Scand J Work Environ Health 1991;17(6):369-379

<https://doi.org/10.5271/sjweh.1691>

Issue date: Dec 1991

Toxicology and occupational hazards of new materials and processes in metal surface treatment, powder metallurgy, technical ceramics, and fiber-reinforced plastics.

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This article in PubMed: www.ncbi.nlm.nih.gov/pubmed/1788529

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Toxicology and occupational hazards of new materials and processes in metal surface treatment, powder metallurgy, technical ceramics, and fiber-reinforced plastics

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MIDTGÅRD U, JØRGENSEN JE. Toxicology and occupational hazards of new materials and processes in metal surface treatment, powder metallurgy, technical ceramics, and fiber-reinforced plastics. *Scand J Work Environ Health* 1991;17:369-79. Many new materials and processes are about to find their way from the research laboratory into industry. The present paper describes some of these processes and provides an overview of possible occupational hazards and a list of chemicals used or produced in the processes. The technological areas that are considered are metal surface treatment (ion implantation, physical and chemical vapor deposition, plasma spraying), powder metallurgy, advanced technical ceramics, and fiber-reinforced plastics.

Key terms: carbides, chemical vapor deposition, fibers, high-tech ceramics, ion implantation, nitrides, oxides, physical vapor deposition, plasma spray.

Technological advancement implies that new processes and materials are constantly being developed. This development involves several industries and scientific disciplines, and the research is often carried out as part of governmental programs. For example, some of the Nordic countries have encouraged research and development in new material technologies by allocating large sums of money for this field. As a result of such programs, several new technological processes are about to find their way from the research laboratory into more general use in industry.

It is the purpose of the present paper to provide an overview of the different kinds of materials and potential workplace hazards associated with some technologies which are more or less new. The technologies that are considered in this report are metal surface treatment, powder metallurgy, advanced technical ceramics, and fiber-reinforced plastics. These areas were chosen since they are about to have a major industrial breakthrough in the Nordic countries.

As an initial step in identifying the chemicals used or produced in the various processes and their potential workplace hazards, we have consulted handbooks, information booklets, and research proposals from various technology centers. Information has also been gathered from meetings and visits to some of the research centers.

In being engaged at an early stage, it is our hope that new hazards are foreseen so that serious occupa-

tional injuries can be prevented. Furthermore, we hope that designers, engineers, and industrial hygienists will be alerted to the new hazards that are inevitably coupled with new technologies.

New materials

Very often new processes and materials are introduced into the workplace before their impact on industrial hygiene is fully understood (1). In fact, scientists are able to create new materials and new chemicals at a much faster rate than the toxicologist can evaluate them. Consequently, many of the substances currently handled or produced in industrial processes are toxicologically unknown. This problem may be of limited concern to designers and research scientists, who are generally not subjected to serious or long-term exposure to hazardous agents. However, in large-scale industrial applications the risk of long-term exposure, and accidental overexposure, is ever present. Therefore, protection of the employees becomes very important, especially when one is dealing with substances that are toxicologically unknown.

New chemicals are by definition almost unknown, and the majority have never been subjected to adequate laboratory tests for biological effects before they are placed on the market. However, new materials are not necessarily synonymous with new chemicals. Very often new materials consist of well-known substances which are mixed or prepared in a manner which leads to a material with new and attractive properties. New materials emerge as a result of intense research and development, and they are characterized by a rapidly growing market. Furthermore, it is characteristic of many new materials that different compounds have been combined in a composite material with unique

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properties. In product design, this development means that there is a tendency towards a breakdown of the divisions between the traditional groups of materials such as metals, ceramics, and plastics. New materials as a concept varies both temporally and geographically. What is considered new in Scandinavia may have been used industrially for many years in other countries.

The different chemicals or substances encountered in the literature search on new materials have been listed in the appendix. The presence or absence of toxicological data was inferred from a check of all the chemicals against the Registry of Toxic Effects of Chemical Substances (2), and, for some of the chemicals and substances, a special search was performed in the data base TOXALL. Apparently, many of the chemicals are toxicologically unknown although they can hardly be considered new. In the following discussion, some of these chemicals and the technologies using them will be considered in more detail.

Figure 1. Typical device for ion implantation. Adapted from reference 3.

