An investigation on microwave sintering of Fe, Fe–Cu and Fe–Cu–C alloys

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Abstract. The powder characteristics of metallic powders play a key role during sintering. Densification and mechanical properties were also influenced by it. The current study examines the effect of heating mode on densification, microstructure, phase compositions and properties of Fe, Fe–2Cu and Fe–2Cu–0.8C systems. The compacts were heated in 2.45 GHz microwave sintering furnaces under forming gas (95% N₂–5% H₂) at 1120 °C for 60 min. Results of densification, mechanical properties and microstructural development of the microwave-sintered samples were reported and critically analysed in terms of various powder processing steps.

Keywords. Powders; processing; particle morphology; microwave sintering; densification; mechanical properties.

1. Introduction

The powder metallurgy (P/M) is one of the most widely used methods to produce complex shapes of automobile components with good dimensional accuracy (Šalak 1995). In ferrous powder metallurgy, Fe–Cu–C system has been a subject of intense research for the past decades (Bockstiegel 1962; Berner *et al* 1973; Jamil and Chadwick 1985). Bockstiegel (1962) proposed solid-state diffusion of Cu into iron grains, leaving large stable pores at Cu sites. Berner *et al* (1973) suggested that the expansion occurring in the compacts is due to the penetration of molten Cu into the interparticle surfaces and also along some of the grain boundaries of the iron particles. Further, the maximum swelling occurs at around 1150 °C. Jamil and Chadwick (1985) reported that the volume expansion is less in Fe–Cu compacts containing iron particles with substantial amount of internal porosity. Wanibe *et al* (1990) found that swelling was controlled by internal porosity left in iron particles after compaction. Other researchers reported that the addition of graphite to Fe–Cu compacts reduces the expansion of compacts (Lawcock and Davis 1990; Griffo and German 1994; Kuroki *et al* 1999). Graphite prevents the grain boundary penetration of a Cu-rich liquid phase. In conventional furnace, electrically heated compacts are radiation-heated during sintering. In order to prevent thermal gradient within the compact, a moderate heating rate (5 °C/min) coupled with an isothermal hold at intermittent temperatures has been followed. But, that has resulted in considerable increase in processing time, thereby contributing to grain coarsening. To

overcome this problem, a rapid heating and shorter sintering periods are envisaged. Faster heating rates (~35 °C/min) in a conventional furnace, however, results in a thermal gradient within the compacts and lead to distortion of the compact and inhomogeneous microstructure. Microwave sintering is now well recognized to offer rapid heating rates and shorter sintering times than the conventional route and still maintaining temperature and microstructural uniformity (Clark and Sutton 1996). Microwave heating is recognized for its various advantages, such as time and energy saving, very rapid heating rates and significantly reduced processing time. Microwave energy is defined as part of electro-magnetic spectrum having a wavelength typically ranging from about 1 mm to 1 m in free space, and the frequency ranging from about 300 MHz to 300 GHz. However, only narrow frequency bands centred at around 915 MHz, 2.45, 28 and 80 GHz are actually permitted for microwave heating and sintering purposes (Wroe 1999). Materials do not reflect microwaves when they are in powder form while bulk metallic parts instantly reflect microwaves (Cheng *et al* 2000). Microwaves directly interact with the particulates within the pressed compacts and thereby provide rapid volumetric heating (Xie *et al* 1999). Few materials do not absorb microwave energy at low temperatures. This problem has been overcome by using a susceptor, which absorbs microwave energy at low temperatures. Therefore, the temperature of the susceptor first increases and then the temperature of the inside sample increases, and the sample efficiently absorbs microwave energy at high temperatures (Mizuno *et al* 2004; Breval *et al* 2005). The mechanical properties of microwave-sintered samples were superior to that of conventionally-sintered samples (Panda *et al* 2006). Ferrous PM alloys are widely used for a variety of structural applications, and the predominant one is in the automotive industry. The copper steel PM parts are used extensively for their

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properties such as high mechanical strength and excellent dimensional control (Anklekar *et al* 2001). However, till date as per the author's knowledge, no investigation was done to observe effect of powder processing on microwave sintering of iron alloys. This study investigates the effect of heating mode on densification, microstructure and properties of specially prepared Fe, Fe-2Cu and Fe-2Cu-0.8Gr powder compacts.

