A PRELIMINARY INVESTIGATION OF LIQUID PHASE
SINTERING IN FERROUS SYSTEMS

Contents

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A PRELIMINARY INVESTIGATION OF LIQUID PHASE
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Liquid phase sintering was utilized to achieve, by a simple compaction and sintering procedure involving short times and moderate temperatures, a virtually full dense high carbon Fe:C alloy and high boron Fe:B alloy. Parameters such as powder characteristics and mixing, compacting pressure, heating program and the liquid phase fraction were found to influence the sintered density. The response of the Fe:C alloy to a heat treatment is reported along with preliminary experiments in the iron base ternary system Fe:W:C. Residual porosities observed in microstructures of certain liquid phase sintered compacts were accounted for by a proposed capillary flow of the liquid phase and a local densification competing against an overall densification. Some general recommendations are made for liquid phase sintering of powder aggregates.

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1. INTRODUCTION

The primary objective of this work was to develop iron base materials with useful mechanical properties from a commercially acceptable powder metallurgical process.

Residual porosity has been identified as a fundamental cause for the mechanical properties of P/M materials falling short of those that may be attained in corresponding wrought materials. The particular circumstances are that from a moderate pressure compaction and solid state sintering the highest densities that have been achieved even with the most active iron powder are 90% theoretical. Mechanical properties have shown appreciable sensitivity to this 10% residual porosity.^{1, 2} Other techniques to produce pore free materials such as high compacting pressures, sintering-repressing-resintering, hot isostatic pressing and infiltration of ferrous parts with copper tend to be rather involved and are used only in special circumstances. In contrast to these, a simple and attractive approach yet to be fully exploited is liquid phase sintering. Looking in this direction for a solution note was taken to two relevant aspects. The first is, an intense densification is observed when sintering occurs in the presence of a liquid phase which wets and to some degree dissolves the solid phase. Of particular interest is the work performed by J. A. Lund³ in which a 1080 steel powder was sintered loose at temperatures that ranged from 1350-1450°C. Appreciable densification was observed when the sintering temperatures were supersolidus: only when partial melting of the compact occurred. The second aspect is that phase diagrams indicate the phase equilibrium which the material tends to achieve.

The actual phases which are present may, over a period of time, drastically differ from those of equilibrium. An example of this is the sintering of iron-nickel-aluminum powder compacts,⁴ where complete densification occurs as a result of a transient liquid phase followed by the development of equilibrium homogeneous material during the sintering process. After some consideration, liquid phase sintering seemed promising as a versatile means of attaining high densities at moderate temperatures, temperatures in the range of commercial furnaces. In summary, attention was focused on designing powder aggregates such that high densities and useful properties develop from a simple process involving reasonable compacting pressures and a moderate temperature liquid phase sintering.

The first phase of this research dealt with attaining some understanding of moderate temperature liquid phase sintering in a simple system. The technologically important Fe:C system was investigated for this purpose, in particular iron graphite compacts; for the purpose of comparison, similar experiments were performed with iron boron compacts. A fully dense high carbon alloy and high boron alloy were produced where in doing so parameters such as powder characteristics, mixing, compacting pressure, heating program and the liquid phase fraction were found to influence the sintered density. While this approach has led to virtually fully dense materials, the carbon or boron addition required for a liquid phase at moderate temperatures results in an undesirable microstructure.

In the second phase of this research the focus was on microstructural improvement with particular emphasis on the use of ternary additions.

II. SOME QUALITATIVE ASPECTS OF DENSIFICATION IN THE PRESENCE OF A STEADY STATE LIQUID PHASE

During sintering a decrease in free energy is achieved by, for example, diffusion, stress relief, reduction in surface areas and densification. Of interest is the intense densification caused by the presence of a liquid phase which wets and to some degree dissolves the solid phase. A typical density response to isothermal liquid phase sintering is an initial rapid densification followed by an abrupt decrease in rate and an asymptotic approach to theoretical density as shown in Fig. A. In general it has been found that densification increases with decreasing initial particle size.

Fig. A.

A detailed presentation of liquid phase sintering was compiled by V. N. Eremenko, Yu. V. Naidich and I. A. Lavrinenko.⁵ The following is a summary of some of the important mechanisms pertaining to liquid phase sintering which were considered during the course of this research.

Three mechanisms proposed to account for densification in the presence of a liquid phase are particle rearrangement, solution-reprecipitation and coalescence.

Particle rearrangement, caused by capillary pressure, is the relative motion of solid particles dispersed in the liquid phase from phase from which an increase in solid particle packing and a reduction in pore surface area occurs. For solid particles to be dispersed in the liquid phase the system must possess appropriate interfacial energies and a solid solubility in the liquid phase such that the liquid wets the solid (Fig. B) and penetrates existing interparticle bonds (Fig. C).

If $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$, then complete wetting occurs.

Fig. B.

If $\gamma_{\text{interparticle bond}} > 2\gamma_{SL}$ then the liquid will penetrate

Fig. C.

Based on the preceeding, with particle rearrangement viewed as a viscous flow, Kingery⁶ proposed a theoretical model which predicts densification of this type to be rapid; from experimental data densification rates of the order of those predicted by the model have been observed in the initial stage of liquid phase sintering.⁷ From considering the solid particle size and shape alone there is a conceivable maximum solid particle packing that may be attained by a particle rearrangement. If this maximum particle packing occurs and the liquid phase fraction is sufficient to fill the remaining interparticle regions then complete densification occurs. This indicates the liquid phase fraction's lower limit for complete densification by a particle rearrangement. Other extenuating circumstances may require even higher liquid phase fractions for complete densification under this mechanism. Complete wetting, liquid phase interparticle penetration and appreciable solid solubility in the liquid are highly probable in the iron graphite and iron boron compacts investigated in this research.

