RECEIVED
LAWRENCE
BERKELEY LABORATORY

LBL-8001

DEC 22 1978

LIBRARY AND
DOCUMENTS SECTION

HIGH DENSITY SINTERING OF IRON-CARBON ALLOYS VIA
TRANSIENT LIQUID PHASE

Tin Tseuk Lam
(M. S. thesis)

June 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782

LBL-8001
c2

— LEGAL NOTICE —

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

LBL #8001

HIGH DENSITY SINTERING OF IRON-CARBON ALLOYS VIA
TRANSIENT LIQUID PHASE

Tin Tseuk Lam

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Mechanical Engineering
University of California
Berkeley, California 94720

June 1978

HIGH DENSITY SINTERING OF IRON-CARBON ALLOYS VIA
TRANSIENT LIQUID PHASE

Contents

Abstract	v
I. Introduction	1
II. Experimental Procedure	4
III. Experimental Results and Discussion	8
IV. Conclusions	11
Acknowledgement	12
References	13
Figure Captions	14
Figures	17

HIGH DENSITY SINTERING OF IRON-CARBON ALLOYS VIA
TRANSIENT LIQUID PHASE

Tin Tseuk Lam

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Mechanical Engineering
University of California
Berkeley, California 94720

ABSTRACT

Because of the transient presence of a liquid phase during sintering of graphite coated iron powder, a high percentage (95% ~ 99.4%) of theoretical density can be achieved in a short time (~10 min.) and at a moderate temperature (1175°C). As a result, the mechanical properties of the graphite coated sintered steel are close to those of commercial plain carbon steels and much better than those of commercial powder metallurgy sintered steels. In addition, the physical and mechanical properties of Fe 2%C 20%W were studied in the as-sintered condition.

I Introduction

The primary objective of this research project was to develop iron base materials with useful mechanical properties via a practical powder metallurgical process.

Steels are very useful engineering materials. They can be formed by the powder metallurgy process and are widely employed in industry. However, the densities of the sintered steel are poor, usually in the range from 6.8 gm/cc to 7.1 gm/cc, depending on the characteristics of the powders, compacting pressure, sintering temperature, sintering time and sintering atmosphere. The 10% porosity in the sintered steel decreases the mechanical strength and ductility directly, because of the stress concentration and crack initiation due to pores.

Liquid phase sintering is a technique to increase the sintered density of P/M products. L. Cambal and J. A. Lund¹ performed an experiment on liquid phase sintering of loose steel powder (0.95%C) at supersolidus temperatures ($1350^{\circ}\text{C} \longleftrightarrow 1450^{\circ}\text{C}$). Even though appreciable densification was achieved by the supersolidus sintering, the high sintering temperature required is not practical and economical, especially in a period of energy shortage.

With these considerations in mind, John Klein² performed experiments on liquid phase sintering of Fe-C compositions at a moderate temperature. A fully dense sample of Fe 2.3%C was achieved by sintering at 1175°C for 10 min. Because of the high carbon content in the sample, a cementite (Fe_3C) network

around pearlite grain(s) characterized the microstructure (Fig. 1), making this an undesirable material.

Breaking up the cementite network should provide a solution to this problem. Two ideas have been proposed. The first one² is to add a third element to the Fe 2.3%C composition that reacts with carbon to break the cementite network. The second one is to decrease the carbon content such that the cementite network cannot be formed under the equilibrium cooling condition.

(A) The first approach

Tungsten powder was mixed with graphite coated iron powder to give a composition of Fe 2%C 20%W. A fully dense sample of the above composition was achieved by sintering at 1250°C for 30 min. Tungsten powder reacted with carbon to form tungsten carbide (WC) during sintering. Tungsten carbide and pearlite are evident in the microstructure (Fig. 2). According to the microstructure, the sintered material should be useful, since tungsten carbide is extremely hard (~ 800 VH) and pearlite can be heat treated to provide a range of properties. A series of experiments was performed for the measurement of mechanical properties, and the results are presented in part III.

