A Thesis entitled

THE SINTERING OF METALLIC POWDERS

submitted by

Robert Laidlaw Craik, B.Sc. A.R.T.C.

for

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Glasgow University.

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Metallurgy Department,
Royal Technical College,
GLASGOW, C.1.

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THE SINTERING OF METALLIC POWDERS.

CHAPTER 1.

Introduction.

Sintering in powder metallurgy consists of annealing metallic powders, previously pressed into some desired shape, at temperatures generally lower than the melting points of the constituent metals. As sintering progresses, the physical properties of the pressed compact may be improved and ultimately may approximate to the properties of the metals in their massive state. Porosity, however, cannot be completely eliminated and hot-pressing techniques have been devised to reduce the porosity, enhancing still further the physical properties of the pressed compact. Sintering may be controlled to obtain desired properties and to alloy different metals. These considerations also apply in the fields of ceramics, where ceramic oxides and glass powders may be sintered in a similar fashion.

To discuss the subject more fully, the following definitions have been adopted. The term "sintering" has been applied to the heating of uni-metallic powder compacts and "alloy-sintering" to that of compacted powder mixtures of different metals.

Sintering:

Of the properties of compacts, density measurements have been /

been found to serve as a measure of the degree of sintering attained on heating compacted metallic powders. These measurements may by obtained directly from the sintered compact or be dilatometric studies during the heating of a pressed shape. Gradual densification has been observed on heating and is attributed to the sealing, gradual isolation and finally elimination of the internal pores in the compact. To explain the increase of density of the sintered product, several theories of sintering have been proposed, each stressing one or other of the following mechanisms of atomic movement.

(1) Evaporation-condensation.
(2) Self-diffusion.
(3) Surface tension forces, causing plastic flow of the metal.

The energy gradient for atomic movement is attributed to the reduction in surface free energy of the metallic powder during densification.

Alloy-sintering:

Since the additional factors of interdiffusion of metals and the possibility of intermetallic compound formation, have to be considered, alloy-sintering is a more complex process. The present investigation has been concentrated on the nature of alloy-sintering and the possible information which cah be obtained from following experimental methods.

(1) /

CHAPTER 1. (Cont'd)

(1) Dilatometric analysis.
(2) Differential thermal analysis.
(3) Electrical resistance measurements.
(4) X-ray analysis.

CHAPTER 2.

Review of the literature.

Sintering:

Analysis of the experimental and theoretical data on sintering has been reviewed by Roberts(1) and Goetzel(2) who concluded that the evaporation-mechanism played a minor role in sintering. The mechanism was analysed from the behaviour of small metal spheres placed upon a plane of the same metal as shown in Fig.(1). On heating this model of Sintering to various temperatures for different times, interfacial growth was observed, the growth of the interface being measured directly by metallographic methods. Kucszynski(3) concluded that the rate at which interfacial growth proceeded at the various temperatures could be explained by the mechanism of self-diffusion. Surface diffusion was considered to create the initial interface across which volume diffusion occurred to increase the strength of this sinter bond. It was further observed that the growth of the interfacial contact was a function of the particle size of the metal spheres, and that surface diffusion predominated, the smaller the size of the metal spheres.

Cabrera(4) reconsidered Kucszynski's results and showed /

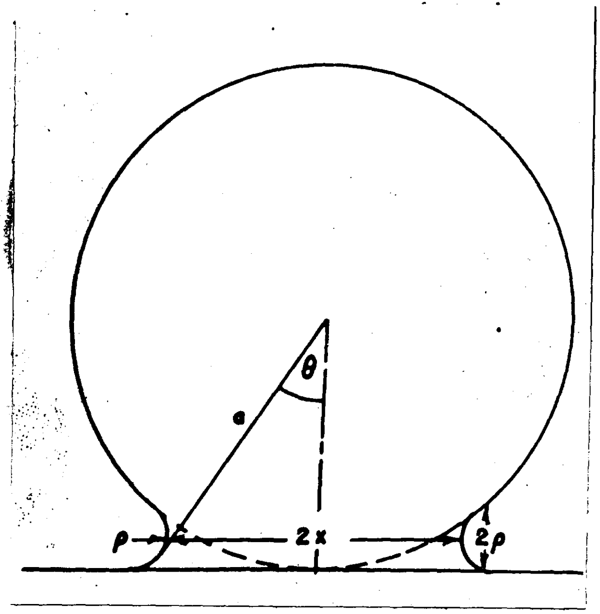


Fig (1) : Diagram illustrating the sintering of a metal sphere to a plane of the same metal. (Kucszynski(3))

a = radius of metal sphere
x = radius of the interface caused by sintering
ρ = radius of curvature of the sinter bond
2θ = angle subtended by the sinter interface.

Interfacial growth was determined by the relationship of the ratio x/a with time 't'. It was found that the logarithm of the ratio x/a could be expressed as a linear function of time (t) and that it was possible to determine the mechanism of atomic movement causing interfacial growth from this mathematical relationship.

showed mathematically that surface tension forces could produce similar rates of interfacial growth and also that the influence of the size of the metal particles could be attributed to its effect on the surface tension force since this force is dependent on the initial radius of the spherical metal particle. Sintering of compacts composed of regular spherical particles of copper have been studied dilatometrically by Jones (5) whose results favour the theory that sintering is caused by surface tension forces.

At this point, it is necessary to distinguish between surface diffusion and the atomic movement caused by surface tension. Surface diffusion is restricted to the surface layers of atoms of a metal and is the most rapid of the diffusion processes. Flow of metal atoms in layers is caused by surface tension. Atomic movement is not confined to the surface of a metal but extends to a depth below the metal surface, by an amount which depends on the physical strength of the metal at the various possible sintering temperatures. This is the basis of the phenomenological theory of sintering proffered by MacKenzie and Shuttleworth (6) who proposed that the mechanism of sintering of metals, ceramic oxides and glass powders was the same. Investigations by Clark and White (7) on ceramic oxides and glass powders appear to substantiate this theory.

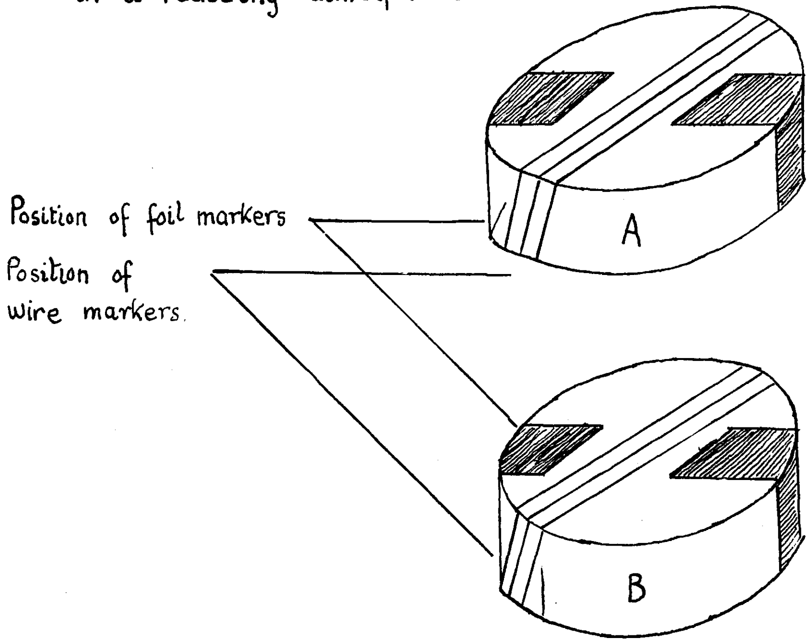
Alloy-sintering: /

Alloy-sintering:

Both interdiffusion of metals and the behaviour at the interfaces of different metals have been the subject of research. The marker method studying interdiffusion, first employed by Smigelskas and Kirkendall (8) and recently by Da Silva and Mehl (9) has yielded useful information. This method consists of placing an inert material e.g., molybdenum, platinum, carbon etc., between the polished surfaces of the metals and the external surfaces of the couple as shown in Fig. (2). The external markers are found to remain stationary on heating the welded assembly whereas the interfacial markers are subject to movement. Movement of the interface can be measured by reference to the external markers and this has been performed with various metal couples. At the various metal interfaces movement of the markers occurs in the opposite direction to that associated with the more rapid diffusion of atoms and has been related to the transfer of excess atoms which depends on the relative rates of interdiffusion of the various matals.

Le Claire and Barnes (10) have found in the study of interdiffusion of copper and nickel by this method that whilst no change in the bulk volume of the couple occurs, the total movement of the markers can be attributed to the expansion /

(a) Component metals of the interdiffusion couple before hot-pressing in a reducing atmosphere.



(b) The interdiffusion couple after hot-pressing in a reducing atmosphere.

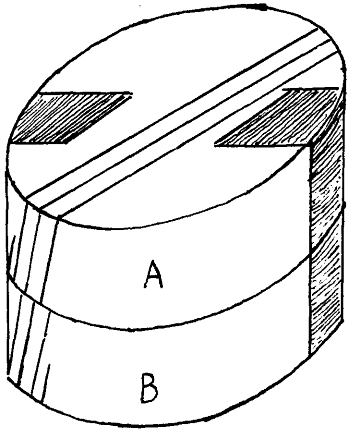


Figure (2): Diagram of metal couple arrangement employed in the study of the interdiffusion of metals. (Da Silva and Mehl (9)) expansion of the nickel which is caused by the transfer of excess copper atoms since copper diffuses more rapidly into the nickel than nickel into the copper.

Interdiffusion experiments of this nature have revealed that diffusion porosity occurs in the neighbourhood of the original interface, given by the marker and is associated with structural degeneracy of the metal from which greatest transfer of metal atoms occurs e.g., in the copper-nickel couples porosity is developed on the copper rich side of the interface.

Compacted mixtures of different metal powders possess similar features to these diffusion studies except that, due to the particle size of the metallic powders, the degree of interfacial contact is much greater and much smaller distances have to be traversed for homogenisation by interdiffusion of the metals.

Dilatometric studies:

Duwez and Martens (11) first investigated expansion and shrinkage changes associated with the continuous heating of compacted binary metallic powder mixtures in a reducing atmosphere. Their work has been confirmed by the investigations of Raube and Plate (12) who have studied a wide range of systems of bimetallic compacts. It would appear from these investigations that the dilatometric characteristics are determined by the equilbrium systems formed by the /

the components of the compact.

Two types of alloy-sintering may be inferred from the dilatometric of compacts during heating.

(1) Where the components of the compact form a complete or partial solid solution system, sintering may be associated with interdiffusion and that shrinkage, accompanying sintering, may proceed without interruption.

(2) Where the components are capable of forming an intermediate compound phase, intermetallic compound formation was held responsible for the abrupt expansions which were observed to accompany the sintering of such compacts.

Moar and Butler (13) have reported that an abrupt expansion of 6-7% occurred during the sintering of copper-nickel compacts. This was not observed by Duwez and Martens (11) who, however, employed much slower heating rates in their experiments. Although expansion may be expected when copper and nickel interdiffuse, this discrepancy cannot be readily discussed until the influence of compacting pressure and particle size has been determined. Furthermore, gas entrapment occurs during compaction and Warren and Libsch, (14) employing permeability and density measurements, have found that under conditions of rapid rates of heating, anomalous permeability and density effects are observed. These effects were attributed to the entrapped gases which develop sufficient internal pressures to cause the expansion of the internal pores of the compact.

Electrical /

Chapter 2. (Cont'd)

Electrical resistance measurements:

Rhines and Colton,(15) and Rhines and Meussner,(16) employing resistance measurements, have studied alloy-sintering of copper-nickel compacts. It was concluded that interdiffusion could be associated with the resistance changes which accompanied sintering, although the authors stressed that the effects of entrapped gases and the surface conditions of the metallic powders e.g., tendency for oxidation, absorbed gases etc., were not to be overlooked. Otherwise little investigation has been performed upon systems which may introduce intermediate phase formation.

Metallographic studies:

General metallographic investigation by Duwez and Martens,(11) Raube and Plate,(12) Hoar and Butler(13) and others have shown the development of porosity during alloy-sintering, particularly when intermediate phase formation occurred. In the case of copper-nickel compacts, this porosity may be associated with "diffusion porosity" which has been found during the interdiffusion of these metals in the solid state. Changes in crystal structure, accompanying intermetallic compound formation, would be expected to develop marked porosity. The complicated metallographic structures, obtained by different staining and etching techniques, do not permit complete identification of the alloy phases produced by sintering.

X-ray studies: /

X-ray studies:

The alloy-sintering of copper-nickel compacts has been investigated by Duwez and Jordan (17) who concluded that interdiffusion occurs and assists the normal sintering process.

With binary metallic powder compacts in which intermetallic compound formation id possible, alloy-sintering may involve the combination of the metals. Duwez and Jordan (18), in a study of a copper-gold compact containing 25 atomic % gold, determined that there was initial formation of the intermetallic compound CuAu at 315 °C and that this compound could exist in apparent equilibrium with any residual copper. Complete homogenisation did not occur until the sintering temperature exceeded the order-disorder transformation temperature of CuAu at 424 °C. Rhines and Colton (19) have confirmed intermediate phase formetion within copper-zinc and copper-tin compacts during sintering. In a copper-zinc compact which contained 70 % copper and was heated to 400 °C, they identified the initial formation of alpha-brass and the eta-compound phases. Further heating resulted in the appearance of the gamma and epsilon compounds. Similar behaviour was also observed during the heating of a copper-tin compact, although the process was more complicated due to the complex intermediate phase formation which prevails in the copper-tin equilibrium system. It has also been observed that when copper and zinc powders were mixed, accurate /

accurate X-ray measurements revealed the formation of traces of the beta-CuZn compound,(20)

Conclusions:

The general features of sintering of metallic powders and the factors which influence the process, have been summarised. Before any investigation of alloy-sintering may be made, the effects of several factors have to be determined. Consequently, a prelimnary investigation of the alloy-sintering of copper-zinc compacts in vacuo has been performed, employing the following experimental methods.

(1) Dilatometric analysis.
(2) Differential thermal analysis.
(3) Electrical resistance measurements.
(4) X-ray analysis.

The object was to study the effect of particle size and compaction upon the alloy-sintering of copper-zinc compacts. Vacuum sintering with low rates of heating was adopted to offset the possible effect of entrapped gases. Since zinc is characterised by its volatility, its effect should be assessed. The influence of the vapour pressure of metals during alloy- sintering as yet has received little attention.

Duwez and Martens(11) observed that the abrupt thermal expansions associated with the heating of binary metallic compacts in which intermetallic compound formation was postulated,were accompanied by indications of heat evolution. Differential thermal analysis seemed a convenient method of studying /

studying such effects.

X-ray measurements could be used for positive identification of the new phases produced during sintering. No extensive metallographic examination was made as the main purpose of phase identification could be secured from X-ray data.

CHAPTER 3.

Prelimnary investigation of the alloy-sintering of copper-zinc compacts in vacuo.

1. Dilatometric analysis:

Dilatometric studies of the heating of copper-zinc compacts in vacuo were performed not only to investigate phase formation but also to determine the influence of the following factors.

(1) The vapour pressure of the metal components.
(2) The particle size of the powders.
(3) The compacting pressure.
(4) The composition of the compact.

Experimental procedure:

Three different batches of atomised copper powder were employed. The screen analysis of these are as follows, (all sizes referred to B.S.S. screens):-

Copper powder (A)	-300 mesh	
Copper powder (B)	+100 mesh	0.09%
	100/150 mesh	9.93%
	150/200 mesh	21.15%
	200/300 mesh	17.02%
	-300 mesh	51.80%
Copper powder (C)	-100 mesh (separated into size grades)	

Two batches of zinc powder were used and possessed the following screen characteristics.

Zinc powder (A)	-300 mesh
Zinc powder (B)	-100 mesh (separated into size grades)

Compacts, weighing 10 gms, were prepared by cold pressing the blended powders into the shape of flat discs in a cylinder mould, 3.25 ins. external diameter, 2.4. ins. length and with an internal bore diameter of 1.15 ins.

