Rapid Prototyping using Electrodeposition of Copper

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Abstract

Injection mould cavities and EDM electrodes were produced from High Speed Selective Jet Electrodeposition (HSSJE). The performance of the electrodes in the EDM process and the surface finish of the tools produced were studied. Studies were made into optimising the HSSJE build process.

Introduction

More and more emphasis is now being placed on Rapid Tooling as a means of creating parts. The current emphasis is on downstream processes from established RP techniques. In contrast, this paper looks at the usage of High Speed Selective Jet Electrodeposition (HSSJE), using copper as a deposition element and its application to create SFF parts directly for injection moulding tools and EDM electrodes.

Conventional Electrodeposition

Electroplating is a process whereby a potential is applied between two conducting electrodes placed in a solution containing metal ions (electrolyte). As a result of an excess of electrons, metal ions are reduced at the surface of the negative electrode (cathode) and form a deposit of metal atoms on the surface. This grows at a rate proportional to the current passed. Metal ions from the positive electrode (anode) dissolve into the electrolyte. However, this process causes a depletion of copper ions in the electrolyte in the vicinity of the cathode as the rate of deposition tends to be significantly faster than their rate of replacement by migration due to the electric field. As a consequence, a concentration gradient develops which results in a diffusion flux. This electrolyte layer adjacent to the electrode is referred to as the Diffusion Layer. Fick's First Law of Diffusion states that the mass transport of ions by diffusion is proportional to the concentration gradient. A limiting current exists beyond which the rate of deposition would be such that diffusion and migration cannot re-supply the metal ions fast enough to maintain an excess concentration of ions. At the limiting current (i_L) as soon as metal ions reach the surface they are reduced and the metal ion concentration at the surface approaches zero. The thickness of the diffusion layer δ is governed by both the hydrodynamic conditions of the electrolyte and the bulk metal ion concentration (c_b). Higher rates of bulk electrolyte movement result in a thinner diffusion layer. The maximum concentration gradient (c_b/δ) is thus governed by the hydrodynamic conditions and the bulk concentration and this determines the limiting current density which can be expressed by equation [1].

$$i_L = \frac{-\,n\,F\,D\,c_b}{\delta\,(1-t)} \qquad [1]$$

where n is the number of electronic charges carried by each metal ion, F is Faraday's Constant, D is the diffusion coefficient and the term $(1 - t)$ accounts for the migration of the ions under the electric field, where t is the transport number of the metal ion concerned.

In general, within electrolytes, metal ions are usually surrounded by charged or polarised molecules. In an aqueous solution these are usually water molecules. Other species such as CN^- ions can be made to form complex molecules around the metal ions, often resulting in a net negative charge (in this case the complexes are still reduced at the cathode despite their electrostatic repulsion to it). Usually the complexes adsorb onto the cathode (via weak Van der Waals type bonds) allowing surface diffusion, where the complexes move to more energetically favourable sites such as steps or holes. Finally, electrons are donated by the cathode and the metal ions are reduced to atoms which are then held by metallic bonds to the cathode.

High Speed Selective Jet Electrodeposition

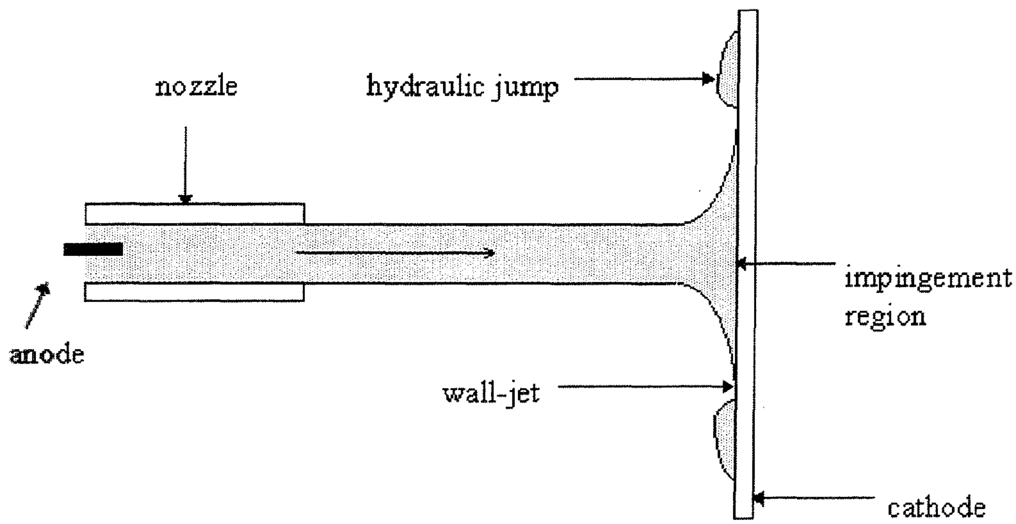

Figure 1. Schematic of the high speed selective jet electrodeposition process.

