Environmental, Resource and Health Impacts of Hard Materials
The Case of Cemented Tungsten Carbide with Cobalt

ANNA FURBERG

Department of Technology Management and Economics
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2018
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Cover:
Picture showing a saw cling with cemented tungsten carbide bits on the cutting edges, surrounded by worn tire studs with cemented tungsten carbide pins. The cemented tungsten carbide material is the focus of this thesis and tire studs specifically are investigated in two of the appended papers.
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ABSTRACT
The importance of hard materials for society is illustrated by the fact that entire historical time periods have been named after the predominant hard material used at that time. In the latest century, the introduction of the hard material cemented tungsten carbide with cobalt (WC-Co) has contributed to the economic growth we have seen and this material is crucial for the manufacturing industry of today. At the same time, knowledge about its environmental, resource and net environmental impacts is limited and a number of important knowledge gaps exist. Chinese WC-Co production has been assessed in detail, but not production outside China. Resource impacts in terms of dissipation and recycling rates exist for tungsten in general but not for specific products containing tungsten. In addition, whether the use of WC-Co in products contribute to net improvements in environmental, resource and health impacts have not been assessed. This study applies the methods of life cycle assessment (LCA) and material flow analysis (MFA) in order to address these knowledge gaps. Environmental impacts of a typical non-Chinese WC-Co production have been assessed using LCA, while resource and net human health impacts are assessed for the WC-Co-containing product tire studs specifically using MFA and LCA, respectively. Results show that a few inputs and outputs dominate the life cycle environmental impacts of the non-Chinese WC-Co production and that recycling greatly reduces these impacts. The MFA study on tire studs showed that tungsten dissipation rate is notably higher than for the average tungsten product (98% vs >60%) and that the functional recycling of tire studs is effectively non-existent. Furthermore, results from the LCA study showed that the purpose of the tire studs to save lives and prevent injuries in traffic is not justified, since negative life cycle human health impacts (mainly from use phase emissions and occupational accidents in artisanal cobalt mining) outweigh the use phase-benefits of reduced accidents. A number of alternatives to WC-Co has been suggested in literature. However, the substitution potential varies due to often higher costs and reduced performance. Further research, applying a life cycle perspective, on the environmental, resource and human health impacts of such alternatives is recommended.

Keywords: life cycle assessment; LCA; material flow analysis; MFA; disability-adjusted life years; DALY; cemented carbide; hard metal; tire stud
LIST OF PUBLICATIONS

Appended papers

Paper I
Anna Furberg, Rickard Arvidsson and Sverker Molander
“Life Cycle Environmental Impacts of Cemented Carbide Production”
Manuscript

Paper II
Anna Furberg, Rickard Arvidsson and Sverker Molander
“Dissipation of Tungsten and Environmental Release of Nanoparticles from Tire Studs”
Submitted to scientific journal.

Paper III
Anna Furberg, Rickard Arvidsson and Sverker Molander
“Live and Let Die? Life Cycle Human Health Impacts from the Use of Tire Studs”
Manuscript

Other related publications


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1 INTRODUCTION

1.1 Hard Materials

Over two million years ago, humanoidts at first acquired the knowledge of how to create tools (Headrick, 2009). These tools were made out of stone or flint and used for hunting. The introduction of new hard materials has shaped entire civilizations, why certain ancient periods have been named after the predominant material used at that time, e.g. the stone age, bronze age and iron age (Hummel, 2004). In more recent times, the cost of producing everyday-life products was significantly reduced in the 1940s when a new, much tougher and harder material compared to steel and high-speed steel was introduced (Ettmayer et al., 2014). This material have had a critical role in enabling the economic growth that we have seen over the latest century (Ettmayer et al., 2014). The hard material making this development possible was cemented carbides, also referred to as hard metals. In applications where wear resistance, toughness and strength are needed at higher temperatures, cemented carbides, consisting of a hard and wear-resistant phase, in the majority of cases tungsten carbide (WC), and a metallic phase, most often cobalt, is the typical choice (Prakash, 2014). WC-Co constitutes the backbone of today’s tool manufacturing industry (Prakash, 2014). Cermet is another type of hard material that is a particulate composite of ceramic particles bonded with a metal matrix (Ettmayer et al., 2014). Examples of cermets include carbides, nitrides or carbonitrides of, for example, titanium, tantalum and molybdenum which have partially replaced the WC phase of cemented carbides in e.g. metal cutting. However, the use of cermets has so far only been restricted to niche markets (Prakash, 2014). Other examples of cermets include alumina, niobium carbide, silicon nitride and silicon carbide (Hampshire, 2014). A group of even harder materials are the so-called superhard materials, e.g. diamond, cubic-boron-nitride (c-BN) and ternary compounds such as B-N-C (Lowther, 2014). Diamond is currently limited to industrial niche applications due to its high unit cost and is used in e.g. sawing or drilling of concrete or asphalt, where there is a requirement of extreme hardness of the tool material (Konstanty, 2005). Examples of the varying properties of some hard materials are presented in Table 1.

Table 1. Hardness and compressive strength of some hard materials represented by Vickers hardness and Young’s modulus, respectively (Fang et al., 2014; Prakash, 2014). WC-Co=cemented tungsten carbide with cobalt, TiC= titanium carbide. Al₂O₃=alumina, SiC=silicon carbide, c-BN=cubic boron-nitride.