(B) The second approach

Decarburization experiments were carried out in a hydrogen atmosphere (7" of Hg gauge pressure and -45°C dew point). A sample with composition of Fe 2%C 20%W was placed in the heating zone of the furnace under the stated hydrogen atmosphere. The heating program was the following: from 100°C to 1200°C in about one hour, 1200°C

for a half hour and cooled down to 300°C in about two hours. The carbon content was reduced from 2% to 0.2% according to chemical analysis, and the microstructure showed no porosity with a ferrite matrix and a tungsten network (Fig. 3). This phenomenon suggested a new idea which was to decarburize a fully dense sample of Fe 2.3%C, to improve the mechanical properties. After a careful series of experiments, the following facts have been found out.

- (1) Decarburization takes place from the outer layer to the core section of a sample (Fig. 4) such that a non-uniform carbon distribution exists.
- (2) Decarburization takes place before and after the presence of liquid phase, and the samples have good sintered density.

It was concluded from these observations that green compacts with low carbon contents should densify very well. To understand how the graphite coated iron compact densifies so well during sintering, an idealized schematic of the process is shown in Fig. 5. The explanation is as follows: Since each iron particle is coated by graphite, the outer layer of each particle must become liquid phase if the temperature is higher than 1154°C regardless of the overall carbon percentage of the samples. Therefore localized transient liquid phase sintering occurs even though the carbon content is less than 2% at 1175°C. Because of the presence of a liquid phase, the green compacts densify easily and uniformly,^{2,3,4,5} in contrast to the conventional commercial green compacts which are composed of steel powder or a mixture of iron powder and graphite powder.

A green compact formed by 75 ksi isostatic-pressure and with the composition of Fe 0.43%C was densified to 7.56 gm/cc under the sintering condition of rapid heating to 1175°C and holding for 1/2 hour in a helium atmosphere. The microstructure of the above sample consisting of pearlite and ferrite grain(s) is shown in Fig. 6. This agrees with the assumed sintering mechanism. The experimental results are presented in part III.

II Experimental Procedure

(A) Powder preparation:

EMP brand atomized elemental iron powder and GAF brand carbonyl elemental iron powder were used with Acheson D 154 colloidal graphite in these experiments. Coating the iron powder with graphite is the principal technique employed to achieve good distribution of the mixture. In preparing blends, an appropriate amount of D154 suspension (depending on the percentage of carbon desired) was placed into a beaker containing the iron powder and diluted with acetone or alcohol to facilitate coating. The resulting slurry was hand mixed for a certain time, vacuum dried and passed through a 100 mesh sieve. The effective weight percentage of graphite in D 154 is about 20%. The final carbon content of graphite coated iron powder was determined by chemical analysis. After preparing the fine graphite coated iron powder, tungsten powder can be added if desired, and tumble mixed for uniform distribution. The specifications of the powders supplied by the manufacturers are as follows:

Atomized Iron Powder
Grade 300 M (A.O. Smith Corporation)

<u>Chemical Analysis</u>		<u>Screen Analysis</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 (General Analine and Film Corp.)

Grade Hp

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

Fansteel Tungsten Powder

99.9+ pure

1-10 μm average particle size

(B) Green compact preparation

In general, green compacts were made by isostatic pressing. The tensile and transverse rupture specimens were molded by double acting steel dies, using a hydraulic press, and then repressed isostatically for better results.

(C) Sintering conditions

Green compacts were sintered in different furnaces depending on the size and atmosphere desired. Usually, small samples were sintered in a Brew furnace which provides a vacuum of about 10^{-6} mm Hg absolute pressure.

A helium backfill at 200°C was used to improve heat transfer in some experiments. Large samples were sintered in a hydrogen furnace which provides a large uniform hot zone (Fig. 7). Nitrogen and/or hydrogen could be backfilled into the furnace depending on the desired atmosphere. The hydrogen was purified by a Matheson 8362 Purifier for a dry and clean atmosphere (~-40°C to -50°C dew point). The sintering temperature was determined by a thermocouple set inside the hot zone of the furnaces.

