Peer-reviewed version available at *Recycling* **2018**, *3*, 59; doi:10.3390/recycling3040059

Article

Recycling-Cum-Manufacturing Process for Utilization of Finely Divided Ferrous Metallic Scrap

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Abstract: The issues of metallic scrap management and its utilization in manufacturing plants are nowadays intensely considered to address essential sustainability guidelines. Efficient recycling procedure for shop floor metallic scrap is not yet available because of abundance and contamination of nonmetallic constituents. Other ferrous metallic scrap are melted and purified during secondary steelmaking to get products in the form of blooms and billets are obtained. This study illustrates the potential of powder technology (powder metallurgy (PM) and metal injection molding (MIM)) based process for solid-state recycling and attainment of usable products. Industrially downgraded grinding sludge is pulverized and used as a raw material. Results showed properties of sintered parts are significantly improved due to in-situ reduction and densification during sintering. Recyclability Index (RI) was created to compare the effect of process variables on obtained products. Based on RI, recycled ferrous parts have about 70% comparable properties with equivalent pure iron parts. Complex reduction and sintering behavior in MIM, particularly, diffusion and pore volume kinetics limits applicability of MIM with this recycling approach. However, few industrial parts were developed and manufactured by PM based approach to validate the applicability of this novel recycling-cum-manufacturing process for the production of porous parts.

Keywords: solid state recycling; metallic scrap/sludge; powder metallurgy; in-situ reduction

1. Introduction

Recent developments in conventional recycling allow achieving comparable properties of metals derived from secondary sources (scraps and industrial waste) with metals from the primary sources. Nearly 40 percent of worldwide steel is produced from secondary sources [1, 2]. The ability to recycle a metal depends upon the ease with which it can be obtained and the demand for that metal once it has been recycled. Steelmaking process using the electric arc furnace (secondary steelmaking) uses scrap metal as the primary raw material. This process is found to be feasible and economical when a large quantity of identical scrap is available and provide secondary raw material for subsequent operations [3]. Solid state approaches used for recycling of non-ferrous metallic scrap on the other hand process scrap available in limited quantities but requires high capacity presses and furnaces for deformation and bonding [4]. Powder technology based novel solid-state recycling process has following advantages for recycling of particulate ferrous metallic scrap,

1. Alloying powders allows achieving unique properties and microstructure
2. Sintering stage can be used for the thermochemical treatment of materials
3. Low energy consumption and shorter overall production time
4. Significant cost benefits as major subsidence of powder cost
5. Net-shape manufacturing

Though powder technology based recycling process has benefits mentioned above, characteristics of products after recycling are not yet discussed in the available literature to quantify the effect of process characteristics on properties attained. It curtails implementation in possible varieties of applications. For instance, particulate raw material (powders), inability to manufacture large and complex shaped parts, low ductility and strength of parts, health hazards due to atmospheric contamination of powder/dust and emissions from furnaces are commonly faced issues [5, 6].

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Currently, applications of powder metallurgy (PM) may be classified into four major groups, structural, tribological, cutting tools and magnetic parts. However, parts produced by PM based recycling may not be suitable for all of these application domains. Powder Metallurgy based recycling technique yields parts of limited strength due to a higher level of porosity. Thus, these parts suit only applications where porosity is desirable and limited structural strength is expected [7, 8].

Metal injection molding (MIM) is best suited for the high-volume production of small metal parts. As with injection molding, these parts may be geometrically complex and have thin walls and fine details. As powdered metal is not melted in the MIM process (unlike metal casting processes), high-temperature alloys can be used without any adverse effect on tool life [9].

The brief overview of PM and MIM process steps in the context of in-process recycling of shop floor ferrous metallic scrap is given below,

Processing and pulverization of identified metallic scrap (a mixture of oxides of iron in various proportions depending on the source of scrap) is carried out by crushing and ball-milling. Brittle iron oxide (forging scale) is crushed by a jaw crusher followed by ball milling. In ball-milling, harder ceramic (ZrO_2) balls strike on iron oxide stock refining the particle size. After sieving the powder, coarser particles are used for PM. In the MIM process, fine particles are used to get adequate mouldability during injection step, besides excellent mechanical properties and dimensional stability of sintered parts.

Phases of iron oxide in scrap are determined quantitatively to calculate the quantity of (carbonaceous) reducing agents required for carbothermic reduction during sintering. A calculated amount of reducing agent (here carbonaceous materials) is mixed with iron oxide powder for in-situ carbothermic reduction during sintering. Mixing is performed using any of the mixing techniques; low-energy ball milling, mixer grinder mixing or turbula mixing, or a combination of these. The powder mixture is uniaxially compacted using hydraulic and mechanical presses which enabled compaction at different strain rates. Compaction of powder mixture to different sample shapes such as a solid cylinder and cylindrical bushes of various dimensions is also performed using cylindrical dies. Compacted samples are then heated to have in-situ reduction and densification during PM sintering cycle. A laboratory scale tubular furnace with inert gas flow arrangement and vacuum is utilized [10]. A series of reduction reactions are taking place for the initial phase of sintering in the samples is represented schematically in Figure 1.

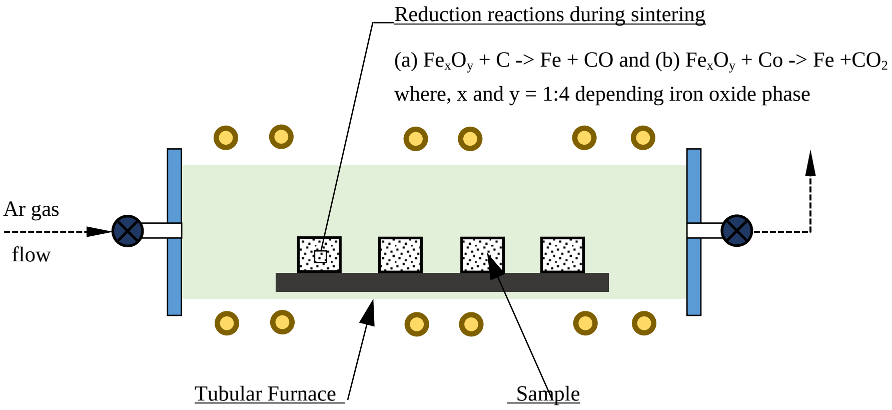

Figure 1. Schematic representation of in-situ carbothermic reduction during sintering of PM compacts

The first step of MIM process is to create a powder mixture of metal and polymer. The metal powder is mixed with a thermoplastic binder, cooled, and then granulated into a homogeneous feedstock in the form of pellets.

