

Cobalt skin dose resulting from short and repetitive contact with hard metals

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Summary

Background. Many daily contacts with metallic items are short and repetitive, and result in metal release; material, sweat, friction and wear may all be important.

Objectives. To study cobalt release and skin deposition as a result of many short and repetitive contacts with two cobalt-containing materials.

Materials/methods. Study participants ($n = 5$) handled two types of hard metal disc (Co 6% and Co 15% Cr 0.6%) for 30 min. Deposited cobalt skin doses were measured with acid wipe sampling and chemical analysis. Cobalt release from the hard metal discs in artificial sweat was measured under conditions simulating those present during the handling of discs.

Results. Average cobalt skin doses from discs containing 6% Co and 15% Co 0.6% Cr were $1.1 \mu\text{g}/\text{cm}^2$ [standard deviation (SD) $0.4 \mu\text{g}/\text{cm}^2$] and $0.7 \mu\text{g}/\text{cm}^2$ (SD $0.5 \mu\text{g}/\text{cm}^2$), respectively. More cobalt was released from hard metal discs containing 6% Co [$11.4 \mu\text{g}/\text{cm}^2$ (SD $1.2 \mu\text{g}/\text{cm}^2$)] than from discs containing 15% Co 0.6% Cr [$4.8 \mu\text{g}/\text{cm}^2$ (SD $0.6 \mu\text{g}/\text{cm}^2$)]. 10% to 15% of the potentially available cobalt was deposited on the skin during handling.

Conclusions. It is likely that the cobalt deposited as a result of short and repetitive contact with hard metals may cause harm. Research regarding cobalt exposure, metal release and the deposition of skin-sensitizing metals resulting from short and repetitive contact is needed for a better understanding of the allergy risk.

Key words: acid wipe sampling; artificial sweat; cemented carbide; cobalt; cobalt release; risk assessment; skin dose.

The nature of much daily contact with metallic items is short and repetitive. Even brief skin contact with metal may result in metal release from the material surface. The type of material and its form, age and surface condition, the properties of sweat and the characteristics of the

contact event (friction, wear, etc.) may all be important for metal release. As a result, metal from short and repetitive contacts is deposited on the skin, and amounts of metals sufficient to cause dermatitis are accumulated on the skin surface (1–4). At present, experimental data are lacking regarding contact dermatitis caused by skin exposure to short and repetitive contact with metallic items.

Contact allergy to nickel, chromium and cobalt is prevalent in the general population. Approximately 17% of women and 3% of men are allergic to nickel, and 1–3% are allergic to chromium and cobalt in some northern European countries (5). To reduce nickel allergy and nickel dermatitis, a limitation on nickel use was adopted in 1994 in the EU (the Nickel Directive) (6). It entered into full force in 2001, and has since 2009 been part of

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REACH, the European chemicals regulation (7). Release of nickel from items intended to come into prolonged contact with the skin is limited to $0.5 \mu\text{g}/\text{cm}^2/\text{week}$. However, items that come into brief and repeated skin contact are not covered by the regulation. It has been shown that handling of nickel-containing coins results in high doses of nickel on the skin (1, 8). The large differences in skin dose from some coin materials could not be foreseen from the results of nickel release tests in artificial sweat after only 1 week. Hence, skin dose assessment was stated to be necessary to evaluate the allergy risk from short and repetitive skin contact with nickel-releasing materials.

Cobalt is a potent skin sensitizer, but little is known about sources and levels of skin exposure to cobalt. Data on contact allergy in dermatitis patients indicate that the rate of cobalt allergy is remaining fairly stable, whereas that of nickel allergy is decreasing slowly (9). Cobalt allergy is well recognized in hard metal workers, pottery workers, construction workers, and electronics workers (10–14).

Hard metal workers come into direct contact with the cobalt-containing materials that they are manufacturing, and those who use the manufactured tools may also be exposed. Information on how much cobalt may be deposited onto skin in such work is of interest.