(D) Metallography

Samples were prepared for metallographic examination by mounting in koldmount self-curing resin or bakelite. The mounted specimens were abraded on silicon carbide paper down to 600 grit and carefully polished on a 1µ diamond wheel. A 2% nital etch was used.

(E) Mechanical property tests

Sintered tensile test bars conforming to MPIF standard 10-63 (Fig. 8) were tested with an Instron testing machine using a crosshead speed of 0.05 cm/min. ASTM standard E8 was used to choose gripping devices and methods of determining tensile strength and elongation. Transverse rupture test bars conforming to MPIF standard 13-62 (Fig. 9) were also tested with the Instron testing machine using a three point bending fixture, (Fig. 10). A Leitz Wetzlar miniload hardness tester and a Rockwell hardness tester were used to determine the hardness of the sintered parts for different purposes.

(F) Density determination

- (1) The determination of the theoretical density of a sample is based on the rule of mixtures. For example, the theoretical

$$\begin{aligned} \text{density of FeC 2.5\% is } & 100 / \left(\frac{M_{\text{Fe}}}{\rho_{\text{Fe}}} + \frac{M_{\text{C}}}{\rho_{\text{C}}} \right) \\ &= 100 / \left(\frac{97.5}{7.87} + \frac{2.5}{2.2} \right) \frac{\text{gm}}{\text{cc}} \\ &= 7.4 \quad \text{gm/cc} \end{aligned}$$

- (2) The water displacement method was used to measure the volume and density of the green and sintered compacts. Before immersing the compacts into the water, they were first vacuum impregnated with epoxy which filled up the pores to prevent the penetration of water. The interaction between the suspension wire and the water's surface, resulting from surface tension, influenced the weight measurements of the immersed compacts; a few drops of kodak 200 photo-flow solution was added to 100 ml of water to eliminate the problem.

III Experimental Results and Discussion

The results of the mechanical property tests of the as-sintered compacts of the two different systems confirm the properties suggested by their microstructures (Fig. 1, 2 and 6). The density and mechanical properties, such as tensile strength, transverse rupture strength, hardness and elongation are presented graphically in Fig. 11 to Fig. 23.

(A) Fe 2%C 20%W system:

From Figs. 11, 15 and 17, the property curves show that these alloys need one hour sintering time for a given sintering temperature and compacting pressure. This is a long sintering time compared with that required for the Fe-C system.

The presence of tungsten carbide in a pearlite matrix makes the material harder, stronger and more brittle than the pearlite with a cementite network. The elongations in a one inch gauge length of Fe 2%C 20%W samples are in the range from 0.1% to 0.4%. The poor elongations restrict the applications of the material. Since pearlite can be heat treated to form tempered martensite or ferrite and graphite, the Fe-C-W system might have better elongation after appropriate heat treatment. However, this system may not be practical from the economical view point. First of all, tungsten powder is expensive. Secondly, the long sintering time and high sintering temperature along with the additional heat treatment increases the cost.

(B) Fe-C system

Figure 18 shows that the densification by transient liquid phase sintering takes place rapidly. In only 10 minutes the sintered densities of graphite coated iron easily achieved 95% to 99.4% of the theoretical densities at 1175°C. The heating rate is not a critical factor for transient liquid phase sintering. Two 75 ksi green compacts with compositions of 0.43%C and 0.68%C densified to 7.49 gm/cc and 7.47 gm/cc, respectively. The sintering was done in a helium atmosphere, with a slow heating rate (200°C → 1175°C in 1/2 hr.) and a hold at 1175°C for 1/2 hr.

