

Nanometric Surface Modification of Iron and Steel Powders

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Abstract

Surface modification of iron powders via displacement and electroless (autocatalytic) depositions of copper from aqueous solution were studied in the concentration range of 1-4wt% Cu. It was found that while both methods result in complete Fe particle coverage, displacement depositions present a rougher surface morphology while electroless coatings exhibit a smoother, thin film configuration. This in turn influenced all green and sintered properties of the resulting specimens. The samples obtained from displacement Cu coated powders showed the highest green strength, at the expense however of powder compressibility. The highest Cu containing sample obtained via electroless deposition (E-4% Cu) presented the best mechanical properties: TRS – 1163 MPa; HRB – 87; and the highest sintered density. The dimensional change was 3 times lower than that in specimens prepared with half the amount of admixed Cu.

Introduction

With the ever increasing demand of powder metallurgy products, superior mechanical properties in conjunction with high dimensional accuracy in the final part are always important requirements of the end user and the primary concern of the powder metallurgy (PM) producer. In ferrous PM, additions of alloying elements such as graphite (0.5 - 1%), Cu (1 - 4%) and Ni (1- 4%) are of utmost importance in obtaining high performance materials. The positive influence of alloying elements on mechanical properties is ultimately related to their homogeneous diffusion into the iron matrix during sintering. It is undeniable that in the pre-alloyed powders this is readily achieved but it comes at the expense of powder compressibility and at relatively elevated costs. A more cost effective method is via the admixing route, in which elemental powders are blended together to the required nominal composition. This method presents excellent powder compressibility but introduces different, undesirable, effects such as segregation of added elements, dusting during handling and operation, and finally variations in dimensional change of the components during sintering. Copper is one of the most important alloying elements of ferrous PM. It brings in the net advantage of transient liquid sintering which facilitates a better distribution and diffusion, in addition to a more rounded pore microstructure. It does, however, present a drawback: when copper is introduced as elemental powder, it triggers the permanent expansion of the sintered component also known as “copper swelling”. It has been reported that the expansion increases with Cu content [1] and it becomes excessive above 2.5wt% [2]. There are two operative mechanisms in copper swelling: as liquid Cu appears, it rapidly penetrates between the grain boundaries of the iron particles causing grain separation – penetration mechanism; it thereafter diffuses into iron causing lattice expansion – diffusion mechanism [1]. While both mechanisms are in effect, it has been demonstrated that the former brings the highest contribution to dimensional change [3]. Obviously, Cu is not the only contributor to the dimensional change and it interacts with the added graphite and commonly added nickel powders. Graphite, normally added to the mix as a strengthening agent, also reduces copper growth [4]. Its presence hinders liquid Cu penetration between iron grains by increasing the dihedral angle between the molten copper and iron [5]. When nickel is added to iron PM, it promotes shrinkage as the sintering of Fe-Ni system is governed by solid state mechanism. Owing to this effect Ni is commonly used in Fe-Cu admix to counter balance the Cu swelling effect. However, Ni addition is not straightforwardly accompanied by a proportional shrinkage due to its interaction with copper [5]. Additionally the size and distribution of the Ni powders also play a role on the degree of shrinkage [6].

In order to address the challenges associated with the admixed route, we explored an alternative method to introduce copper as alloying element via surface modification of iron particles. The method entails direct deposition of Cu from aqueous solution and directly alleviates copper dusting. It can also decrease the Cu swelling effect, providing a coherent coating that is achieved and preserved thereafter in the compaction step. Two routes have been examined: displacement deposition and electroless plating. Even though sometimes the name *electroless* is generically used to define both processes in order to highlight the absence of an external power supply, the clear differences between the two methods must be emphasised. Both methods are based on the oxido-reduction concept of metal salts in aqueous solutions. While in the displacement method the electrons necessary for