2. Experimental

The as-received powders were characterized for particle morphology, size, purity and flow behaviour as per MPIF standard and the data is shown in table 1 (MPIF Standard 3, 1991; MPIF Standard 46, 1991; MPIF Standard 48, 1991). The morphology of the powders was obtained by scanning electron microscope (Zeiss Evo 50, Carl Zeiss SMT Ltd., UK) and is shown in figure 1. The powders were mixed in the required proportions (Fe-2Cu, Fe-2Cu-0.8Gr) in a turbula mixer (model: T2C, supplier: Bachoffen, Switzerland) for 60 min. The mixed powders were pressed at 600 MPa to make cylindrical pellets (height, ~6 mm, diameter, ~16 mm) using an uniaxial semi-automatic hydraulic press (model: CTM-100, supplier: Blue Star, India) using zinc stearate as a die wall lubricant. The green (as pressed) compacts were sintered in microwave furnaces. Microwave sintering of the green compacts were carried out using a multimode cavity 2.45 GHz, 6 kW commercial microwave furnace (Cober Electronics, Ct, USA). The samples were sintered at 1120 °C for 1 h in forming gas 95% N₂ and 5% H₂. The temperature of the sample was monitored using an infrared pyrometer (Raytek, Marathon Series) with the circular cross-wire focused on the sample cross-section. The pyrometer is emissivity based; direct temperature measurement was measured above 700 °C (Lide 1998; Pert *et al* 2001) by considering emissivity of steel as (0.35) (Nayer 1997). Typically, emissivity varies with temperature. However, as very little variation in the emissivity was reported in the temperature range used in the present study, hence, the effect of

variation in emissivity was ignored. Further details of the experimental setup of microwave sintering are described elsewhere (Anklekar *et al* 2001). The sintered density was obtained by dimensional and weight measurements as well as Archimedes' density measurement technique. The sintered density normalized with respect to the theoretical density based on the weight fraction (w) of the respective component. The theoretical density for a given composition (ρ_{th}) was calculated using inverse rule of mixture and is expressed as:

$$\frac{1}{\rho_T} = \sum_{i=1}^N \frac{w_i}{\rho_i}.$$

The sinterability of the compact was also determined through a densification parameter which is expressed as:

$$\text{Densification parameter} = \frac{\text{Sintered density} - \text{Green density}}{\text{Theoretical density} - \text{Green density}}.$$

The sintered samples were polished on a series of SiC emery papers (paper grades 220, 320, 500 and 1000), followed by cloth polishing using a suspension of 0.05 μm alumina diluted with water and the polished samples were etched with 3% nital to examine the microstructures. The microstructural analysis of the samples was carried out through optical microscope (model: DM2500, supplier: Leica Imaging System Ltd., Cambridge, UK). The pore size was estimated by measuring the pore area, while pore shape was characterized using a shape-form factor, F , which is related to the pore surface area, A and its circumference in the plane of analysis, P , as follows:

$$F = \frac{4\pi A}{P^2},$$

where A is the area of pore (μm^2) and P the circumference of pore in plane of observation (μm).

Both pore-area distribution and shape factor were directly measured using an image analyser. The pore measurement

Table 1. Characteristics of experimental powders.

