism of sintering is only vaguely understood. There is no general agreement about the mechanism of sintering even after more than thirty years of continued efforts. This is, however, not surprising since sintering does not involve one simple and straight forward process, but consists of many simultaneously occurring phenomena. The The phenomenon dominating at any instant during the process depends on a great variety of factors(1, 11), e.g.,

(i) History and other characteristics of powder;

(ii) Density of the sintering compact;

(iii) Sintering temperature and time;

(iv) Impurities;

(v) Doping agents;

(vi) Sintering atmosphere etc.

Various sintering theories have been proposed to relate the rate of shrinkage, the rate of neck growth or the change in pore shape, size and distribution to the mechanism of material transport operative during sintering. At present there are two major schools of thought viz. assuming either a diffusion mechanism(2, 3, 6, 9, 10) a plastic flow mechanism(4, 5, 13). It is now universally accepted that the driving force for the material transport during sintering is the lowering in total surface energy of the perticulate system.

The sintering of metal powders depends to a large extent on the surface state of the powder. Migration of atoms along surfaces is usually fast, but owing to the small quantity of material involved, and also the presence of contamination, it does not contribute materially to sintering consequently, to attain the desired properties, long times and high temperatures are usually required.

To achieve faster rates of sintering and to improve the physical and mechanical properties of the powder compacts, a substantial amount of material must be moved in a short time and the lattice as a whole must contribute to the process of transport$^{(12)}$. The concept of "activated sintering" was developed in this connection.

To 'activate' sintering it is necessary to increase the driving forces for sintering and to decrease the resistance to material transport. It refers to the sintering operations in which the rate has been modified by some chemical or physical means$^{(30)}$.

Physical methods of activation include the use of varying magnetic field, deformation, irradiation, static loading, cyclic heating or ultrasonic vibrations$^{(23)}$.

Chemical methods, which appear to be more practical, may involve dissociation of hydrides, sintering under atmospheres containing a reactive (aggressive) gas, sintering in the presence of very small quantities of alloying elements or sintering of metal powders having reactive surface layers(22).

CHAPTER - II

REVIEW OF LITERATURE

II.1 All the recognisable factors influencing the pattern of material transport during sintering have been recently classified by Thummler and Thomma(1) are given in Table I.

Table - I

A. Temperature dependent properties of the metals

- (i) Free surface and interfacial energy, including the pore surfaces.
- (ii) Diffusion Coefficients (lattice, grain boundaries, surfaces)
- (iii) Viscosity Coefficients (with amorphous substances)
- (iv) Critical shear stresses (combined with the action of plastic flow)
- (v) Vapour pressure and rate of vaporisation (combined with the action of vaporisation and condensation)

(vi) Crystal structure and state of bonding

(vii) Nascent state conditions, modification changes

B. Powder properties, pretreatment and sintering conditions

(i) Effective integral area of contact

(ii) Surface activity

(iii) Lattice activity (cold working, tensile and compressive stress, lattice defects governed by manufacturing conditions, crystallite sizes)

(iv) Reciprocal orientation of the contact faces

C. Foreign constituents (including those introduced by sintering conditions)

(i) Soluble (homogeneously or heterogeneously)

(ii) Insoluble

(iii) As surface layers (e.g., oxide films, soluble and insoluble, reducible and non-reducible, dissociating and non-dissociating under sintering conditions)

(iv) Gases (adsorbed, occluded and dissolved and effects of sintering atmospheres)

The quantities listed under (A) govern essentially the transport processes and are responsible for their relative importance.

(B) also includes, though not mentioned, the particle size, particle size distribution, and pressing conditions.

Numerous possibilities exist of influencing, the promotion or inhibition of sintering, either deliberately or otherwise. These include all the secondary factors listed above in (B) and (C) which relate both to powder and processing criteria.

These factors may influence the sintering process in positive or negative direction and can take place in the following ways:(1)

(a) The surface or contact conditions between the particles are altered.

(b) The activation energies of the transport mechanisms are raised or lowered.

(c) The type of particle transport or of transport path is changed.

(d) The number of particles capable of migration is changed.

In general it is not always possible to predict which of these factors exert a promoting or inhibiting impulse.

The influence of important variables and the probable mechanism of "activation" has been explained in the following lines.

(1) Effect of Structure, state of bonding and modification changes

A comparison between metals possessing cubic, hexagonal and tetragonal lattices shows that the temperature at the start of sintering, referred to the relevant melting point, increases with decreasing symmetry i.e. the sinterability decreases correspondingly(47, 48). This could be due to occurrence of non-metallic homopolar bonding constituents, at any rate with less closely packed structures.

The allotropic modifications and transformations also influence the sintering rate. During transformation the sintering contacts can be destroyed or distorted by reason of volume change(49).

(2) Effect of Powder activity(52, 53)

The total activity of powder particles is composed of the surface and lattice activities.

(a) Surface activity :- This is directly related to the particle size and shape and hence to the scientific surface.

High surface activity powders are characterized by sharp surface irregularities, as well as by a high specific surface area. Atoms are particularly mobile on surfaces having a strongly convex curvature, which leads to the initiation of sintering at very low temperatures with such powders. An increase in surface values naturally gives lower sintering temperatures and a higher shrinkage(51).

(b) Lattice activity :- This depends on -

(i) Particle and crystallite sizes

(ii) Lattice defects, arrangement of dislocations and internal stresses

(i) Particle and crystallite sizes :- Generally, finer powders give higher shrinkage than coarser material and that favourable distribution functions improve the apparent powder density, tap density and green and sintered density, on the other hand, fine powders give lower apparent and green densities.

Atomic processes in fine materials usually take place more rapidly and easily during sintering, because surfaces, grain boundaries, and all lattice distortions are present within a more restricted space and hardly any undistorted region exists(1).

The finest powders, especially in the pressed state also have a large "integral contact area" per unit volume, provided that their surface is not too severely fissured.

It has been established(28) that powder from single crystal particles exhibits slight grain growth at high sintering temperatures, while polycrystalline particles show a strong grain growth, corresponding to their higher activity.

(ii) Lattice defects, arrangement of dislocations and internal stresses :-

Nonequilibrium states within the volume (e.g., excess vacancies, dislocations and internal stresses) also arise from the method of production. Excess energy can be introduced into powders especially by cold working (i.e. grinding)(54).

An increase in densification with grinding time was found in the case of Al_2O_3 powder (calcined at high temperature)(55, 56). The results on the influence of deformation-induced stresses in metals are not in agreement. The stresses are eliminated at temperatures much lower than those at which densification begins, and are thus without o practical importance so far as sintering processes are concerned.

(3) The influence of stoichiometry

Special type of lattice activity is obtained with certain oxide compounds, as a result of the presence of the non-stoichiometric states in the cation or anion sub lattice. In the case of uranium-dioxide (UO_{2+x}) excess oxygen is present at elevated temperatures in the form of interstitials, which are extremely mobile(57). Due to this uranium dioxide (UO_{2+x}) sinters more easily than ordinary stoichiometric oxide under many, if not all conditions(58).

(4) The influence of foreign constituents

The sintering process can be affected in various ways by foreign atoms and foreign constituents, which are present in different forms. These factors are described below :-

(a) Oxide layers

In some cases e.g., in copper and iron it was found that an optimum thickness of oxide layer promotes sintering. Only those oxide layers which are reducible or soluble or dissociated during sintering are beneficial(14, 59).

A sinter promoting effect has been reported(60) with metal/oxide mixtures (of Cu - CuO, Fe - Fe_2O_3, W - WO_3) as long as the water vapour formed and other enclosed gases could be removed sufficiently easily.

Oxides that are not removable under sintering conditions have in general an inhibiting effect, because they act as diffusion barriers. In the case of aluminium, stainless steel and uranium powders(61) their respective oxides (e.g., Al_2O_3, Cr_2O_3 and UO) show inhibiting effect in practice.

(b) The influence of sintering atmosphere(31, 62)

Inert or reducing gases are generally preferred for metals. Addition of aggressive or nascent gases promote the reactions. In removing enclosed or adsorbed gases from the compact a vacuum is superior to other sintering atmospheres.

Sintering was frequently promoted by the addition of chlorine, HCl and reactive nascent hydrogen (e.g. by the decomposition of TiH_2). In such cases new sinter active surfaces are continually formed, thus accounting for the promotion of sintering. This method proved successful in the case of iron powders(27, 42, 63).

Chlorine contained sintering atmospheres promote the sintering process in iron and steel by the formation of volatile or low melting point halides, especially in the early stages of sintering.

(c) Small additives

Strongly inhibiting or promoting effects of the second component were observed, according to the materials used, sintering conditions and stage of sintering. Here the deciding factor is not the solid solution formation, as such, but the different partial diffusion coefficients (hetero-diffusion effect) occurring in each case in practice. New vacancies are constantly being produced in this way. These can assist the process by increasing the effective atom mobility, provided that they remain "dissolved" in the lattice. If vacancies coagulate to form new pores, they naturally have an inhibiting action by producing the well known Kirkendall effect. Favourable results have been reported in the systems Fe-Ni, Co-Ni and Ag-Cu(1) and also in tungsten with small additions of metals of the iron group and platinum group(23, 24).

The marked promotion of tungsten sintering by small additions of the iron group metals, especially nickel, can be considered as a special case, in which the temperature of extensive densification can be decreased to 1100°C. With about 0.25 % Ni addition, almost theoretical density of tungsten have been obtained(64). It is explained that metal addition should be effective only upto the point where a continuous surface layer is formed on tungsten particles, a further addition appears to have no effect(65). Tungsten diffusion is these layers should be rate determining, because tungsten is soluble in the added metals but iron-group metals do not dissolve much in tungsten. Larger additions hafe a very minor effect or may even prove inhibiting if intermetallic phases, with a high bonding energy are formed.

More recently the inhibited sintering characteristics of powder mixtures, e.g., in the Cu-Ni system, have been investigated. Under certain conditions expansion phenomena were observed instead of contraction(73, 74).

According to Fisher and Rudman(66) these are directly related to the degree of homogenisation. The expansion is also attributed to other factors such as preferential gas evolution during the formation of solid solutions(67).

(5) Other factors which may promote sintering

(a) Formation of new phases (reaction sintering)

The formation of new phases during sintering is associated in many cases with particularly marked expansion phenomena,(68, 69). By using specific pressure sintering conditions, sound and fairly pure phases can be manufactured by such 'reaction sintering' e.g., UC from uranium and carbon mixture is obtained.

(b) Sintering process in the presence of liquid phase

This is occupying a special position because of ease of diffusion process and of the possibilities of reordering of the phase remaining solid in the melt and of rapid dissolution and reprecipitation. The process can be divided into three stages(70, 71, 72) as follows.

(i) Particle rearrangement stage

The rearrangement of the particles of the residual solid phase by viscous flow in the liquid phase, helps in densification.

(ii) Dissolution and reprecipitation stage

For these to take place, at least a limited solubility of the solid in the liquid phase is necessary. This stage promotes densification with slower rate. Small grains, with strongly convex curvatures then disappear while larger ones assume a more regular shape.

The driving force for material transport results from the increased compressive stresses and hence from the enhanced chemical potential and higher solubility in the contact zones. The solid substance is then carried away and precipitated again at location of lower stress.

(iii) Coalescence Stage

In case of incomplete wetting (angle of contact 90) the solid grains are partly in contact without the interposition of the melt. A non-wetting liquid phase (contact angle 90°) is ineffective or inhibiting and usually exude partially from the sintered compact in the form of droplets.

II.2 ACTIVATED SINTERING OF METALS AND ALLOYS

Maurer(12) has shown that physically absorbed gases can help migration of atoms at relatively low temperatures. A greater effect may be expected when chemisorption preceeds the formation of a new phase. In this case, a large scale atomic rearrangement in the surface occurs. Also chemisorption involves transfer or sharing of electrons between the metals and the adsorbate. This reduces the surface bond energy of the substrate, which may thus provides the surface with increased numbers of atoms to participate in material transport if the newly formed phase is removed before or during the sintering cycle.

Surface cleaning (to remove impurity) like absorbed films etc., is necessary to activate the sintering process. One method of cleaning is to oxide the layer and reduce it (oxidation is done so that reduction will be easier) to get a fresh surface. Metallic crystals are activated by alternate oxidising and reducing.

Copper, and iron powders sinter best(14) when they have optimum amount of oxide, they are capable of reducing. This of course limit the cold welding. Also much oxide will give much water vapour (when hydrogen is used for reduction). This gas will rupture the compact.

Clasing(59) suggested that optimum oxide layer on copper to get good compact properties in vacuum sintering is about 400-500 Å. We must have low oxide and low temperature treatment in air so that activated sintering is possible. This practice does not require lubricants. For iron powder 300 - 350°C is favourable for activated sintering and the optimum oxide layer is about 400-600 Å. If oxides are not reducible then other compounds are formed on the surface.

In case of molybdenum we add controlled amount of oxygen in hydrogen atmosphere, possibly OH (volatile) takes part in the reaction. Molybdenum is sintered at 1630° C in hydrogen saturated with H_2O at 400°C. These have similar density of compact sintered at 2200°C with dry hydrogen. The same case has been noted in the case of tungsten.

Another method by Eudier(42, 43) is to introduce liquids into the system by using halide compounds (NH_4F and NH_4Cl). This gives more extended range of operative temperature. $Fe-S_1$ and Fe - Al alloys have been tried by this technique.

Use of bromine atmosphere for chromium alloy was suggested by Galmiche (probably oxybromide is formed).

The literature on catalysis reports(12) that formic and acetic acid vapours decompose catalytically via chemisorbed formate or acetate intermediates on the surfaces of copper powder, leading to the formation of microcrystals of copper formate and acetate, respectively, after prolonged exposure to the vapours. It is also known that these newly formed phases can be removed by heating at low temperatures.

According to Koróvesky(63) activation technique during sintering is same as infiltration. Despite the improved properties industrially it is not used due to dangerously halogen attack. Chemical reactions by diffusion is inside the compact and this has good possibility similar to surface treatment of fused material.

By alloying the powder surface characteristics can be changed and accelerated sintering can be achieved.

In the case of few ferromagnetic materials sintering under magnetic field has been done and accelerated rate has been reported.

The effect of ultrasonic vibrations on the sintering efficiency have also been studied and some improve properties have been reported.

An attempt was made by G.V. Samsonov to explain the activating phenomenon on the basis of 'stable Electron

Configuration Model'. He suggested that during the formation of condensed solid state, valency electrons can be divided into localized and non-localized parts.

His model is based on the results obtained by Morsunskii & Jenkin about the distribution of valency electrons by X-ray studies in the following transition metals.

Metal	Electronic Structure in Free atom.	No. of valency electrons ds	Localized part	Non-localised part
Zr	$4d^2\ 5s^2$	4	2.6	1.4
Nb	$4d^4\ 5s^1$	6	3.8 - 3.9	1.2 - 1.1
Cr	$3d^5\ 4s^1$	6	3.5	2.5
Mo	$4d^5\ 5s^1$	6	4.1 - 4.2	1.9 - 1.8

According to Samsonov the localised fraction of these electrons (valency electrons) forms a fairly broad spectrum of configurations. These configurations differ in their energetic stability i.e. in their stock of free energy, so that along with the very stable configurations there appear some which are less stable or even unstable. In view of the fact that the statistical weight of most energetically stable electronic configurations are considerably greater than the statistical weight of the unstable ones, each atom can be assigned state of a limited number of stable configurations. Between the stable configurations as the nonlocalized fraction of the valency electrons, there occur exchanges, which are responsible for the bonds between the pair of stable configurations. Stable electronic configurations, according to the degree of descending energy stability are $d^5 \longrightarrow d^{10} \longrightarrow d^o$.

The statistical weight of atoms having stable electron configuration (SWASC) in the metallic crystals can be obtained with the help of following expressions.

$$\text{SWASC} \quad d^5 = \frac{q}{5} \times 100 \; \%$$

$$\text{"} \quad d^o = \frac{5 - q}{5} \times 100 \; \%$$

if $o \leqslant q \leqslant 5$

where, q = No. of localised electrons.

$$\text{and SWASC} \quad d^5 = \frac{10 - q}{5} \times 100 \; \%$$

$$d^{10} = \frac{q - 5}{5} \times 100 \; \%$$

if $5 \leqslant q \leqslant 10$

G. V. Samsonov and V. I. Yakovlev studied the activating effect of iron group metals (Fe, Co & Ni) and platinum group metals (Ru, Rh, Pd & Os) on the sintering of tungsten. They observed that the activating effect increases from Fe → Co → Ni direction and also optimum quantity decreases in the forward direction. In the other case they found that activating effect rose from Os → Ru → Rh → Pd direction. They explained these results on the basis of stable electron configuration model as follows :-

Tungsten atoms are showing very little donar characteristics, since with increase in SWASC (shown in TABLE II) the donar capacity of various transition metal atoms decreases. The attainment of d^{10} configuration is easily achieved in the case of Ni, Pd & Rh additives, because they are having higher SWASC d^{10}. It is difficult to achieve in the case of elements which have lower SWASC d^{10}. This is the reason why in the series Ni → Co → Fe and Pd → Rh → Ru → Os, the optimum quantity of additive increases.

TABLE - II Electronic Structure, Solubilities and SWASC of some additive metals in Tungsten ($SWASC\ d^5 \sim 96$)

Additive element	Electronic structure in free atom	Solubility in Tungsten	Solubility of Tungsten in additive	SWASC		
				d^0	d^5	d^1
Fe	$3d^6\ 4s^2$	0.8 wt. %	32.5 wt. %	0	44	56
Co	$3d^7\ 4s^2$	0.3 "	45.0 "	0	28	72
Ni	$3d^8\ 4s^2$	0.3 "	42.0 "	0	16	84
Os	$5d^6\ 6s^2$	15 Atomic %	48 Atomic %	0	84	16
Ru	$4d^7\ 5s^1$	18 "	48 "	0	80	20
Rh	$4d^8\ 5s^1$	Negligible	12 "	0	60	40
Pd	$4d^{10}\ 5s^0$	~ 0.3 Atomic %	10 "	0	18	82

The various results on activated sintering of metals and alloys as reported in various literatures are being summarized in Table III.

