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Rhenium as a Hard Chrome Replacement for Gun Tubes

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Hard chrome plating processes expose workers to toxic chromium compounds and are under a federal mandate for replacement with more environmentally friendly processes. In addition, hard chrome as a gun bore coating does not provide acceptable performance when used with modern ammunition. Replacement coating materials to date have been considered as too expensive, do not meet performance requirements, or have processing temperatures that exceed heat treatment limits of the steel barrels. Low-temperature chemical vapor deposition applied rhenium coatings should solve the environmental issues and the cost-to-benefit problems while meeting performance expectations for modern medium and large caliber ammunition.

Keywords Chrome replacement; Gun bore coatings; Gun tube wear; Rhenium coatings; Rhenium CVD; Rhenium gun liner.

1. Introduction

The current state-of-the-art medium and large caliber gun barrels employ an electrolytic hard chrome metal coating on the gun bore as a resistant layer against thermomechanical and chemical attack from gun propellants. For two primary reasons the chrome coating is insufficient for continued use. First, hexavalent chromium chemistry as used in chrome plating operations is toxic, and a federal mandate to eliminate chrome-VI requires a replacement. Secondly, the current state-of-the-art gun propellants are not especially compatible with the properties of a chrome-plated gun tube surface, and therefore the lifespan of current gun tubes is short enough to warrant an intensive search for a chrome replacement material.

The research project of concern is an Army-funded Phase II SBIR program investigating the applicability of low-temperature CVD rhenium metal and rhenium alloys as suitable chrome replacement materials. The M242 25-mm automatic gun system as employed in the Bradley Fighting Vehicle is the test bed for replacement coatings developed in this program.

2. Background

Previous SBIR work [1] performed by Ultramet engineers suggests that rhenium and its alloys are quite suitable for use in gun tube coatings and liners. A gun tube liner materials matrix was examined in vented bomb combustor testing for material erosion (Table 1) [1]. The materials matrix itself was chosen using criteria of desired properties and materials compatibility with the gun tube steel substrate. These criteria include high melting point, above 2500°C (preferably above 3000°C) stability in double base and RDX/HMX propellant environments at bore temperatures [2], high hot hardness, high ductility and toughness, compatibility with gun steel and ability to adhere strongly to gun steel, low/controlled coefficient of thermal expansion to reduce thermomechanical fatigue and buckling stresses, and low thermal conductivity to reduce heat load into the gun tube preventing substrate melting. In these criteria, rhenium shines as a coating material because of its superiority, and past application in rocket nozzle environments has demonstrated an excellent stability in hostile environments. Rhenium has the highest work hardening coefficient of any metal, is very ductile, has a high tolerance for carbon and hydrogen, a high melting point, and no brittle-to-ductile transformation.

Rhenium may be alloyed with other metals to reduce material cost while maintaining the desirable performance properties of rhenium itself. Optimal alloy compositions should be single phase and have solubility with the steel substrate without brittle intermetallic compounds. The molybdenum–rhenium system has good solid solubility below 25% Re, and any molybdenum added to a rhenium coating will reduce the materials cost. Tungsten is a brittle metal, but is frequently ductilized with 5% or 25% rhenium, and costs much less than rhenium. Tantalum is also less expensive than rhenium and is often alloyed with 10% rhenium. The oxidation resistance of rhenium can be improved by adding cobalt, but at some penalty to the melting point with large cobalt compositions.

Also very important to a gun tube coating is the adhesion between the coating and the gun tube steel (vanadium-modified 4340 steel). The carbon content of the steel is high enough to cause problems with carbon poisoning the coating interface at elevated temperatures (600°C+) seen in most CVD operations. Two methods of defeating this problem are to perform the coating process at low-temperatures, or to add a carbon getter or diffusion barrier at the interface. Ultramet addressed this problem by the second method and utilized an electroless nickel interlayer between the steel and the rhenium [1, 3] (Fig. 1). The nickel served to increase the solubility of the rhenium and the steel and behaved as a barrier to diffusing carbon.

Until now, the preferred methods of depositing rhenium by CVD have been from the halides, high-temperature processes. The decomposition of rhenium carbonyl is a low-temperature method of rhenium deposition, but a 20 at.

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TABLE 1.—Ultramet vented bomb combustor test results on a materials matrix of potential gun liner materials [1].

Material	Erosion rate	Thermomechanical damage
CVD Re coated Mo	+2 mg/shot	none
PM rhenium	+2 mg/shot	none
Mo-49Re	−26 mg/shot	mild heat checking
TZM (Mo)	−39 mg/shot	intermediate heat checking
W-26Re	−40 mg/shot	severe heat checking
Ta-10W	−122 mg/shot	mild heat checking
EHC*	−480 mg/shot	
4340 steel	−1120 mg/shot	

*Electrolytic hard chrome.

% residual carbon content destroys the high-temperature properties. The biggest problem with high-temperature CVD on gun tubes is the annealing of the autofrettage treatment on the steel substrate. A short time at 600°C is acceptable (especially in the smaller caliber barrels), but really any process above 357°C may relax the desired residual compression stresses. Unfortunately, most CVD processes and a few surface treatment processes require temperatures above 600°C.