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Usually, sigma blade mixer is used to prepare feedstocks. The resulting feedstock typically has 60% metal and 40% polymer by volume. The feedstock is shaped using the similar equipment and tooling that are used in plastic injection molding. However, the mold cavities are designed approximately 20% larger to account for the part shrinkage during sintering. During molding cycle, the feedstock is melted and injected into the mold cavity, where it cools and solidifies into the shape of the part. The molded "green" part is ejected. In the subsequent step, polymer binders are removed from the metal. In some cases, solvent debinding is first performed in which the "green" part is placed in water or chemical bath to dissolve the sacrificial binder component. After this step, thermal debinding or pre-sintering is performed. The solvent debinded part is heated in a low-temperature oven, allowing the polymer binder to be removed via evaporation. Thermal debinding is usually carried out in a vacuum. As a result, the remaining "brown" metal part contains approximately 40% empty space by volume. The final step sintering is required to consolidate the loosely bound powder in the "brown" part, resulting in a high-density (95-99%) metal part. Sintering usually carried out in the inert gas atmosphere or in the vacuum. Sintering temperatures are usually close to 85% of the metal's melting point [11, 12].

Literature available so far does not contribute to the knowledge of the effect of process variables on the process as well as part characteristics after solid state recycling. To establish a correlation between these characteristics and to appreciate in-situ reduction during sintering for purification of iron constituents are the initial objectives of this work. Moreover, comparative assessment of these characteristics with process variables (mainly, thermal debinding stages and temperature, sintering temperature, sintering time, thermal debinding atmosphere and sintering atmosphere) on the properties of sintered products is also discussed. Finally, an attempt is made to analyse the recyclability of metallic scrap by the PM and MIM process.

2. Materials and Methods

Metallic waste generation in a forging plant at every intermediate process starting from cutting to final finishing operation was analyzed. Oxide scales, chips, and flashes are usually recycled in steel making process whereas metallic constituents in grinding sludge are dumped as a landfilling material. Grinding sludge/swarf is a crude mixture of metallic (about 50 wt. % of iron oxides and pure metal particles) and nonmetallic constituents such as dust, cutting fluids and lubricants. Many new techniques are adopted for recycling of such a scrap by hot consolidation, pigments for paint industry, etc. These processes do not provide direct applicability of these essential metallic resources. Powder technology (particularly PM and MIM) as discussed in the previous section is applied to get usable products directly after recycling. Selected grinding sludge is dried to remove moisture, roasted in controlled conditions to obtain pyrolytic carbon from nonmetallic constituents and ball milled for pulverization. Table 1 provides chemical composition of powdered grinding sludge which considered as a starting material for this study.

Table 1. Semi-quantitative abundance (by EDS analysis) of major and minor elements in the powder sample

Elements	C	O	Al	Si	Mn	Fe
wt. %	6.21	29.03	0.39	0.57	0.42	63.38

Iron (Fe) and oxygen (O) are the major constituents in powder sample whereas carbon (C) is a minor element. The presence of alloying elements such as Mn, Si, Al in powder from grinding sludge conforms that scrap is derived from finishing operations of micro-alloyed steel. The XRD analysis also confirmed the presence of Fe_3O_4 (92.8 wt.%), FeO (1.9 wt.%), $Fe(CO)_5$ (1.5 wt.%) and negligible portion or absence of Fe_2O_3 in Grinding Sludge (GS). Determined values of iron oxide phases were used to calculate the amount of carbon needed for carbothermic reduction.

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The theoretical requirement of carbon for reduction of 1gram of Grinding Sludge powder (92.78% Fe_3O_4, 1.92% FeO, 1.44% Fe and 3.84% C by wt.) may be calculated as:

2 Fe_3O_4 (0.9278)[*1]	+	C 0.0247	=	6 FeO [0.864]	+	CO_2 0.088
FeO (0.0192) + [0.864]	+	C 0.0738	=	Fe [0.692]	+	CO_2 0.272

∴ Total theoretical C needed per gram of grinding sludge (by wt.) = 0.0247+ 0.0738 = 0.0985 g…………… (1)

As carbon is the limiting reactant (controls carbothermic reduction reaction) and stoichiometric proportion of carbon may not produce the desired degree of reduction [13]. Carbon is mixed with powdered scrap in 25% excess than that theoretically calculated based on above reactions [14, 15]. For comparative assessment of properties, commercial pure iron powder commonly used in powder metallurgical applications and carbonyl iron powder (as detailed in Table 2) were processed likewise for PM and MIM purpose respectively.

Table 2. Physical properties of source material used in the present study

Process	Material	Particle shape	Mean / Avg. particle size (μm)	Density (g/cc)	Identifier	Powder Loading by wt. %
PM	Commercial Pure (CP) Iron	Spherical	48.03	7.73	CPI	----
PM	Grinding Sludge (GS)	Irregular	45.84	5.61	GS	----
PM	GS - Graphite (GR)	Irregular - Flakes	45.84 - < 5	5.61 - 2.26	GSGR	----
MIM	Carbonyl Iron (CI)	Spherical	3.29	7.60	CI90	90
MIM	Grinding Sludge (GS)	Irregular	2.64	5.71	GS75	75
MIM	GS - Graphite (GR)	Irregular - Flakes	2.64 - < 5	5.71 - 2.26	GSGR75	75

CP, GS, and GSGR powder mixtures were compacted to cylindrical shaped samples having 10 mm height as well as diameter. Sintered cylindrical samples (CP iron, GS, and GSGR) obtained after conducting 3^3 full factorial experiments were used for characterization of properties. Significant process parameters compaction pressure (levels: 900, 1050, 1200 MPa), sintering temperature (levels: 1100, 1200, 1300°C), sintering atmosphere (levels: vacuum, argon gas, nitrogen gas) were varied according to experimental settings (as given in Appendix A). Other parameters such as graphite addition (25% excess than a stoichiometric requirement), reduction temperature (100°C below sintering temperature), reduction time 30 min and sintering time 60 min were kept constant. Three samples per experimental condition were used for measurement of Degree of Reduction, i.e. DOR (for GS and GSGR), sintered density, hardness, and yield strength (in compression).

[*1] ( ) represents mass obtained from source, [ ] represents mass obtained from reaction

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An organic binder system having 70 wt. % paraffin wax, 25 wt. % HDPE and 5 wt. % stearic acid (S.A) was mixed with metallic powder for preparation of two separate MIM feedstocks, one designated as CI90 (90% solid loading of Carbonyl Iron powder) and the other GSGR75 (75% solid loading of a mixture of 65.77 wt. % Grinding Sludge and 9.22 wt. % GRaphite) using a Sigma Blade Mixer running at 50 rpm. Dogbone shaped and cylindrical samples were injection molded for tensile and compression testing respectively. Solvent debinding was performed on parts of different shapes and feedstock materials. Parts were debinded in n-Heptane at 56ºC. To analyze the sintered properties of MIM test samples with varying sintering temperature, and sintering atmosphere, a full factorial (3^2) design was used. Nine experiments with three repetitions per experiment were performed to study the effect of sintering atmosphere and temperature, each at three levels. Nine experimental (sintering cycles) settings used to perform debinding and sintering of samples are given in Appendix B. Three samples per experimental condition were used for measurement of DOR (for GSGR75), sintered density, yield strength, UTS, elongation and elastic modulus. The average values and standard deviation of properties were determined to represent the corresponding experimental characteristics.

