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INVESTIGATION OF SILVER METAL CLAYS USING SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE SPECTROSCOPY

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Abstract

Precious metal clay is a popular material with jewellery makers. Its plasticity permits the creation of intricate designs practically indistinguishable from pieces produced by ordinary metalsmithing techniques. Metal clays may not have entered museum collections yet but will inevitably do so as single or composite objects – but should they be conserved like ordinary metal objects? This study examines the morphology and inorganic composition of two brands of silver metal clay using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). Fired silver clay tablets were also submitted to Oddy testing in an attempt to determine the corrosive effect of any remaining organic binder. The results confirm that both brands of metal clay are composed of silver and they can be displayed and stored alongside other metal objects. However conservation treatments must be designed to take into account their porosity.

Keywords*: Silver; Metal clay; Powder metallurgy; Oddy test; SEM-EDS.*

Introduction

The production of materials from powdered metal without passing through a molten state is known as Powder Metallurgy (PM). In PM, ground metals are mixed with a lubricant and transformed into a *compact* which can be moulded. Heating the *compact* causes the metal particles to fuse in a process called *sintering.* Because the sintering temperature is below the metal's melting point the particles are joined together by a process known as *atomic diffusion in solid state* - although in the case of alloys, this may involve a liquid phase [1].

One of the manufacturing methods in PM is Metal Injection Moulding (MIM). MIM was developed in the 1970s, permitting for the first time the production of intricate metal pieces out of powdered metals [2]. The process combines very small metal particles (of between 1-10μm) with a binder, resulting in a plasticized feedstock that is then injected into moulds [2]. The production of objects using metal clays can be interpreted as a simple version of MIM.

Silver metal clay was developed in the 1990's in Japan by Mitsubishi Materials as Precious Metal Clay (PMC™) followed by a version from Aida Chemical Industries under the name of Art Clay Silver™ [3]. Gold, bronze and more recently silver/bronze metal clays have been developed by both companies. There are various types of silver metal clays on the market.

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Whilst essentially the same product (i.e. silver, organic binder and water) their firing temperature and shrinkage rates vary.

Metal clay objects are produced using moulds or shaped freehand. Shaped pieces are allowed to dry then fired in an electric kiln - a gas hob or a butane torch can also be used [3, 4]. As metal particles sinter the object shrinks. Fired metal clay objects have a matt-white colour as its irregular surface traps light instead of reflecting it [3]. In order to display a metallic shine, the surface of fired metal clay must be smoothed out with abrasives and polishing material. Figure 1 illustrates the manufacture of one of the pieces from Sima Vaziry's 2012 Hajj Collection, commissioned by the British Museum (BM).

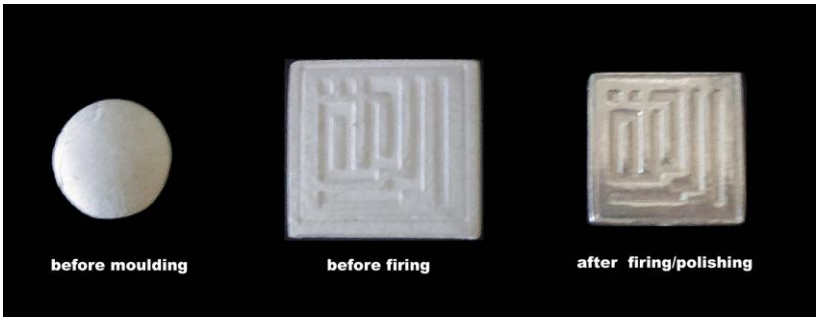

Fig. 1. Creating a metal clay piece

Users of metal clays have developed their own techniques and tools for manipulating the material and reducing shrinkage. For instance Mrs. Vaziry uses graphic design techniques to ensure reproducibility of features – a particular concern given that her BM pieces are produced in large numbers [5]. Although these objects are produced using metal clays the description of the pieces featured on the BM's website does not mention it specifically [6]. In Mrs. Vaziry experience the main reason for the omission is that objects made of metal clay are composed of pure metal once fired and are thus hallmarked accordingly [5, 7]. Another reason for the omission may be that precious metal clay is commonly associated with handcrafts, not designer jewellery [5]. But do objects produced from metal clay share the same characteristics as those produced by conventional methods? Should they be subjected to the same conservation interventions?

