An Explanation of Wettability Problems When Brazing Cemented Carbides

Alumina that forms on cemented carbide surfaces (through the oxidation of aluminum dissolved in the binder) prevents wetting

BY K. Aa. THORSEN, H. FORDSMAND, AND P. L. PRAESTGAARD

ABSTRACT. Problems encountered when brazing cemented carbide tools such as saw blades and masonry drills are often related to low wettability; the reasons for these are not well understood. Accordingly, wetting studies involving the brazing of cemented carbides were conducted wherein wettability was determined using a modified Leitz hot stage microscope. This was especially the case with carbide parts that had been sintered in hydrogen furnaces, packed in alumina sand, and suffered from low wettability.

By SEM, microprobe and auger analysis on specimens from the hot stage, the following conditions were found to lead to difficulties:

1. At the high temperature and strong reducing environment of the sintering furnace, the degree of dissociation of the Al_2O_3 of the sand according to $Al_2O_3 + 3\ H_2 \rightleftarrows 2\ Al + 3\ H_2O$ is not insignificant, and a rather high aluminum activity is achieved.

2. By diffusion through the vapor phase, aluminum is transferred to the cemented carbide, where it dissolves in the molten cobalt-binder in amounts corresponding to the activity.

3. In the cooling zone of the sintering furnace, the above-mentioned equilibrium shifts to the left, and Al_2O_3 is formed on the surface of the cemented carbide specimens. Removal of this skin will improve wettability. However, the aluminum contents of the binder is still so high that a new alumina layer that hinders wetting is formed on heating.

Treatments to improve wettability are discussed, but the ideal solution is, of course, to produce aluminum-free carbides. Reference is made to the problems that may arise from the recycling of Al_2O_3-coated carbides.

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Introduction

In the manufacture of cemented carbide-tipped tools such as circular saws for cutting wood and masonry drills, the cemented carbide bits are joined to the steel base materials by brazing. To accomplish this, torch and induction brazing involving the use of a flux, as well as furnace brazing without a flux, are being used. However, for many years the wetting of cemented carbide parts by molten brazing filler metal—usually a silver brazing alloy—has posed a problem, particularly when brazing without a flux.

Mahler (Ref. 1) points out that the sintering process influences the wettability. Carbides packed in alumina and sintered in hydrogen furnaces can present surprisingly great wetting difficulties. Nonetheless, items such as saw and drill tips are normally produced by this method.

Evaporation of cobalt from the surface in vacuum furnaces or the uptake of carbon from graphite in vacuum furnaces can also cause problems. Brookes (Ref. 2) states that, before brazing, the sintering "skin" which often contains diffused excess graphite or aluminum should be removed to provide a "key" for brazing.

According to Ruža (Ref. 3), wetting difficulties also are caused by surface contamination with oxides such as ZrO_2 and ZrW_2O_8 or with free or bound carbon. The origin of the ZrO_2 was not stated; however, a source might be the antisticking agents used for impregnation of graphite plates in vacuum furnaces. Alumina pickup also is troublesome according to Matharu (Ref. 4), who also pointed to an apparently positive effect of carbon-pickup in cobalt on the ability of a silver brazing filler metal to wet cemented carbides.

To eliminate the above-mentioned difficulties and improve wettability, cemented carbide surfaces are cleaned or modified in the following ways:

1. Mechanical cleaning by rough-grinding or shot-blasting with SiC-grit as mentioned by Brookes (Ref. 2) and Růza (Ref. 3).

2. Modification of the surface so that it consists solely of the cobalt binder. A high-temperature salt bath treatment has been described by Toney (Ref. 5). It is stated that some of the cobalt is made to migrate to the surface to form a continuous cobalt case to a depth of approximately 2.5 μm.* Also, Hirschfeld and Kolaska at Krupp (Ref. 6) developed an electrolytic method by which the carbide phase was dissolved anodically in an alkaline KOH-solution leaving a 0.1-10 μm thick spongeous cobalt layer.

3. Coating of the surface with an easily wettable material, such as nickel or cobalt, has been suggested. With this method, surface wetting by the molten braze filler metal is ensured. However, according to Mahler and Zimmermann (Ref. 1), the benefit of this procedure is in dispute, because the adhesion of the surface layer to the cemented carbide might be weak. A diffusion heat treatment might be applied to improve bonding. Also, Kalish (Ref. 7) has described how coating with iron, cobalt or nickel may be applied by PVD or by electroplat-

**1 μm = 1 micrometer (0.000001 m) = 0.001 mm = 0.000039 in.*

Table 1—Cemented Carbides Used For Wetting Experiments

A	93		7	Fine
B	93	2	5	Fine
C	94		6	Coarse
D	92		8	Coarse
E	63.6	26.4	10	Medium

[a]WC—tungsten carbide; TiC/TaC—titanium carbide/tantalum carbide; Co—cobalt

Table 2—Wetting Angles of Hydrogen Sintered Carbides, deg

	Silvery surfaces		Dull dark grey surfaces	
Grade	Sintered	Polished	Sintered	Polished
A	50	85	106	81
B	71	81	94	102
C	[a]	[a]	108	100
D	[a]	[a]	120	99
E	116	110	119	100

[a]A silvery surface was not found on these grades.

ing. Electroless cobalt-plating is described by Ritsko (Ref. 8).

