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Improving iron compact green strength using powder surface modification

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In powder metallurgy, green strength has important consequences for part production rates and product end quality. Mechanical interlocking and interparticle cold welding are the main mechanisms responsible for green strength. These mechanisms are a ected by compaction pressure, temperature, amount of lubricant and additives admixed to the powder, and surface characteristics of the powder. The present paper describes the e ect of iron powder surface modification on the green strength of compacted specimens. The green properties of compacts fabricated from iron powder treated with diluted sulphuric acid and coated with copper by a non-catalytic displacement plating method are presented. The results indicate that surface modifications strongly influence the green strength of the compacts. PM/0831

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INTRODUCTION

Green strength is an important property a ecting powder compact manufacturing. It is defined as the ability of a green compact to maintain size and shape during handling.[1] The importance of green strength is becoming increasingly apparent as PM parts increase in size and geometry becomes more complex.[2] High green strength allows the production of sound parts (with no cracks or lamination) and makes the handling (including green machining) before sintering easier.

Crack formation in PM components is an important quality issue in the PM industry. Formation of cracks in PM processing has a great impact on the production rate and the quality of the final products. Zenger and Cai[3] reviewed the physical mechanisms by which cracks are formed. Cracks in PM components primarily originate during consolidation or handling before sintering. The root cause is most likely poor interparticle bonding before the sintering stage. In other words, the propensity to form cracks depends on the green strength of the compacts. Cracks will form if the internal stresses produced during ejection or handling are beyond the green strength of the compacts. Klar and Shafer[4] classified the powder variables a ecting green strength into three distinct groups: geometric factors, e.g. particle shape, size distribution, surface area, and roughness; intrinsic factors, e.g. bulk composition, impurities, texture, grain structure, and cold work; and surface related factors, e.g. surface composition, adsorbed species, and lubricants.

Surface related factors might a ect the formation of good interparticle bonds during compaction. The presence of oxide film, for example, may inhibit cold welding between the particles during compaction and reduces compact green strength. Additives (metallic, graphite, and lubricants) also generally reduce the green strength of the compacts by impeding the formation of good interparticle bonds during compaction.

Coleman and Foba[5] studied the e ect of di erent copper coatings (6–14 wt-%) on the properties of composite powders. The results showed that copper coating improves the strength of green iron compacts. The authors studied the e ect of di erent coating techniques (electrolytic, electroless, and displacement methods) and showed that the composite powders fabricated using the displacement methods have the highest green strength. Their results also showed that the amount of copper deposed at the surface of the powder does not strongly a ect the green strength of the compacts.

Lashmore[6] also worked on copper coated powders. He developed di erent coatings on di erent types of particles to produce cold formed materials. The technique includes the use of a proprietary activation solution before compaction. The author discloses that the solution dissolves the oxide film at the surface of the powder, enhances the interparticle welding during compaction, and increases the green strength and other properties depending on interparticle bonding (e.g. thermal and electrical conductivity).

Little work has been carried out on the e ect of powder surface treatment on the green strength of ferrous powder blends designed for traditional press and sintered applications. The copper content in most of these blends is lower than 2%. For traditional press and sinter applications, these powder blends usually contain additives and admixed lubricants to facilitate the compaction and ejection process.

This paper shows the e ect of di erent powder surface treatments on the properties of green iron powder compacts fabricated using uniaxial compaction. The e ect of an H_2SO_4 acid etching treatment and di erent copper coatings ($<2\%$Cu) on the properties of specimens fabricated with and without admixed additives is presented and discussed.