TABLE - III

Metal powder.	Activating agent	Temperature °C	Experimental details	Observations	Proposed mechanism	Ref.
1	2	3	4	5	6	7
W	H_2 + Br_2 gas	1200-1700	H_2 + Br_2 atmosphere was used	(i) The presence of Br_2 increased densification rates. (ii) Densification is more effective at about 1500°C. (iii) Load to fracture improved, but failed under bending test.	No explanation	(15)

1	2	3	4	5	6	7
"	Ni	Above 1000	Ni added in powder form as well as in aqueous salt solution	(i) Even at 1100°C shrinkage occurred containing Ni upto 0.5% (ii) Increased rate of densification obtained.	The principal condensation ~~mechanism~~ mechanism was presumably of the dislocation type.	(19)
"	Pd	1600	————	(i) Relative density upto 90-95% obtained. (ii) 0.2 wt. % of Pd was found optimum for ~~denset~~ densest and strongest.	Stable electron configuration model	(21)
"	Iron group metals (Fe, Co, Ni)	1000-2000	(i) H_2(pure) atmosphere (ii) Co & Fe added in powder form (0.05 to 1.0 wt%)	(i) Activating effect increases from Fe Co Ni direction (ii) Optimum quantity decreases in the forward direction.	Stable electron configuration model	(21)

1	2	3	4	5	6	7
			(iii) [illegible] as aqueous solution (iv) Time 1 hr.			
"	Platinum group metals (Ru, Rh, Pd & Os)	1000-2000	(i) H_2(Pure) atmosphere. (ii) Ru, Rh & Os added in powder form(0.05 to 1.0 wt %) (iii) Pd as Pd Cl_2 aqueous solution (iv) Time 1 hr.	(i) Activating effect rose from Os → Ru → Rh → Pd direction. (ii) Promotes mutual dissolution by increasing SWASC.	Stable electron configuration model	(24)

2	3	4	5	6	7
Ni	-	Fine W powder coated with a uniform Ni layer of the order of atomic thickness	(i) Rapid densification achieved at unusually low temperature. (ii) Density, 92% of theoretical, achieved at 1100°C after 30 Mts. (iii) 98% of theoretical density obtained after 16 hrs. at 1100°C. (iv) Activation energy for sintering - 68 k Cal/mole.	Activation takes place by movement of W through or on a thin Ni carrier phase. Ni remains on particle surface because of its small solubility in W (i.e. 0.3 wt. % at 1500 °C) But W issoluble in Ni to greater than 38 wt. % at temperatures about 970°C.	(35)
Ni	-	Sintering and strength of coated and ~~CO~~reduced Ni-W powder was studied CO reduced	W sintering can be ~~xxxx~~ activated with minimum amount of Ni, if coating process, rather than CO-reduction process is used.	No explanation	(36

	2	3	4	5	6	7
	Pd, Rh Ru & Pt	1100	-	(i) Sintering of W at low temperature accelerated by addition of Pd, Rh, Ru & Pt. (ii) Densification retards at 1100°C.	Cause is related to enhancement of grain boundary diffusion	(37)
	~~Tungsten~~ Group VIII transition elements	~~Moist~~ H_2 -	Small additions	Pd appears to have greatest effect, followed in order by Ni, Rh, Pt & Ru	No explanation	(39)
ungsten horia owder lende	Moist H_2	1100	-	Severe coarsening of thoria observed at low temperature (1100°C)	This behaviour involves the formation of "liquid" type interparticle films associated with an interaction between thoria & a tungsten oxide derived from oxygen initially chemiabsorbed on the particle surface.	(32)

1	2	3	4	5	6	7
Fe	Ni, Co, Mn, Cu and Chlorides of these elements & $BaCl_2$	-	-	(i) Activation efficiency depends on mobility of atoms. (ii) Efficbency depends on dissolution of additive in Fe (iii) $CoCl_2$ & $MnCl_2$ give fine grains. (iv) $NiCl_2$ & $BaCl_2$ give coarse grains	Partial diffusion coefficients of additives exceeds that of Fe. This creates structural defects and accelerates sintering. Interaction of associated structural defects facilitates diffusive creep. As chlorides reduce, create surface defects & facilitate diffusive creep.	(17) (25) (27)
"	Sn	1000	2% Sn	(i) Sn is more effective than Cu. (ii) Sintering rates very high at 2% Sn (Wt. %) (iii) Temperature and time both can be reduced	No explanation	(18)
"	~~[illegible]~~ NH_4F NH_4Cl	-	~~[illegible]~~ -	(i) Range of operative temperature increases (ii) Sintering rate accelerated.	-	(1)

1	2	3	4	5	6	7
	Various activating methods	-	Sintering in (i) Dry H_2 (ii) H_2 with 2% & with 10% moisture (iii) Initial oxidation + dry H_2 (iv) H_2 for 7 ~~Mts.~~ minutes then water for 3 ~~Mnts.~~ minutes. (v) H_2 + HCl atmosphere. (vi) Same as (v) but oxidized sample. (vii) Under powder alumina + 0.1% NH_4Cl. (viii) Under powder alumina + 0.1% NH_4F.	Comparative study of relative activating efficiency was made. Most favourable effect on magnetic properties obtained by adding Hcl to sintering atmosphere	-	(40)

1	2	3	4	5	6	7
"	HCl	-	Optimum HCl content in continuous current of gas being 5 - 10 %	Most favourable influence on magnetic permeability & coercive force was obtained	-	(41)
Cu	Cu_2O	-	(i) H_2(pure dry) atmosphere (ii) Coated with critical oxide film (Cu_2O-thickness 500°A)	(i) Activation energy for Cu(Pure) 55 Kcal/mole (ii) Activation energy of oxide coated Cu-37 K cal/mole	Surface cleaning by oxidising and reducing accelerates sintering.	(14) (33)
"	Aqueous formic and acetic acid	-	-	Densification, hardness and tensile properties improved	Explained on the basis of chemisorption which preceeds the formation of a new phase.	(12)
Re	Pd	~~1900 - 2000~~ 1900 to 2000	Optimum 0.2 to 0.4 wt %	(i) 92% relative density achieved at 1900-2000°C (Pure Re (without Pd) gave only 80%) (ii) Density goes up with temperature upto 2000°C.	-	(20

&	NH_4Cl & $CoCl_2$	2000-2600	-	(i) Satisfactory density at 2500-2600°C. (ii) Shrinkage starts even at 2000°C (iii) Activation energies of sintering TaC & HfC with $CoCl_2$ fillers being 24.8 & 30.5 K Cal/mole respectively.	NH_4Cl forms respective chlorides as intermediate layer which promotes diffusion. $CoCl_2$ forms a surface layer, which reduces slip resistance.	(16)
aze	Boron	-	Traces of ~~Pd~~ B	(i) Maximum increase in shrinkage and the highest mechanical strength of the alloys corresponded to the limiting solubility of B in copper. (ii) B reduces the tendency towards grain growth on sintering by forming an adsorption layer on the surfaces of the grains.	Development of structural defects at the particle boundary during the diffusion of Boron.	(26)
$_2$ der	Ni & TiO_2	-	Small additions	(i) TiO_2 addition relatively ineffective till temperature approaches UO_2 - TiO_2 eutectic (1550°C) and improved rapidly with further rise of temperature.	-	(46)

				(ii) At 1700°C, W - UO_2 powders in equal proportions by volume could achieve near theoretical density with addition of 0.05 - 0.10% TiO_2 (iii) Equal addition of both Ni & TiO_2 speed up densification.		
2	TiO_2, BeO, Al_2O_3, MgO, V_2O_5, ZrO_2, CaO & CeO_2	-	H_2 atmosphere	(i) Results indicated that TiO_2, BeO, Al_2O_3 and MgO had pronounced accelerating effect. (ii) Minor effects were noted for V_2O_5, ZrO_2 CaO, and CeO_2	-	(29)

II.3 SCOPES OF THE PRESENT WORK

In view of the wide applicability of aluminium bronze and the difficulties encountered during its casting, it is worthwhile to develop powder metallurgical techniques for the fabrication of such alloys. This will definitely have much saving in the waste scraps.

Some work has already been conducted(26) on the study of activating effect of Boron on the sintering of tin bronze. A similar study was planned in the present investigation for Aluminium bronze. The progress of sintering was followed by studying parameters such as volume change, hardness - maro as well as micro, porosity and degree of homogenisation. A comparative study was made on the sintering behaviour of aluminium bronze with or without Boron addition.

CHAPTER - III

EXPERIMENTAL DETAILS

III.1 METAL POWDER SPECIFICATIONS

Riedel copper powder of 99.99 % purity was used in the present investigation. The size of the copper powder was - 200 mesh.

Aluminium powder of 99.9% purity (laboratory chemical) manufactured under arrangement with E Merck AG. Darmstadt (Germany) by SARABHAI M. CHEMICALS LIMITED, BARODA (Batch number OE 00493) was used. The size of this powder was - 100 mesh.

Boron crystalline powder manufactured by Koch-Light Laboratories Ltd., Coinbrook, Bucks, England was used. The size of the Boron powder was approximately - 65 mesh.

III.2 PREPARATION OF GREEN COMPACTS

A composition of 7% Aluminium-bronze (rest 93% copper by weight) was selected in the present investigation.

Boron powder was chosen to study the effect of its addition (0.05% by weight) on the sintering characteristics and mechanical properties of the Aluminium-bronze alloy.

III.2.1 Mixing of Powders

The first lot of powder mixture (i.e. 7% Aluminium bronze in which Boron was not added) was mixed by passing through 100 mesh screen about 5 times and then 25 times through 65 mesh screen.

The second lot of powder mixture in which Boron has been added, was first mixed in batches (about 20 gms. of powder mixture in each batch) with the help of pestle and mortar with a view to reducing thesize of boron powder and avoiding the segregation of the Boron particles in the powder mixture and then finally the same procedure was adopted as in the first lot of powder mixture.

III.2.2 Making of green compacts

Universal Testing Machine and high speed steel die and punch were used for making cylindrical green compacts of powder mixture of approximately 1.0 cm. diameter and 1.5 to 2.0 gms weight.

Three compacting pressures i.e., 3.82, 5.09 and 6.36 tonne/sq.cm. were selected for making these compacts.

Desired compacting pressures were obtained slowly (in about 1½ to 2 minutes) and then were kept constant for 2 minutes in each case. Pressures were also released with the same rate as these were applied initially.

III.3 SINTERING

Before each sintering operation, entrapped gases in the green compacts were removed by heating these samples at 250°C under vacuum for 1 hr.

Sintering of the green compacts was performed under vacuum of the order of 5 microns at temperatures of 550°C and 700°C respectively. These temperatures were selected with a view to making comparative study of solid phase sintering (at 550°C) and liquid phase sintering (at 700°C) of the alloy under investigation.

Liquid phase sintering was done for five different periods i.e., 1/2, 1, 1½, 2 and 2½ hrs. In the case of solid phase sintering comparatively longer periods were chosen viz. 1/2, 1, 5 and 10 hrs.

III.4 VOLUME CHANGE MEASUREMENTS

The dimensional changes of the samples after sintering were measured with the help of micrometer screw gauge (least count = 0.001 cms).

Difficulty was encountered in the case of Boron added samples that the liquid phase exuded in the form of droplets and solidified on the outer surface of the specimen. Thus before any measurement to be taken, this oozed out material was removed by gentle rubbing and polishing.

About 5 to 7 readings were taken for diameter measurements, whereas 10 to 15 readings were taken for height measurement in order to get an average picture.

III.5 HARDNESS MEASUREMENTS IN V.P.N.

Sintered specimens were properly polished upto 3-zero emery paper and then the hardness was measured along the diameter at about 5 to 7 points by the Vickers Diamond Pyramid hardness tester using a load of 5 Kg. The median of these readings was taken as the hardness value of the specimen concerned.

III.6 MICRO-HARDNESS MEASUREMENTS

Sintered samples corresponding to only 6.36 tonne/sq.cm. pressure were selected to analyse the pattern of microhardness variation.

Microhardness Tester Model D 32 attached with large Incident-Light Camera Microscope "NEOPHOT 2" was used for measuring microhardness.

Sintered specimens were properly polished (mechanically) and then etched with ferric chloride solution.

Three different loads viz. 10.78, 21.96 and 45 gms. were applied for making indentation in the selected area of the microstructure. But the results of microhardness were reported in this work for intermediate load.

After measuring the length of diagonal of indentation, calculations were made as follows :

$$Hm = \frac{1854.4\ P}{d^2}\ (Kg/mm^2)$$

where, Hm = general microhardness in kg/mm^2

P = Test load in gms i.e. 21.96 gms (obtained with the help of Calibration Curve)

The micrometer reading and the scale interval yield the indentation diagonal as,

$$d = m\,\delta$$

where,

m = Reading of indentation size, expressed in drum division.

δ = Scale interval (varies with magnification used)

d = Length of diagonal of impression in μ (microns)

III.7 MICROSTRUCTURAL STUDIES

Metallographic studies were conducted on the Large Incident-Light Camera "NEOPHOT 2". The microstructures were examined at different magnifications and microphotographs of selected specimens corresponding to 6.36 Tonne/sq.cm. pressure were also taken.

III.8 X-ray STUDIES

Required quantities of powder samples for X-ray studies were obtained by filing the sintered specimens and then passing through 150 mesh screen.

X-ray diffraction patterns of powder samples of some of the sintered specimens were taken on the X-ray unit model No. XR-DA-2 with the help of two camera's of diameters 90 mm. and 114.6 mm respectively, for the sake of estimating the extent of solid solution formation of the component powder mixture.

The time of exposure was tried from 8 to 25 hrs. and the rating was varied from 20 M.A., 35 K V. to 25 M.A., 40 K.V.

CHAPTER - IV

RESULTS

IV.1 VOLUME CHANGE

In this multicomponent system volume expansion was observed instead of contraction in the solid phase as well as in the liquid phase sintering. Thus the density of the sintered product decreases in this alloy.

The results of volume expansion (as percentage) of simple and boron added aluminium bronzes are given in Table IV and V respectively.

TABLE IV - Variation in % volume change of simple and B-activated Al-Bronze specimens sintered in solid state at 560°C

	Simple Al-Bronze				B-activated Al-Bronze			
Sintering time in hrs. / Pressure of compacting in Tonne/sq.cm.	0.5	1	5	10	0.5	1	5	10
3.82	0.66	0.66	0.67	0.67 ~~0.44~~	0.44	0.42	1.51	1.41
5.09	0.68	0.69	0.71	0.68	0.42	0.61	1.55	1.65
6.36	0.80	0.69	0.69	0.78	0.46	0.65	1.55	2.32

TABLE V - Variation in % volume change of simple and B-activated Al-Bronze specimens sintered in Presence of liquid phase at 700°C

Sintering time in hrs. ssuro compact- in ne/sq.cm.	Simple Al-Bronze					B-activated Al-Bronze				
	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
3.82	3.26	3.04	3.14	3.96	3.31	5.67	5.55	5.33	5.49	5.22
5.09	3.41	3.21	3.21	3.05	2.45	6.25	6.11	6.37	6.32	6.22
6.36	4.6	4.39	4.89	5.42	6.27	6.58	6.61	6.50	6.62	6.43

IV.1.1 Volume change during solid state sintering

Volume expansion results of simple aluminium bronze sintered at 550°C for various periods are shown in Fig. 1. Here the initial volume expansion is comparatively very large in each sample. The 6.36 tonne/sq.cm. pressure compacted samples show a typically more expansioninitially, but at 1 hour of sintering all these samples show almost equal expansion irrespective of compacting pressure. In the later stages of sintering only ~~sight~~ slight expansion was noted in 6.36 tonne/sq.cm

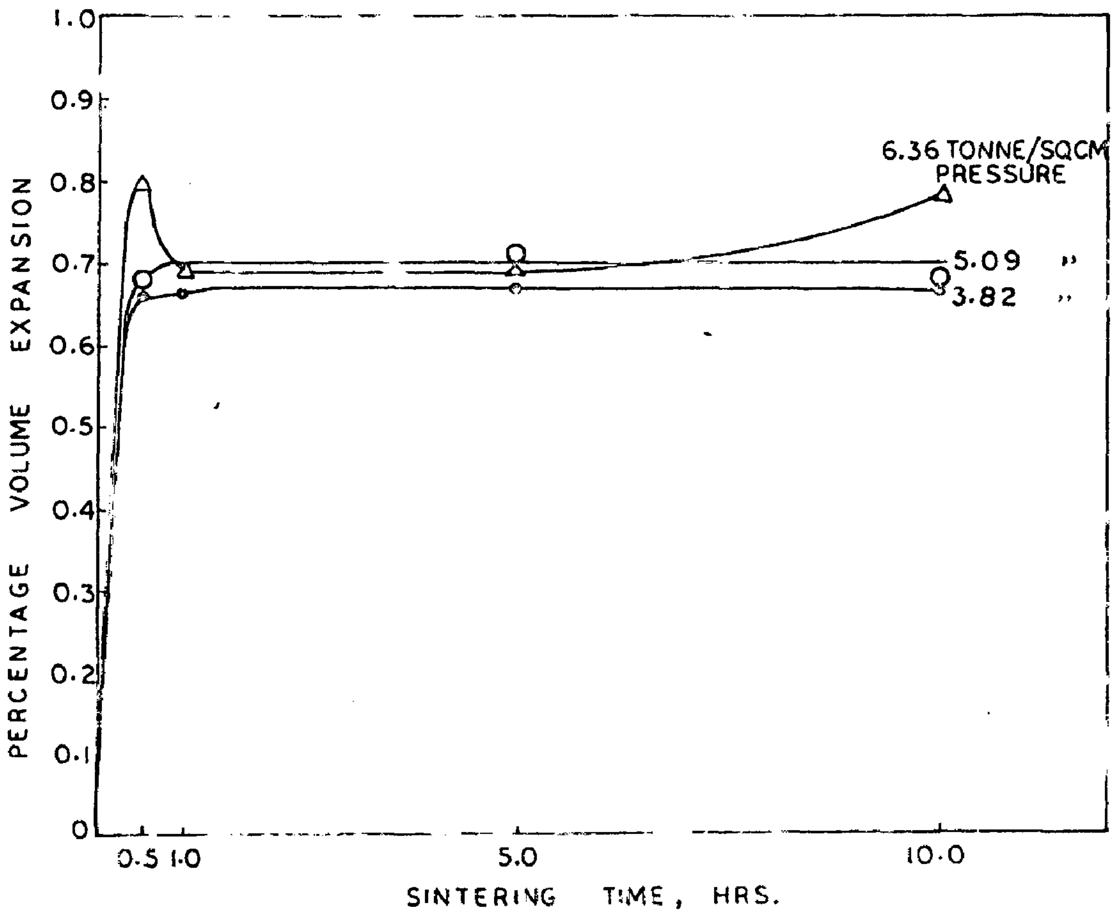


FIG. I. VOLUME EXPANSION OF SIMPLE Al-BRONZE DURING SOLID PHASE SINTERING AT 550 °C.

pressure compacted samples and no expansion was detected in 3.82 and 5.09 tonne/sq.cm. pressure compacted samples.