4. Thermo-chemical treatments of the cemented carbides have been suggested. Oxidation and pickling are recommended by Tengler (Refs. 9, 10). The cemented carbide is kept for a short time at 850–900°C (1562–1652°F) in air; the oxides formed at the surface are dissolved in a boiling alkaline NaOH-solution at 120–140°C (248–284°F). Beginning with Mahler and Zimmermann (Ref. 1), heat treatment for ½ h at 700–900°C (1292–1652°F) in a hydrogen atmosphere has been reported by several sources to improve the brazeability. According to Sawashima and Sugawara (Ref. 11), the effect of this type of treatment can be traced back to the fact that carbon-contamination on the surface is removed as CH_4.

The literature survey discussed here led to the conclusion that there was inadequate information on the problem and lack of an explanation on the fundamental mechanisms behind the wetting difficulties. There was a further discrepancy between the problems described and the fact that Ramqvist (Ref. 12) found massive tungsten carbide (WC) to be easily wettable by molten copper, with wetting angles of 10-25 deg being obtainable; moreover, Gilliland and Adams (Ref. 13) reported wetting of cemented carbides by copper to be almost instantaneous.

As a consequence of inadequacies and discrepancies in the literature, it was decided to launch an investigation, the results of which are reported in this paper.

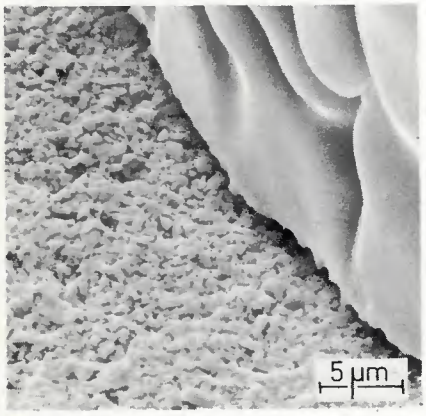

Fig. 1—SEM of poor adhesion of solidified copper droplet to surface of grey sintered grade A cemented carbide

Experimental Procedures

Methods

The cemented carbides used for the investigations were sintered either in a hydrogen furnace working with pure H_2, graphite boats and packing in alumina, or in a vacuum furnace. The wetting of the surfaces by copper that was used as brazing filler metal was studied using a Leitz 1750 hot stage microscope. The processes were observed in a stereo microscope or through the camera of macro-photographic equipment mounted on the hot stage. The method has been described in detail elsewhere (Ref. 14).

During the experiments the stage was flushed with pure hydrogen at a pressure of 1 atm. The copper was normally kept molten only for ½–5 min; this was found to be sufficient to be able to decide whether the specimen could be wet or not. The temperature was recorded for only a few of the experiments, since this variable was found not to be of primary importance.

Crucible and tube furnaces were used for salt bath treatments and experiments requiring controlled oxidation. Alumina crucibles proved to be suitable containers for the molten salts. Scanning electron microscopy, microprobe analysis, and, in a single case, auger-analysis were used for examination of the specimens after the wetting test. Wetting angles were measured after the experiments using an optical microscope with a rotating specimen stage.

Materials

The cemented carbides listed in Table 1 were utilized during the investigation. Furthermore, the following materials were also used:

1. Electrolytic cobalt.
2. A plate of tungsten with a surface layer of tungsten carbide made by carburization.
3. Copper with 1% of silver and OFHC copper as brazing filler metals; no difference in wetting ability was found between the two materials.
4. 99.99 vol-% hydrogen with the following impurities (maximum):

H_2O .... 5 ppm
N_2 .... 100 ppm
O_2 .... 3 ppm

Results

Wetting of Hydrogen Sintered Cemented Carbides

The cemented carbides from the hydrogen sintering furnace had different appearances in the as-sintered state; these were classified as a bright silvery group and a dull dark grey group. Surface structure investigations on the SEM revealed that the surface of the former type mainly consisted of cobalt, and of the latter type mainly of tungsten carbide. In order to eliminate the influence of different surface conditions, a set of samples were rough-ground and polished with diamond to expose the intrinsic structure of the cemented carbide to the molten copper brazing filler metal.

The cemented carbides were tested in the sintered as well as in the polished state. After having been in contact with molten copper containing 1% silver for 30 seconds(s), the specimen was cooled and the wetting angle measured. Prolonged contact time did not change the results. The wetting angles of this series of experiments are shown in Table 2.

SEM examination revealed that copper does not really wet the dull dark grey sintered surfaces very well. Figure 1 demonstrates the bad contact between the

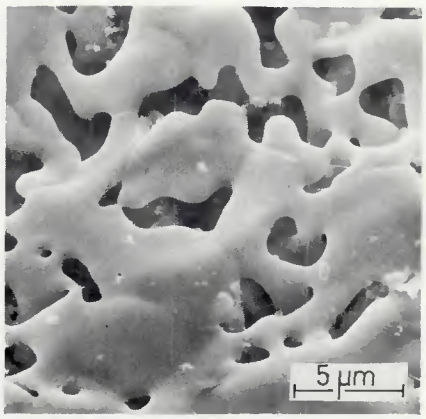

Fig. 2 — SEM of surface of grade C carbide after treatment in molten $CaCl_2$. The cobalt network has been transformed to rounded aggregates by solid-phase sintering

foot of a solidified copper droplet and the totally tungsten carbide dominated surface of a grade A cemented carbide. The titanium carbide-containing grade had big wetting angles in any case.

Solidified copper droplets with contact angles of about 90 deg could usually be pulled up from the carbide surface with ease, without leaving any copper sticking to the carbide. Inspection of the contact area by SEM showed the existence of a very few and small copper "feet" that had been torn, leaving ductile fracture wedges sticking up from the carbide.