deposition are supplied by the substrate, electroless plating occurs via the oxidation of a reducing agent added to the solution. The biggest advantage of the displacement method is the simplicity of the bath which contains only the dissolved salt of the metal to be deposited (e.g. CuSO_4). The coating occurs very fast, within minutes, by a replacement reaction between the Cu ions in solution and Fe substrate which dissolves stoichiometrically. The biggest drawback of the process is the limited control over the parameters which in turn influences the amount and characteristics of the deposit. In contrast, the electroless method offers an excellent process control owing to the complexity of the bath. Additions of stabilisers, accelerators, complexing agents, and pH regulators, all contribute to a precise adjustment of reaction rates and by-products which could be fine-tuned to obtain pore-free thin coatings. For instance, ductility promoters such as hexacyanoferrate, 2,2' dipyridyl, added to the bath in very small concentrations as well as complexing agents such EDTA inhibit both void formation and hydrogen incorporation which result in Cu deposits with high ductility (3 to 8% elongation) [7]. A drawback of the method is that the reducing agent, under specific temperature conditions, will liberate electrons only on the surface of the metal to be deposited which entails prior surface activation with catalytically active metals, usually Pd nuclei, in order to initiate the reduction.

Several attempts of Cu coating on iron particles have been reported in the literature. In one study, Cu coating via different methods was performed [8]. The authors examined the properties of the green compacts resulting from coated powders and concluded that electroless specimens (8wt% Cu) did not affect powder compressibility while displacement samples exhibited the highest green strengths. High green strengths for displacement coated samples (1wt% Cu) were also obtained by Lefebvre et al. [9], which accounted for the surface roughness of the powders and particles interlocking effect. More recently [10-12] it has been reported that Fe displacement coated samples of 3wt%, 8wt% and 12wt% Cu show better dimensional stability and improved properties for higher Cu content specimens when compared with their admixed counterparts.

In the light of these findings, we believe that a comparison between the characteristics of Cu coating produced from both methods and their influence on mechanical properties of the resulting compacts both in green and sintered states is needed. Moreover, owing to the lack of information for this application, the electroless method needs to be thoroughly examined. In the present study, coatings without surface activation were attempted and a mechanism is proposed. All depositions via both methods were performed within the traditional industrial range (1-4wt% Cu) and the resulting samples were processed within industrial parameters.

Experimental Methodology

The base powder used in this study was unalloyed water-atomised iron powder ATOMET 1001HP (Rio Tinto Metal Powders) with an average particle size $D_{50} = 75 \mu\text{m}$. Coating experiments were carried out on powder in the "as received" condition with no surface activation, preparation or cleaning. The chemical compositions of displacement and electroless solutions as well as the experimental parameters for a 4wt% Cu content are given in Table 1.

Table 1 Chemical compositions and experimental parameters for electroless and displacement coatings

Electroless (E)			Displacement (D)					
Bath Chemistry			Parameters		Bath Chemistry		Parameters	
Metal Salt	Copper sulfate, pentahydrate	8 g/l	pH	12.08	Copper sulfate, pentahydrate	8 g/l	pH	3.95
Reducing Agent	Formaldehyde, 37% solution	7 m/l	T (°C)	70			T (°C)	r. t.
Complexing Agent	EDTA, disodium salt	32 g/l	time (min)	25			time (min)	5
Stabilizer	2,2'-Dipyridyl	20 mg/l	RPM	300			RPM	300
Accelerator	Potassium hexacyanoferrate	60 mg/l	Fe (g/l)	50			Fe (g/l)	50
pH Regulator	Sodium hydroxide		Cu (wt %)	3.98			Cu (wt %)	4.29

Subsequent dilutions of the parent baths were performed thereafter. The Cu contents were determined via ICP-AES. The deviations from the targeted compositions were ± 0.3 and ± 0.1 wt% Cu for displacement and electroless, respectively. The coatings were analysed via SEM, EDS, XRD and optical microscopy. For comparison purposes, a reference sample with no added-Cu was prepared as well as two premixes containing 2% Cu; one with a fine (F) Cu grade ($D_{50} = 12 \mu\text{m}$) and the other with a regular (R) Cu grade ($D_{50} = 54 \mu\text{m}$). All samples: coated, admixed and reference were thereafter blended with 0.75% EBS wax and 0.6% synthetic graphite. Specimen denomination and Cu contents are shown in Table 2. The samples were compacted to a target green density of 7.00 g/cm^3 into standard test bars and sintered at 1120°C for 25 min. in a $90:10\text{N}_2:\text{H}_2$ atmosphere. Hardness and TRS

testing were performed in accordance with MPIF Standard 43 and 41, respectively. Optical microscopy was used for porosity evaluation in as-polished condition and to observe the microstructure of 3% Nital etched specimens. SEM was employed for fracture surface examinations.