EXPERIMENTAL PROCEDURE

All specimens were prepared with water atomised iron powder (Atomet 1001 from QMP). Acid treatments were carried out by immersing the iron powder for a few minutes in an acidic solution of pH 2·0 made of 0·75 g L^{-1} of H_2SO_4. After immersion, the powder was filtered, rinsed, and dried at room temperature. Copper coating was applied using the non-catalytic displacement plating method[7] on as received powder and H_2SO_4 treated powder. The plating solution has the same concentration of sulphuric acid as the acidic solution. To coat 1 kg of iron powder with 1 wt-%Cu, the powder was immersed in 1 L of a $CuSO_4.5H_2O$ (39·3 g L^{-1}) aqueous solution. The iron powder was thoroughly stirred until the bluish tint of the solution vanished. The copper deposits on iron according to the following reaction[7]

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0$$

Hydrogen evolution also occurs when iron powder is immersed into the acidic solution

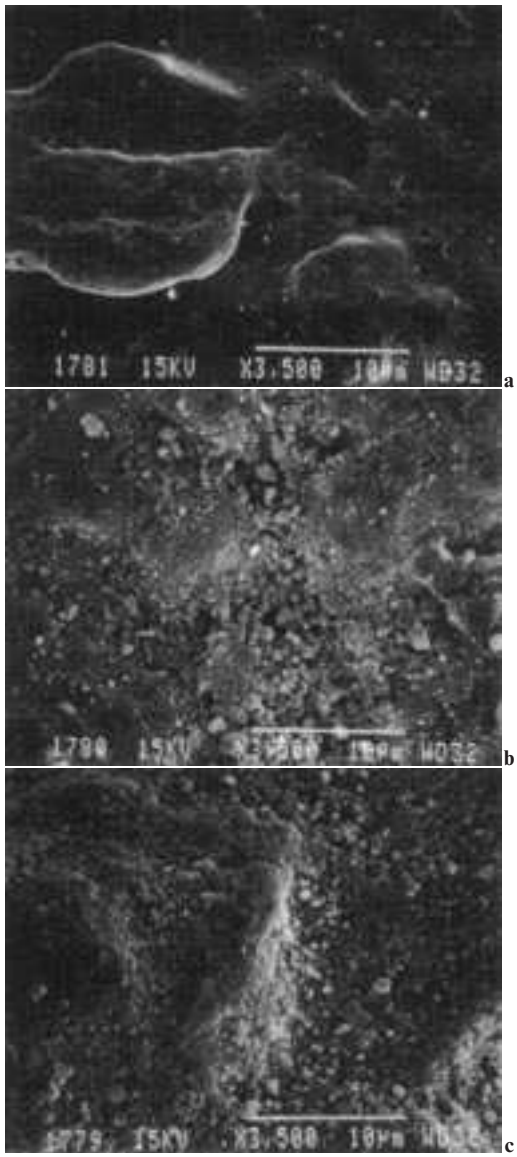
$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$

The powder surface was observed with a SEM and was analysed using a Kratos Axis HS X-ray photoelectron spectrometer (Kratos, Manchester, UK). Monochromated Al K_α radiation was used for excitation and a 180° hemispherical analyser with a three channel detector was employed for the survey and high resolution spectra. The spectrophotometer was operated in fixed analyser transmission mode throughout the study. The pressure in the analyser chamber was 10^{-6}–10^{-7} Pa. An electron flood gun was used to neutralise the charge during the experiment. Binding energies were referenced to the carbon–carbon bond, which was assigned a binding energy of 285 eV. Peak deconvolution was performed using the standard programs provided with the instrument.

Transverse rupture strength (TRS) test bars (3·175 × 1·27 × 0·635 cm) were pressed at 620 MPa at 25°C in a floating die using a hydraulic press. Specimens were compacted with powder containing no additives (die wall lubrication) and powder containing di erent additives (lubricant, graphite, and copper powder). Five specimens were prepared for each experimental condition. Electrical resistivity, and transverse rupture strength were all evaluated on the same specimens. Electrical resistivity was evaluated using a four point contact probe (0·8 cm between contact points) and a micro-ohmmeter (Ultra-Optec PM0 450) adapted for this application. Side and thickness e ects were taken into account in the electrical resistivity calculations. Five readings were taken on the top and bottom faces of each TRS bar and averaged. Green strength was evaluated according to MPIF standard 15.