Solution-precipitation requires interfacial energies such that solid particles are separated at contact areas by a thin liquid film where the liquid phase must have a low solubility in the solid phase. Aside from this, as a result of the porosity a hydrostatic pressure acts on the compact; for a spherical porosity the pressure is predicted by the relation $P = -2 \gamma LV / r_p$. In view of these factors, according to Kingery,⁸ this pressure is transmitted through the thin liquid film and is balanced by compressive forces at contact areas between particles resulting in a higher chemical potential in these areas. A mass transfer then occurs from areas of contact to free surfaces, allowing

the centers of particles to approach, by a dissolution of contact areas, diffusion through the liquid film and reprecipitation on free surfaces (Fig. D).

Arrows indicate mass transport and associated approach of particle centers.

Fig. D.

Based on this along with certain geometric idealizations, a theoretical model proposed by Kingery predicts densification rates of the order of those observed immediately after particle rearrangement.⁹ Although the expected densification rate resulting from this mechanism is considerably slower than that of particle rearrangement it is appreciable when compared to solid state sintering since diffusion through the solid.

Where the system is coalescent, densification is similar to that of solid state sintering since solid state diffusion is the only mechanism available for a mass transport which would allow the approach of particle centers. Aside from this, as a result of no liquid inter-particle separation, considerable neck growth between particles occurs by a rapid diffusion through the liquid phase of atoms from convex regions of the solid particles to concave neck regions (Fig. E).

Dotted arrows indicate solid state diffusion with the associated approach of particle centers. Solid arrows indicate diffusion through liquid phase resulting in neck growth.

Fig. E.

Pertaining to a noncoalesced system, with a liquid phase present, the size and shape of particles which comprise the solid phase may be influenced by a number of factors. The initial particle size will have some bearing on the size of the solid particle, but during the course of sintering dissolution of the smaller particles and reprecipitation on the larger ones can be expected. If no solid crystalline plane is thermodynamically favored, the solid particles will have a tendency of spheroidize achieving a corresponding reduction in free energy. If solution precipitation occurs it will be accompanied by a reduction in the index of sphericity of the solid particles due to the nature of this mass transport shown in Fig. D. In some systems, such as the Fe:Cu system, microstructures are consistent with those that would be anticipated if mechanisms such as these occurred: grains with an index of sphericity depending on the liquid phase fraction are found imbedded in a continuous network consisting of the liquid phase components. For systems where the solid phase has a thermodynamically favored crystalline plane, angular solid particles would be expected such as WC in cobalt bonded WC materials. For a coalesced system considerable grain growth takes place.

There have been few studies concerned with the case where the liquid phase is transient.

III. EXPERIMENTAL METHODS

A powder compact's preparation involved a judicious choice of powders followed by blending and compaction. The compact was subsequently annealed in a suitable atmosphere. Reliable temperature measurements were desired. Density measurements and metallographic examination were used to evaluate the sintered material.

A. Powder and Powder Characteristics

Depending on the nature of the experiment, appropriate use was made of Emp atomized elemental iron powder as received (henceforth referred to as atomized iron powder) and carbonyl elemental iron powder. Data supplied by the company on both powders is as follows:

Atomized Iron Powder

Grade 300 M

<u>Chemical Analysis</u>		<u>Screen Analysis</u>	<u>(Tyler Sieve Series)</u>
Fe	99.5%	+ 80	0.0%
C	<0.01%	-80 + 100	2.0%
Mn	0.20%	-100 + 150	14.0%
P	0.005%	-150 + 200	22.0%
S	0.010%	-200 + 250	10.0%
Si	0.02%	-250 + 325	22.0%
H ₂ loss	0.12%	-325 +	30.0%
O ₂ content	0.08%		
(Vacuum Fusion)			

GAF Carbonyl Iron Powder

Grade Hp

<u>Chemical Analysis</u>		<u>Average Particle Diameter</u>
Fe	99.5% min.	6-8
C	0.1% max.	
O	0.3% max.	
Ni	0.1% max.	

Alloying elements used are as follows:

Dixon Microfyne Graphite Powder

United Mineral Boron Powder

99.5% pure

1-3

Fansteel Tungsten Powder

99.9+ pure

1-10

B. Blending and Compaction

Since powder blending procedures became a major aspect of this research, their descriptions are in Sections IV and V.

With respect to the compaction, note was taken of the work of Price and coworkers¹⁰ who showed that the sintered density of liquid phase sintered compacts is not influenced by green density. Circular cylindrical specimens of approximately 1 cc obtained from a compaction of powder blends in a 0.5 inch diameter double acting steel die; in

view of the atomized iron powder's high compressibility, a 20 kpsi compaction was used, unless otherwise mentioned, to minimize gas entrapment.

C. Sintering Environment

All samples were individually sintered in a relatively inert atmosphere of 10^{-5} mm of Hg. A vacuum atmosphere was used to remove evolved gases from the compact. The specimens were positioned in the center of the hot zone and contained in an alumina crucible. Sintering was performed in a Brew furnace.

