FINAL REPORT

Development of Environmentally Friendly Projectiles

SERDP Project WP-2756

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This SERDP Special Study will focus on the science needed to achieve success in this area, as well as the environmental impact this topic encompasses. What exactly is the environmental impact of metal cobalt? Is research needed to determine what the function of cobalt is in this material system? What does cobalt accomplish? Is there a drop-in replacement? Has anyone looked into the science behind the addition of cobalt? Also, is this just an Army problem, or does it affect all services? An impartial study will be undertaken by ARL to answer these questions, to determine whether this is an appropriate SERDP Statement of Need for the future.

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ACRONYMS AND ABBREVIATIONS

BLUF	bottom line up front
Co	cobalt
CoNi	cobalt nickel
DoD	Department of Defense
DNA	deoxyribonucleic acid
EU	European Union
ESTCP	Environmental Security Technology Certification Program
Fe	iron
FeNi	iron nickel
GPa	gigapascal
$MPa\sqrt{m}$	megapascal square root meter
Ni	nickel
NiAl	nickel aluminide
OSD	Office of the Secretary of Defense
RAC	Risk Assessment Committee
SERDP	Strategic Environmental Research and Development Program
SoN	statement of need
STTR	Small Business Technology Transfer
UHCS	ultra-high carbon steel
VC	vanadium carbide
WC	tungsten carbide
Wt%	weight percent

Development of Environmentally Friendly Projectiles

SERDP Special Study WP-2756: Determination of Potential for Future Statement of Need
by Marc Pepi

31 July 2018

Problem Statement: There is currently approximately 10% cobalt (Co) in the matrix of tungsten carbide (WC) cermet armor piercing projectiles. The US Department of Health and Human Services has classified cobalt as “reasonably anticipated to be a human carcinogen”. The classification of cobalt as an “anticipated carcinogen” has resulted in subsequent complications (i.e. strict industrial controls) in the production and machining of cobalt-containing bodies for all applications, not just armor-piercing cores (e.g. tooling, jewelry, abrasives, etc.), where the inhalation of airborne dust can be hazardous to persons handling or machining these materials. The objective of this topic is to identify non-hazardous alternative matrix materials for tungsten carbide cermets that will yield materials with the necessary properties for use in armor-piercing projectiles.

Impact: The DoD purchases a large quantity of M993/M995 armor-piercing rounds containing a WC-Co core. Development of a non-hazardous material would lead to the removal of over 1.5 tons of cobalt from the environment from just this single munition system. Across the product lifecycle, this would translate to improved health effects during manufacturing, and no cobalt leaching into the ecosystem in regions where there is an accumulation of these projectiles (i.e. target range). To date, there has been no reported success in the area of cobalt replacement for this application.

Questions: A review of this topic by the SERDP/ESTCP Technical Committee has raised some questions that will be addressed by this study. These include: how special is the cobalt addition to tungsten carbide? Is there a drop-in replacement? What is the true environmental impact of cobalt usage in this material system?

Objective: This SERDP Special Study will focus on the science needed to achieve success in this area, as well as the environmental impact this topic encompasses. What exactly is the environmental impact of metal cobalt? Is research needed to determine what the function of cobalt is in this material system? What does cobalt accomplish? Is there a drop-in replacement? Has anyone looked into the science behind the addition of cobalt? Also, Is this just an Army problem, or does it affect all services? An impartial study will be undertaken by ARL to answer these questions, to determine whether this is an appropriate SERDP Statement of Need for the future.

Bottom Line Up-Front (BLUF): This topic appears worthy of a SERDP SoN, in that there is certainly a link to “weapon systems”, and there would definitely be a requirement for sound scientific research to further the state-of-the-art. In addition, it has been shown that there is an environmental impact of this study. Future work would need to build off the related research highlighted herein.

Background: Tungsten carbide (WC) cermets are among the most successful composite materials yet developed, with a unique combination of high hardness, strength, and fracture toughness. This combination of properties, along with exceptionally high density, provides a superior material for small caliber armor-piercing projectiles. The current state of the art is ≈10% cobalt (Co) matrix. Cobalt is a critical and strategic material for the US military due to its utilization in tungsten carbide munitions, however, cobalt supply is influenced by economic, environmental, political, and technological factors affecting exploration for and production of copper, nickel, and other metals as well as factors affecting the cobalt industry [1]. Moreover, The United States is predominately import dependent for cobalt [2]. Much of the cobalt supply is derived as a byproduct of copper and nickel mining. Consequently, economic, environmental, political, and technological factors affecting copper and nickel exploration and production may also affect cobalt supply [2]. The demand for cobalt raw materials has increased, due to the emergence of China as a major producer and consumer of refined cobalt, primarily for rechargeable batteries [2]. Figure 1 shows the cobalt supplying countries by year, in metric tons of production. In 2012, worldwide estimates of the amount of cobalt mined/refined were estimated to be ≈92,000 tons/year.

