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Publisher's version / la version de l'éditeur:

Proceedings of the International Thermal Spray Conference (ITSC 2006), 2006-05-15

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imi 2006-112584 - 9
CNRC 48853

Metallic fume emission and operator exposure during WC-10%Co-4%Cr spraying by HVOF

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Abstract

The increasing use of HVOF coatings to replace hard chrome plating was initially motivated by the environmental and health risks associated with hexavalent chromium (Cr^{6+}) emissions during the plating process. Following performance optimization and proper coating selection, it has been found that the potential increase in performance and the cost/process-time reduction offered by the HVOF process often justifies its application. Recently, the use of Cr-containing alloys processed by HVOF has drawn attention to the potential release of Cr^{6+} during heating of metallic chromium. For instance a new California regulation for airborne toxic control measures to reduce emission of hexavalent chromium from thermal spraying is in preparation.

The present study focused on monitoring operator exposure during the HVOF spraying of WC-10%Co-4%Cr. The spraying was performed using a JP-5000 HVOF gun in a spray room in which a ventilation flow rate of 10 000 scfm was imposed. Air sampling was taken in the spray room as well as in the adjacent control room in accordance with the NIOSH 7300 and 7600 standard methods. A portable sampler attached on the operator's chest was also used to monitor the operator exposure during a typical workday. Results indicate that even though metallic fumes of Co and Cr are present in the spray room during spraying, the hexavalent form Cr^{6+} is not detected. It was concluded that an operator entering the spray room for a limited amount of time with the gun in operation would be exposed to only low fume levels that can be still reduced by wearing an appropriate respiratory mask.

Introduction

HVOF Coatings are the solution of choice for the replacement of electrolytic hard chrome plating. The initial efforts to implement this technology have initially been environmentally motivated by the need to reduce Cr^{6+} toxic emission. It has since been established that proper process optimization and coating selection, can lead to increased performance and cost/process-time reduction. These interesting attributes offered by the HVOF process now often justifies its application. In order to fulfill the various needs dictated by the increasing number of application a larger variety of feedstock materials are considered, for example: Cr-containing alloys for corrosion resistance. The usage of these alloys have drawn attention to the potential release of Cr^{6+} during heating of metallic Cr. This attention has triggered regulatory activities, for an example the preparation of the new Californian regulation for airborne toxic control measures to reduce emission of hexavalent chromium from thermal spraying.

During the HVOF process, small particles (10 to 45 μm diameter) are injected into a supersonic flame by which they are heated and accelerated. Upon impact on a substrate, the particles flatten, solidify and form a coating. During spraying of chrome-containing materials metallic fumes as well as oxides of various valance states can be formed. Consequently, the formation of Cr^{6+} during the spray process is possible. The health risks associated with Cr^{6+} exposure are well established and have lead to the initiative to replace hard chrome plating technologies by alternative methods, such as, for instance HVOF thermal spraying. In this paper, we will present results of a study measuring operator exposure to metallic fumes and oxides, including those in the Cr^{6+} state, during HVOF processing.

Methodology

Air samples were taken for analysis during the spraying operation of a typical Cr-containing cermet material. Sampling was performed over a period of 6.5 hrs to monitor exposure during a typical work day. The sampling procedure and analysis were undertaken by a qualified industrial hygienist in accordance to accepted practices and in compliance with NIOSH 7300 [1] for the total Co and Cr and NIOSH 7600 [2] standards for the Cr⁶⁺.

Spray conditions

The spray experiment was performed using the JP-5000 HVOF gun for a WC-10%Co-4%Cr powder (1350 VM from Praxair). This is an agglomerated and sintered powder with particle size between 15 to 45 μm .

Typical spray conditions for this kind of materials were used and are listed below:

Spray distance:	38.1 cm (15 in.)
Kerosene:	22.7 LPH
Oxygen:	1038 LPM
Powder feed rate:	75 g/min
Barrel length:	10.16 cm (4 in.)

Air sampling

Four air samples were taken and analyzed.

- Two samples, one for Cr⁶⁺ analysis and one for the total Cr and Co emission, were taken simultaneously inside the spray booth during a continuous spray period of two hours.