RESULTS

Figure 1 shows the surface of as received, H_2SO_4 treated, and copper coated powders. The surface of the as received powder is smooth while the surfaces of the H_2SO_4 treated and copper coated powders are irregular. The surface roughness of the H_2SO_4 treated powder may come from the attack on the powder during the acid treatment and from oxidation that appeared after the treatment. The appearance of the copper coated powder is similar to the surface of the H_2SO_4 treated powder and to the surface of the copper coated powder prepared by Coleman and Foba.[5] The modification of the surface may come from the acid attack, the powder oxidation after the coating treatment, and from the deposition of copper crystals.



a as received; *b* H_2SO_4 treated; *c* 1 wt-%Cu coated

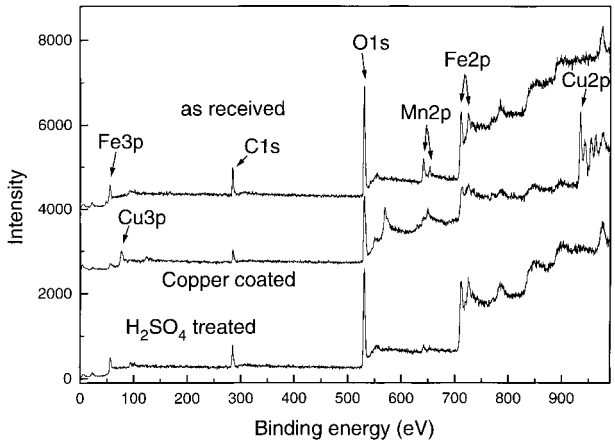
1 Micrographs showing surface of powders

Table 1 Surface composition (at.-%) of di erent powders evaluated by XPS: relative concentration in respect to one specific element is given in parenthesis

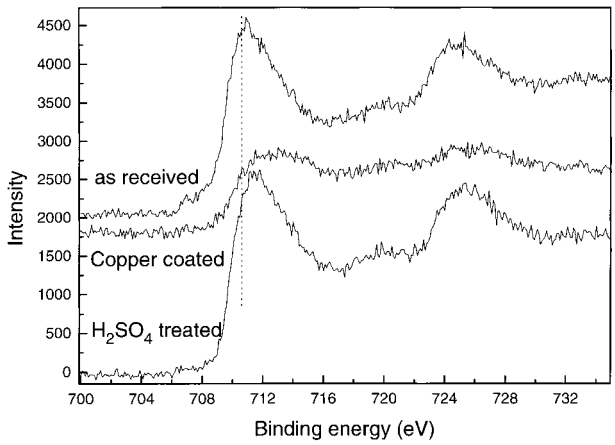
	As received	H_2SO_4 treated	1 wt-%Cu coated
Total carbon	30·5	25·8	22·6
Total oxygen	48·7	50·8	49·1
O 1s at 530·1 eV	21·5 (56·4%)	22·2 (43·8%)	18·8 (38·2%)
531·3 eV	13·7 (28·2%)	19·7 (38·7%)	18·0 (36·6%)
532·3 eV	5·3 (10·9%)	6·4 (12·6%)	8·4 (17·1%)
533·7 eV	2·2 (4·5%)	2·5 (4·9%)	3·7 (7·5%)
Total iron	17·0	22·1	16·0
Fe 2p at 710·6 eV	8·7 (51·6%)	10·4 (46·8%)	7·0 (43·7%)
724·1 eV	3·5 (20·4%)	4·1 (18·5%)	3·1 (19·5%)
712·9 eV	3·3 (19·4%)	5·0 (22·6%)	4·2 (26·4%)
726·4 eV	1·5 (8·6%)	2·5 (11·3%)	1·7 (11·5%)
Total manganese	3·8	1·3	...
Total copper	...	...	12·3
Cu 2p at 934·7 eV	...	...	5·2
940·9 eV	...	...	1·6
943·9 eV	...	...	1·7
954·6 eV	...	...	2·2
962·7 eV	...	...	1·5

