Fig. 4
The present invention relates to an improved process and electrolyte for the electrolytic grinding of metals or for other electrolytic and electro-chemical metal working processes, for example electrolytic sinking.

For several years the electrolytic and electro-chemical metal working processes have found increased adaptation, particularly the grinding of hard metals or alloys such as "cemented carbides" by means of metal bond grinding disks provided with diamonds as the abrasive material is already widely in application.

Initially, the present day state of the art for electrolytic grinding will be briefly considered. One process for electrolytic grinding is based upon the fact that a strong direct current is simultaneously delivered during grinding through the arrangement including grinding disk, ion conducting fluid and workpiece. The electron conducting grinding wheel or disk, generally a metal bound diamond disk, provides the negative electrode in the arrangement, namely, the cathode. The workpiece to be processed is then the positive electrode, namely, the anode. The electrolyte, which simultaneously undertakes the function of cooling, is generally an aqueous salt solution. Since these electrolytes come into contact with portions of the grinding machine important for the operations thereof, such must be as little corrosive as possible, which then considerably limits the number of useable salts. Under consideration come solutions of nitrates, phosphates and borates having slight to medium alkalinity. The corrosion resistance of a part of certain other salts can be suppressed or dampened by the addition of nitrates, phosphates, chromates or other corrosion inhibitors. This holds particularly true for carbonates, nitrates, tartrates, and to a reduced degree also for sulphates.

If the electrolyte under the above-described electrical conditions possesses a pronounced solvating action for the metal to be worked, there then results a new type of metal working or shaping or duplication, which has been termed in the art as sinking. The electrode serving for working or sinking is applied to the workpiece to be treated while maintaining a small work gap. The electrolyte is introduced in suitable manner, for example through the electrode itself into the work gap. During the working process the work gap is held constant by means of a suitable feed-control mechanism. The metallic displacement or removal is only conditioned upon the current.

During electrolytic grinding the width of the grinding gap is given by the diamond grains of the grinding disk and by the externally effective contact pressure of the workpiece. The chemical reactions caused by the passage of current consists, according to previously expounded views, in a dissolving of the anode, whereas the cathodic processes have hardly been considered. The products of the anode dissolution are, according to the views of several authors, soluble materials, whereas other publications speak in terms of insoluble oxidic-like substances.

The function of the grinding disk is to continuously conduct new electrolyte into the grinding gap and, at the same time, to remove or carry away the formed anodic products. On the other hand, with electrolytic sinking a prerequisite is the existence of soluble products or products which can be washed away.

The investigation of grinding disks has been of particular interest to those skilled in the art. Such investigations or studies have led to the commercial availability of present day disk types. They contain relatively coarse diamond grains embedded in a disk bonding material possessing porous structure. By virtue of this porosity the receiving capacity of the disk for electrolyte is supposed to be improved. Such types of grinding disks are indeed very practical, yet, however, are also very sensitive to mechanical overload or stress. The viewpoint has also been advanced that the pores and the free spaces between the protruding diamond points fill with worked away oxide material, so that the grinding process ultimately is effected only by this so-called "semi-conductive" layer.

The term "semi-conductive" should, for the purpose of the present invention, be understood to only imply poor conductivity. Insulating of the insert and plastic edges at the grinding disk should suppress the formation of sparks which then appear when the workpiece is applied to the disk or removed therefrom, or when the portion of the workpiece to be ground has which has left the grinding surface is again brought in contact. A considerable advantage of the electrolytic working process resides in the feature that, the removal of metal takes place without appreciable heating, which obviates thermal damage to the tool.

The views regarding the wear of the diamond disks are again divided. One opinion propounds that the disk wear is approximately of the same magnitude as with electrolytical grinding, affecting however improved material removal capability or efficiency and surface quality, whereas the other opinion expresses the belief that disk wear is very small and, at most, only amounts to a few pro mille of the removed hard metal. With sinking, in contradistinction to grinding, no electrode wear can be ascertained. A current of 100 amperes gives a removal of 80 to 150 cubic millimeters (mm.\(^3\)) per minute with hard metal e.g. of the sinter type such as so-called "sintered carbides" or "cemented carbides" whereas for hardened steel there are present removal values of 180 to 360 cubic millimeters (mm.\(^3\)) per minute per 100 amperes.

The present invention contemplates as one of its primary objects the provision of an improved process and electrolyte for the electrolytic working of metals in an efficient and reliable manner within relatively broad ranges of contact pressure and voltage.

Another important object of this invention is to provide improved process and electrolyte for electrolytic metal working, resulting in excellent surface qualities at the workpiece as well as improved metal removal capacity.