3. Results and Discussion

Process quality characteristics like Degree of Reduction (DOR), Degree of Densification (DOD) were determined by (2) and (3).

$$\text{Degree of Reduction (DOR)} = \left(\frac{\text{Actual weight change}}{\text{Theoretical weight change}}\right) \times 100\ \% \ \ldots\ldots (2)$$

$$= \left(\frac{\text{Initial weight} - \text{Final weight of the sample}}{\text{Initial weight} - \text{Theoretical reduced weight}}\right) \times 100\ \%$$

$$\text{Degree of Densification (DOD)} = \left(\frac{\rho_{\text{Sintered}} - \rho_{\text{Green}}}{\rho_{\text{Iron}} - \rho_{\text{Green}}}\right) \times 100\ \% \ldots\ldots (3)$$

During carbothermic reduction, the weight of sample progressively decreases as oxygen from the oxide is lost. The initial and final weight of the sample was measured. Weight change is the total of the weight change of the ingredients (oxide powder plus graphite). The ideal (theoretical) weight of the reduced sample was obtained.
For example, the compacted sample weighed 3g having 86.9565 wt. % iron oxide powder and 13.0435 wt. % graphite (if 25 % excess graphite added) then theoretical reduced weight of iron = 3 × 0.8695 × 0.704*[2] = 1.8363g. “Degree of Densification” of the sintered iron sample was determined as the difference between the density before sintering (green density) and that after sintering (sintered density).

DOR, DOD and mechanical properties of sintered parts are influenced by material and process parameters (such as the composition of the scrap, reducing agent and reducing gas, sintering time, compaction, injection, sintering and debinding temperatures, the particle size of iron oxide, compaction pressure, etc.) of the recycling process. Effect of these parameters on process characteristics and mechanical properties of recycled and sintered parts are discussed elsewhere [16, 17]. However, the correlation between process characteristics, particularly Degree of Reduction (DOR) and properties of sintered parts is essential to understand the improvement in properties of GSGR and GSGR75 via in-situ carbothermic reduction by selected powder technology (PM and MIM) based recycling approach in the present study. To apply the recycling approach, the recycled material and part should have comparable properties as that of virgin wrought material besides equivalent energy consumption. Following sections discuss the correlation between Degree of Reduction (DOR) and sintered properties along

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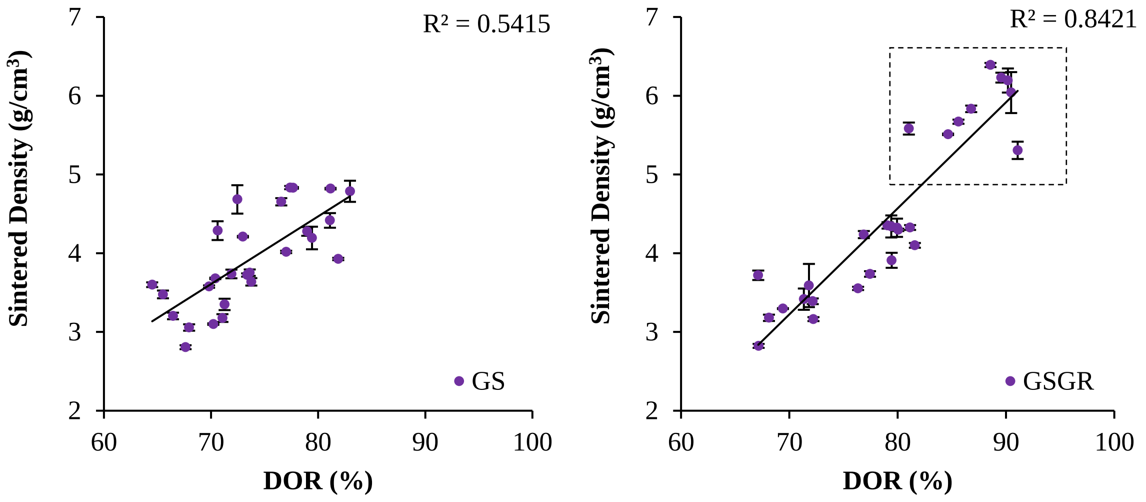
*[2] Amount of iron obtained after reduction of 1g of scrap powder (considering iron oxide phases in scrap and stoichiometric calculations)

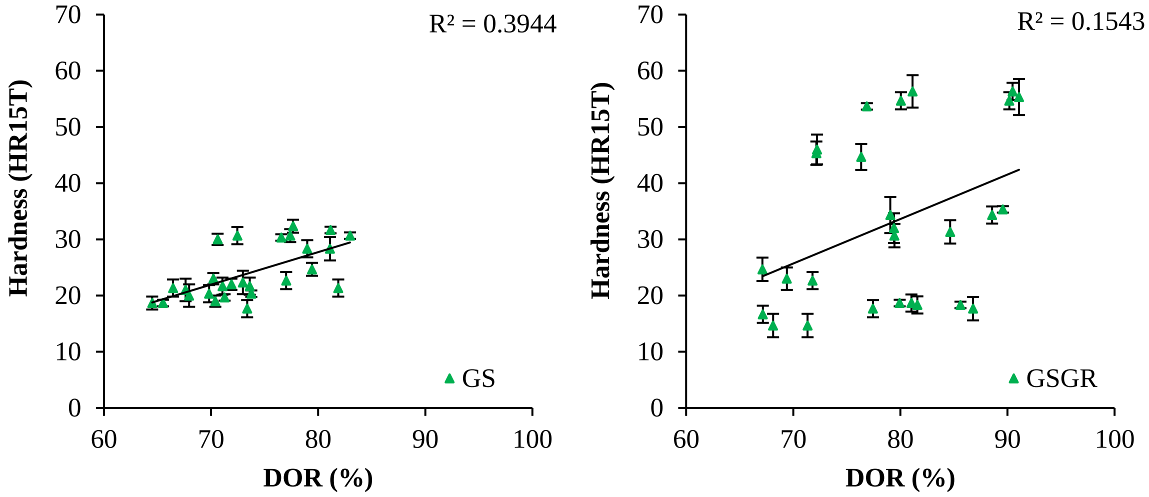
with quantification, evaluation of recyclability using the novel Powder Technology based recycling approach. An optimized material and process parameter settings for Powder Metallurgy based recycling were selected based on process characteristics (DOR and DOD), and properties of compacted and sintered PM parts as illustrated in [10] and [15] are considered. The latter part of this section demonstrates the suitability and prospective applications of established recycling technique.