Cemented carbides (often called hard metals or hard materials) constitute a family of hard and tough (wear-resistant) composite materials used in tools for drilling, milling, turning, threading, and sawing. The basic cemented carbide consists of hard grains of tungsten carbide (WC) embedded in cobalt as a ductile binder (15). The tungsten carbide grain size has a strong influence on the mechanical properties of the material, and the cobalt binder can be alloyed or replaced by other metals to improve corrosion resistance (16–18). The material is manufactured powder metallurgically; the appropriate blend of tungsten carbide and cobalt powder particles is pressed into the desired shape (compacting), and then heated in a controlled atmosphere to bond the materials (sintering) (15).

In this study, we performed manipulation tests to measure the amount of cobalt deposited on skin, accumulated during a period of many short and repetitive contacts with hard metal. In parallel, we performed metal release experiments under conditions simulating those present during skin dose measurements. The aim of the study was to explore cobalt release and skin deposition as a result of many short and repetitive contacts, involving wear, with a cobalt-containing material. This is of importance for further understanding of potential allergy risks related to short, repetitive skin exposure to sensitizing metals.

Materials and Methods

Study participants

Five volunteers, who were healthy persons without a history indicating cobalt allergy, ongoing dermatitis, or skin lesions on their hands, participated in this study. All were right-handed. The study was approved by the KI Nord ethics committee at Karolinska Hospital, Stockholm, and all participants gave their informed consent.

Hard metal materials

Hard metal (cemented tungsten carbide) discs of two different compositions were used. The discs were manufactured and provided by Sandvik AB (Sandviken, Sweden). Discs of the same materials and batches were previously studied by Julander et al. and Thyssen et al. (19, 20). Discs denoted 'A' contained Co 6%, and discs denoted 'F' contained Co 15% and Cr 0.6%. The diameter of the discs was ~ 11 mm, and the total surface area of one disc was estimated to be 2.7 cm^2 (19).

Prior to any use, the discs were degreased with a sodium dodecylbenzene sulfate solution [5 g of $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, technical grade (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) in 1 l of distilled H_2O] for 2 min in an ultrasonic bath, rinsed with distilled water until no foam from the anionic surface-active agent was present, and then gently dried with laboratory paper tissue (Kimtech Science precision wipes; Kimberly-Clark Professional, Roswell, GA, USA). The discs were left to dry on paper tissues overnight, before being tested the next day. The same sets of discs were used for manipulation tests, and thereafter in the metal release experiments.

All test tubes and other laboratory utensils used in experiments were acid-washed; submerged in 10% HNO_3 for 24 hr, rinsed four times in deionized water, and dried in ambient air in the laboratory. The laboratory bench in contact with the discs or skin was cleaned with 1% HNO_3 before each experiment. The discs were handled with protective gloves and plastic forceps by the operator.

Skin exposure and skin dose assessment

In experiments for the assessment of cobalt skin dose, the participants ($n = 5$) handled the discs for 30 min in the laboratory, which is similar to 'counting coins' using both hands (Fig. 1a). On the first day, they handled one type of disc, and on the following day the other type. Twenty-seven discs of type A and 28 discs of type F were used. The same discs were used by all participants, and the discs were cleaned as described above between the sessions.

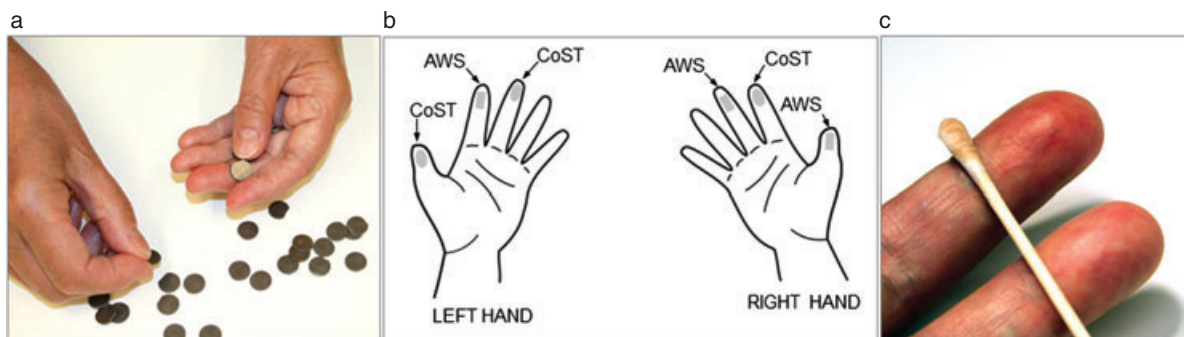


Fig. 1. The manipulation of hard metal discs was performed by the participants similarly to 'counting coins' for 30 min (a). Acid wipe sampling (AWS) was performed on the right thumb, the left index finger, and the right middle finger. The left thumb, right index finger and left middle finger were spot tested for cobalt (CoST) (b). The cobalt spot test was used directly on the skin, in order to explore its ability to detect cobalt deposited on fingers (c).