High Speed Selective Jet Electrodeposition (HSSJE), patented by NASA in 1974, uses a free standing jet of electrolyte impinging onto the cathode substrate as shown in Figure 1. A current is passed from an anode which is placed upstream from the nozzle. Away from the impingement region an extremely thin radial wall jet layer of electrolyte forms. The electrical resistance of this wall jet is high in comparison to the impingement region so no deposition can occur there. As a result, deposition occurs mainly in the impingement region and the immediately surrounding area. Furthermore, due to the continual supply of fresh electrolyte and the hydrodynamic conditions created the thickness of the diffusion layer δ is smaller and hence the mass transport of metal ions to the surface of the cathode can be made substantially higher than in the case of traditional electroplating. Consequently, higher current densities and thus higher deposition rates can be achieved than is conventionally possible. A more detailed discussion of the process is given by Bocking(1) and Chen(2). By moving the nozzle in relation to the substrate whilst deposition is occurring, it is possible to selectively "write" tracks and patterns at relatively fast rates without the need for masking the substrate.

However, at the very high current densities found with HSSJE, the time allowed for surface diffusion is much lower and deposits can be rough, porous, hard and contain higher internal stresses. Also, since the diffusion layer is much thinner any small elevation in the cathode surface will protrude into a region of higher metal ion concentration. This produces a locally enhanced current density and the protrusion is magnified. By this effect, the maximum current density that produces a good deposit is set well below the maximum current density as described earlier. In order to facilitate higher speeds of deposition, higher concentrations of metal ions are often used. In addition, higher temperatures increase the diffusion rate of metal ions and jet deposition benefits from electrolytes operating at elevated temperatures. Also many electrolytes contain constituents that are corrosive to the metal that is deposited. Consequently, deposits produced by HSSJE may be re-dissolved by the flowing electrolyte during "writing" operations.

As organic additives used in conventional techniques (brighteners, levellers etc.) are usually adsorbed onto the cathode (a time dependant phenomenon), their fraction of incorporation is largely dependent on the current density. High current densities and thus high rates of deposition will result in less incorporation into the deposit. Hence at high current densities these additives are less effective. Conventional electrolytes are very different from good HSSJE electrolytes, to the extent that HSSJE electrolytes often will not work in conventional plating baths.

Due to the low currents (despite the high current densities) associated with HSSJE, build rates are measured in grams per hour. Hence it would take an extremely long time to build a large metal tool using a single nozzle. Either improvements must be made in the deposition rates or multiple nozzles must be used, possibly with varying apertures for combined dimensional accuracy and speed. Feedback/levelling systems are required to build large deposits due to the factors that amplify surface imperfections. However, provided the parts are reasonably shallow, this could be omitted. Also, overhangs and support structures may prove difficult to produce and indeed deposits will have profiles fitting Gaussian functions(4) which slope asymptotically towards the substrate surface. Hence it is likely that the edges of layers and parts will not have straight vertical sides. Overhangs could be produced from a nozzle to substrate angle of less than 90°. The mass transfer characteristics of an oblique jet have been previously documented by Chin & Agarwal(3). This method may not be amenable to the usual CAD $\Rightarrow$ STL $\Rightarrow$ SLI $\Rightarrow$ vector file process found with other RP systems. Hence this process is suited to small complex tools and EDM electrodes rather than prototypes as these will require overhangs and support structures.

Experimental

The electrolyte composition used was 0.5M sulphuric acid and 0.8M copper sulphate. No organic additives were used. The gantry system used was based upon a Roland Plotter DXY 885, controlled via a QBASIC program running on a PC through a RS232C interface with the pen up/down function modified to switch on and off the current to the nozzle. The temperature was controlled via a thermocouple and 200W collar heater through which the electrolyte was pumped en route to the nozzle and the flow rate monitored using the same PC. The QBASIC program was written to draw the particular geometry of the shape to be produced, although more recently a program has been written to slice ASCII .STL files and use the data to create a 'vector file' to control the motion of the plotter.