3.1 Correlation between DOR and sintered properties of PM and MIM parts

In PM sintering, in the absence of separately added graphite powder, in-situ reduction in a grinding sludge (GS) sample occurs by carbothermic reduction of iron oxide through pyrolytically generated carbon. Carbon (~4.32% by wt.) in grinding sludge is generated by pyrolytic transformation of nonmetallic constituents during roasting of the GS. In the GSGR samples, carbothermic reduction of iron oxide occurred due to both, pyrolytically generated carbon and 25% excess graphitic carbon added for carbothermic reduction.



(a) Improvement in sintered density with Degree of Reduction (DOR)



(b) Variation in hardness of sintered samples with Degree of Reduction (DOR)

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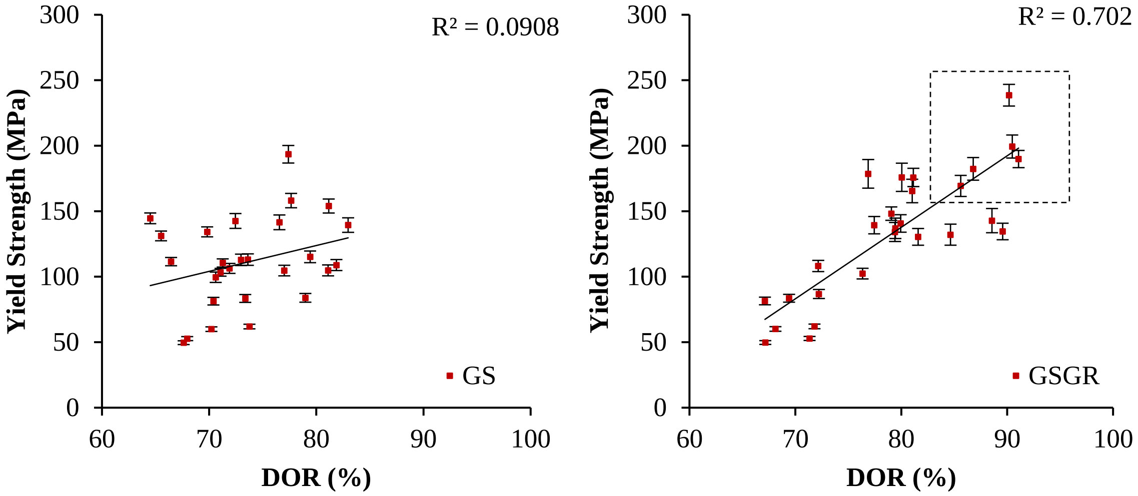

(c) Variation in yield strength of sintered samples with Degree of Reduction (DOR)

Figure 2. Influence of Degree of Reduction on sintered properties of GS and GSGR parts manufactured via Powder Metallurgy route

Sintered density, hardness, and yield strength show an increasing trend with DOR. The reason is the characteristics (properties and DOR) are simultaneously influenced by in-situ reduction and setting of control parameters. Sintered densities of GS and GSGR samples were similar for 65% to 80% DOR (Figure 2 (a)). However sintered density of GSGR samples further improved from 5.5 to 6.5 g/cm^3 with an increase in DOR enabled by 25% excess (compared to stoichiometry) carbon, compaction pressure (1050 MPa), sintering temperature (1200-1300ºC) and argon gas atmosphere in sintering. Hardness measured on the surface of cylindrical sintered samples does not correlate well with DOR (which is bulk characteristics) [18]. The yield strength of sintered samples also correlated well with DOR because the increase in the metallic transformation resulted after reduction and densification enable a proportional increase in yield strength of the GSGR samples. The effect of sintering parameters (sintering temperature and sintering atmosphere) on CI90 and GSGR75 feedstocks were studied for suitability of MIM for recycling. These parts were characterized to recognize the physical and mechanical properties changes with sintering parameters and feedstock materials. Properties of sintered samples of CI90 are used as a reference to appreciate the improvement in properties of sintered GSGR75 samples obtained from MIM process.

In-situ reduction of grinding sludge was taken place in GSGR75 samples by carbothermic reduction of iron oxide during sintering of MIM parts. The carbon is sourced from pyrolytically generated carbon and externally added graphite in 25% excess for carbothermic reduction. The trend of increasing sintered properties of GSGR75 parts with DOR is similar to that of GSGR as shown in Figure 2. However, the correlation between sintered properties and DOR is weak in MIM-based GSGR75 parts as compared to PM based GSGR. The weak correlation is because of the heterogeneous distribution of graphite in grinding sludge (arises from low solid loading in GGS75 i.e.75 wt. %) limits the carbothermic reduction, densification, and properties of sintered parts. The quantification (DOR and DOD) for recycling process via PM and MIM suggest a lower degree of completion of reduction and densification. During recycling, though the optimal parametric setting provides ~92% DOR and ~70% DOD by PM technique and ~69% DOR and ~74% DOD by MIM technique, additional improvement in these characteristics is not possible because,

1. The residue carbon after carbothermic reduction during sintering hinders the physical contact between iron particles which limits the extent of reduction and prolongs the process of necking for densification

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in PM. Particle contact developed during sintering of injection molded part of GSGR75 feedstock is even weaker due to substantial pore volume created during debinding, i.e., before the start of the sintering stage.

2. The existence of pores during sintering is prolonged because of the presence of irregularly sized and shaped pores which hinders even volumetric diffusion during densification.
3. The energy change during carbothermic reduction is considerably higher than the interfacial energy of particles. This is not in support of pore removal mechanism (requires high interfacial energy) and hence leads to decrease in densification. The more substantial volume difference between reactant (iron oxide and carbon) and product (iron) decreases reduction and densification due to high energy required to enhance the volumetric diffusion.
4. In the case of MIM, finer powder particles accelerate densification because of higher activation energy for surface diffusion compared to reduction reaction rate. This lowers the coinciding completion of carbothermic reduction.
5. If densification started earlier to complete reduction (in the case of very high sintering temperatures), bulk diffusion and grain coarsening would enhance the densification rate of reduced iron which tends to entrap the unreduced portion and decreases reduction extent and sintered density.
6. The growing preliminary iron grains surround the secondary (small) pores formed in a close-packed arrangement leading to low shrinkage. A considerable shrinkage is observed when large pores get eliminated.

