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[54] **RUTHENIUM OR OSMIUM ON HARD METAL**

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[58] **Field of Search** 75/203, 208, 204; 29/182.7, 182.8

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[57] **ABSTRACT**

Bodies having osmium or ruthenium at the surface are found to give improved service as cutting tools, dies, bearings and the like. Best results are obtained when the body consists of a hard metal consisting of a carbide and a cobalt binder, and osmium or ruthenium is caused to combine with the bonding metal by interdiffusion of a surface coating of the precious metal and underlying bonding metal or by using mixtures of cobalt and osmium or ruthenium or both as the bonding metal.

5 Claims, No Drawings

RUTHENIUM OR OSMIUM ON HARD METAL

The present invention is concerned with articles which present one or more working surfaces subject to wear in use. As is well known, the most common articles of this kind are cutting tools having at least one cutting edge between rake and flank faces, the actual cutting edge and parts of these faces being working surfaces subjected to considerable wear, which limits the cutting life. The whole of the tool may be made of sintered hard metal consisting essentially of a metal carbide and a metal binder of the iron group, but usually only the tip of the tool is made of hard metal and is carried by a steel or other support.

Other articles which are subjected to wear and become heated in use are drills, wire-drawing dies, powder-compacting and metal-forming dies and some journal bearings, the bores and surfaces of which become worn in use.

As is well-known, sintered carbide is a product of powder metallurgy made of finely divided, hard particles of a carbide of a refractory metal sintered with one or more metals of the iron group. The hard particles are, most advantageously, tungsten carbide, usually in combination with lesser amounts of other carbides. The additional carbides are those of titanium and tantalum with some occasional specialized use being made of the carbides of niobium, molybdenum, vanadium, chromium, zirconium and hafnium. For most commercial purposes, the binder metal is cobalt.

The carbides are present as individual grains and also as a finely dispersed network resulting from the precipitation during cooling of carbide dissolved in the cobalt during sintering. Table I sets forth in percent by weight the composition of certain types of carbide compositions to which the present invention is applicable.

TABLE I

Carbide Group	% Co	% TaC+ TiC	% WC
1	2.5–6.5	0–3	Bal.
2	6.5–15	0–2	Bal.
3	15–30	0–5	Bal.
4*	3–7	20–42	Bal.
5*	7–10	10–22	Bal.
6*	1–12	8–15	Bal.
7**	4.5–8	16–25	Bal.
8**	8–10	12–20	Bal.
9***	5.5–16	18–30	Bal.

* Added carbide is predominantly TiC
** Added carbide is predominantly TaC
*** Added carbide is exclusively TaC

The carbide groups set forth in Table I are generally used for cutting purposes for various types of metal. The carbides of group 3 are especially useful for high-impact die applications and the carbides of group 9 are specifically applicable for wear-resistant applications particularly involving heat. One common hard metal used for cutting tips consists of 94 percent tungsten carbide and 6 percent cobalt, and another of 83 percent tungsten carbide, 12 percent titanium carbide and 5 percent cobalt, known to the trade as grade C–6.

It is an object of the present invention to provide novel wear-resistant articles, particularly cutting tools, having improved resistance to wear.

It is another object of the present invention to provide a novel process for providing an improved surface on carbide and other cutting tools.

Other objects and advantages will become apparent from the following description.

According to one aspect of the invention, in a hard metal article presenting one or more working surfaces subjected to wear in use, in at least that part of the hard metal which presents the working surface or surfaces the binder consists of cobalt together with a lesser or equal amount of weight of ruthenium or osmium or both. It is found that by thus modifying the binder either the life of the article or the cutting or other working speeds can be greater than those attained under similar conditions when the binder is cobalt alone.

An article according to the invention may be produced by forming a mixture of particles of ruthenium or osmium or both with carbide and cobalt particles, compacting the mixture and sintering the compact. If the cobalt is to be modified only at the working surface or surfaces, a mixture of carbide and cobalt particles may be compacted, and with or without first presintering the compact one or more surface layers of a mixture of particles of ruthenium or osmium or both with carbide and cobalt particles may be applied to the compact, which is then sintered. Such a surface layer may be applied as a slurry.

An article according to the invention may also advantageously be made by coating a sintered body of carbide and cobalt with ruthenium or osmium or both and heat-treating the coated body to cause partial diffusion of the coating into the cobalt. Such a coating may be formed in any convenient way, for example by electrodeposition, plasma-spraying or vapour deposition; or by applying a slurry of powder and sintering; or by applying liquid-bright (a ruthenium-bearing liquid) and subsequently decomposing this to metal by heating. The coating may also be formed while the article is being made in that it may be applied for example by plasma-spraying to a compact of the carbide and binder metal before this is sintered, or that a layer of ruthenium or osmium may be put on a compact and compacted, again before the compact is sintered.