Volume expansion results of boron added aluminium bronze sintered at 550°C for various periods are shown in Fig. 2. In this case volume expansion occurs almost continuously (with a slight deflection in samples compacted at 3.82 tonne/sq.cm. pressure between 0.5 & 1 hr. duration) at the constant rate upto 5 hour of sintering in all the samples. Beyond this period, a slight contraction has been observed in samples compacted at 3.82 tonne/sq.cm. pressure, but further expansion has been noted in the case of samples compacted at 5.09 and 6.36 tonne/sq.cm. pressures. The rate of % volume expansion for 6.36 tonne/sq.cm. pressure compacted samples is fairly high than the expansion rate of 5.09 tonne/sq.cm. pressure compacted samples in the later stages of sintering.

IV.1.2 Volume Change during liquid phase sintering

Volume expansion results of simple aluminium-bronze sintered at 700°C for various periods are shown in Fig. 3.

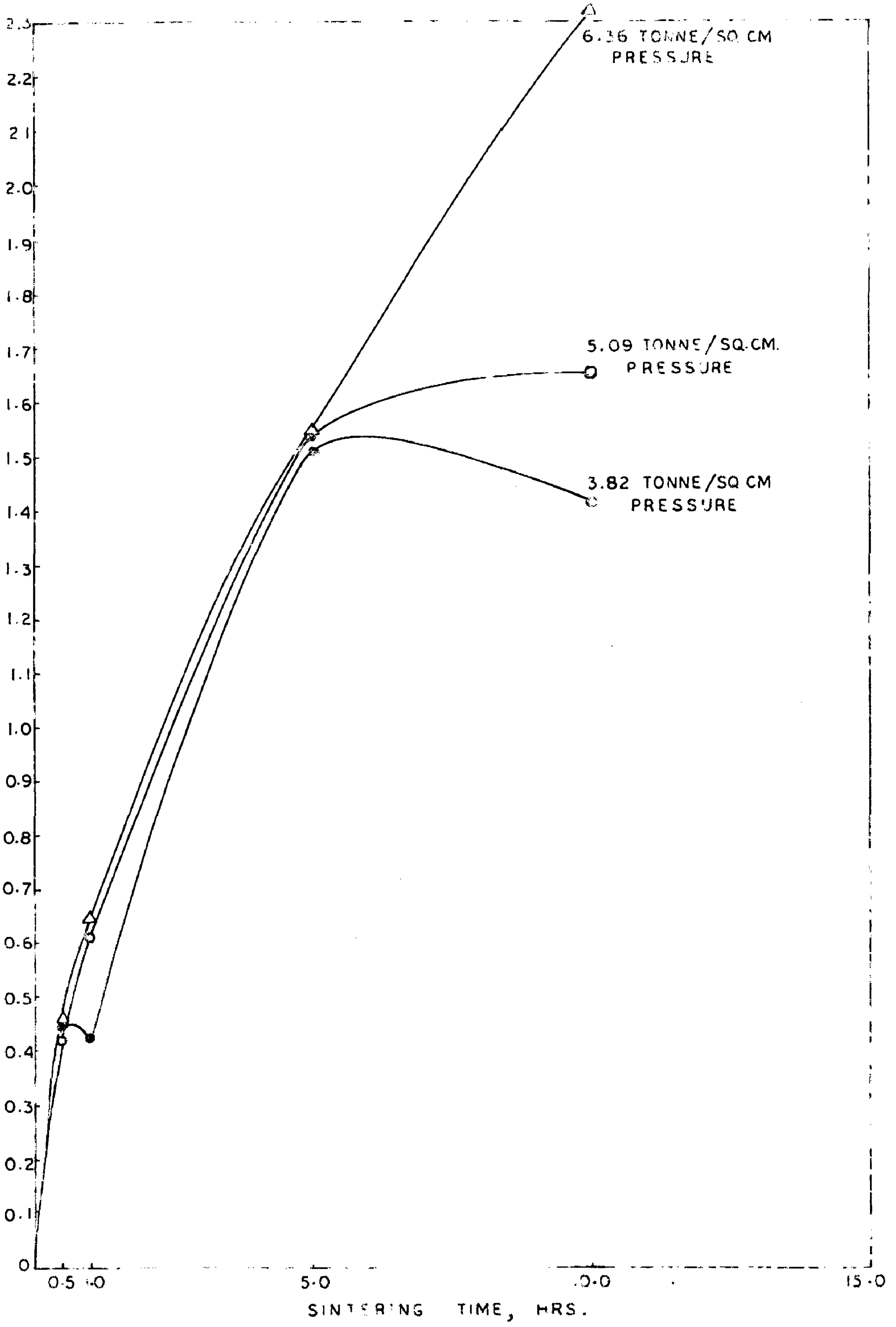


FIG. 2. VOLUME EXPANSION OF BORON ADDED AL-BRONZE DURING SOLID PHASE SINTERING AT 550 °C.

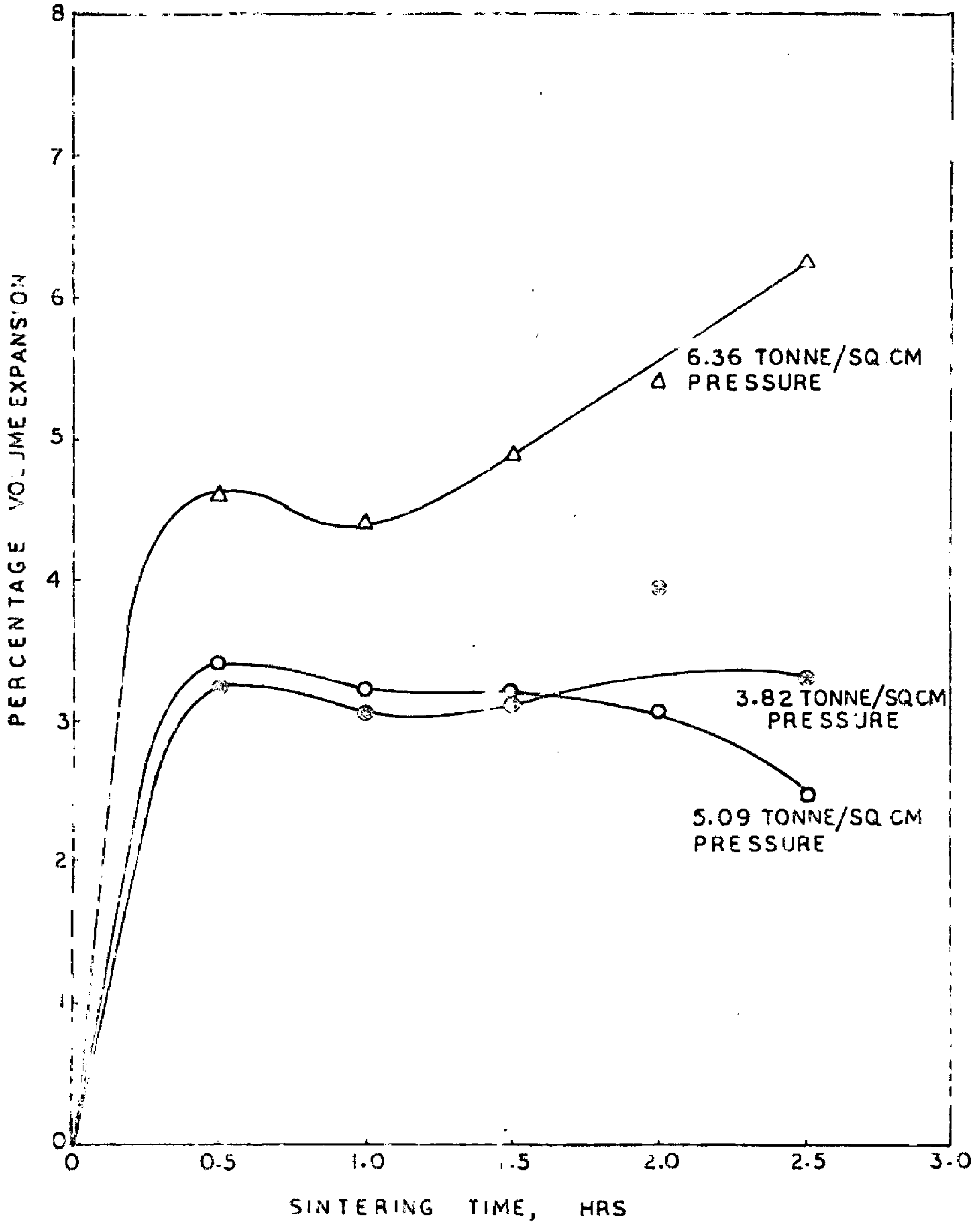


FIG. 3. VOLUME EXPANSION OF SIMPLE AL-BRONZE DURING LIQUID PHASE SINTERING AT 700 °C.

In this case also initial volume expansion is comparatively large in each sample. But the expansion behaviour of 6.36 tonne/sq.cm. pressure compacted samples is quite different from samples compacted at 3.82 and 5.09 tonne/sq.cm. pressures. Initial expansion itself in 6.36 tonne/sq.cm. pressure compacted samples is comparatively more and remains constant upto 1 hour, but beyond this expansion occurs continuously at constant rate upto the end of sintering time. However, volume expansion is almost constant with sintering period in samples compacted at 3.82 and 5.09 tonne/sq.cm. pressures. In the later stages of sintering a slight contraction has been noted in samples compacted at 5.09 tonne/sq.cm. pressure.

Volume expansion values of boron added aluminium bronze sintered at 700°C for various periods are shown in Fig. 4. Here also it is very large in the initial stages of sintering itself and remains almost constant with sintering time in each case irrespective of compacting pressure. It is comparatively more with higher compacting pressures. In this

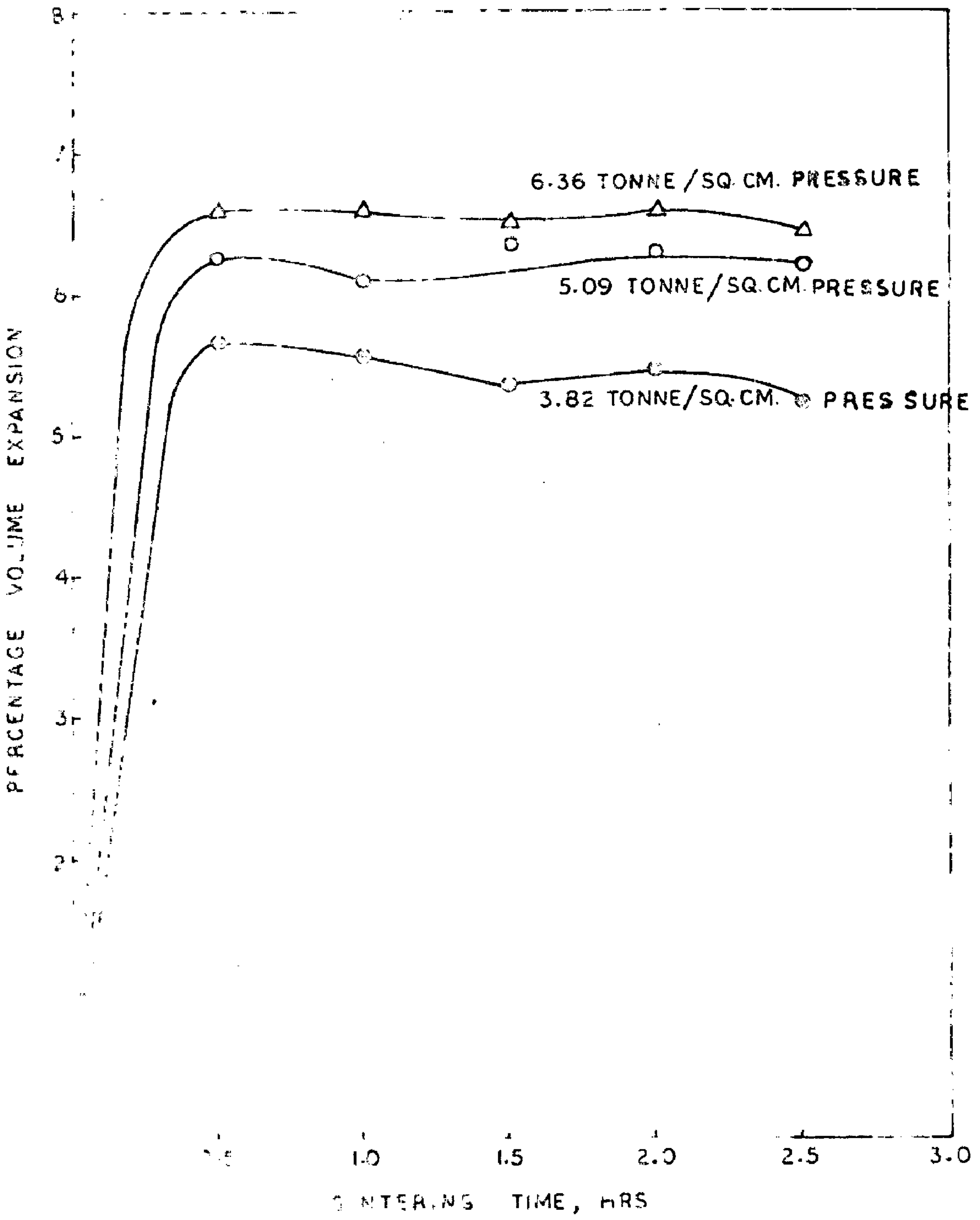


FIG 4. VOLUME EXPANSION OF B-ADDED AL-BRONZE DURING LIQUID PHASE SINTERING AT 700 °C.

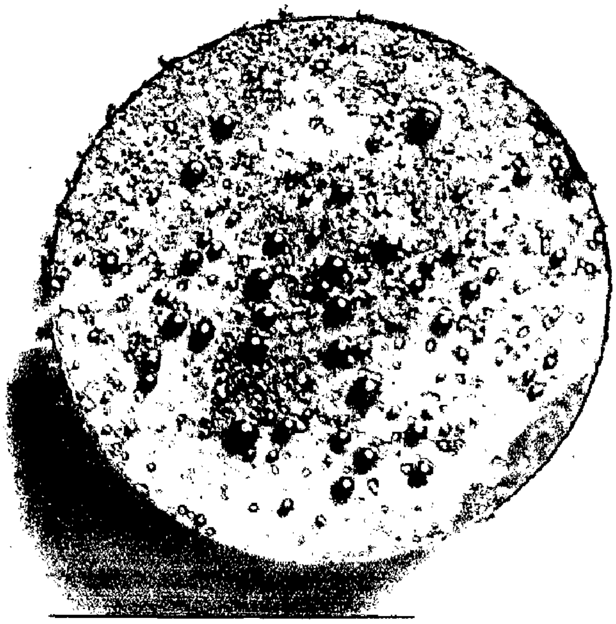


FIG. 5. VIEW OF THE B-ADDED ALUMINIUM BRONZE SPECIMEN SHOWING THE PRESENCE OF EXUDED MATERIAL DURING LIQUID PHASE SINTERING.

case one peculiar phenomenon has been observed almost in all the sintered compacts. Liquid phase exudes in the form of droplets and solidifies at the surface of the samples. One photograph of such sample with its oozed out liquid phase has been taken and shown in Fig. 5.

Thus in general we find that volume expansion is comparatively very low in solid phase sintering than in liquid phase sintering. Initial volume expansion of boron added aluminium bronze in solid phase sintering is comparatively slightly less, but beyond 1 hour it is quite higher than that of simple aluminium bronze.

Initial as well as overall volume expansion is comparatively more in case of boron added aluminium bronze than simple aluminium bronze when liquid phase sintering is done.

IV.2 HARDNESS

Hardness values (median of various readings) in V.P.N. of sintered specimens of simple aluminium bronze and boron added aluminium bronze are given in Tables VI & VII respectively.

TABLE VI - Variation of hardness (V.P.N.) of simple and B-activated Al-Bronze specimens sintered in solid state at 550°C.

Pressure of compacting in tonne/sq.cm. \ Sintering time in hrs.	Simple Al-Bronze				B-activated Al-Bronze			
	0.5	1.0	5.0	10.0	0.5	1.0	5.0	10.0
3.82	54 ± 10	56 ± 5	56 ± 14	54 ± 7	43 ± 3	53 ± 8	45 ± 5	52 ± 3
5.09	75 ± 3	73 ± 3	71 ± 6	66 ± 8	61 ± 6	63 ± 8	60 ± 10	62 ± 8
6.36	81 ± 19	80 ± 8	81 ± 7	73 ± 7	67 ± 6	76 ± 10	73 ± 5	67 ± 9

TABLE VII - Variation of hardness (V.P.N. of simple and B-activated Al-Bronze specimens sintered in presence of liquid phase at 700°C.

Sintering time in hrs. / Pressure of compacting in tonne/sq.cm.	Simple Al-Bronze					B-activated Al-Bronze				
	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
3.82	66 ± 7	67 ± 9	56 ± 6	68 ± 8	64 ± 2	57 ± 11	44 ± 2	46 ± 12	55 ± 13	46 ± 2
5.09	81 ± 7	69 ± 16	75 ± 9	81 ± 6	86 ± 9	58 ± 10	54 ± 3	60 ± 8	44 ± 10	58 ± 14
6.36	109 ± 26	91 ± 11	81 ± 15	99 ± 19	92 ± 4	63 ± 10	53 ± 5	54 ± 22	51 ± 9	74 ± 16

IV.2.1 Hardness of solid phase sintered specimens

Hardness values (in V.P.N.) of simple aluminium bronze sintered at 550°C for various periods are shown in Fig. 6. A slight decrease in hardness occurs in the initial stage in case of samples compacted at 5.09 and 6.36 tonne/sq. cm. pressures and then it remains constant almost upto 5 hrs. of sintering. Further a slight decrease in hardness has been noted in the last stage of sintering. The hardness values of samples compacted at 3.82 tonne/sq.cm. pressure remain almost constant at 55 V.P.N. throughout the sintering period of 10 hrs. Hardness level in general is high in case of samples compacted at higher pressures.