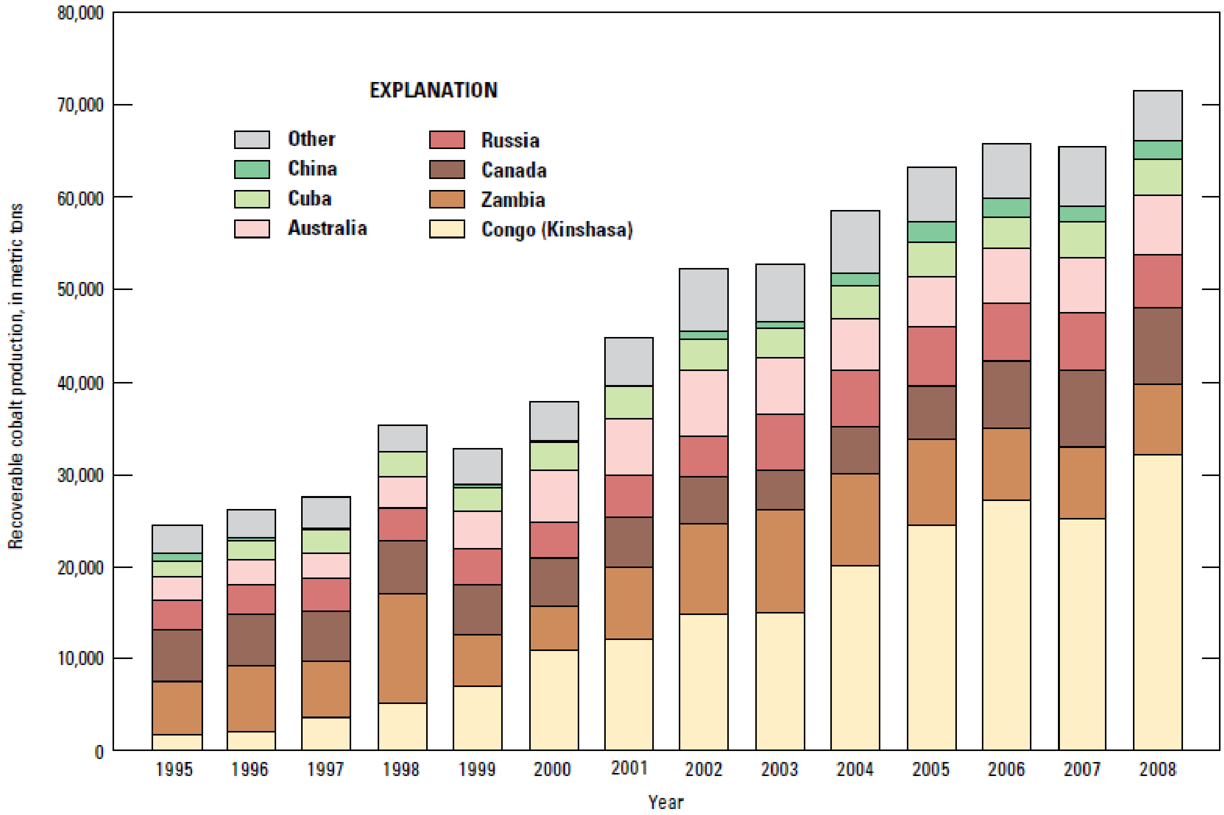

Figure 1 Cobalt supplying countries by year [2].

Cobalt Health Effects: The US Department of Health and Human Services has classified cobalt as "reasonably anticipated to be a human carcinogen". In addition, the EU Risk Assessment Committee (RAC) agreed on the following for cobalt metal classification [3]:

- Carcinogen Cat 1B for all routes of exposure and with specific concentration limit of 0.01%;
- Reprotoxic Cat 1B
- Mutagen Cat 2

Canada concluded that solubility is a crucial factor in the environmental risk posed by cobalt-containing substances. Cobalt and soluble cobalt compounds are harmful to organisms in the environment and should be subject to regulatory risk management under paragraph 64(a) of the Canadian Environmental Protection Act of 1999. Environment and Climate Change Canada and Health Canada published a risk management approach document outlining their proposed measures [4].

Adverse health effects, such as cardiomyopathy and vision or hearing impairment, were reported at peak blood Co concentrations typically over 700 µg/L (8–40 weeks) [5]. It has been found that cobalt is acutely toxic in larger doses, and in mammalian in vitro test systems cobalt ions and cobalt metal are cytotoxic and induce apoptosis and at higher concentrations necrosis with inflammatory response. Cobalt metal and salts are also genotoxic, mainly caused by oxidative DNA damage by reactive oxygen species, perhaps combined with inhibition of DNA repair [6].