Unfortunately, the minimum scan speed allowed by the plotter was $10mms^{-1}$. This is above the optimum scan speed due to the finite nucleation time for copper deposition. If the speed is too fast then only the trailing side of the substrate under the jet will have had enough time for full nucleation to occur. This results in a lower effective surface area of deposit and, therefore, a higher current density and a lower quality of deposit(4).

For all experiments, a nozzle of internal orifice diameter 820 ± 20μm was used with a nozzle to substrate distance of between 1 and 3mm. A polished copper block was used as a substrate for the deposition of EDM test electrodes and untreated copper clad PC board as a substrate for all other experiments. An electrolyte flow rate of 180 ± 40 $mlmin^{-1}$ was used and the temperature was kept at 22.7°C with a standard deviation of 0.8 . The current was controlled by a current source circuit with a FET at its heart.

The production of the shape shown in Figure 2 was undertaken using HSSJE except the central pins radii were decreased and the outer square perimeter shrunk by 0.4 mm to allow for the approximate width of the deposit. The circle was left unaltered due to difficulties with the software although with the .STL file slice routine, this has since been rectified. All nozzle scanning was carried out horizontally as shown in Figure 2. Electrodeposited copper tracks were laid with a lateral spacing of 0.025mm. It was intended to create an injection moulding tool cavity from this and to test its performance in the EDM process.

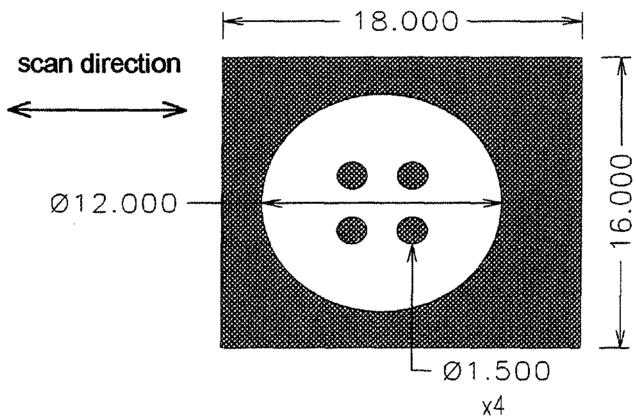

Figure 2. The first test piece.

The piece shown in Figure 3 was built at 30 mA (56.8 $mAmm^{-2}$) with 40 layers. The build height was approximately 0.15mm. It was noticed that the central pins were beginning to roughen in the centre and tiny spots were beginning to build disproportionately high. Three theories were considered for this phenomenon.

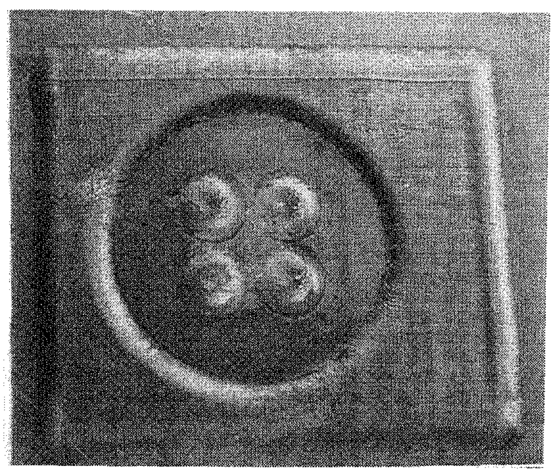

Figure 3. A sample built at 30mA (56.8 $mAmm^{-2}$) for 40 layers.

Firstly, too high a current will produce a rough surface as described above and eventually vertical columnar growth will occur. Secondly, once a track is deposited the substrate surface is no longer flat. A second track next to the first track will not produce an identical profile as the first track (being slightly raised from the surface) will tend to attract the current from the second, slightly raising it above the second track. Edge effects occur in a similar fashion. Even if the deposited surface is perfectly flat, the edges will be slightly rounded, eventually asymptotically approaching the initial substrate surface. As a result of this rounding, the edge of the deposit will attract more current from the interior of the deposit. This produces edges which are higher than the interior of the deposit with corners being higher still. The nature of the pins are that they have a large edge to deposit area ratio and hence this unevenness of the surface is exaggerated.