Table 2 Preparation method and Cu content of tested specimens

Electroless (E)		Displacement (D)		Reference and Admixes (M)	
Sample	Cu (wt %)	Sample	Cu (wt %)	Sample	Cu (wt %)
E-1%Cu	1.11	D-1%Cu	0.88	Fe - Blank	-
E-2%Cu	2.04	D-2%Cu	1.70	M-2%Cu (F)	2.00
E-2.5%Cu	2.59	D-4%Cu	4.29	M-2%Cu (R)	2.00
E-4%Cu	3.98				

Results and Discussion

Coating Evaluation

The exterior appearance of copper coated iron particles (4wt% Cu) via displacement and electroless methods are shown in Figures 1a and 1b respectively; their corresponding cross-sections are depicted in Figures 1c and 1d. As observed in the images, a coherent Cu coating was obtained via both methods. However, there are clear differences in the morphology and characteristics of the two coatings.

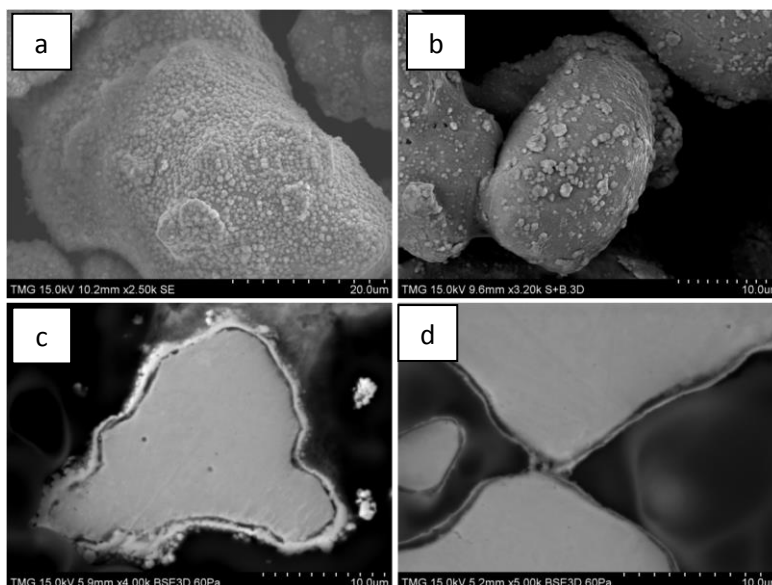


Figure 1 Iron particles 4wt% Cu coated : (a) displacement and (b) electroless; (c) displacement Cu coated particle cross-section; (d) electroless Cu coated particle cross-section

The exterior surface of the coating obtained via displacement method shows a “spongy” particulate-type morphology, whereas electroless depositions present a more rounded “island”-type characteristic. As a result of the rougher morphology, the thickness of the displacement coatings as measured by SEM appeared to be double (439 ± 84 nm), those of the electroless film (205 ± 32 nm) for the same amount of copper deposited. The differences between the two coatings reside in the disparity of the deposition mechanisms of the two methods. As observed in Table 1, the time required for electroless plating is 25 min., in a strongly alkaline bath (pH 12.08), whereas displacement deposition occurs in 5 min. in an extremely acidic solution (pH 3.95). The difference in the reaction rates of the two processes influences the resulting deposit. For instance displacement deposition takes place as a replacement between $\text{Cu}^{2+}_{(\text{aq})}$ ions in solution and $\text{Fe}_{(\text{s})}$ substrate. The red-ox potential between the two species is large and the exchange of charges will occur fast. As a result, the freshly generated Cu particles will rapidly agglomerate stochastically on the substrate creating a porous structure. Moreover, at high reaction rates, favoured by the low pH, hydrogen evolution occurs fast and is easily absorbed in the coating. All these factors render a porous coating structure and a rough appearance, which in turn influences the physical properties of the deposit. Moreover, the formation of defects due to precipitation of absorbed atomic hydrogen alters the ductility of the coating [13]. It has been reported