New surface treatment techniques

Metal surface treatment comprises a variety of methods in which a metallic substrate is coated with another material either for decorative purposes or for the production of corrosion-resistant or wear-resistant objects. Metal surface treatment may also be performed to reduce friction or improve the adhesion of a following layer. It includes well-known methods such as electroplating and electroless plating, but during the last couple of decades more sophisticated techniques have come into use, especially in the manufacture of wear-resistant tools. Numerous compounds are currently being used as coating materials (see the appendix), but the refractory coating of wear-resistant tools usually consists of either carbides, nitrides, or oxides.

In some processes (eg, electroplating and physical vapor deposition), the material is simply deposited directly on the substrate, and in others (eg, ion implantation), a surface layer consisting of both the substrate and the added material is produced.

It is not the purpose of the present survey to review the occupational hazards of all techniques for metal surface treatment. This contribution will be restricted to the occupational hazards of ion implantation, chemical and physical vapor deposition, melt spraying, and the toxicity of some of the compounds being produced or used in these processes.

Ion implantation

General aspects. In the ion implantation technique, the surface of an object is bombarded with high-energy ions which penetrate into the material to depths of up to 0.5 μm . Unlike other metal surface treatment processes, ion implantation does not produce dimensional changes in the object, and the protective layer does not break off. Furthermore, ion implantation is a low-temperature process that allows treatment of practically all materials — even plastics (3).

Ions from a gaseous material are produced in the ion source and are accelerated towards a separation magnet (figure 1). The beam then passes into a column where the ions are accelerated through an electrical

Table 1. Occupational hazards associated with different techniques in metal surface treatment.

Technique	Hazard	Preventive measure
Ion implantation	High voltage (electrical shock)	Grounding procedures
	Ionizing radiation	Shielding
	Toxic gases and liquids	Exhaust ventilation
	Electromagnetic fields	Shielding
Physical vapor deposition	Solvent cleaning of objects	Exhaust ventilation
	High voltage	Shielding, grounding
	(Dust from cleaning of reaction chamber)	Dust control
Chemical vapor deposition	Irritative compounds (eg, titanium tetrachloride)	Exhaust ventilation
	Toxic gases (eg, carbon monoxide)	Exhaust ventilation
	Explosive gases (hydrogen + air)	Exhaust ventilation
Plasma spray	Noise	Acoustical protection
	Toxic fumes	Exhaust ventilation, air-line ventilator
	Ultraviolet light	Visual protection
	Heat	Shielding, gloves

potential of up to 150 kV. The ion beam is then focused on the target, which is placed on a computer-controlled manipulator in the end station. For producing wear-resistant tools, the ions (N^+ , Ti^+ , Cr^+ , B^+) are produced from nitrogen, titanium tetrachloride, chromium (VI) dioxychloride, and boron trichloride. In the semiconductor industry ion implantation is used to produce arsenic- or phosphide-doped silicon, and the dopant ions are generated from arsine and phosphine (4).

Hazards. The occupational hazards associated with ion implantation are summarized in table 1. The personnel operating the ion implanter are, first of all, at risk from contact with the high-voltage unit and exposure to ionizing radiation. To avoid accidents, access to the high-voltage unit should be prevented by enclosure of this part of the equipment during operation, and regular or emergency shut-down of the ion implanter must include grounding procedures. Ionizing radiation should be measured after an implanter has been installed, and lead shielding should be applied if necessary. However, results of badge dosimetry monitoring of personnel operating ion implanters indicate that serious exposure to ionizing radiation normally does not occur (4).

Some of the chemicals used in the process of ion implantation in the semiconductor industry are very toxic (eg, arsine and phosphine). Workplace monitoring has shown that workers are continuously exposed to low-level concentrations of the dopants (4). However, the occupational exposure limits were not exceeded. Apparently, the exhaust ventilation near the ion source and vacuum pumping system provides sufficient protection of the personnel.

Boron trichloride and titanium tetrachloride, which are used for producing refractory coatings, are strongly irritant, and chromium (VI) dioxychloride contains hexavalent chromium, which is carcinogenic and allergenic. Although these compounds are used in very small amounts, they should be handled with care, and it is recommended that a ventilated face mask and gloves be used as protection against accidental leaks during the change of the gas cartridges.

The surface layer of the final ion-implanted product constitutes only a very small fraction of the entire product, and after-treatment is generally not necessary. Therefore, it is believed that the added material in the final product does not present any health risks.