Apparent partial wetting of cemented carbide surface thus did not necessarily imply the establishing of metallic contact over the total area covered. Grinding and polishing appeared to provide no direct improvement; wetting behavior might be said to have become more homogenous after this treatment, with angles of 80–100 deg being found. Sandblasting was also tested but was found not to have any effect on wetting behavior.

In order to study the effect on wetting of transforming a surface consisting of

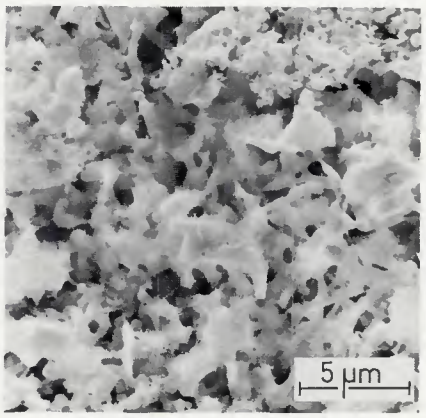

Fig. 3 — SEM of surface of grade C carbide after electrolytic dissolution of tungsten carbide. Remaining spongeous skeleton of cobalt binder

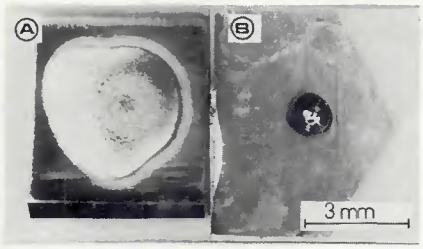

Fig. 4 — View after wetting tests on cut surfaces. A — vacuum sintered grade B carbide; B — hydrogen furnace sintered grade C carbide

tungsten carbide into one of cobalt, surface treatments discussed by Toney (Ref. 5) as well as Hirschfeld and Kolaska (Ref. 6) were tested.

Salt Bath Treatment of Hydrogen Sintered Cemented Carbides

Treatment at 1180°C (2156°F) in molten $CaCl_2$ of grade C specimens, originally with dull dark grey surfaces, produced perfect wettable surfaces. On the basis of loss of weight measurements, it was found that about 4 µm of surface was removed in 10 min.

The surface structure of the cemented carbide after the salt bath treatment is seen in Fig. 2. The tungsten carbide has probably been oxidized and, simultaneously, the oxides have been dissolved in the molten salt. The remaining former intercarbidic network of cobalt binder has sintered together into rounded aggregates by solid-phase sintering.

When close-packing the specimens, surfaces shielded from the salt were unchanged. Thus, the effect of this treatment can apparently be traced back to a chemical effect of the salt and is not only a physical effect.

Electrolytic Dissolution of Tungsten Carbide from Hydrogen Sintered Cemented Carbides

Anodic dissolution of the tungsten carbide in a grade C cemented carbide in an alkaline solution of 4 n. NaOH at 300 mV SCE produces a dark grey surface. The remaining spongeous skeleton of cobalt binder is seen on Fig. 3.

After two hours of electrolysis, the tungsten carbide had been dissolved to a depth of about 5 µm. Then satisfactory but rather slow wetting was found to have occurred, and the end result was a wetting angle of 20-30 deg.

Dross on the surface of the solidified copper-droplet contained titanium, aluminum and tungsten.

Comparison Between Vacuum and Hydrogen Sintered Cemented Carbides

Vacuum sintered cemented carbides were easily but slowly wetted after a slight sandblasting, even if they originally had a dark grey surface. This was in contrast to the hydrogen sintered carbides.

Cemented carbides of grade C from the hydrogen sintering furnace and of grade B from the vacuum furnace were cut through with a diamond saw, and the surfaces of the cuts tested for wetting. Figure 4 demonstrates the very different behavior of the two specimens as seen after the experiment. Wetting of the vacuum sintered specimen (Fig. 4A) is perfect but slow. On the hydrogen sintered specimen (Fig. 4B) the wetting angle exceeded 90 deg.

A surface of pure tungsten carbide was tested and behaved very much like the vacuum sintered surface. After being passed through the hydrogen sintering furnace, pure tungsten carbide still showed very good wetting behavior. Pure cobalt wetted perfectly.

Microprobe-analysis on the polished surfaces of the cuts at this stage of the investigation pointed to the following differences in the aluminum contents between the interior of the various specimens: vacuum sintered carbide — 0% Al; hydrogen sintered carbide — 0.07% Al; hydrogen sintered carbide after being heated to about 1200°C (2192°F) — 1.84% Al.

The rise in the Al contents due to the heating can only be explained by the formation of an alumina layer due to selective oxidation of Al diffusing to the surface from the bulk material.

Aluminum in Cemented Carbides

Tungsten, cobalt, oxygen and graphitic carbon were found in a freshly polished surface of a cut in hydrogen sintered grade C cemented carbide that was subjected to auger analysis. The O- and C-signals stemmed from contamination of the surface. After brazing at about 1200°C (2192°F), a similar surface contained small amounts of tungsten and cobalt but large amounts of aluminum and oxygen. The aluminum was in its oxidized state.

A depth profile revealed that the Al_2O_3 layer was about 180 nm* thick and that the aluminum- and oxygen-signals were completely absent from 210 nm inwards. The profile is shown on Fig. 5. The high cobalt-intensity on the uttermost 50 nm may be caused by copper contamination of the surface from copper vapors from the molten brazing filler metal droplet present on the specimen during heat treatment. Secondary lines from copper can coincide with the primary line of cobalt.