The /

The mould was fitted with a tapered base plug, 1 ins long. The compacting pressures used covered the range of 5-80 tons/ins^2.

Dilatometric studies during heating, were made under conditions of less than 1 mm. Hg., produced by an Edward's Hyvac pump. The furnace arrangement which is shown in Fig.(3) was compased of a Nichrome wound furnace, containing a fused silica tube of 2 ins. internal diameter. Measurements were over a range of temperature extending from 0-800°C with a constant heating rate of 3°C/minute. Temperature readings were obtained by a Chromel-Alumel thermocouple.

Dimensional changes were indicated by a thin fused silica tube, the lower end of which passed through a drilled hole in a split Inconel container within which the pressed compact was placed vertically as shown in the diagram. The upper end of the silica tube was contained within a wide closed end glass tube which passed through the rubber bung. Any dimensional changes in the compact were observed by a cathetometer, focussed on the knife edge.

The end of the thermocouple was inserted through another hole, drilled in the container so that the junction was as close as possible to the specimen under test. During experiments, cathetometer readings were taken at 0.1. mv. intervals of temperature. The experimental results of the dimensional changes, caused during the heating of the copper-zinc compacts are given in Fig. (4)-(5) and condensed in tables /

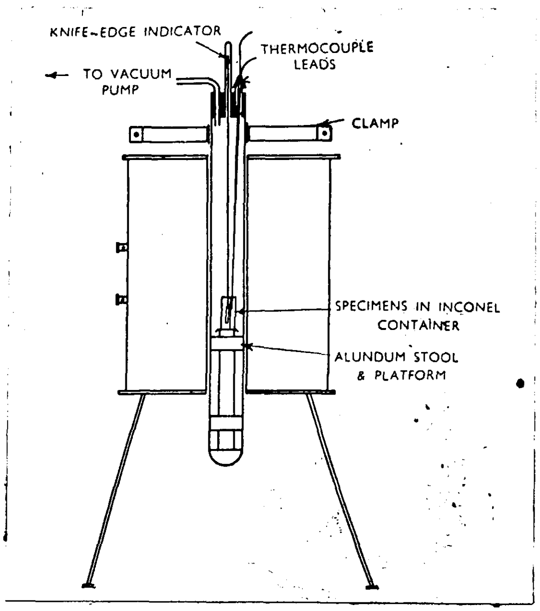


Fig. (3): Apparatus for studying dilatometric changes.

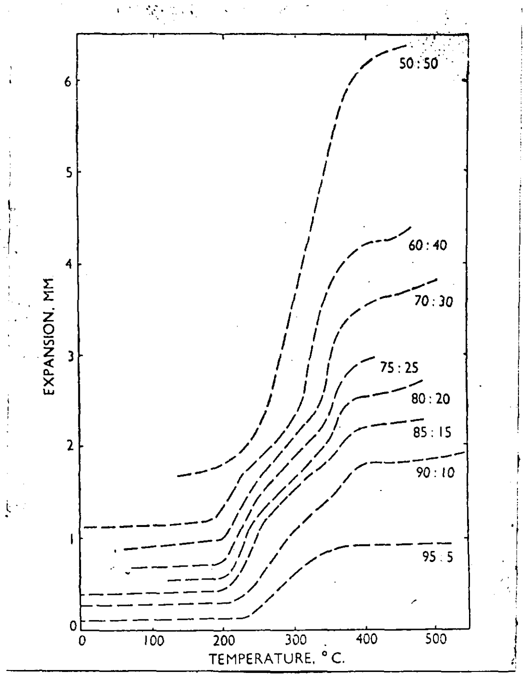


Fig (4): Thermal expansion curves for copper-zinc compacts. Pressed at 20 tons/in.^{2} and heated in vacuo.

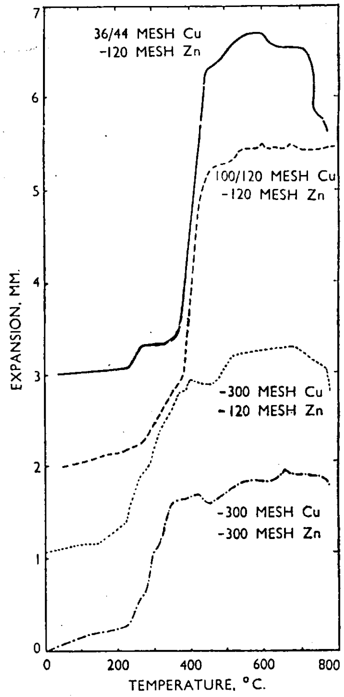


Fig. (5) : Thermal expansion curves for 50:50 Copper-zinc compacts with Varying mesh grades of powders. Pressed at 50 tons/in.² and heated in vacuo.

Copper Particle Size	Zinc Particle Size	Observed Expansion	
		mm.	%
36/ 44 mesh	— 120 mesh	3·66	12·52
100/120 mesh	,, mesh	3·38	11·57
— 300 mesh	,, mesh	2·52	8·63
,, mesh	— 300 mesh	1·96	6·71

Table (1): Effect of particle size on expansion of 50:50 copper-zinc Specimens.

Compacting Pressure, tons/in.²	Expansion in Range 180°–380° C.		Temp. of Start of Expansion, °C.	Temp. of End of Expansion, °C.	Rate of Expansion, mm./°C.	Temp. Range of Expansion, °C.
	mm.	%				
	2·31	7·91	216	324	0·021	108
10	2·27	7·78	215	332	0·019	117
20	1·69	5·78	226	346	0·014	120
30	1·32	4·52	200	385	0·007	185
50	1·50	5·13	200	385	0·008	185
70	1·72	5·88	179	385	0·0085	206

Table (2): Effect of compacting pressure on the expansion of 70:30 copper-zinc compacts.

tables (see Tables (1)-(2)).

Results:

(1) The dilatometric behaviour of compacts, composed of copper powder (A) and progressively increasing amounts of zinc powder (A), pressed at 20 tons/ins.^{2}, are given in Fig.(4). (4). An abrupt expansion begins about 200°C and becomes more marked as the temperature increases until it is complete about 380°C. The compositions of the compact varied from 5-50 % zinc and within these limits the total expansion varies directly with the zinc content.

(2) The effects of particle size are shown in the dilatometric curves, given in Fig. (5) and Table (1) for compacts which were composed of 50 % zinc powders, pressed at 50 tons/in.^{2} Mixtures of varying size grades of copper powder (C) and zinc powder (B) were employed. Similar abrupt expansions were observed within the temperature range noted previously (200°-380°C). As the particle size of the powders is decreased, the total expansion is diminished as shown in Table (1).

(3) The influence of compacting pressure may be observed from a study of the dilatometric behaviour of compacts, composed of 70% copper and 30% zinc powders (A), formed under different compacting pressures, ranging from 10-70 tons/in.^{2} The total expansions observed for the different pressures are /

are shown in Table (2). As the compacting pressure is increased, the initial temperature of expansion falls and the temperature at which expansion ceases, becomes constant at 385°C. The total expansion decreases to a minimum at compacting pressures about 30 tons/in.^{2} and thereafter gradually increases with increase in compacting pressure up to 70 tons/in.^{2} The rate of expansion in mm./°C gradually fails to a constant value for compacting pressures of 50-70 tons/in~~s~~.^{2}

2. Differential thermal analysis:

Experimental procedure:

Compacts, weighing 25 gms., were prepared and halved, each half disc being used as a test specimen. Differential thermal curves were obtained by comparing the rate of heating of the test specimen with that of a copper standard of identical weight and shape within the Nichrome wound furnace arrangement shown in Fig. (6). The standard and test specimen were placed inside an alundum container, made with appropriate recesses. The junction of the Chromel-Alumel Thermocouple was located in a central hole within the alundum container as shown in the diagram. The differential thermocouple junctions were inserted into central holes drilled in both the standard and test specimens. The differential thermocouple bridge was composed of Chromel-Alumel-Chromel wires and the difference in e.m.f. ac~~r~~ross its leads measured by a Tynsley potentiometer, fitted with a null point /

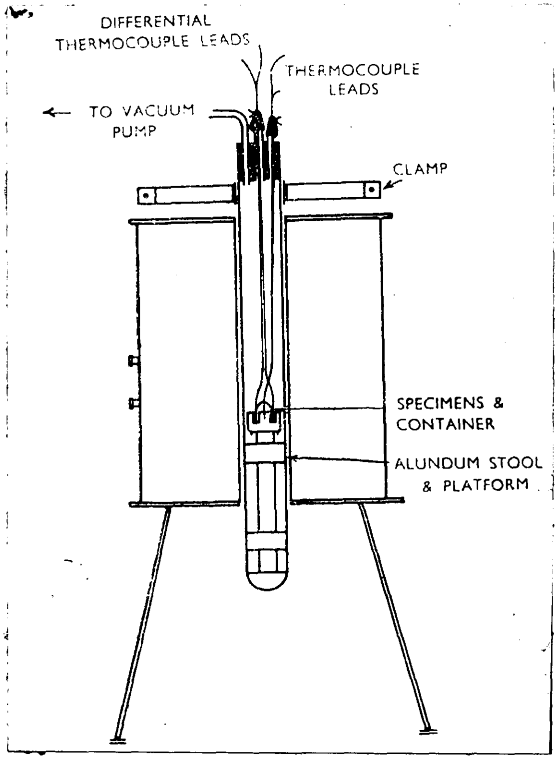


Fig.(6) : Apparatus for studying thermal changes.

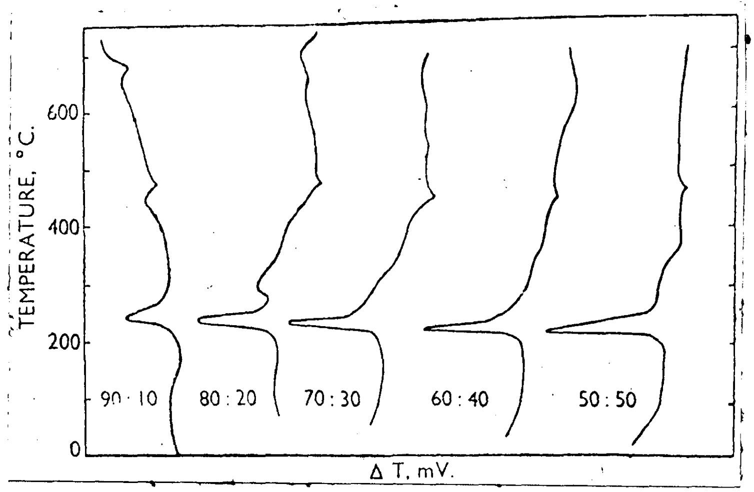


Fig (7): Differential thermal curves for compacts of varying composition made from -300 mesh copper and -120 mesh zinc powders. Pressed at 50 tons/in.^{2} and heated in vacuo.

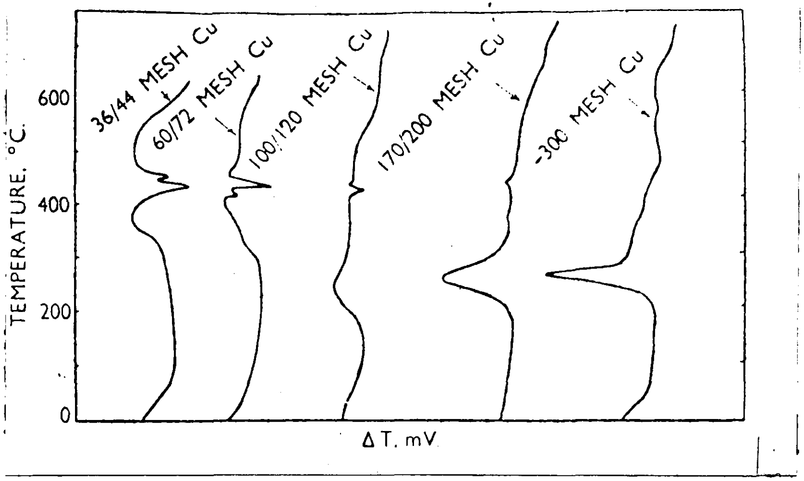


Fig.(8): Differential thermal curves for 50:50 compacts, composed of -120 mesh zinc powder with various grades of copper powder. Pressed at 50 tons/in². and heated in vacuo.

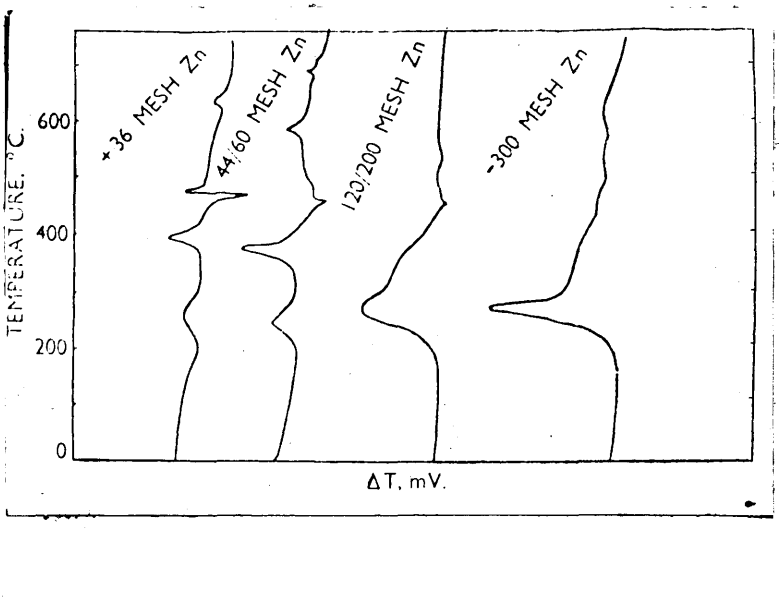


Fig.(9): Differential thermal curves for 50:50 compacts, composed of -300 mesh copper powder with various grades of zinc powder Pressed at 50 tons/in² and heated in vacuo.

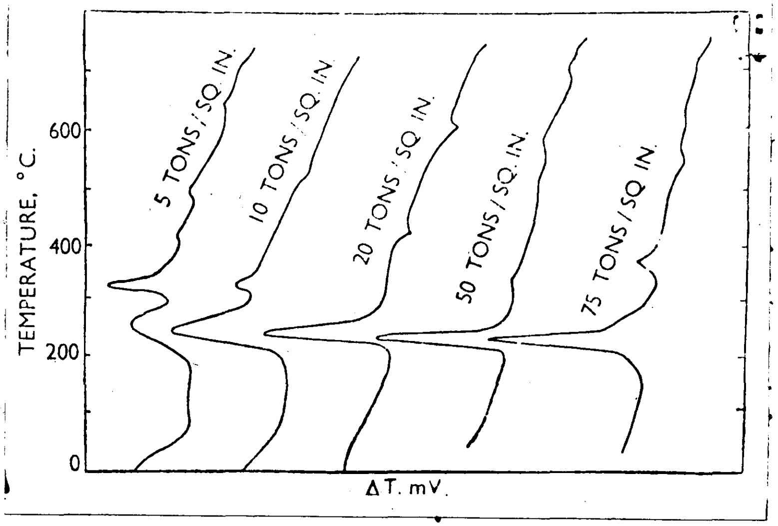


Fig. (10): Differential thermal curves for 50:50 compacts made from -300 mesh copper and zinc powders with varying compacting pressures and heated in vacuo.

point Cambridge galvanometer.

Readings of the differential e.m.f. were taken at 0.1 mv. temperature intervals under vacuum and heating conditions, identical to those observed during the dilatometric studies.

Differential thermal curves are given in Fig. (7)-(10).

Results:

(1) Differential thermal results obtained from compacts, composed of copper powder (A) and -120 mesh zinc powder (B), pressed at 50 $tons/in.^2$ are given in Fig. (7). The composition of the compacts varied from 10-50 % zinc. A marked exothermic change, the intensity of which was proportional to the zinc content, occurred at 240 ^oC followed by a slight endothermic change at 480 ^oC. The exothermic change began at 200 ^oC and the endothermic change at 450 ^oC being completed by 490 ^oC. In the case of compacts, containing 20% and 50 % zinc, evolution of heat appeared complete by 300 ^oC.

