Wear-Resistant WC Composite Hard Coatings by Brazing

J. Bao, J.W. Newkirk, and S. Bao

(Submitted February 10, 2004)

A wear-resistant tungsten carbide/copper (WC/Cu) brazing alloy coating was deposited onto a steel substrate by high-temperature furnace brazing. Compared with other hard surfacing processes, much larger WC particles could be used to make a metal layer with higher wear resistance. ASTM G-65 wear test results for the brazed composite coating showed a higher wear resistance when compared with some WC-Co hard coatings that are commonly used. In this paper, the brazing alloy, the brazing process, and the after-brazing heat treatment are studied. The microstructure of the brazing alloy and the as-deposited coating were characterized, and no significant porosity was found. A good metallurgical bond was formed at the WC/Cu alloy interface and at the composite coating/substrate interface. Little or no dilution was observed. The bond strength between the Cu alloy and substrate is also much higher than for a thermal spray coating.

Keywords copper brazing alloy, furnace brazing, tungsten carbide, wear-resistant coating

1. Introduction

Surface coating techniques have been developed and widely used in industries to improve service lifetimes through applying a layer with superior physical or mechanical properties than the underlying substrate. Numerous surface coating techniques, including thermal spray, chemical and physical vapor deposition, and laser beam cladding have been widely used in various applications. Each coating technique has its own specific use area. Thermal spraying, thermal welding, and laser cladding are common methods to improve the surface wear characteristics of materials by depositing relatively thick coatings (i.e., several millimeters).[1] Thermal spray techniques consist of spraying the substrate with a molten stream of particles at high speeds. A mechanically bonded coating is formed, and the bond strength is approximately 30-50 MPa at best. [2] A stronger metallurgical bond between the coating and the substrate is formed during thermal welding and/or laser cladding. However, there is a high dissolution of the substrate material by the coating due to the high energy input needed for melting both the powder and the substrate. Residual stresses and distortion of the work piece are unavoidable due to the high temperature, rapid cooling, and nonuniform temperature field generated during the process. Therefore, it is significant to explore alternative wear-resistant coating processes that might lead to better performance at lower costs.

Recently, studies have been conducted on a brazing process as a means to deposit thick coatings. [2,3] Brazing is a traditional process of joining metals or ceramics by melting a filler metal. The substrate is wetted by the filler metal, and a good metallurgical bond is formed. The brazing temperature is less than

This paper was presented at the 2nd International Surface Engineering Congress sponsored by ASM International, on September 15-17, 2003, in Indianapolis, Indiana, and appeared on pp. 592-96.

J. Bao and J.W. Newkirk, Department of Metallurgy, University of Missouri-Rolla, Rolla, MO 65401; and S. Bao, Shijiazhuang Iron & Steel Corp., Mechanical Department, Hebei, 050051 People's Republic of China. Contact e-mail: jbao2000@yahoo.com.

the melting point of the substrate, and the cooling rate after the brazing process is slow. As a result, there is little dissolution of the substrate or creation of residual stresses. The coating can also be deposited on a curved surface, in addition to flat surfaces, and is well suited for depositing the coating over large surface areas. A much thicker coating can be readily deposited so that the wear protection can last longer in comparison to the other coating techniques.

Composite coatings with WC as the hard phase and alloys with good toughness are used extensively for numerous wearresistant applications. Several factors, such as carbide grain size or carbide volume fraction, play important roles in determining the wear performance of the coatings. The wear mechanism for WC composite layers has been shown to involve the extrusion of the binder phase, leaving the carbide grains unsupported. This subsequently leads to fracture. [4,5] The relationship between the abrasive grit size and the dimensions of the composite microstructure is also important to overall wear behavior. [6,7]

In this study, a mixture of different sized WC powders was deposited onto a low carbon steel substrate by the Cu alloy brazing process. Relatively large WC particles (i.e., up to 850 µm) were used as the reinforcements. The compact was then infiltrated with a Cu brazing alloy with good toughness. A composite coating was formed that bonded firmly with the base metal. The as-deposited coating was then evaluated by mechanical and abrasive wear tests and compared with some commonly used WC-Co coatings.

2. Experimental Study

During the abrasion wear process, small WC particles can be pulled from the matrix after the binder around them has been worn away. Better abrasion resistance is expected by using relatively larger WC particles. Smaller WC particles are also added to create a higher carbide volume fraction in the composite layer. A mixture of WC powder in 20-30 mesh range (57%) is combined with WC powders in the 40-60 mesh (29%) and 60-80 mesh (14%) ranges. This creates a composite with a relatively larger average particle size with a more carbide compacted microstructure when compared with other carbide mixture ratios.