3.2 Evaluation of Recyclability Index of GS, GSGR (PM) and GSGR75 (MIM)

As a general observation from Figure 2, measured properties were improved in GSGR than GS with DOR though samples of the both were processed at identical conditions. To evaluate relative improvement of properties by in-situ carbothermic reduction of grinding sludge for recycling process, samples of CP iron with the identical condition were characterized and used as a reference. Sintered properties of GSGR samples were normalized with CP iron properties for similar experimental setting (Exp. No. 1-27) and plotted as shown in Figure 3. Normalized properties of GSGR show an increasing trend with sintering temperature from 1100°C to 1300°C for any of the selected compaction pressure. The variation in compaction pressure does not show significant improvements in relative properties improvement of GSGR samples. Furthermore, these individual normalized properties were averaged and represented as a Recyclability Index (relation 4) corresponding to the experimental setting for GS and GSGR samples. For example, Recyclability Index for corresponding to Exp. No.14 for GSGR is calculated as,

$$\text{Recyclability Index} = \frac{\text{Normalized Density+Normalised Hardness+Normalised YS}}{3} \text{ ………....................................} \quad (4)$$

$$\text{Recyclability Index (for GSGR at Exp. No. 14)} = \frac{0.61 + 0.69 + 0.45}{3} = 0.58$$

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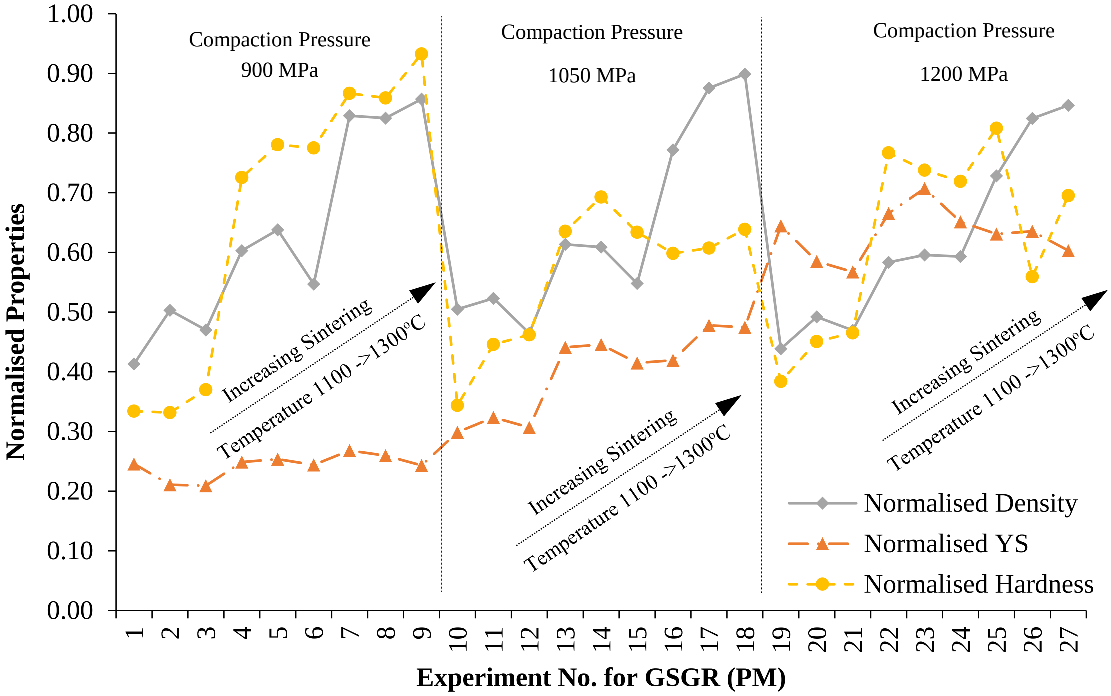

Figure 3. Variation in normalized properties of GSGR (PM) sintered samples with experimental condition (parametric setting corresponding to the Exp. No. is given in Appendix G1)

Recyclability Index (averaged properties) quantifies the overall normalized property of sintered samples for a given experimental setting. This quantification is performed to get an effective improvement of properties by a carbothermic reduction in GSGR than GS as the energy input for processing CP iron, GS and GSGR are identical. This Recyclability Index is only used to categorize the relative improvement in properties (for structural strength) of GS and GSGR with corresponding properties of CP iron at identical processing conditions. Recyclability Index is arranged in ascending order with corresponding experiment number for GS and GSGR and given in Figure 4. Except for four experimental conditions (Exp. 1, 2, 3 and 10), Recyclability Index of GSGR is higher than GS. These experimental conditions have a sintering temperature of 1100ºC and lower compaction pressure which resulted in a limited carbothermic reduction, residues of graphite and partial metallic transformation of grinding sludge. In the rest of the experiments, the experimental settings are operational for improvement of the Recyclability Index. Highest magnitude of Recyclability Index is observed in GSGR samples from experiments 25 and 27 which is almost 17% more than corresponding highest for GS samples.

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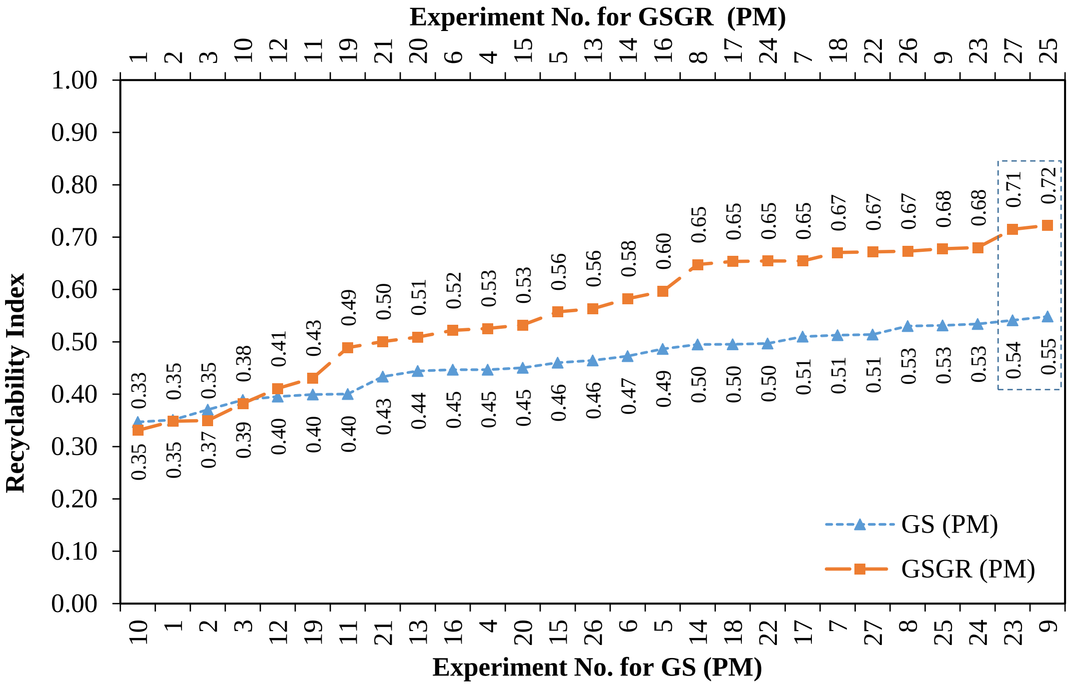