Yet another noteworthy object of the present invention is directed to the provision of an improved electrolyte for electrolytic metal working which is characterized by the feature that its essential component contains water soluble fluorides or fluoride compounds.

Still another important object of the present invention is the provision of an improved process and electrolyte for electrolytic metal working or the like ensuring for less wear at the grinding or working tool.

A further object of the invention contemplates the protection of the surfaces of the workpiece which are not to be worked, by applying thereto a coating composition containing an electron-conductive pigment and a binding agent of an organic or inorganic nature.

Other features, objects and advantages of the invention will become apparent as the description proceeds, and the invention will now further be described in conjunction with certain graphs depicted in FIGURES 1 to 4 of the drawings, wherein FIGURES 1 to 3 graphically depict results with electrolytes proposed in publications.
or obtainable on the commercial market and thereby provide an illustration of the state of the art, whereas FIGURE 4 graphically illustrates results obtained by employing the inventive process and electrolyte.

Directing attention now to the drawings and, more specifically, to the graph of FIGURE 1, it will be seen that four curves are plotted thereon for respective contact pressures of 3 k.p./cm.², 5 k.p./cm.², 7.5 k.p./cm.² and 10 k.p./cm.². These pressures with a 15% potassium nitrate electrolyte give the depicted removal capacity in mm.³/cm.² per minute at the workpiece with changed voltage (V) in the generator. These curves show for different voltage ranges a different behavior. Only in the range of the full-line portion of the curves are the conditions for a faultless working operation of electrolytic grinding good. In the dotted or dashed portion of the curves there appear increasing spark discharges. In the chain-dot range of the curves the number of spark discharges is so large that it is no longer possible to work satisfactorily. The effects of the spark discharges increase the wear of the grinding disk and form spark erosion locations at the workpiece.

In FIGURE 2 there is shown in similar manner the operation of a commercial electrolyte on the basis of the sodium nitrite-sodium nitrate with organic additives. In this case there were processed two hard metal samples of type P10, these materials being well known "cemented carbides." From this figure is also discernible the fact that a good operating region only lies in a very narrow voltage range.

FIGURE 3 contains the same data for a commercial electrolyte available only as a particular trademark which is on the basis of the sodium nitrite-sodium dihydrogenphosphate-sodium tetaborate. Out of this figure there is likewise discernible that for the most different working materials the useable range is present only within very narrow limits.

It will thus be seen from FIGURES 1, 2 and 3 that the range of application of the electrolytes is limited. In particular, the working pressure (k.p./cm.²) and the voltage in the grinding gap must be very exactly accommodated to one another, since otherwise, in consequence of the pronounced electric spark discharge, a satisfactory working operation is impossible. Thus, the normal working conditions are only attainable within a narrow range.

Concerning the possibility of simultaneously removing hard metal and steel, the most common view is that the simultaneous working of hard metal and steel is indeed possible, yet not economical however. Electrolytes developed for hard metal working give unfavorable results when working steel.

To provide a fuller explanation there will subsequently be given several considerations regarding the passive layers on the workpieces which have to be processed. The formation of passive layers shows considerable similarity with annealing layers and scaling layers. The transport of ions through these passive layers formed by oxidation becomes that much easier and results quicker, the thinner such layer and the greater the potential drop. If the passive layer is not attacked either chemically or mechanically, then it increases and the effect of ion inclusion in the layer ultimately comes to standstill. The anode processes resulting during electrolytic grinding in addition to the formation of the passive layer lead to the formation of hydrogen ions, namely to the formation of an acid. The type of the thus formed acid depends upon the type of anions contained in the solution. Thus there is provided the possibility to specifically act upon the formed passive layer or cover layer, that is to say, to attack them more or less strongly chemically, or to create reverse conditions which protect them.

In unbuffered systems including salts of strong acids the electrolyte in front of the anode becomes strongly acidic. If the acid possesses a solvating capability for the components of the passive and cover layers, then initially there occurs a pronounced attack of the layers. In addition thereeto there appears a further effect. In a given solution with known pH-value the passivity appears at a rather well defined and reproducible anode potential. With the electrolyte becoming acidic in front of the anode the necessary potential for the passification is also displaced towards a more positive value. Due to this displacement or change from a passive to an active mechanism of the anodic dissolution there result particularly advantageous working conditions. The latter observations are particularly valid aso for electrolytic sinking.