(2) The influence of particle size on the thermal behaviour of the compacts was investigated in a series of compacts, containing 50:50 ratio of copper-zinc powders. The compacts, produced at a compacting pressure of 50 $tons/in.^2$ were made up from powders of varying size grades as follows,

(a) -120 mesh zinc powder (B) with varying grades of copper powder (B).
(b) -300 mesh copper powder (A) with various grades of zinc powder (B) and zinc filings of a given size range.

The /

The differential thermal curves for these compacts are given in Fig. (8)-(9).

With large sized copper particles of 36/44 mesh and 60/72 B.S.S. mesh size, a marked heat absorption occurred at 420° C and must be attributed to the melting of zinc and zinc-rich phases. With 100/120 mesh copper powder, this endothermic change diminshes and a slight exothermic change occurs about 240° C. With copper powder of still finer size grading, the exothermic change becomes more marked.

In compacts made up of fine copper powder and zinc powder of varying size grades, similar effects are observed. In compacts containing large zinc particles (+36 and 44/60 mesh), two exothermic changes are observed, the first occurring at 240° C and the second at 380°-390° C. In compacts containing zinc powder of progressively finer sizes, this second exothermic change diminishes until in compacts containing -300 mesh zinc only one exothermic change is observed.

(3) The effect of compacting pressure has been investigated, using compacts composed of 50/50 mixtures of -300 mesh copper and zinc powders (A). Compacting pressures of 5,10,20,50 and 70 tons/in.^{2} were employed to prepare the compacts. As shown in Fig. (10), a definite exothermic change occurs at 240° C, the heat evolution becoming more pronounced once the compacting pressure was greater. With compacting pressures up to 10 tons/in.^{2}, two exothermic changes /

changes occur, one at 240°C and the other at 320°C. Over 10 tons/in^{2}, only one exothermic change occurs. Slight endothermic changes at 420°C were observed on some of the curves.

3 Electrical resistance measurements:

Experimental procedure:

A horizontal furnace arrangement was adopted as shown in Fig. (11) to study the changes in relative electrical resistance of compacts during heating. Two holes of approximately 3/32 in. diameter were drilled through a compact at a distance of 3/4 in. apart. The compact was bolted by Inconel screws to the ends of two lengths of 1/4 in. copper rod, the ends of which had been drilled and tapped. The copper rods were held rigid by two asbestos clamps and emerged via the rubber bung as shown in the diagram. Temperature reading were obtained by a Chromel-Alumel thermocouple placed as near the specimen as possible.

A constant current was passed through the discs via the copper rods and the potential drop across the rods measured by a Tynsley potentiometer at 0.1. mv. intervals of temperature. This permits the measurement of the disc in milli-volts since the expansions associated with the vacuum sintering of copper-zinc compacts prevent even an approximation of the true electrical resistance value.

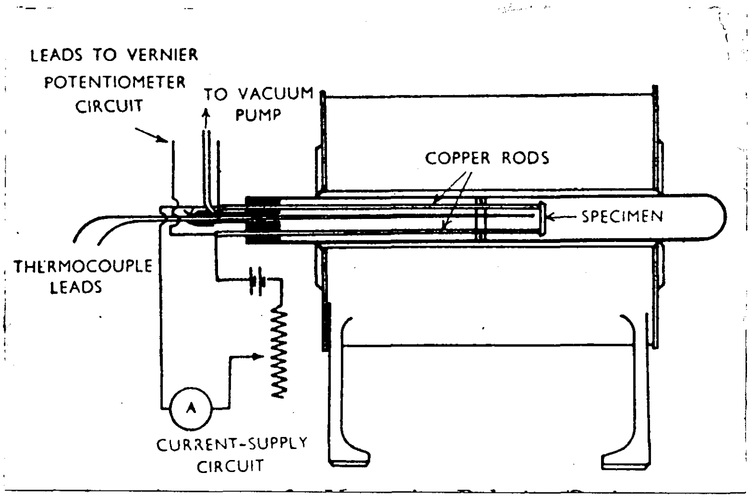


Fig. (11): Apparatus for measuring relative resistance.

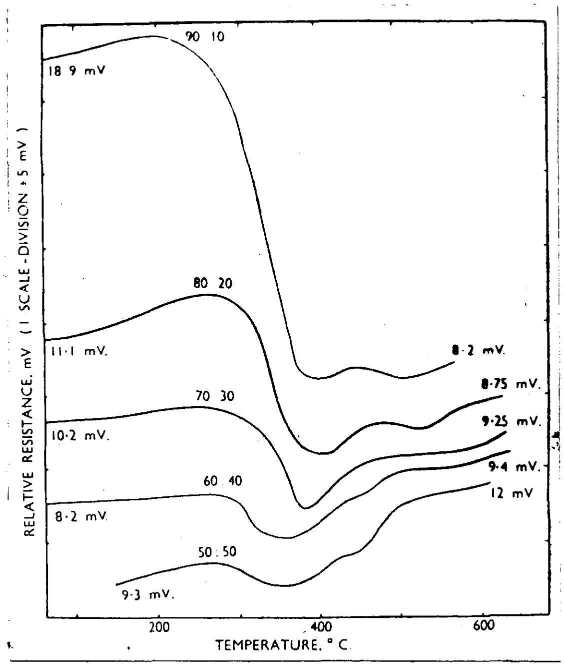


Fig. (12): Relative resistance curves for compacts composed of coarse copper powder (B) with -300 mesh zinc powder. Pressed at 50 tons/in^2 and heated in vacuo. Initial and final resistance values are given for each curve.

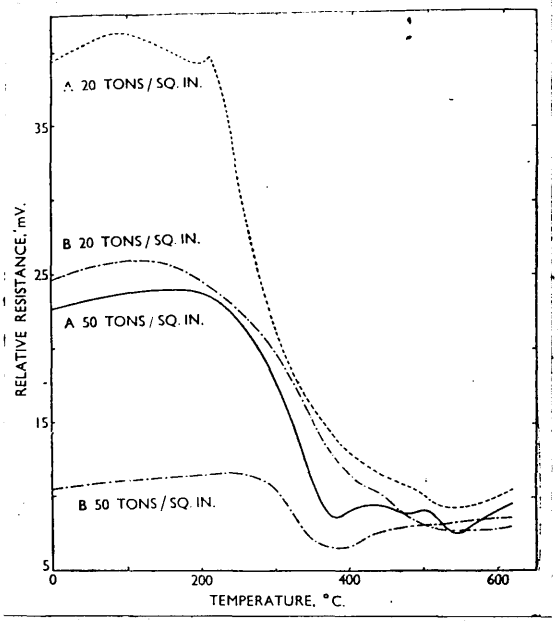


Fig. (13): Relative resistance curves for 80:20 compacts composed of fine copper powder (A) and coarse copper powder (B) with -300 mesh zinc powder. Pressed at 20 and 50 tons/in.² and heated in vacuo.

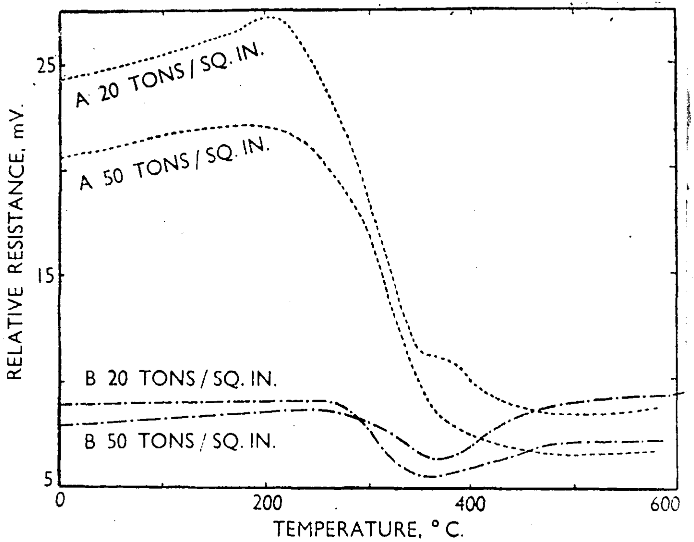


Fig (14): Relative resistance curves for 60:40 compacts composed of fine copper powder (A) and coarse copper powder (B) with -300 mesh zinc powder. Pressed at 20 and 50 tons/in.² and heated in vacuo.

value. Relative electrical resistance values were determined for a number of copper-zinc compacts under varying conditions of composition compacting pressure and particle size of the constituent powders. The results which have been obtained are presented in Fig. (12)-(14) as a plot of relative resistance against temperature.

Results:

(1) The observed relations between the electrical resistance and the composition of the compacts during heating are given in Fig. (12) for compacts, composed of copper powder (B) and -300 mesh zinc powder, pressed at 50 tons/in.^{2} Initially, there is a linear relationship between the resistance and temperature until in all cases within a temperature range of 200°--250°C, an abrupt drop in resistance is observed. The total resistance drop decreases as the zinc content increases. At 380°C this fall in resistance ceases and an irregular variation in resistance follows before a final constant value of resistance is obtained at 500°C. This final value of electrical resistance depends on the zinc content, generally becoming higher as the zinc content of the compact is increased.

(2) Changes in compacting pressure and particle size cause variations in the electrical resistance behaviour as shown in Fig. (13)-(14) for varying grades of powder mixtures, compacted at 20 tons/in.^{2} and 50 tons/in.^{2} As the compacting pressure is increased, the initial value of resistance is decreased, /

decreased, and the lowest initial resistance value is associated with compact containing the coarser grade of copper particles. The drop in resistance which begins at 200°-250°C decreases with the increase in the compacting pressure and the particle size, At temperatures above 380°C, the fall in resistance ceases and then tends to a constant value 500°C.

6. X-ray analysis:

Experimental procedure:

10 gm. samples of various copper zinc powder mixtures were prepared in the form of discs which were heat treated in vacuo at the various temperatures associated with the dilatometric and thermal changes. The following procedure was adopted.

(1) Compacts, composed of varying amounts of fine copper powder (A) and zinc powder (A), compacted at 50 tons/in.^{2} were treated under the same conditions of vacuum and heating rate as prevailed during the previous experiments. The compacts were heated to 750°C and cooled slowly in the furnace.

(2) Compacts, containing 50/50 ratio of copper powder (A) and zinc powder (A) were compacted at 50 and 100 tons/in.^{2} and heated to temperature of 250°C, 305°C and 525°C. The specimens were cooled slowly in the furnace in all cases

(3) 50/50 copper-zinc powder compacts were prepared from different size grades of copper and zinc powders. These mixtures of powders were compacted at 50 tons/in.^{2} and heat treated at 250°C, 350°c, and cooled slowly in the furnace.

After sintering the specimens were inevitably distorted, to a certain extent by the thermal expansions which occurred during heating and prior to X-ray studies, the /

2θ Values, degrees	Miller Indices
Copper Lines	
43·2	222
50·2	211
73·4	111
β-Phase Lines	
43·4	110
62·76	200
79·8	211
Zinc Lines	
36·3	204
38·95	222
42·25	300
54·20	402
69·90	... *
70·40	501
81·80	510

* Line probably due to Cu K_{α_1} radiation.

Table (3): X-ray lines used in phase identification.

the surfaces of the compacts were machined and then polished with successive grades of emery paper down to 000 grade.

X-ray back reflection technique was adopted and measurements made by means of a Phillips X-ray machine, equipped with a Geiger-Muller counter. By means of this instrument, planes of reflection between 10-45° angles could be obtained and were sufficient to permit definite phase identification within the sintered compact. Copper radiation of wavelength 1.5412 Kx units, produced by a high tension voltage of 5Kv, and a filament current of 6.0 milliamps., was employed.

For phase identification, planes of reflection were measured from prepared specimens of copper..zinc powders and beta-CuZn filings which had been pressed into compacts. These reference lines are given in Table (3). Analysis of the copper and zinc powders 99.9% purity and consequently were sufficiently pure for the determination of the X-ray pattern of these elements. Filings of the beta-copper-zinc solid solution were obtained from a prepared alloy, the analysis of which corresponded to the stoicheiometric proportions of the formula-Cu Zn.

The Geiger-counter readings, taken at intervals of 0.2° were plotted as shown ina typical set of results in Fig. /

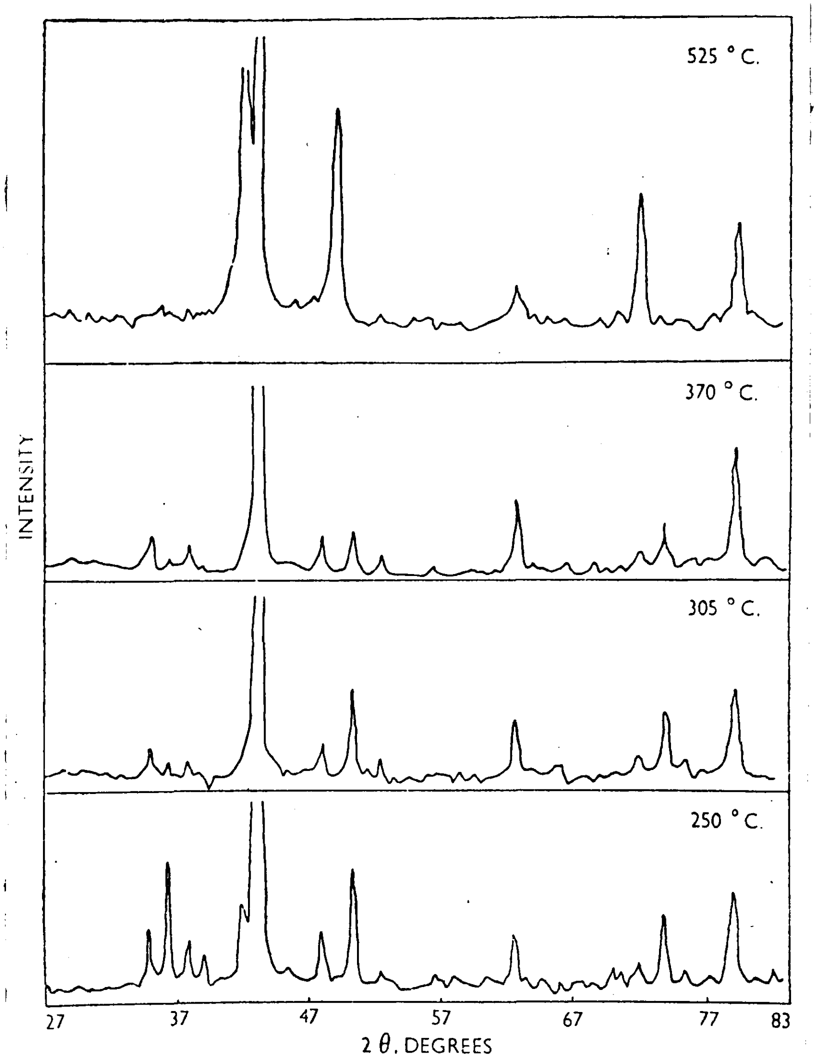


Fig.(15): X-ray diffraction curves for 50:50 Compacts made from -300 mesh copper powder and -120 mesh zinc powder. Heated for 2 hr. at the temperatures indicated.

Composition of Compact, %	Major Lines in X-Ray Spectra		
	Angle, degrees	Plane of Reflection	Phases Present
Cu 100	43·3	222	...
	50·3	211	...
	73·9	111	...
Zn 100	43·3	...	...
	36·3	...	...
	39·0	...	...
	54·2	...	...
	69·9	...	...
	81·9	...	...
Cu 90 Zn 10	42·9	222	α
	50·0	211	
	73·3	111	
Cu 80 Zn 20	42·7	222	α
	49·7	211	
	72·9	111	
Cu 70 Zn 30	42·5	222	α
	49·4	211	
	72·4	111	
Cu 60 Zn 40	42·2	222	α
	43·3	110	β
	49·2	211	α
	71·9	111	α
Cu 50 Zn 50	43·3	110	β
	62·5	200	
	79·1	211	

Table (4): X-ray data for copper-zinc powder compacts.