D. Temperature Measurements

Accurate temperature measurements were desired since the liquid phase fraction may vary appreciably with temperature: with respect to equilibrium states of an Fe:2.5%C material a 0.33 vol.% change in the liquid phase corresponds to a 1°C temperature variation from 1175°C . Two platinum-platinum 10% rhodium thermocouples were used. The hot junction of the first was encapsulated in a thin piece of alumina and maintained in contact with the sample throughout the experiment by a cantilever spring mechanism. The second thermocouple was positioned $1/8 - 3/8$ inches directly above the sample. To determine the reliability of the temperature measurements a blend of eutectic composition, 4.26% C was prepared by tumble mixing elemental iron powder and graphite: this composition was chosen since copious amounts of liquid phase would readily indicate that the eutectic temperature has been achieved. The blend was compacted at 50 kpsi and vacuum sintered at 1140°C for 60 min. followed by a 2°C increase in temperature. The specimen was visually observed for melting; after

TABLE I

Eutectic Temperature (atomized iron powder + 4.26% Dixon graphite)

Sample No.	Size	Eutectic Temperature		Placement of Thermocouple (2)
		Thermocouple in Contact (1)	Thermocouple (2)	
(1)	0.501 x 0.505	1155°C	1155°C	1/8 in. at room temperature
(2)	0.500 x 0.495	1152°C	1152°C	1/4 in. at room temperature
(3)	0.506 x 0.498	1152°C	1141°C	3/8 in. at room temperature
(4)	0.501 x 0.750	1152°C	1132°C	3/8 in. at room temperature

5 min. the temperature was again increased by 2°C. This procedure was continued until incipient melting of the sample was observed. The specimens obtained were slightly spheroidized. Similar checks were made periodically throughout the research. From Table I it may be noted that a discrepancy existed between thermocouple (2) and the reported iron graphite eutectic temperature, (1154°C). This discrepancy varied depending on the initial placement of the thermocouple and the sample size and was, therefore, considered unreliable. The eutectic temperature recorded by thermocouple (1) agreed closely with the reported iron graphite eutectic temperature; a thermocouple maintained in contact with the specimen, accordingly, a relied upon for accurate temperature measurements.

E. Volume Determination of Sintered Compacts

The sintered compact's volume was determined from its weight in air and while immersed in water. The interaction between the suspension wire and the water's surface, resulting from surface tension, influenced the weight measurements of the immersed compact; a few drops of Kodak 200 photoflow solution added to 100 ml of water corrected this. Close agreement (± 0.05 cc) between a volume measurement determined as above and with a micrometer was achieved for compacts of densities greater than 92% theoretical. For those compacts of densities less than 92% theoretical close agreement was achieved only when the specimens were vacuum impregnated with either epoxy or molten wax; epoxy was used for compacts intended for metallographic examination.

F. Metallography

Samples were prepared for metallographic examination by mounting in Koldmount self-curing resin powder. The mounted specimen was abraded on silicon carbide paper down to 6000 grit and carefully polished on a 1 μ diamond wheel after which the specimen was micro-polished in a thick 0.05 μ alumina slurry, the duration of which depended on the material. A 1-2% nital etch was used.

TABLE II
Atomized Iron Powder Sintered
at 1175°C for 60 Minutes

Sample No.	Compacting Pressure	Green Density	Sintered Density
(5)	30 kpsi	77.3%	77.2%
(6)	50 kpsi	82.3%	83.1%
(7)	75 kpsi	88.4%	89.6%
(8)	100 kpsi	91.3%	90.5%

TABLE III

Atomized Iron + Dixon Microfyne Graphite,
Rapid Heating to 1175°C (held 60 minutes)

Sample No.	Composition	Green Density	Sintered Density
(9)	Fe:0.8%C	70.5%	71.3%
(10)	Fe:1.8%C	69.2%	69.8%

IV. FIRST PHASE - MODERATE TEMPERATURE LIQUID PHASE SINTERING OF IRON GRAPHITE AND IRON BORON COMPACTS

A. Experimental Approach

For a free flowing blend, low die abrasion, and good compacting characteristics, Dixon microfyne graphite and atomized iron powder were used, as recieved, in a first attempt at liquid phase sintering.

The data shown in Table II were obtained to establish the compressibility of the atomized iron powder and densification resulting from sintering at 1175°C; very little densification occurred.

Subsequently compacts of 0.8% and 1.8 wt.% graphite were obtained from a compaction of blends that were tumble mixed for 30 minutes. The lowest temperature for a liquid phase to be possible in this system is the iron graphite eutectic temperature, 1154°C. Instead of following the normal practice of gradual heating to sintering temperatures, these compacts were rapidly heated to 1175°C (1 min.). The results are recorded in Table III; appreciable densification, as would be expected if a liquid phase to some had been present, was not observed. This may be attributed to the rapid achievement of equilibrium with no appreciable intermediate liquid phase, as a result of the fine powders used and the high diffusion rate of carbon in iron ($D = 10^{-6.5} \text{ cm}^2/\text{sec.}$ at 1000°C).¹¹ In order to achieve a liquid phase for compacts of less than 2.0 wt.% graphite it would be necessary to go to increasingly higher temperatures for decreasing carbon contents, as indicated by the phase diagram shown in Fig. 1; these are temperatures far beyond the range at commercial furnaces.

Compacts with 2-2.5% graphite were used for the desired liquid phase sintering at moderate temperatures. With a 10^{-5} mmHg vacuum and a heating rate of 60°C/min. the first critical observations were violent fluctuation of the vacuum needle and complete compact distortion 2 minutes after the achievement of supersolidus temperatures. The same observations were made when the heating rate was 30°C/min. It was found that compact distortion could be circumvented by a 60 min. presintering at 1135°C prior to reaching supersolidus temperatures: this was attributed to the fact that at subsolidus temperatures an interconnected pore network is available to vent gaseous products. At supersolidus temperatures the liquid phase forms and evolving gases distort the compact. The nature and source of the gaseous products were investigated more thoroughly. For this purpose a detailed analysis of the atomized iron powder by chemical analysis, vacuum fusion, and hydrogen weight loss methods were considered inadequate. A slightly indirect approach was taken.