that displacement Cu has a high specific area $1\text{m}^2/\text{g}$ [14] reaching up to 30% porosity with nearly no ductility at this porosity level [15]. In contrast, electroless deposition proceeds with no substrate sacrifice but rather by oxidation of the reducing agent. This imposes high pH levels in the bath which considerably decreases the speed of the reaction and allows the freshly precipitated Cu particles to arrange on the substrate in a more orderly fashion. As the deposition proceeds, the island structure observed in Figure 1b merges to form a continuous film until complete coverage of the substrate. Thereafter, new islands nucleate and grow on top of the already deposited Cu layer. This “building block” mechanism reduces the porosity and roughness of the layer. Additionally, some ductility promoting additives such as 2,2' – dipyridyl and EDTA added in the bath, inhibited both the inclusion of hydrogen and the voids formation [7]. It has been reported that ductility of copper electrolessly deposited in the presence of these additives could range from 3 to 11% [17]. It is based on fine tuning of experimental parameters that electroless Cu coating presents a continuous thin film appearance (Fig. 1d) contrasting with the roughness of the displacement coating (Fig. 1c). In the present study the electroless Cu depositions were obtained on a non-activated substrate surface. The operating mechanism could be regarded as two consecutive steps. In the first step, the reduction of Cu^{2+} is initiated by galvanic displacement with the substrate until the newly formed Cu nuclei trigger the oxidation of the reducing agent. In the second step the deposition proceeds autocatalytically by oxidation of the reducing agent.

The impurity levels of the two coatings were examined via EDS analysis. The only impurity detected was oxygen. While electroless depositions showed an average of 1.25wt% oxygen, a high percentage averaging 5.9wt% was observed in the displacement coatings. Although not detected in the XRD scans, it is believed that the high levels of oxygen are related with Cu_2O formation. It has been reported that Cu can corrode at extreme pH with hydrogen evolution [18]. According to Pourbaix diagram at pH 3.95 at which displacement reaction took place, Cu is stable up until a cell potential of 0.34 V. Higher oxidation potentials triggered by the existence in the solution of various other species such as, for example, water saturated with air or oxygen, will move the system closer to the oxidation of Cu to cuprous oxide Cu_2O . At high pH of 12.08, at which electroless depositions occurred, Pourbaix diagram indicates that $\text{Cu}(\text{OH})_2$ could precipitate. However, this is prevented by the existence in the bath of complexing agents such as EDTA and therefore a higher purity Cu deposit is obtained.

Green and Sintered Properties of the Tested Materials

The properties of the specimens resulting from the as-coated powders, the two premixes and the reference sample are presented in Table 3.

Table 3 Green and sintered properties of the materials pressed to $7.00\text{g}/\text{cm}^3$

Sample	Green Strength (MPa)	Compacting Pressure (MPa)	Spring-back (%)	Sintered Density (g/cm^3)	Dimensional Change Green (%)	Dimensional Change Die (%)	TRS (MPa)	Apparent Hardness (HRB)
D-1%Cu	21.1	827*	0.19	6.87	-0.27	-0.08	472	47
D-2%Cu	22.8	827*	0.21	6.85	-0.23	-0.02	559	61
D-4%Cu	22.3	818	0.17	6.93	+0.15	+0.32	826	83
E-1%Cu	12.1	514	0.16	6.98	-0.04	+0.13	844	70
E-2%Cu	13.0	512	0.17	6.97	+0.05	+0.22	995	81
E-2.5%Cu	-	491	0.09	6.96	+0.11	+0.20	1071	83
E-4%Cu	-	503	0.13	6.99	+0.08	+0.21	1163	87
Fe -Blank	9.8	490	0.10	6.97	+0.03	+0.13	651	55
M-2%Cu (F)	10.0	481	0.09	6.89	+0.32	+0.41	943	78
M-2%Cu (R)	10.3	478	0.08	6.90	+0.23	+0.31	1002	80

*Maximum pressure allowed by the equipment. The requested density of $7.00\text{g}/\text{cm}^3$ was not reached by these samples.