Figure 4. Improvement in Recyclability Index of grinding sludge by carbothermic reduction for different experimental settings using Powder Metallurgy route

In order to evaluate the suitability of MIM-based recycling approach, sintered properties of GSGR75 samples were normalized with C90 properties for corresponding experimental setting (Exp. No. 1-9 from Appendix B) and plotted in Figure 5. Normalized properties of GSGR75 show an increasing trend with sintering temperature from 1100°C to 1300°C especially in experiments wherein samples were thermally debinded in vacuum followed by immediate sintering in argon.

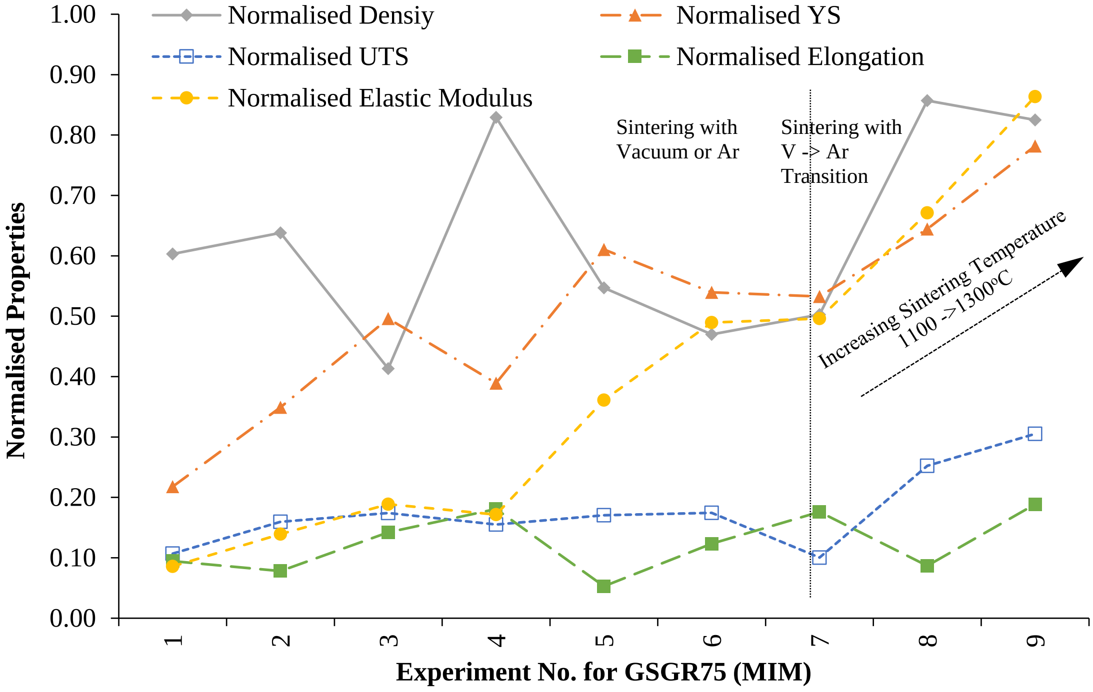

Figure 5. Variation in normalized properties of GSGR75 (MIM) sintered samples with experimental condition

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Furthermore, these individual normalized properties were averaged and represented as a Recyclability Index (see relation 4) corresponding to the experimental setting for GGSR75 samples. These averaged numbers (Recyclability Index) quantify the overall normalized property of sintered samples for a given experimental setting (Exp. No. 1-9 from Appendix B). This Recyclability Index is useful for comparison between the overall structural strength of GSGR75 and CI90 with equivalent energy input for MIM processing. Recyclability Index is arranged in ascending order with corresponding experiment number for GSGR75 and given in Figure 6.
Maximum Recyclability Index (0.59) of GSGR75 is observed from Figure 6 with Exp. No. 8 (sintering temperature: 1300ºC and sintering atmosphere: V-Ar wherein samples were thermally debinded in vacuum followed by immediate sintering in argon). Experiments (Exp. No. 1, 4, 7) with a sintering temperature of 1100ºC and vacuum sintering result in limited carbothermic reduction and formation of highly porous structure.

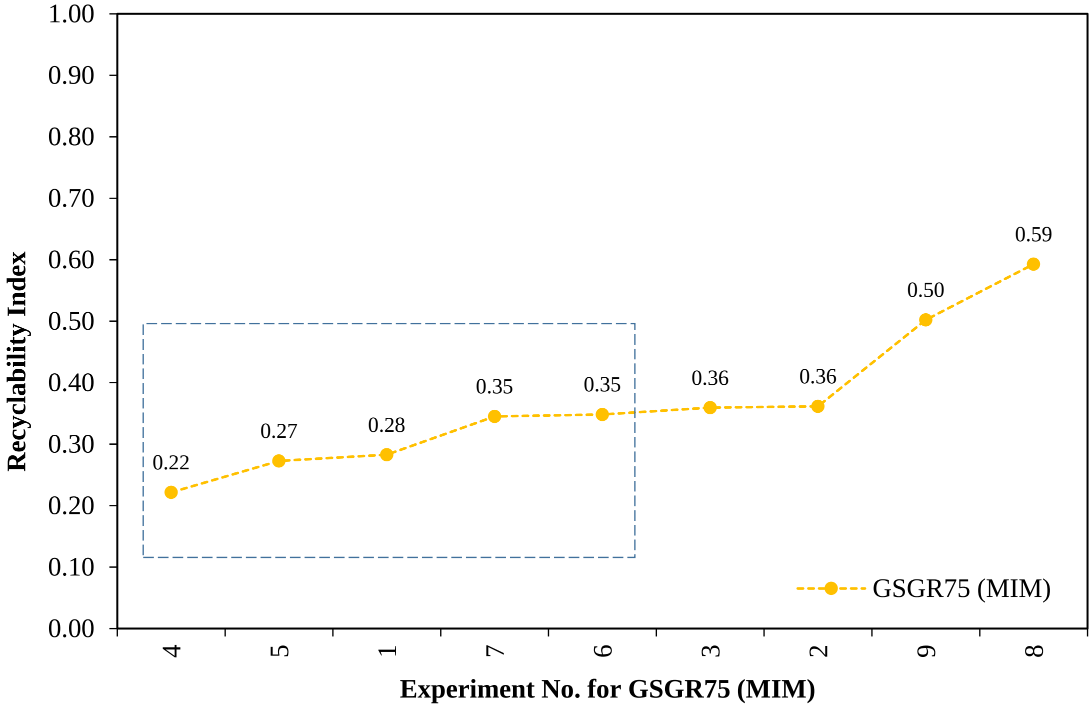

Figure 6. Recyclability of grinding sludge by carbothermic reduction for different experimental settings using Metal Injection Molding (MIM) route