Characteristics	Water-atomized Fe	Sponge Fe	Carbonyl Fe	Cu	Graphite
Apparent density (g/cc)	2.90	2.60	3.6	4.58	0.17
Tap density (g/cm)	3.40	3.20	4.3	5.35	0.33
Flow rate in s, 50 g	26	29.29	Non-flowing	Non-flowing	Non-flowing
Particle size (μm)					
D_{10}	35.31	32.68	4.40	13.82	3.90
D_{50}	78.73	90.12	11.37	30.53	8.84
D_{90}	160.8	179.80	35.01	62.02	17.77
Theoretical density (g/cm ³)	7.86	7.86	7.86	8.96	2.32
Surface area (m ² /g)	0.10	0.107	0.668	0.246	0.842
Shape	Irregular	Spongy (porous)	Spherical	Spherical	Flaky
Purity	>98.89%	99.14%	99.99%	>99.43%	99.99%

Figure 1. Scanning electron micrographs of as-received (a) water-atomized Fe, (b) sponge Fe, (c) carbonyl Fe, (d) Cu and (e) graphite powder.

was performed on un-etched samples. For each sample, pore shape quantification was done on 10 photomicrographs captured randomly. On the whole, between 3,500 and 5,700 pores were quantified for statistical accuracy. The shape factor of a feature is inversely proportional to its roundness. A shape factor of one represents a circular pore in the plane of analysis and as it reduces, the pores tend to become more irregular. Bulk hardness of the samples was measured using a semi-automatic Rockwell hardness tester (4150AK, Indentec hardness testing machines Ltd., UK) at 100 kg load with a 16-inch ball indenter. The observed hardness values are the averages of ten readings taken at random spots throughout the sample. The load was applied for 5 s. For measuring the tensile properties, flat tensile bars were pressed as per MPIF standard 10 (MPIF Standard 3, 1991; MPIF Standard 46, 1991). Tensile testing and transverse rupture strength was carried out after each sample marked with 25.4 and 26 mm gauge length using universal testing machine (1195, Instron, UK) of capacity 20 kN at a strain rate of $3.3 \times 10^{-4} \text{ s}^{-1}$ (cross-head speed, 0.5 mm/min) (Standard Test Methods for Metal Powders and Powder Metallurgy Products, 1991). In order to ensure repeatability, for each condition, three samples were evaluated. To correlate the tensile properties with the microstructure, fractography analyses of the samples were carried out using SEM imaging (Zeiss Evo 50, Carl Zeiss SMT Ltd., UK).

Figure 2. Thermal profiles of different Fe powder compacts sintered in microwave furnace.

3. Results and discussion

3.1 Heating profiles

Figure 2 compares thermal profiles of the Fe, Fe–2Cu, Fe–2Cu–0.8C alloy compacts sintered in microwave furnace. It

was observed that all water atomized, sponge and carbonyl iron powders couple well with the microwave. In order to maintain the uniform as well as higher heating rate than conventional route without any intermediate hold, SiC rods were used as susceptor. The sintering was done at 1120 °C for 60 min. This method is consistent with the methodology adopted by other researchers. As compared to water atomized and sponge samples, the carbonyl samples couple well with microwave. It is proposed that the fine particle size of carbonyl powder may be causing faster sintering rates.

3.2 Densification response

The densification data of microwave-sintered samples are shown in table 2. Water atomized (WA) iron powders (irregular shape) give low apparent densities and hinders achieving a high-pressed density, but it will give higher green strength than regular shaped powders because of mechanical interlocking. A high-green strength depends upon attaining a large degree of interparticle contact during pressing. An increase in the particle roughness aids green strength through mechanical interlocking of particles. Sponge powders formed by oxide reduction had shown a lower green density. Sponge particles with internal porosity were difficult to compact. The large interparticle pores cause initial compression of the powder. Sponge powder shows a high initial compressibility but resist compaction to high final densities. Whereas spherical powders (carbonyl) exhibit high initial packing densities, but do not provide the acceptable green strength. A carbonyl iron powder has a high sinter densification rate because of alpha to gamma transformation temperature, differentiating it from other powders that reach greater increase in density. Fine particle size gives more interparticle bonding during sintering and improvement in sinter density has been observed. Fine powders resist deformation and harden during sintering.

The density is consistently increased in Fe–Cu compacts. It is due to the fact that the fine particles aid densification in even shorter sintering times in the presence of liquid phase.