Series made from atomised copper powder (A) and Schori grade A zinc powder
All compacts were made under a compacting pressure of 50 tons/in.^{2}, heated gradually to 750°C and allowed to cool slowly in vacuo.

Compact No.	Composition, %	Particle Size (B.S. Mesh Sieves)	Compacting Pressure, tons/in.^{2}	Time of Annealing at Temperature, hr.
1	Cu 90 Zn 10	— 300 — 300	50	2
2	Cu 70 Zn 30	— 300 — 300	50	2
3	Cu 50 Zn 50	60/72 — 120	50	2
4	Cu 50 Zn 50	170/200 — 120	50	2
5	Cu 50 Zn 50	— 300 — 120	50	2
6	Cu 50 Zn 50	170/200 — 120	100	2
7	Cu 50 Zn 50	170/200 — 120	50	4
8	Cu 50 Zn 50	— 300 — 120	50	4
9	Cu 50 Zn 50	100/120 — 120	50	12
10	Cu 50 Zn 50	36/44 — 120	50	2

Table (5): Data on copper-zinc compacts prepared for X-ray examination.

Compact No.	Possible Phases Present	Temperature to Which Compact was Heated			
		250° C.	305° C.	370° C.	525° C.
1	Cu	Strong	Strong	Strong *	Absent
	Zn	Absent	Absent	Absent	,,
	β	Very slight	Slight	Very slight	,,
	α	Absent	Absent	Absent	Strong
2	Cu	Strong	Strong *	Absent	Absent
	Zn	Weak	Absent	,,	,,
	β	Slight	Moderate	Weak	,,
	α	Absent	Absent	Strong	Strong
3	Cu	Strong	Strong	Moderate *	Absent
	Zn	,,	Weak	Absent	,,
	β	Very slight	Moderate	Moderate	Strong
	α	Absent	Absent	Absent	Slight
4	Cu	Strong	Strong	Moderate *	Absent
	Zn	Moderate	Absent	Absent	,,
	β	Slight	Strong	Strong	Strong
	α	Absent	Absent	Absent	Slight
5	Cu	Strong	Strong *	Absent	Absent
	Zn	Weak	Absent	,,	,,
	β	Moderate	Strong	Strong	Moderate
	α	Absent	Absent	Slight	Strong
6	Cu	Strong	Moderate	...	...
	Zn	Moderate †	Absent	...	...
	β	Strong	Strong	...	...
	α	Absent	Absent	...	...
7	Cu	Moderate	Moderate	...	...
	Zn	Absent	Absent	...	...
	β	Strong	Strong	...	...
	α	Absent	Absent	...	...
8	Cu	Moderate	...	...	...
	Zn	Absent	...	...	...
	β	Strong	...	...	...
	α	Absent	...	...	...
9	Cu	Strong	...	...	...
	Zn	Weak	...	...	...
	β	Moderate	...	...	...
	α	Absent	...	...	...
10	Cu	Strong	Strong	...	...
	Zn	Moderate	Moderate	...	...
	β	Very faint	,,	...	...
	α	Absent	Absent	...	...

* Indicates that the copper lines showed very slight displacement owing to the beginning of the formation of α. When this displacement becomes more pronounced with rise in temperature, α is recorded as present and copper as absent.

† Absent after 4 hr. at 250° C.

Table (6): X-ray data for copper-zinc powder compacts.

Fig. 15. The lines obtained are sufficiently strong to permit positive identification. The X-ray data which has been obtained, has been summarised and compiled in tabular form (see Tables) (4)-(6).

Results:

(1) From the data recorded in Table (4), it appears that Copper-zinc compacts, pressed at 50 tons/in.^{2} and heated to 750°C, are in general composed of those phases which would be expected in an alloy of the same composition, prepared by melting and casting. Loss of zinc by volatisation alters the composition of the compact. A compact, containing 50/50 copper and zinc powders may contain slight traces of the alpha-phase but there was no indication of the gamma compound phase.

(2) Investigation of the test specimens, heat treated according to the data in Tables (5) and (6) indicate the following results.

(a) The initial cause of alloy-sintering is the formation of beta-Cuzn phase and even in compacts where the alpha-phase is the equilibrium state, beta-Cuzn forms primarily whilst no appreciable quantities of the alpha-phase appear until almost all the zinc has combined to form the beta-phase.

(b) The rate of beta-Cuzn formation is assisted by the increase of compacting pressure and the decrease of particle size of the copper and to a lesser extent, of the zinc. A higher temperature appears to be required for the combination of all the zincto beta-CuZn as the particle size of the powder was increased.

(c) /

(c) The lowest temperature at which beta-CuZn lines appear is at 170°C whilst with the finest powders, The maximum rate of beta-CuZn formation occurred at 250°c.

CHAPTER 4.

Further investigations of the alloy-sintering of bi-metallic compacts in vacuo by differential thermal analysis.

From the results of this preliminary investigation of copper-zinc Powder compacts, the high vapour pressure of zinc may be considered the important factor in promoting compound formation in the solid state. Abrupt expansions, however, have been observed by Duwez and Martens,(11), and Raube and Plate(12) during the heating of bimetallic compacts the components of which are ~~C~~characterised by their extremely low vapour pressures at the temperatures associated with sudden expansion e.g., Nickel-aluminium, nickel-Silicon and others. It was therefore decided to examine the possibility of intermetallic compound formation within such systems as the initial cause of sintering. The systems investigated were, copper-nickel, copper-aluminum, nickel-aluminium and nickel-zinc. The differential thermal analysis method was used to determine the temperatures at which any combination of the metallic powders occurred.

Experimental procedure:

The apparatus for differential thermal analysis was redesigned. By arranging the furnace horizontally, more uniform heating was obtained throughout the container with consequent reduction of the drift previously experienced. Better control of vacuum conditions was secured by the use of /

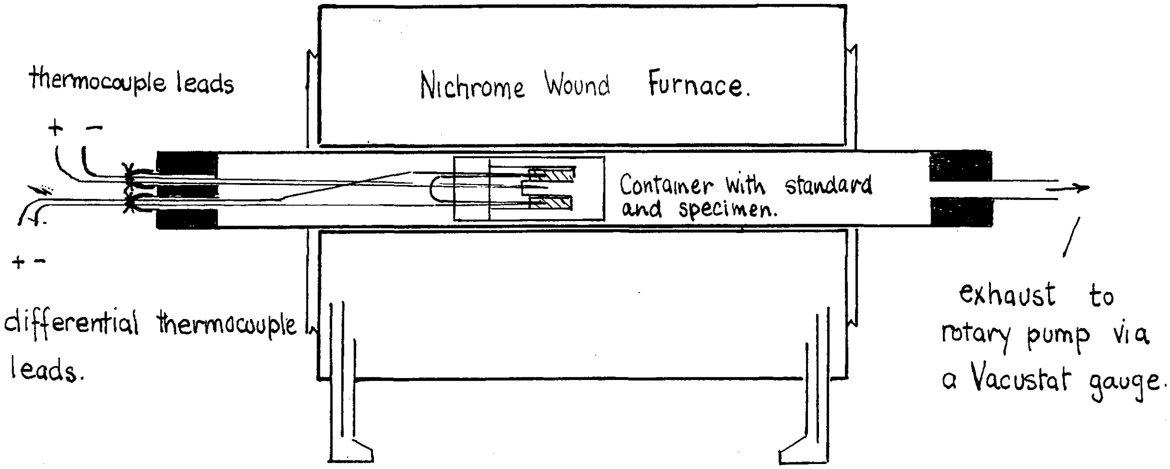


Fig.(16): Redesigned apparatus for studying thermal changes.

of an Edward's Vacustat gauge. This experimental arrangement is shown in Fig.(16)

Cylindrical 25 gm test compacts were prepared and drilled to receive the junction of the differential thermocouple. A copper disc of the same size and weight was employed as the standard.

The powders used with their particle size charactistics are as shown below.

POWDER	Characteristics
Carbonyl nickel powder	-120 mesh (B.S.S.)
Aluminum powder (produced by the stamp process)	-300 mesh (B.S.S.), composed of flakes, of approx.,5 Mu. diam.
Electrolytic copper powder	-300 mesh (B.S.S.)
Zinc powder (A)	-300 mesh (B.S.S.)

Specimens, corresponding to the compound compositions of NIAL, beta-Cu$_3$Al and a copper-nickel composition of 50/50 ratio by weight were pressed at 50 tons/in^2. The differential thermal curves obtained using these compacts, are presented in Fig. (17)-(19).

Results:

(1) No exothermic change was determined over the range of temperature of 0-700°C in the copper-nickel compact.

(2) Fig. (17) shows the thermal curve for the copper-aluminium compact and reveals the appearance of a sudden exothermic change at 500°C. The reaction appeared to be instantaneous and the rapidity with which it proceeded, was /

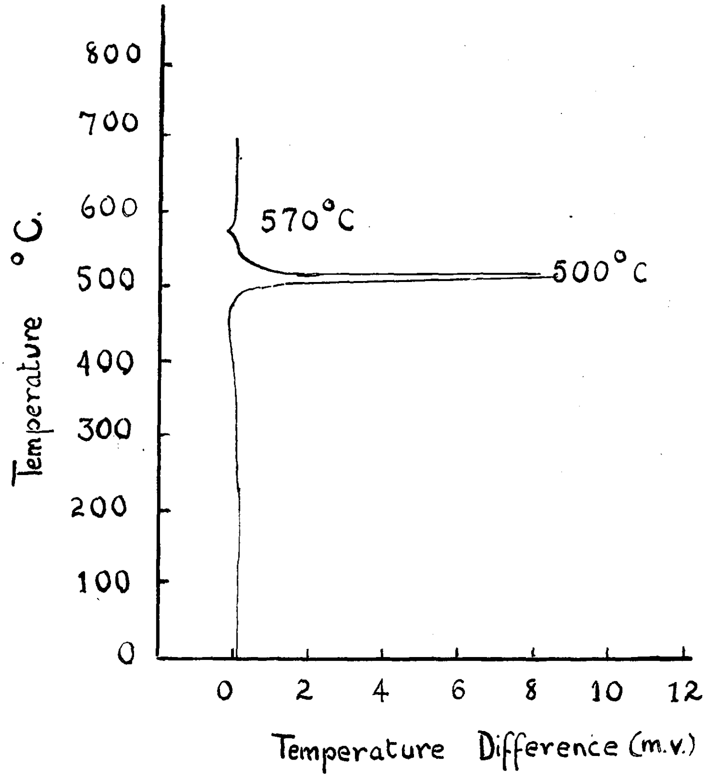
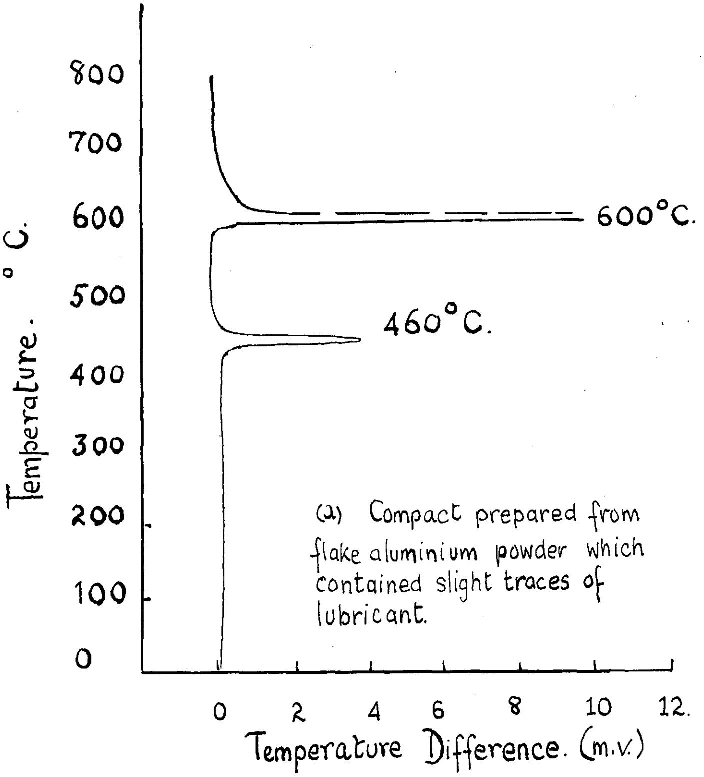
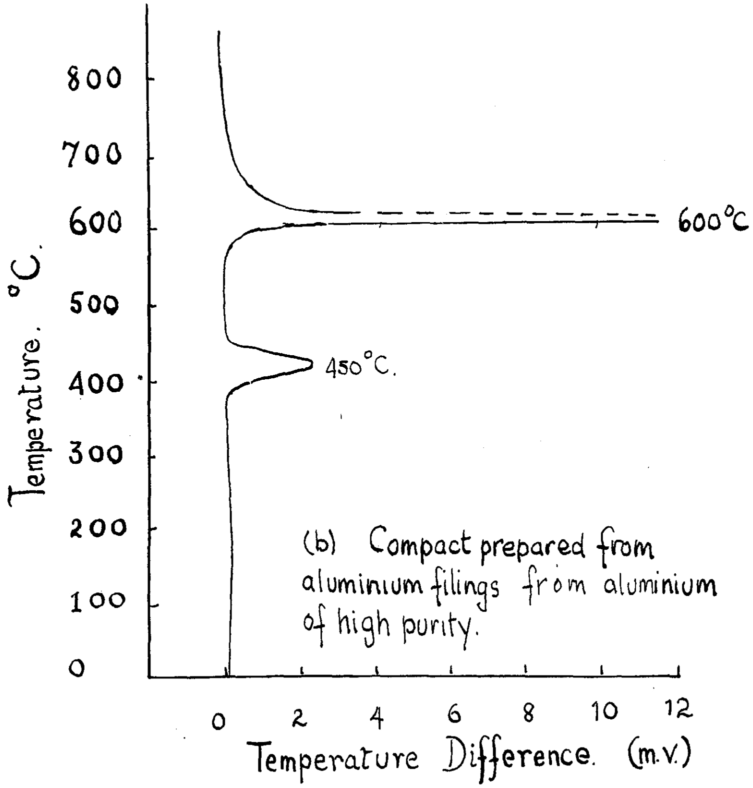


Fig (17): Differential thermal curve of a copper-aluminium compact, corresponding in composition to the compound formula - Cu_3Al



(a) Compact prepared from flake aluminium powder which contained slight traces of lubricant.

Fig (18a): Differential thermal curve of a nickel-aluminium compact of composition corresponding to the compound formula- NiAl.



(b) Compact prepared from aluminium filings from aluminium of high purity.

Fig.(18b): Differential thermal curve of a nickel-aluminium compact, of composition corresponding to the compound formula- Ni Al.

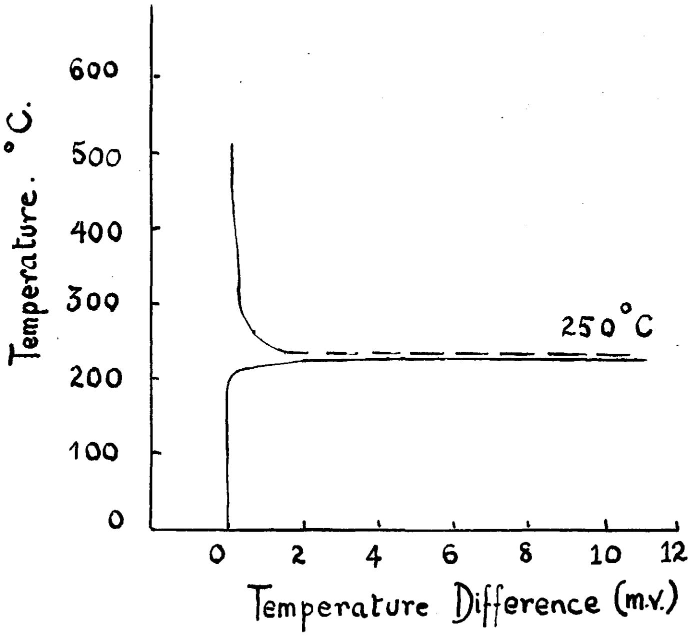


Fig (19): Differential thermal curve of a nickel-zinc compact, of composition corresponding to the compound formula - NiZn was indicated by the temperature difference of 175C$^{\circ}$ between the standard and the test specimen. An endothermic change was observed at 570°C but ~~none~~ not at the melting point of aluminum.