Experimental

The aim of this experimental procedure is to look at the physical and chemical changes undergone by two brands of silver clay during three distinct stages in the production of a metal clay piece: moulded or unfired, fired and polished.

The clays analysed in this study are Art Clay™ 650 and PCM™3. These clays were selected because of their low firing conditions.

Preparation of metal clay tablets for analysis

Below is a detailed description of how the two brands of silver clay were prepared in each of the stages prior to SEM-EDS analysis.

Moulding

Each metal clay brand was rolled out on a plastic mat and cut into three small tablets (50x50x3mm) using a scalpel. Tools and work surfaces (including hands) were coated in olive oil to prevent the clay sticking to them [4]. All tools and surfaces were washed with soapy water between metal clays to avoid cross contamination. The tablets were allowed to dry away from direct sunlight for two days (one day on each side to allow uniform drying). The outline of each

tablet was traced on paper as a way to verify shrinkage after firing. These tablets are henceforth referred to as *unfired tablets*.

Firing

The unfired tablets were supported by ceramic tiles and fired in an electric kiln. The Art Clay™ 650 tablets were fired at 650^{o}C for 30 minutes and the PCM™3 tablets at 700^{o}C for 10 minutes, being the lowest recommended settings for each clay. The tablets were placed in the middle of the kiln to ensure an even heat distribution. The increase in the kilns' temperature was gradual so that any remaining water could turn into steam and escape the tablets without causing damage [3]. The kilns were switched off once the firing time had elapsed and the tablets taken out after 30 minutes and allowed to cool in open air. These tablets are henceforth referred to as *fired tablets*.

Polishing

Each set of fired tablets was polished with Highflex® sponge sanding pads of 180, 220 and 280 grits - one grade per tablet. To standardize the procedure each tablet was polished 100 times in one direction only to facilitate the comparison between the different abrasives. Care was taken to maintain the same level of pressure on all tablets. Two sets of sponges were used - one for PCM™3 and another for Art Clay™ 650 and the polished tablets stored in different containers to avoid cross contamination. These tablets are henceforth referred to as *polished tablets*.

SEM-EDS Analysis

Unfired, fired and polished tablets were analysed by JEOL Superprobe JXA – 8600 operating at an accelerating voltage of 20kV with a beam current of 0.5nA. High magnification images were obtained by JEOL JMS-6301F Scanning Microscope operating at 10kV with a beam current of 0.5nA. Low beam energies reduce the electron penetration into the specimen thus increasing the emission from the surface, resulting in images with improved definition [8]. A low beam current was adopted to minimize beam-induced damage which could cause material loss of organic components during analysis [9]. This loss would hinder the identification of the binder which is an organic compound. A number of surface areas in each tablet were imaged so that the images reproduced in this article are typical of the images taken during analysis. Images and spectra were manipulated using INCA™ software.

The tablets were analyzed without further sample preparation. Carbon coating the samples was not necessary given their natural electrical conductivity. Polishing the samples further - normally a requirement for achieving high definition images - was deemed problematic due to the material's porosity and softness [9]. The tablets were analyzed perpendicularly to the electron beam, with images created using the secondary electrons (SE) mode. This mode was chosen because it yields the clearest surface topographical imaging amongst all scanning techniques [8]. Backscattered electrons (BSE) mode, widely used for metals and alloys analysis was also considered [8]. In BSE mode, image contrast is a result of differences in atomic number, albeit elements with atomic numbers lower than sodium cannot be detected. Thus the image produced can be interpreted as a distribution map of the components within a sample. Unfortunately trial runs on the tablets using the BSE mode did not yield new information on their composition.