In the end, the Ultramet vented bomb combustor tests showed that the rhenium and molybdenum rhenium alloys experienced the least degradation in vented bomb combustor testing (Table 1), and that the current hard chrome coating was exceeded in performance by all of the refractory coatings tested. It should be noted that this vented bomb combustor test was much more severe than what is seen in actual gun firings as the average gas exposure time in the test was 20–30 msec per shot as opposed to 3–5 msec in an actual gun.

3. CURRENT WORK

It is understandable that the cost of a gun tube is important, and it is, but if the cost/(lifetime*performance) ratio is comparable to the current chrome plate system, the benefit of reduced cost of gun tube transport and supply logistics far exceeds the value of the gun tubes themselves, as the gun tubes themselves are always less expensive than the cost of actually using one in the field. So, for a rhenium-coated barrel that costs 3 times what a current chrome barrel costs but lasts 4 times longer and uses current high-performance ammunition, all of the cost-based criteria have been justified.

Often the greatest challenge with coating processes is to achieve adequate coating adhesion. With low-temperature CVD methods this is especially true because of inadequate energy to promote interdiffusion and metallurgical bonding between the coating and the substrate. Various techniques have been employed to enhance adhesion. In the gun tube environment, good adhesion means adhesion in one of the most difficult environments possible.

Traditional CVD processes of refractory metals utilize the metal halides. These processes are inefficient, require high-temperatures, and have dangerous acidic byproducts such as HF, HCl, and HBr in addition to toxic, unreacted metal halides. These chemicals are much more dangerous than hexavalent chrome and where possible should be replaced with green processes.

Rhenium CVD from the carbonyl has been performed below 450°C, but the residual carbon content degraded mechanical properties (Fig. 2). As long as the high-temperature and ductility properties of rhenium are not important for the application, the carbonyl CVD technique is acceptable. Though the rhenium carbonyl CVD is low-temperature, it is expensive. A vertically integrated precursor generation and CVD process could eliminate materials costs, but in any appreciable amount paying \$6/g vs. \$12/g for a precursor with a 50% yield at high deposition rates is still a steep cost. Improved recovery and recycling processes can also lower cost. Regardless of the materials costs of rhenium carbonyl, the low-temperatures and nontoxic byproducts make it a highly competitive alternative to the Re halide CVD processes. From the

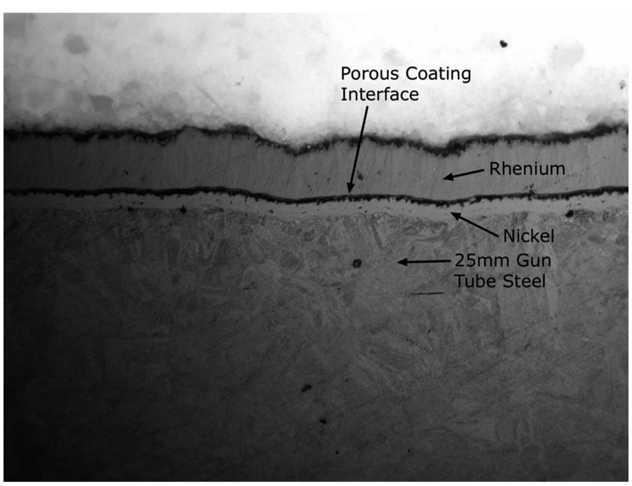

FIGURE 1.—Ultramet deposited rhenium on an electroless nickel interlayer on 25-mm gun tube steel in two stages, first from ReF6 and then from ReCl6. The interface between the rhenium and the nickel was very porous. 200x.

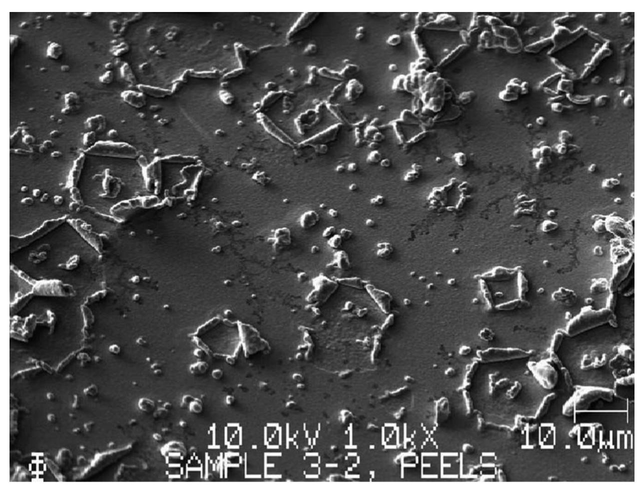

FIGURE 2.—Rhenium carbonyl decomposes to form a rhenium coating at below 450°C, but high carbon and oxygen concentrations make a brittle, layered microstructure with high residual stress. This image is of the growth surface of a 1–5-μm coating on quartz.

carbonyl route, this computes to about 280 g of rhenium and approximately 350 g CO_2 gas per five-foot barrel for a 100-μm coating.