X-ray photoelectron spectroscopy (XPS) analyses were conducted to evaluate the surface composition of the di erent powders (Table 1). Figure 2 shows the survey spectra of as received, H_2SO_4 treated, and copper coated powders. The spectrum of the as received powder shows the presence of iron, oxygen, carbon, and manganese at the surface of the powder. The spectrum of the H_2SO_4 treated powder is similar to the spectrum of the as received powder. However, the spectrum of the copper coated specimen shows the presence of copper at the surface of the powder. It is suspected that copper does not entirely cover the surface of the iron powder since iron peaks are also observed for this specimen. It is interesting to mention that no sulphur was observed at the surface of the H_2SO_4 treated and copper coated powders. This observation indicates that the cleaning procedure was e ective and no residues of the solutions remained on the powder surface after washing.

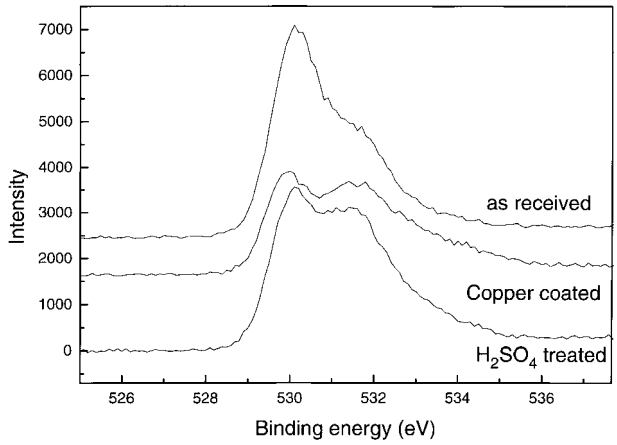
The high resolution spectra of iron (Fig. 3) show that the chemical state of the iron compounds is similar for the three powders. Most of the iron signal comes from the Fe 2p at 710·6 eV (and 724·1 eV), which corresponds to the



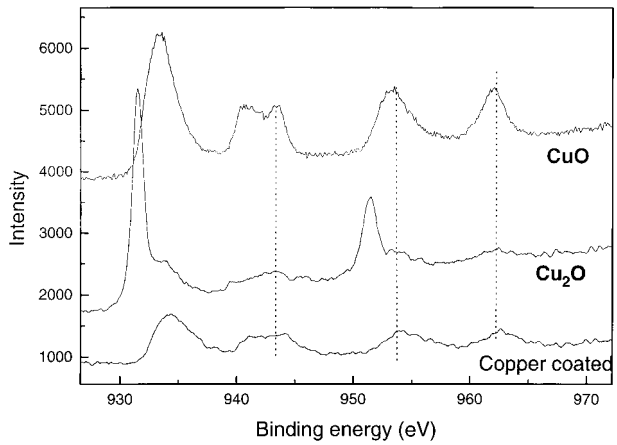
2 XPS survey spectra of as received, H_2SO_4 treated, and 1 wt-%Cu coated powders



3 XPS high resolution spectra of iron on as received, H_2SO_4 treated, and 1 wt-%Cu coated powders



4 XPS high resolution spectra of oxygen on as received, H_2SO_4 treated, and 1 wt-%Cu coated powders



5 XPS high resolution spectra of copper on the surface of copper coated powder and surface of CuO and Cu_2O standards

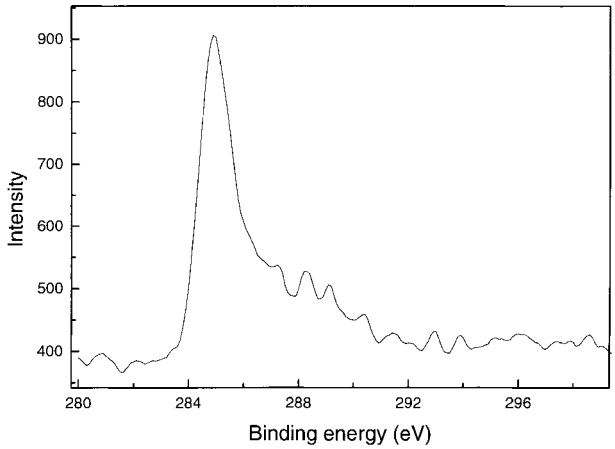
energy of iron atoms in the Fe(III) state.[8] It is not possible to discriminate whether the surface is composed of Fe_2O_3 or $Fe(OH)_3$ using the iron spectrum peak since the Fe(III) state corresponds to both Fe_2O_3 and $Fe(OH)_3$. The iron spectrum suggests, nevertheless, that Fe^0 (706–707 eV), FeO (709 eV), and Fe_3O_4 (708·2 and 710·8 eV) were not present on the surface of the powders.