(3) According to Fig. (18) in the nickel-aluminium compact, equivalent to the NiAl composition, two well defined exothermic changes occurred at 460°C and 605°C, the latter temperature being associated with the greatest liberation of heat. The initial change created a temperature difference of 115 $^{\circ}$C between the standard and the test ~~a~~specimen, whilst the second caused a difference of 610 C$^{\circ}$, which was sufficient to upset the heating conditions within the furnace.

Since the aluminium powder was produced by the stamp process it contained slight traces of lubricant and so roused the suspicion that the presence of this carbon-aceous material might have affected the magnitude of the heat change in the presence of a very slight leak in the vacuum. Another differential thermal analysis was performed on a compact, containing filings obtained from a small ingot of super-purity aluminium (99.99%). As shown in Fig. (18b) an identical curve was obtained, revealing the same exothermic changes.

(4) The nickel-zinc compact, on heating in vacuo, displays a strong evolution of heat at 250°C as shown in Fig. (19) and /

and the reaction was sufficient to cause a temperature difference of 350 C° between the standard and the test specimen. No endothermic change was found at the melting point of zinc at 420°C.

CHAPTER 5.

Further X-ray studies of the alloy-sintering of bi-metallic compacts in vacuo.

X-ray meaaurements were performed on heat treated compacts of mixtures of two component metals. The systems investigated, were those in which intermetallic compound formation is known to occur when alloys are produced by fusion and casting. The systems examined, were those of iron,nickel and copper with magnesium, aluminium, silicon and tin. The transition elements iron and nickel along with copper form intermediate phases with the latter group of metals and the nature and stability of these phases are known. X-ray analysis may be employed to determine whether compound formation has occurred and to identify the phases produced.

Experimental procedure:

A Phillips X-ray machine, fitted with a Geiger-Muller counter, was employed as indicated earlier. Copper K-alpha radiation was generally employed excepting those specimens containing iron when cobalt radiation was employed due to the unfavourable absorption charactistics at the wavelengths of copper radiation for any reflection from the lattice planes of iron. Compacts, containing iron, were examined by the normal photographic technique, using a Straumanis camera and the X-rays generated by a Newton-Victor machine. Otherwise, the back reflection technique was /

was considered suitable for the remainder of the bimetallic compacts, since a number of planes of reflection are present within range of 5-45° angles of reflection as the lattice parameters of the intermetallic compounds which may form are large even although their crystal structures may be complex.

To assist the identification of the phases produced during heating of the compacts, alloys of the appropriate compositions were prepared by melting and casting, since their structures have not been fully established within the present classification index of X-ray diffraction patterns. Filings or turnings from these alloys were then examined to determine their X-ray patterns.

Bi-metallic compacts were prepared in the normal manner and heat treated in vacuo to the various temperatures associated with heat evolution as obtained by differential thermal analysis.(21) A compacting pressure of 50 tons/in.^{2} and as fine size grades of metallic powders as possible were employed in order that a general survey of alloy-sintering could be made. Test specimens of varying composition were used and the sintered products were crushed and ground to a powder of -170 mesh particle size wherever this was deemed necessary for X-ray measurements. The powdered product was mounted in diakon and /

and after polishing, was found to give good reflection characteristics. This procedure was also adopted for the standard alloys prepared by fusion since they could usually be readily crushed.

The results of the X-ray analysis have been tabulated and are given by Tables (7)-(19). The analysis of the Straumanis diffraction patterns have been summarised as the film negative could not be readily reproduced.

Results:

The different systems of bi-metallic compacts may be classified into three groups, (1) copper-base compacts, composed of copper with magnesium or aluminium powders; (2) nickel-base compacts containing nickel with magnesium, aluminium, silicon or tin powders; (3) iron-base compacts, consisting of iron and aluminium powders.

Each of these alloy systems comprise intermetallic compounds in the alloys prepared by melting and casting. Powder compacts of the metals have displayed marked expansion and exothermic changes during heating.(11,12,21)

The X-ray patterns of back reflection have been presented in the following fashion. A comparison of the reference alloy patterns, obtained from the alloys prepared by fusion, is given to confirm the reflection lines of the different /

Specimen	Treatment	Angles of Reflection (1) Line Intensity (2)
Copper	Compacted powder	44.2 Strong 74.8 Medium. 51.2 Medium
Magnesium	Compacted powder	33.0 Weak 57.0 Weak 35.2 Medium 63.8 Weak 37.6. Strong 69.4 Weak 48.6 Weak 70.7 V. Weak
84.0 % Copper Alloy (Cu_2Mg)	(a) Cast alloy ground to -170 mesh powder and mounted in diakon. Chemical analysis 84.0% copper (b) Alloy powder, obtained by alloy-sintering in vacuo the specimen, being used for differential thermal analysis.	(a) (b) 22.8 Strong 22.8 Strong 43.5 Strong 43.7 Strong 45.5. Strong 45.4 Strong 52.6 Weak 53.0 Medium 70.1 Medium 70.0, 70.3) V. Weak 77.3 Weak 77.3. Weak.
57.0 % Copper Alloy ($CuMg_2$)	(a) Cast alloy ground to -170 mesh powder and mounted in diakon Chemical analysis. 57.0% Copper (b) Alloy powder, obtained by alloy-sintering in vacuo the specimen, being used for differential thermal analysis.	(a) (b) 21.0 Medium 20.3, 20.5) Strong 38.2 Medium 38.2 Weak 40.1, 40.4) Strong 40.1, 40.3) Strong 43.1 Strong 43.2 Medium 45.3. Strong 45.3 Strong 54.3 V. Weak 54.7 Weak 65.4 V. weak 72.0 Weak 49.7 (?) Weak 76.0. V. Weak. 59.5 (?) Trace.

(1) Angles of Reflection are given by 2θ where θ = Bragg Angle.

(2) Terms of Intensity are,
Strong ≥ 100 Geiger counts.
Medium ≥ 50 Geiger Counts
Weak ≥ 20 Geiger counts
V. Weak < 10 Geiger counts.

Table (7): X-ray back reflections of copper, magnesium and alloys.

different intermetallic compounds and to determine the degree of homogenity of alloys prepared by sintering. Sufficient characteristic lines were generally obtained to permit the identification of the phases produced by the different heat treatments. Phase identification has also been tabulated to outline the general trend of the alloying mechanism.

(1) Alloy-sintering of copper-base compacts:

From the thermal analysis data(21) the heating of compacted powder mixtures of copper with magnesium or aluminium, is accompanied by marked heat evolution and X-ray measurements have been confined to these systems.

(a) Copper-magnesium:

The back reflections of copper, magnesium and their two intermetallic compounds, Cu_2Mg and $CuMg_2$, are shown in Table (7). Cast standard alloys were prepared and their compositions checked by the electrolytic estimation of their copper content.

Compacts of copper and magnesium powder mixtures, containing 90/10, 81/19, 75/25, and 70/30 compositions, were heated to 475°C and 520°C and permitted to cool in the furnace. The 81/19 and 70/30 compositions of powder mixtures are equivalent to the compositions(21) of the formulae of Cu_2Mg and $CuMg_2$. The temperature 475°C is below whilst 520°C is above the reaction temperature of the compacted /

(a) Specimens, slowly cooled in vacuo from 475°C.

X-ray Analysis: Copper) present Cu_2Mg) absent.
Magnesium) $CuMg_2$)

(b) Specimens, slowly cooled in vacuo from 520°C.

Composition %	X-ray Analysis.	
90/10. Cu/Mg.	Copper: 44.2 Strong 51.0) 51.3) Medium (broad) 74.2) 74.8) Weak (broad). Cu_2Mg: Absent.	Magnesium: Absent. $CuMg_2$: 37.2 Trace 40.3 Trace 45.4 Weak 72.1 Trace (broad)
84/16 Cu/Mg	Copper: 44.2 Strong 51.2 Medium (broad) 74.8 Medium (broad) Cu_2Mg: 22.8 Strong 43.4 Strong 53.0 Medium 63.0 Weak (broad) 70.0) 70.2) Medium 77.3. Weak (broad)	Magnesium: 43.9 Strong (displaced) 51.0 Medium (displaced) 74.2) 74.5) Weak (broad & displaced) $CuMg_2$: 21.0 V. Weak (diffuse). 37.0 Weak 45.3 Weak
75/25 Cu/Mg.	Copper: 44.1 Medium 51.3 Weak 74.6) 74.7) V. Weak Cu_2Mg: 22.8 Medium 43.3 Strong 52.4 Medium (displaced) 63.0 Weak 69.0 Weak 77.0 Weak	Magnesium: Absent $CuMg_2$: 20.3 Strong 36.9 Weak 40.1 Strong 45.3 Strong 49.7 Weak (?) 58.7 Weak (?).
57/43 Cu/Mg	Copper: 44.2 Strong 51.2 Medium 74.7) 74.9) Weak Cu_2Mg: Absent	Magnesium: 35.3 Medium 37.5 Medium 48.6 Weak 63.9 V. Weak (diffuse) $CuMg_2$: 20.3 Strong 21.0 Weak (broad) 36.3 Weak 40.1 Medium 40.3 Strong 43.2. Weak

Table (8): X-ray analysis of heat-treated copper-magnesium compacts.

compacted powders at 500°C. It may be observed that the temperatures were below the melting point of each metal, the various compounds and the lowest eutectic level within the copper-magnesium equilibrium system. The results of the X-ray examination are presented in Table (8).

Compacts, cooled in the furnace from 475°C, revealed only the presence of strong copper and magnesium reflections and there was no indication of line displacement or broadening. Compacts, heat treated to 520°C, show lines characteristic of a compound. Copper lines were found to persist although they had broadened and their intensities had diminished whilst no line displacement occurred. Magnesium lines were absent in all cases except the $CuMg_2$ specimen. The reflection pattern of the $CuMg_2$ compound was observed in all the compacts whilst Cu_2Mg phase reflection lines appear only in those compacts, containing 75/25 and 84/16 copper- magnesium powder mixture compositions.

A general conclusion of the analysis is that the formation of the $CuMg_2$ phase initiated alloy-sintering and may be followed by the formation of Cu_2Mg where sufficient copper and magnesium were present to promote the reaction. This would explain the absence of Cu_2Mg within the 57/43 and the 90/10 compacts.

(b) Copper-aluminium:

Specimen	Angles of Reflection	Line Intensity.		
Copper: Pressed compact.	44.2 74.8	Strong Medium.	51.2	Medium.
Aluminium: Pressed compact.	~~32.0~~ 65.7	Medium 39.4 Medium.	45.4 78.9	Strong Medium.
(a) 87.5% Cu-(Cu_3Al) (b) 86.6% Compacted alloy powders, severely quenched from 900°C into ice and water.	(a) 41.5 45.5, 45.7 47.8	 Medium Weak (?)	(b) 41.2 45.5. 45.7 47.3	 Medium Weak Medium
82.4% Cu - (Cu_9Al_4) Alloy powder obtained from cast alloy.	43.5, 43.8	V. Weak	44.9 46.0	Strong. V. Weak.
77.6% Cu - ($Cu_{16}Al_9$?) Alloy powder obtained from cast alloy.	26.0 44.2 45.0	V. Weak V. Weak Strong	49.7 65.0	Weak Weak.
75.2% Cu - (Cu_3Al_2) Alloy powder obtained from cast alloy.	26.0 44.1 45.1	Strong V. Weak Strong	65.0, 65.3	Weak
72.5% Cu - (Cu.Al) Alloy powder obtained from cast alloy.	24.5 26.1 44.5	Weak Weak V. Weak	45.25 65.0, 65.5	Strong Weak.
54.5% Cu - ($CuAl_2$) Alloy powder obtained from cast alloy	21.7 30.3 38.8	Strong Weak Medium.	42.9 43.5 46.5 48.2.	Strong Strong Trace Medium
49.0% Cu- alloy. Alloy powder obtained from cast alloy.	21.7 30.4 38.8 42.2 43.0 43.5	Strong V. Weak Medium V. Weak Medium Strong	45.2, 45.6 48.2 48.7 57.8 74.2	(?) Medium. Weak Medium Medium

Table (9): X-ray back reflections of copper, aluminium and alloys.

(b) Copper-aluminium:

In Table (9) is given the back reflection patterns of copper, aluminium and their intermetallic compounds which were prepared by fusion and casting. Their compositions were verified by the electrolytic estimation of the copper content. Of the various phases, beta Cu_3Al ~~Al~~ which is unstable below 570°C, presented the greatest difficulty and the X-ray pattern of this phase was obtained by experiments involving the repeated drastic quenching of alloys from temperatures above 900°C into ice and water.

Test specimens of a powder mixture, containing 87/13 ratio by weight of copper-aluminum powders, were water-quenched from 540°C, 700°C, and 900°C. It was observed that after a period of several hours at room temperature the compact, quenched from 540°C, was found to expand and finally crumble into a powder. This tendency still persisted in the compact quenched from 700°C but was not apparent in that quenched from 900°C.

Consideration of this effect would suggest that quenching had interrupted the initial stages of the mechanism but was insufficient to suppress the reaction from occurring even at room temperature.

From Table (10) immediate X-ray analysis of the specimen, /

(a) All specimens are of composition corresponding to the formula Cu_3Al (87% Copper).

Treatment	X-ray Analysis
1 Water-quenched from 540°C and immediately X-rayed	Copper: 44.2 Strong 51.2 Medium 74.8 Weak (broad) Aluminium: Absent Unidentified 62.1 V. Weak (broad) Attributed to Al-rich solid solution. $CuAl_2$ 21.0 21.5) V. Weak 21 6 37.4 Strong(3) 33.4 Weak 43.1 43.5) V. Weak (broad) 74.2 V. Weak (broad)
2 Water-quenched from 540°C. Specimen found to disintegrate after several hours, the disintegrated powder was then X-rayed	Copper: 44.2 Stong 51.3 Weak (broad) 74.8 Weak (broad) $CuAl_2$: 21.7 Weak (3) 37.2 Medium 43.0 Medium (broad) 48.6 Weak (broad) 74.8 V. Weak (diffuse) Aluminium: Absent Cu_9Al_4: 43.5. Medium 44.9 Indefinite. 46.0 (?).
3. Water-quenched from 700°C. Specimen showed tendency to crumble after several hours, the specimen was then X-rayed.	Copper: 44.2 Strong 51.2 Medium (broad) 74.8 Weak (broad) $CuAl_2$: 21.7 Weak 37.3 Medium (3) 43.0 Weak (broad) 45.2 Weak (broad) 48.6 Weak (Indefinite) 74.2 Weak (broad) Aluminium: Absent Unidentified: (4) 62.1 V. Weak (broad) 50.7 Weak (broad) Cu_9Al_4: 43.5 V. Weak 44.9 Weak 46.0 Trace.
4. Water-quenched from 900°C. Specimen showed no tendency to crumble.	Copper: 44.2 Medium 51.2 Trace 74.8 Trace Cu_9Al_4 43.5. Indefinite 44.9 Strong 46.0 V. Weak Aluminium: Absent. $CuAl_2$ Definite traces Lines of copper-rich primary solid solution at, 44.0 Strong 50.7 Weak (broad) 74.1 Weak (broad)

(3) This line cannot be rigidly identified as a $CuAl_2$ line. Further investigation has suggested that it may be due to a transient phase, introduced by water-quenching.

(4) Lines attributed to primary Al- and Cu-rich solid solutions.