Qualitative compositional analysis of the metal clay tablets was carried out using an EDS x-ray emission detector. EDS x-ray is good for detecting constituents of a sample but only if these are present in high concentrations. Elements present in small quantities may not be detected as the resolution of the SEM-EDS equipment is around 0.5%. Nonetheless SEM-EDS is a versatile, simple and inexpensive analytical technique widely available in material science laboratories [9].

Oddy test

Oddy Testing a material helps to identify if the material could cause harm to metal objects. The material is placed in a test tube also containing a pure metal coupon (silver, lead

and copper are used) and submitted to high humidity and high temperature conditions over a period of time. The test is positive if the metal coupon changes appearance in comparison with a control. The fired silver clay tablets were tested using the "3 in 1" method, as proposed by *Robinet & Thickett* [10]. This method was chosen because it saves time as all three metal coupons are placed in the same test tube.

Results & Discussion

Surface imaging

In this section the morphology of the unfired, fired and polished tablets are investigated using SEM. The images of the unfired tablets are shown in Figure 2. Both clays are composed of spherical powdered metallic silver in sizes varying between 1.8µm-11µm. Art Clay™ 650 appears to have a marginally higher proportion of smaller particles than PCM™3 in all images analysed.

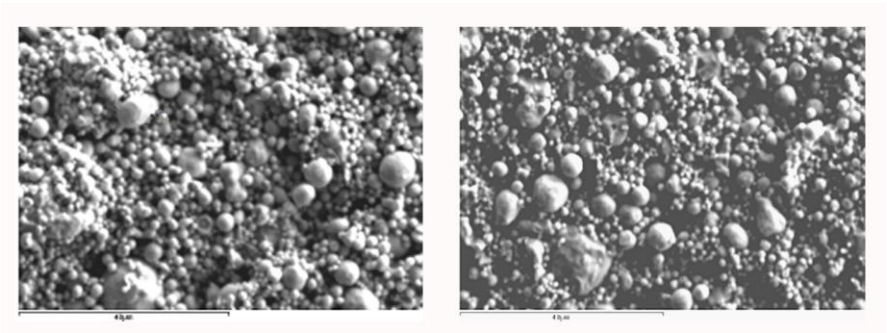

Fig. 2. Unfired Art Clay™ 650 (left) and Unfired PCM™3 (right)

Particle size is a crucial factor of MIM. Small spherical particles tend to facilitate the sintering process because they have greater potential energy across their curved surface than larger particles [1, 2]. During sintering, "necks" form between the particles at the point of contact. Neck growth is a result of grain boundary diffusion and surface diffusion in silver powders sintered in air [11]. The "necks" progressively thicken, leading to a reduction in porosity [12]. Eventually the rounded outlines of the particles disappear as re-crystallization and grain growth takes place [1].

The fired Art Clay™ 650 and PCM™3 are shown in Figure 3. In these pictures, the characteristic face-centred cubic crystalline structure of pure silver is recognizable, particularly for Art Clay™ 650.

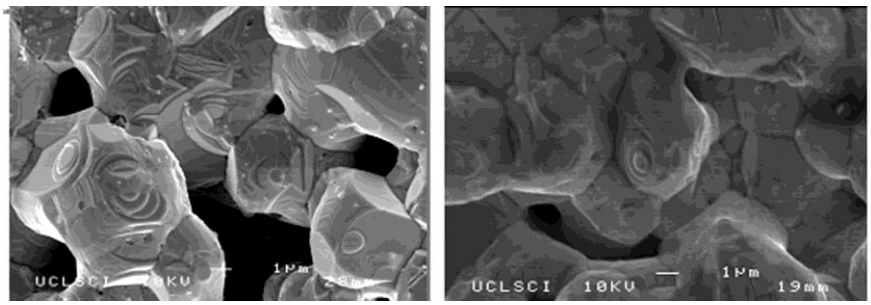

Fig. 3. Fired Art Clay™ 650 (left) and Fired PCM™3 (right)

Art Clay™ 650 appears to be more porous than PCM™3. All three Art Clay™ 650 unfired tablets shrunk by 11% in one direction and all three unfired PCM™3 tablets shrunk by 10% in all directions. These shrinkage rates are close to the manufacturer's rates for each brand of clay (8-10% and 10-15% respectively).