After the discs had been handled for 30 min, acid wipe sampling (AWS) was performed on three fingers (right thumb, left index finger, and right middle finger) (Fig. 1b). Then, three fingers (left thumb, right index finger, and left middle finger) were rubbed with the cobalt spot test reagent (Fig. 1b,c).

Acid wipe sampling

To measure the amount of cobalt deposited onto the fingers, AWS of defined, exposed skin areas was performed (21). The recovery rate of cobalt was previously found to be dose-dependent, with 90–100% being in the dose range of 0.5–1.7 $\mu\text{g Co/cm}^2$ (21, 22).

Before manipulation of the discs, the participants washed their hands with soap and water. Their hands were then rinsed by the operator with 1% HNO_3 [65% HNO_3 for analysis (Merck, Darmstadt, Germany) and deionized water], followed by deionized water, and dried with a paper towel. After handling of the discs, the areas for AWS were marked on the skin by indicating the corners of a 2-cm² template. Each area was then wiped with three consecutive wipes (injection wipes; Paper-Pak Sweden AB, Sundbyberg, Sweden), each moistened with 0.5 ml of 1% HNO_3 . The three wipes were pooled in the same container (60 ml, PP; Nalgene® Labware, OH, USA), and 23.5 ml of 1% HNO_3 was added for extraction of metal from the wipes. Blank samples, containing the 1% HNO_3 used for sampling in duplicate and 1% HNO_3 plus three wipes (duplicates), were prepared for each of the experiments assessing cobalt skin dose. After shaking of the containers for 30 min with an orbital shaker (Gesellschaft für Labortechnik m.b.H. & Co., Burgwedel, Germany), the extract solutions were poured into new test tubes (25 ml, PP; Sarstedt, Nümbrecht, Germany).

The solution samples were stored in a refrigerator (+ 5°C) until chemical analysis.

The results, in terms of a 'cobalt skin dose', represent the measured level of cobalt skin deposition divided by the recovery efficiency of the sampling method. As the AWS recovery rate in the measured dose range was considered to be high, the measured levels of cobalt skin deposition are referred to as cobalt skin doses without any further correction for recovery rate in this case.

A paired sign test (non-parametric) was applied to data of mean individual cobalt skin doses originating from handling A discs and F discs.

Cobalt spot test

The cobalt spot test indicates the presence of cobalt ions by a colour change from yellow to orange-red (20, 22). The cobalt spot test reagent was prepared in our laboratory as previously described, by dissolving 100 mg (corresponding to 0.1 wt%) of oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, purified; Sigma-Aldrich Chemie), 20 mg (0.02 wt%) of nitroso R salt (disodium-3-hydroxy-4-nitrosophthalene-2,7-disulfonate, for analysis; Fluka Analytical, Sigma-Aldrich Chemie) and 5 g of sodium acetate (CH_3COONa , for analysis; Merck) in deionized water (16.7 M Ω /cm), making up 100 ml of solution (20).

The test was performed by rubbing a cotton wool stick moistened with 50 μl of cobalt spot test reagent over a 2-cm² demarked skin area for 30 seconds. Any colour change was recorded within 10 min.

Metal release in artificial sweat

Metal release experiments were performed with the discs in order to compare the skin doses of cobalt deposited on fingers with the amount of released cobalt that is

potentially available for deposition onto hands. The metal release tests were performed by shaking the discs in artificial sweat for 30 min. This experimental procedure was a rough attempt to simulate the handling of discs, which involved mechanical wear of the test material.

The artificial sweat solution was prepared according to the reference test method EN1811:2011, by mixing urea (0.1 wt%), NaCl (0.5 wt%) and lactic acid (0.1 wt%) in distilled water [a Sartorius balance (Sartorius, Göttingen, Germany) was used for weighing of the chemicals]. The pH of the solution was adjusted with 1 M NaOH, 0.1 M NaOH and 0.1 M HCl to 6.5 ± 0.05 (PHM 210 Standard pH Meter; Radiometer, Copenhagen, Denmark).