The coating can be very thin, say 2 or 3 microns thick or less, but the thickness is in part dependant on the way in which the coating is produced. When it is produced electrolytically it is found that the quality tends to be inconsistent when the thickness is greater than 6 microns, and the preferred thickness is from 2 to 10 microns. However, so far as the improvement in life is concerned coatings of equal quality from 2 to 30 microns thick give substantially the same improvement. Coatings applied by plasma spraying are inevitably thicker by nature of the process and may be, for example, as great as 125 microns thick.

If the coating is formed by the application of a liquid-bright' (a ruthenium-bearing liquid produced by the reaction of a ruthenium halide with an ether), a single application followed by drying and heating at say 600°C yields a coating about 0.5 microns thick, and it is desirable to repeat the process several times in order to produce a thicker final coating.

Most electrolytic baths from which ruthenium or osmium can be deposited are so acidic as to attack the binder in the hard metal, and when such a bath is used a flash coating of a resistant metal, which may be gold or palladium, should first be applied.

The heat-treatment to cause partial diffusion of the ruthenium or osmium into the hard metal should not be such as to cause migration of the cobalt or other binder metal out of the hard metal or result in substantial coarsening of the carbide grain. The temperature of the

heat treatment is in the range 1250° to 1400°C, and the duration is broadly inversely proportional to the temperature. At temperatures up to 1300°C the diffusion is slow, and when the temperature is raised above 1350°C degradation of the carbide occurs with loss of cutting properties. The durations at different temperatures are as follows:

Temperature	Duration range in hours	Optimum duration in hours
1400°C	<1	½
1375°C	<2	1
1350°C	1 to 4	2
1335°C	1 to 5	2
1325°C	1 to 24	6
1300°C	1 to 24	24
1250°C	1 to 30	>24

The temperature is preferably from 1335° to 1350°C, and the duration from one to two hours. It is desirable to cool slowly from temperature (taking about one hour to cool) to avoid embrittlement of the metal matrix.

We believe that the reason for the improvement is increase in the transition temperature of cobalt as the result of alloying it with ruthenium or osmium. Pure cobalt has a close-packed hexagonal structure which gives the hard metal low friction characteristics, and this changes to a face-centred cubic structure at about 400°C, with loss of the desirable low friction characteristics. Typically a cutting edge attains a temperature of about 1000°C. As the cobalt becomes increasingly rich in ruthenium or osmium the transition temperature rises, and is 1100°C in an alloy containing 70 percent cobalt and 30 percent ruthenium. Thus by raising the transition temperature the hexagonal structure is at least partly maintained despite the heat developed in use, and the working life is prolonged or the cutting speed can be higher. Support for this theory is to be found in the fact that the other metals of the platinum group, which do not have the same effect on the transition temperature of cobalt, do not give improvement similar to that produced by ruthenium or osmium.

Whether or not this theory is correct, it is desirable to ensure that the proportion of ruthenium to cobalt by weight in the binder at least at the working surface or surfaces is at least 1:6 though even a lesser amount of ruthenium alloyed with the cobalt gives some improvement. Normally the proportion is no more than 1:1.5 but may be as high as 1:1.

The proportion of osmium to cobalt is preferably at least 1:4 and may be as high as 1:1.

The invention is primarily useful in prolonging the life of cutting tips, and numerous tests have been made on tips of the hard metal composed of 83 percent tungsten carbide, 12 percent titanium carbide and 5 percent cobalt. In these tests the conditions were severe, the tips being used to cut bars of EN30B steel (an alloy steel containing 0.3 percent carbon, 4 percent nickel, 1.25 percent chromium and 0.3 percent molybdenum) hardened and tempered to 500 Hv. The majority of the tests were carried out without cutting lubricant and coolant. The angle of approach of the tip to the work was 75°, the cut being made by one edge of the tip. The feed was 0.3 mm/rev. and the depth of cut was 1.3 mm. The life as determined when the tool tip broke off or 0.4 mm. average flank wear was observed or 0.8 mm. localised flank wear was observed or the tip was observed to be no longer making a cut to a given diameter.