Hardness values (in V.P.N.) of boron added aluminii bronze sintered at 550°C for various periods are shown in Fig. 7. Here a slight increase in hardness in initial stage of sintering was noted in all the three types of samples, but hardness goes down beyond 1 hr of sintering. Samples compacted at 6.36 tonne/sq.cm. pressure show a further drop in hardness beyond 5 hours of sinterigg. Whereas in samples compacted at 3,82 and 5.09 tonne/sq.cm. pressure, a slight increase in hardness beyond 5 hour of sintering was observed

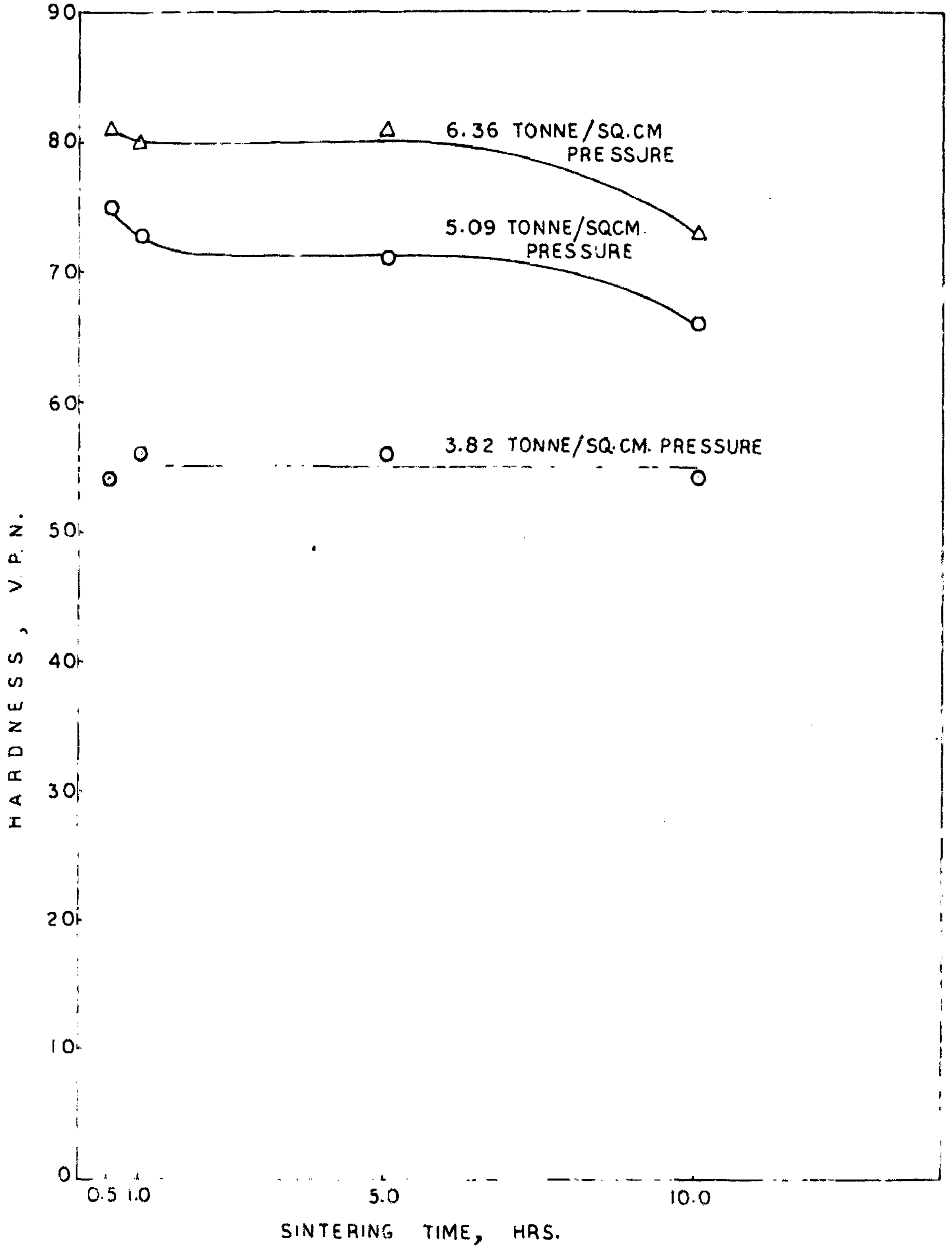


FIG. 6. HARDNESS VARIATION OF SIMPLE Al-BRONZE SPECIMENS DURING SOLID PHASE SINTERING AT 550 °C.

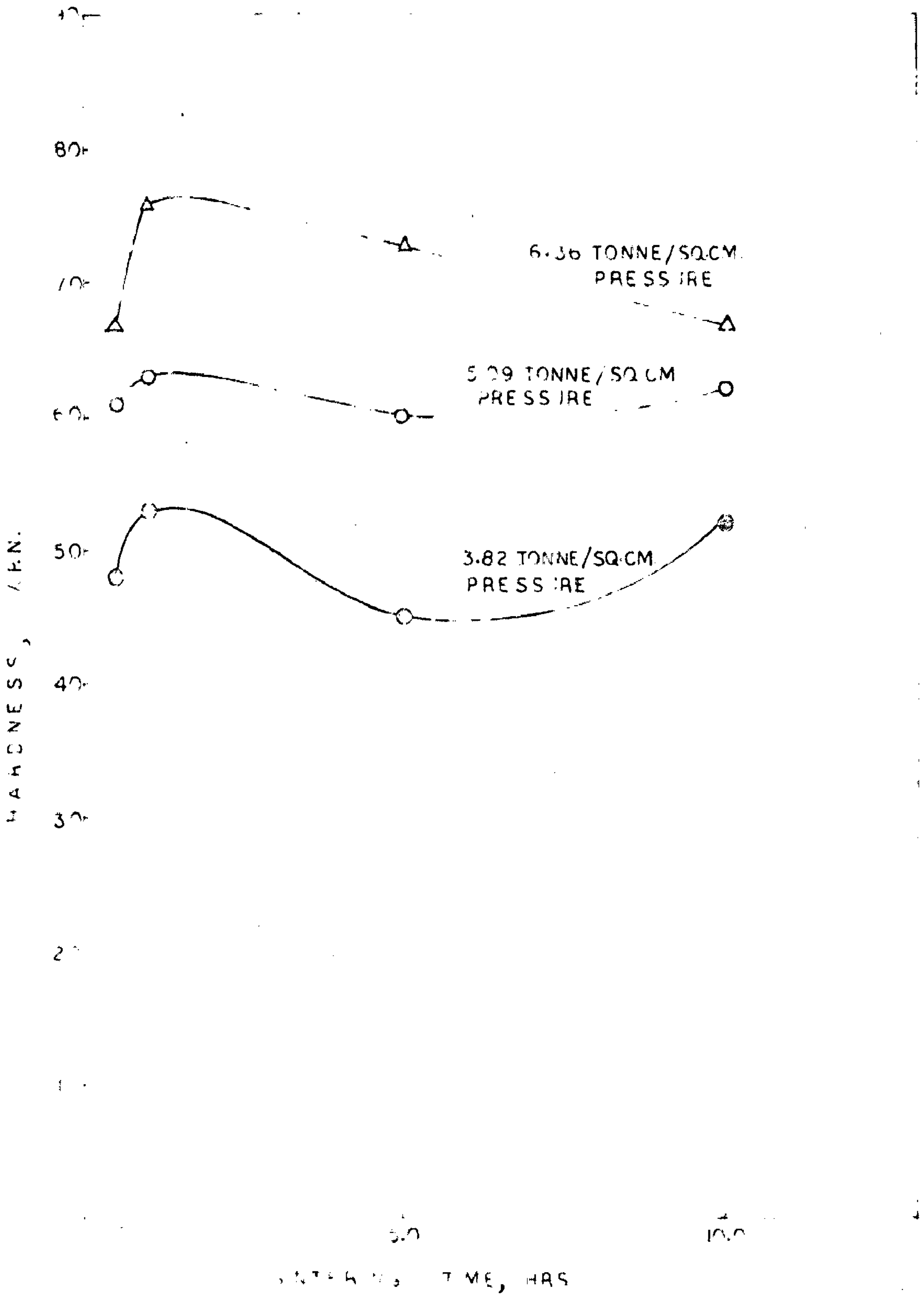


FIG. [illegible] HARDNESS VARIATION OF B- ADDED AL-BRONZE SPECIMENS DURING SOLID PHASE SINTERING AT 550 °C

IV.2.2 Hardness of liquid phase sintered specimens

Hardness values (in V.P.N.) of simple aluminium bronze sintered at 700°C for various periods are shown in Fig. 8. Here in the initial stages of sintering the hardness values were found to be very high in all the three types of samples, but the hardness drops rapidly as sintering proceeds further. After 1 to 1½ hour of sintering an increasing trend in hardness values has been found in all the samples. In general, we observe that the hardness curves are of U-shape in all the three cases.

Hardness values (in V.P.N.) of boron added aluminium bronze sintered at 700°C for various periods are shown in Fig. 9. The nature of hardness curves shown in Fig. 9 is similar to that of Fig. 8. Thus we find that the hardness level of liquid phase sintered simple aluminium bronze is highest in comparison to others. In general Boron added aluminium-bronze is showing lower hardness values as compared to the simple aluminium bronze if sintered under similar conditions.

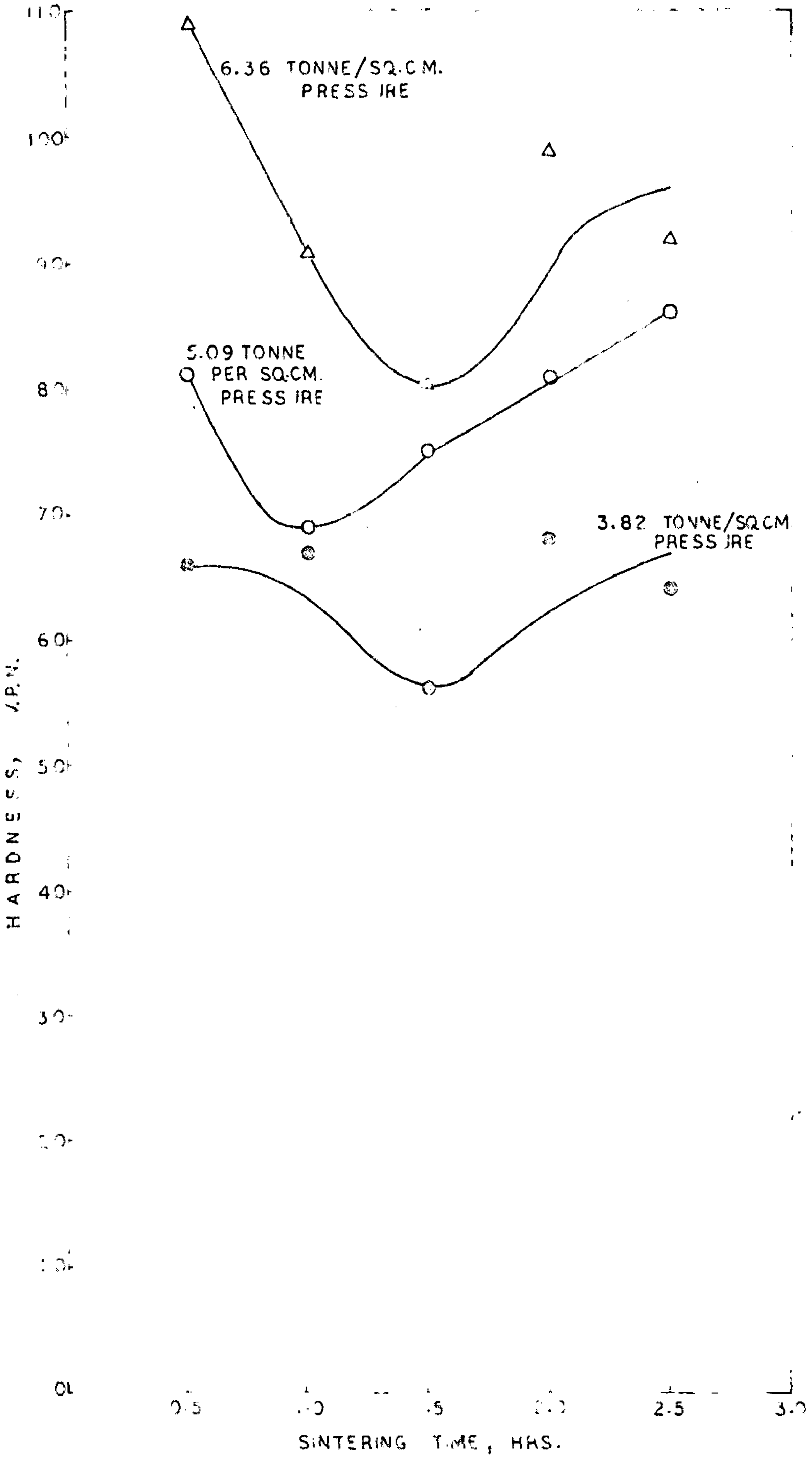


FIG. 8. HARDNESS VARIATION OF SIMPLE Al-BRONZE SPECIMENS DURING LIQUID PHASE SINTERING AT 700 °C

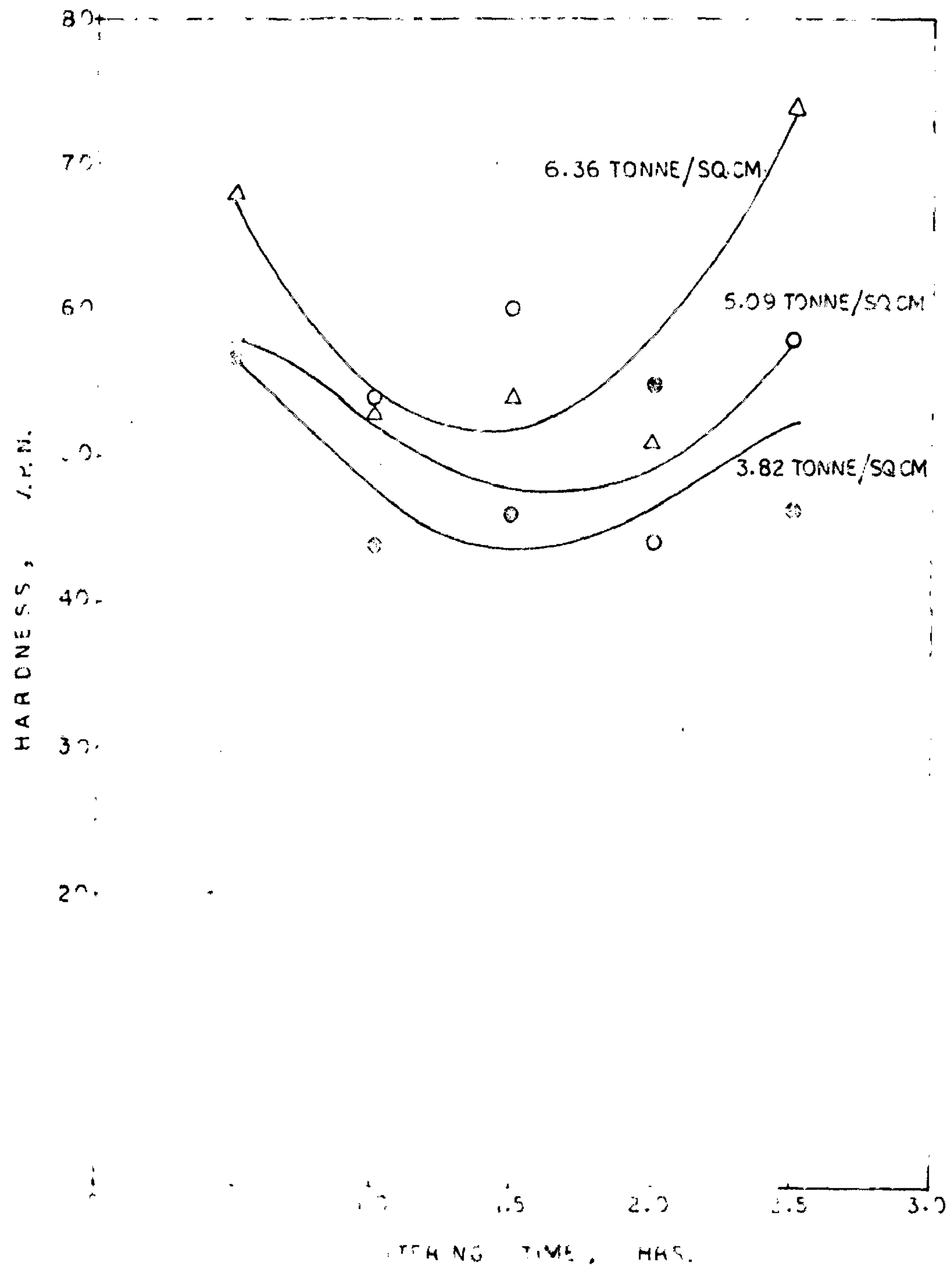


FIG. 5 HARDNESS VARIATION OF B-ADDED AL-BRONZE SPECIMENS DURING LIQUID PHASE SINTERING AT 700 °C.

Though the nature of the hardness curves for compacts sintered at 700°C is almost similar for simple as well as for boron added aluminium bronze, but the level of hardness is low in the boron added bronze.

The nature of the hardness curves for specimens sintered at 550°C is not similar for simple and boron added aluminium bronze. In the case of simple aluminium bronze the hardness goes down initially whereas it increases in boron added aluminium bronze. The hardness level in both cases is not much different from the other.

IV.3 MICROHARDNESS

Microhardness results of some selected sintered compacts of simple aluminium bronze and boron added aluminium bronze are given in Tables VII & IX respectively.

IV.3.1 Microhardness ~~result~~ of solid phase sintered sintered specimens

Microhardness results of solid phase sintered specimens, corresponding to 6.36 tonne/sq.cm. pressure of simple aluminium bronze are shown in Fig. 10. The level of microhardness values of copper rich region is quite higher

Region / Sintering time in hrs.	Simple Al-Bronze			B-activated Al-Bronze		
	0.5	5.0	10.0	0.5	5.0	10.0
Copper rich	105 ± 7	94 ± 7	95 ± 11	75 ± 11	70 ± 14	75 ± 8
Aluminium rich	38 ± 1	43 ± 2	68 ± 6	53 ± 7	93 ± 12	78 ± 10

Table VIII - Variation of microhardness (kg/mm^2) of simple and B-activated Al - Bronze specimens (Corresponding to 6.36 T/sq.cm. compacting pressure) sintered in solid state at 550°C.