Physical vapor deposition

General aspects. Physical vapor deposition includes several coating processes (eg, evaporation, ion plating, sputtering) in which an object is coated with a thin film in vacuum. Briefly, the material to be deposited is evaporated by resistance heating or bombardment with electrons or argon, after which it is transferred to the

object where it creates a thin surface film. In ion plating, the ionized evaporant is transferred to the object by means of an electrical potential, but the potential is considerably lower (<7 kV) than in ion implantation and the ions do not penetrate the surface of the object (5, 6).

The physical vapor deposition process is advantageous in that the temperature is considerably lower than in chemical vapor deposition. However, the surface coatings produced by physical vapor deposition are less resistant than those made with chemical vapor deposition, and the object must be completely free from dust and grease to secure a good result.

Hazards. The pretreatment of objects with solvent cleaning probably constitutes the most serious health risk in physical vapor deposition (table 1), and appropriate exhaust ventilation must be associated with this part of the system. In large-scale industrial use of the physical vapor deposition process, the equipment needed for cleaning objects is usually more expensive and voluminous than the physical vapor deposition apparatus.

The materials that can be deposited as films by the physical vapor deposition processes include metals, alloys, oxides, carbides, and nitrides. For many of the compounds, there is practically no toxicological data (eg, chromium carbide, iron carbide, titanium nitride), and it is therefore not clear whether they constitute an occupational hazard to the worker or consumer. Deposition of refractory coatings inside the reaction chamber may sometimes require cleaning by sand blasting. During this process dust is released to the work environment with the risk of inhalation.

Chemical vapor deposition

General aspects. In chemical vapor deposition, a surface coating is produced at high temperatures (500—1100°C) by means of a chemical reaction between gaseous reactants and the substrate. Due to the high temperatures needed in the process, suitable substrates are restricted to metals and alloys with high melting points. However, in plasma-assisted chemical vapor deposition, a low substrate temperature can be used due to microwave or electrical-discharge plasma activation. The chemical vapor deposition processes are used particularly for producing wear-resistant coatings, but optical films and semiconductors may also be produced (6).

Wear-resistant coatings consisting of nitrides are produced by the process of bubbling hydrogen and nitrogen through liquid chlorides (eg, titanium tetrachloride or vanadium tetrachloride) and then passing the gas mixture over the objects in the reaction furnace (figure 2). Carbon nitride coatings are produced through the addition of methane (or carbon monoxide) to the reaction gas (7, 8).

Figure 2. Technique for producing a titanium nitride coating by chemical vapor deposition. Adapted from reference 8. (H_2 = hydrogen, N_2 = nitrogen, CH_4 = methane, $TiCl_4$ = titanium tetrachloride)

rachloride are strongly irritant, as is hydrochloric acid, which is produced in the process.

Plasma spraying

General aspects. In plasma spraying a gas is directed through a direct-current arc, which results in a high-temperature plasma that expands rapidly and is capable of melting any material. The material used for coating is fed as a powder into the plasma and is ejected at high speeds towards the object. The melted material impinges on the object, where it coalesces and solidifies (6).

Plasma spraying techniques are advantageous because the substrate is kept at relatively low temperatures (about $100^\circ C$) and all kinds of material can be used for coating. Moreover, the adhesion to the substrate is very good, and the coating permits patchy repair.

Hazards. Plasma spraying generates considerable noise, and the use of a direct-current arc results in ultraviolet radiation, ozone, and nitrous gases (6). The process room, therefore, requires exhaust ventilation, and the workers should be equipped with both acoustical and visual protection, as well as an air-line respirator (table 1).

Figure 3. Main steps in manufacturing powder metallurgy products. Adapted from reference 9.

Hazards. Several hazardous chemicals are used in chemical vapor deposition (table 1). For example, carbon monoxide has a high acute toxicity by inhalation, and hydrogen mixed with air is explosive. Exhaust from the reaction furnace to the open environment is therefore needed, and installation of carbon monoxide sensors in the room is recommended. In addition, the furnace should be ventilated with nitrogen before being opened. Titanium tetrachloride or vanadium tet-

Powder metallurgy

General aspects

Powder metallurgy is defined as the production of metal powders and their utilization for the manufacture of massive materials. Powder metallurgy techniques are used to produce a wide variety of products consisting of metals, alloys, or metals in combination with nonmetals, as for instance cermets. Powder metallurgy techniques are both economically and technically advantageous. They are well suited for mass production, and it is possible to produce objects that cannot be made with conventional techniques. Furthermore, the powder metallurgy process is generally "clean" as compared with ordinary metal casting (9).