The sampling location was behind the robot as shown in Figure 1 a). The fume samplers remained stationary and attached on the top of the stepladder. This location was selected for its proximity to the gun without impeding the robot movement.

- Another sample was also taken in the breathing space of the operator using a portable filtration unit that monitors exposure to during the work day (6.5 h in this case). The sampler was attached on the operator chest as shown in Fig. 2b).
- Finally, a test was conducted in the spray room without spraying to assess the level of background contamination. This sampling was performed for 105 min.

In order to evaluate the time required for the complete air exchange and evacuation of metallic fumes from the spray areas, CO₂ was introduced and then monitored as the spray room is ventilated. CO₂ was selected as a marker since it is easily tracked by electronic sensors.

A typical spray operation was realistically replicated by coating flat coupons. The setup is shown in fig 1c). During spraying, the operator entered the spray room ten times, replicating typical coupon exchange steps during production. The ventilation flow rate in the spray hood was 289 m³/h (10 200 scfm) creating an air flow velocity of 3 m/s (600 FPM) over the front surface of the spray hood.

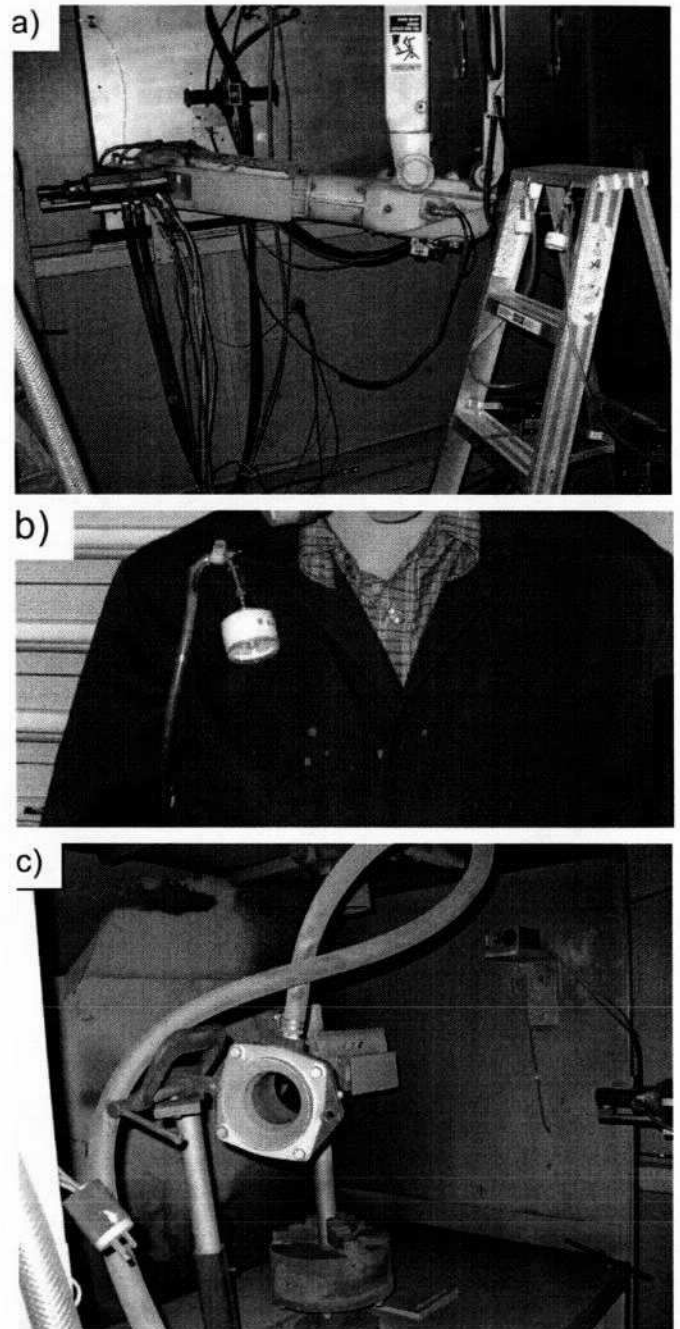


Figure 1: Air sampling during spraying. a) Stationary sampling in the spray room b) operator with its sampling unit. c) Spray booth configuration.