Dimensional changes occur in all stages of sintering, often leading to shrinkage and densification of the material [13]. However entrapped gases, water vapour and binder's decomposition products may inhibit densification and even promote growth during sintering [2]. Any one or a combination of these factors could explain why experimental shrinkage rates for both clays differ from the manufacturers' rates.

The image of the fired Art Clay™ 650 at higher magnification exemplifies how the atoms of silver move along the crystal boundaries, flowing into the pores. The image of the fired PCM™3 may represent the stage where most pores have been filled. Mrs. Vaziry explained that to achieve a high density all metal clays should be fired at 900^{o}C for 2 hours [5]. This temperature is very close to the melting point of Sterling silver at 920^{o}C. Therefore it could be argued that Art Clay™ 650 is more porous than PCM™3 because it was fired at a lower temperature. On the other hand the Art Clay™ 650 tablets were fired for longer than the PCM™3 ones thus perhaps compensating for the 50^{o}C difference in firing temperatures.

The influence of temperature and firing time in the density of Art Clay™ 650 and PCM™3 has been studied by *McCreight & Burks* [14]. The researchers identified that Art Clay™ 650 remains comparatively less dense than PCM™3 regardless of the firing temperature. Although they emphasize that the performance of any metal clay is a function of firing temperature and time i.e. if firing at lower temperatures the time must be extended [14].

Although small particles tend to facilitate sintering the porosity of the fired metal clays must also relate to the size and distribution of metal particles within the unfired clay. A mixture of particles sizes facilitates powder compaction as small particles fall into the gaps between the larger particles during sintering thus explaining the apparent higher density of PCM™3 over Art Clay™ 650. A porosity test would be required to confirm this hypothesis.

Another factor that influences the physical properties of metal clays is the composition of the binder. Binders used in MIM must adhere mainly to two requirements. Firstly, the binder and the powder metal must form a homogeneous mass. Secondly, the binder must be removable from the piece without causing damage or deformation [15]. Unsurprisingly the chemical composition of the binders used in PM is often an industrial secret [2]. The same applies to precious metal clays. Identification of the metal clays' organic binders was not included in this study because the binder is supposed to decompose completely during firing. However any partially decomposed binder can be a cause of concern if it promotes metal tarnishing/corrosion – thus justifying the inclusion of Oddy testing the fired tablets as part of this study.

The apparent higher porosity of Art Clay™ 650 has important implications. PM materials are known to be less resistant to corrosion than wrought pieces [16]. Their porous nature means that there is more surface area exposed to attack by corrosive agents. Moreover the pores' morphology must also be considered as, depending on the environment, certain shapes may promote pit corrosion [16]. Given these considerations, it is likely that Art Clay™ 650 is more susceptible to corrosion than PCM™3. However this can only be confirmed by submitting both clays to porosity and corrosion tests. Undertaking porosity analysis of the metal clays could predict the way they corrode, providing information for the design and evaluation of specific corrosion tests [17].

Subjecting PM objects to simple treatments such as oil immersion and mechanical plating can confer them corrosion resistance [17]. More complex treatments like plasma

nitriding modify the surface porosity of the piece by sealing it with a nitride layer [16]. German & Campbell found that PM bronze art pieces become as corrosion resistant as their wrought counterparts once a corrosion layer is formed [19]. This layer fills the pores on the surface of the piece thus decreasing the surface available to corrosion attack. Polishing was also found to be effective against corrosion as it makes the surface of the objects less porous [19]. By analogy it is possible that polishing the fired metal clays may make them more resistant to corrosion.

The changes to the surface of metal clay caused by polishing are shown in Figure 4 – the unpolished portion on the left and the polished one on the right. The image was taken from the edge of the metal clay tablet, hence the difference in depth between the surfaces.