Table (10): X-ray analysis of heat-treated copper-aluminium compacts.

specimen, water-quenched from 540°C, indicated the presence of copper and possible traces of an aluminium-rich solid solution, otherwise there were no apparent traces of aluminium. The formation of $CuAl_2$ was apparent but no other intermediate phase could be detected. Examination of the disintegrated compact revealed the presence of a copper-rich intermediate phase to which the expansion of the compact may presumably be attributed. X-ray studies of the other specimens which were water quenched from 700°C and 900°C, showed more definite indications of the copper-rich intermediate phase and the formation copper-rich alpha solid solution, with consequent depletion of the copper lines. In the latter specimen, water-quenched from 900°C, there were possible traces of the Cu_9Al_4 phase but the lines were too indefinite to establish its presence.

This examination inferred that alloy-sintering was began with the formation of the compound $Cu\,Al_2$ followed by the appearance of a copper-rich intermediate phase which however could not be positively identified. The mechanism can occur at a temperature below the melting points of the component metals and lowest eutectic level of the copper-aluminium system.

(2) Alloy-sintering of nickel-base bimetallic compacts:

According /

Specimen	Angles of Reflection Line Intensity			
Nickel: Pressed compact	45.4	Strong	52.7	Strong
	77.1	Medium		
Magnesium: Pressed compact	33.0	Weak	57.0	Weak
	35.2	Medium	63.8	Weak
	37.5	Strong	69.4	Weak
	48.6	Weak	70.7	V. Weak
78% Nickel alloy (Ni_2Mg)	(a)		(b)	
(a) Alloy powder produced by alloy-sintering in vacuo at 450°C for 100 hours.			23.0 23.4	Weak
			24.9	V. Weak
			35.5	V. Weak
(b) Alloy powder obtained from cast alloy	43.7	Weak	41.5	V. Weak
Chemical analysis 78.1% Ni	45.3	Strong	44.9	Strong
			45.8	Weak
	52.6	Strong	52.4 52.5	V. Weak
	62.5	V. Weak	64.5	Trace
	63.0	Weak	67.2	Trace
	75.5	Weak	76.8	V. Weak
	76.9	Medium	80.1	Weak.
54% Nickel alloy ($NiMg_2$)	(a)		(b)	
			21.0	Strong
(a) Alloy powder produced by alloy-sintering in vacuo at 450°C for 100 hours.			23.0	V. Weak
	37.9	Weak	37.9	Weak
	40.4	V. Weak	40.2	Weak
	40.8	Weak	41.2	V. Weak
(b) Alloy powder obtained from cast alloy	45.9	Medium	44.5	V. Weak
			45.9	Strong
	58.1	Weak	47.5	V. Weak
Chemical analysis 54.0% Ni.	67.6	V. Weak.	53.0	Trace
	73.1.	V. Weak.	73.0	V. Weak.

Table (11): X-ray back reflections of nickel, magnesium and alloys.

According to differential thermal analysis data[(21)], compacted powder mixtures of nickel with magnesium, aluminium, silicon or tin, are accompanied by heat evolution during heating.

(a) Nickel-Magnesium:

Nickel and magnesium form two intermatallic compounds, Ni_2Mg and $Ni Mg_2$, which were prepared by direct alloying and casting. The composition of the cast alloys was verified by chemical analysis of nickel by the gravemetric precipitation of nickel demethyl-glyoxime from solution.

In Table (IV) are presented the back reflection data of nickel, magnesiume and their two compounds. An alloy of Ni_2Mg composition could not be prepared by prolonged sintering in vacuo since the annealed compact was found inhomogeneous, as indicated by the presence of nickel and $Ni Mg_2$ lines.

Powder mixtures, containing nickel-magnesium compositions of 90/10, 81/19; 75/25 and 70/30 proportions by weight were compacted and then water-quenched from 450°C which was the observed reaction temperature associated with heat evolution.(21) The powder mixtures of 81/19 and 70/30 correspond to the compositions of the Ni_2Mg and $NiMg_2$ compounds.

The /

(a) All specimens, water-quenched from 450°C.

Composition %	X-ray Analysis.
90/10 Ni/Mg	Nickel: 45.3 Strong (sharp) 52.7 Weak (broad) 77.0 Weak (broad) $NiMg_2$: 37.9 V. Weak 40.7 V. Weak) Indefinite 45.9 V. Weak Magnesium: Absent. Ni_2Mg: Absent.
81/19 Ni/Mg	Nickel: 45.3 Medium (sharp) 52.7 Weak (broad) 77.0 Weak (broad) $NiMg_2$: 37.9 V. Weak (broad) 40.2 V. Weak (broad) 40.7 Weak (broad) 45.9 Medium (sharp) 65.5 V. Weak } Indefinite 73.0 (?) } Indefinite 67.4 V. Weak } Indefinite Magnesium: Absent Ni_2Mg: 44.0 - (?) otherwise no trace.
75/25 Ni/Mg	Nickel: 45.3 Weak (broad) 52.6 Weak (broad) 76.9) V. Weak (diffuse) 77.2) V. Weak (diffuse) $NiMg_2$: 36.0 - Indefinite.(5) 37.9 Weak (broad) 40.2 Weak (broad) 40.8 Weak (broad) 45.9 Medium (sharp) 58.1 (?) Indefinite. 65.5 Weak (broad) 67.6 Weak (broad) 73.1 Weak (sharp). Magnesium: Absent Ni_2Mg: Absent.
69/31 Ni/Mg.	Nickel: Absent Magnesium Absent $NiMg_2$: 37.9 Weak 40.4 V. Weak 40.8 Weak 45.9 Strong 58.1 V. Weak (broad) 65.6 Weak (broad) 67.6 Weak (broad) 73.1 V. Weak (broad) Ni_2Mg: Absent

(5) Attributed to Mg-rich solid solution.

Table (12): X-ray analysis of heat-treated nickel-magnesium compacts.

The X-ray reflections obtained are shown in Table (12). (12). The investigations revealed that, except for the compact of 69/31 composition, nickel lines persist although their intensities diminish and they become slightly broadened. Magnesium lines were absent and in all specimens it was observed that the nickel lines were not displaced. There were no apparent indications of the magnesium-rich solid solution. Characteristic lines of the compound $NiMg_2$ were very evident and only traces of Ni_2Mg were found. It is to be concluded that the formation of $NiMg_2$ was responsible for the initial stages of the alloy-sintering, similar to that of the copper-magnesium compacts. No apparent magnesium-rich solid solution preceded the reaction, inferring that there was rapid diffusion of magnesium into the nickel. Since the specimens have been water-quenched, the reaction to form Ni_2Mg has possibly been deterred. The inhomogeneity of the prolonged sintered Ni_2Mg compact, however, would suggest that this alloy cannot be readily prepared by this method.

(6) Nickel-Aluminium:

Two intermetallic compounds occur in this system, Ni_3Al and NiAl and alloys corresponding to those compositions were prepared. The alloy composition was checked by the gravimetric estimation of nickel as in the previous case.

Back /

Specimen	Angles of Reflection. Line Intensity.			
Nickel: Pressed compact.	45.4	Strong	77.1	Medium.
	52.7	Strong		
Aluminium: Pressed compact.	39.2 40.3)	Strong	67.7	Weak
	45.4	Strong	78.9	Medium.
Ni_3Al alloy powder: Prepared by alloy-sintering for 180 hours at 1000°C.	44.6	Medium	75.6	V. Weak
	45.1	Strong	76.5	(?) Trace.
	51.7	Weak		
	52.1	Weak		
NiAl alloy powder: (a) prepared by alloy-sintering for 180 hours at 1000°C. (b) Obtained from cast alloy. Chemical analysis 67.8% Ni.	(a)		(b)	
	31.8	Weak	31.0	Trace
	45.2	Strong	31.9	medium
	65.2 65.6)	Weak	35.0	Trace
			36.1	Weak
			44.5	Strong
			45.4 45.8)	Strong
			65.2 65.4)	Trace
			79.0	V. Weak
50/50 ratio alloy of Ni_3Al and NiAl. Prepared by alloy-sintering for 180 hours at 1000°C.	Ni_3Al		NiAl	
	44.6	Strong	32.0	(?) Trace.
	45.1	----	45.5.	Strong
	51.6	Weak	65.9	(?) Trace.
	75.4	Weak		

Table (13): X-ray back reflections of nickel, aluminium and alloys.

Back reflection patterns of nickel, aluminium and the two intermediate phases are given in Table (13). Comparison of the patterns reveal little difference between them, NiAl may omly be distinguished from Ni_3Al by the presence of two weak lines at 32.0 and 65.5 degrees angle of back-reflection. The Ni_3Al pattern differed from that of nickel by the appearance of super-lattice lines at angles slightly less than those associated with a primary nickel-rich solid solution. An alloy of 50/50 ratio of Ni_3Al and NiAl composition, was therefore prepared to determine whether any clearer defination between the patterns could be obtained. The reference patterns were sufficiently different to permit a qualitative identification of the phases whose formation was responsible for the exothermic changes, observed at 500°C.

Test specimens, containing nickel-aluminium powder mixtures of 95/5, 86/14, 70/30 and 68/32 compositions, were prepared and water-quenched from 500°C and 600°C. The 86/14 and 68/32 compositions correspond to the compound formulae. Ni_3Al and NiAl. The X-ray data for these compacts are shown in Table (14)-(15).

Investigation of the compacts water-quenched from 500°C indicated the presence of both nickel and aluminium lines. These were broad and of diminished intensity but were /

(a) All specimens water-quenched from 500°C.

Composition %	X-ray Analysis.	
95/5 Ni/Al	Nickel: 45.4 Strong 52.6 Medium (broad) 77.0 Weak (broad).	Aluminium 39.4 Trace (?) 78.9 (?). 45.4 Strong 67.7 (?)
	Ni_3Al: 44.6 Trace (?) 45.4 Strong 51.8 Trace (?) 76.5 Trace (?).	NiAl: 32.0 (?) 45.4 Strong (?) 65.2 (?).
88/12 Ni/Al	Nickel: 45.4 Strong 52.6 Medium 77.0 Weak (broad)	Aluminium: 39.4 Trace (?) 78.9. (?) 45.4 Strong 67.0 (?)
	Ni_3Al: 44.6 V. Weak (diffuse) 45.4 Strong. 51.7 V. Weak (diffuse) 76.5 (?)	NiAl: 32.0 (?) 45.4 Strong. 65.7 Trace.
70/30 Ni/Al	Nickel: 45.4 Strong (broad) 52.6 Weak (broad) 77.1 Weak (broad)	Aluminium: 39.4 Weak (broad) 45.4 Strong (broad) 79.0 V. Weak (broad).
	Ni_3Al 44.6 Weak 45.4 Strong 51.6) 51.8) Weak (diffuse)	NiAl: 32.0 Trace 45.4 Strong. 65.8 V. Weak.
68/32 Ni/Al	Nickel: 45.4 Strong (broad) 52.6 V. Weak (broad) 77.1 V. Weak (broad).	Aluminium: 39.4 V. Weak 45.4 Strong (broad) 79.0 Indefinite
	Ni_3Al: 44.6) 44.9) Weak 45.4 Strong (broad) 51.6) 51.8) Weak 76.5 Indefinite.	NiAl: 32.0 (?) 45.4 Strong (broad) 65.8 V. Weak.

Table (14): X-ray analysis of heat-treated nickel-aluminium compacts.

(b) All specimens water quenched from 600°C.

Composition %	X-ray Analysis.	
95/5 Ni/Al	Nickel: 45.3 Strong 52.6 Medium (broad) 77.0 Medium (broad) Ni_3Al: 44.6 Medium 45.3 Strong 51.6 Weak (broad) 75.6 V. Weak	Aluminium: Absent. Ni Al: 32.0 Weak (broad) 45.3 Strong. 65.2 (?) indefinite
88/12 Ni/Al	Nickel: 45.4 Strong (broad) 52.6 Medium (broad) 77.0 Weak (broad) Ni_3Al: 44.6 Medium 45.4 Strong (broad) 51.6 Weak (broad) 75.6 Weak (broad)	Aluminium: Absent. Ni Al: 32.0 (?) 45.4 Strong (broad) 65.2 Trace.
70/30 Ni/Al	Nickel: 45.4 Strong 52.6 V. Weak 77.0 Trace Ni_3Al: 44.6 Medium 45.4 Strong 51.7 Weak (broad) 75.6 Weak (broad)	Aluminium: Absent. Ni Al: 32.0 Weak 45.4 Strong 65.4 Weak (broad)
68/32 Ni/Al	Nickel: Ni_3Al: Aluminium } Absent.	Ni Al: 31.9 Weak 45.3 Strong 65.7 Weak.

Table (15): X-ray analysis of heat-treated nickel-aluminium compacts.

were not displaced. In all cases lines of Ni_3Al were determined although there were occasional traces of the NiAl pattern.

Examination of the second series of compacts, water-quenched from 600°C was marked by the complete disappearance of the aluminium lines and the more definite appearance of the phase NiAl. In general, it was observed that the pattern tended to conform to that which could be associated with the equilibrium alloy.

Since no formation of an aluminium-rich solid solution was determined in either of the series, it would appear that the formation of Ni_3Al initiated the reaction at 500°C. The major heat change at 600°c is to be linked with the formation of NiAl.

(c) Nickel-silicon:

Nickel and Silicon form a number of intermediate phases and of these Ni_3Si, Ni_5Si_2, Ni_2Si and Ni Si were prepared by melting and casting. The compositions of the cast alloys were checked by analysing for nickel as in the previous two cases. Compacted nickel-silicon powders, corresponding not only to the compositions of these compounds but also of Ni_3Si_2 and $NiSi_2$ were subjected to a prolonged sintering treatment in vacuo, as shown in Table (16).

Comparison of fused alloy reflection lines with those of the prolonged sintered products, as given in Table (16), indicated /

Specimen	Angles of Reflection	Line Intensity.	Angles of Reflection	Line Intensity.
Nickel: Pressed compact.	45.4	Strong	77.1	Medium
	52.7	Strong		
Silicon Pressed compact.	29.5	Strong	57.0	Weak
	48.2	Medium	77.1	V. Weak
Ni_3Si alloy: (a) Prepared by alloy-sintering for 48 hours at 700°C and then 250 hours at 1000°C. in vacuo. (b) Prepared by melting, Chemical analysis - 86.4 %Ni	(a)		(b)	
	45.5	Strong	45.4	Strong
	53.0	Weak	52.9	Weak (diffuse)
	77.0	V. Weak	76.7 77.2 77.8	V. Weak (broad)
	27.6	V. Weak	39.4	Trace
	30.5	V. Weak	42.6	Trace.
	35.0	Trace		
	42.9	V. Weak		
	43.9	V. Weak		
	46.8	Weak		
	48.0	Weak		
	68.7	Trace		
	76.0	Trace		
Ni_5Si_2 alloy: (a) Prepared by alloy-sintering for 48 hours at 700°C and then 250 hours at 1000°C in vacuo. (b) Prepared by melting. Chemical analysis 83.8%Ni	(a)		(b)	
	42.8	V. Weak	42.8	V. Weak
	43.2	Weak	43.9	Weak
	45.4	Medium	46.9	Medium
	46.8	Medium	47.9	Medium
	48.0	Medium.	68.6	Medium
	52.2 52.7	Trace	30.1	V. Weak
			31.5	V. Weak
	60.5 66.8 67.1 68.7	Indefinite.	43.0	V. Weak
			53.0	Indefinite
			72.6	Trace
			78.9 79.2 79.6	Weak (diffuse)
Ni_2Si alloy: (a) Prepared by alloy-sintering for 350 hours at 750°C in vacuo. (b) Prepared by melting. Chemical analysis - 81.4%Ni	(a)		(b)	
	27.9	V. Weak		
	40.4	V. Weak	40.3	Weak
	43.2	V. Weak	43.2	Weak
	44.3	V. Weak.	44.3	V. Weak
	45.2	Indefinite	45.2	Weak
	46.4	Strong	46.3	Strong
	48.0	Weak	48.1	V. Weak
	49.6	Medium	49.6	Strong
	62.0	V. Weak	62.0	Trace.

(P.T.O.)