Outgassing of the compact during heating was indirectly followed by vacuum readings for runs in which a specimen containing 2.5° C was in the hot zone and for comparison when no sample was in the hot zone. The furnace element's contribution to the vacuum variations was negligible. Appreciable out gassing after an initial outgassing, began at 555°C, again at 720°C (approximately the eutectoid temperature of 710°C) and at 900°C (approximately the α - γ transition temperature). One source of gas is surface oxide reduction by carbon; the vacuum was recovered after 22 min. at 1135°C. The vacuum recovery rate of the Brew furnace, when no specimen was contained, was tested by

backfilling with helium; the vacuum was recovered in 3-5 min.

Upon metallographic examination of the atomized iron powder, pores and unidentified nonmetallic inclusions were observed, Fig. 4. Since sintering was done in a vacuum and a rapid reduction of the limited amount of surface oxides can be expected at 1135°C it was considered plausible that the rate determining step of the prolonged high temperature outgassing is the diffusion through the iron lattice of gaseous elements possibly located in the observed porosity or non-metallic inclusions of the powder. In consideration of these factors it was felt that a 30 min presintering at 1135°C would be necessary to avoid the deleterious affects of the outgassing.

Accordingly, compacts of 2.2, 2.3 and 2.5% graphite were pre-sintered and then sintered at 1175°C for 30 min.; they showed increased densification with increasing carbon content. The highest density achieved, 95% of theoretical, was for the compact containing 2.5% graphite. Based on the rapid diffusion of carbon in iron and the fine powders used, it's highly probable that equilibrium was rapidly approached where for a material of this composition at 1175°C a 25 vol. % liquid phase is present. The second critical observation made were large pores in the microstructure as shown in Fig. 5.

According to the Fe:C phase diagram, Fig. 1, at 1135°C austenite can contain a maximum of 2 wt.% carbon. Since the temperature has not exceeded that of the eutectic and the carbon was introduced as graphite, which is thermodynamically favored over cementite, the carbon in excess of 2 wt.% at 1135°C will be in the form of graphite.

Upon heating, after complete outgassing has occurred, to 1175°C and the achievement of equilibrium, the solid phase is austenite containing approximately 2 wt.% C. Concurrent with the achievement of the equilibrium solid phase the liquid phase containing approximately 4.26% C, forms by the reaction of the austenite with the free graphite. If the free graphite is nonuniformly distributed throughout the compact, melting would be local and subsequently a capillary flow of the liquid phase into the pore network and a local densification would compete against an overall densification establishing the observed isolated porosity, Fig. 5.

In a first attempt to correct this situation, for graphite additions of 2-2.5 wt. % C, numerous mixing techniques including wet mixing were employed; all resulted in a mix for which segregation was visually observed during handling. It was found that the addition of 0.0003 cc mineral oil per gram contributed sufficient interparticle cohesion for a stable blend to result from a standard mixing procedure. The stability of the blend was investigated by passing it through a funnel and observing it under an optical microscope for possible segregation, as suggested by J. C. Williams.¹² Similarly large pores were observed in the microstructure of the sintered compacts. Where the quality of this blend would be acceptable for solid state sintering, in liquid phase sintering it proved to be responsible for a coarse 5% residual porosity.

These observations were followed by a number of relevant experiments.

The first experiment was designed to eliminate the need for an extremely intimate blend of constituents. The same constituent powders and mixing procedure were used to prepare samples of 2% C. A sample was vacuum presintered for 60 min. at 1135°C; a complete thermal homogenizing is possible since 2% C is soluble in austenite at this temperature. The temperature was subsequently increased to 1250°C: a 20 vol. % liquid phase is present at equilibrium for this composition and temperature. A liquid phase was visually observed. For a sample that was held at this temperature for 30 min. a 99% theoretical density was attained where the resulting microstructure was relatively pore free and uniform as shown in Fig. 6.

The following two experiments were designed so that an extremely intimate blend of constituent powders is attained.

Atomized iron powder was coated with a colloidal graphite by using Acheson Dag 154, a colloidal graphite suspended in isopropanol which also contains a thermoplastic. It was felt that a most a slight carbon residue would result from the vaporization of the thermoplastic during sintering. In preparing blends, the appropriate amount of Dag 154 solution was placed in a beaker after which the iron powder was added: the resulting slurry was hand mixed for 15 min., vacuum dried, and passed through a 100 mesh sieve. The effective weight percent graphite contained in Dag 154 (15%) was determined from a calculation based on the Dag 154 addition to atomized iron powder which resulted in sintered samples of eutectoid composition; the microstructure consisted of a coarse pearlite. Accordingly, samples were prepared by compacting iron powder with a 2.5 wt. % graphite coating at 20 kpsi.

They were then vacuum presintered for 30 min. at 1135°C followed by 30 min. at 1175 C. A liquid phase was visually observed. The sintered density was 99% theoretical where the resulting microstructure was uniform and relatively pore free as shown in Fig. 7. Higher compacting pressures resulted in the abrasion and segregation of the graphite coating, evidence of which were large pores in the microstructure of the sintered sample.

The conventional means of attaining an intimate blend of powder constituents intended for liquid phase sintering is a mechanical homogenizing which involves the milling of a hard compound such as WC with a ductile metal such as Co: the ductile powder is smeared onto the hard particles by extensive milling. Domtar white cast iron powder, as received, and the appropriate amount of atomized iron powder for a 2.5% carbon content were ball milled under hexane for 40 hours. A steel drum with a 4 inch internal diameter 2 inches and 7 one inch steel balls were used. To achieve sufficient green strength a 2 wt.% methyl cellulose addition was necessary. The sample was presintered for 30 min. at 1135°C followed by 30 min. at 1175°C. A liquid phase was visually observed. The resulting microstructure was uniform and pore free.