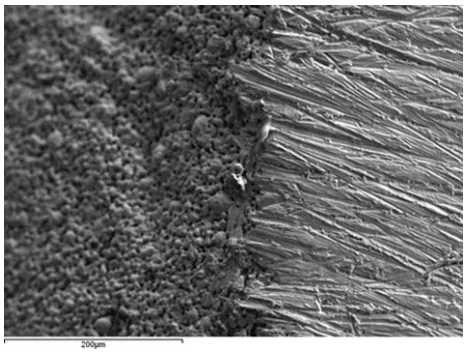

Fig. 4. Fired Art Clay™ 650 during polishing

Polishing moves the metal particles around the surface of the metal clay, filling its pores. It also scratches the surface of the material, the size of which depends on the type/size of grit of the abrasive material.

Figure 5 shows both metal clays after polishing with Highflex™ 220. Art Clay™ 650 appears to have acquired the smoothest surface out of the two brands of clay. Possibly its higher porosity facilitates polishing as there is less silver in contact with the abrasive. The apparent deeper grooves in PCM™3 may be the result of extra pressure applied during polishing, which cannot be quantified in the absence of a control. Although a thorough assessment of the effects of polishing on metal clays could only be achieved using profilometry or confocal microscopy.

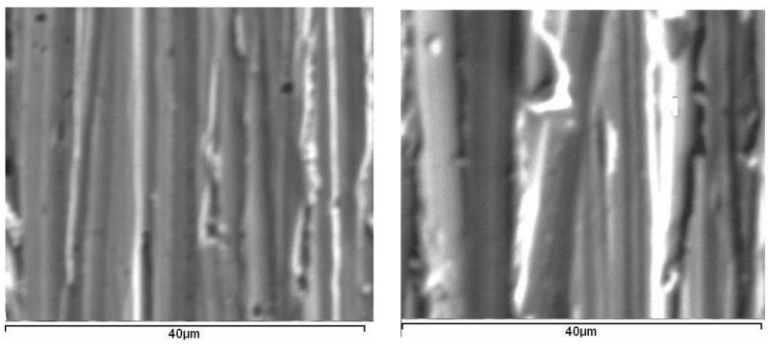

Fig. 5. Polished Art Clay™ 650 (left) and polished PCM™3 (right)

Compositional analysis

The EDS analysis confirmed the presence of large quantities of silver and small quantities of carbon in both unfired and fired tablets. The presence of carbon can be assigned to the organic binder. As expected, the amount of carbon in the fired tablets is lower than in unfired tablets – an indication of the binder's partial decomposition. Another possibility is that some traces of carbon will always remain in metal clays given their porosity. Moreover the firing conditions adopted may have hindered the de-binding process as the tablets were not fired in an upright position.

Magnesium (Mg) and Oxygen (O) were identified only in the fired Art Clay ™650 (Fig. 6). The inclusion of magnesium in the metal clay formula could be justified on at least two grounds. The first relates to magnesium's hardness. Pure silver is very weak so silverware is made out of alloys which are stronger. The presence of magnesium in the clay would play the same role as copper in sterling silver. Another possibility could be related to magnesium's high flammability. Under this scenario the magnesium would act as a catalyst to the thermal decomposition of the binder during firing. In fact the bright light flashes that occur during torch firing of the metal clay pieces look characteristic of magnesium [20]. The resulting magnesium oxide would then explain the presence of the O peak. Further analysis of both clays perhaps using an alternative analytical technique such as X-ray fluorescence is required to ascertain their elemental composition.