EXAMPLE 1

The tips were coated electrolytically with ruthenium in an aqueous electrolyte containing 30 g/l $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ and 10 g/l ammonium sulphamate, at a pH adjusted to 1.5 by the addition of sulphamic acid, the temperature of the electrolyte being 70°C and the current density from 1 to 2 amp/dm². Prior to ruthenium plating the hard metal was given an initial flash coating of gold in an alkaline gold cyanide bath to avoid attack of the cobalt by the acid electrolyte. Ruthenium coatings of different thicknesses were produced and the coated tips were heat-treated at 1325°C for two hours. Tips having coatings six microns and 10 microns thick had nine times as long as those of uncoated commercial tips. when the machining speed was 92 metres per minute.

EXAMPLE 2

The tips were electrolytically coated with osmium in an aqueous electrolyte containing 10 g/l potassium hexachloro-osmate, 15 g/l potassium chloride and 60 g/l potassium hydrogen sulphate, adjusted into the pH range of 1.2 to 1.5 by potassium hydroxide. The temperature of the electrolyte was 70°C, the cathode current density from 1 to 2 amps/dm² and the anode current density less than 0.5 amp/dm². This electrolyte also attacks hard metal, so all the tips were initially flash-coated with gold. The coated tips were heat-treated as in Example 1. The improvement in life given by an osmium coating three microns thick after heat-treatment was greater than seven times those of the uncoated tips when machining at 67 m/min.

EXAMPLE 3

The tips were coated as in Example 2 in a mixed chloroosmate/chloro-ruthenate electrolyte to give a coating of 3.5 μm of an alloy composed of 50 percent ruthenium and 50 percent osmium. After heat-treatment for two hours, 1325°C, the cutting life was 10 times greater than that of the uncoated tips when machining at 49 m/min.

EXAMPLE 4

The tips were coated with ruthenium to a thickness of about 125 microns by plasma-spraying ruthenium powder of particle size from 50 to 150 microns through a standard plasma-spray gun. After heat treatment for two hours at 1325°C, an improvement of nine times in the life was obtained when machining at 64 m/min.

EXAMPLE 5

The tips were painted with ruthenium liquid bright, dried in air and fired in air at 600°C, and the process was repeated four times to build up the thickness to 1.5 microns. The coated tips were heat-treated at 1325°C for two hours. An increase in life of six times was obtained on machining at 49 m/min.

EXAMPLE 6

A powder mixture of 82.3 percent tungsten carbide, 13 percent titanium carbide, 3.8 percent cobalt and 0.9 percent ruthenium was ball-milled for 48 hours in acetone, dried and sieved. 1 percent paraffin wax in carbon tetrachloride was added, and the mixture was compacted at 77 MN/m², heated slowly in hydrogen to 600°C to remove the wax, pre-sintered for one hour at

900°C and finally sintered for one hour at 1425°C, all in hydrogen. The resultant article was ground to a tool tip or bit 12.5 × 12.5 × 3 mm. in size with an 11° relief angle. This tip, when used in machining at 67 metres per minute had a life 11 times that of a similar tip bonded only by cobalt.

EXAMPLE 7

The binder in Example 6 contains about 20 percent ruthenium. Tips made as in Example 6 but with other proportions of ruthenium in the binder gave life improvements as follows:

90% Co – 10% Ru	5 times
70% Co – 30% Ru	11 times
60% Co – 40% Ru	10 times
50% Co – 50% Ru	7 times

EXAMPLE 8

A tip containing 82.1 percent tungsten carbide, 13 percent titanium carbide, 3.9 percent cobalt, 0.5 percent ruthenium and 0.5 percent osmium, used as in Example 6, gave an improvement in life of six times.

EXAMPLE 9

A tip containing 81.6 percent of tungsten carbide, 13 percent titanium carbide, 3.8 percent cobalt and 1.6 percent osmium used as in Example 6, gave a life improvement of two times.

Although the majority of the machining tests were carried out dry, some comparative data were obtained using a water-soluble oil (diluted 150:1) as coolant/lubricant. On machining at 67 meters per minute with coated and uncoated tips in both cases the use of the coolant/lubricant increased tool life by a factor of 2, compared with the dry machining results. Hence the use of a coolant/lubricant will increase the life, but does not affect the relative lives of coated and uncoated tips.

It has also been found that the provision on cutting tools, whether of hard metal or of other materials commonly used for this purpose, of a surface coating of ruthenium or osmium or an alloy of these two elements gives the tool a longer life or enables it to be worked at a higher speed without loss of life even when this coating is not caused to diffuse into the underlying metal.