Ten discs of each type were placed in a 60-ml flask, and 10 ml of artificial sweat solution was added with a vollpipette. Duplicates were prepared with A discs, F discs, and blank solution. The six flasks were bundled together, and the six-pack was shaken manually for 30 min at room temperature ($\sim 20^\circ\text{C}$) in the laboratory. The movement can be described as being similar to gently playing maracas in a common time rhythm. The discs were then removed from the artificial sweat solutions, and rinsed with deionized water. Fine, suspended particles resulting from the wear of discs during shaking remained in the artificial sweat solution, giving it a greyish appearance. The artificial sweat samples were acidified with 150 μl of 65% HNO_3 , and stored in refrigerator prior to chemical analysis.

The same procedure was repeated for three consecutive days with the same discs (which were degreased, rinsed and dried between the experiments) and freshly prepared artificial sweat solution each day.

By combining the results from skin dose assessment experiments and metal release experiments, it is possible to estimate the proportion of metal released and deposited. The metal released in artificial sweat during the shaking experiments for 30 min represents 'the potentially available metal that could be released during skin contact'. A quantitative relationship between released and deposited cobalt is achieved by dividing the deposited cobalt dose by the released cobalt ($\mu\text{g}/\text{cm}^2$).

$$\begin{aligned} & \% \text{ of released Co deposited on skin} \\ &= \frac{\text{average Co skin dose}}{\text{average Co release}} \frac{(\mu\text{g}/\text{cm}^2_{\text{skin}})}{(\mu\text{g}/\text{cm}^2_{\text{sample}})} \times 100 \end{aligned}$$

Chemical analysis

The concentration of cobalt in acid wipe samples was analysed by means of graphite furnace atomic absorption spectroscopy (GF-AAS) (AAnalyst 800; Perkin Elmer,

Waltham, MA, USA). The cobalt concentration in samples from metal release experiments was measured by using the flame mode of the atomic absorption spectrometer (flame-AAS). Reference solutions for calibration were prepared from a cobalt standard solution (1000 mg/l in 2% HNO_3 ; atomic Spectroscopy Standard; Perkin Elmer) diluted in 1% HNO_3 to 35, 10 and 3.5 mg/l, and to 100, 30 and 10 $\mu\text{g}/\text{l}$, for flame-AAS and GF-AAS analysis respectively. The limits of detection [calculated as three standard deviations (SDs) in blank samples] were 0.3 $\mu\text{g}/\text{l}$ with GF-AAS for skin dose assessments, and 16.5 $\mu\text{g}/\text{l}$ with flame-AAS for metal release samples. The measured results are based on three replicate readings of each sample, and quality control samples of known cobalt concentration (reference solution diluted in 1% HNO_3 to 20 mg/l for flame-AAS and 10 $\mu\text{g}/\text{l}$ for GF-AAS) were analysed consecutively. The cobalt concentration in blank samples was below the detection limit, except in a few cases where the cobalt contribution of the background (blank samples) was subtracted from the samples associated with this blank.

Material characterization

The surface morphology and appearance of A and F discs were studied with field emission gun scanning electron microscopy (LEO 1530) and a Gemini column (Zeiss, Oberkochen, Germany). Discs in as-received condition, after manipulation tests and after metal release testing, were studied. High-resolution images were obtained in high-vacuum mode with an accelerating voltage of 10.00 kV by use of a backscatter detector. Energy dispersive X-ray spectroscopy analysis was performed on selected areas to verify the chemical composition of the hard metal samples (silicon drift detector and INCA software from Oxford Instruments, Abingdon, UK).

To study the microstructure of hard metals A and F, one non-used disc of each material was moulded into a conducting polymer (acrylic resin with iron filler, ConduFast; Struers, Ballerup, Denmark) with a Prontopress (Struers). The discs were then ground and polished by use of standard metallographic techniques (600 SiC, 1200 SiC, 1 μm diamond paste, and finally 0.05 μm Al_2O_3 in acidic slurry) to a surface finish that enabled an overview evaluation and comparison of the microstructure.