In the second phase of this research, powder aggregates consisting of appropriate elemental powders are rapidly heated to temperatures at which a liquid phase forms. The outgassing associated with the use of the atomized powder precludes its use in these experiments. Carbonyl iron, a nonporous powder, was selected for this purpose. From preliminary experiments it was found that, in contrast to when

atomized iron was used, when carbonyl iron and graphite compacts were rapidly heated to 1175°C no compact distortion or fluctuation of the vacuum needle was observed. Similar to when atomized iron powder was used, when carbonyl iron was admixed with 2.4% graphite macropores were observed in the microstructure of a sample that was sintered at 1175°C. To circumvent the macropore format , samples were subsequently obtained from a compaction of 2.4% graphite coated carbonyl iron powder; they were then rapidly heated to 1175°C and held for 30 min. According to the phase diagram for a material of this composition in equilibrium at 1175°C there is a 20.9% liquid phase present. A liquid phase was visually observed. A pore free material with a uniform microstructure was attained as shown in Fig. 8.

In addition to investigating iron graphite compacts, iron compacts containing elemental boron were also investigated where reasonably good results were attained by a normal mixing procedure. Carbonyl elemental iron powder and United Mineral elemental boron powder were mixed in a steel container (internal dimensions: 2 inch diameter x .5 inches) on a Geos planetary ball mill where 1/8 inch steel balls were used to achieve a blending rather than a milling action. A sample containing 0.97% B was rapidly heated to 1175°C and held for 30 min. On the basis that fine powders were used and the rapid diffusion boron in iron ($D = 6.1 \times 10^{-7} \text{ cm}^2/\text{sec. at } 1100^\circ\text{C}$) it was also considered highly probable that equilibrium is rapidly approached; according to the phase diagram shown in Fig. 2, for a material of this composition in equilibrium at 1175°C there is a 25% liquid phase present. A liquid

phase was visually observed. The resulting microstructure of the sintered sample was relatively pore free as shown in Fig. 9.

A simple mixing of elemental carbonyl iron powder and boron was not accompanied by macropores in the microstructures of sintered samples which was not the case when carbonyl iron was admixed with an appropriate amount of graphite. The specific gravity of the graphite and boron powders are respectively 2.1 and 2.37 gm/cc with the particle size of both the 1-10 μ range. The only apparent major difference to which the drastically differing results may be accounted for, is the graphite addition, exceeding the boron addition by approximately 2.3%, saturated the iron powder; evidence of which was an observed segregation. It is plausible that while the mineral oil additions improved the graphite distribution it had not done so to the extent required for liquid phase sintering.

TABLE IV

Atomized Iron Powder + Acheson Day 154,
Green Density $\approx 70\%$, Sintering Temperature 1175°C

Sample No	Composition	Duration	Liquid Phase Fraction	Sintered Density ($\pm 1\%$)
(11)	Fe:2.2%C	30 min.	11.6%	91.0%
(12)	Fe:2.2%C	60 min.	11.6%	92.0%
(13)	Fe:2.3%C	15 min.	16.3%	95.0%
(14)	Fe:2.3%C	30 min.	16.3%	95.0%
(15)	Fe:2.4%C	10 min.	20.9%	99.0%
(16)	Fe:2.4%C	30 min.	20.9%	99.0%

TABLE VI

Carbonyl Iron Powder + Elemental Boron -

Green Density $\approx 65\%$ - Heating Program, Rapid Heating to 1175°C

Sample No.	Composition	Duration	Liquid Phase Fraction	Sintered Density	Hardness
(22)	Fe:0.21%B	30 min.	5%	94.6%	57.0 RB
(23)	Fe:0.40%B	30 min.	10%	97.0%	72.5 RB
(24)	Fe:0.97%B	10 min.	25%	99.2%	98.0 RB
(25)	Fe:0.97%B	30 min.	25%	99.4%	98.0 RB

TABLE V

Carbonyl Iron Powder + Acheson Day 154-heating
Program, Rapid Heating to 1175°C (Green Density $\approx 64\%$)

Sample No.	Composition	Duration at 1175°C	Liquid Phase Fraction	Sintered Density	Hardness
(17)	Fe:2.05%C	30 min.	5.11%	94.5%	14.0 RC
(18)	Fe:2.17%C	10 min.	10.2%	98%	19.2 RC
(19)	Fe:2.17%C	30 min.	10.2%	99.2%	20.0 RC
(20)	Fe:2.4%C	10 min.	20.1%	99.7%	23.0 RC
(21)	Fe:2.4%C	30 min.	20.1%	99.6%	23.0 RC

B. Composition vs. Sintered Density

Compacts consisting of graphite coated atomized iron powder with varying compositions were presintered for 30 minutes at 1135°C prior to sintering, for moderate durations, at 1175°C. The results are recorded in Table IV along with the vol. % liquid phase that is present at equilibrium according to the phase diagram shown in Fig. 1. In view of those samples with a fixed composition of 2.2% graphite, samples (11) and (12), an increased sintering duration at 1175°C from 30 to 60 minutes resulted in the sintered density increasing from 91.0 to 92.0%. In contrast to this, with respect to samples with a fixed sintering duration at 1175°C (samples (11), (14) and (16)), increasing graphite additions (respectively 2.2, 2.3 and 2.4%) were accompanied by increasing sintered densities (respectively 91.0 95.0 and 99.0%). With particular reference to samples (15) and (16) approximately a 2.4% graphite addition resulted in the attainment of near theoretical density with most of the densification taking place within the first 10 min. at 1175°C.

Similarly, compacts consisting of graphite coated carbonyl iron powder with varying compositions were rapidly heated to 1175°C. The results are recorded in Table V. With respect to 1175°C. The results are recorded in Table V. With respect to samples with a fixed sintering duration at 1175°C (samples (17), (19) and (21) increasing graphite additions (respectively 2.05, 2.17 and 2.40%) were accompanied by increasing sintered densities (respectively 94.5, 99.2 and 99.6%). With specific reference to samples (.8) and (19) near theoretical density was attained for a 2.17% graphite addition with most of the

densification occurring in the first 10 minutes.