Ferrous powders in general are sintered at higher temperatures where significant grain boundary diffusion occurs, leading to large shrinkages. Less swelling was observed with large copper particles and longer sintering times. Fine iron powder produces shrinkage especially at lower green densities. Higher green density of the material lowers the shrinkage. The presence of the carbon content promotes the finer-gamma iron grain phase and thus providing a greater grain boundary volume that facilitates increased material diffusion, and enhancement in the sintering behaviour of sintering mechanisms. It increases the self diffusion coefficient of gamma iron by about one order of magnitude.

3.3 Microstructure evaluation and phase composition analysis

The unetched optical micrographs of the microwave sintered samples are shown in figure 3. In water atomized samples a large number of small pores and a small number of large pores are observed. The large pores are the former sites of the copper particles which moved into the small pores by capillary action after melting. In case of atomized iron powders, the penetration of the liquid-Cu phase into the grain boundaries results in sample swelling. There are long pores lying normal to the pressing direction and also normal to the surface. It may be due to the fact that during compact ejection, a number of microcracks or flat pores might have developed normal to the pressing direction. In case of the sponge iron powder at high compaction pressures, the liquid-Cu phase had penetrated the Fe/Fe grain boundaries, thereby pushing the grains apart and causing swelling at the very early stages of sintering. When carbonyl iron powder was used, the pore size was reduced due to the increase in packing and the larger driving force for the reduction in the surface area. Figure 4(a and b) compares shape factor and pore area distribution of microwave sintered ferrous samples.

The etched optical micrographs of the microwave sintered compacts are shown in figure 5. It is clear from micrographs that as compared to pure Fe, Fe–2Cu has more pores of larger

Table 2. Densification response on effect of powder processing of Fe, Fe–2Cu and Fe–2Cu–0.8C. Compacts sintered at 1120 °C with 60 min soaking time.

Composition	Green density (g/cm ³)	Sintered density (g/cm ³) ρ_s	Sintered density, % theoretical	Densification parameter
Water-atomized Fe	6.68 ± 0.1	6.78 ± 0.1	84.06 ± 0.1	–0.001
Water-atomized Fe–2Cu	6.78 ± 0.02	6.84 ± 0.04	85.33 ± 0.2	–0.002
Water-atomized Fe–2Cu–0.8C	6.76 ± 0.06	6.82 ± 0.09	87.08 ± 0.5	–0.003
Sponge Fe	6.41 ± 0.24	6.62 ± 0.09	84.10 ± 0.6	0.008
Sponge Fe–2Cu	6.62 ± 0.1	6.70 ± 0.09	85.29 ± 0.2	0.001
Sponge Fe–2Cu–0.8C	6.63 ± 0.01	6.68 ± 0.09	86.76 ± 1.0	0.0001
Carbonyl Fe	6.32 ± 0.01	6.97 ± 0.04	88.79 ± 0.6	0.008
Carbonyl Fe–2Cu	6.31 ± 0.02	6.92 ± 0.02	88.09 ± 0.2	0.007
Carbonyl Fe–2Cu–0.8C	6.50 ± 0.01	7.14 ± 0.04	92.75 ± 0.5	0.008

Figure 3. Unetched optical micrographs of ferrous alloy compacts sintered in microwave furnace, water atomized (left), sponge alloys (middle) and carbonyl alloys (right) at (a) Fe, (b) Fe–2Cu and (c) Fe–2Cu–0.8C, respectively.

Figure 4. Comparison of (a) shape factor distribution and (b) pore area distribution of ferrous compacts sintered in microwave furnaces.