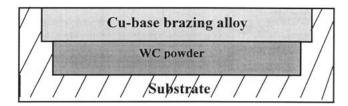


Fig. 1 Schematic illustration of an assembled specimen's cross section before brazing

The coating quality depends on the properties of the brazing alloy to a great extent. The brazing alloy bonds with the substrate due to thermal diffusion, so a good wetting brazing filler alloy is required to keep WC bonded firmly to the substrate. Because Cu and iron (Fe) can partly dissolve in each other, the wettability of Cu on a steel surface and its ability to fill gaps are well known. Therefore, Cu was chosen as the base filler metal. Nickel (Ni) was added to improve the high temperature strength and wettability. However, it also raised the melting point of the brazing alloy. Manganese (Mn) was then added to form a low melting point solid solution with Cu and to provide additional solid solution strengthening. A small amount of silicon (Si) was added to reduce the surface tension of the alloy, thereby improving metal flow characteristics. Thus, a Cu-Mn-Ni-Si brazing alloy was developed with the following composition (vol.%): Cu balance, Mn 19%, Ni 21%, and Si 0.4%. The melting temperature of the brazing alloy is approximately 1050 °C.

Brazing was carried out in a high-temperature furnace. A mold was made of low carbon steel according to the required geometry and desired coating thickness (Fig. 1). The mixture of WC powders was put into the lower part of mold with the brazing alloy on top of it. The weight of brazing alloy is about 70% that of the WC powders. The mold was then placed into the furnace and heated at 150 °C/h. To prevent oxidation of the WC powder at this high temperature, it is very important to shield the mold/sample from oxygen during the thermal cycle. As the temperature reached 1050 °C, the Cu brazing alloy melted. The specimen was then heated to 1150 °C and held for 1-2 h. During this time, the Cu brazing alloy wetted and infiltrated into the WC powder and the substrate/coating interface. The specimen was then cooled to room temperature in the furnace. Upon subsequent examination, a good metallurgical bond between the WC and the base metal formed.

The brazing alloy's hardness and strength have a significant effect on the wear performance of the composite coating. So solution heat treatment and age hardening was performed on the Cu brazing alloy to improve composite wear performance by precipitation hardening. The heat treatment process is shown in Fig. 2. The composite specimen was heated to between 850 and 890 °C and held for 2 h. The sample was furnace cooled to between 400 and 430 °C and held for additional 48-72 h. Finally, the specimen was air-cooled to room temperature.

After the heat treatment, the composite coating layer was machined to the substrate/composite coating interface. It was then prepared into several standard test specimens for mechanical testing, including microhardness, elastic modulus, and fracture toughness tests. The G-65 standard wear test of the composite coating was conducted on a dry sand/rubber wheel abrasive wear tester, with specimen dimensions of $76 \times 25 \times 8$

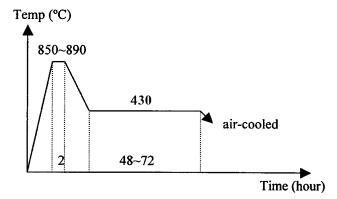


Fig. 2 Heat treatment after brazing process

mm. The microstructure of the coating was examined using optical microscopy. Scanning electron microscopy (SEM) was used to investigate the wear mechanism.

3. Results and Discussion

3.1 Microstructure Examination

The wear characteristics of a deposited coating depend on the average size of the carbides and the carbide distribution. A composite coating with a larger average WC size, and a higher volume fraction of carbide, is expected to have better abrasive wear performance. Therefore, smaller sized carbide powders were added to produce a higher carbide volume fraction. An optimum mix of different size carbides was used so that both of these factors could be optimized. Figure 3 shows the distribution of carbides in the coating. The carbides of different sizes are evenly distributed in the matrix. The average carbide particle size was measured to be 0.677 mm, which is much larger than most of the commonly used WC powders for deposited coatings. The volume percent of carbide was measured to be 80.5 and the mean separation distance between the carbides was 94 µm. This spacing is quite small compared with the carbide size. An optical photograph of the coating is shown in Fig. 4. Little porosity is found either in the matrix or carbides.