Recorded in Table VI are the results of sintering carbonyl iron compacts containing varying amounts of boron; the mixing procedure used is the one previously described for these powders. Samples were rapidly heated to 1175°C. With respect to those samples with a fixed sintering duration (samples (22), (23) and (25) an increasing boron content (respectively 0.21, 0.40 and 0.97%) was accompanied by an increasing sintered density (respectively 94.6, 97.0 and 99.4%). With specific reference to samples (24) and (25) near theoretical density was attained for a boron content of 0.97% with most of the densification taking place within the first 10 min.

With respect to the microstructures of sintered samples, those of the iron boron samples are most readily interpreted on the basis of the densification mechanisms introduced in Section II. Since all the requirements are met, some degree of particle rearrangement and solution-precipitation mechanisms would be expected in this system. Fig. 9, 10 and 11 display the microstructures of samples (24), (23) and (22) respectively where grains imbedded; for the most part, in a continuous network consisting of the components of the liquid phase are observed. Accompanying an increase in the boron addition was an increase in the grain sphericity. This is consistent with the proposed densification mechanisms since with increasing boron additions, with a correspondingly increasing liquid phase fraction, the extent to which particle rearrangement may occur increases and consequently solution-precipitation to a lesser extent is relied upon for further densification: a mechanism which involves a mass transport which

would decrease the sphericity of the solid particles. In particular for a 0.97% boron addition, Fig. 9, the grains have a high degree of sphericity; the preceeding, the high densification rate and the near theoretical density are consistent with what would be expected if a particle rearrangement predominated.

C. First Phase Conclusions

- 1) For iron graphite compacts, graphite additions in excess of 2.0 wt.% were necessary for the achievement of a fully dense material from a moderate temperature sintering, 1175°C. With respect to compositions less than 2.0%, the lack of an appreciable densification was attributed to the high diffusion rate of carbon in iron resulting in a rapid approach of equilibrium with no appreciable intermediate liquid phase. For compositions in excess of 2.0% there is a liquid phase present at equilibrium, according to the phase diagram, which was visually observed and accompanied by an appreciable densification.
- 2) Deleterious outgassing was associated with the use of the atomized iron powder in powder aggregates rapidly heated to temperatures at which a liquid phase forms. This was attributed to a prolonged high temperature outgassing with the rate determining step being the diffusion through the iron lattice of gaseous elements located in the porosity and nonmetallic inclusions of the atomized iron powder. It is felt that in view of the 0.3% surface oxide content of carbonyl iron (which is appreciable when compared to the .08% oxide content of the atomized iron), the successful use of it in iron graphite samples rapidly heated to supersolidus temperatures further justified the exclusion of surface oxide reduction by carbon as a source for a deleterious outgassing.
- 3) It is felt that the blending of powders is an important step, particularly if the achievement of near theoretical density with a minimum liquid phase fraction is desired. General powder blending

recommendations were based on the interpretation of a macropore formation in iron graphite compacts and the relevant experiments which followed. In general, for alloy systems which are amenable to a thermal homogenization the use of elemental powders and a normal mixing technique is sufficient. For systems where normal mixing techniques are found to be responsible for nonuniform microstructures and residual porosities, techniques such as powder coating, the use of prealloyed powders and/or milling are recommended. Care should be taken that segregation does not occur during compaction. With respect to the iron graphite compacts, the simple procedure of graphite coating is a more desirable recourse than the others presented, since it resulted in blends with good flow and compacting characteristics, low die abrasion and moderate sintering requirements. With respect to the sintered iron boron compacts, pore free microstructures were attained for compacts consisting of blends prepared by a normal mixing procedure. From signs of nonuniformly distributed liquid phase in the sintered microstructures as shown in Fig. 9, it was considered plausible that with the use of more homogeneous blends similar results could have been achieved with a reduction in the boron content (reduction in the liquid phase fraction).

4) Assuming that equilibrium was rapidly attained, which is somewhat justified by the reasons mentioned, a 20.9% liquid phase fraction was required for a complete rapid densification for compacts consisting of graphite coated atomized iron powder. In contrast to this a 10.9% liquid phase fraction was required when graphite coated carbonyl iron powder was used in place of the graphite coated atomized iron powder.

This was roughly attributed to carbonyl iron powder being a finer powder where the solid phase during liquid phase sintering will consist of correspondingly finer solid particles: in this case a more efficient solid particle packing by a particle rearrangement is possible.

V. Second Phase: Microstructural Improvement

A continuous carbide or boride network is unfavorable with respect to mechanical properties since the material will most likely adopt their brittle behavior.¹³ The second phase of this research essentially dealt with deriving a useful material directly from those developed in the first phase of this research by various means of microstructural improvement.

A. Heat Treatment of Specimen (21)

The first step was to convert the massive free carbides observed in the microstructure shown in Fig. 8 to thermodynamically favored free graphite and ferrite by heat treatment similar to the one used to malleabilize white cast iron. Specimen (21) was heat treated under vacuum in the following manner: 1125 C for 2.5 hours, 925 C for 2 hours and finally after 2 hours at 720 C the sample was cooled slowly to room temperature. The microstructure achieved is shown in Fig. 12. The microhardness of the pearlitic and ferritic regions are respectively 175 VH and 95.8 VH determined by a Leitz microhardness tester. With respect to this approach the resulting volume percent and morphology of the graphite nodules, analogous to a porosity, provides no apparent major advantage over a compacting and subsolidus sintering program with appropriate carbon additions, where densities of 90% theoretical can be achieved. For the development of fully dense materials with desirable microstructures some preliminary experiments were performed with the use of ternary additions.