Figure 5. Optical micrographs of ferrous alloy compacts sintered in microwave furnace, water atomized (left), sponge alloys (middle) and carbonyl alloys (right) at (a) Fe, (b) Fe-2Cu and (c) Fe-2Cu-0.8C, respectively.

size since Cu powder melts at 1083 °C and liquid Cu spreads between the Fe particles leading to its swelling and leaving behind large pores at the former sites. On examination of the micrograph of Fe-2Cu, homogeneously distributed copper clusters are observed in Fe-matrix after sintering. Because, the solubility of copper in iron at room temperature is around 0.4% which is very less as compared to initial amount, hence the excess copper precipitates out and the region of higher copper concentration appears more brownish in the micrograph. During sintering, above the melting point of copper, the liquid copper wets the iron. The reported dihedral angle is around 0–34° in the temperature range of 1120–1180 °C. Copper does not uniformly diffuse into iron at shorter time of sintering. Longer times are required to attain homogeneous microstructure. Carbon is added in the form of graphite and it dissolves into Fe to stabilize austenite phase field. Carbon diffusion rates are high and hence homogenizes easily during sintering. Rounded pores are mostly desirable and often formed at high sintering temperatures. Samples containing

angular pores exhibit low strength and poor fatigue resistance as they may act as stress raisers.

The scanning electron micrographs of the microwave sintered compacts are shown in figure 6. Here it can be seen that the interparticle bonds are broken in some regions. Some of the cracks are formed along the grain boundaries within the particle. These cracks are believed to have formed due to the penetration by liquid copper along the grain boundaries and subsequently its dissolution in the iron lattice. It is also observed that microwave sintering restricts microstructural coarsening. Furthermore, optical and SEM micrographs of the sintered compacts reveal distinct differences in the pore morphology of microwave compacts. Microwave sintering resulted in narrow pore-size distribution which is indicative of more regular pores.

Figure 7 compares XRD patterns of the composition in both the heating modes. From XRD patterns, as far as phase evolution is concerned, no difference was observed. Also, there was no noticeable shift in XRD peaks.

Figure 6. SEM micrographs of ferrous alloy compacts sintered in microwave furnace, water atomized (left), sponge alloys (middle) and carbonyl alloys (right) at (a) Fe, (b) Fe–2Cu and (c) Fe–2Cu–0.8C, respectively.

Figure 7. X-ray diffraction pattern of microwave-sintered ferrous alloy compacts.

3.4 Mechanical properties

Figure 8 shows effect of microwave heating mode on the bulk hardness and microhardness of sintered ferrous compacts. It

is clearly seen that the alloying elements and the microwave heating increase hardness of the ferrous compacts. The hardness indentation is large enough to take into account size of the pores and if the pores are uniformly distributed, the hardness values will depend only on the total amount of porosity. Figure 9 shows effect of heating mode on the tensile strength and yield strength of ferrous alloy compacts. Tensile strength and yield strength values of iron are improved upon the addition of copper and carbon. These results can be attributed to increased sinter bonding by liquid phase sintering, copper-solid solution hardening and the formation of pearlite structure due to addition of carbon. Samples that are sintered with powders through water atomization route were found to have low tensile strength. This can be attributed to the presence of pores which in turn is due to the reduced amount of metal. These pores act as local stress raisers at the interparticle bonds. Figure 10 shows effect of heating mode on the transverse rupture strength (TRS) of ferrous alloys. TRS value increases in a similar manner as the hardness trend. There is significant effect of the microcracks existing in the material thus reducing the transverse rupture strength. Carbonyl sample exhibits lower ductility as compared to water atomized and sponge samples. Figure 11 shows a cup and cone type fractured surfaces of sponge and carbonyl samples which is

Figure 8. (a) Bulk hardness value, HRB scale and (b) Vickers microhardness value of ferrous alloy compacts consolidated in microwave furnace.

Figure 9. (a) Ultimate tensile strength MPa and (b) yield strength, MPa of ferrous alloy compacts consolidated in conventional and microwave furnace.

Figure 10. (a) Transverse rupture strength and (b) ductility of ferrous alloy compacts consolidated in microwave furnace.

Figure 11. SEM fractographs of ferrous alloy compacts sintered in microwave furnace, water atomized (left), sponge alloys (middle) and carbonyl alloys (right) at (a) Fe, (b) Fe–2Cu and (c) Fe–2Cu–0.8C, respectively.

a typical feature of ductile failure whereas water-atomized samples resulted in mixed mode fracture (brittle and ductile).