Metal powders can be produced by several different methods (eg, reduction from metal oxides and atomization of molten metal by air or water jet and by electrolytic deposition). The production of powders also involves milling and screening to obtain powders with the required particle dimension.

The particles in the powders are generally in the size range of $100\text{--}200\text{ }\mu m$, but fine particles ($1\text{--}10\text{ }\mu m$) and ultrafine particles ($1\text{--}100\text{ nm}$) are also used.

For producing massive objects, the metal powders are mixed, and a lubricant is added (metal stearate, paraffin, molybdenum disulfide). The mixture is then passed into a die where it is consolidated by the application of heat and/or pressure (cold isostatic pressing

or hot isostatic pressing). Afterwards, the compact object is sintered at temperatures ranging from 760°C to 2400°C depending on the material (figure 3). In another variation of the method, injection molding, very fine powders are mixed with a thermoplastic resin, and the mixture is injected into the replica. The resin may be extracted with solvents before the sintering, or it is simply pyrolyzed during the sintering. The finishing treatments of the powder metallurgy products include grinding and surface treatment such as plating or coloring (9).

In addition to the more common metals (iron, copper, aluminum, lead, tin, nickel, tungsten, cobalt, chromium) and their alloys, powder metallurgy techniques also make use of various rare earths (samarium, cerium, thorium) and molybdenum, vanadium, niobium, tantalum, titanium, and zirconium, especially as carbides. Objects which are produced by mixtures of a ceramic material (eg, chromium carbide, titanium carbide, titanium nitride, or a metal oxide) and metals (nickel-chromium, cobalt-chromium, nickel-molybdenum) are called cermets or metal-matrix composites, depending on the amount of metal in the product (10). In these products, the high-temperature resistance of the ceramics is combined with the high-fracture resistance of the metals.

Hazards. The most important occupational hazard in powder metallurgy is probably exposure to dust (table 2). Airborne dust can develop during the production and mixing of the powders and during the grinding of the consolidated or sintered objects.

The powders used in powder metallurgy have a tremendously high surface area:volume ratio which increases properties such as explosiveness and toxicity. Furthermore, the use of fine and ultrafine powders increases the risk of inhalation. Consequently, effective dust control is of paramount importance as a preventive measure against accidents and work-related dis-

eases. Very fine powders should, as far as possible, be handled in closed systems, and operations that create airborne dust should be avoided.

The toxicology of many of the metals used in powder metallurgy is well known (eg, lead, cadmium, beryllium, cobalt, nickel) and the health hazards associated with the handling of these metals are generally acknowledged (11). Exposure to chromium and nickel, which are strong sensitizers, increases the risk of occupational dermatitis, and cobalt dust plays a central role in the development of asthma and hard metal disease among workers in the cemented carbide industry (12, 13, 14).

The biological effects of oxides appear to be well known (see the section Advanced Technical Ceramics), whereas information on the carbides is very limited. Chromium carbide has been reported to produce thickening of the alveolar septa in rats after intratracheal instillation (15), whereas tantalum carbide, tungsten carbide, and titanium carbide are considered inert (16). However, due to the lack of long-term inhalation experiments with animals, it is not possible to decide whether or not the different types of carbide dust constitute an occupational hazard.

Advanced technical ceramics

General aspects

Ceramics are defined as inorganic, nonmetallic materials that are processed at high temperatures. While traditional ceramics (pottery, tiles, etc) are made from naturally occurring minerals (clay, silica, feldspar), advanced technical ceramics encompass a wide range of compounds such as carbides, nitrides, oxides, and titanates. More than 450 compounds are used in the manufacture of ceramic products (17), and only a fraction of these compounds are listed in the appendix.

Advanced technical ceramics are particularly known for their extreme heat resistance and hardness, which

Table 2. Occupational hazards associated with powder metallurgy, advanced technical ceramics, and fiber-reinforced plastics.