The classification of cobalt as an "anticipated carcinogen" has resulted in subsequent complications (i.e. strict industrial controls) in the production and machining of cobalt-containing bodies for all applications, not just armor-piercing cores (e.g. tooling, jewelry, abrasives, etc.), where the inhalation of airborne dust can be hazardous to persons handling or machining these materials. Air concentrations of cobalt in these occupational settings generally range from 1.0×10^4 to 1.7×10^6 ng/m^3 [7]. Additionally, cobalt is known to be toxic to aquatic life, therefore spent projectiles could be an environmental hazard by increasing the cobalt concentration in the soil and water.

Why Cobalt?: Cobalt provides high hardness and wear resistance properties to WC at 10%, as the binder phase. Cobalt is the preferred binder because [8]:

- Cobalt has a high melting point 1493°C (2719°F)
- Cobalt has excellent strength at high temperature
- It forms a liquid phase with WC at a suitable temperature of 1275°C. This pulls the sintered part together by surface tension and eliminates voids
- Cobalt dissolves WC. Cobalt forms a eutectic with WC at 1275°C/1350°C and at that temperature dissolves 10% WC
- On cooling, WC should reprecipitate in the Cobalt bond giving hardness combined with toughness

- Cobalt can be produced as a very fine powder well under 1 micron. The binding agent should be capable of being ground very finely to mix with the hard carbide particles. Cobalt can be produced very finely and grinds down to << 1µ. On grinding, it reverts to the close packed form which is brittle although in the carbide product, it retains the more ductile cubic form at room temperature
- Cobalt fulfills all the needs of a binder while others, like Ni, Fe, etc., only fulfill some. It is this fact that has kept it irreplaceable in carbides. However other binders such a nickel and chrome can add corrosion resistance and toughness. They are harder to use and thus more expensive but the increased performance can be well worth it.

Cobalt not only affects the sinterability of WC parts subjected to powder metallurgy, but also, abnormal grain growth is often observed in sintering WC with small amounts of Co [1]. In this study (Singapore/Taiwan collaboration), vanadium carbide (VC) was added to inhibit the grain growth of WC. However, final hardness was affected by addition of VC. Co content affects the hardness, fracture toughness and wear resistance of WC–Co-cemented carbides [9]. The hardness and wear resistance of WC–Co-cemented carbides decrease as the Co content increases [10]. However, the fracture toughness is improved as the Co content increases, which ensures a certain impact resistance of the WC–Co-cemented carbides. Therefore, Co addition should be controlled within a certain range and a 0.2 wt% Co sample possesses a high hardness, good fracture toughness and wear resistance.

Is there a Drop-In Replacement for Cobalt? Although many alternatives have been researched (NiAl, Fe, Ni, FeNi, CoNi, as well as V and Ta additions), there does not appear to be a drop-in replacement that satisfies all properties (ballistic performance, manufacturing/machining characteristics, hardness, strength, fracture toughness), based on literature review, and personnel interviews.

<u>Benchmark Properties</u>: Any replacement alloy, or newly developed drop in cobalt replacement material will need to exhibit the following benchmark property requirements: 1) a Knoop hardness of 15 GPa, 2) a fracture toughness of 11 MPa√m, and 3) a flexure strength of 3 GPa. These baseline values were selected to be equal to current WC-Co properties for munitions.

<u>Related Efforts</u>: As part of an OSD Small Business Technology Transfer (STTR) program, three Phase I efforts were funded to research possible non-hazardous replacements for cobalt as a binder for WC munitions. These three companies were Advanced Materials and Devices, UES, Inc., and Thor Technologies, and their final reports are listed in references [11], [12] and [13]. The aforementioned benchmark property requirements (Knoop hardness of 15 GPa, fracture toughness of 11 MPa√m, flexure strength of 3 GPa) was utilized as the go-/no-go. Advanced Materials and Devices focused on an ultra-high carbon steel (UHCS) matrix, UES, Inc. looked at “binderless” WC/W, and Thor Technologies researched a titanium silicon carbide matrix. None of the research by these contractors yielded alternatives that met all of the benchmarks, and as such, no Phase II contracts were awarded.

Suggested Efforts if Funding Available? Through interviews, it became clear that research should focus on two new areas, not previously looked at, if funding became available. These areas include:

- Thermodynamic modeling of new alloys using Thermocalc modeling for focusing on wetting, compaction/consolidation of powders, melting temperature and viscosity properties as well as mechanical properties.
- How best to modify ternary alloys.

Conclusion: Elimination of cobalt-containing materials is essential and advantageous from two perspectives, reduction of potential health risks associated with these materials as well as stabilization of the supply chain and cost. Efforts need to be initiated to identify non-hazardous alternatives to cobalt that will yield materials with the necessary properties for use as armor-piercing projectiles. Attention is slowly starting to focus on cobalt-free compositions for economic, as well as, environmental reasons. It is anticipated that the results of this work will also benefit industrial applications, because tungsten carbides containing cobalt are also widely used in the commercial sector in cutting tools, coatings, saw blades, and wear-resistant components in industrial machinery, as well as in sporting goods and surgical equipment. Based on this study, it appears this topic would be worthy of a SERDP Statement of Need.

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