TABLE VII Fe:W:C System

Sample No.	Composition	Heating Program	Duration	Sintered Density	Hardness
(25)	Fe:20%W:2.20%C	rapid heating →1175°C	30 min.	89.4%	14 RC
(26)	Fe:20%W:2.20%C	rapid heating →1200°C	30 min.	91.5%	20 RC
(27)	Fe:20%W:2.20%C	rapid heating →1225°C	30 min.	95.5%	32 RC
(28)	Fe:20%W:2.20%C	rapid heating →1250°C	30 min.	99.4%	40 RC
(29)	Fe:20%W:2.20%C	rapid heating →1275°C	5 min.	99.2%	40 RC
(30)	Fe:20%W:2.20%C	slow heating →1140°C	60 min.	--	--
		slow heating →1250°C	30 min.	99.0%	60 RC

TABLE VII Fe:W:C System (Continued)

Sample No.	Composition	Heating Program	Duration	Sintered Density	Hardness
(31)	Fe:15%W:2.34%C	rapid heating +1175°C	30 min.	99.0%	90 RB
(32)	Fe:17.5%W:2.22%C	rapid heating +1175°C	30 min.	97.0%	16 RC

B. Ternary Additions

The second step, in this phase of the research, was to include in the powder aggregate a refractory carbide forming element in an amount such that the continuous iron carbide network would be exchanged for a dispersed refractory carbide phase. It was felt that if the formation of the refractory carbide was sluggish enough the remaining material would have a composition, for a period of time, in the range of a cast iron from which a liquid phase would develop at moderate temperatures. In view of the near theoretical density attained in sample (18) it was considered plausible that if the liquid phase fraction is sustained slightly greater than 10% for 10 min. near theoretical density would be highly probable.

A series of experiments followed where W was chosen since H is the most refractory of carbide forming elements. The first composition investigated was Fe:20%W:2.20%C. According to the phase diagram shown in Fig. 3 the lowest temperature at which a liquid phase will be present at equilibrium is approximately 1400°C. To establish a good graphite distribution in the powder aggregate and to avoid a deleterious outgassing the following mixing procedure and powders were used. Blends were attained by hand mixing the slurry resulting from the appropriate amounts of the Dag 154 solution, carbonyl elemental iron powder and Fansteel W. Samples of this composition, (25) - (30), were individually heated to temperatures ranging from 1175-1275°C as recorded in Table VII. With respect to samples (25) - (28), with increasing sintering temperatures from 1175-1250°C sintered densities

increased from 89.4% to 99.4% and accompanying this was an increase in the furnace cooled hardness from 14RC to 40RC. Figure 13 shows the microstructure of sample (28) where a reasonably good distribution of WC (small angular particles) was attained in a pearlitic matrix along with a third unidentified microconstituent. The overall uniformity of the microstructure was, for the most part, attributed to the nature of the mixing procedure used. A 60RC hardness was attained by a water quench of sample (28) from 1140°C the microstructure of which is displayed in Fig. 14. From the three hour annealing at 1250°C of sample (3) with no apparent change in the microstructure and the persistence of the liquid phase, it was concluded that either equilibrium was not achieved since the phase diagram does not indicate the presence of a liquid phase or the phase diagram is in error. As a whole the material looks promising, where the WC should contribute considerable wear resistance: this requires further investigation. Figure 15 displays the microstructure of sample (31) in which the composition was adjusted to attain a liquid phase at 1175°C, a moderate temperature. The morphology of the graphite nodules resemble those which nucleate from the melt. The remaining microconstituents of this material are WC and ferrite. The 90RB furnace cooled hardness of this material was attributed to the fact that the microstructure consisted primarily of ferrite. Sample (32) is the result of adjusting the composition of Fe:17.5%W:2.22%C; the results of this are shown in Table VII.

C. Conclusions of the Second Phase

- 1) The fully dense Fe:2.4%C alloy developed in the first phase of this research, by liquid phase sintering, responded to the described heat treatment in a manner similar to that which would be expected of a cast iron of the same composition.
- 2) The results obtained when W was included in iron graphite compacts indicate that there are possibilities of deriving a useful material directly from the first phase of this research.

VII. AREAS FOR FURTHER STUDY

1) Densification has been found to increase with a decreasing powder particle size, where this has normally been attributed to the fact that corresponding to an initially finer particle size is a solid phase consisting of finer particles: in this case a greater amount of densification is possible during the regrouping of the solid particles in the presence of the liquid phase. Another aspect which may be relevant to the particle size of the powders being used is, corresponding to finer initial powder sizes and an appropriate mixing procedure may be an improved distribution throughout the powder aggregate of the alloying components primarily responsible for the liquid phase. More specifically, an important factor may be this distribution immediately prior to liquid phase formation which will considerably influence the distribution that the liquid phase assumes in the powder aggregate. The liquid phase distribution will in turn determine the effectiveness of the liquid phase in causing an overall densification to take place. An ideal liquid phase distribution would be expected when each particle acts as a source for the liquid such as supersolidus sintering of a prealloyed powder. As the liquid phase distribution deviates from the ideal case interparticle bonds requiring the penetration of the liquid phase are initially more extensive. Concurrently, a capillary flow of the liquid phase and local densification may compete against an overall densification resulting in the development of a coarser porosity. The implication of this with respect to the subsequent overall densification is a lower

hydrostatic pressure acts on the compact corresponding to a coarser porosity: for a spherical porosity this is predicted by the relation $P = -2 \gamma LV / rp$ introduced in Section II.