**1 nm = 1 nanometer = 1×10^{-9} m = 1×10^{-6} mm = 4×10^{-8} in.*

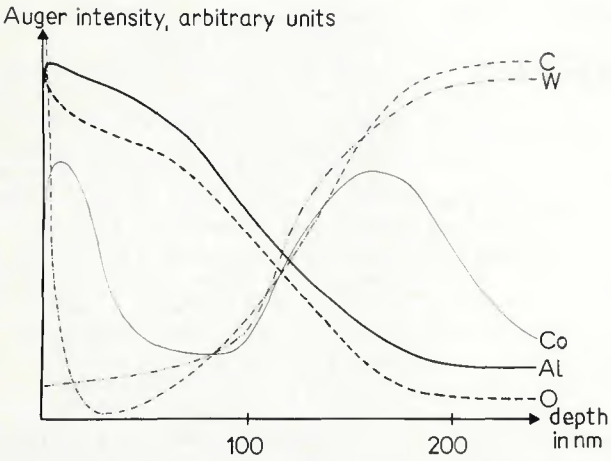

Fig. 5 — Auger analysis depth profile of grade C carbide showing oxide layer being formed on original polished surface by heating to 1200°C (2192°F) in hydrogen

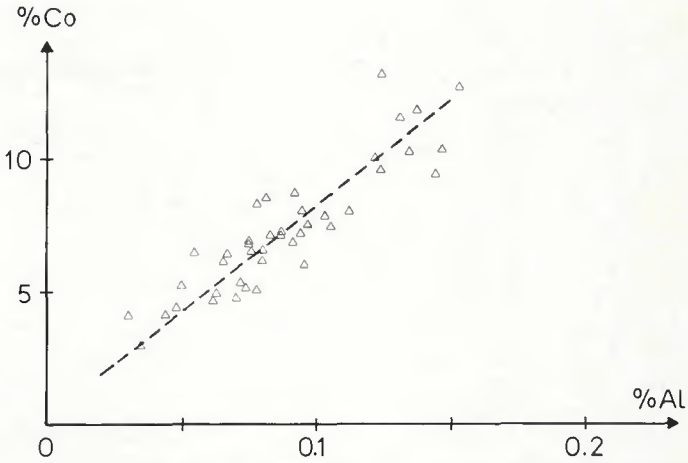

Fig. 6 — Spot analysis by microprobe on polished surface of grade C carbide. Interdependence between cobalt and aluminum indicate that aluminum is dissolved in the binder

Spot analysis by the microprobe on a specimen of grade C pointed to a connection between the concentrations of cobalt and aluminum as shown on Fig. 6. The microstructure of the specimen consisted of the two phases, tungsten carbide and cobalt, and was coarse. Consequently, the focused electron beam of the microprobe hit areas with different cobalt contents; this is the reason for the variation in cobalt contents seen in Fig. 6.

The connection between the contents of aluminum and cobalt indicate that the aluminum in the cemented carbides is dissolved in the binder. The slope of the curve points to an aluminum content in the binder of about 1.2 wt-%. This value only applies to the specimen that was made object of the analysis and cannot be considered a general value.

By heat treating grade C specimens in graphite at 1090 and 1210°C (1994 and 2210°F) for 18 h, aluminum (but not cobalt and tungsten) was oxidized. Aluminum diffused through the binder phase of the cemented carbide to the surface where it was oxidized to Al_2O_3. An aluminum profile made by the microprobe from the surface inwards after heat-treating at 1090°C (1994°F) is seen in Fig. 7; it demonstrates the draining of aluminum from the carbide.

Calculations on the basis of a limited amount of experimental results point to diffusion constants of the following magnitudes:

$D_o = 9.4 \cdot 10^{-4}\ m^2/s$ and $Q = 270$ kJ/mol.

Combination of the above experimental evidence points to the fact that the serious wetting problems often met with cemented carbides sintered in hydrogen furnaces can be traced back to contamination of the binder phase with aluminum. The aluminum is found throughout the material and is not restricted to the surface alone.

The most probable source of the aluminum is the packing sand. At the high temperature and strongly reducing environment of the high-temperature zone of the sintering furnace, aluminum is generated in the metallic state by dissociation of Al_2O_3 according to:

$$Al_2O_3 + 3H_2 \rightleftarrows 2\ Al + 3\ H_2O$$

A partial pressure of aluminum is built up corresponding to the aluminum activity. Aluminum is absorbed by and dissolved in the molten binder and completely penetrates the small specimens that are normally produced by this method. Thermodynamic calculations were carried out to verify the experimental evidence.

Thermodynamics of Aluminum Activity During Sintering at 1400°C in Hydrogen Furnaces

Based on equilibrium conditions, which were thought to be a fairly good approximation, the activity of aluminum in the metallic state was calculated. Some quantities were presumed to be stable in that the activities of Al_2O_3 and carbon are both equal to unity since alumina and graphite are present. The partial pressure of hydrogen was 1 atm.