Finally edge effects occur due to the finite acceleration/deceleration time of the gantry system. As the nozzle moves to the end of the piece, the current is switched off but since the nozzle does not stop immediately, a higher charge per unit area is delivered to the substrate. This can easily be solved by lowering the current proportionally as the velocity decreases, however, it was intended to see if the process could work with a minimum of complexity. In addition to these three effects, once any surface protrusion occurs it begins to attract more current due to the nature of the electric field, further increasing the deformity of the surface.

To determine which of these effects is responsible for the degradation of the surface of the pins, or if a mixture to what extent each are responsible, it was decided to build the same height at the lower current (and lower current density) of 20mA (37.9mAmm^{-2}) for 60 layers. It was noticed that this system still showed the same uneven growth. Therefore, the effect cannot be due to an excessive current density.

Surface Roughness

The surface roughness of the samples were measured in a region away from any edges. Two samples, one with 140 layers at 7mA (13.26 mAmm^{-2}), one with 10 layers at 20mA (37.9mAmm^{-2}) were found to have Ra values of 0.32 and 0.27 μm respectively. The surface appeared shiny with an almost mirror finish.

EDM Performance

The test geometry was deposited onto a solid copper block at 20mA (37.9mAmm^{-2}) for 40 layers and used as an electrode to spark erode into a block of mild steel. A pulse

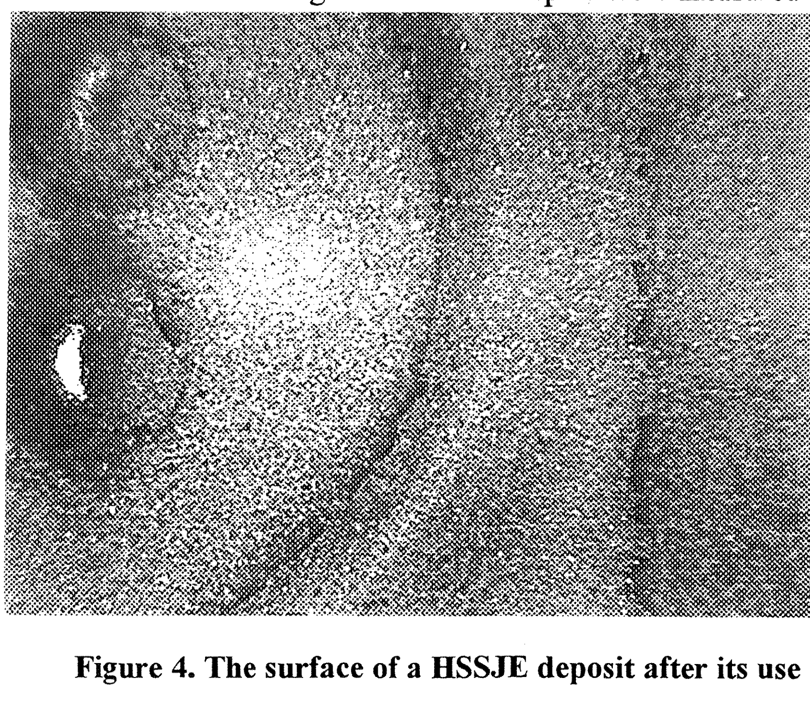

Figure 4. The surface of a HSSJE deposit after its use as an EDM electrode.

current of 5A was used and the electrode was plunged into the steel by approximately 0.3mm. The results were good and the electrode after sparking is shown in Figure 4. The electrode showed some wear especially around the outer edge of the deposit. This may be due to poor adhesion or internal stress in the deposit.

Edge effects

A second test piece was created to investigate the edge effects. The piece was as shown in Figure 5 with the dimension x being variable. All experiments on this piece were performed using the same experimental conditions except the track spacing was 0.1mm. Current (densities) of 7 mA (13.26 $mAmm^{-2}$) and 14 mA (26.52 $mAmm^{-2}$) were used with between 500 and 3000 layers. All scanning was performed left and right as shown in Figure 5. With each sample produced, the heights at each of the points displayed 1 to 11 in Figure 5 were measured from the bottom of the substrate (epoxy/glass fibre PC board) using a micrometer with a conical probe with a flat circular tip of 0.5 mm diameter. It was generally found that the two corners (points 11 and 12) were the highest (merely an addition of two edge effects), the ridge at the end (point 10) was next, followed by the sides (points 8 and 9), followed by the top of the flat (points 5, 6 and 7). This indicated that both edge effects are significant. The three values of interest for each deposit were the difference between the average height of the middle of the flat top of the deposit (points 5, 6 and 7) and the average height of the top of the substrate (points 1, 2, 3 and 4), the standard deviation of the average height of the middle of the flat top of the deposit (points 5, 6 and 7) and the standard deviation of all the flat top (points 5, 6, 7, 8, 9, 10, 11 and 12). These three values were named the useful height, the S.D. of useful height and the total S.D. of the deposit respectively.