The peaks at 712·9 and 726·4 eV correspond to Fe(OOH). The O 1s peak at 531·3 eV (Fig. 4) corresponds to atoms involved in hydroxyl bonds while O 1s peak at 530·1 eV corresponds to atoms in Fe_2O_3. The variation of the ratio of iron oxide/hydroxide peak intensity suggests that the relative concentration of iron oxide/hydroxide is a ected by the treatments.

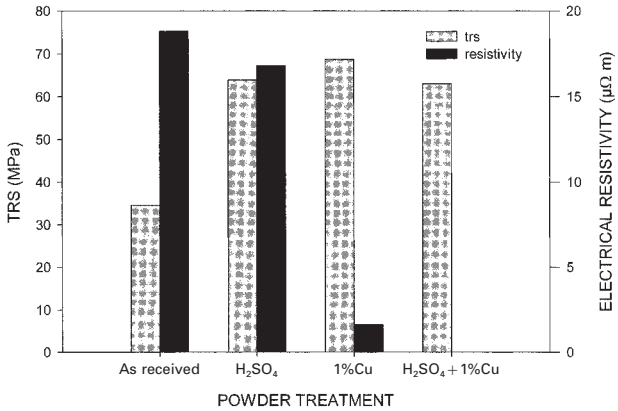
The copper peaks (Fig. 5) show that copper is mostly in the CuO form (933·5 eV). The peaks in the 940–945 eV range are in fact characteristic of CuO (*see* Fig. 5 which displays control spectra of CuO and Cu_2O). However, CuO has little probability of being present at the surface of the powder since this oxide is usually formed at high temperature. The CuO may come from a copper carbonate ($CuCO_3.Cu(OH)_2$ or $2Cu.H_2O.CO_2$), which has a higher probability of being formed when the copper coated powder is exposed to air. Since no carbonate peak (290·3 eV) is observed on the high resolution carbon spectrum taken on the copper coated powder (Fig. 6), it is believed that the carbonate was decomposed when the powder was exposed to high vacuum before the XPS analysis. Additional experiments should however be carried out to confirm that hypothesis.

It is di cult to confirm the presence of Cu^0 (932·7 eV) and Cu_2O (932·5 eV) at the surface of the powder since there is a convolution with the CuO signal. Since the peak at 933·5 eV is quite symmetrical and does not seem to have a bump on the left hand side, it is believed that the amount of both Cu^0 and Cu_2O is low, at least within the first 5 nm at the surface of the powder. As depth profiles were not investigated in this study, for the moment it is not possible to determine if there is some metallic copper beneath the CuO or copper carbonate layer.