The air intake of the stationary Cr⁺⁶ sampler, as well as of the mobile Co and Cr samplers, which were attached to the operator chest, were 1.7 L/min.

A higher sampling rate of 20 l/min was used for the stationary Co and Cr samplers. The total air volumes sampled per device were 0,208 m³, 0.663 m³ and 2 m³, respectively.

A smaller sample was used for the Cr⁺⁶ detection due to the limited filter flow capacity imposed by the types of filter required for Cr⁺⁶ analysis.

Analysis

Following the air sampling, the filters were chemically dissolved and the solution analyzed by atomic emission spectroscopy (ICP-AES) for total Cr and Co content. Visible absorption spectrophotometry was used for Cr⁶⁺ detection. Table 1 presents the detection limits that are obtained with these techniques.

Table 1. Techniques and detection limits

Element	Détection limit (µg) on filter	Method
Cr,	1	atomic absorption
Co	1	atomic absorption
Cr ⁺⁶	0.5	visible absorption spectrophotometry

Since the detection limit is dictated by the total amount of material caught in the filter, the volume of air sampled during the tests plays a significant role in terms of the detection and precision of the analysis.

The results for the average operator exposure were corrected for a 8-hr period, even though the actual test was conducted for only 6.5 hrs.

Results

The results are presented in Table 2. For comparison purpose, the recommended ACGIH (American Conference of Governmental Industrial Hygienists) exposure limit are also included in the table. The sign (<) indicates a lower level than the detection limit. This detection limit is corrected from the value in Table 1 for the actual sample volume, which was always below 2 m³. Longer sampling or adaptation of the filters to higher flow rates would reduce this detection limit.

During spraying, significant amounts of both Co and Cr have been detected in the spray room. This result is somewhat unexpected considering the strong ventilation in the spray room. In addition, the gun and substrate were installed inside a hood, which further confines the overspray. The elevated

concentrations of airborne metals may be caused by a recirculating air flow and rebounding particles. Figure 2 shows an example of a particles spray, using Fe powders. The photograph illustrates the presence of particles rebounding from the substrate during spraying. The resulting dust tends to accumulate on the floor in front of the hood during extended operation, which is a strong indication that not all particles are captured by the dust collection system. It is therefore likely that a portion of the generated metallic fume also bypasses the collection system.

Table 2: Results of the air sampling analyses

		Detection	Average exposure for 8 h	ACGIH threshold limits*
		µg/m ³	µg/m ³	µg/m ³
Spray room during operation (120 min.)	Co	461		20
	Cr	98		500
	Cr ⁶⁺	< 2.4		10
Operator (390 min.)	Co	3.9	3.2	20
	Cr	1.8	1.5	500
Spray room after spraying (105 min)	Co	< 0.5		20
	Cr	< 0.5		500

*As reported from Threshold Limit Values and Biological Exposure Indices of the The American Conference of Governmental Industrial Hygienists (ACGIH)

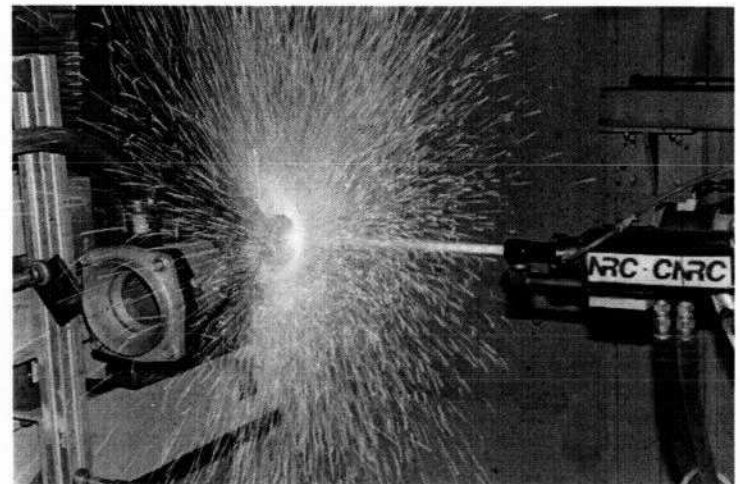


Figure 2. HVOF Spraying of Fe particle.