The weight loss of the compacts resulting from displacement coated powders (D) is almost double than of all other samples. As the sintering process takes place in N_2/H_2 atmosphere, Cu_2O will be reduced in the presence of H_2 at temperatures above 250°C back to Cu with elimination of water (weight loss). These findings confirm Cu oxidation occurring in the displacement bath. Sample oxidation was also reported by Strobl et al. [12] in specimens obtained via a similar method. In contrast, electroless samples (E) show a weight loss in range of admixed (M) specimens and reference material. Despite a high compacting pressure, D specimens could not reach the $7.0\text{g}/\text{cm}^3$ targeted density. Two factors are believed to contribute to this effect: the inherent porosity of the coating which reduces the ductility of the deposit, as previously explained, and the powder oxidation occurring in the bath. In contrast, the E specimens required much lower compacting pressures, in the same range as pure iron and the premixes. This is attributed to the purity and high ductility of the

coating associated with the electroless process. Doubling in the green strength was observed for displacement specimens as compared to admixes and reference materials, the interlocking mechanism proposed by Lefebvre et al. [3] due to surface roughness of the powders to be in effect. Additionally, it is believed the high compacting pressure applied in an attempt to reach 7.0 g/cm^3 density is promoting the interlocking and/or powder to powder contact increasing green strength. The specimens obtained via the electroless method presented a much lower green strength than the displacement samples, which is related to the smoothness of the coating. Nevertheless these values were higher than those of the premixes (M) and iron (Fe – Blank). For the same nominal 2wt% Cu, the admixed specimens exhibited green strength of $\approx 10 \text{ MPa}$ whereas the electroless sample (E – 2% Cu) a value of 13 MPa , which represents a 30% increase in green strength.

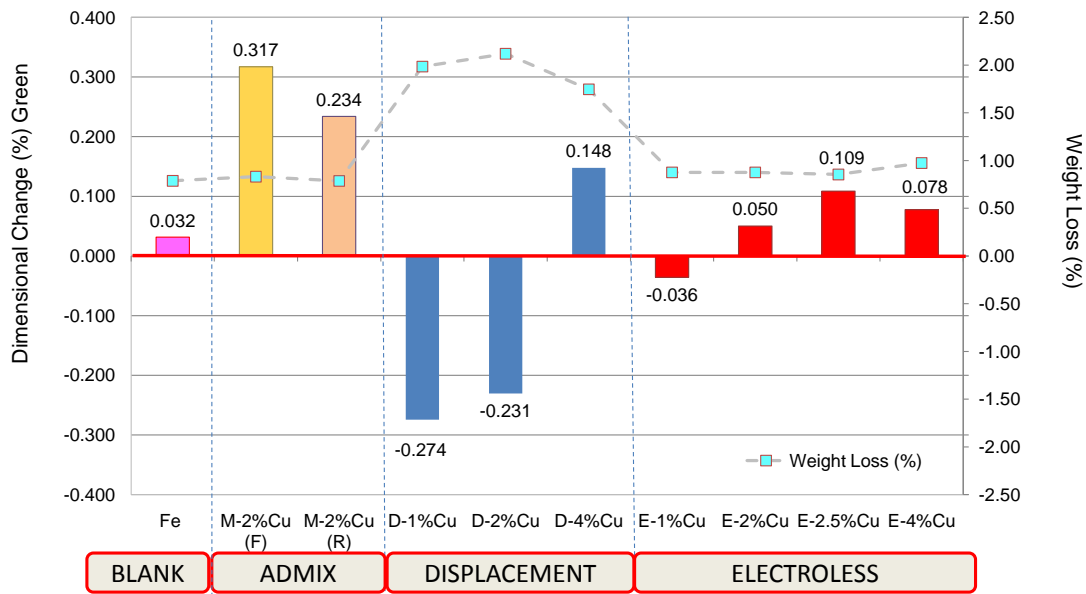


Figure 2 Dimensional change from green size and weight loss for all samples after sintering