Technique	Hazard	Preventive measure
Powder metallurgy	Respirable dust	Shielding, exhaust ventilation, protection masks
	Sensitizing metals (cobalt, nickel) (asthma, dermatitis)	Gloves, exhaust ventilation
	Toxic metals (eg, cadmium, lead)	Protection masks, exhaust ventilation
	Pyrophoric metals (fire, dust explosions)	Exhaust ventilation, avoidance of flames, protection against sparks
Advanced technical ceramics	Compact presses	Shielding
	Respirable dust (pneumoconiosis, fibrogenic material, carcinogenic agent)	Protective masks, exhaust ventilation
	Toxic elements (lead in different compounds)	Protective masks, exhaust ventilation
	Irritative compounds (cadmium oxide, magnesium oxide)	Protective masks, exhaust ventilation
Fiber-reinforced plastics	Toxic solvents (eg, neurotoxic, carcinogenic, irritating agents)	Shielding, exhaust ventilation
	Sensitizing compounds	Exhaust ventilation, gloves
	Dust from machining (fibers, matrix)	Exhaust ventilation, protection masks, gloves
	Flammable solvents	Avoidance of flames

Figure 4. Main steps of the traditional and chemical way of processing ceramic powders. Adapted from reference 21.

make them attractive as engineering materials. These structural ceramics are increasingly used as components in engines, where they replace high-performance metals (eg, in exhaust manifolds, piston caps, turbocharger blades, etc). Other types of ceramics have unique electrical or optical properties, and some are used as surgical implants (bioceramics). Electrical ceramics include passive materials such as alumina and silicon dioxide, but also more active compounds which are used in pressure transducers and solar cells (10, 18, 19, 20).

Ceramic powders, which constitute the raw materials, are produced by grinding or milling or by chemical methods (gel-sol processing), in which the particles are formed by polymerization. Gel-sol processing results in homogeneous particles with sizes in the sub-micron range (10, 21).

The overall process in the manufacture of ceramic products resembles that of powder metallurgy. The ceramic powders are mixed and consolidated into compacts by dry pressing followed by sintering (figure 4). Compacts may also be produced from colloidal suspensions of the powders ("slurries") by slip casting, in which the liquid is absorbed by the porous mold before the sintering (21).

During sintering, the ceramic particles coalesce, and the density of the product increases. Due to their extreme hardness, ceramics are generally not subjected to further treatment after being sintered. However, the surface of the object may be polished if required, and smaller items may be cut with lasers.

Electronic ceramics, which are generally used in smaller amounts, may be produced as thin films by techniques such as physical vapor deposition, ion beam sputtering, and chemical vapor deposition (22).

Many ceramic compounds are available as fibers or whiskers, which are used particularly for purposes of insulation (eg, furnace linings) and as reinforcing inclusions in resins, metals, and ceramics. Ceramic fibers can be classified into two groups, oxide fibers, which include alumina, zirconia, and chemically modified alumina-silica fibers, and nonoxide fibers such as silicon carbide, silicon nitride, and boron nitride. The diameter of the fibers range from 1 μm to about 10 μm , but whiskers are usually somewhat thinner (10). The fibers are commercially available in bulk material or come as blankets or felts. Continuous fibers may even be twisted into yarns and woven into heat-resistant clothing (23).

Hazards

The most important health hazard in the manufacture of advanced technical ceramics is probably the inhalation of dust (table 2). The storing and mixing of ceramic materials in a dry, powdered form increases the risk for developing airborne dust that may be inhaled. The use of ceramic powders with particle size in the submicron range further increases the risk of inhalation. Protective measures should therefore include effective dust control, local exhaust ventilation, and the use of respirators during operations that are likely to create airborne dust.

Except for beryllium oxide, most of the compounds used in advanced technical ceramics have only limited acute toxicity, and titanium dioxide, zirconium silicate, and titanium carbide are considered biologically inert (16, 24, 25, 26). Inhalation of cerium oxide and tin dioxide has been reported to result in benign pneumoconiosis (11, 27), and nickel monoxide and beryllium oxide have the potential of inducing cancer (28). Furthermore, some of the compounds (eg, calcium oxide, cobalt oxide, zirconium oxide) may cause irritation or allergic reactions (29–31). More important, however, is that next to nothing is known about the biological effects of several of the compounds (eg, some nitrides, carbides, niobates, and titanates), and dust of these materials should be considered hazardous until proved otherwise.

Information on the toxicology of ceramic fibers appears to be very limited (32), except for those made of glass and asbestos. Fibers with diameters below 3 μm are classified as respirable (33), and long and thin durable fibers (diameter < 0.25 μm , length > 8 μm)

appear to be carcinogenic (34). Very thin ceramic fibers or whiskers should accordingly be considered as potentially hazardous, as they might turn out to be carcinogenic. Recent animal experiments seem to confirm this possibility since it has been found that inhalation of kaolin-based ceramic fibers (diameter 1 μm , length 25 μm) produced pleural mesothelioma in 36 out of 102 animals (35). Furthermore, in vitro experiments have shown that silicon carbide whiskers are more cytotoxic than crocidolite fibers (36).