To determine the influence of this factor on densification, the following experiments are proposed. The densification of Fe:Cu powder aggregates for an ideal situation, where Cu coated Fe powder is used, can be compared to the densification of Fe:Cu powder aggregates of lower homogeneity. A controlled reduction of the blend homogeneity can be attained by tumble mixing Cu coated Fe powder with elemental Fe powder, the overall composition being the same. A series of micrographs of these samples displaying their porosity at different stages of sintering may elucidate the role played by this factor. Other factors to be considered are, for example, properties of the alloy system, powder characteristics and compacting pressure. The extent to which deviation from the ideal case may occur without an appreciable loss in densification would be of interest in more complicated systems where coating and thermal homogenizing are no longer feasible.

2) Experiments similar to the ones mentioned above with iron-nickel-aluminum would also be of interest: for these alloys, densities of 98-99% theoretical have been reported as a result of a transient liquid phase followed by the development of a homogeneous solid solution alloy during the sintering process.¹⁴

3) The diffusion rate of carbon or boron in iron requires considerable additions of these elements for a moderate temperature liquid phase. The use of alloying components with lower diffusion rates and/or the design of powder aggregates with diffusion barriers to modify reaction

rates may be a possible recourse. A preliminary experiment was performed along these lines. A 9 mil iron wire was coated with 1 mil Ni, followed by a 1 mil Fe coating and finally a Dag 154 coating for a 0.8%C overall composition. The composite was rapidly heated to 1175°C where it was felt that if the Ni acted as a diffusion barrier against carbon, the outer Fe shell, for a period of time, would be carbon rich from which a liquid phase would develop at moderate temperatures. After 10 min. at 1175°C the wire was cooled to room temperature and examined metallographically. For the most part, the inner Fe core had developed into a eutectoid composition which discouraged effects to reproduce this in a powder aggregate. When this had failed, possibly the substitution of a more refractory metal such as Mo, Ta or W for Ni would improve results. One precaution is that when substitutional diffusions are involved diffusion voids and swelling may develop if diffusion rates differ appreciably.

4) With respect to the experiments in which elemental W was included in iron graphite compacts, the next step may be the use of, for example, Mo, Ta or Nb in place of W. Following this, would be the selection of a material on the basis of microstructure and overall promise for a detailed investigation of mechanical properties.

5) Spherical graphite nodules were observed when the composition was Fe:15%W:2.34%C. Another approach would be the use of some inoculant in a manner which results in a coarse spherical graphite; this would be desirable with respect to mechanical properties.

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Figure Captions

- Fig. 1. Fe:C phase diagram. [Metals Handbook, vol. 8 (American Society for Metals) p. 275.]
- Fig. 2. Fe:B phase diagram. [Metals Handbook, vol. 8, (American Society for Metals) p. 270.]
- Fig. 3. Fe:20%W:C phase diagram. [Metals Reference Book, (Smithells, vol. 1) p. 520.]
- Fig. 4. Microstructure of the atomized iron powder - arrows indicate pores and unidentified nonmetallic inclusions.
- Fig. 5. Macropores in liquid phase sintered Fe:2.5%C sample:
Tumble mix of atomized iron powder and Dixon microfyne graphite-heating program, 1135°C for 30 minutes, 1175°C for 30 minutes.
- Fig. 6. Fe:2.0%C, fully dense: tumble mix of atomized iron powder and Dixon microfyne graphite - heating program, 1140°C for 60 minutes, 1250°C for 30 minutes.
- Fig. 7. Fe:2.5%C, 99% theoretical density: graphite coated atomized iron powder - heating program, 1135°C for 30 minutes, 1175°C for 30 minutes.
- Fig. 8. Fe:2.4%C, fully dense: graphite coated carbonyl iron powder - heating program, rapid heating to 1175°C and held for 10 minutes.
- Fig. 9. Fe:0.97% B, sample (24), fully dense: tumble mix of carbonyl iron powder and United Mineral Boron - heating program, rapid heating to 1175°C and held for 10 minutes.
- Fig. 10. Fe:0.40%, Sample (23), 97% theoretical density: tumble mix

of carbonyl iron powder and United Mineral Boron - heating program, rapid heating to 1175°C and held for 30 minutes.

Fig. 11. Fe:0.21%B, Sample (22), 94.6% theoretical density: tumble mix of carbonyl iron powder and United Mineral Boron - heating of 1175°C and held for 30 minutes.

Fig. 12. Microstructure of sample (21) after heat treatment (Fig. 8 displays microstructure of sample (21) before heat treatment) - arrow 1 indicates graphite nodule, arrow 2 indicates ferrite hallow, arrow 3 indicates a pearlitic region.

Fig. 13. Fe:20%W:2.20%C, Sample (28), fully dense: hand mix of carbonyl iron, Fansteel W and Dag 154 - heating program, rapid heating to 1250°C and held for 30 minutes, arrow 1 indicates WC, arrow 2 indicates pearlitic region, arrow 3 indicates unidentified microconstituent.

Fig. 14. Fe:20%W:2.2%C, Sample (28): reheated to 1140°C and water quenched.

Fig. 15. Fe:15%W:2.34%C, Sample (31), fully dense: hand mix of carbonyl iron, Fansteel W and Dag 154 - heating program, rapid heating to 1175°C and held for 30 minutes.

C-Fe

Phase Diagrams of Binary Alloy Systems

C-Fe Carbon-Iron

XBL 754-6206

Fig. 1.

B-Fe Boron-Iron

XBL 754-6204

Fig. 2.

XBL 754-6205

Fig. 3.

Section
at 20% W

Fig. 4.

XBB 735-3270

Fig. 5.

Fig. 6

XBB 735-3274

Fig. 7.

Fig. 8.

XBB 735-3269

Fig. 9

Fig. 10.

XBB 735-3272

Fig. 11.

XBB 735-3276

Fig. 12

Fig. 13.

XBB 735-3271

Fig. 14.

XBB 735-3277

Fig. 15.