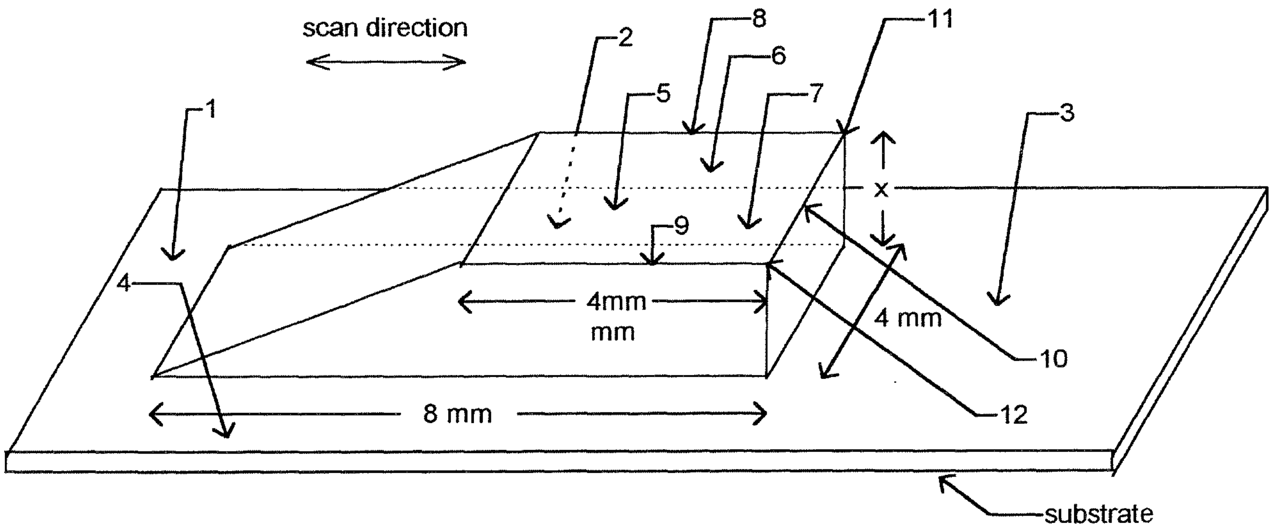

Figure 5. The second test piece.

Figure 6 shows the variation of the useful height with number of layers. The graph shows that for the range of samples shown, the useful height remains linear with a build of 0.2 μm per layer (at 7mA) indicating that if the surface were to be levelled (e.g. by milling) then any build height in the region studied could be used between each milling operation.

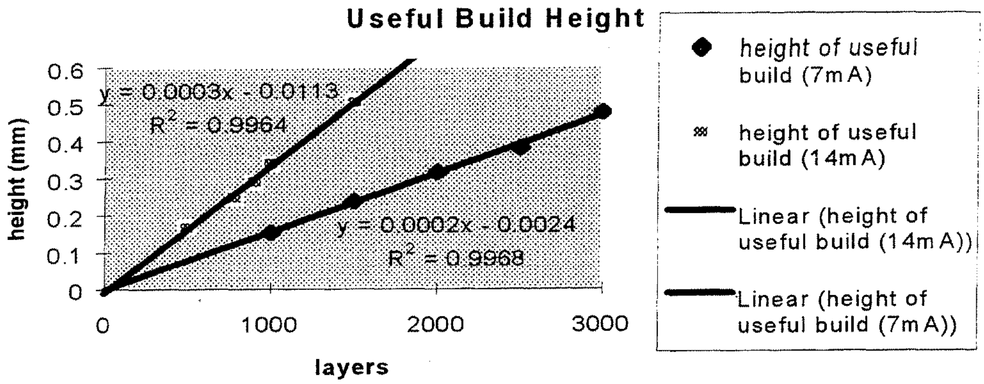

Figure 6. The variation of the useful build height versus number of layers at 7 and 14mA (current density at the nozzle exit is 13.26 and 26.52 $mAmm^{-2}$ respectively).