It should also be noted that the Cr to Co ratio in the emission is about 20% instead of 40% which would be dictated from the initial powder composition. As a consequence, the global composition of the feedstock may not readily serve to extrapolate emission levels of contaminants that are not directly measured. In this case, it seems that the exposure to Cr in the spray room is about half that may be estimated if applying the initial compositional ratio to the Co emission.

The relatively high detection limit for Cr⁺⁶ (2.4 µg/m³) in this study, which is primarily due to the low volume (0.208 m³) of sampled air in our case, prevents to accurately measured the low level of emission, which is far below the exposure limit. However, an approximation can be made, based on the total chromium emission and using the guidelines expressed in the new California regulation [3], which establish a conversion factor of Cr⁺⁶ to total Cr of 0.62%. According to this conversion, using 98 µg/m³ total Cr (see Table 2), a concentration of 0.61 µg/m³ of Cr⁺⁶ in the spray room can be estimated. This value is indeed 4 times lower than our detection limit. This concentration has to be confirmed experimentally if information about long-term generation of pollutants is to be sought.

As reported in Table 2 the operator exposure is very low, 3.9 and 1.8 µg/m³ for the Co and Cr, respectively. Exposure levels are even lower when they are corrected for an 8h work shift. It should be noted that the operator entered the spray room 10 times during the test. These short peak exposures are taken into account. However, the operator is mostly in the control room, which is separated from the spray room. Previous studies have established that the control room is free of any contamination. Assuming that the operator peak exposure corresponds to the level measured in the spray room (461 µg/m³ for the Co) we can estimate an average time of 20 s as the time spent inside the spray room to change one sample. This estimate is close to the actual value since the substrate replacement step during production is very fast. Nonetheless, the operator should wear respiratory protection when entering the spray room during gun operation.

After spraying, the level of contamination inside the spray room drops to undetectable levels, indicating that after the gun is shut down it is safe to enter the room without protective gear. The results of the CO₂ monitoring are presented in Figure 3. The initial value of CO₂ was 1500 ppm and reached a stable value, corresponding to that in air, in less than 60 seconds ventilation. As a good practice it was establish to wait 2 minutes after spraying to enter the room.

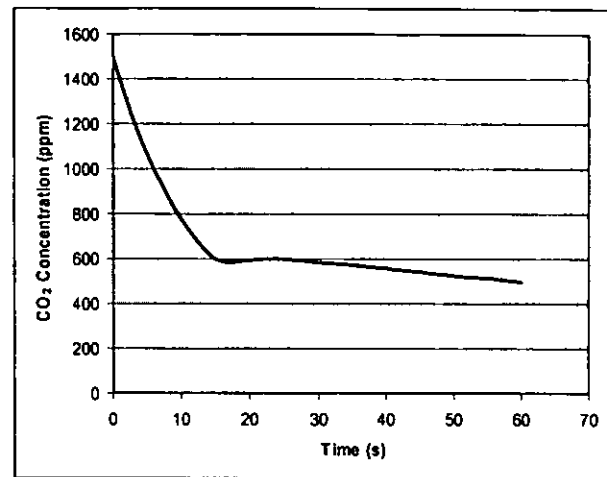


Figure 3. Evolution of CO₂ concentration

Summary

For HVOF Spraying of WC-10%Co-4%Cr powders:

- There is a significant concentration of metal fumes in the spray room during operation even at maximum air exchange. This emphasizes the need to have a booth configuration separating the operator from the spray areas.
- For the HVOF process investigated, no Cr⁺⁶ was detected in the spray room even though considerable amount (98 µg/m³) of Cr is detected.
- During a work day, the exposure of the operator to Co or Cr is far below established levels.
- Even if the operator enters the spray area several times for a short period there is no significant accumulative exposure.
- After spraying, the spray room is free of metallic fumes after 60 sec ventilation.

References

- 1) NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, METHOD 7300, Issue 3, 15 March 2003
- 2) NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, METHOD 7600, Issue 2, 15 August 1994
- 3) 93102.5 "Airborne Toxic Control Measure to Reduce Emissions of Hexavalent Chromium and Nickel from Thermal Spraying. Proposed new section 93102.5", title 17, California Code of Regulations,