An SEM image of one of the carbides is shown in Fig. 5. No porosity or defect was found. Porosity is very common in macrocrystalline carbide powders (without binder). Since there is no binder (Co) in the carbide, the microhardness of the carbides should be higher than that of sintered WC. Figure 6 is an SEM image of the carbide/matrix interface area. Chemical analyses by energy-dispersive spectroscopy (EDS) of areas A and B in this image are shown in Table 1. There is a small amount of Cu, Mn, and Ni in area A of the interface, suggesting that the Cu alloy melted and diffused into the WC, subsequently forming a good metallurgical bond at the contact surface. The bond strength depends on the extent of melting that occurs and varies with the holding time during brazing. EDS analysis of area B in Fig. 6 shows that there is some Fe from the substrate that dissolved into the liquid alloy and subsequently forms a new phase with WC.

3.2 Mechanical Properties and Abrasive Wear Behavior

The mechanical properties, including Vicker's hardness (HV), elastic modulus, and fracture toughness, of the compos-

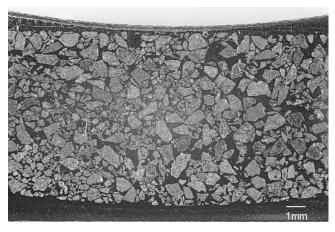


Fig. 3 Cross section of the deposited coating shows carbide distribution

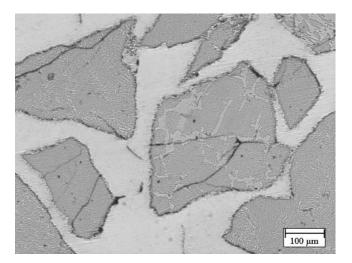


Fig. 4 Optical pictures of deposited coating shows microstructure

ite coating were determined. The Vicker's hardness of the carbide and the matrix were measured with a load of 100 g. Young's modulus was determined by dynamic excitation, using the ultrasonic frequencies of the longitudinal oscillations in a test bar, and ascertaining the resonance frequency of its natural oscillations. The tensile strength of the coating and the bond strength of the coating/substrate interface were tested with a tensile tester. Fracture toughness was calculated using a four-point bend test on standard "b-type" chevron-notched bars prepared according to ASTM C 1421. [8] The mechanical test results were compared with those of sintered WC-6Co materials. These results are shown in Table 2.

The WC-Cu composite coating shows relatively higher fracture toughness than WC-6Co due to the higher binder volume percent. The microhardness of carbides in the coating is also higher compared with the sintered WC in the conventional coating. The coating density is a little lower than that of sintered WC-6Co. Also, due to the nonuniform deformation between WC particles and the brazing alloy when the composite coating is under a tensile load, an internal stress concentration is induced. As a result, cracks are more likely to be initiated at the WC/Cu alloy interface and then propagated through the

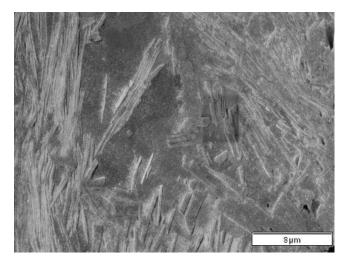


Fig. 5 SEM image of cast WC carbide in the coating at 5000×

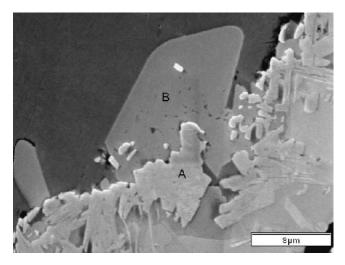


Fig. 6 SEM image of carbide/matrix interface at 5000×

Table 1 EDS Analysis of Carbide/Matrix Interface Shown in Fig. 6

	Carbide/Matrix	Phase in the	
Element	Interface (A)	Matrix (B)	
W	89.08	59.99	
Cu	4.24	5.98	
Mn	0.47	4.04	
Ni	2.74	13.04	
Fe	3.46	22.15	

WC particles during a tensile test. So the tensile strength of the coating mainly depends on the bond strength between the carbide and matrix. The bond strength between the brazed composite coating and the substrate is much higher than that formed during thermal spraying, and it can be increased with increased temperature or holding time during postbraze heat treatment.^[2]

During the brazing process, the brazing alloy melts at a high temperature and then solidifies as the furnace cools down. The

Table 2 Mechanical Properties Compared to Sintered WC-6% Co^[9]

	WC-Cu Composite	
Property	Coating	WC-6%Co
Density, g/cm ³	13.15	14.80
Microhardness, HV	2261 (carbide)	1600
	430 (matrix)	
Elastic modulus, GPa	492	620
Fracture toughness, MN/m ^{3/2}	14.2	11.0
Tensile strength, MPa	122	
Coating/substrate bond strength, MPa	185	

properties of as-cast Cu brazing alloy can be evaluated by testing as-cast Cu braze alloy bars. In this study, the effect of heat treatment is evaluated by comparing the properties of Cu brazing alloy bars before and after heat treatment, as shown in Table 3. Inspection shows that the microhardness and tensile strength of Cu brazing alloy were improved substantially after the heat treatment. The extent to which the properties improved depends on the length of the heat treatment. With even longer aging times, better results are expected.