TABLE IX - Variation of microhardness (kg/mm^2) of simple and B-activated Al-Bronze specimens corresponding to 6.36 tonne/sq.cm. Compacting pressure sintered in liquid phase at 700°C.

Region / Sintering time in hrs	Simple Al-Bronse			B-actuated Al - Bronze Specimens					
				Outer surface			~~Inner surface~~ Interior		
	0.5	1.5	2.5	0.5	1.5	2.5	0.5	1.5	2.5
Copper rich	54 ± 2	53 ± 12	61 ± 3	72 ± 4	74 ± 12	75 ± 7	77 ± 8	98 ± 5	87 ± 6
Aluminium rich	113 ± 31	116 ± 16	135 ± 54	104 ± 5	115 ± 24	138 ± 19	125 ± 15	167 ± 20	163 ± 2

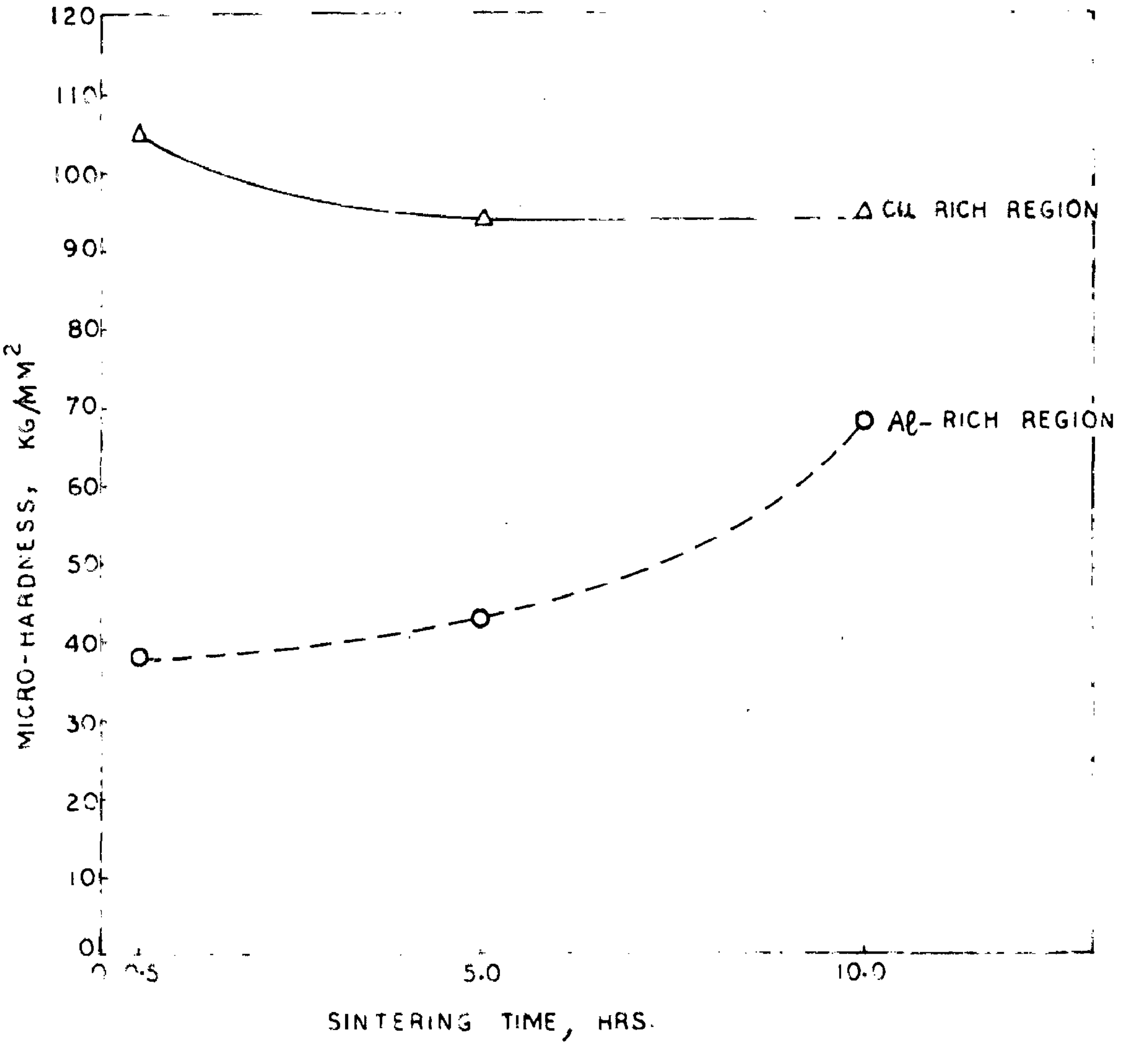


FIG. 10. MICROHARDNESS VARIATION DURING SOLID PHASE SINTERING OF SIMPLE Al-BRONZE SAMPLES COMPACTED AT 6.36 T/SQ.CM. PRESSURE.

than that of aluminium rich region. The microhardness of copper rich region in initial stages of sintering decreases from 105 kg/mm^2 to 94 kg/mm^2 and then remains almost constant. The microhardness of aluminium rich region, which is quite low (38 kg/mm^2) initially, continuously increases first with slower rate and in the later stages with faster rate and finally reaches a level of 68 kg/mm^2. Thus a large difference of about 67 kg/mm^2 in microhardness values, which existed initially between the two regions, has reduced to only 27 kg./mm^2 in the last stage of sintering.

Microhardness results of boron added aluminium bronze compacts corresponding to 6.36 tonne/sq.cm. pressure, sintered at 650°C for various durations are shown in Fig.11. Although in the initial stage of sintering the microhardness values of copper rich region are higher (about 17 kg/mm^2) than the aluminium rich region, in the intermediate stage the microhardness of aluminium rich region goes upto 93 kg/mm^2 and that of copper rich region goes down to 70 kg/mm^2. At a later stage of sintering the hardness of copper rich region

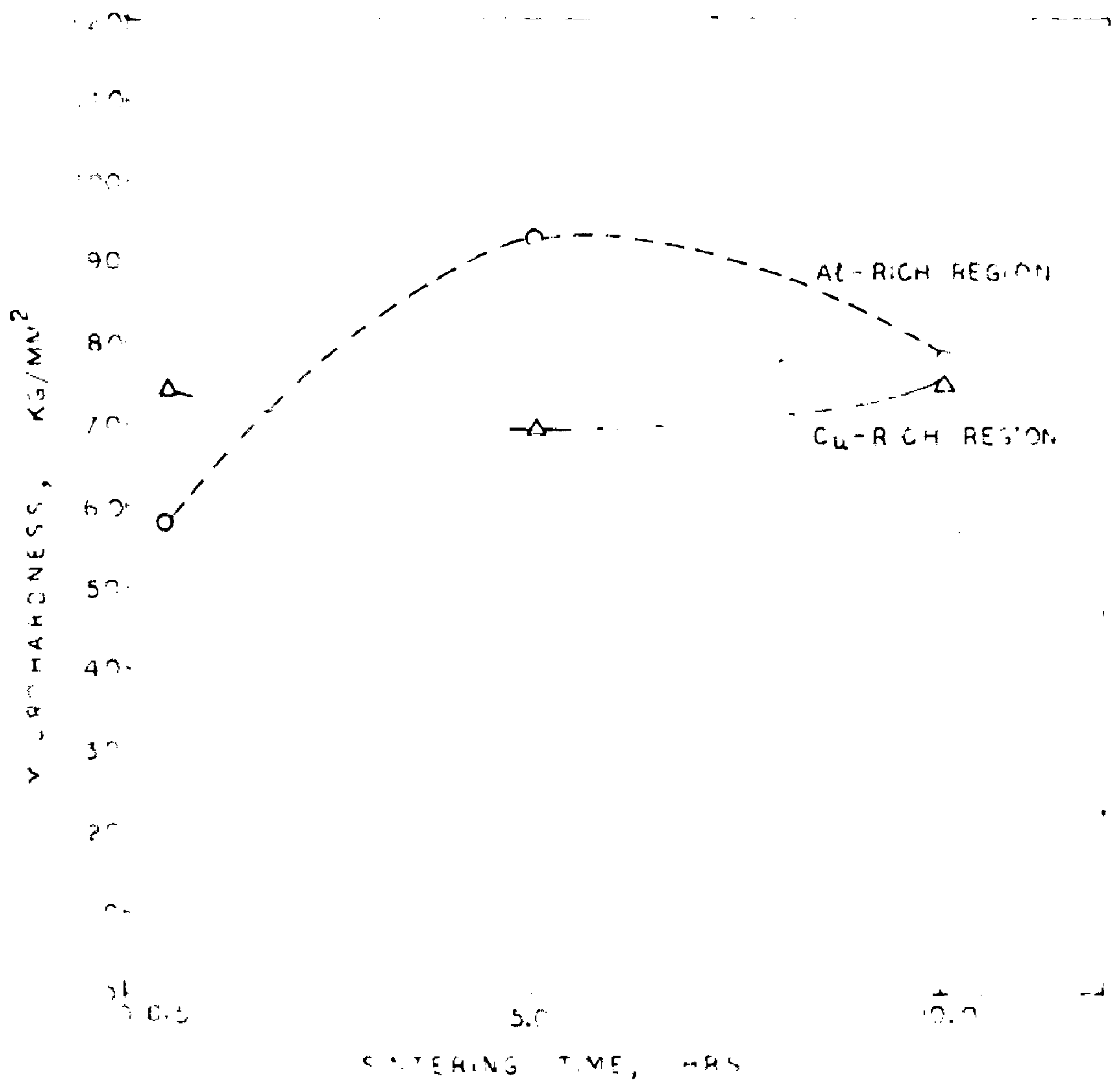


FIG. 11. MICROHARDNESS VARIATION DURING SOLID PHASE SINTERING OF B-ADDED Al-BRONZE SAMPLES COMPACTED AT 6.36 T/SQ.CM PRESSURE.

increases slowly and that of aluminium rich region decreases rapidly and consequently in the end of sintering i.e. after 10 hours, the microhardness of both the regions are almost the same.

IV.3.2 Microhardness of liquid phase sintered specimens.

Microhardness results of simple aluminium bronze compacts, corresponding to 6.36 tonne/sq.cm. pressure, sintered at 700°C for various durations are shown in Fig. 12 Here the microhardness level of copper rich region is about 60 to 70 kg/mm^2 lower than the aluminium rich region. The microhardness of both copper and aluminium rich regions increases with sintering time although with different rates.

Microhardness values of the outer surface and of the interior of the specimens (boron added aluminium bronze) obtained by sectioning are shown in Fig. 13 and 14 respectively.

In both the cases the level of hardness of copper rich region is much lower than that of aluminium rich region

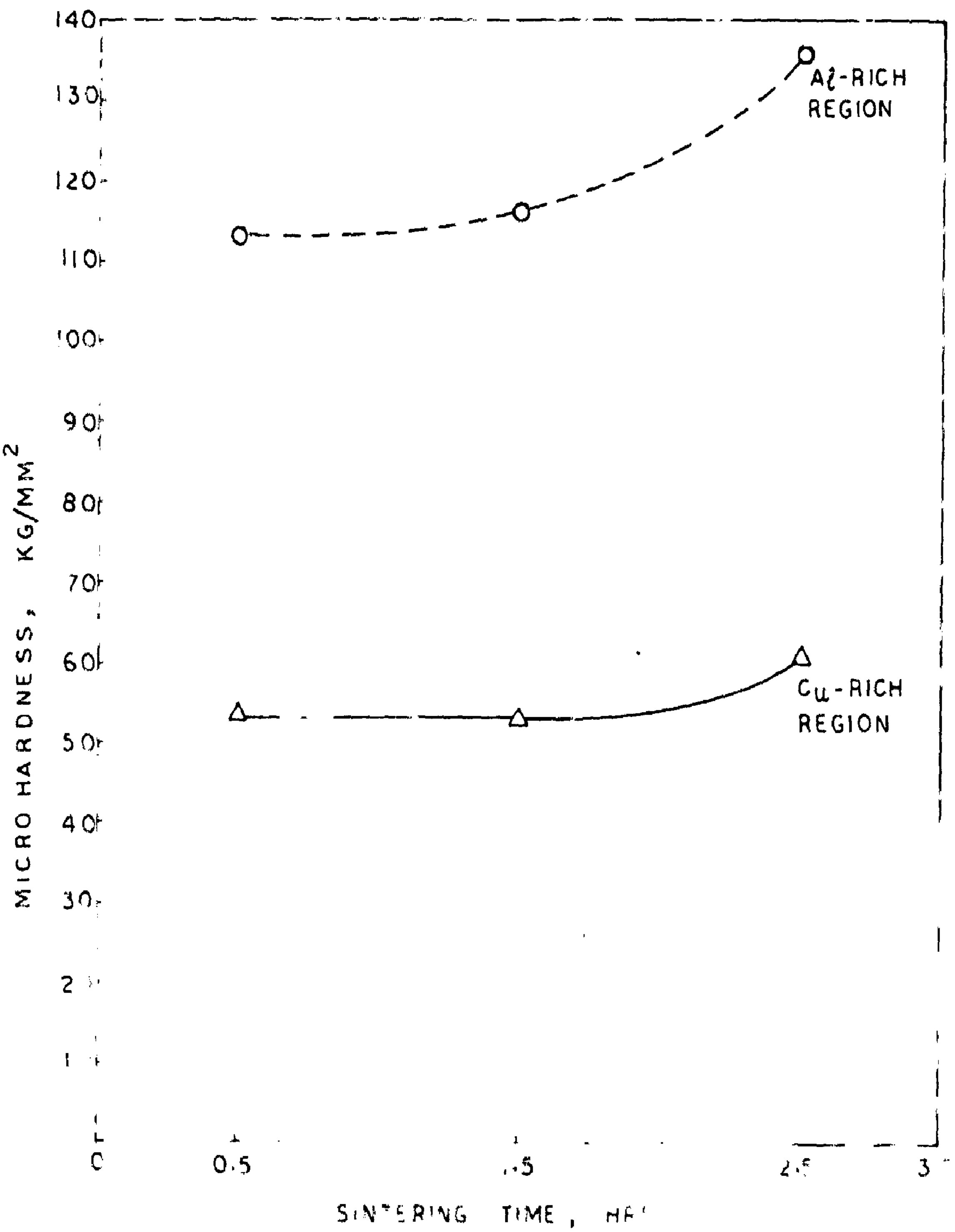


FIG. 12. MICROHARDNESS VARIATION DURING LIQUID PHASE SINTERING OF SIMPLE AL-BRONZE SAMPLES COMPACTED AT 6.36 T/SQ CM PRESSURE.

which increases with sintering time.

Fig. 13 shows that the hardness of both the regions increases continuously upto the end of sintering, but at a faster rate in the case of aluminium rich region, whereas very slowly in case of copper rich region.

Fig. 14 shows that the microhardness of both regions first increases and then decreases with sintering time. Here also the rate of hardness increase of aluminium rich region is faster than the other region. The rate of fall of microhardness observed during the later stage of sintering is almost equal for both the curves.

IV.4 MICROSTRUCTURE

Microphotographs of simple and boron added aluminium bronze compacts, corresponding to 6.36 tonne/sq. cm. pressure, sintered at 550°C for various periods are shown side by side in Fig. 15 (a, b and c).

It is evident from Fig. 15 (left) that there is no detectable change in microstructure with sintering time. Only in the later stages of sintering, some smaller

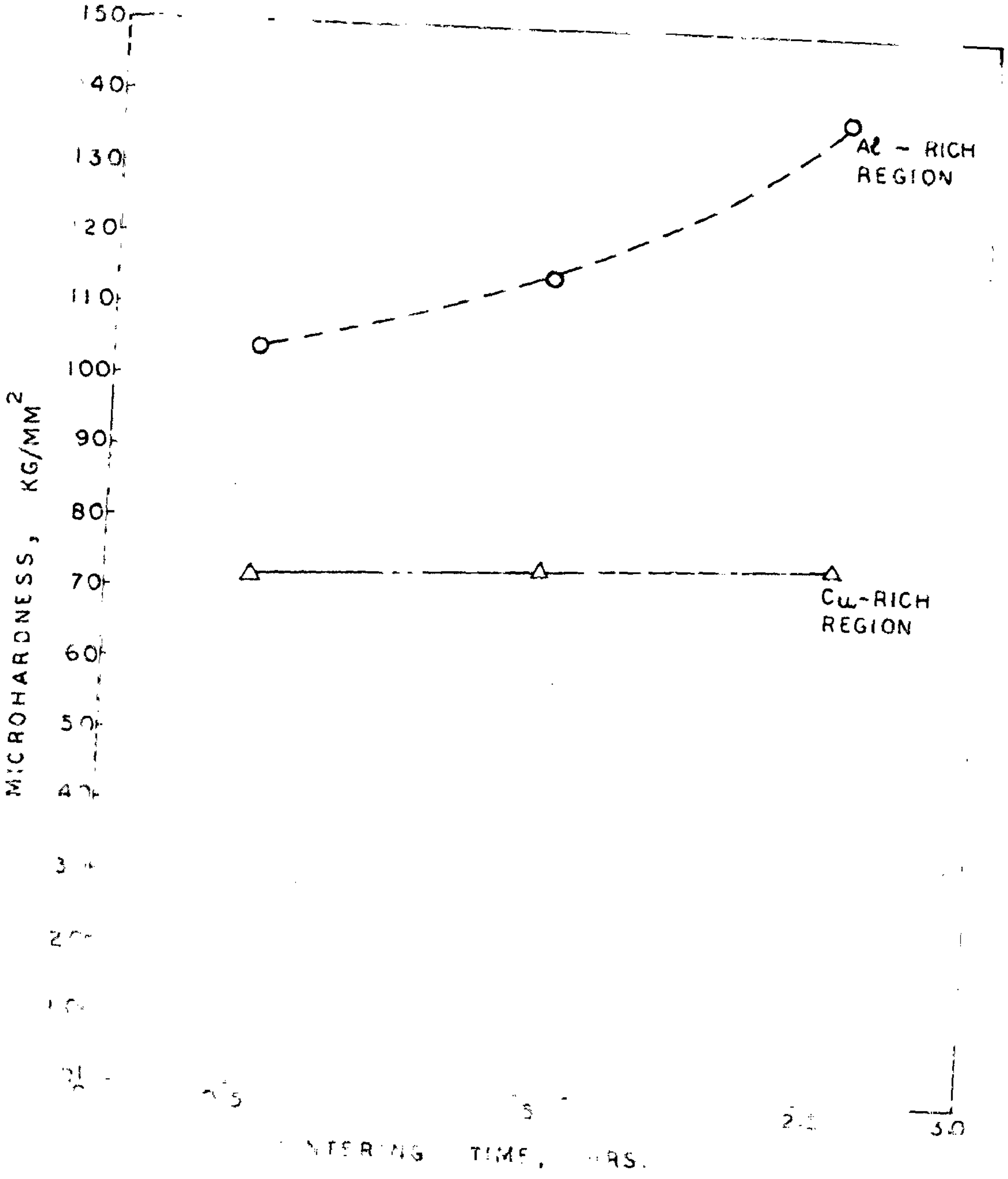


FIG [illegible] MICROHARDNESS VARIATION DURING LIQUID PHASE SINTERING OF B-ADDED AL-BRONZE SAMPLES COMPACTED AT 0.36 [illegible] PRESSURE.