As a result, the mechanical properties are very close to commercial plain carbon steel and much better than the commercial P/M sintered steel. For example, the yield strengths of the commercial P/M sintered steel ($\sim 0.4\%C$), the AISI 1040 hot rolled steel and the graphite coated sintered steel (0.4%) are 25 ksi 44 ksi and 40 ksi respectively. Moreover, the elongations of the commercial P/M sintered steel (0.4%), AISI 1040 hot rolled steel and the graphite coated sintered steel are 2%, 18% and 20% respectively. The complete comparisons of the mechanical properties of these three different steels are shown in Fig. 18 to Fig. 22. The stress-strain curves of the graphite coated sintered steel of $0.2\%C$ and $1\%C$ are shown in Fig. 23. They represent the characteristics of low carbon steel and high carbon steel respectively. Some advantages foreseen of the graphite coated steel are as follows:

- (1) This system has all the advantages of the P/M process.
- (2) The procedure for producing this material is relatively simple.
- (3) The sintering time is short.
- (4) The sintering temperature is moderate ($\sim 1175^{\circ}C$).
- (5) The mechanical properties vary with the carbon content, such that a wide variation of mechanical properties can be achieved for different applications.
- (6) Because of some micropores in the material, they can provide for some strain adjustment.

Disadvantages:

- (1) Due to the existence of micropores in the material, applications

in aggressive atmospheres are not suggested, unless with surface coating.

(2) The micropores may cause crack initiation.

(C) Suggestions for further study:

- (1) Different types of mechanical tests can be conducted for a more detailed understanding of the mechanical behavior of the graphite coated sintered steel. Fatigue tests and charpy tests are highly recommended. Wear tests on the Fe-C-W system would be very useful.
- (2) Use the same technique of coating for other systems to study the kinetics of transient liquid phase sintering.
- (3) A third material added to the Fe-C system may benefit densification and strengthening. Ni is suggested for the above purpose.
- (4) From the viewpoint of practical application, the coefficient of shrinkage in different directions and in different shapes should be known.

IV Conclusions

The simple press and sinter method used for the graphite coated sintered steel results in good mechanical properties. This method does not require high compacting pressures, high sintering temperatures, long sintering times and rapid heating rates, and makes the process practical and economical.

ACKNOWLEDGMENT

The author is sincerely grateful to Professor Milton R. Pickus for his advice and guidance. Special thanks to Dr. John Ling-Fai Wang for his encouragement and valuable directions throughout the project. The technical assistance rendered by Mr. John T. Holthuis and Mr. John A. Jacobsen and the technicians in the Materials and Molecular Research Division is greatly appreciated.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

References

1. L. Cambal, J. A. Lund, Int'l J. of Powder Metallurgy, 8, (3) 1972.
2. John Klein, A preliminary investigation of liquid phase sintering in ferrous system. LBL-3549, April 1975.
3. V. N. Eremenko, Yu, V. Naidich, I. A. Lavrinenko, Liquid phase sintering, Consultants Bureau, N. Y. 1970.
4. W. D. Kingery, J. of Applied Physics, 30, (3) March 1959 pp. 301-306.
5. W. D. Kingery, J. of Applied Physics, 30, (3) March 1959 pp. 307-311.
6. Van Vlack, Materials Science for Engineers, Addison Wesley, 1969.
7. Robert E. Reed-Hill, Physical Metallurgy Principles, 2nd Edition, D. Van Nostrand Co. 1973.
8. Albert Gagnebin, The Fundamentals of Iron and Steel Casting, The Int'l Nickel Co. Inc., 4th Edition, Oct. 1968.
9. A. H. Rauch, Source Book on Ductile Iron, ASM, 1977.
10. A. Stosuy and J. Marsden, Metallography of Sintered Ferrous Materials, Hoeganaes Corp.
11. Joel S. Hirschhorn, Introduction to Powder Metallurgy, American P/M Institute, 1976.