The dimensional change from green size for all samples and its associated weight loss are shown in Figure 2. The highest expansion is exhibited by the admixed specimens and is more pronounced in the sample where fine Cu particles were used. This is associated with the existence of free Cu in these specimens. During sintering, Cu melts at 1085°C and rapidly penetrates between the grain boundaries of the iron particles causing grain separation and permanent expansion of the compacts. For Cu coated specimens, the iron particles are already separated by a layer of copper provided the integrity of the coating was preserved in the compacting step and hence a smaller dimensional change is expected. In displacement coated samples, due to the excessive weight loss observed as a result of Cu_2O reduction, the dimensional change could not be directly correlated with the coating effect. However, for electroless coated powders, which presented similar weight losses as the reference or admixes, reduced expansion is clearly observed. For the electroless 2% Cu sample, the dimensional change is similar to that of the reference material (Fe – Blank), that is approximately six times smaller than for the premixes. Similarly, the highest Cu coated sample (E-4% Cu) shows a fourfold decrease in growth compared to the premixes. As reported in Table 3, the electroless samples exhibit very decent mechanical properties. The highest TRS and hardness values at 1163 MPa and 87 HRB , respectively, were obtained for the E-4% Cu sample.

Figure 3 presents the pore structure, microstructure and fractured surface characteristic of electroless coated samples. The microstructure of E-4%Cu on Figure 3a shows the typical remnant porosity comparable to sintered admixed Cu samples.

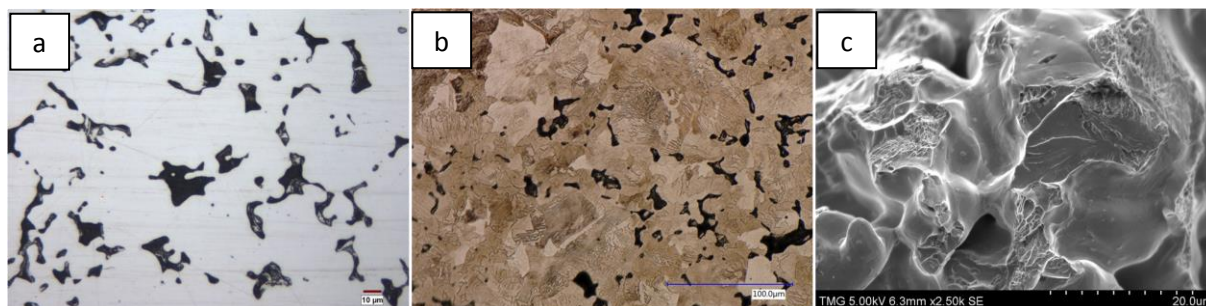


Figure 3 E-4%Cu sample: (a) pore structure; (b) microstructure; (c) and fracture surface

The microstructure shown in Figure 3b depicts homogeneous diffusion of C in the iron matrix. The micrograph shows primarily pearlite with very limited amount of primary ferrite while the fracture surface is a combination of ductile rupture and brittle modes.

Conclusions

Copper coatings ranging between 1 and 4 wt% were successfully deposited on iron particles via displacement and electroless methods. Electroless Cu coatings were performed without any surface activation of the iron particles. The deviations from the targeted compositions were ± 0.3 wt% for displacement and ± 0.1 wt% for electroless. The coating morphology obtained via the displacement method showed increased roughness and a greater variation in thickness whereas the electroless coating presented thin film characteristics and limited thickness variation. It is believed that in displacement coatings the detriment properties is related to the difference in morphology and quality of the deposited Cu. The highest green strength was shown by the displacement coated samples as a result of increased surface roughness and interlocking mechanism which was favoured by the high compacting pressure. However, as the displacement coating significantly decreased compressibility, even with high compacting pressures the targeted density of 7.00 g/cm^3 was not attained. On the other hand, for similar compacting pressure and density, compacts obtained from Cu coated powders via electroless (E) method showed a 30% increase in green strength compared with admixes.

As with admixes, coating powders with increasing Cu amounts improve the mechanical properties. The highest Cu containing sample via electroless (E-4% Cu) presented therefore the highest mechanical properties: 1163 MPa in TRS and 87 HRB in apparent hardness. Additionally, the growth during sintering was greatly reduced for electroless coated samples. For instance, dimensional change was + 0.05% for E- 2 %Cu (nearly the same as pure iron +0.032%) while the regular copper admix attained 0.234%Cu(R), increasing green strength by ~30% and without compromising mechanical properties.

While electroless coating should not be regarded as a replacement route for the admixing method, it certainly represents an avenue worth exploring if one wants to preserve mechanical properties while increasing green strength and improve dimensional precision.

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