4. Conclusions

In summary, this study showed that the Fe, Fe–Cu and Fe–Cu–C alloys can be successfully consolidated through microwave sintering route. Regardless of the composition difference, all samples showed nearly similar sintered densities. Iron copper (Fe–2Cu) showed less densification response than others. This confirms compact swelling due to copper growth phenomenon whereas copper steel increasing response is due to the role of carbon which restricted growth of copper. All the compacts had undergone shrinkage due to sintering effect which yielded better densification. Irrespective of the Cu and carbon content, carbonyl powder microwave-sintered compacts had higher densification and a more uniform microstructure. Consequently, the mechanical properties of carbonyl powder compacts sintered using microwaves were higher than their counterparts processed through water atomized and sponge powders.

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References

- Anklekar R M, Agrawal D K and Roy R 2001 *Powder Metal.* **44** 355
- Berner D, Exner H and Petzow G 1973 *Mod. Devel. Powder Metal.* **6** 237
- Bockstiegel G 1962 *Metallurgia* **3** 67
- Breval E *et al* 2005 *Mater. Sci. Eng. A* **391** 285
- Cheng J *et al* 2000 *J. Mat. Proc. Tech.* **108** 26
- Clark D E and Sutton W H 1996 *Ann. Rev. Mater. Sci.* **26** 299
- Griffo A and German R M 1994 *Int. J. Powder Metal.* **30** 399
- Jamil S and Chadwick G 1985 *Powder Metal.* **28** 65
- Kuroki H, Gang Han and Kenji Shinozaki 1999 *Int. J. Powder Metal.* **35** 57
- Lawcock R and Davis T 1990 *Powder Metal.* **33** 147
- Lide D R (ed) 1998 *CRC handbook of chemistry and physics* (Boca Raton, FL: CRC Press) 79th edn

- Mizuno M *et al* 2004 *J. Eur. Ceram. Soc.* **24** 387
- MPIF Standard 3 1991 Determination of flow rate of free flowing metal powders using the Hall apparatus. Standard test methods for Metal Powders and Powder Metallurgy Products, Metal Powder Industries Federation, NJ, Princeton
- MPIF Standard 10 1991 Tension test specimens for pressed and sinter metal powders. Standard test methods for Metal Powders and Powder Metallurgy Products, Metal Powder Industries Federation, NJ, Princeton
- MPIF Standard 41 1991 Determination of transverse rupture strength of sintered metal powder test specimen. Standard test methods for Metal Powders and Powder Metallurgy Products, Metal Powder Industries Federation, NJ, Princeton
- MPIF Standard 46 1991 Determination of tap density of metal powder. Standard test methods for Metal Powders and Powder Metallurgy Products, Metal Powder Industries Federation, NJ, Princeton
- MPIF Standard 48 1991 Determination of apparent density of metal powders using the Arnold meter. Standard test methods for Metal Powders and Powder Metallurgy Products, Metal Powder Industries Federation, NJ, Princeton
- Nayer A (ed) 1997 *The metals data book* (NY, USA: McGraw-Hill)
- Panda S S, Singh V and Upadhyaya A 2006 *Metal. Mater. Trans. A* **37A** 2253
- Pert E, Carmel Y, Birnboim A, Olorunyolemi T, Gershon D and Calame J 2001 *J. Am. Ceram. Soc.* **84** 1981
- Šalak A 1995 *Ferrous powder metallurgy* (England: Cambridge International Science Publishing) 1st edn
- Standard Test Methods for Metal Powders and Powder Metallurgy Products 1991 Metal Powder Industries Federation, NJ, Princeton
- Wanibe Y, Yokoyama H and Itoh T 1990 *Powder Metal.* **33** 65
- Wroe R 1999 *Metal Powder Report* 24
- Xie Z, Yang J, Huang X and Huang Y 1999 *J. Eur. Ceram. Soc.* **19** 381