The activities of metal carbides and oxides can be found as functions of the oxygen potential on the basis of the equilibrium constants:

$$H_2 + \tfrac{1}{2}O_2 \rightleftarrows H_2O \qquad K_{H_2O} = 6.74 \cdot 10^4$$
$$C + \tfrac{1}{2}O_2 \rightleftarrows CO \qquad K_{CO} = 1.2 \cdot 10^8$$
$$C + O_2 \rightleftarrows CO_2 \qquad K_{CO_2} = 2.27 \cdot 10^{12}$$

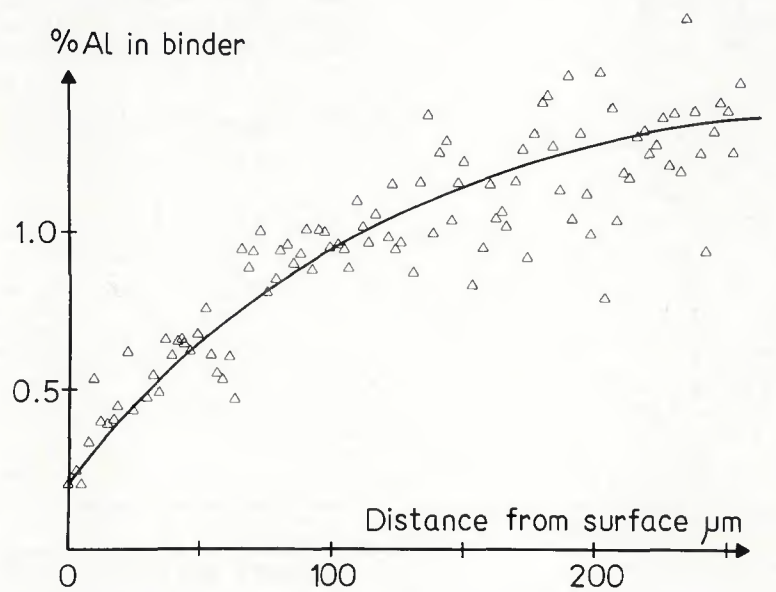

Fig. 7 — Spot analysis by microprobe. Aluminum profile at surface of grade C carbide after selective high-temperature oxidation of aluminum

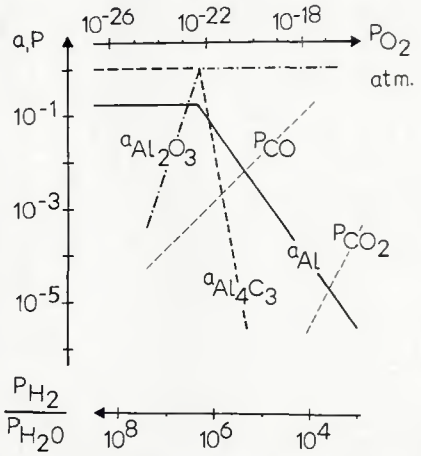

Fig. 8 – Double-logarithmic plot of calculated activities at 1400°C as functions of P_{O_2}. Representative of the chemical environment of the high-temperature zone of a hydrogen sintering furnace

$$2\ Al + \tfrac{3}{2}O_2 \rightleftarrows Al_2O_3 \quad K_{Al_2O_3} = 3.55 \cdot 10^{35}$$
$$4\ Al + 3\ C \rightleftarrows Al_4C_3 \quad K_{Al_4C_3} = 1.98 \cdot 10^{3}$$

The equilibrium constants are calculated by application of:

$$\Delta G^\circ = -RT \ln K$$

ΔG° values are presented in handbooks (Refs. 15, 16) as functions of temperature. With $2\ Al_L + \tfrac{3}{2}O_2 \rightleftarrows Al_2O_{3,S}$ as an example, $\Delta G^\circ = -407{,}950 - 6.19 \cdot T \cdot \log T - 0.78 \cdot 10^{-3} \cdot T^2 + 3.935 \cdot 10^5 \cdot T^{-1} + 102.37 \cdot T$ cal/mol.

As an example of activity (a), calculations in the aluminum-carbon-oxygen system at 1400°C, Al_2O_3 and Al_4C_3 will have the same activity when $a_{Al_2O_3} = a_{Al_4C_3} = 1$.

This occurs when:

$$P_{O_2} = \left[\frac{K_{Al_4C_3}}{K_{Al_2O_3}^{\ 2}}\right]^{1/3} = 2.5 \cdot 10^{-23}\ \text{atm}$$

At lower values of P_{O_2}, $a_{Al_4C_3} = 1$, and thus:

$$a_{Al} = (K_{Al_4C_3})^{-1/4} = 0.15 \text{ and:}$$

$$a_{Al_2O_3} = \frac{K_{Al_2O_3} \cdot P_{O_2}^{\ 3/2}}{\sqrt{K_{Al_4C_3}}}$$

At higher values of P_{O_2}, $a_{Al_2O_3} = 1$, and thus:

$$a_{Al} = [K_{Al_2O_3} \cdot P_{O_2}^{\ 3/2}]^{-1/2} \text{ and}$$

$$a_{Al_4C_3} = \frac{K_{Al_4C_3}}{K_{Al_2O_3}^{\ 2} \cdot P_{O_2}^{\ 3}}$$

A double-logarithmic plot of the activities as functions of P_{O_2} will produce straight lines as seen on Fig. 8. A correction for the fact that the total pressure cannot exceed 1 atm would only give insignificant changes.

Since P_{CO} is not expected to exceed 0.1 atm and aluminum-carbide is not formed in the furnace, it is a realistic assumption for sintering in a hydrogen furnace at 1400°C (2552°F) that the partial pressure of oxygen is in the range 10^{-22} to 10^{-18} atm. In this range, the activity of metallic aluminum is from 10^{-1} to 10^{-4} with the activity of pure aluminum in the liquid state as unity. The solubility of aluminum in cobalt is about 10 wt-% at 1400°C (2552°F). Thus, it is realistic to assume that aluminum will go into solution in the molten binder in an amount corresponding to the thermodynamic activity of aluminum in the immediate environment.