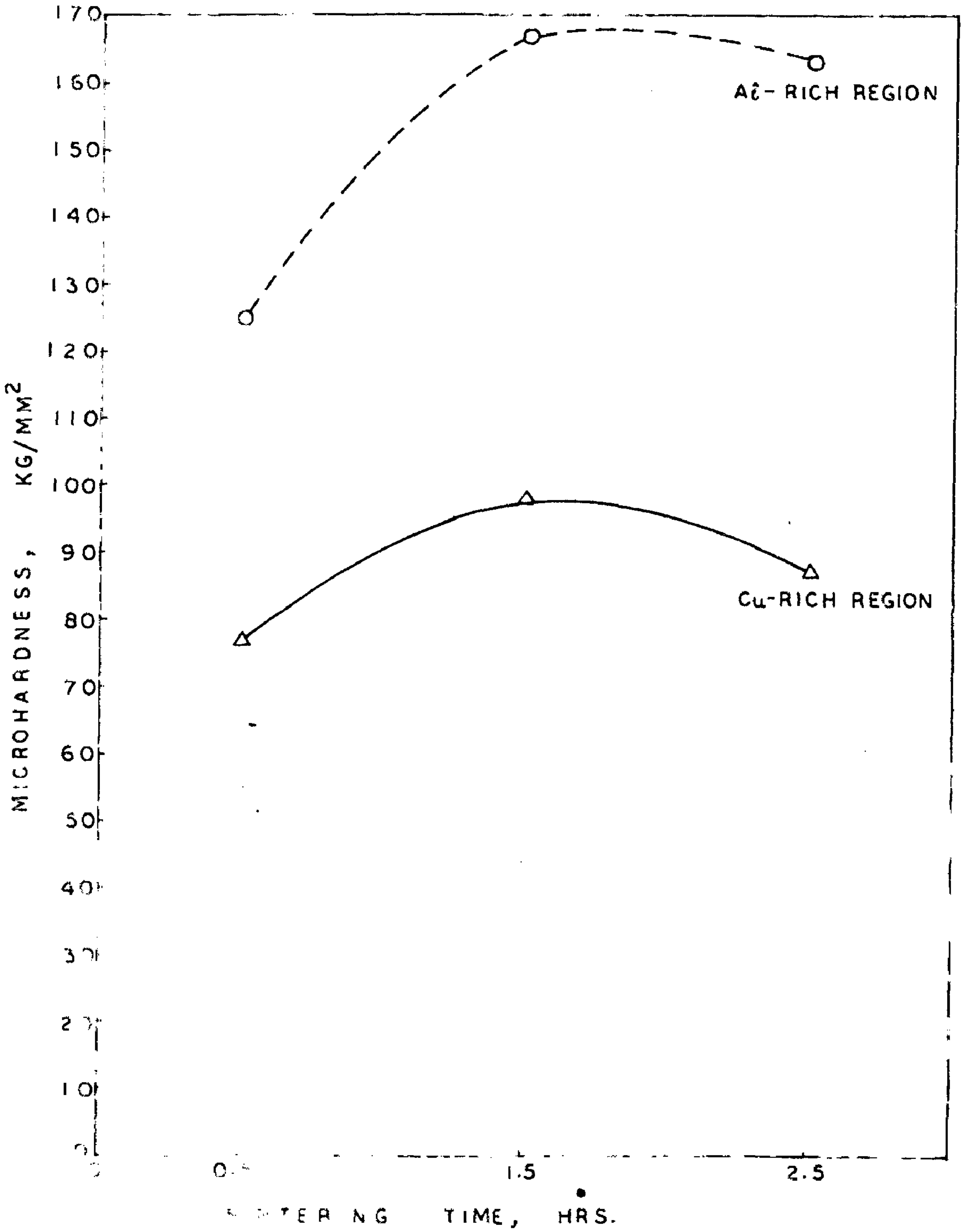


FIG. [illegible] MICROHARDNESS VARIATION IN THE INTERIOR DURING LIQUID PHASE SINTERING OF B-ADDED AL-BRONZE SAMPLES COMPACTED AT 5.36 T/SQ.CM. PRESSURE.

which increases with sintering time.

Fig. 13 shows that the hardness of both the regions increases continuously upto the end of sintering, but at a faster rate in the case of aluminium rich region, whereas very slowly in case of copper rich region.

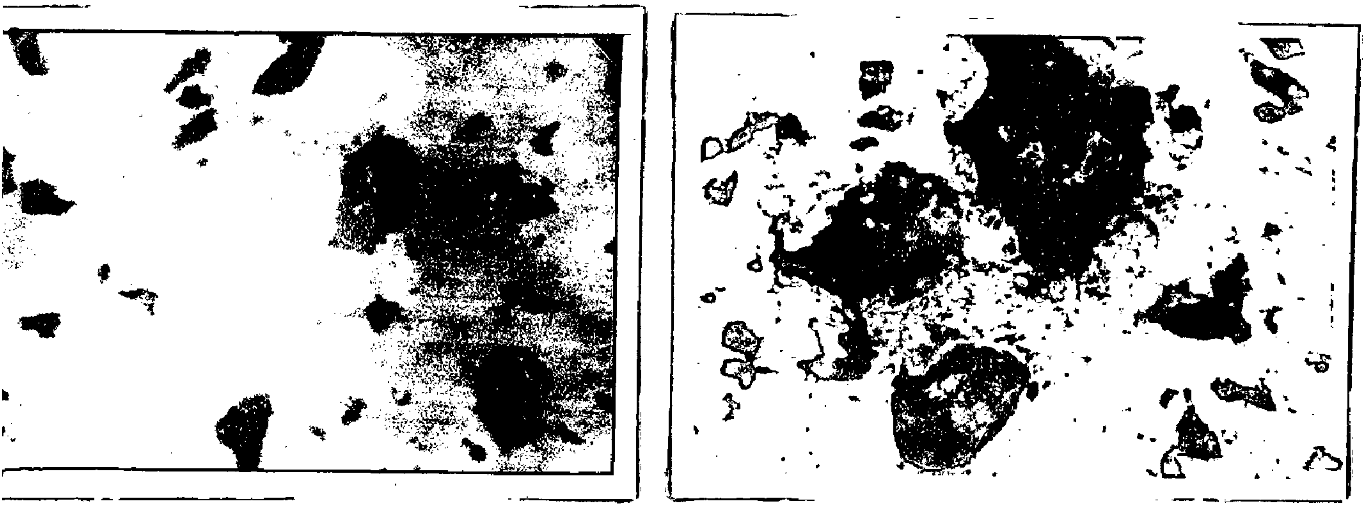
Fig. 14 shows that the microhardness of both regions first increases and then decreases with sintering time. Here also the rate of hardness increase of aluminium rich region is faster than the other region. The rate of fall of microhardness observed during the later stage of sintering is almost equal for both the curves.

IV.4 MICROSTRUCTURE

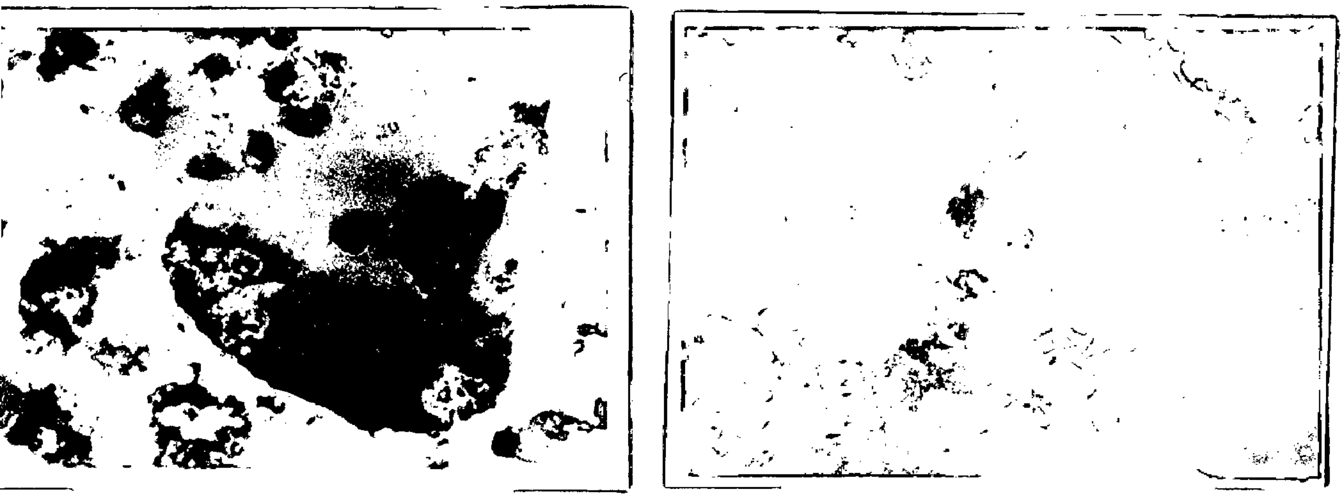
Microphotographs of simple and boron added aluminium bronze compacts, corresponding to 6.36 tonne/sq. cm. pressure, sintered at 550°C for various periods are shown side by side in Fig. 15 (a, b and c).

It is evident from Fig. 15 (left) that there is no detectable change in microstructure with sintering time. Only in the later stages of sintering, some smaller

(a) SINTERING TIME 1/2 HOUR



(b) SINTERING TIME 5 HOURS



(c) SINTERING TIME 10 HOURS

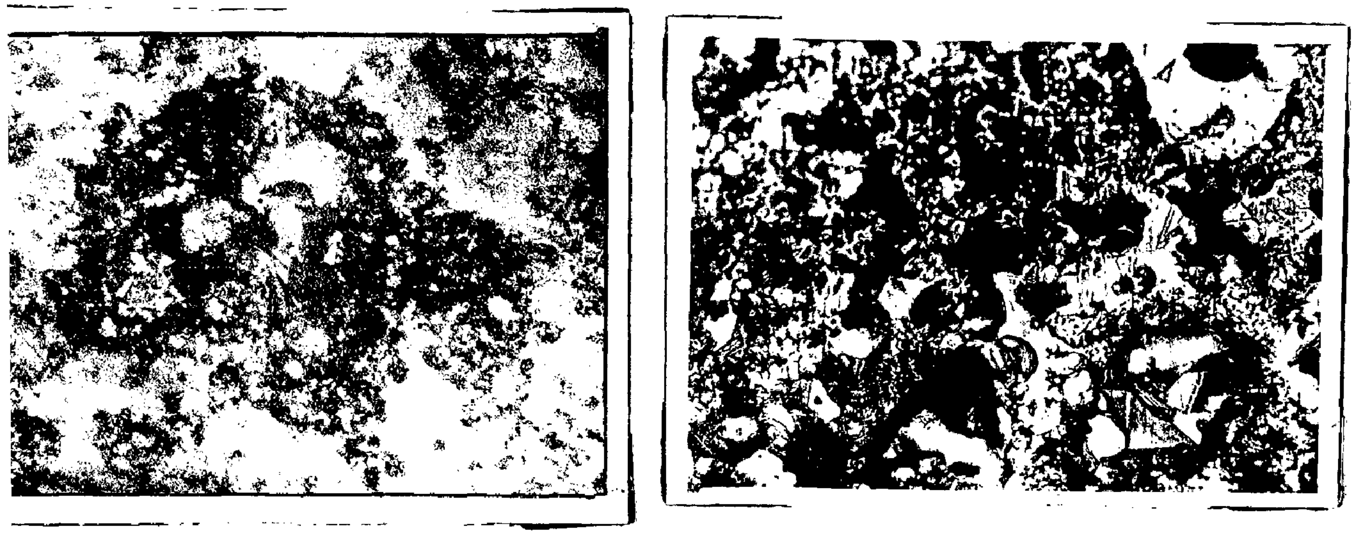
. 15. MICROSTRUCTURES OF SOLID PHASE SINTERED 7% Al-BRONZE AT 550° C FOR SIMPLE (LEFT) AND B-ADDED (RIGHT) SAMPLES AT DIFFERENT SINTERING PERIODS (X 250) aluminium particles are showing a change in their etching behaviour.

The microphotographs on the right of Fig. 15 (a, b and c) reveal that in the initial stages of sintering only very fine aluminium particles are prone to alloying, which is manifested by distinction in the etching behaviour. The alloying tendency is naturally more in case of compacts sintered for longer ~~terms.~~ times From Fig. 15(b, c) (right) it is evident that there is a sort of rim formation around the aluminium particles, suggesting the solid solution formation. But in case of fine aluminium particles this tendency is so great that it is difficult to identify the same from the copper matrix. At the same time it is observed that around all boron particles a dark region is present.

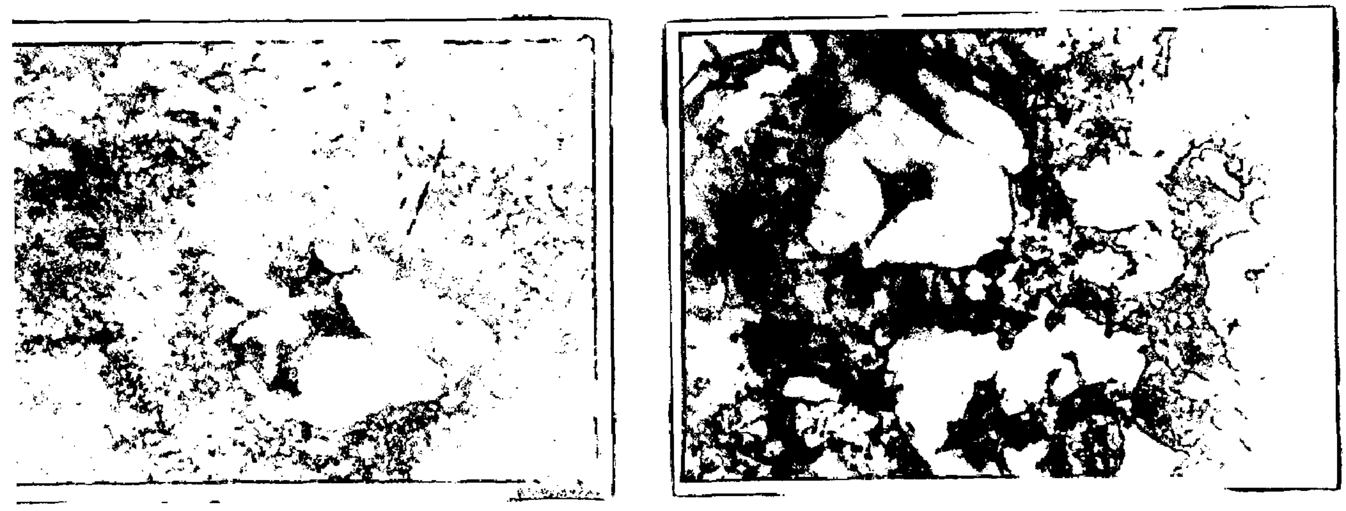
Microphotographs of simple and boron added aluminium bronze compacts corresponding to 6.36 tonne/sq.cm. pressure, sintered at 700°C for various periods are shown side by side in Fig. 16 (a, b, c).

It is obvious that the aluminium particles have lost their individual identity. Fig 16(a)(left) shows two

(a) SINTERING TIME 1/2 HOUR



(b) SINTERING TIME 1½ HOURS



(c) SINTERING TIME 2½ HOURS

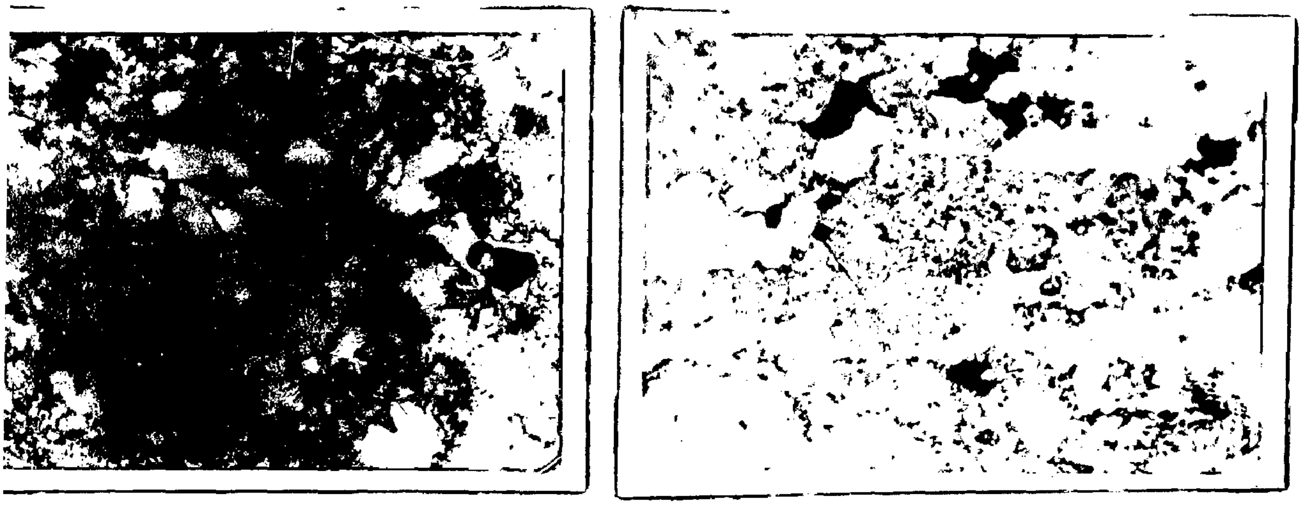
. 16. MICROSTRUCTURES OF LIQUID PHASE SINTERED 7% Al-BRONZE AT 700° C FOR SIMPLE (LEFT) AND B-ADDED (RIGHT) SAMPLES AT DIFFERENT SINTERING PERIODS (X 250) distinct regions - one darker and the other lighter in shade. The darker region is around the site of aluminium particles in the green compact and the lighter one is copper rich region.