Results

Skin dose assessment

The average skin doses of cobalt on the fingers in 5 participants, as assessed with AWS, are shown in Fig. 2,

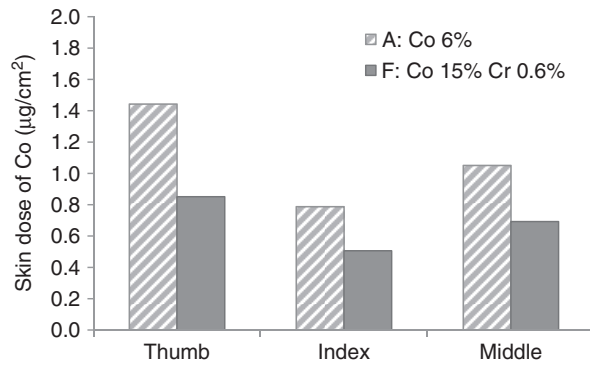


Fig. 2. Measured average skin doses of cobalt ($\mu\text{g}/\text{cm}^2$) deposited from hard metal discs A and F on the right thumbs, left index fingers and right middle fingers of 5 participants after manipulation for 30 min.

which compares the skin doses originating from handling A and F discs for 30 min. The deposited cobalt doses were higher from A discs than from F discs. The skin doses of cobalt were highest on the thumbs $1.4 \mu\text{g}/\text{cm}^2$ (SD $0.6 \mu\text{g}/\text{cm}^2$) for A discs, and $0.9 \mu\text{g}/\text{cm}^2$ (SD $0.7 \mu\text{g}/\text{cm}^2$) for F discs and lowest on the index fingers $0.8 \mu\text{g}/\text{cm}^2$ (SD $0.3 \mu\text{g}/\text{cm}^2$) for A discs, and $0.5 \mu\text{g}/\text{cm}^2$ (SD $0.3 \mu\text{g}/\text{cm}^2$) for F discs in all participants. The level of cobalt deposited on the middle fingers was intermediate: $1.1 \mu\text{g}/\text{cm}^2$ (SD $0.7 \mu\text{g}/\text{cm}^2$) for A discs, and $0.7 \mu\text{g}/\text{cm}^2$ (SD $0.7 \mu\text{g}/\text{cm}^2$) for F discs.

The cobalt spot test indicated, by an orange–red colour, that cobalt was deposited on the fingers in all participants (Fig. 1c).

The individual deposited cobalt skin dose, based on the total dose from three fingers of each participant (I–V) handling A and F discs during different sessions, is shown in Fig. 3. More cobalt was deposited on the skin from A discs than from F discs. On application of the sign test to these data, this difference was found to be statistically significant at a 5% level. The average cobalt skin doses deposited during 30 min on the three fingers of all participants were $1.1 \mu\text{g}/\text{cm}^2$ (SD $0.4 \mu\text{g}/\text{cm}^2$; range 0.5 – $1.7 \mu\text{g}/\text{cm}^2$) from A discs and $0.7 \mu\text{g}/\text{cm}^2$ (SD $0.5 \mu\text{g}/\text{cm}^2$; range 0.3 – $1.6 \mu\text{g}/\text{cm}^2$) from F discs.

Metal release

The results from metal release experiments with 10 discs shaken in 10 ml of artificial sweat for 30 min are shown in Fig. 4. The level of cobalt release per unit surface area of the discs was in the same order of magnitude in consecutive experiments. More cobalt was released from A discs than from F discs. This is consistent with the deposited skin doses from the same discs. The mean release

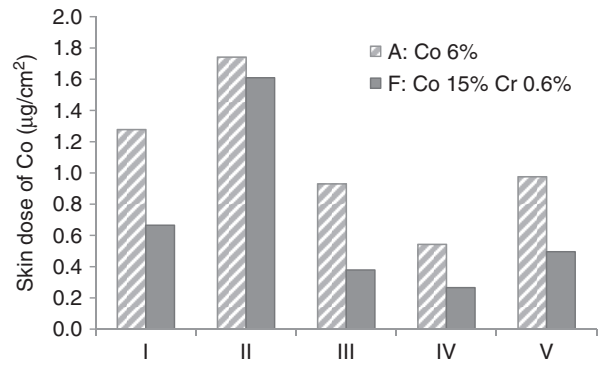


Fig. 3. The individual average skin dose of cobalt (from right thumb + left index finger + right middle finger) expressed in mass per surface unit area ($\mu\text{g}/\text{cm}^2$) deposited onto fingers from hard metal discs during 30 min of manipulation. The same discs were used by all participants ($n = 5$, indicated by roman numerals) in sessions on different days.