Table (16): continued on next page.

	(a)		(b)	
Ni_3Si_2 alloy: (a) Prepared by alloy-sintering for 350 hours at 750°C in vacuo	43.2	V. Weak		
	44.5	Indefinite		
	45.2	Medium		
	45.9	Medium		
	46.3	Weak		
	46.7	Medium		
	48.4	Weak		
	52.9	Trace		
	53.6			
	66.4			
	74.4			
NiSi alloy: (a) Prepared by alloy-sintering for 350 hours at 750°C in vacuo.	32.2	Strong	32.0	Weak
	35.4	Weak	32.2	
	46.6	Medium	35.4	Weak
	48.0	Strong	36.8	Weak
	52.6	Weak	37.2	Weak
(b) Prepared by melting Chemical analysis 67.2% Ni	44.0	Traces	46.5	Medium
	45.3		48.1	Strong
	45.9		52.6	Strong
	48.8		36.0	Traces.
	51.0		63.0	
	61.0			
$NiSi_2$ alloy: (a) Prepared by alloy-sintering for 350 hours at 750°C in vacuo.	29.4	Strong		
	37.2	Weak		
	46.6	Weak		
	48.4	V. Strong		
	57.1	Medium		
	66.0	V. Weak		
	66.2			
	66.4			
	77.4	Trace		

Table (16): X-ray back reflections of nickel, silicon and alloys.

(a) All specimens slowly cooled in vacuo from 675°C.

Composition %	X-ray Analysis.	
95/5 Ni/Si	Nickel: 45.4 Strong (broad) 52.7 Strong (broad) 77.1 Medium (broad) $NiSi$: 32.0 V. Weak (broad) 46.6 Weak (broad) 48.0 Medium 52.6 Indefinite 44.0 Trace	Silicon: $NiSi_2$: Ni_2Si: Ni_5Si_2: Ni_3Si: } Absent. Ni_3Si_2: (?) Principal lines coincide with those of $NiSi$ but subsidiary lines are absent.
85/15 Ni/Si	Nickel: Lines have shifted to coincide with Ni_3Si: 45.6 Strong 52.9 Medium 77.4 Weak (broad) $NiSi$: 32.0 V. Weak (broad) 46.6 Medium (displaced) 48.0 Medium 52.5 Trace Ni_5Si_2: Major lines coincident with those of $NiSi$ observed but presence of line at 68.7 suggests that this phase has formed.	Silicon: $NiSi_2$: Ni_3Si_2: } Absent. Ni_2Si: 40.4 Trace 43.2 V. Weak (broad) 45.2 } 46.4 } Indefinite 48.0 Medium 49.6 V. Weak (broad) 62.0 Trace
81/19 Ni/Si	Nickel: Lines have shifted to coincide with Ni_3Si:- $NiSi$: 32.0 Indefinite 40.4 Trace 46.3 Strong 48.1 Strong 49.6 Medium. Ni_2Si: 43.0 Trace 46.3 Strong 48.1 Strong 49.6 Medium.	Silicon: $NiSi_2$: } Absent Ni_3Si_2: 44.4 Weak 45.3 Strong 45.9 Indefinite 46.3 Strong 46.7 Medium 48.5 Trace Ni_5Si_2: Presence indicated by line at 68.7.

(P.T.O.)

Table (17): continued on next page.

75/25 Ni/Si	Nickel: Absent NiSi: (?) 46.6 Weak (broad) 48.1 Weak (broad) Ni_3Si_2: 43.2 Trace 44.4 Weak 45.3 Medium 45.9 Weak 46.3 Strong 48.4 Trace.	Silicon: Absent except for traces at, 29.0 Trace 48.1 V. Weak (broad) Ni_2Si: 40.4 Trace 46.3 Strong 48.1 V. Weak (broad) 49.6 Weak Ni_5Si_2 Ni_3Si } Absent.
65/35 Ni/Si	Nickel: 45.4 Weak 52.7 Weak (broad) 77.1 V.Weak (broad) NiSi (?) 32.5 Trace 46.6 Trace 48.1 Medium. Ni_3Si_2: All lines of this phase are present but are of weak intensity	Silicon: 29.4 Weak 48.1 Weak 56.9 V. Weak 77.1 V. Weak Ni_2Si: Ni_5Si_2: Ni_3Si: } Absent.
55/45 Ni/Si	Nickel: 45.4 Weak (broad) 52.7 Weak (broad) 77.1 V. Weak NiSi : Ni_3Si_2: } Lines of these phases are present but are of weak intensity	Silicon: 29.4 Strong 48.1 Medium 77.1 V. Weak. Ni_2Si Ni_5Si_2 Ni_3Si } Absent.
45/55 Ni/Si	Nickel: 45.4 Medium 52.7 Weak (broad) 77.1 V. Weak (broad) No compound phase lines were found present.	Silicon: 29.4 Strong 48.1 Weak 56.9 V. Weak 77.1 V. Weak.

Table (17): X-ray analysis of heat-treated nickel-silicon compacts.

indicated that the sintered alloys contained traces of incomplete alloying by the presence of faint lines which could be accredited to neighbouring intermediate phases at the alloy compositions which were prepared. Otherwise, there was good agreement between both sets of alloys. Sufficient referance lines were available to identify the new phases formed at 670°C, the reaction-temperature of nickel-silicon powder compacts.(21)

A range of test compacts were made, containing mixtures of powders, as given in Table (17), along with X-ray data of the heat-treated compacts. The nature of the reaction can be best realised by considering first those specimens, containing a high proportion of silicon. After heating, the 45/55 compact of nickel-silicon powders displayed only the lines of nickel and silicon, whereas the 55/45 mixture revealed weak traces of Ni Si and Ni_3Si_2 along with the component elements. As the proportion of nickel increased, the patterns were characterised by the disappearance of the nickel and silicon lines which were replaced by the appearance of the other intermediate phases in the order Ni_2Si , Ni_5Si_2 and Ni_3Si along with the other previous compounds. Nickel lines, slightly broadened and of diminished intensity, reappeared in the 95/5 specimen along with faint traces of Ni Si.

Interpretation /

Interpretation of the data indicated that the reaction, although complicated, possibly began with the formation of Ni Si which promoted a series of reactions, resulting in the formation of the other phases. Sufficient nickel and silicon must be present to maintain the reaction. This may account for the absence of the compounds in the higher silicon compacts and the isolated presence of Ni Si in the 95/5 compact. In all cases no traces of primary silicon rich solid solution were determined nor was there any displacement of either the silicon or the nickel lines, inferring that rapid combination of the metals had occurred.

(d) Nickel-tin:

Nickel and tin form two stable intermetallic compounds, Ni_3Sn_2 and Ni_2Sn3, which were prepared by prolonged sintering treatment. Back reflection patterns of nickel, tin and their two compounds are presented in Table (18); the patterns were weak but were of sufficient strength to permit identification of the phases formed at 180 °C, the temperature at which reaction occurs according to differential thermal analyses data.(21)

Table (19) shows the results of the various nickel-tin powder compacts after heating to 250 °C and cooling in the furnace. This has revealed that Ni_2Sn_3 was initially formed. Nickel lines persisted in all cases except in the compact /

Specimen	Angles of Reflection. Line Intensity.			
Nickel: Pressed compact	45.4 52.6	Strong Strong.	77.1	Medium.
Tin : Pressed compact.	31.6 32.9 44.7 45.8 56.1 63.3.	Medium Medium V. Weak Weak V. Weak Trace	64.5 65.3 73.1 73.9 80.2	Trace V. Weak Trace Trace Trace.
Ni_3Sn_2 alloy obtained by alloy-sintering for 48 hours at 200°C and then 180 hours at 400°C.	31.0 31.2 31.7 32.0 44.3 44.6	Weak Weak Weak	45.3 55.9 59.8 62.5.	Weak (broad) Trace Trace Trace
Ni_2Sn_3 alloy: Obtained by alloy-sintering for 48 hours at 200°C and then 180 hours at 400°C.	31.2 31.6 32.5 44.1 45.3	Weak Indefinite V. Weak Weak Weak.	55.8 59.0 73.0	Indefinite Traces.

Table (18) : X-ray back reflections of nickel, tin and alloys.

(a) All specimens slowly cooled in vacuo from 250°C.

Composition %	X-ray Analysis.
80/20 Ni/Sn	Nickel: 45.3 Strong 52.6 Strong 77.1 Medium Tin : } Absent. Ni_3Sn_2: } Absent. Ni_2Sn_3: 31.2 } Weak 31.6 } 32.5 } Weak 32.6 } 44.2 Weak 45.3 ......
60/40 Ni/Sn	Nickel 45.4 Strong 52.6 Medium 77.1 V. Weak (broad) Tin: } Absent Ni_3Sn_2 : } Absent Ni_2Sn_3 31.3 } Weak 31.6 } 32.5 } Weak 32.7 } 44.2 Weak 45.4 .....
40/60 Ni/Sn.	Nickel : } Absent Tin : } Absent Ni_3Sn_2: } Absent Ni_2Sn_3 31.5 Weak 32.5 } Trace 32.7 } 44.2 Weak 45.4 Medium.
66/34 Ni/Sn. (6)	Nickel: 45.4 Strong 52.6 Medium 77.1 Medium. Tin : } Absent. Ni_3Sn_2 : } Absent. Ni_2Sn_3: 31.3 } Weak 31.6 } 32.5 Trace 44.1 } Medium. 44.4 }

(6) This specimen was used for differential thermal analysis ~~and~~ which had revealed an exothermic change at 185°C. The specimen has been allowed to slowly cool in vacuo from 220°C.

Table (19) : X-ray analysis of heat-treated nickel-tin compacts.

compact, corresponding to the Ni_2Sn_3 composition. No displacement of the nickel lines was found nor were there lines of any primary tin-rich solid solution, preceding the reaction as indicated by the X-ray patterns.

(3) Alloy-sintering of iron-base bi-metallic Compacts. Differential thermal analysis has established that compacted iron-aluminium powder mixtures reacted on heating with marked liberation of heat at 600°C. Since copper radiation is unsuitable in studying iron, the compacts were tested by normal X-ray diffraction technique, using a Straumanis Camera with cobalt radiation.

(a) Iron-aluminium:

Two compacts of 86/14 and 67.5/32.5 ratios (corresponding to the compositions of the intermetallic compounds Fe_3Al and $FeAl$) which had been previously employed for differential thermal analysis experiments, were examined. The various lines in the diffraction patterns were identified by comparison with similar patterns of iron and aluminium.

The specimen of $FeAl$ composition gave no lines, corresponding to those of iron and aluminium but a new pattern appeared in the diffraction photograph. This pattern could be associated with the intermetallic compound $FeAl$. On the other hand, the compact of Fe_3Al composition was characterised by the presence of iron lines along with diffraction /

diffraction pattern which is associated with Fe Al There was no indication of the presence of primary aluminum rich solid solution. The reaction would therefore appear to consist of the formation of Fe Al.

Discussion of experimental results.

(1) Preliminary investigation of the alloy sintering of copper-zinc Compacts in vacuo.

(a) Dilatometric analysis:

The sudden expansions, approximately proportional to the zinc content of the compacts and occuring over the temperature range of 200°- 380°C agree with the results which have been determined by other investigators(11,12,22) Raube and Plate (12) have found that maximum total expansion occurred with a zinc content of 80%. These investigators concluded that expansion was due to the formation of a copper-zinc compound, containing approximately 80%, and the internal pressure created within the pores of the compact by the volatileation of the zinc. Duwez and Martens (11) proposed that a number of intermediate phases were being formed at overlapping stages. The initial phase formed, was not considered until Cranston (22) claimed, from metallographic studies that beta-CuZn was initially formed and that this phase possessed a degree of stability over the expansion range observed by the dilatometric studies. No other intermediate phases were reported by Cranston.

Ref?

The effect of particle size of the powders had not been previously examined. As the particle size diminished, swelling of the compacts decreased. This may be explained on the basis of phase formation. Decrease in particle size /

size of the powders causes an increase of the surface area on which zinc vapour may be absorbed and from which zinc may volatilise. This promotes greater phase formation and consequently less free zinc ia available to create internal swelling pressure within the compact. The volatilization of zinc and its subsequent absorption by the copper particles is believed to have a larger expansion effect than the changes of crystal structure which accompany phase formation . From geometrical considerations of packing, the growth of larger sized copper particles during phase formation, may be accompanied by a greater decrease in the packing density.

The pressed compact has a certain green strength and consequently, the higher the compacting pressure, the greater the resistance against swelling that would be developed. An increase in the degree of cold welding at the metal particle interfaces would also be expected so that interdiffusion causing phase formation, may be enhanced and there would be less free zinc to cause swelling of the compact. The increase in expansion noted when the compacting pressure exceeds 30 tons/in.^{2} can only be attributed to the nature of phase formation which will be discussed later. The initial temperature of expansion fell as the compacting pressure increased, and this may be attributed to the greater degree of pressure-welded interfacial contact of the

powders /

powders.

(b) Differential thermal analysis:

The marked exothermic change at 240°C tended to confirm the assumption of intermetallic compound formation during the alloy-sintering of copper-zinc compacts. It is apparent that the possibility of this reaction was largely dependent upon the two main physical variobles of the campact, namely, the inherent particle size of the powders and the compacting pressure employed.

The differential thermal analysis of a series of compacts, composed of varying blends of finer sized powders which had been pressed at 50 tons /in.^{2} reveals the general behaviour to be expected during the alloy-sintering of copper-zinc compacts. A compound is initially formed at 240°C, independent of the composition of the compact. The extent of the reaction, as measured by the intensity of the heat change, increases with the zinc content and appears to reach a maximum intensity with a zinc content of 50%. Since this heat libration is associated with the abrupt expansions which have been observed, expansion must be partially due to the initial formation of a copper-zinc compound. Traces of a minor exothermic change occur at 300°C for compacts~~,~~ containing 20% and 50% zinc. A second phase may form but it would be more probable that a more rapid rate of heating during sintering prevented the /

the majob change at 240°C from being complete. This suggests that in the study of alloy-sintering, the rate of heating may be critical. The endothermic changes at 420°-480°C are attributed to the melting of residual uncombined zinc.

The differential thermal measurements during the heating of compacts, comprised of a 50/50 mixture of copper-zinc powders of varying size grades and compacted under different compacting pressures, support the conclusions which have been obtained from dilatometric studies. The possibilities of intermetalic compound formation are enhanced by decreasing the particle size of the powders and increasing the compacting pressure. When relatively coarse powder mixtures were investigated, there was little evidence of compound formation and since such compacts were associated with very marked expansion, the internal swelling pressure of zinc vapour may perhaps be regarded as the major force causing expansion of the compacts during heating.

The particle size of the powders had to be less than -170 mesh and the compacting pressure greater than before appreciable heat liberation occurred at 240°C. This implies that the mechanism of alloy-sintering is linked with the nature of the metallic powder surfaces and the /

and the formation of cold-welded interfaces between the metal particles.

Differential thermal analysis appears a very suitable method of studying the mechanism of alloy-sintering within bi-metallic compacts in which compound formation may occur.

(c) Electrical resistance measurements:

The resistance of a compact may be considered as being dependent upon two factors

(a) The resistance of the metallic particles.

(b) The interfacial contact resistance between neighbouring particles.

The latter factor can cause the largest variation due to its dependency on surface conditions of the powders and the degree of cold-welding, effected during compaction.

The resistance of zinc is higher than that of copper and the decrease of the initial resistance of the compact with increasing proportions of zinc, may be explained by the packing of the - 300 mesh zinc powder within the voids, presented by the relatively coarser copper particles. The initial resistance of the compact becomes correspondingly lowered until the voids have been completely filled with the finer powder. Once the zinc content exceeds 40%, the continuity of the copper particles is disrupted and the interfacial resistance of /

of the-300 mesh zinc powder causes the resistance to increase.