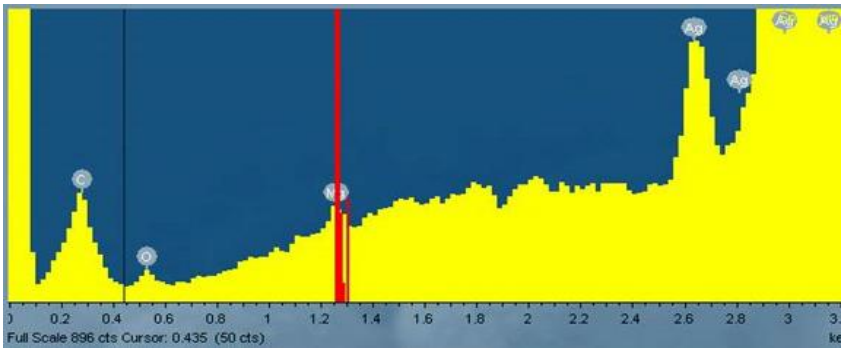

Fig. 6 – Spectrum of fired Art Clay™ 650 with magnesium peaks (marked in RED)

When analyzing the polished samples aluminum and silica peaks appeared in the spectrum. Their presence could be linked to the abrasive. Table 1 lists the grain types for each abrasive sponge. The aluminum and silica peaks appeared only in certain polished clay tablets, those that corresponded to the type of sponge used for polishing that tablet. Consequently these peaks must relate to a grain of grit embedded in the silver clay tablet. The EDS analyses therefore confirm that both brands of metal clay are mainly composed of silver confirming the manufacturers' product description.

Table 1. Grain type of abrasive sponges used for polishing the silver metal clay tablets

Abrasive sponge	Grain type
Highflex™ 180	Al/Oxide
Highflex™ 220	Al/Oxide
Highflex™ 280	Si/Oxide

Source: http://www.abrapower.co.uk/highflex.htm

Oddy test

Both silver clays tested negative as none of the metal coupons tarnished. This result points to the total combustion of the organic binder during firing and/or that any remaining binder does not contain corrosive agents. However as the clay tablets were removed from the test tubes they felt slightly wet to the touch, indicating water absorption.

To ascertain the degree of water absorption the clay tablets were weighed on an electronic scale then heated for 10 minutes on a hot plate and weighed again. The Art Clay™650 tablets showed a 2% weight loss while the weight of the PCM™3 remained unchanged. Because the tablets are roughly the same size the experiment demonstrated that Art Clay™650 absorbed more water than PCM™3, another indication of its higher porosity inferred from the SEM images. If this is the case, it is likely that the clays behave in different ways in spite of having similar chemical compositions. Art Clay™650 being more porous would be less resistant to shock and more prone to corrosion than PCM™3.

Conclusion

This study presented SEM images and EDS analysis of two brands of silver metal clays – Art Clay™650 and PCM™3. Results have shown that both silver clays remain porous after firing, with Art Clay™650 appearing to be slightly more porous than PCM™3. Moreover the results appear to indicate that the two brands of silver clay have different chemical compositions although this must be verified by other analytical methods.

The porosity of metal clays facilitates the embedment of abrasive material during polishing which may develop into galvanic corrosion if the material contains metals. Porosity also poses challenges to tarnish removal as the process removes material from the object [21]. Consequently successive removal of tarnish from metal clay objects could yield a matt finish as the porous core underneath is revealed.

In order to decrease the frequency of tarnish removal museums such as the V&A in London have adopted the practice of lacquering silver objects [22]. Lacquering also have drawbacks. Its effectiveness relies on the chemical stability of the lacquer as well as its even application [21, 23]. As the surface of silver clay pieces remains uneven still after polishing extra care must be taken when lacquering these objects.

This study demonstrated that metal clay objects pose a challenge to conservators given their porosity and uneven polished surface. Existing treatments for metal objects will need to be adapted and perhaps new treatments developed taking these characteristics into account.

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References

[1] G. Downson, **Powder Metallurgy: The Process and its Products**, Adam Hilger, Bristol; New York, 1990, p. 2, 34 and 58.

[2] G. Downson, D. Whittaker, **Introduction to Powder Metallurgy: The Process and its Products** (revised edition), European Powder Metallurgy Association, 2008, p. 2, 7, 9, 17-28.

[3] T. McCreight, **Working with Precious Metal Clay**, A & C, London, 2000, p. 11, 94, 96 and 121.

[4] * * *, **Metal Clay Academy,** http://www.metalclayacademy.com/metal-clay-resources/metal-clay-beginners-information.html [accessed on 10.02.2011].