In the case of boron added aluminium bronze [Fig. 16(a, b, c) (~~left~~ Right)] we find one marked difference that the porosity is much more as compared to simple aluminium bronze [Fig. 16(a, b, c) (left)] sintered under the same conditions.

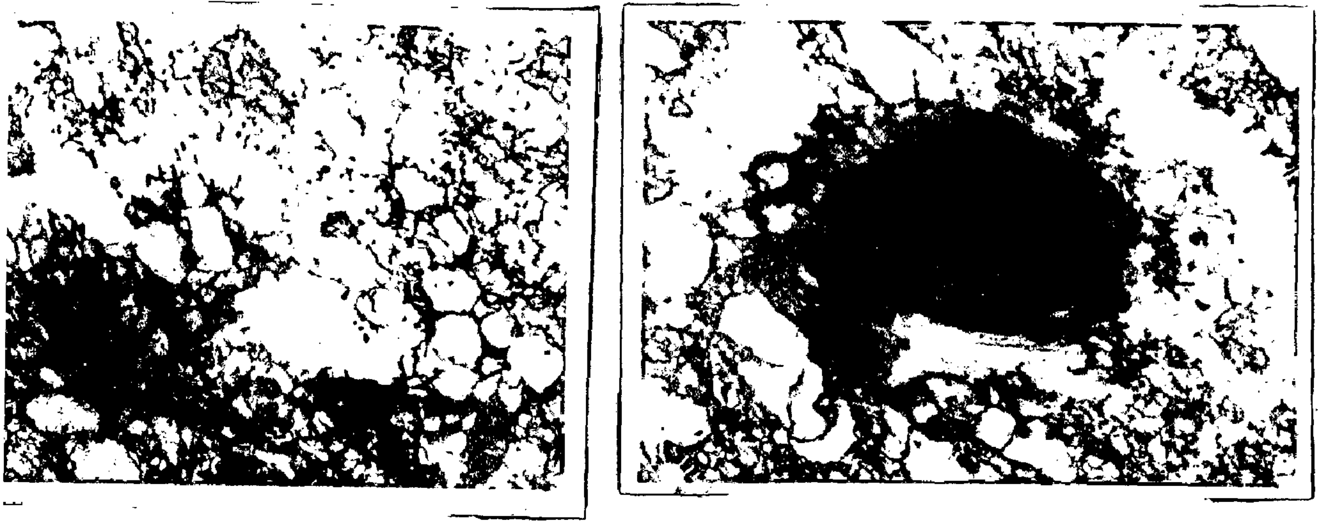
In general homogenisation is more in the case of boron added aluminium bronze.

Microphotographs of the interior of the liquid phase sintered compacts of simple and boron added aluminium bronze are shown in Fig. 17(a, b, c). The comparative study of these microphotographs showed the following features :-

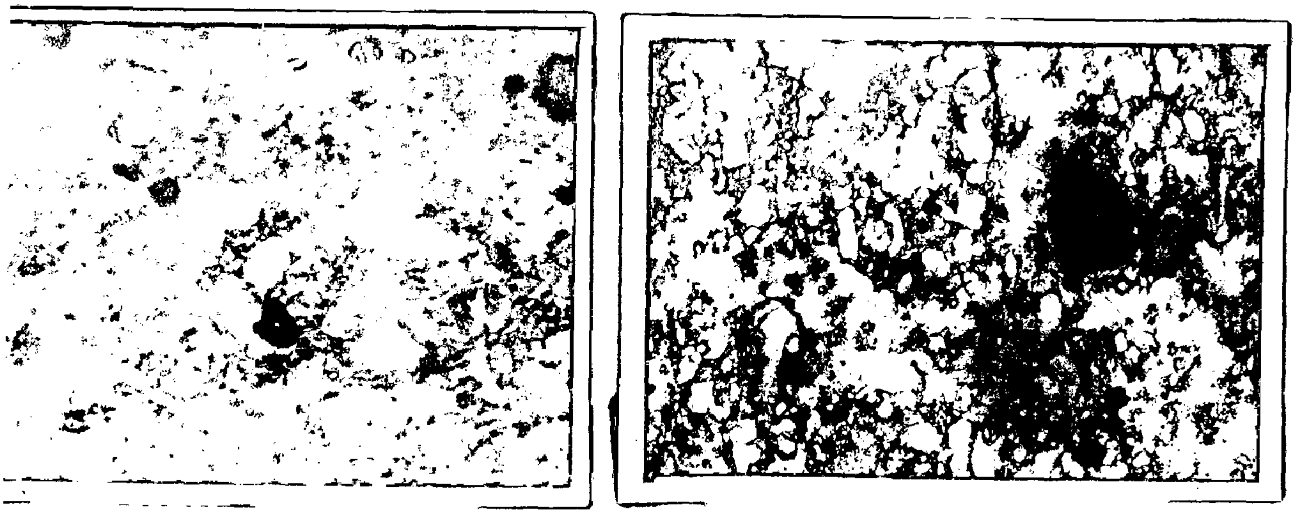
~~(i) Porosity in the interior is comparatively more in the boron added aluminium bronze.~~



(a) SINTERING TIME 1/2 HOUR



(b) SINTERING TIME 1½ HOURS



(c) SINTERING TIME 2½ HOURS

17. MICROSTRUCTURES OF THE INTERIOR OF LIQUID PHASE SINTERED 7% Al-BRONZE AT 700° C FOR SIMPLE (LEFT) AND B-ADDED (RIGHT) SAMPLES AT DIFFERENT SINTERING PERIODS (X 200)

(i) Porosity in the interior is comparatively more in the boron added aluminium bronze;

(ii) Homogenisation is more in case of boron added aluminium bronze than the simple aluminium bronze; and

(iii) If we compare the amount of porosity present in the interior [Fig. 17(a, b, c) (Right)] with that of the exterior [Fig. 16(a, b, c) (right)] of the liquid phase sintered compacts of boron added aluminium bronze, we find that at the outer surface the amount of porosity is much more than the interior.

7.5 X-RAY STUDIES

As previously reported the X-ray patterns for the ntered specimens were taken and an attempt was made to find e relative changes in the lattice parameter with respect to ntering variables. The expected lattice parameter for 100% mogenised structure of 7% aluminium bronze is 3.77 Å(76) whereas the lattice parameter of pure copper is 3.60 Å(75). This consequently means a percentage shift of line position in the X-ray patterns would be 4.74 for 100% homogenised alloy (7% aluminium bronze), whereas the % error expected in the measurement of line positions is about 2. As far as the present sintered samples are concerned, the extent of homogenisation is not more than 20 to 25%. Thus it is obvious that the % shift in these samples will not be more than 2% in any case. Since the % shift being of the same order as that of % error, no concrete conclusion could be drawn regarding the line shift/lattice parameter with respect to different sintering variables.

It was also found inadequate to assess qualitatively the relative changes in the intensity of the different lines of the pattern with respect to sintering variables as the large X-ray exposure time was involved and in this duration very large power fluctuations in the X-ray generator were noticed. However, line broadening was noticed in the patterns of sintered specimens indicating that the lattice was heavily deformed as a result of residual compacting stresses and perhaps due to the inter diffusion of copper and aluminium in each other.

CHAPTER - V

DISCUSSION

During the sintering of two component mixture in our case copper and aluminium one has to note the following important features :-

(i) Aluminium bearing higher coefficient of thermal expansion than copper will definitely cause some overall expansion of the specimen which may or may not be compensated during sintering.

(ii) Aluminium being lower melting constituent than copper, the structural changes in aluminium rich regions would be evident at an earlier stage of sintering, whereas the changes in copper rich regions for the same sintering period may not be observed.

(iii) The overall mechanical properties of the specimen would basically depend on the actual amount and nature of porosity and so also for the various phases present in the system.

(iv) In order to understand the interaction between the components and hence the mechanism of sintering, effect of presence of porosity must be eliminated as far as possible.

(v) Any third addition in the binary system might alter the reaction rate between copper and aluminium and hence will produce changes in all the properties related with this reaction. It may also alter the sintering characteristics at the surface and interior of the specimen.

While discussing the various results obtained an attempt will be made to correlate all these features in order to assess an overall performance of this system during sintering.

It is evident from Fig. 1 to 4 that there is an overall volume expansion instead of contraction at both sintering temperatures (i.e., 650°C and 700°C) in the binary system under investigation. The cause of volume expansion may be,

(i) Due to escape of entrapped gases, if any;

(ii) Due to expansion caused by more and more alloying;

(iii) Due to large difference in values of intrinsic diffusivities of aluminium and copper, the diffusion rates of aluminium and copper atoms vary very widely and therefore causes the development of additional pores in the structure by coagulation of newly formed vacancies just similar to that observed in Kirkendall effect.

(iv) Due to the difference in the coefficient of thermal expansion of the components, presently aluminium and copper at the sintering temperatures.

SOLID STATE SINTERING

Since all the specimens of simple aluminium bronze show regular volume expansion during solid state sintering (Fig. 1) and as such is never compensated during the entire sintering period, it is very likely that this volumetric expansion takes place before the sintering starts. The idea of such an expansion is further supported by large difference in linear coefficients of thermal expansions* of aluminium

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*Coefficient of linear thermal expansion
of aluminium at 20°C = $23.6 \times 10^{-6}/^{\circ}C$

" " 550°C = $27.7 \times 10^{-6}/^{\circ}C$

Coefficient of linear thermal expansion
of copper at 20°C = $16.5 \times 10^{-6}/^{\circ}C$

(Data from - Metals Hand Book Vol. I, 8th edition; A.S.M. 1962) and copper. Volume expansion due to the escape of entrapped gases is ruled out for all practical purposes, as the entrapped gases have been removed by heating the specimens at 250°C under vacuum for 1 hr.

Considering that each aluminium particle pushes the neighbouring copper particles away from their original sites occupied in the green compact to the new sites in the sintered specimen during sintering and that the copper particles get sintered at least partially, in these new sites as a result of thermal diffusion during sintering, a net expansion of specimen would be resulted. On cooling the specimen after completion of sintering, the contraction of all the particles would occur without causing any shift in their positions. Thus overall volume expansion in the sintered specimens is expected.

It is possible to develop a model based on volumetric thermal expansion data with following assumptions.

(i) Cumulative volumetric thermal expansion of all the individual aluminium particles present in a specimen is equal to the net volume expansion of the equivalent volume of aluminium.

(ii) All the aluminium particles remain fixed in their original sites, while copper particles shift their positions as a result of relative expansion caused by a nearby aluminium particle.

(iii) On cooling the specimen after sintering, copper particles contract at their new sites only.

(iv) The expansion of aluminium particles is free of any constraint.

Thus with the help of these assumptions theoretical values of volume expansion for each specimen were calculated and are given in Table X.

Theoretical values of volume expansion of specimens keeping in view the above assumptions were plotted against the weight of the specimen and shown in Fig. 18. In the same figure actual expansion values of various specimens have also been plotted. While comparing the theoretical and experimental values of volume expansion following facts are evident.

(1) For a given compacting pressure, the curve representing actual volume expansion with respect to the weight of the specimen is a straight line similar to the theoretical curve.

TABLE X - Theoretical and Observed volume changes due to higher coefficient of thermal expansion of aluminium than copper (sinter at 550°C) for various specimens.

Pressure of compacting (~~Gms/sq~~) T/sq cm.	Sample No.	Weight of sample in gms.	Weight of Al in the sample in gms.	Theoretical volume change in cc at 550°C	Observed volume change in cc at 550°C
6.36	1	1.8734	0.131133	0.002150	0.002123
"	2	1.8573	0.130732	0.002133	0.001900
"	3	1.8333	0.120424	0.002127	0.002134
"	4	1.8631	0.130067	0.002122	0.001939
5.09	1	1.8327	0.121739	0.002149	0.00193
"	2	1.8812	0.127484	0.002079	0.00190
"	3	1.6843	0.117336	0.001328	0.00132
"	4	1.8341	0.128337	0.002094	0.00121
3.82	1	1.9305	0.132335	0.002158	0.00300
"	2	1.9357	0.135439	0.002210	0.00232
"	3	1.8634	0.130088	0.002121	0.00133
"	4	1.8233	0.127931	0.002087	0.00127

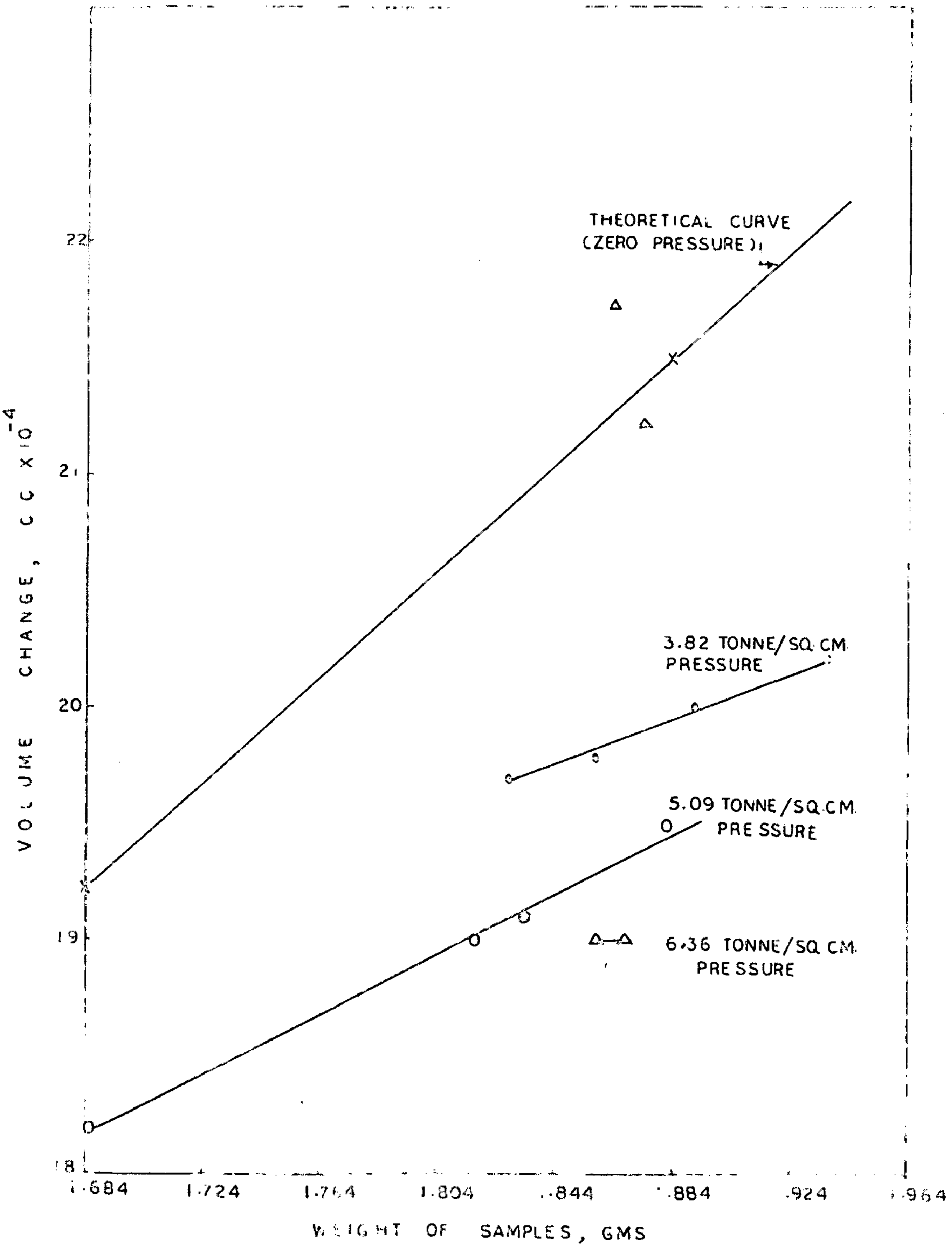

FIG. 18. THEORETICAL AND OBSERVED VOLUME CHANGES DUE TO HIGHER COEFFICIENT OF THERMAL EXPANSION OF ALUMINIUM THAN COPPER (SINTERED AT 550°C.) FOR VARIOUS SPECIMENS.

(2) In general the actual expansion of the specimen is lower than that predicted by the theoretical curve. This is obvious because the expansion of aluminium particles in compacted samples during heating is taking place under constrained conditions, whereas, in the proposed model expansion is assumed to occur freely.

(3) The expansion of specimen also decreases with increasing pressure. It is due to the fact that during the expansion of aluminium particles in compacted samples, copper particles offer more and more resistance as the compacting pressure is increased.

The initial volume expansion in the solid phase sintering of boron added aluminium bronze (Fig. 2) is again mainly due to the difference in coefficients of thermal expansion of component metals, whereas larger volume expansions at longer periods of sintering is perhaps mainly due to the enhanced rate of alloying as a result of activating effect of boron. It has been metallographically observed that a phase probably solid solution is present practically around all the aluminium particles in the boron activated samples sintered for 8 hrs and 10 hrs, whereas only negligible alloying has been noticed in the case of simple aluminium bronze samples when sintered for 10 hrs.

Thus the expansion in solid state sintering of the binary system results in,

(i) the creation of macro-porosity due to differences in coefficients of thermal expansion, and

(ii) the creation of micro-porosity due to coagulation of vacancies in the region of that component whose diffusion coefficient is comparatively more.

The porosity in general affects adversely the mechanical properties of the product. The amount, shape, size and distribution of porosities affect the macro as well as micro-hardness results. If the size and amount of porosities are large then the same will have adverse effect on macro-hardness, whereas the presence of microporosity will have comparatively more adverse influence on microhardness results.