3.3 Wear Test Results

The standard dry-sand, rubber-wheel abrasion test, ASTM G-65 (procedure A), was performed and the results compared with some commonly used WC-6Co with different grain sizes. The WC-6Co alloys had a much smaller grain size compared with the one used in this study and a lower binder content. The results are shown in Fig. 7. It shows that the WC-Cu composite coating has a relatively higher wear resistance in pure abrasion despite having a higher binder content. This is primarily due to the large WC particles and the good bond strength between the carbides and the matrix. In addition, the hardness of the Cu brazing alloy after precipitation hardening contributes to the overall wear resistance. The wear loss was mainly from the binder being abraded by the silica sand particles, not as a result of the deterioration of the WC particles. To some extent, the distribution of WC was also helpful in protecting the Cu binder from abrasion by the silica sand particles, thereby reducing wear loss.

4. Conclusions

Hard WC/Cu composite coatings have been produced using a Cu brazing alloy and a low carbon steel substrate. A mixture of different sized WC powders was used to create a larger average carbide size and a higher carbide volume fraction in the composite coating. The Cu brazing alloy was developed to have better wettability, a lower melting point, and good mechanical properties, especially after a precipitation hardening heat treatment. ASTM G-65 test results for the composite coating show higher wear resistance than several commonly used WC-6Co alloys. A good metallurgical bond was formed at the interface between the WC and the Cu brazing alloy, and between the coating and substrate. The relatively large average size of the carbides is effective in improving abrasive wear resistance because the particles are harder to pull out of the

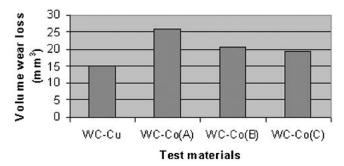


Fig. 7 ASTM G-65 wear test results compared with WC-6%Co coatings

Table 3 Mechanical Properties of Cu Brazing Alloy Before and After Heat Treatment

Property	Cu Brazing Alloy Bar (before HT)	Cu Brazing Alloy (after 72 h aging treatment)
Microhardness, HV	217	517
Tensile strength, MPa	375	870

matrix when the binder around them has been worn away. Since the brazing mold can be designed specifically for many different surface geometries and coating thicknesses, surface coating by brazing would be very effective in depositing thick coatings, particularly on curved surfaces or on large surface areas.

Acknowledgment

The authors would like to thank Dr. J.A. Hawk from the Albany Research Center, U.S. Department of Energy, for performing the G-65 tests and help with the interpretation.

References

- 1. M.Cadenas and R. Vijande: "Wear Behavior of Laser Cladded and Plasma Sprayed WC-Co Coatings," Wear, 1997, 211, pp. 244-53.
- S. Lu and O. Kwon: "Microstructure and Bonding Strength of WC Reinforced Ni-Base Alloy Brazed Composite Coating," Surf. Coat. Technol., 2002, 153, pp. 40-48.
- 3. S.C. Lim and M. Gupta: "Wear Resistant WC-Co Composite Hard Coatings," Surf. Eng., 1997, 13, pp. 247-50.
- R. Blombery and C. Perrot: "Abrasive Wear of Tungsten Carbide-Cobalt Composites. I. Wear Mechanisms," *Mater. Sci. Eng.*, 1974, 13, pp. 93-100.
- H. Engqvist: "Tribological Properties of a Binderless Carbide," Wear, 1999, 232, pp. 157-62.
- S. Bahadur: "Friction and Wear Behavior of Tungsten and Titanium Carbide Coatings," Wear, 1996, 196, pp. 156-63.
- Q. Yang and T. Senda: "Effect of Carbide Grain Size on Microstructure and Sliding Wear Behavior of HVOF-Sprayed WC-12%Co Coatings," Wear, 2003, 254, pp. 23-34.
- S. Freiman and E. Fuller: Fracture Mechanics Methods for Ceramics, Rocks and Concrete, ASTM Special Technical Publication 745, American Society for Testing and Materials, Philadelphia, 1981, pp. 69-84.
- K.A. Brookes: Hardmetals and Other Hard Materials, 3rd ed., International Carbide Data, Metal Powder Industry, Herefordshire, UK, 1998