Given calculations for an ideal solution as a first approximation, aluminum contents of an order of magnitude from 0.005 to 5 wt-% should be found. Existence of the intermediate aluminum-cobalt phase in the aluminum-cobalt system indicates, however, that the activity coefficient is less than unity. The concentrations of aluminum might thus be higher than those stated above.

The transport mechanism for aluminum from Al_2O_3-sand to carbide would probably be diffusion in the vapor phase. Pure aluminum having a vapor pressure at 1400°C (2552°F) of about 13 N/m², 2.7 to 2.7 · 10^{-3} N/m² of aluminum pressure could be expected.* By way of comparison it may be mentioned that the pressure of pure Al_2O_3 at 1400°C (2552°F) is 0.2 N/m² and of pure cobalt about 0.1 N/m². The vapor pressure of aluminum thus seems to permit ample transport by vapor phase diffusion.

Aluminum Activity in Al_2O_3 as a Function of Temperature for $a_C = 1$, and $P_{H_2} = 1$ atm

On the basis of variation of $K_{Al_2O_3}$ with the temperature, this function was calculated for different values of P_{CO} and the results are displayed in Fig. 9. The stabilization of Al_2O_3 with decreasing temperature is clearly seen.

Design of an Optimum Surface Treatment Process on Basis of Acquired Knowledge

Consideration of the investigative results described previously logically lead to certain steps for achieving an optimum surface treatment; these are:

1. Removal of Al_2O_3 from the surface. Pickling in strong alkaline solution would be necessary.
2. Removal of aluminum in the carbide immediately under the surface. Treatment at high temperature would be necessary to bring about diffusion of the aluminum, and the oxidation potential should be powerful enough to oxidize aluminum. Thereafter, pickling is to be recommended as in step 1 above.
3. Removal of the tungsten carbide of the surface layer. Although this constituent is wettable, it leads to the wetting being slow. The oxidation potential should be kept powerful enough to oxidize tungsten carbide. Pickling in a strong alkaline solution would remove the oxidation products.
4. No attack on cobalt either at high-temperature oxidation or during pickling.
5. The largest surface area possible to provide as large a driving force for wetting as possible.

Thermodynamic calculations showed that an atmosphere of hydrogen with a dew point of 90-95°C (194-203°F) would oxidize tungsten carbide but not cobalt. On this basis, the following treatment was thought to comply with the above-mentioned demands:

1. Heating at 1000°C (1832°F) for 1 h

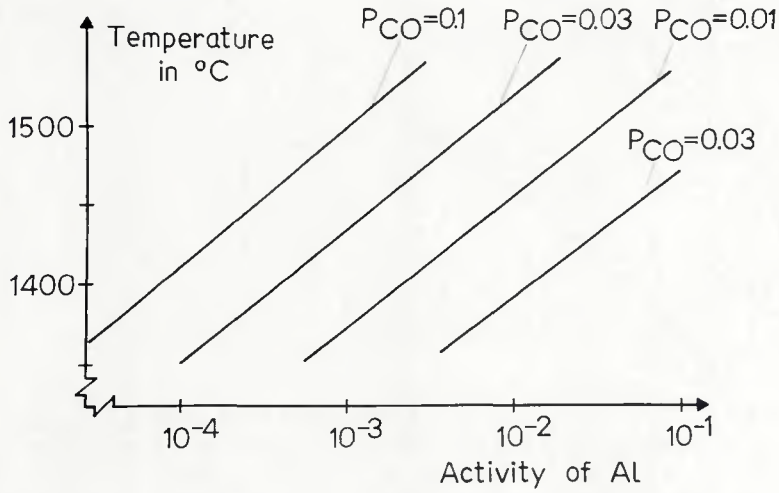

Fig. 9 – Aluminum activity in Al_2O_3 as functions of temperature and P_{CO} for $a_C = 1$ and $P_{H_2} = 1$ atm

**1 N/m² = 1 Pa and 1 psi = 1 Pa ÷ 6895, or psi = 0.000145 Pa*

in hydrogen with a dew point of 90-95°C (194-203°F).

2. Pickling in molten NaOH (melting point of 318°C, *i.e.*, 604°F) followed by a water rinse.

The surface of a grade C specimen treated for 315 min at 1000°C (1832°F) in H_2 with a dew point of 90°C (194°F) and then pickled as described above has the structure shown on Fig. 10. The structure consists of weakly agglomerated small cobalt crystals with diameters of ½-1 μm and is very different from the structure obtained by salt bath treatment—Fig. 2. This might be ascribed to the metal oxides formed during oxidation by the wet hydrogen; these remain on the surface and impede the sintering of the cobalt network that remains embedded in oxides till the pickling. It was found that the tungsten carbide was oxidized at a rate of 1-3 μm/h. In addition, wetting was unique. The surface was wetted instantaneously when the melting point of copper was reached, and the designed method came up to expectations fully.

Summary and Discussion of Results

In the investigation described in this paper, attention focused on the significant thermodynamic instability of alumina at high temperatures. This phenomenon was found to offer a good frame for a theory of the mechanisms leading to the poor wettability encountered when brazing cemented carbides.