Based on the experimental observations, following mechanism of solid state sintering for recycling based on powder technology is proposed. Evolution of properties is also consistent with the degree of physical changes after sintering. The carbothermic reduction involves about 17 to 23 (depending upon the presence of iron oxide phase and corresponding reaction rate favoring conditions) volume percent change due to rearrangement iron lattice and atomic oxygen transport [19, 20].
In the present study, densification proceeds through the following stages during sintering:

1. Particle contact developed during compaction and injection starts necking by surface and grain boundary diffusion and thereby formation of distinct pores of various sizes.
2. Pores tend to become rounded to lower the surface energy which decreases the porosity further. The pore elimination rate for smaller pore is higher than that of larger pores because of higher activation energy needed to eliminate larger ones.
3. Combination of volumetric (bulk) diffusion and grain coarsening further enhances the densification rate and tends to eliminate the remaining porosity.

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3.3 Applicability of recycling and manufacture of porous PM parts

Solid state recycling attempted in the present study involves in-situ carbothermic reduction of iron oxide from a source of scrap and densification during sintering of PM and MIM stage. Full reduction and densification is not possible at the same time in such a complex (involves multiple stages and modes reduction) carbothermic reduction system of study. However, based on the experimental observations and characterization of sintered properties some optimal parametric settings were reported.

In recycled parts, a maximum of 70% of the properties of sintered iron can be achieved in PM while about 59% properties of the sintered carbonyl iron can be achieved in MIM after recycling. The deviation in the properties of recycled parts from sintered iron properties is caused by comparative chemical composition and level of porosity after sintering. The chemical composition of recycled iron (PM) parts (1.12 wt.% C, 0.42 wt.% Si, 0.76 wt.% Mn and balance Fe) is similar to high carbon steel which contains approximately 0.7–2.5 wt.% carbon. Recycled iron parts obtained by MIM process have even higher carbon content (1.37 wt.%).

Downgraded metallic scrap (grinding sludge) for powder technology based recycling process as per the outcomes (from above experimental results pertaining to the degree of reduction, the degree of densification, sintered density and mechanical properties quality characteristics) can be used to appreciate the merits of attainment of usable products. Material and processing conditions of sintered samples of ~0.7 Recyclability Index is further utilized for simultaneous powder metallurgy based recycling (in which in-situ reduction of grinding sludge and manufacturing of parts is attainable) and manufacturing of porous products. Proposed recycling technique is used in manufacturing commonly applicable shapes like a solid cylinder, bush and circular ring and plain bearing.

A mixture of grinding sludge and graphite (25% excess than the stoichiometric requirement for carbothermic reduction) GSGR was prepared. The mixed powder was then compacted at 1050 MPa compaction pressure. Compacted (green) samples were then sintered in a tubular furnace with a constant flow of argon gas at 150 ml/min. Parts sintered at 1200^{o}C are porous and shows considerable shrinkage as shown in Figure 7.

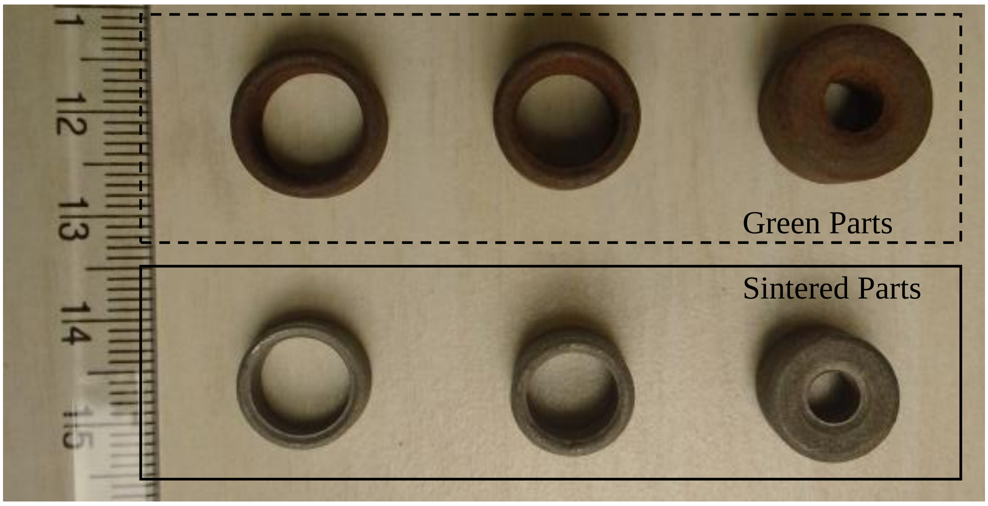

Figure 7. Green and sintered PM parts of GSGR material

Compaction die design considerations needs to be developed for implementation of PM based recycling-cum-porous product manufacturing. This is because GSGR parts show significant volumetric shrinkage after sintering than CI parts because of simultaneous effect of carbothermic reduction and densification during sintering. These porous parts may work well for air film rolls/bearings, instrument filters, flow restrictors, flame arrestors, etc. in view of the performance characteristics like filtration, flow control, porosity, and distribution.

Peer-reviewed version available at Recycling 2018, 3, 59; doi:10.3390/recycling3040059

However, structural characteristics in term of sintered density and mechanical properties may have some limitations for suitability to a particular application.

4. Conclusions

Extensive experimental studies were conducted to confirm possible implementation of powder technology (powder metallurgy and metal injection molding) for the development of a recycling-cum-manufacturing process. The degree of reduction (DOR) and mechanical properties of GSGR (PM) parts are well correlated than GSGR75 (MIM) parts because of controlled carbothermic reduction and pore volume shrinkage in sintering step of PM process. A quantitative measure “Recyclability Index” was established to relate the effect of process parameters and process characteristics (DOR and DOD) with sintered properties.

Recyclability Index of GSGR (PM) samples is significantly higher (~17%) than GS (PM) samples thanks to stoichiometric added carbon (for completing in-situ carbothermic reduction). Recyclability Index of GSGR75 at an optimal parametric setting is 59% (meaning parts produced from this recycling technique have 59% physical and mechanical properties than the pure iron dense part parts), the proposed MIM-based recycling approach would not be practically suitable for manufacturing of usable products. However, RI of GSGR parts is enough to implement powder metallurgy route for recycling-cum-manufacturing. Thus, PM based recycling of grinding sludge is possible for manufacturing of net-shaped porous products. Significantly high volumetric shrinkage during sintering also demands further optimization of compaction die design for dimensional control of sintered products.