Figure Captions

- Fig. 1. Fe 2.5% C (sample #39), fully dense, graphite coated iron (GAF) compact (20ksi), sintering condition: vacuum, rapid heating rate, 1175°C for 10 min.
- Fig. 2. Fe 2%C 20%W (sample #35), fully dense, graphite coated iron (GAF) powder tumble mixed with Fansteel tungsten powder, compacted at 30 ksi, sintering condition: vacuum, 1200°C for 10 min.
- Fig. 3. Fe 2%C 20%W (Sample #13), fully dense; graphite coated iron (GAF) powder tumble mixed with Fansteel tungsten powder, compacted at 30 ksi, sintering condition: Hydrogen atmosphere, slow heating rate, 1135°C for 1/2 hr. 1265°C for 1/2 hr, decarburized to 0.2%C.
- Fig. 4. Fe 2.5%C, (Sample #47), graphite coated iron (GAF) compact (20 ksi), sintering condition: Hydrogen atmosphere, 1175°C, 10 sec.
- Fig. 5. Schematics of liquid phase sintering for production of sintered carbon steel.
- Fig. 6. Fe 0.43%C (Sample # B-6), graphite coated iron (GAF) compact (75 ksi), sintering condition: helium atmosphere, rapid heating rate, 1175°C for 1/2 hr sintered density 7.56 gm/cc.

- Fig. 7. Schematic diagram of hydrogen furnace.
- Fig. 8. MPIF standard 10-63 tensile test specimen.
- Fig. 9. Die and punches for making MPIF Standard 13-62 transverse rupture test specimen.
- Fig. 10. Fixture for transverse rupture test.
- Fig. 11. Sintered densities vs sintering time of Fe 2%C 20%W system (GAF) at 1250°C and different compacting pressures sintered in vacuum atmosphere.
- Fig. 12. Sintered densities vs sintering temperature of Fe 2%C 20%W system (GAF) at different compacting pressures and sintering times sintered in vacuum atmosphere.
- Fig. 13. Hardness of sintered Fe 2%C 20%W vs sintering time and temperature, sintered in vacuum atmosphere.
- Fig. 14. Ultimate strength of sintered Fe 2%C 20%W vs sintering temperature, sintered in vacuum atmosphere.
- Fig. 15. Ultimate strength of sintered Fe 2%C 20%W vs sintering time, sintered in vacuum atmosphere.
- Fig. 16. Transverse rupture strength of sintered Fe 2%C 20%W vs sintering temperature, sintered in vacuum atmosphere.
- Fig. 17. Transverse rupture strength of sintered Fe 2%C 20%W vs sintering time, sintered in vacuum atmosphere.

Fig. 18. Densities of graphite coated sintered steel* vs carbon content, sintered in helium atmosphere.

Fig. 19. Hardness of graphite coated sintered steel vs carbon content, sintered in nitrogen atmosphere.

Fig. 20.** Yield strengths of different steels vs carbon content.

Fig. 21.** Ultimate strengths of different steels vs carbon content.

Fig. 22.** Elongations of different steels vs carbon content.

Fig. 23.** Stress-strain curves of graphite coated sintered steels.

Fig. 24. Fe-C phase diagram (Metals handbook, Vol. 8, ASM p. 275).

* The graphite coated sintered steels are made from GAF iron powder.

** The graphite coated sintered steels were sintered in nitrogen atmosphere.

XBB 770 11572

Fig. 1

XBB 770 11571

Fig. 2

XBB 785 5729

Fig. 3

XBB 785 5731

Fig. 4

Fig. 5

XBL 786-5117

XBB 785 5730

Fig. 6

XBL 772-355

Fig. 7

MPIF Standard 10-63

Flat unmachined test bar

Pressure area = 1.00 sq. in.

Dimensions specified are those of the
compact when in the die.

XBL772-356

Fig. 8

XBL 772-358

Fig. 9

Details of fixture for testing bending strength

All dimensions in inches.

XBL 772-357

Fig. 10

XBL 786-5105

Fig. 11

Fig. 12

XBL 786-5104

Fig. 13

XBL786-5110

Fig. 14

XBL 786-5106

XBL786-5107

Fig. 15

XBL 786-5108

Fig. 16

XBL 786-5109

Fig. 17

XBL 786-5111

Fig. 18

Fig. 19

XBL 786-5116

XBL 786-5114

Fig. 20

Fig. 21

XBL 786-5115

Fig. 22

XBL 786-5113

Fig. 23

C-Fe

Phase Diagrams of Binary Alloy Systems

C-Fe Carbon-Iron

XBL 754-6206

Fig. 24

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720