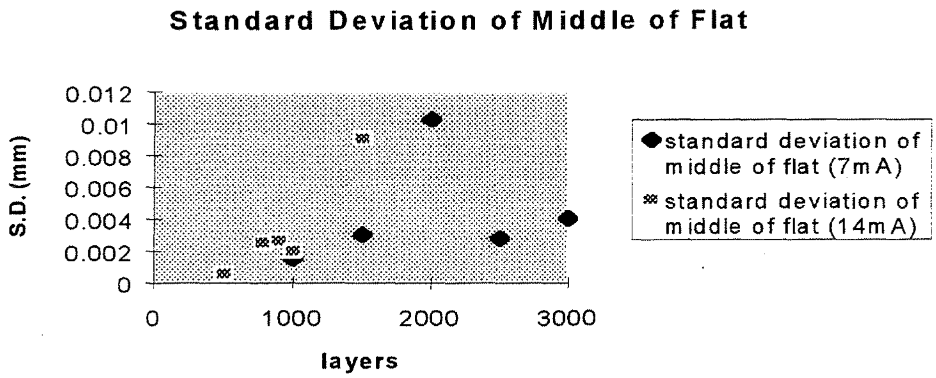

Figure 7. The variation of the standard deviation of the height of the flat section versus number of layers at 7 and 14mA (current density at the nozzle exit is 13.26 and 26.52 $mAmm^{-2}$ respectively).

Figure 7 shows the variation of the standard deviation of the useful height with the number of layers. It suggests that the unevenness of the flat top of the deposit increases with the number of layers although the data shows no clear trends. This is probably because three measurements is not enough to calculate each standard deviation point accurately.

Figure 8 shows the variation of total standard deviation (points 5, 6, 7, 8, 9, 10, 11 and 12) of all available samples against the useful build height. The useful build height was used instead of the number of layers as it allows for the different build rates associated with different currents used. It also allows for any minor deviation in current from that stated and for deviations in the build time (i.e. the plotter moving too fast/slow causing less/more deposit per layer). It shows that the data is fairly consistent for both currents used although more data is needed at the high end of the graph. It also suggests that the deposit becomes more deformed with increasing thickness in an exponential manner confirming that any surface imperfections attract more current and are thus further magnified.

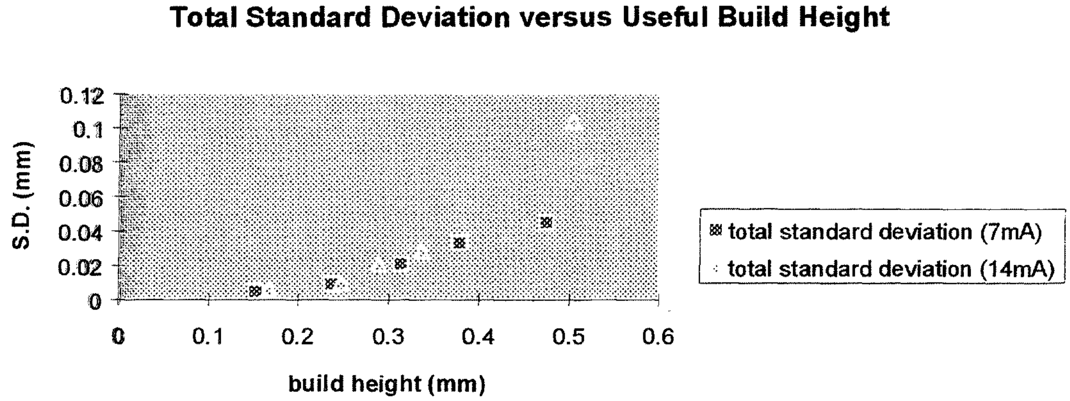

Figure 8. Graph showing the useful build height against the total standard deviation of all measurements of the deposit.

The results indicate that for a particular height of build, the size of the deformities in the deposits are independent of the current used (for the currents used) up to approximately 0.4 mm, beyond which further results are required.

Discussion

The results also indicate that parts higher than 0.5mm cannot be built without a levelling system or active current control. Parts that are less than 0.5mm will have a horizontal inaccuracy proportional to nozzle diameter. Build speed is ultimately inversely proportional to nozzle area. Hence, a compromise is necessary unless multiple nozzles are to be used. In addition, some geometries are more problematic than others, e.g. small pins. Other inaccuracies exist, including the shallow sloping sides. However, the possibility exists to make SFF parts with micron layer thickness. The process produces adequate EDM electrodes directly although care must be taken. For parts larger than 0.5mm high active current control or a levelling system is necessary.

References

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