Other problems with low-temperature CVD have been residual stress, adhesion, and adsorbed and trapped gases such as hydrogen, oxygen, and halide gases. The residual stresses may be due to any number of phenomena depending on the process and parameters. At low-temperatures, adequate metallurgical bonding and adhesion between the coating and the substrate may not be sufficient to overcome thermal mismatch stresses at the interface during a temperature change, i.e., a gun shot. Also at low-temperatures, it is difficult to purge the coating surface of precursor ligands and other reaction gases. Fast deposition rates may compound the problem by not allowing adequate desorption time.

Rhenium CVD research has generated new techniques and rhenium precursors that promise to reduce cost, deposition temperature, and increase deposition efficiency while retaining environmentally friendly properties. Already, rhenium metal coatings have been deposited below 600°C on quartz with acceptable impurity levels of carbon, oxygen, and halides. Experiments with molybdenum precursors and a similar technique have shown some promise for low-temperature codeposition with rhenium. Further work will determine optimum deposition parameters and deposition rates, address residual stress and adhesion issues, and advance the techniques to become commercial processes.

One of the undesirable properties of a CVD coating in a gun tube application is the columnar grain structure. In this configuration, the grain boundaries are continuous from the coating surface to the substrate. As fast diffusion paths, the grain boundaries fail and allow hot combustion gases to reach the substrate and decompose the steel along the coating interface. After a few shots, the coating loses adhesion and begins to spall, exposing more steel directly to the hot gases, which further accelerates barrel wear. Interrupting the growth of the coating by chemical or mechanical means provides a solution to this columnar dilemma by encouraging new grain nucleation once the coating growth is underway.

Another low-temperature means of applying rhenium coatings is by nonaqueous electrodeposition. Low-temperature fused salt baths and organic solvent baths are under investigation for rhenium plating suitability. Current industrial rhenium plating processes require high-temperatures that will damage heat treatments and refined grain structures in steel. Lowering the temperatures of such processes to below 400°C will enable low-temperature substrate materials to be coated. Aluminum, copper, and magnesium and possibly polymers may be rhenium coated.

Interlayer deposition and choice is also quite important. Nickel as an interlayer is covered by a patent developed by Andrew J. Sherman and held by Ultramet [3]. Nickel provides a good barrier to carbon diffusion and increases the solid solubility between rhenium and steel. Other metals such as cobalt and possibly CVD chromium may behave well as an interlayer. In addition to providing a carbon diffusion barrier, the nickel or cobalt surface is nobler than the steel surface, so its preparation for coating should not be as difficult. The interlayer can be deposited by CVD, electroplating, or electroless processes. Aqueous and nonaqueous plating processes should be chosen for pure depositions, because impurities common to most plating processes will lower the melting point of the interlayer. For instance, the electroless nickel phosphorous plating system leaves 1–3 at% P behind in the nickel, and though the coating is very hard, it has a low melting point. Other nickel systems, such as nickel chloride electroplating and electroless nickel boron, deposit very pure coatings. Also, solution-based surface preparation is common and known to produce good adhesion as is seen in the current hard chrome plating.

Chemical vapor deposition is also a likely candidate for the application of a nickel interlayer. The decomposition of nickel carbonyl occurs below 200°C and is exclusively used at Powdermet, Inc. for high-purity nickel deposition. Nickel carbonyl is quite toxic but is unstable and decomposes easily with environmentally safe byproducts (CO_2). Cobalt carbonyl is more difficult to work with as it is a solid with a narrow sublimation to decomposition temperature window, but other precursors exist for cobalt deposition.

4. Conclusions

Rhenium is an excellent material choice for a pure metallic gun tube coating, and there are many viable methods of adding a rhenium lining to a gun tube. Manufacturing powder metallurgy liners, and CVD coatings are two of the most popular alternatives. As research continues, we expect the state-of-the-art, low-temperature, rhenium CVD coated gun tubes will become an economically attractive and performance demonstrated system. Advances made in low-temperature rhenium CVD are significant, and new materials systems are now possible. Previously, refractory metal CVD was limited to high-temperature materials substrates, but now, materials such as aluminum and some polymers are coatable.

As ceramic materials compete with metals systems for application in gun tubes, it becomes apparent that no single material will likely provide the ultimate performance. It will probably be a refractory cermet composite structure that meets all of the performance goals of medium and large caliber gun tubes. Even so, it will be difficult for such systems to compete performance wise with a pure rhenium coating, though the economics of the situation will likely be the driving force behind a move in the direction of cermets. Efficient composites of silicon nitride or titanium nitride and moly-rhenium will provide chemical, wear, and thermal resistance while possibly reducing materials costs and increasing component lifespan.

References

1. Sherman, A. J. *Advanced Materials and Fabrication Processes for Gun Barrels*, SBIR Final Report. U.S. Army ARDEC. Report DAAA21-93-C-0036. April–December, 1993.
2. Ahmad, I. *The Problem of Gun Barrel Erosion: An Overview*; Benet Weapons Laboratory Watervliet Arsenal, Watervliet: NY.
3. Sherman, A.; Arrietta, V. Method for Making a High Temperature, High Pressure, Erosion and Corrosion Resistant Composite Structure. United States Patent 5,935,351, August 10, 1999.