The abrupt change at 200° - 250°C can only be associated with the previous dilatometric and thermal changes. As the zinc content is increased, the expansion of the compact increases. This offsets any resistance drop which may be expected. Nevertheless, a resistance precedes the alloy-sintering mechanism and would suggest interfacial growth prior to the expansion of the compact. Irregular resistance variation beyond 380°C is attributed to the internal pressure of entrapped zinc vapour and the melting of residual zinc. The final alloy is assumed homogenous as indicated by the regular behaviour of the final resistance of the compact during heating.

Increased compaction decreases the interfacial resistance of the particles by the greater degree of cold welding effected. Since finer powders are more susceptible to surface impurities such as oxide films, high resistance values were to be expected.

Electrical resistance measurements suggested, therefore, that a somewhat complex surface rearrangement preceded the possible formation of a copper-zinc intermediate phase but due to the complex nature of the several factors which may /

May affect the resistance of a powder aggregate, little further information could be deduced.

(d) X-ray analysis:

From X-ray data, the liberation of heat and abrupt expansions on heating, are associated with the formation of beta-CuZn which may persist since it possess a degree of stability under the conditions, prevailing within the powder aggregate

General Summation:-

The mechanism suggested, is the transfer of the zinc to the surface of the copper particle, this transfer occurring largely through the vapour phase. The absorption of the zinc results in the formation of the beta Cu Zn phase. Two factors contribute to the rapid rate of formation of the compound, beta-Cu Zn. First, the transfer of zinc through the vapour phase implies that virtually the whole surface of the copper particles is available as a diffusion interface. Second, as shown by the work of SmigilsKas and Kirkendall(8), zinc diffuses into copper much more rapidly than copper into zinc. Admittedly, this is a comparatively simplified picture of the reactions taking place as some slight formation of the alpha solid solution is almost inevitable but the known rates of diffusion suggest that this film or layer of alpha solid solution may be very thin. In addition, the X-ray results show no evidence of alpha-solid solution.

Complete /

Complete alloy-sintering of copper-zinc compacts, in contrast to the work, reported by Rhines and Coltonn(19), appeared to be exceptionally rapid. By heating in vacuo up to 750°C, it was shown that the compacts consisted of those phases which would be found in the corresponding alloy prepared by melting and casting. The heat treatment, imposed by Rhines and Coltonn on their copper-zinc compacts, consisted of rapidly heating to 400°C so that the reaction between copper and zinc powders was possibly incomplete. Build-up of Zinc by its high vapour pressure possibly promoted the introduction of a further zinc-rich phase as indicated by their observed formation of the gamma-copper-zinc phase. Comparison of their results with the present work is further impaired by the possible variations introduced by differing compaction and size grades of powders. Although the nature of alloy-sintering is complex, it may be inferred that the surface conditions at the metal interfaces within a pressed powder aggregate can interfere with the accepted interdiffusion mechanisms of metals in the solid state.

2. Further differential thermal analysis:

Since the compacts were composed of very fine powders and were pressed at a high compacting pressure, 50 tons / in^2, the behaviour of the thermal curves represents the reactions which may be expected during the alloy-sintering of such systems.

Since /

Since the alloy-sintering of Copper-nickel compacts was not accompanied by any heat change, this supports the assumption that heat changes may only occur within compacts, containing two metals which are capable of forming intermetallic compounds in their alloys. It would, therefore, tend to confirm the distinction drawn between alloy-sintering of complete or partial solid solution systems and those displaying possible compound formation, As was discussed in the review of the literature and shown by the preliminary investigation of the alloy-sintering of copper zinc compacts in vacuo.

The large exothermic changes observed in the copper-aluminium and nickel-aluminium compacts would suggest that the vapour pressure of the metals may be relatively unimportant and that other factors accelerate compound formation. Since compound formation occurs at temperatures below the nelting points of either of the constituent metals, the mechanism must be governed by diffusion processes which depend on the physical nature of the metallic powders and the area of interfacial contact between the particles.

The copper aluminium compact revealed a slight endothermic change at 570 °C and it was thought that Delta $Cu_9 Al_4$ and alpha copper solid solution had formed and that these phases later combine to form beta $Cu_3 Al$.

In /

In the case of the nickel-aluminium compacts, the two exothermic changes may possibly be attributed to the formation of more than one intermetallic compound or to effects introduced by compaction and size grading of the metallic powders.

Marked heat evolution was noted in the nickel-zinc compact. The vapour pressure of zinc, whilst it must accel~~l~~erate the reaction, cannot be as important as other factors which may be associated with the surface of the powders and the conditions introduced by compaction. Rapid interdiffusion processes must be involved under conditions which facilitate the movement of different metallic atoms in the neighbourhood of one another.

3. Further X-ray studies:

X-ray examination of compacted metallic powder mixtures in which compound formation may be possible on heating, suggested that alloying began with the formation of a compound phase at a temperature below the melting points of the component metals or of any other combination of phases in the alloy system. The reactions within these compacts were not prece~~e~~ded by any signs of primary solid solution formation since there was no apparent displacement of the principal line of X-ray reflection of the component elements. The lower melting point elements e.g. Magnesium, Aluminium, Tin etc., were rapidly absorbed in the formation of the compound phase /

phase as shown by the disappearance of the characteristic lines of their X-ray spectra . The higher melting-point elements copper, nickel and iron displayed lines which had become slightly broadened but diminished in intensity. Extensive primary solid solution formation was not possible within the alloys studied and consequently very little displacement could be expected to occur. Line broadening may indicate solid solution formation but normally this is associated with the presence of internal lattice strains.

Comparable intermetallic compounds were formed in the systems, copper-magnesium, copper-alumimium and nickel-magnesium powder mixtures when in each case the compounds $CuMg_2$, $Cu\ Mg_2$, $Cu\ Al_2$, and $Ni\ Mg_2$ were initially formed. Considering the alloy-sintering of copper-zinc and copper-gold compacts in which alloy-sintering began with the formation of the phases beta-Cu Zn and Cu Au (18), the appearance of a stable intermediate phase could only be found in the case of nickel-aluminium, iron-aluminium and nickel-tin compacts where Ni Al, Fe Al and Ni_2Sn_3 were the major phases involved during heating. The behaviour of nickel-silicon and copper-aluminium compacts which have been examined, suggested that a series of rate reactions may be involved. An initial compound may be considered to form such that further reaction could be promoted. In the nickel-silicon compacts, the Ni Si phase appeared to form initially and this resulted /

resulted in a series of reactions wherebye the other nickel-silicon compounds were produced. Compacted copper-aluminium powder mixtures interreacted to produce $Cu\,Al_2$, initially, followed by the possible ultimate formation of Cu_9Al_4.

Thus, alloying of metallic powders during sintering, may be considered as an activated rate process, the kinetics of which are not solely dependent on interdiffusion but also upon the activational and free energies involved in the formation of the various intermetallic compounds. The new phases which were formed, were characterised by their large heats of formation. The initial compound formed could not always be associated with that possessing the maximum heat of formation. Nevertheless sufficient local heat must be generated to promote further reaction.. Where insufficient local energy was liberated, it may be possible that an apparent state of stability could produce one intermetallic compound such as has been observed in the formation of the compounds Cu Zn, Cu Au(18), Fe.Al, Ni Al and Ni_2Sn_3 during the heating of compacted powder aggregates of these metals.

Such a mechanism would imply that the marked expansion and thermal changes, caused by the formation of intermetallic compounds during sintering, may not necessarily be attributed to the formation of any one particular phase. Therefore, /

Therefore, although these methods of studying alloy sintering, determine the reaction temperature, the dilatometric and thermal effects, only qualitative evidence of the mechanism can be gained since these methods are dependent to a large extent in the degree of compaction and size grading of the metallic powders. The varations introduced by these physical factors can be assessed by their influence on the dilatometric and thermal characteristics, as has been found in the case of copper-zinc compacts.

CHAPTER 7

Final conclusions and general summations.

The alloy-sintering of compacted metallic powder mixtures has been distinguished from sintering of unimetallic powders by the possibilities of interdiffusion of the metals and compound formation. Previous investigations of alloy-sintering appear to indicate that according to dilatometric evidence, two mechanisms of alloying were involved, depending on the nature of the equilibrium system formed by the components of the compacted aggregate; Where intermetallic compounds were present in the system, heating of the compact was accompanied by marked growth of the compacts. In systems exhibiting complete or partial solid solubility, this marked growth was not observed. Discrepancies, however, existed but little could be postulated since no consideration of the physical conditions of compaction and the particle size of the powders had been determined. Volatility of the metals was known to exert an effect on growth during alloy-sintering but its exact influence on the mechanism had not been established.

Consequently, a preliminary study of the alloy-sintering characteristics of copper-zinc compacts in vacuo was performed to determine these factors and also the most advantageous methods of conducting a general survey of the process of alloy-sintering. Of the experimental methods employed./

employed in this investigation, dilatometric and differential thermal analysis coupled with X-ray measurements were the most successful.

In heating copper-zinc compacts exothermic changes and expansion of compacts were observed at temperatures of 240°C to 320°C. The growth of the compacts was dependent on the proportion of zinc present, the compacting pressure and the size grading of the metallic powders. X-ray measurements proved that the intermetallic compound Cu Zn was formed and that alloying of the copper and the zinc was almost complete once a sintering temperature of 750°C had been attained. The growth of the compacts was attributed to the adsorption and absorption of the zinc by the copper particle with accompanying formation of beta-CuZn, and the pressure developed by the zinc vapour, entrapped within the pores of the compact. Evolution of heat was associated with the combination of copper and zinc to form the beta Cu Zn phase. The effects of compacting pressure and particle size of the powders were assessed by their influence on the dilatometric and differential thermal characteristics, displayed during the heating of the compacts. Increase of the compacting pressure and decrease of the particle size of the powders resulted in a decrease of the volume expansion and an increase in the heat evolution. It was concluded that rapid formation of the compound Cu Zn. occurs /

occurs with quick absorption of the zinc. The tendency to develop internal pressure of Zinc vapour was, therefore, diminished. It was also thought that increased compacting pressures endowed the green compact with greater cold strength so that growth during sintering was restricted.

Results of the electrical resistance studies were interpreted on the assumption that the resistance of a compacted powder was dependent on two factors, the contact resistance of the metal interfaces and the inherent resistance of the metal. Of these, the former was considered the more important. Since this was subject to extreme variation, depending on the surface conditions of the powder, the nature of the cold welded interface etc., the information deduced from changes in resistance, could only be tentatively interpreted. Nevertheless it was postulated that a surface rearrangement of atoms prece~~e~~ded the alloying reaction, causing the resistance of the compact to drop. This was associated with some form of interfacial growth which caused a decrease of the contact resistance of the interfaces present within the compacts.

The apparent rapidity with which alloying of the metals occurred, was considered due to the high vapour pressure of the zinc which permitted rapid transport of the zinc atoms to the surface of the copper particles so that there was created a large interface across which interdiffusion could proceed. /

proceed. Differential thermal analysis was also performed to study alloy-sintering and investigate the possible intermediate phase formation within a number of other bi-metallic compacts.

No exothermic reaction occurred during the sintering of a copper-nickel compact but marked heat evolution was apparent in the case of copper-aluminum, nickel-zinc compacts. Differential thermal analysis of a wider range of bi-metallic compacts, comprised of elements characterised by their relatively low vapour pressures and their ability to form intermetallic compounds, have been found to be accompanied by similar exothermic changes at relatively low temperatures,(21) It was observed that all indications of heat evolution occurred at temperatures below the melting points of the different elements concerned. Unusually rapid interdiffusion was considered to have occurred due to the interfacial conditions introduced by compaction, whereby movement of different metallic atoms in the neighbourhood of one another was facilitated.

From further X-ray investigations, as already stated only one compound was found to be formed in certain systems e.g. copper-zinc, nickel-aluminium, nickel-magnesium, iron-aluminium, etc., but in other instances e.g. copper-aluminium, nickel-silicon, more than one intermetallic compound appeared at an early stage, depending on the composition /

composition of the compact. In certain cases, all the parent metals had combined to form the equilibrium alloy.

Rapid formation of the intermetallic compounds may be associated with ability of one metal to diffuse more rapidly into another. The other apparent feature which was noticeable is that very little primary solid solution is formed.

Considerations of the behaviour of nickel-silicon and copper-aluminium compacts suggested that the alloying mechanism could be regarded as a series of rate processes. A compound was considered to form initially by rapid interdiffusion and was presumably to be associated with the lowest activational energy of combination. The heat energy liberated by its formation was regarded as sufficient to promote further reaction in a manner akin to that of "ignition".

From the experimental evidence it would possibly seem that interdiffusion within powdered metal aggregates, differs from that which had been determined across the interfaces of two "hot pressure" welded metals, as has been investigated by various authors. According to these investigations, volume changes were not unexpected in either of the systems of complete or partial solid solubility on those displaying intermetallic compound formation, since growth was caused by the unequal rates of diffusion between the component elements as well as through any new phase /

phase formed.

Interdiffusion cannot solely explain the extremely rapid rates of reaction between the various elements which have been investigated. It may be possible that cold-welded interfaces behave differently to that of hot-welded metals since, in the latter, stress conditions have been removed by recovery and recrystallization. Indirect evidence can be obtained by considering alloy sintering under conditions of hot-pressing. Goetzel (22) has compared the sintering behaviour of both cold and hot pressed copper-zinc compacts. The cold pressed compacts displayed the same general effects, observed in the present investigation. Hot pressing, however, apparently, deterred alloying and this would imply that the nature of cold-welded interfaces exerts a considerable influence on the initial stages of alloy-sintering.

Since interdiffusion may cause porosity in the sintered product, interdiffusion may possibly be regarded as unrelated to the mechanism of sintering. This porosity effect does not necessarily mean that growth of the original metal interfaces has not occurred, otherwise it would be difficult to visualise the rapid solid-state reactions which have been ascertained by this investigation.

Apart from the factor of time, homogenisation of the compact by interdiffusion also depends on (1) the interfacial area /

area across which atomic movement can occur and (2) the depth to be traversed by the diffusing elements for complete alloying to occur. Within compacted power aggragates, this interfacial area is large and the distances to be penetrated for complete alloying small; they are governed by the inherent particle size of the metallic powders, and the conditions caused by compaction. Under such conditions within compacts, composed of metals which are capable of forming intermetallic compounds, an intermetallic compound may be formed provided that the combination requires low energies of activation. If the resultant intermetallic compound formation is accompanied by an exothermic change, local heat may be sufficient to promote further interreaction of the metallic powders and produce other new phases.

This mechanism would account for the appearance of a number of different phases within some of the compacts, examined by X-ray measurements and the variation of the reaction with the composition of the compact. Considering the phases which were identified, each possessed a high heat of formation. Only one compound would be formed where further phase formation requires greater energy than is available from the initial compound formation. This may account for the pseudo- stability of the intermetallic compounds e.g. Cu Zn , $Ni Mg_2$, Ni Al , Fe Al , Fe Al and $Ni_2 Sn_3$/

Ni_2Sn_3. The alloying process, however, would probably proceed to completion if sufficient time was permitted for interdiffusion to occur under the experimental conditions which have been employed.

Differential thermal analysis indicated that the reactions occured at a characteristic temperature. Since the process has been regarded as a rate-process, this temperature may only be characteristic under the experimental conditions which have been adopted. It may be possible that at the observed temperatures, interdiffusion of the various metals can occur at a rate favourable for the reaction to proceed. It was noted that in the case of copper zinc compacts, the reaction temperature may be dependent on the experimental rate of heating. Further isothermal studies are necessary to elucidate this possibility.

Growth of bi-metallic compacts during sintering can possibly occur where simple interdiffusion is involved, e.g. copper-nickel compacts; Marked expansion is to be more associated with those in which compound formation may possibly occur since definite changes in crystal structure are incurred and cannot be restricted to any extent by increasing the cold-strength of the compact. It would therefore appear that whilst dilatometric measurements establish the nature /

nature of growth accompanying sintering, intermediate phase formation can only be rigidly determined by differential thermal analysis. Furthermore, the expansion and heat evolution effects which have been determined, vannot be attributed in every case to the formation of any one particular phase but rather to a series of reactions which are contributing their effects.

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(See overleaf)

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