Fiber-reinforced plastics

General aspects

Fiber-reinforced plastics are composite materials consisting of fibers embedded in a matrix of plastic. Their products combine high strength with low density and can serve as substitutes for steel and other construction materials where weight is critical. These composite materials were originally developed for use in the aerospace industry, but, since more fiber types have become available commercially, fiber-reinforced plastics are now being used increasingly. In addition to the use in the aerospace industry, fiber-reinforced plastics occur in land vehicles, boats, sporting goods, and prostheses (37).

The most commonly used fibers are made of glass, carbon, boron, or aramid. The fibers are embedded in a matrix of a thermosetting resin (eg, polyester, epoxy) or a thermoplastic (eg, polyether etherketone, polyether imide), depending on the physical characteristics that are needed. The fiber and matrix are often combined in tapes (prepregs) containing about 60 (volume) % fibers and ranging in width from about 3 mm to 1 m. Prepregs may then be stacked together to form a laminate component. Fiber-reinforced plastics can also be produced by a process called filament winding, which is particularly useful for cylindrical objects.

Cured objects made of fiber-reinforced plastics can require machining such as drilling, sawing, or grinding before the final product is obtained. In these processes, large amounts of dust can develop.

Hazards

The occupational hazards associated with the production of fiber-reinforced plastics are those which apply to the plastics industry in general. In other words, there can be exposure to many solvents and liquids that may be neurotoxic, carcinogenic, irritating, or sensitizing (table 2). Although these problems are important and serious, the present paper is restricted to the toxicology of the fibers and the possible health effects of handling fibers and machining the cured fiber-reinforced plastics objects.

Carbon fibers. There are several papers concerning the toxicological effects or health implications of exposure to dust from carbon fibers. Inhalation experiments with animals (rats and guinea pigs) indicate that carbon fiber dust does not produce systemic toxicity or pathological changes in the lungs (38, 39). However, a Soviet animal study indicates that dust from carbon fibers produces slight pulmonary fibrosis and irritation of the respiratory tract (40). Medical examination and respiratory symptom questionnaires of workers engaged in carbon fiber production have revealed no adverse effects on the lungs (41).

Carbon fibers tend to break laterally rather than longitudinally when milled (38, 41). Fibrous dust consisting of long and thin fibers, which are generally believed to be carcinogenic (34), is therefore not likely to develop. However, it has been reported that the sawing and drilling of carbon/epoxy composites produce free fibers, some of which show evidence of longitudinal cleavage (42).

Taken together, these studies indicate that carbon fibers present little or no chronic health risk during manufacture and use. Dust from carbon fibers may, however, present an indirect fire hazard, since it can cause short-circuiting in electrical installations (43).

Aramid fibers. Aramid fibers do not produce allergic reactions on skin contact, and inhalation experiments with rats show only minimal tissue reaction in response to the dust. In addition there is only little or no collagen deposition in the lungs (44, 45). Furthermore, intraperitoneal injections of dust from aramid fibers do not appear to increase the rate of tumors in rats (46).

Boron fibers. In a literature search, no papers related to the toxicology of this fiber type were identified.

Glass fibers. Since glass fibers can hardly be considered a new material (they have been in use for more than 50 years), the occupational hazards will be outlined only for comparative purposes. Skin irritations and itching are common complaints of workers exposed to dust either from handling the fibers or from machining plastics reinforced with glass fibers (47). Glass fibers may also produce a transient irritation of the mucous membranes of the eyes, nose, and throat (48), but adverse effects such as lung fibrosis, lung cancer, or mesothelioma have not been observed either in epidemiologic studies or in inhalation experiments with animals (49). Furthermore, the latest critical review of epidemiologic data shows that the standard mortality rate for lung cancer is not significantly increased by exposure to fine glass fibers (50). In animal experiments it has been found that very thin glass fibers (diameter < 1.5 μm) are highly carcinogenic after intrapleural implantation (51). However, these ex-

periments are unrelated to occupational exposure. Glass fibers used for reinforced plastics have diameters of 9–24 μm , and an examination of dust shows that longitudinal splitting of the fibers does not occur during grinding (52).