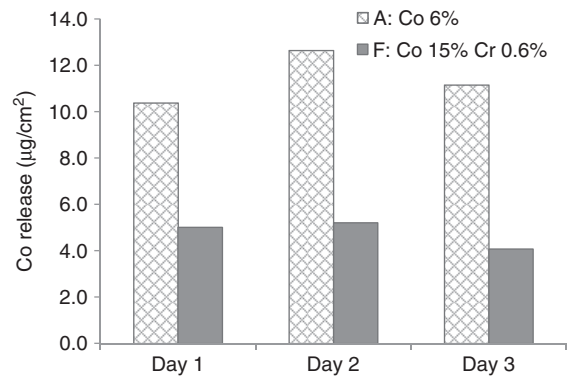


Fig. 4. Measured amounts of cobalt released, per surface area unit ($\mu\text{g}/\text{cm}^2$), from hard metal discs after 30 min of shaking in artificial sweat solution. The experiment was repeated on three consecutive days.

of cobalt from A discs was $11.4 \mu\text{g}/\text{cm}^2$ (SD $1.2 \mu\text{g}/\text{cm}^2$; range 10.4 – $12.6 \mu\text{g}/\text{cm}^2$), and that from F discs was $4.8 \mu\text{g}/\text{cm}^2$ (SD $0.6 \mu\text{g}/\text{cm}^2$; range 4.1 – $5.2 \mu\text{g}/\text{cm}^2$).

The proportions of the metal released and deposited on skin were 10% and 15% for A discs and F discs, respectively. A general estimate would be that 10–15% of the potentially available cobalt was deposited on the skin during 30 min of handling of hard metals, under the conditions of the experiment and assuming a 100% recovery rate of the skin sampling method.

Material characterization

The size of tungsten carbide grains in a hard metal material is crucial for its hardness and performance in

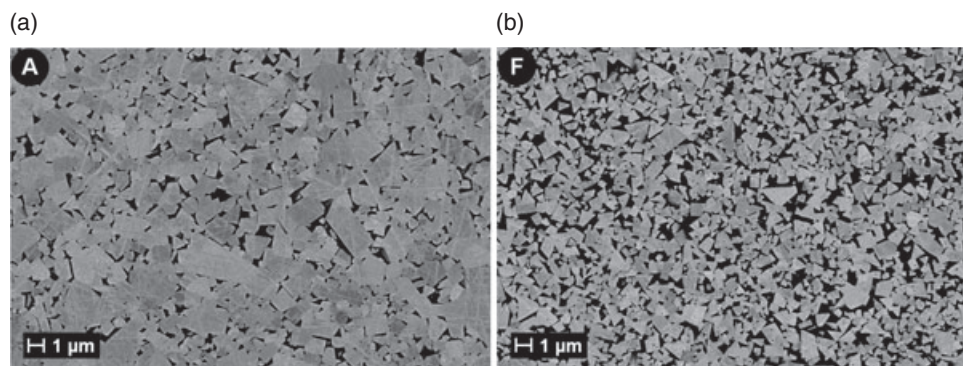


Fig. 5. High-resolution scanning electron microscopy images of hard metal A (a) with coarse tungsten carbide particles and 6% Co in the matrix (cobalt is seen as black fields in between the lighter tungsten carbide particles in the image) and hard metal F (b) with finer tungsten carbide particles and a higher cobalt content (15% Co 0.6% Cr).

different applications. High-resolution scanning electron microscopy images showed larger particles of tungsten (typical particle size in the range of 1–3 µm) in material A than in material F (typical particle size of < 1 µm) (Fig. 5).