In the high-temperature zone of the hydrogen sintering furnaces, the alumina in the packing sand dissociates to some degree according to the equation:

$$Al_2O_3 + 3\ H_2 \rightleftarrows 2\ Al + 3\ H_2O.$$

At this stage of the sintering process, the binder is molten and metallic aluminum is dissolved in the binder and will diffuse into the material along the path formed by the binder. However, in the cooling zone of the hydrogen sintering furnace the above-mentioned equilibrium shifts to the left, and alumina is formed on the surfaces of the cemented carbides. The Al_2O_3 found on these surfaces is not simply packing sand sticking to or picked up by the surface. Instead, it is alumina bonded directly on the surface by the partial oxidation of aluminum diffusing to the surface from the cemented carbide beneath the surface.

Not all aluminum is consumed during passage through the cooling zone. A fair amount still remains in solution in the binder. Even if the specimen is cleaned, a new Al_2O_3 layer can, therefore, be formed on the surface during heating to the brazing temperature.

The reduction and re-formation of Al_2O_3 are primary factors relative to wetting barriers. Other factors, such as carbon and titanium carbide, are secondary. In the investigation described here no reaction could be traced to such secondary effects.

Irrespective of the fraction of the surface covered by tungsten carbide, hydrogen sintered carbides with raw sintered or polished surfaces exhibited wetting angles of 50-120 deg. These were much too large when compared with the perfect wettability of Co and the wetting angle of 20-30 deg found on pure tungsten carbide.

The original surface of vacuum sintered cemented carbides, which could not absorb aluminum during processing, showed a wettability very similar to that of pure tungsten carbide. On cuts through hydrogen and vacuum sintered cemented carbides, the same results as on the outer surfaces were found.

Using microprobe analysis, no aluminum was found in the vacuum sintered cemented carbide. However, there was about 0.07 wt-% in the hydrogen sintered carbide, and in the latter 1.84 wt-% of aluminum was found after heating to the brazing temperature of about 1200°C (2192°F). The last result can only be explained by the formation of an Al_2O_3 layer on the surface due to selective oxidation. Auger analysis confirmed the existence of such a layer, the thickness of which was found to be about 180 nm.

Spot analysis by the microprobe revealed that metallic aluminum dissolved in the cemented carbide was to be found in the binder phase of cobalt. This was in agreement with the fact that, after passing through the hydrogen sintering furnace packed in alumina, pure tungsten carbide exhibited a wetting angle of 20-30 deg. Tungsten carbide simply cannot dissolve metallic aluminum or Al_2O_3. After several hours of selective oxidation at high temperatures of aluminum, a concentration gradient of aluminum could be measured by the microprobe and the diffusion constants could be calculated.

The experimental evidence was confirmed by thermodynamic calculations based on equilibrium conditions in the high-temperature zone of a hydrogen sintering furnace. The activity of aluminum in the metallic state at 1400°C (2552°F) due to decomposition of Al_2O_3 was calculated to be 10^{-4} to 10^{-1}. At the same time the vapor pressure of aluminum and the solubility of aluminum in cobalt reached such magnitudes that unexpectedly high concentrations of aluminum could be found in the cobalt binder.

The substantial variation in the activity of aluminum (caused by relatively minor fluctuations of the partial pressure of oxygen in the sintering furnace) might be reflected in a substantial disparity between the products from various

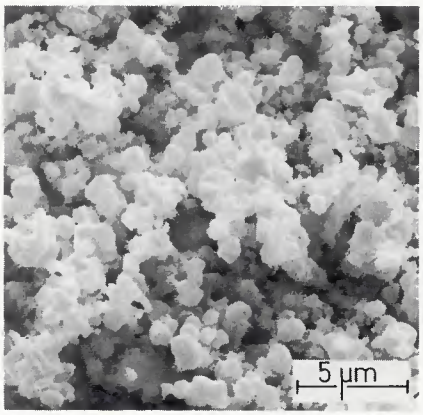

Fig. 10—SEM of surface of grade C carbide after 315 min at 1000°C (1832°F) in wet hydrogen and pickling in molten NaOH. Weakly agglomerated ½-1 μm cobalt crystals

sources. The activity of aluminum is diminished by about one half for each 25°C (45°F) reduction of the sintering temperature. This circumstance too must be taken into consideration when trying to understand regular practice.

The use of cemented carbides with high cobalt contents is generally considered beneficial as seen from a brazeability point of view. Apart from the better and more rapid wetting of cobalt, such grades are sintered at lower temperatures, *i.e.*, at lower aluminum activities.

Some practical consequences of the investigation described here are outlined below. Wetting problems may be of minor importance when brazing with a flux. When selecting flux, however, it might be advantageous to have the possible existence of an Al_2O_3 layer in mind.

Brazing without a flux can be more of a problem. Here great differences in the wettability can be found; as already mentioned these can sometimes be traced back to the sintering conditions (partial pressure of oxygen, temperature).

In cases of poor wettability, various surface treatments have been referred to in the literature. One of these is mechanical cleaning. Here, rough grinding would take away all alumina on the surface, although sandblasting would probably leave some alumina especially in the gaps between the tungsten carbide grains. In any case, problems could arise due to renewed formation of Al_2O_3 during heating to the brazing temperature. Moreover, the experiments described here indicate that mechanical cleaning is inadequate.

Modification of the surface to consist solely of the binder metal is more successful. By salt bath treatment at high temperatures, tungsten carbide and aluminum from the binder are oxidized and the oxides simultaneously dissolved in the molten salt. The cobalt binder is left

untouched and is gradually transformed to rounded aggregates by solid-phase sintering. The surface obtained is easily wettable. Statements that Co migrates to the surface cannot be confirmed.