Matrix dust. The sawing and drilling of cured composites produce dust in the respirable size range, and it appears that several chemical agents, some of which have a sensitizing capacity, are released from the dust (43, 53). Although exposure to chemicals degassing from the dust occurs on a minor scale compared with the prepregging and lay-up processes, the hazard should not be ignored. In fact, there are reports of allergic contact dermatitis due to trace amounts of epoxy in the finished product (43). The intratracheal instillation of dust from carbon fiber epoxy composites in rats showed that some fabrics were inert, while others produced slight fibrotic changes in the lungs (53). This result has been supported by in vitro experiments with rabbit alveolar macrophages (54). However, it has not been established which component of the fiber-reinforced plastics (fiber, matrix, or additive) is responsible for the toxic effect.

To minimize exposure to fiber fragments produced in the machining of cured fiber-reinforced plastics, local exhaust ventilation should be applied. There is evidence that the occupational exposure limit for dust is frequently exceeded during the grinding of fiber-reinforced plastics, even though the machines are equipped with an exhaust device (52). Therefore, it is recommended that workers wear gloves and respiratory protection masks during grinding.

Acknowledgments

This work is part of a project supported by the Nordic Council of Ministers. We gratefully acknowledge the help and advice of the steering group, which consisted of Dr S Krantz (Stockholm), Dr D Ryberg (Oslo), Dr P Wilhardt (Copenhagen), and Dr A Zitting (Helsinki).

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Appendix

Materials used in metal surface treatment, powder metallurgy, advanced technical ceramics and fiber-reinforced plastics

The following table lists materials used in metal surface treatment, powder metallurgy, advanced technical ceramics, and fiber-reinforced plastics. In the last column + indicates the existence of toxicological data and — indicates that there is no or only very little information on the toxicity. Note: The list is not intended to be exhaustive. (The compounds have been identified from various handbooks, information booklets, and from research descriptions from technology centers.)

Compound	Formula or abbreviation	Metal surface treatment	Powder metallurgy	Advanced technical ceramics	Fiber-reinforced plastics	Toxicological data
<i>Metals and alloys</i>						
Aluminum	Al	+	+			+
Aluminum-magnesium	Al-Mg	+				+
(continued)						

Continued.

Compound	Formula or abbreviation	Metal surface treatment	Powder metallurgy	Advanced technical ceramics	Fiber-reinforced plastics	Toxicological data
Cadmium	Cd	+				+
Chromium	Cr	+				+
Chromium-molybdenum	Cr-Mo	+				+
Cobalt	Co	+	+			+
Cobalt-tin	Co-Sn	+				+
Cobalt-tungsten	Co-W	+				+
Copper-tin	Cu-Sn	+				+
Copper	Cu	+				+
Gold	Au	+				+
Indium	In	+				+
Iron-nickel	Fe-Ni		+			+
Iron-zinc	Fe-Zn	+				+
Lead	Pb	+				+
Lead-tin	Pb-Sn	+				+
Molybdenum	Mo	+	+			+
Nickel	Ni	+	+			+
Nickel-aluminum	Ni-Al	+				+
Nickel-cadmium	Ni-Cd	+				+
Nickel-chromium	Ni-Cr	+				+
Nickel-graphite	Ni-C	+				+
Nickel-palladium	Ni-Pd	+				+
Nickel-tin	Ni-Sn	+				+
Nickel-phosphorus	Ni-P	+				+
Nickel-tungsten	Ni-W	+				+
Nickel-zinc	Ni-Zn	+				+
Silver	Ag	+				+
Tantalum	Ta	+				+
Tin	Sn	+				+
Titanium	Ti	+				+
Tungsten	W	+				+
Yttrium	Y	+				+
Zirconium	Zr	+				+
<i>Boron-containing substances</i>						
Boron	B	+	+			+
Ferri boride	FeB	+				-
Lanthanum boride	LaB ₆			+		-
Niobium boride	NbB	+				-
Tantalum boride	TaB ₂	+				-
Titanium boride	TiB ₂	+		+		-
Tungsten boride	WB	+				-
Zirconium boride	ZrB ₂	+				-
<i>Carbides</i>						
Boron carbide	BC			+		-
Calcium carbide	CaC ₂	+				+
Chromium carbide	Cr ₃ C ₂ , CrC	+	+			-
Chromium carbide	Cr ₇ C ₃	+	+			-
Iron carbide	FeC	+				-
Molybdenum carbide	Mo ₂ C		+			-
Niobium carbide	NbC	+	+			-
Silicon carbide	SiC	+		+		+
Tantalum carbide	TaC	+	+			+
Titanium carbide	TiC	+	+			+
Tungsten carbide	WC	+	+			+
Tungsten carbide-cobalt	WC-Co	+	+			+
Vanadium carbide	VC		+			-
Zirconium carbide	ZrC	+				-
<i>Nitrides</i>						
Aluminum nitride	AlN	+		+		-
Boron nitride	BN	+				-
Chromium nitride	CrN, Cr ₂ N	+				-
Lithium nitride	Li ₃ N			+		-
Silicon nitride	Si ₃ N ₄			+		-
Tantalum nitride	TaN	+				-
Titanium nitride	TiN	+	+			-
Zirconium nitride	ZrN	+				-
<i>Oxides</i>						
Aluminum oxide	Al ₂ O ₃	+		+		+
Beryllium oxide	BeO			+		+
Lead oxide	PbO	+				+
Calcium oxide	CaO			+		+
Cerium oxide	CeO ₂			+		+