In addition to the chemical attack upon the workpiece surface there also comes into consideration the mechanical removal effected by the grinding disk wheel. Passive layers are dense, free of pores and generally rigidly adhere to the parent metal. If the grinding disk is no longer able to remove the passive layer quickly enough, then the current drops considerably. If the contact pressure is increased then there is thereby also increased the mechanical removal of the passive layer. Such becomes thinner, at some places being in fact removed. Consequently, the total resistance becomes smaller so that with the current the removal again increases. Thus there are again provided the conditions for a stronger passiveness. If the grinding disk with its mechanical effect cannot follow or not rapidly enough follow subsequently, then the workpiece is again entirely passified. The current drops sharply so that the induced voltage force causes a spark discharge, which is mostly followed by an entire cascade of further sparks. As a result, there appear spark erosion locations in line pattern, with the line arranged behind one another. Such effects are not only undesirable at the workpiece, but also are an essential cause of diamond disk wear. If there is ensured that the passive layer will be sufficiently strongly mechanically attacked, then a new effect becomes operative: The exposed locations of the workpiece surface become localized anodes, whereas the locations which are still covered with the passive layers become localized cathodes. Such an activation of the surface of the workpiece appears especially then, when the direct current applied to the grinding gap is wave or undulating-like or impulse-like. Basicallly the following measures or steps arise for the influencing of the working conditions at the grinding gap or work gap, respectively:

(a) Utilization of acid to strongly acidic electrolytes.
(b) Utilization of neutral to slightly alkaline electrolytes or electrolytic solutions which possess no or very small buffer action, and which by consequence of the passive layer mechanism become acidic in front of the anode.

(c) Electrolytes as mentioned in item (b) which themselves possess only small or no oxidative properties.
(d) Electrolytes which contain components which advance the chemical corrosion of the passive layer, e.g. formation of complexing agents.
(e) Electrolytes which contain components which are incorporated in the passive or cover layers and influence the characteristics of the layers such that they can be easier removed or carried away mechanically.

(f) Electrolytes which contain components which are incorporated in the double layer, cover layer or passive layer, and which influence the transport of the cations or anions or both through this layer.

(g) Electrolytes as mentioned under items (e) and (f) which change the electric properties of the layers, as for example the electric conductivity.

(h) Electrolytes according to items (c) to (g) can be effective even if they have buffering properties or oxidize the effects.

(i) Influencing the action at the anode in that a stronger wave-like or impulse-like direct current is used, the current and voltage amplitudes of which at times are small or in fact null, or for very small periods of time are in fact negative.
(k) It is possible to also work such that the smoothed or wave-like or impulse-like direct current has superimposed in specific time intervals an impulse of opposite polarity.

(l) With the aid of such cathodic current surges it is possible to blow-off or suddenly remove the anodic generated layers, or to limit or extinguish the passivity to a desired degree.

(m) The blowing-off or sudden removal can be carried out particularly easy with passive layers and cover layers which in their characteristics are similar to those of aluminum.

(a) In order to increase the mechanical effect the grinding disks available nowadays on the commercial market normally contain corundum diamond grains than normal grinding disks. Such together with the intentionally contained porous bonding render such disks very sensitive to mechanical overload.

(o) Increasing the contact pressure results in a more pronounced increase of the removal effect. The formation of particularly declines to a minimum, yet with increasing contact pressure against increases, and finally shortens. The mechanical grinding portion and the disk wear increase in the same manner.

(p) An increase of the mechanical attack of the passive and cover layers also brings about an increase of the displacement work or velocity of the grinding body, for example the rotational speed of the grinding disk.

(q) It is evident that also two or more of these measures can be combined, which, in fact, is the rule. Only then it is possible to achieve with electrolytic grinding really satisfactory results.

On the basis of experiments it has been determined that the measures set forth in items (d), (e), (f) and (g) are particularly suitable for electrolytic grinding. For electrolytic sinking the measures of items (a) to (m) are of particular importance. The invention is concerned with the problem of fulfilling these measures. Such as achieved by virtue of the fact that, the electrolyte or electrolytic solution in its essential component contains water soluble fluorides or fluoro or fluoride compounds.

It has been found that these solutions, in particular potassium fluoride in medium and high concentrations, work absolutely in faultless manner in very broad ranges of the contact pressure (kp/cm²) as well as the voltage. In addition to excellent surface quality there result removal capacity or efficiencies which have not even been closely approached by any of the previous known electrolytes.

There will now be explained an inventive embodiment in conjunction with the graph of FIGURE 4. This figure illustrates the behavior of a potassium fluoride electrolyte with 15% potassium fluoride in accordance with the Invention. Along the abscissa there is plotted the different voltages (V) regulated in the generator. Along the ordinate there is plotted the material removal capacity (mm²/cm²/min.). The individual curves were plotted with different contact pressures (kp/cm²) as indicated thereat. Of particular value is the very pronounced dependency of the removal capacity (mm²/cm²/min.) upon the voltage in the generator and the contact pressure (kp/cm²), indicated by the steepness or inclination of the curves. The region in which it is possible to work without trouble is considerably larger than illustrated. It is to be understood that FIGURE 4 is only a small portion of the possible working range of the inventive electrolyte. Such larger trouble-free zone is clearly perceivable by comparing FIGURES 1, 2 and 3 which depict the previous known electrolytes, with FIGURE 4 representing the electrolyte according to the invention. A further advantage of the electrolyte according to the present invention resides in the fact that, the wear of the grinding disks is smaller. For this reason there can be advantageously selected a material for the grinding disks which no longer corresponds to a diamond. According to the invention it has become possible to submit grinding wheels or disks to shaping operations.