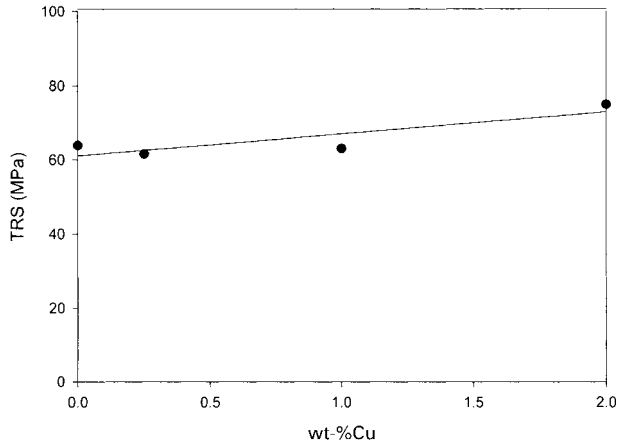
Figure 7 shows the e ect of di erent surface treatments on the green strength and electrical resistivity of bars. Specimens fabricated with the H_2SO_4 treated powder exhibit a much higher green strength compared with the specimens fabricated with the as received powder. The increase of the green strength after the acid treatment must be associated with a modification of the surface of the powder. The e ect of surface composition should not be important since the XPS measurements have shown that the surface composition of the as received and the H_2SO_4 treated powder is similar. In fact, the oxide removed during the acid treatment is rapidly reformed after the treatment, probably after washing or when the powder is exposed to air. This hypothesis is confirmed by the electrical resistivity measurements which show that the resistivity of the specimens fabricated with the H_2SO_4 treated powder is similar to the resistivity of the specimens fabricated with the as received powder (suggesting that the insulative iron oxide layer is present on both type of powder). Accordingly,



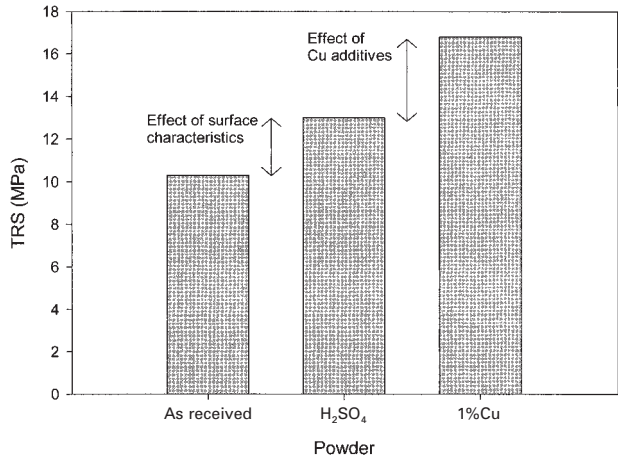
6 XPS high resolution spectra of carbon on 1 wt-%Cu coated powder



7 E ect of di erent surface treatments on green strength and electrical resistivity of compacts fabricated at 620 MPa at 25°C using die wall lubrication: electrical resisistivity of H_2SO_4 was not evaluated



8 E ect of copper content on green strength of compacts fabricated at 620 MPa with copper coated powder at 25°C using die wall lubrication: powder was pretreated with sulphuric acid

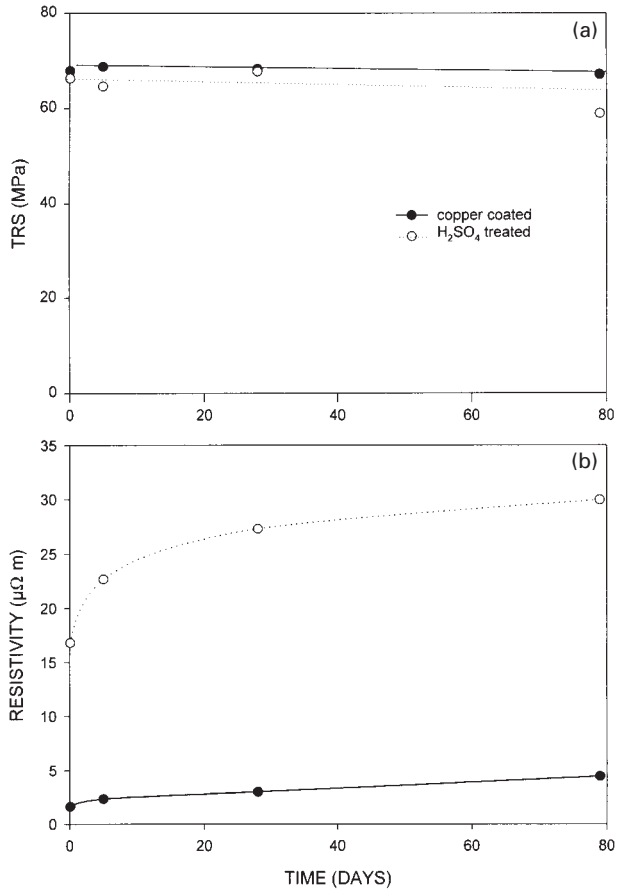


9 Green strength of specimens compacted at 620 MPa at 25°C with powders admixed with 0·6 wt-% graphite and 0·75 wt-% Acrawax C: specimens fabricated with as received powder and H_2SO_4 treated powder were admixed with 1 wt-%Cu additives