(continued)

Continued.

Compound	Formula or abbreviation	Metal surface treatment	Powder metallurgy	Advanced technical ceramics	Fiber-reinforced plastics	Toxicological data
Chromium oxide	Cr_2O_3 , CrO_2	+				+
Cobalt oxide	CoO			+		+
Magnesium oxide	MgO			+		+
Manganese oxide	MnO			+		+
Nickel monoxide	NiO			+		+
Niobium pentoxide	Nb_2O_5		+			+
Silicon dioxide	SiO_2			+		+
Tantalum oxide	Ta_2O_5		+			+
Tin dioxide	SnO_2			+		+
Titanium dioxide	TiO_2	+		+		+
Tungsten oxide	WO_3		+			+
Vanadium oxide	VO_2 , V_2O_3		+			+
Yttrium oxide	Y_2O_3			+		+
Zinc oxide	ZnO			+		+
Zirconium oxide	ZrO_2	+		+		+
<i>Fibers/whiskers</i>						
Aluminum oxide	Al_2O_3		+	+		+
Aramid (Kevlar®)	..				+	+
Beryllium oxide	BeO					-
Boron/boron carbide	B/BC				+	-
Carbon	C				+	+
Glass					+	+
Iron carbide	FeC		?			-
Ceramic fibers (Nextel®)	..			?		+
Potassium octatitanate	..					+
Potassium titanate	..					+
Silicon carbide	SiC		+	+		+
Zirconium oxide	ZrO_2			+		-
<i>Polymers</i>						
Epoxy					+	+
Nylon block copolymer	..				+	-
Polyamide	PA				+	+
Polybutylene terephthalate	PEBT				+	-
Polyether etherketone	PEEK				+	-
Polyether imide	PEI				+	-
Polyether sulfone	PES				+	+
Polyphenylene oxide	PPO				+	+
Polyethylene terephthalate	PETP				+	+
Polyphenylene sulfide	PPS				+	+
Polypropylene	PP				+	+
Teflon	PTFE	+				+
<i>Miscellaneous</i>						
Barium titanate	BaTiO_3			+		-
Boron trichloride	BCl_3	+				+
Cadmium sulfide	CdS			+		+
Calcium fluoride	CaF_2	+				+
Carbon	C	+				+
Chromium dioxichloride	CrO_2Cl_2	+				+
Copper selenide	CuSe , Cu_2Se			+		-
Ferrite	$(\text{Zn}, \text{M}) \text{Fe}_2\text{O}_4$			+		+
Ferrite	$\text{M Fe}_{12}\text{O}_{19}$			+		+
Gallium arsenide	GaAs			+		+
Krypton	Kr	+				+
Lead titanate	PbTiO_3			+		+
Lead-zirconium titanate	$(\text{Pb}, \text{Zr}) \text{TiO}_3$			+		+
Lithium niobate	LiNbO_3			+		-
Lithium tantalate	LiTaO_3			+		-
Magnesium fluoride	MgF_2			+		+
Molybdenum disulfide	MoS_2	+				-
Molybdenum selenide	MoSe_2	+				-
Molybdenum silicon	MoSi_2					-
Nitrogen	N	+				+
Phosphorus	P		+			+
Titanium tetrachloride	TiCl_4	+				+
Tungsten selenide	WSe_2	+				-
Vanadium tetrachloride	VCl_4	+				+
Zirconium fluoride	ZrF_2			+		-
Zirconium silicate	ZrSiO_4			+		+

Received for publication: 8 March 1991