Discussion

This study shows that considerable amounts of cobalt were deposited onto the skin after handling of hard metal discs containing 6% and 15% cobalt. Cobalt release from the materials was measured in metal release experiments in which shaking was also performed, as a first attempt to simulate wear resulting from contact between discs during handling. The proportion of cobalt deposited on the skin, in relation to released cobalt, was 10–15% under the test conditions. Neither the amount deposited nor the amount released was directly related to the cobalt content in the hard metal materials. Cobalt deposited on the fingers was, in all cases, detected with the cobalt spot test directly on the exposed skin surfaces. Sometimes, the tip of the cotton wool stick was discoloured (greyish) but with an orange–red halo indicating cobalt (22).

The experimental design of the study was based on previously published results on occupational exposure to sensitizing metals involving brief and repeated skin contact with metals, such as in cashiers, metal workers, and locksmiths (2, 3, 8, 23, 24). The purpose was to study cobalt skin exposure resulting from the handling of cobalt-containing materials, as data regarding skin doses of cobalt are scarce. Intense handling of hard metals occurs during manufacture and tool sharpening. The two types of hard metal used in this study (6% Co and 15% Co 0.6% Cr) represent commercial grades for typical applications that are well studied with regard to wear characteristics and corrosion resistance (16, 25–28). In this study, the

surface finish of our test materials was not identical, the manual shaking of samples during release testing was a rough, first attempt to introduce wear into the experiment, and handling varied between participants. The test conditions may thus be modified and better standardized in future experiments, if considered necessary.

Measured cobalt skin doses show individual variations

The level of cobalt deposited on skin varied between individuals. This could be attributable to differences related to frequency, duration and pressure of contact with the discs, amount and composition of the sweat, etc. All participants handled the same sample sets, as we had access to a limited number of discs. It was interesting to determine whether there was any trend related to the repeated use. This could have been the case if the surface layer of the discs had been significantly affected by the release or handling procedures. Metal release on three consecutive days did not show any marked difference. However, owing to the large interindividual variation, it was not possible to assess whether there was any difference in skin exposure related to the repeated use. To some extent, the variation in cobalt skin deposition could also be attributable to individual differences in skin condition that may affect the recovery rate of AWS (90–100% in the measured dose range, which means that up to 10% of the deposited cobalt may remain on the skin after the experiments).

Wear affects cobalt release from hard metals

Test materials of the same batches as used in this study have been used to study patch test reactivity in cobalt-allergic patients and cobalt release under static conditions (19). The released amounts of cobalt measured in this

study after 30 min of shaking in artificial sweat are within the same order of magnitude as after 1 hr under static conditions in the experiments of Julander et al. (19). However, it is not straightforward to evaluate the effect of wear on cobalt release, as the experimental conditions of the static test differ from those of our shaking experiments (the temperature was not the same and, most importantly, the material surface area/solution volume ratio differed).

Cobalt deposition and release are not directly related to cobalt content

Our results showing higher cobalt release and higher cobalt skin doses deposited from hard metal A than from hard metal F are in agreement with the previous results of Julander et al. (19). To determine the reason for the higher cobalt release from a material containing less cobalt, the microstructure of the hard metals was investigated. High-resolution scanning electron microscopy images showed larger particles of tungsten carbide in hard metal A (typical particle size in the range of 1–3 µm) than in hard metal F (typical particle size of < 1 µm) (Fig. 5). This would generally imply that hard metal A is harder (more resistant to deformation) than hard metal F, which, instead, is tougher (higher energy absorption prior to deformation). The chromium in the cobalt binder phase of hard metal F functions as a 'grain growth inhibitor' during the sintering process, but it also improves the corrosion resistance of the hard metal by the formation of a chromium-enriched surface oxide (17, 18). Hence, smaller tungsten carbide grains and greater toughness, together with higher corrosion resistance, are the most likely causes of the lower cobalt release/deposition from hard metal F than from hard metal A. Metal release and

the influence of wear on metal release are dependent on material-specific properties. Results obtained with other types of metallic materials will thus be different from those of this study.

Conclusions

In this study, we have shown that cobalt is deposited onto skin after short and repetitive contact with hard metals. Moreover, cobalt deposition and release are not directly related to the cobalt content in the material. It is very likely that the deposited and accumulated skin doses of cobalt resulting from short and repetitive contact may cause allergic reactions. A combination of release testing and skin dose assessment is of relevance for understanding the risks associated with skin contact with sensitizing metals, even of short duration. However, more research regarding cobalt exposure is needed.

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