the improvement of the green strength with the acid treatment probably did not come from the removal of the oxide but rather from the e ect of the increase of the surface roughness of the powder.

Figure 7 also shows that the green strength of the specimens fabricated with copper coated powder is also significantly higher than the strength of the specimens fabricated with the as received powder and is similar to the strength of specimens fabricated with the H_2SO_4 treated powder. The strength does not seem to be a ected by the sulphuric acid pretreatment carried out before the copper coating procedure. The solution used to coat the iron particles contains sulphuric acid and surface modification occurs with both acid and copper coating solutions. The improvement of the green strength with the copper coated powder may come from the e ect of the surface roughness increase rather than from the presence of copper at the surface of the powders. In fact, the copper content does not strongly a ect the green strength of the specimens as indicated in Fig. 8. These observations are in agreement with the results obtained by Coleman and Foba[5] which showed that the strength was not significantly a ected when the copper content deposited on the surface of iron powder varied from 6 to 14 % (also deposited by the displacement method). The electrical resistivity of the specimens fabricated with the copper coated powder is significantly lower than the resistivity of the specimens fabricated with the as received powder. The di erence may come from the electrical resistivity and thickness of the oxides or carbonate covering the iron powder.

Experiments were carried out to evaluate if the e ect of the powder treatments on the green strength can be seen with specimens fabricated with powder admixed with lubricants and additives. Lubricants are generally admixed with powder for PM press and sinter applications. The lubricant facilitates the compaction and the ejection of the compacts but also reduces significantly the interparticle cold welding and interlocking during compaction.[9] This reduction of the formation of interparticle bonds during compaction explains the relatively low green strength of the specimens fabricated with admixed additives (Fig. 9) compared with the green strength of the specimens fabricated with no admixed additives (Fig. 7). The lower green strength of the specimens fabricated with copper additives may come from two sources: di erence in powder surface roughness between the as received powder and the copper coated powder, and from the negative e ect of the admixed copper additives on the green strength of the material. The di erence in green strength between specimens fabricated with as received and H_2SO_4 treated powder comes from powder surface modification while the di erence between the specimens pressed with H_2SO_4 treated powder



a green strength; *b* electrical resistivity

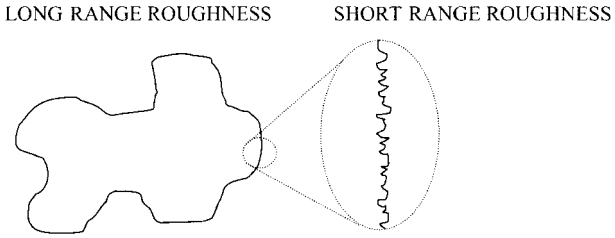
10 E ect of storage period on specimens fabricated using die wall lubrication at 620 MPa at 25°C using H_2SO_4 treated powder and 1 wt-%Cu coated powder

and copper coated powders comes from the presence of copper additives in the specimens fabricated with the H_2SO_4 treated powder. The negative e ect of copper additives on the green strength was observed previously by other researchers.[10]