Concentrated to saturated fluoride-containing solutions are particularly well suited also for sinking. Thus it is also possible to work hard metals such as "cemented carbides." According to the properties of the materials to be worked there are employed acidic, neutral or alkaline solutions. It has been found desirable when potassium fluoride is employed in the electrolyte solution that it be present in a concentration of at least 4%. Moreover, it is possible that the electrolyte, in addition to a water soluble fluoride, also contains other salts, such as nitrates, nitrites, phosphates, carbonates, sulphates or salts of organic acids and bases, whereby the mentioned salts are combined with fluorides. It is also advantageous if the electrolyte possesses a pronounced solvating capacity for the passive layers arising at the anode and which mechanically are very wear resistant, as well as for the carbides contained in the hard metals. Finally, it is desirable if the electrolyte contain ions, in particular fluoro-ions, which are embedded in an anodic produced passive or cover layers and influence such layers in a manner favorable for the execution of the process.

As is generally known with electrolytic and electrochemical metal working, the surfaces and the roundings of the edges of the workpiece which are not in contact, are subjected to an electrolytical removal operation. Attempts to protect these surfaces and edges of the workpiece from material removal by coating with oil, grease or, or coating compositions such as lacquers or paints, have encountered failure. A grease layer is generally pushed away, and lacquer films peel off or roll up. It appears that all such protective layers are pressed away by the oxygen occurring under high pressure. According to an advantageous further development of the invention as relates to a method for protecting the edges and surfaces during electrolytic working, there are employed lacquers or coatings with particularly good electron conductivity.

These lacquers or coatings are grindable after drying or hardening. They exhibit a particularly high content of electron conductive pigment, as for example graphite, carbon or metal powder, as well as a binding agent of an organic or inorganic nature.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

What is claimed is:

1. A process for the electrolytic working of metallic workpieces comprising the steps of providing a workpiece formed of a material selected from the group consisting of steel and cemented carbides as one electrode and spacing said workpiece a small distance from another electrode, filling the space between said electrodes with an electrolyte and removing material from said workpiece by passing a direct current between said electrodes and through said electrolyte, said electrolyte consisting essentially of an aqueous solution of a water soluble fluoride salt having a pH ranging from a generally neutral solution to a mildly alkaline solution.

2. Process for the electrolytic working of metallic workpieces according to claim 1 including the step of driving the other electrode.

3. Process for the electrolytic working of metallic workpieces according to claim 1 including the step of covering the surfaces of the workpiece which are not to be worked with an electron conductive layer in order to limit material removal.

4. Process for the electrolytic working of metallic workpieces according to claim 1 wherein said electrolyte is an aqueous solution of potassium fluoride.

5. Process for the electrolytic working of metallic workpieces according to claim 4 wherein the potassium fluoride appears in a concentration of at least 4% in said electrolyte.
6. Process for the electrolytic working of metallic workpieces according to claim 1 wherein said other electrode comprises a grinding body possessing an abrasive material.

7. Process for the electrolytic working of metallic workpieces according to claim 1 including the step of covering the edges and surfaces of the metallic workpiece which are not to be subjected to the working process with an electron conductive coating composition in order to protect such edges and surfaces.

8. Process for the electrolytic working of metallic workpieces according to claim 7 wherein the coating composition is of the type which is grindable after hardening or drying.

9. Process for the electrolytic working of metallic workpieces according to claim 7 wherein the coating composition contains a binding agent and an electron conductive pigment.

10. Process for electrolytic working of metallic workpieces according to claim 9 wherein said electron conductive pigment is selected from the group consisting of graphite, carbon, metal and alloy particles.

References Cited

UNITED STATES PATENTS

2,469,689 5/1949 Gresham 204—143
2,538,504 6/1951 Aller 204—143
2,766,199 10/1956 Higgins 204—143
2,506,582 5/1950 Mateosian 204—140.5
2,805,197 9/1957 Thibault et al. 204—143
3,088,895 10/1962 Williams 204—143
3,051,494 10/1962 Snyder et al. 156—18
3,088,889 5/1963 LaBoda et al. 204—143
3,130,138 4/1964 Faust et al. 204—143

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