According to another aspect of the invention, therefore, a cutting tool has a coating of ruthenium or osmium or an alloy of these two elements on at least the surfaces adjacent to the cutting edge or each such edge.

The tool may be made of hard metal (consisting essentially of carbide and a binder metal of the iron group, usually cobalt), high-speed steel or any other suitable material.

The coating may be produced by any of the methods set forth above, and its thickness may be the same as those of coatings intended to be heat-treated to cause partial diffusion into the binder of a hard metal tool. It will be appreciated however that according to this aspect of the invention such diffusion is not necessary and in general will not occur, though generally speaking the improvement in tool life obtained is less when such diffusion does not take place.

The provision of coatings of ruthenium or osmium or alloys thereof is primarily useful in prolonging the life of cutting tips, and numerous tests have been made on tips of the hard metal composed of 83 percent tungsten carbide, 12 percent titanium carbide and 5 percent cobalt. The test conditions were the same as described in connection with the preceding examples.

EXAMPLE 10

The tips were coated electrolytically with ruthenium in an aqueous electrolyte containing 30 g/l $(NH_4)_3[Ru_2NCl_8(H_2O)_2]$ and 10 g/l ammonium sulphate, at a pH adjusted to 1.5 by the addition of sulphamic acid, the temperature of the electrolyte being 70°C and the current density from 1 to 2 amp/dm². Prior to ruthenium plating the hard metal was given an initial flash coating of gold in an alkaline gold cyanide bath to avoid attack of the cobalt by the acid electrolyte. Ruthenium coatings of different thicknesses were produced. Tips having coatings six microns and 10 microns thick had lives three times longer than initial tips when the machining speed was 92 meters per minute.

EXAMPLE 11

The tips were electrolytically coated with osmium in an aqueous electrolyte containing 10 g/l potassium hexachlorosmate, 15 g/l potassium chloride and 60 g/l potassium hydrogen sulphate, adjusted into the pH range of 1.2 to 1.5 by potassium hydroxide. The temperature of the electrolyte was 70°C, the cathode current density from 1 to 2 amps/dm² and the anode current density less than 0.5 amp/dm². This electrolyte also attacks hard metal, so all the tips were initially flash-coated with gold. The improvement in life given by an osmium coating three microns thick at a matching speed of 67 meters per minute was three times.

EXAMPLE 12

A hard metal tip consisting of 82 percent tungsten carbide, 13 percent titanium carbide and 5 percent cobalt was electrolytically coated with ruthenium six microns thick as in Example 10. When used as in Example 10 to machine EN30B at a speed of 61 meters per minute the tip had a life three times that of a similar uncoated tip.

EXAMPLE 13

A cutting tool of high-speed steel having the nominal composition 0.8 percent carbon, 21 percent tungsten, 11 percent cobalt, 5 percent chromium, 1.5 percent vanadium, 0.5 percent molybdenum, balance iron, was coated with ruthenium four microns thick as in Example 10. To coat such steel satisfactorily is difficult, and the steel was pretreated in the same way as stainless steel to be coated with nickel. After this pretreatment a flash coating of gold was applied before the steel was coated with the ruthenium. When the coated tip was used to machine EN30B steel of 500 Hv. at 15 meters per minute, the feed at each revolution being 0.25 mm. and the depth of cut at 1.3 mm., the life was four times that of a similar uncoated tip.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. An article made of sintered hard metal consisting essentially of carbide and a metal binder, and presenting one or more working surfaces subjected to wear in use, in which in at least that part of the hard metal which presents the working surface or surfaces the binder consists of cobalt together with metal from the group of ruthenium and osmium and mixtures and alloys thereof said metal from said group being present in an amount of at least about 14.7 percent by weight based on total content of cobalt plus metal of the group, and effective to reduce friction at high temperatures at said working surface or surfaces and up to an amount equal in weight to the amount of said cobalt.

2. An article as in claim 1, being a cutting tool in which at least in the neighbourhood of the cutting edge or each such edge the binder consists of cobalt with a lesser amount of ruthenium.

3. An article as in claim 1 in which at least at the working surface or surfaces the hard metal consists of from 97 to 80 percent carbide and a binder consisting of cobalt and ruthenium, the ratio of cobalt to ruthenium by weight being at least 1.5:1 but not more than 6:1.

4. An article as in claim 1 wherein the layer of metal at the surface of the carbide mass is in a state resulting from heat treating the precious metal-containing article as 1250°C. to about 1400°C.

5. An article as in claim 4 which has been heat-treated at about 1325°C to about 1350°C.

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