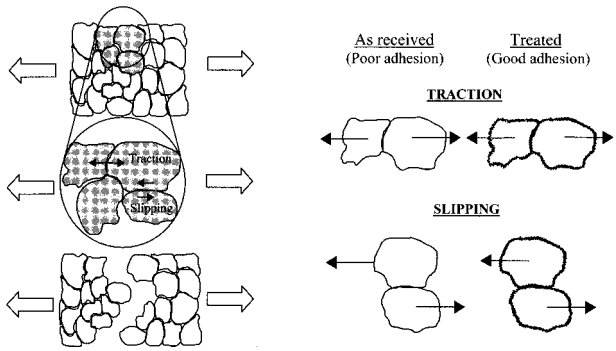
In order to see if the treated powders are stable under atmospheric conditions, specimens were fabricated with H_2SO_4 treated powder and 1 wt-%Cu coated powder and stored in bottles for di erent time periods. The results presented in Fig. 10 show that the green strength of the specimens fabricated with the H_2SO_4 treated and copper coated powder remains stable for at least 80 days. The electrical resistivity increases significantly during the storage period indicating that oxidation took place during that period. It is interesting to note that even if oxidation took place during that period, it did not significantly a ect the green strength of the specimens. This observation confirms the hypothesis that the improvement of the green strength observed after the surface treatments came from the modification of the surface roughness and not from the presence of iron oxide.

DISCUSSION

As described by Klar and Shafer,[4] green strength is influenced by many di erent powder characteristics. Because the green strength of metal powder compacts results mainly from mechanical interlocking, particle shape is the most important factor contributing to green strength. Generally, increasing the powder surface area increases the green strength. This can be achieved by reducing the average particle size and/or increasing the particle surface



11 Schematic diagram of short and long range roughness



12 E ect of particle roughness on particle decohesion during transverse rupture tests

roughness, thus providing more sites for mechanical interlocking.[11]

Roughness can be considered as long and short range. Long range roughness mainly refers to particle shape and irregularity. Short range roughness, however, does not a ect the powder shape and refers to the type of surface roughness modifications observed in this study. A schematic diagram of the two types of surface roughness is presented in Fig. 11. The results obtained in this study suggest that a modification in short range surface roughness strongly a ects the green strength of the powder compacts.

The physicomechanical phenomena involved during the rupture of green powder compacts are complex. Figure 12 is a simplified representation of the interaction of the powder surface during a rupture test. The reality is of course much more complicated and the rupture involves mixed mechanisms. Figure 12 also helps to illustrate the e ect of particle short range roughness on the strength of green powder compacts.

The formation of interparticle contacts plays an important role in compact strengthening when the particles are pulled apart by traction. Surface roughness may influence the strength of the compact if the asperity at the surfaces of adjacent particles interlock. Apart from pure traction, slipping of the powder surface also occurs during rupture tests. The slipping forces are influenced by the formation of interparticle metallic contacts, but also by the surface roughness. In fact, the roughness at the surface of the powders may strongly improve the green strength by increasing the slipping forces during the transverse rupture tests.

Based on the observations in this study, it is believed that the green strength of metallic powder compacts can be significantly increased by modifying short range roughness of the powder surface. Treating the powder with an acid may be one way to do this. Other experiments should however be made to evaluate if other treatments may further increase the surface roughness of the powder.

The modification of the powder surface roughness can be an interesting technique for improving the processability of di cult to shape powders with poor green strength, such

as spherical powders. The benefit of modifying the surface roughness can be observed with powders containing admixed additives. However, the positive e ect of the surface treatments is significantly more important when the powders do not contain admixed lubricant. The use of powder surface modification techniques then becomes an interesting approach to increasing the green strength of PM compacts with the recent developments and commercialisation of die wall lubrication units for PM applications.

CONCLUSIONS

This paper has presented the e ect of di erent iron powder surface modifications on the green strength of compacted specimens and has shown that the green strength of compacts fabricated with H_2SO_4 treated powder and copper coated powder is significantly higher than the strength of specimens fabricated with as received powders. The e ect of the surface modification treatments was observed for mixes with and without admixed additives (lubricant, graphite, and copper powder).

The improvement of the green strength appears to be related to a modification of the surface roughness of the powder. The surface of the treated powder is more irregular than the surface of the as received powder. The surface roughness may influence microinterlocking between adjacent particles and may a ect significantly the green strength of the compacts.

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