The slight lowering of hardness (V.P.N.) in the initial stage of solid state sintering for simple Al-Bronze samples (Fig. 6) compacted at higher pressures (i.e. 5.33 and 6.33 T/sq.cm.) is perhaps mainly due to the creation of more porosity around aluminium particles caused by the unequal expansion of aluminium and copper particles. However, the lowering of hardness in the later stages of sintering (Fig. 6) for simple Al-bronze may be attributed to the relieving of work hardening effect, and perhaps due to development of microporosity in the structure as a result of differential rates of diffusion of copper and aluminium atoms.

The hardness values (in V.P.N.) of solid phase sintered boron added aluminium bronze specimens (Fig. 7) are systematically lower than those of simple aluminium bronze (Fig. 6). This is perhaps due to the creation of large amount of microporosities as a result of coagulation of vacancies in the region of that component whose diffusion coefficient is comparatively more (i.e. in copper rich region which is present in bulk amount).

The various microhardness tests were performed from the view,

(i) to correlate the volume expansion and hardness results more rationally, and

(ii) to study the beneficial effects (if any) of boron addition in the formation of alloy from the mixture of the two components viz. copper and aluminium.

The microhardness values of solid state sintered simple as well as boron added aluminium bronze (Fig. 10 and 11 respectively) suggest that the diffusion of copper in aluminium is faster than vice versa, as a very significant rise in microhardness values with sintering time have been noted in the aluminium rich regions only and at the same time in general a slight decrease in microhardness values of copper rich regions have been noted. Thus as a result of Kirkendall type of effect aluminium rich region suffers compressive stresses due to more than proportionate increase of copper atoms in its lattice, while copper rich region suffers tensile or dilational type of stresses due to coagulation of vacancies in the form of microporosity. Thus the microhardness of aluminium rich region should be obviously higher with respect to sintering time and for copper rich region it should be lower with respect to sintering time.

Although data in literature are available for the activation energy of interdiffusion of copper in aluminium(76,77,7 no such accurate data are available for aluminium into copper. Under such circumstances our explanation is based on observed results only. However, on the basis of stable electronic configuration model it is evident that copper atoms will have a tendency to donate their valence electrons to stabilise the sp^3 configuration of aluminium atoms. This seems to occur at the present temperature range, however, this process may not occur at a still higher sintering temperature.

Marked decrease in microhardness values in the copper rich regions of boron added aluminium bronze (Fig. 11) as compared to simple aluminium bronze (Fig. 10) confirms the large amount of microporosity developed probably due to enhanced rate of diffusion by the activation of boron. The extent of microporosity will depend on the difference in intrinsic diffusion coefficients. Obviously higher the difference, more will be the microporosity. This confirms that here the diffusion process is very fast and consequently alloying occurs (Fig. 18) in solid state sintering of boron added aluminium bronze.

LIQUID PHASE SINTERING

Large volume expansions in liquid phase sintered specimens (Fig. 5 and 6) is perhaps mainly due to large difference in coefficient (volume) of thermal expansion of liquid phase (mainly molten aluminium) and solid phase (copper rich solid).

The liquid phase formed at 700°C pushes the solid (copper rich) particles away to new sites. These displaced particles do not return to their original sites when the samples are cooled and consequently this phenomenon results in large overall expansion. The above analysis suggests the presence of increased porosity in the regions where originally aluminium particles were present. This is confirmed from Fig. 16 and 17.

Overall expansion is obviously higher in case of samples compacted at comparatively higher pressures because of relatively large amount of closed pores and overall less porosity available to accommodate the expanding phase (molten liquid phase of aluminium containing some amount of copper also).

Simple aluminium bronze samples compacted at 6.38 T/sq.cm. pressure have shown an increasing trend of volume expansion even after one hour of sintering period at 700°C, this is attributed mainly to more intensive alloying effect. However, the volume remains almost constant with respect to sintering time in the cases of 3.82 and 5.09 T/sq.cm. pressure compacted specimens of simple bronze (Fig. 3) and also in all the three types of compacts of boron-added aluminium bronze(Fig.4

In all the above cases the amount of porosity is obviously more, which probably accommodates the volume expansion as a result of alloying with increase in sintering time.

Comparatively more volume expansion in the case of boron added aluminium bronze (Fig. 4) than that of simple aluminium bronze (Fig. 3) may be attributed to the more volume of liquid phase formed as a result of activation effect of boron. It is quite probable that it may activate the formation of some ternary alloy (between copper, aluminium and boron) which may result in lowering of the liquidus curve of the liquid alloy formed. Thus the superheating of the liquid phase (ternary alloy) in the boron added bronze may be comparatively more than the liquid phase (binary) formed in simple bronze, thus in turn resulting in comparatively more volume of liquid phase. This superheating may also cause the higher rate of dissolution of copper in the liquid phase, which may increase the density as well as amount of the corresponding liquid phase.

The peculiar phenomenon of oozing out of liquid phase observed presently is probably due to change in wetting characteristics of the molten phase (aluminium rich) with [illegible]

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The peculiar phenomenon of oozing out of liquid phase observed presently is probably due to change in wetting characteristics of the molten phase (aluminium rich) with respect to solid phase (copper rich alloy) by the addition of boron. The spherical shape of exuded material and very small area of contact of these droplets on the outer surface, confirm that the liquid phase has developed non-wetting nature when in contact with the solid phase (copper rich alloy).

Thus due to decrease of wettability, liquid phase gets repelled from the solid surfaces. Although this nonwetting liquid phase cannot enter the interconnected porous channels on its own but owing to its increasing compressive pressure it is forced through these channels and thus whereever the liquid gets such an opportunity, it has a tendency to come out to the surface of the specimen and to solidify later on in the form of spherical drops.

Metallographic examinations have also revealed that in boron added aluminium bronze samples because of coming out of the liquid phase, a large amount of porosity exists near the outer surface (Fig. 16) in comparison to the interior of the specimen (Fig. 17). This is obvious because of lack of interconnected porosity upto the surface, the molten alloy from the interior does not come out and as such it is forced to penetrate into the local interconnected porosity as a result of expansion.

The oozed out liquid phase will be obviously rich in aluminium and thus the overall composition of the material near the outer surface of the specimen appears to be comparatively copper rich than that of the interior of the specimen.

Thus the large expansion in liquid phase sintering of simple and boron added aluminium bronze mainly results in creation of large amount of macroporosity due to the difference in coefficients of thermal expansion. The porosity in general affects very adversely the macrohardness results. Thus hardness variation with respect to sintering variables, in general, depends ~~mim~~ mainly on the following factors;

(i) Distribution, amount and nature (shape and size) of porosities present in the specimen.

(ii) Hardness of different existing phases in the specimen.

Thus much lower values of hardness in the liquid phase sintered specimens than those sintered in solid state (Fig. 8 and 9) are due to the presence of large amount of porosity as discussed earlier. This is evident from the microstructural examination (Fig. 16 and 17).

The nature of hardness curves for liquid phase sintered specimens (Fig. 8 and 9) can be mainly attributed to the alloying effect, which in turn depends on :-

(i) the type of phase or phases present in the sintered specimen,

(ii) distribution and amount of various existing phases, and

(iii) the extent of alloying or overall homogenisation

The extent of alloying and consequently homogenisation naturally increases with increase of sintering period which results in rise of hardness values. Microstructural examination also confirms this view since the amount of porosity does not increase but the extent of alloying and homogenisation at the same time has definitely increased (Fig. 16 and 17).

In addition, the hardness values of boron added aluminium bronze are comparatively lower and show an irregular pattern than the simple aluminium bronze. It may be attributed to,

(i) more expansion in the case of boron added than simple aluminium bronze which results in more porosity.

(ii) the oozing out of the liquid phase resulting in very large, irregularly distributed porosities at the outer, surface.

The presence of liquid phase naturally enhances the inter-diffusion of both components which ultimately results in more solid solution formation in the liquid phase than the solid state sintered specimens. This is evident from the microstructural studies (Fig. 15 and 16). Higher rates of increase of microhardness values of copper rich and aluminium rich regions of liquid phase sintered specimens (Fig. 12 and 13) also suggest that the rates of diffusion of both copper and aluminium have increased.

Beneficial effect of boron addition is evident from the fact that the rates of increase of hardness of Al-rich as well as that of Cu-rich regions in the outer as well as in the interior of the boron added bronze is comparatively more than the simple bronze composition.

Slightly higher rates of increase of microhardness values of Cu-rich/and Al-rich regions in the interior than the outer surface of boron added bronze is attributed to,

(i) the presence of more liquid phase in the interior than the exterior of the boron added bronze samples which enhances the diffusion phenomenon.

(ii) the presence of more aluminium in the interior than the exterior as at the surface some molten metal exudes out in each sintering operation.

CHAPTER - VI

CONCLUSIONS & SUGGESTIONS

(1) Solid state sintering of the powder mixture compacts of 7% Al and 93% copper has not yielded very encouraging results as far as the homogenisation of the structure is concerned.

(2) The liquid phase sintering is more suitable from the point of view of alloying i.e. homogenisation but this results in a product of inferior hardness within the limited period of 2½ hrs. sintering in the present case.

(3) The effect of boron has definitely increased the rate of alloying in the present system consisting of 7% Al and 93% copper, by enhancing the rate of interdiffusion in solid state as well as in the liquid phase sintering. But the boron activated sintered products are poorer in overall hardness than simple aluminium bronze. However, as a result of increased rate of homogenisation, the microhardness of the phases present in Boron added structure are of higher order than simple i.e. without boron added structure.

4. Boron has developed a sort of non-wetting characteristic in the liquid phase (Al-rich) with respect to solid phase (copper rich alloy), which is in general not beneficial as far as better sintering is concerned.

5. In general better sinterability is expected near the outer surface than the interior of the specimen, but the effect of boron addition has yielded opposite results.

Suggestions for Further Work

In selecting the components of the powder system for developing the utilisable sintered products following considerations may be made.

For better sinterability and hence better homogenisation, the diffusion rates of atoms of various components in the mixture should be approximately the same at the sintering temperature.

In general the size of all the powders should be as small as possible, particularly of the components which are to be added in smaller quantities e.g. aluminium and boron in the present case for the purpose of better sinterability.

In further investigation of this present system following points may be taken into consideration.

(i) Temperature of sintering may be selected just above the melting point of aluminium in order to reduce the overall volume expansion.

(ii) Aluminium powder finer than copper may be added.

(iii) Size of the boron must be reduced as far as possible and only screened fraction should be added. Preferably the particle size should be of the order of few microns.

(iv) Quantity of boron in liquid phase sintering may be reduced to 0.01% by weight, in order to observe the optimisation of the activation process.

... and Thomas, W., Metals and Materials, 12, 1967, 0

2. Ichinose, H., and Kuczynski, G.C., Acta. Met., 10, 1962, 209

3. Herring, C., J. Appl. Phy., 21, 1950, 437

4. Early, J.G., Lenel, F.V., and Ansell, G.S., Trans. AIME., 230, 1964, 1641.

5. Weertman, J., J. Appl. Phy., 26, 1955, 1213

6. Johnson, D.L., and Clarke, T.M., Acta. Met., 12, 1964, 1173.

7. Nichols, F.A., and Mullins, W.W., J. Appl. Phy., 36, 1965 1826.

8. Rockland, J.G.R., Acta. Met., 15, 1967, 277

9. Johnson, D.L., J. Appl. Phy., 40, 1969, 192

10. Kuczynski, G.C. and others; Acta. Met., 8, 1960, 209

11. Tikkanen, M. H., and others, Int. Jour. Powd. Met., 6(3), 1970, 43.

12. Reshamwala, A.S., and Tendolkar, G.S., Int. Jour. Powd. Met., No. 25, 13, 1970

13. Dunne, J. J., Lenel, F.V. and Ansell, G. S., Acta. Met., 1970

14. Ramkrishnan, P., and Tendolkar, G. S., Trans. Indian. Inst. Metl., 17, 1964, 115.

15. Toth, I. J., Lockington, N.A. & Perry, L.W., J. Less Common Metals, 9, 1965, 157

16. Pomacyuk, A.D., Izv Akad. Nauk SSSR Neorgan Materialy, No. 7, 1, 1965, 1008

17. Fedorchenko, I.M. and Ivanova, I.I., Poroshkovaya Met. 2, 1963, 17.

18. Duckett, R. and Robins, D.A., Metallurgia, 74(444), 1966, 163.

19. Panichkina, V.V., Poroshkovaya Met., 2, 1967, 1.

20. Dushina, O.V. and [illegible], T.V., Poroshkovaya Met., 2, 1969, 69

21. Samsonov, G.V. & Yakovlev, V.I., Poroshkovaya Met., 7, 1967.

22. Rochanwala, A.S., and Sandolkar, S.S., Powd. Met. Int., 1(2) 1969(Dec), 69.

23. Samsonov, G.V. and Yakovlev, V.I., Poroshkovaya Met., Oct 1969

24. Samsonov, G.V. & Yakovlev, V.I., Poroshkovaya Met., Jan. 1970

25. Fedorchenko, I.M. & Ivanova, I.I., Poroshkovaya Met., 1970

26. Filatova, , et.al., Poroshkovaya Met., May 1970

27. Fedorchenko, I.M., and Ivanova, I.I., Poroshkovaya Met., 1969

28. Yamaguchi, T., J. Amer. Ceram. Soc., 47, 1964, 131

29. Maruya, K. et al, Atomic Energy Soc. of Japan, 4(12), Dec. 1962 846

30. Barta, J., Pow. Met. Int., June 1970.

31. Morton, J. T., Trans. AIME, 203(1), 1966, 49

32. George E. Tardiff, Int. J. Pow. Met., 5, 1969, 89

33. Ramakrishnan, P., Powd. Met., 9(17), 1966, 47

34. Gupta, A., Current Sci (India), No. 2, 21, 1952, 39

35. Brophy, J. H. et al, "Powd Met " Interscience, 1961, 113

36. Brophy, J.H. et al, Tran. Met. Soc. AIME, 221(6), Dec 1961, 1225

37. Brophy, J. H. et al; U.S. Naval Ordnance Weapons, Final Report, AD-421, 1963, 520

38. Gatti, A., U.S. Pat., 2, 1964, 116

39. Hayden, H. W. and Brophy, J. H., J. Electrochem. Soc., 110(7), July 1963, 805.

40. Andrievskii, R. . and Fedorchenko, I.M., Metallovedenie i Term Obrabotka Metallov, No 12, Dec. 1960, 36.

41. Andrievskii, R.A., et al., Metallovedenie i Term. Obrabotka Metallov, No. 7, 1961, 49.

42. Eudier, M., "Symp. on Pow. Met., Special Report 58", Iron & Steel Inst., London, 1956, 59

43. Eudier, M., Proc. Metal Powder Assoc. 13th Meeting, 1957, 5.
44. Fedorchenko, I.M., Soviet Powder Met. & Metal Ceramics, No. 3, May-June 1962, 151.

45. Green Wood, H.W., Engineer, 199, 1955, 749.
46. Lenz, W.H. and Rundiger, P.R., J. Less Common Metals, 5(2), April 1963, 191.

47. Sonch, G.A., Powder Met., 3, 1959, 126
48. Eron, V.A., ibid, 5, 1962, 339
49. Onley, H. and Ciceron, G., Inter J. Pow. Met., 1, 1965, 16
50. Samsonov, G.V., and Verkhoglyadova, T.S., Soviet Pow. Met., 2, 1962, 93

51. Fedorchenko, I.M. and Kostyrko, O.V., Physics Metals Metallography, 12, 1960, 72

52. Murray, P., "Agglomeration" (edited by W.A. Knepper) New York and London (Inter Science Publishers), 1962, 93

53. Blackman, L.C.F., Indust. Chemist, 38, 1962, 620; and 39, 1963, 83.

54. [illegible], [illegible], Scholz, W. and Fiedler, A., ibid, 38, 1962, 820
55. McLaren, R.R., and Atkinson, R.H.W., J. Nuclear Mat., 17, 1965, 142.

56. Dron, V.A. and Semkina, N.V., Soviet Powder Met., 5, 1962, 332
57. Delle, J., Proc. 2nd Internat. Conf. on Peaceful Uses of Atomic Energy, 1, 1958, 599.

58. Fuhrmann, N; Hower, L.D., and Holden, R.B., J. Amer. Ceram. Soc. 46, 1963, 114

59. Clasing, M., Z. Metallkunde, 42, 1953, 69

60. Rutkowski, W., Neue Hütte, 6, 1961, 738

61. Williams, J., Jones, J.W.S., and Westmacott, K. H., Powder Met., 7, 1961, 167

62. Cox, F. G., Metal Ind. 97, 1960, 186, 207, 231

63. Borovsky, Sh. Ya., Doklady Akad. Nauk, U.S.S.R., 97, 1954, 875.

64. Vacek, J., Planseeber, Pulvermet., 7, 1959, 6

65. Prill, A.L., Hayden, H.W., and Brophy, J. H., ibid, 230, 1964, 769.

66. Fisher, R. and Rudman, P. S., Acta. Met., 10, 1962, 37

67. Raichenko, A.I., and Fedorchenko, I.M., Voprosy Poroshkovoi Met. i Prochnosti Materialov, 6, 1958, 3

68. Raub, E. and Plate, W., Z. Metallkunde, 42, 1951, 76

69. Duwez, P., Powder, Met. Bull., 4, 1949, 144, 168

70. Lenel, F.V., Trans. Amer. Inst. Min. Met. Eng., 175, 1948, 1061.

71. Gurland, J. and Norton, J.T., Trans. Amer. Inst. Min, Met. Eng., 194, 1952, 1051.

72. Kingery, W.D., J. Appl. Physics, 30, 1959, 301

73. Lund, J.A., Irvine, W.R., and Maciw, M.M., Powder Met., 11, 1962, 218.

74. Rao, P. R., Trans. Indian Inst. Metals, 17, 1964, 87

75. Kapoor, [illegible], and Madan Lal; Project Report (unpublished work submitted in the Metallurgical Engineering Department, U.O.R., Roorkee, 1970.

76. Peterson, N.L., and Rothman, S.J., Phy. Revue, 2, 1870

77. Kartinski, M., Arch. Huten, 13(1), 1968, 87.

78. Ceresara, S., Phy. Status. Solid, 27(2), 1968, 517