Electrolytic dissolution of the tungsten carbide leaves the cobalt network with its original structural and chemical composition. Experiments showed this kind of a surface to be reasonably well wetted; however, the aluminum dissolved in the cobalt clearly has an unfavorable influence. The coating of surfaces with nickel or cobalt by galvanic processes, or otherwise, creates easily wettable surfaces. However, there is the risk that the adhesion of the coating to the cemented carbide may be weak, especially if there is an intermediate layer of alumina between the cemented carbide and the coating.

A thermo-chemical method such as heat treatment in air followed by pickling in alkaline solutions must be considered to have unpredictable effects in that aluminum, tungsten carbide and cobalt can be oxidized. Heating in hydrogen would oxidize the aluminum and create a continuous layer of alumina on the surface; this would certainly not promote the wettability..

As a result of the investigation described here, a surface treatment was designed to create a surface consisting solely of very fine-grained cobalt without aluminum. This was achieved by heat treatment in wet hydrogen, followed by pickling in molten NaOH. With this method perfect and instantaneous wetting was obtained on previously virtually nonwettable cemented carbide.

As already mentioned and apart from the influence of aluminum, secondary effects that might have an adverse effect on wettability have been described in the literature. One of these has been the carbon contents of the cobalt binder of the cemented carbides. Where the carbon contents of the cobalt may be thought to be a deleterious factor, then there is a possibility that—in reality—tungsten is the decisive factor, because the two elements are interlocked by the solubility product. No reaction in the investigation described here could be traced to such secondary effects, however. It might be added that, when looking for a possible secondary effect, it will be absolutely essential not to have aluminum present in the cemented carbide since this might easily put such secondary effects completely into the shade.

Finally, the possible problems posed by aluminum may have to be taken into consideration when recycling carbides. Alumina-coated indexable inserts entering recycling processes might contaminate the carbide powder from the recycling plant with alumina; this might later create unexpected brazing troubles.

Conclusions

The results of the investigation allow the following conclusions to be made:

1. Poor wettability when brazing cemented carbides sintered in hydrogen furnaces is primarily caused by metallic aluminum dissolved in the cobalt binder of the cemented carbides.

2. The source of the aluminum causing poor wettability is the alumina packing sand normally used in such furnaces. At the high temperature and strongly reducing environment of the high temperature zone of the furnace, the equilibrium position of $Al_2O_3 + 3\ H_2 \rightleftarrows 2\ Al + 3\ H_2O$ shifts to the right, causing a not insignificant activity of aluminum. The aluminum content corresponding to the activity is built up in the molten binder.

3. Minor reductions in the partial pressure of oxygen will cause a substantial increase in aluminum activity a_{Al}. Reduction of the sintering temperature will reduce
a_{Al}. Large variations in the aluminum contents of cemented carbides can thus be expected dependent on sintering practice.

4. On cooling in the sintering furnace the equilibrium, described in Conclusion 2 above, shifts to the left, and Al_2O_3 is formed on the surface of the cemented carbides by the reaction between aluminum from the cemented carbides and oxygen from the surrounding atmosphere. The alumina of the sintering "skin" is either completely or partially formed by in-situ growth; it is not merely packing sand sticking to or picked up by the carbide.

5. After cooling in the furnace, a fair amount of aluminum still remains in solution in the binder. Even if the specimen is cleaned, new Al_2O_3 layers can be formed on the surface during heating to the brazing temperature.

6. The surface layers of Al_2O_3 constitute severe wetting-barriers, especially when brazing without a flux. The barrier effect will be neutralized—at least partly—when using a flux.

7. Mechanical cleaning by grinding or sandblasting will clean the surface at least partially. However, it is considered inadequate since renewed formation of Al_2O_3 during heating has been found to prevent wetting.

8. Salt bath treatment will oxidize tungsten carbide as well as aluminum from the binder and dissolve the oxides leaving a surface of cobalt. Substantial improvement in wettability has been found.

9. Electrolytic dissolution takes away the tungsten carbide phase, leaving the cobalt binder with its contents of aluminum. Reasonably good wettability is achieved. However, the unfavorable influence of the aluminum is still observed.

10. Other surface treatments are mentioned in the literature but have not been tested in the investigation described in this paper. However, comment on them is as follows:

(a) The benefit of coating with nickel or cobalt is in dispute, because the adhesion of the coating to the carbide might be weak, especially if there is an intermediate layer of alumina.

(b) By heating in hydrogen no immediate improvement in wettability could be expected. Alumina cannot be reduced by the dew points and temperatures prevalent during such treatments.

(c) High-temperature oxidation in air followed by alkaline pickling must be expected to have unpredictable effects.

11. A procedure has been designed where the carbides are heat treated at 1000°C (1832°F) in wet hydrogen followed by pickling in molten NaOH. Tungsten carbide and aluminum are oxidized and removed, leaving behind a surface layer of fine-grained cobalt. Unique wetting properties are obtained.

12. Apart from the influence of aluminum, secondary effects having their origin in free or bound carbon, etc., might come into play according to the literature. When sintering in vacuum furnaces where there is no contact with alumina during processing, such secondary effects might be detected; however, in the present investigation no such secondary effect could be traced, although vacuum sintered specimens were tested as well.

13. Attention is called to the risk that powder, which is produced by recycling of cemented carbides, may be contaminated with alumina from coated tools; for this reason brazing troubles might arise.

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WRC Bulletin 296
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Fitness-for-Service Criteria for Pipeline Girth-Weld Quality
By R. P. Reed, M. B. Kasen, H. I. McHenry, C. M. Fortunko and D. T. Read

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WRC Bulletin 292
February, 1984

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