Acknowledgments: The authors of this research paper declare no external funding sought for this work. Department of Mechanical Engineering provided all experimental and analytical resources, Indian Institute of Technology, Bombay.

Author Contributions: Kedarnath Rane designed and performed the experiments. Kedarnath Rane and Prashant Date analyzed the data with equal contribution. Kedarnath Rane wrote the paper, and he is the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Experimental condition for Full Factorial 3^3 experiments conducted for PM study

Experiment No.	Experimental Settings for CP Fe, GS and GSGR		
	Compaction Pressure (MPa)	Sintering Temperature (°C)	Sintering Atmosphere
1	900	1100	Vacuum
2	900	1100	Argon
3	900	1100	Nitrogen
4	900	1200	Vacuum
5	900	1200	Argon
6	900	1200	Nitrogen
7	900	1300	Vacuum
8	900	1300	Argon
9	900	1300	Nitrogen
10	1050	1100	Vacuum
11	1050	1100	Argon
12	1050	1100	Nitrogen
13	1050	1200	Vacuum
14	1050	1200	Argon

15	1050	1200	Nitrogen
16	1050	1300	Vacuum
17	1050	1300	Argon
18	1050	1300	Nitrogen
19	1200	1100	Vacuum
20	1200	1100	Argon
21	1200	1100	Nitrogen
22	1200	1200	Vacuum
23	1200	1200	Argon
24	1200	1200	Nitrogen
25	1200	1300	Vacuum
26	1200	1300	Argon
27	1200	1300	Nitrogen

Appendix B

Experimental 3^2 design matrix and sintering condition for MIM sintering cycle

Cycle	A: Sintering Temperature (ºC)	B: Furnace Atmosphere during Thermal Debinding and Sintering	Coded Representation
1	1100	TD: Vacuum followed by S: Vacuum	1100V
2	1200	TD: Vacuum followed by S: Vacuum	1200V
3	1300	TD: Vacuum followed by S: Vacuum	1300V
4	1100	TD: Vacuum, S: Ar gas separate	1100Ar
5	1200	TD: Vacuum, S: Ar gas separate	1200Ar
6	1300	TD: Vacuum, S: Ar gas separate	1300Ar
7	1100	TD: Vacuum, S: Ar gas immediate transition	1100V-Ar
8	1200	TD: Vacuum, S: Ar gas immediate transition	1200V-Ar
9	1300	TD: Vacuum, S: Ar gas immediate transition	1300V-Ar

where TD: Thermal debinding and S: Sintering

References

1. R. A. Frosch, N. E. Gallopoulos, Strategies for manufacturing, *Scientific American*, Vol. 261, No. 3, 1989, pp. 144-152.
2. Rick LeBlanc, An overview of metal recycling, its importance and recycling processes, retrieved from www.thebalance.com/an-introduction-to-metal-recycling-4057469 on 10 February 2018.
3. S. F. Sibley, W. C. Butterman, Metals Recycling in the United States, *Resources, Conservation, and Recycling*, Vol. 15, 1995, pp. 259-267.

4. V. Güley, A.Güzel, A.Jäger, N.Ben Khalifa, A.E.Tekkaya, W.Z.Misiolek, Effect of die design on the welding quality during solid state recycling of AA6060 chips by hot extrusion, *Materials Science & Engineering A*, Vol. 574, 2013, pp. 163–175.
5. Yu Yao Kebang, Powder Metallurgy Co. Ltd., (2015), retrieved from: www.kbpm.cn/en/th.asp on February 10, 2015.
6. Asian Powder Metallurgy Association (APMA) Report 2009, retrieved form: www.apma.asia/#GlobalTransition on February 10, 2015.
7. R. M. German, Powder metallurgy of iron and steel, Wiley, 1998 - Science - 496 pages
8. P. Ramakrishnan, History of powder metallurgy, *Indian Journal of History of Science* Vol. 18, No. 1, 1983, pp. 109-114.
9. G. S. Upadhyaya, Powder Metallurgy Technology, Cambridge Int. Science Publishing, 1997 - Science - 158 pages.
10. K. K. Rane, P. P. Date, Sustainable Recycling of Ferrous Metallic Scrap Using Powder Metallurgy Process, *Journal of Sustainable Metallurgy*, 3(2) 2017, pp. 251-264.
11. B. Berginc, Z. Kampus , B. Sustarsic, The use of the Taguchi approach to determine the influence of injection-moulding parameters on the properties of green parts, *Journal of Achievements in Materials and Manufacturing Engineering*, Vol. 15, Issue 1-2, 2006, pp. 63-70.
12. D. F. Heaney, Qualification Method for Powder Injection Moulded Components, *P/M Science & Technology Briefs*, Vol. 6, No.3, 2004, pp. 21-27.
13. K. K. Rane, P. P. Date, Pulverisation of forging scales and grinding sludge: A new technique for metallic recycling for Forging Industries, *Waste Management & Resource Utilisation*, 2014, pp. 637-642.
14. F. Demirci, A.Turan, O. Yucel, An investigation on the direct reduction of mill scale from continuous steel casting, *International Iron and Steel Symp*., 2012, pp. 353-359.
15. K. K. Rane, P. P. Date, Reduction and densification characteristics of iron oxide metallic waste during solid state recycling, *Advanced Powder Technology*, Vol. 26, No. 1, 2015, pp. 126–138.
16. R. Urval, S. Lee, S. V. Atre, S. J. Park, R. M. German, Optimization of process conditions in Powder Injection Moulding of Microsystem components using a Robust Design Method: Part I. Primary Design Parameters, *Powder Metallurgy*, Vol. 51 No. 2, 2008, pp. 133-142.
17. A. T. Sidambe, I. A. Figueroa, H. Hamilton, I. Todd, Improved Processing of Titanium Alloys by Metal Injection Moulding, *IOP Conf. Series: Materials Science and Engineering*: 26, 2011, pp. 109-117.
18. M. Laska, J. Kazior, Influence of Various Process Parameters on the Density of Sintered Aluminium Alloys, *Acta Polytechnica*, Vol. 52, No. 4, 2012, pp. 93-95.
19. S. Prakash, Reduction and sintering of Ouxed iron ore pellets-a comprehensive review, *The journal of South African Mining and metallurgy*, 1996, pp. 1-14.
20. N. Srinivasan, Reduction of iron oxides by carbon in a circulating fluidized bed reactor, *Powder Technology*, Vol. 124, 2002, pp. 28-39.