[5] * * *, **Sima Vaziry *perscomm***, *https://www.simavaziry.com/* [accessed on10.05.2016].

[6] * * *, **The British Museum**, http://www.britishmuseumshoponline.org/invt/cmcn447190 [accessed on 10.05.2016].

[7]* * *, **The Goldsmiths' Company Assay Office,** http://www.thegoldsmiths.co.uk/welcome-to-the-assay-office/hallmarking-services/getting-items-hallmarked/faqs/ [accessed on 10.03.2016],

[8] I.M. Watt, **The Principles and Practice of Electron Microscopy**, Cambridge University Press, Cambridge, 1985, p. 106, 112, 206 and 273.

[9] J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, C. Fiori, E. Lifshin, **Scanning Electron Microscopy and X-ray Microanalysis**, Plenum Press, London; New York, 1981, p. 288, 365 and 448.

[10] L. Robinet, D. Thickett, *A new methodology for accelerated corrosion testing*, **Studies in Conservation, 18**, 2003, pp. 263-268.

[11] W.K. Lee, R.L. Eadie, G.C. Weatherly, K.T. Aust, *A study of the sintering of spherical silver powder – II. The Initial stage*, **Acta Metallurgica, 26**(12), 1978, pp. 1837-1843.

[12] R.L. Eadie, G.C. Weatherly, K.T. Aust, *A study of sintering of spherical silver powder – I. The intermediate stage*, **Acta Metallurgica, 26**(5), 1978, pp. 759-767.

[13] F. Thümmler, R. Oberacker, F. Oberacker, **An Introduction to Powder Metallurgy**, Cambridge University Press, The Institute of Materials. Series on Powder Metallurgy, 1993, p. 236.

[14] * * *, **Art Clay Metal**, http://www.pmcguild.com/download/Tech_Data/PMC3vs%20ArtClay650.pdf [accessed on 10.04.2011]

[15] V.M. Kryacheck, *Injection Moulding (Review)*, **Powder Metallurgy and Metal Ceramics**, **43**(7-8), 2004, p. 339.

[16] A. Bautista, F. Velasco, S. Guzmán, D. de la Fuente, F. Cayuela, M. Morcillo, *Corrosion behavior of powder metallurgical stainless steels in urban and marine environments*, ***Revista de Metalurgia,* 42**(3), 2006, pp. 175-184

[17] E.L. Hibner, E. Klar, P.K. Samal, *Chapter 60 - Powder Metallurgy (P/M) Materials*, R. Baboian (ed) **Corrosion Tests & Standards: Application & Interpretation** (second edition), ASTM International Standards Worldwide, 2005, pp. 664-670

[18] R. Marchiori, A.M. Maliska, P.C. Borges, A.N. Klein, J.L.R. Muzart, *Corrosion study of plasma sintered unalloyed iron: The influence of porosity sealing and Ni surface enrichment*, ***Material Science and Engineering: A*, 467**(1-2), 2007, pp. 159-164.

[19] R.M. German, L.G. Campbell, *Technical Note - Atmospheric oxidation corrosion of sintered artistic bronze*, ***Powder Metallurgy,* 49**(2), 2006, pp. 189-191.

[20] * * *, **Art Jewelry - Torch Firing Metal Clay**, https://www.youtube.com/watch?v=4ZRLhX2z6BM [accessed 23.03.2016]

[21] * * *, **Care and Conservation of Silver and Plate**, http://icon.org.uk/system/files/documents/care_and_conservation_of_silver.pdf [accessed 23.03.2016]

[22] * * *, **Silver Conservation - Victoria and Albert Museum**, http://www.vam.ac.uk/content/articles/s/silver-conservation/ [accessed 23.03.2016]

[23] C. Sease, L.S. Selwyn, S. Zubiate, D.F. Bowers, D.R. Atkins, *Problems with Coated Silver: Whisker Formation and Possible Filiform Corrosion*, ***Studies in Conservation*****,** **42**(1), 1997, pp. 1-10.

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