<table>
<thead>
<tr>
<th>Material</th>
<th>Vickers hardness [HV]</th>
<th>Young’s modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>240-300</td>
<td>150-200</td>
</tr>
<tr>
<td>High-speed steel</td>
<td>750-800</td>
<td>210</td>
</tr>
<tr>
<td>WC-Co</td>
<td>700-2200</td>
<td>400-650</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1200-2100</td>
<td>340-390</td>
</tr>
<tr>
<td>TiC</td>
<td>1500-2200</td>
<td>460</td>
</tr>
<tr>
<td>SiC</td>
<td>2300-2600</td>
<td>400-460</td>
</tr>
<tr>
<td>c-BN</td>
<td>4000</td>
<td>~400</td>
</tr>
<tr>
<td>Diamond</td>
<td>8000-10 000</td>
<td>1220</td>
</tr>
</tbody>
</table>
1.2 Cemented Tungsten Carbide with Cobalt

The importance of cemented tungsten carbide with cobalt (WC-Co) for the manufacturing industry of today can be illustrated by the fact that about 70% of the metal cutting tools are made out of this material (Fang et al., 2014). WC-Co is used in a wide range of applications, including cutting tools for metals, plastics, woods and composites; rock drilling tools used for oil and natural gas exploration, mining and construction; and wear parts such as metal forming dies, wire drawing dies and abrasive fluid handling nozzles (Fang et al., 2014). However, knowledge about its environmental, resource and human health impacts is limited. Only a few studies provide life cycle inventory (LCI) data on the production of WC-Co or any of its precursors. LCI data for the production of the precursor tungsten carbide (WC) powder based on two production sites in China was recently provided by Ma et al. (2017). Indeed, China dominates the global tungsten production, but partly due to poor WC quality only 40% of the total tungsten export comes from Chinese tungsten products (Ma et al., 2017). Therefore, WC-Co purchased outside China is more likely to originate from non-Chinese production. Furthermore, there is a major difference in the production technologies applied between Chinese and non-Chinese production of WC, where the former applies solid ion-exchange technology and the latter solvent extraction (Wolfe et al., 2014). Some studies have attempted to gather LCI data for non-Chinese production. However, the data provided from these studies is limited to input materials, excluding energy used, emissions and waste (Syrраков et al., 2005) or is restricted to only a few life cycle processes (Xiong et al., 2008). LCA studies on products containing tungsten largely obtain their LCI data from such limited data sets (Bobba et al., 2016; Wigger et al., 2017). Furthermore, none of these LCI data sets include recycling, despite a global recycling rate of tungsten at 10-25% (Graedel et al., 2011). This is the first knowledge gap identified:

Knowledge gap 1: Life cycle inventory (LCI) data for non-Chinese WC-Co production including recycling is missing.

There are also growing concerns related to the future availability of WC-Co. Tungsten and cobalt are both geochemically scarce metals, present at only 1 and 24 ppm in the Earth’s crust, respectively (Wedepohl, 1995). Both elements are further included on the European Union’s list of critical raw materials due to their high estimated supply risk and economic importance (EC, 2017). The global mine production of these metals are dominated by two countries: China (>80% for tungsten (USGS, 2018a)) and the Democratic Republic of the Congo (DRC) (50% for cobalt (USGS, 2017)). Besides these resource issues related to WC-Co and its constituents, the use of tungsten, which is the main element by mass in WC-Co, is largely dissipative (Zimmermann and Gößling-Reisemann, 2013). This means that the metal is lost in such a way that it is technologically or economically unfeasible to recover, e.g. released to the environment, landfilled or diluted in other material flows. According to Zimmermann and Gößling-Reisemann (2013), the global dissipation rate of tungsten is >60%, while the average functional recycling of tungsten is limited to 10-25% globally (Graedel et al., 2011). Functional recycling of a metal implies that it is returned to a product or material where it has a specific function to fulfil (Guinée et al., 1999). In order to be able to act on this information, knowledge is needed on the societal flows of tungsten. So far, only a few studies of the societal metabolism of tungsten on the United States and global level have been conducted (Leal-Ayala et al., 2015; Harper and Graedel, 2008; Wang et al., 2018). None of these studies focus on specific products. The dissipation of a specific product may vary considerably from the material average, why it is important to also conduct studies having a higher resolution on product-specific material flows. Such studies are further important for the identification and implementation of product-specific measures to reduce dissipative losses (Zimmermann, 2015; Zimmermann, 2016). This is the second knowledge gap identified:

Knowledge gap 2: Dissipation and functional recycling of tungsten in specific products are unknown.

The importance of WC-Co for the manufacturing industry and its economic benefits are obvious (Section 1). However, whether WC-Co also provide net benefits from an environmental, resource and health perspective has so far not been assessed. Tungsten, together with tin, titanium and gold (3TG), is defined as a conflict mineral by the Dodd-Frank Act, since revenues from tungsten mining in the DRC is financing civil warfare in the region (Young, 2015). Other minerals, such as cobalt, mined in the DRC have also been associated with the conflict (Parsmo, 2015). While the global mine production of tungsten from the DRC is limited (USGS, 2018a), the global cobalt mining is dominated by the DRC (USGS, 2017), where artisanal mining, i.e. small-scale mining, prevail under harsh conditions for the miners (Elenge et al., 2013). In general, artisanal mining is a very dangerous activity that cause fatal accidents to 2.5% of the miners.
involved (ILO, 1999). To assess net impacts of products, a number of studies have suggested the application of a life cycle perspective and in particular the use of DALY to quantify net human health impacts of e.g. an airbag system (Baumann et al., 2013), nano-enabled chemical gas sensors (Gilbertson et al., 2014) and a gold ring (Parsmo, 2015). These studies include both positive human health impacts, e.g. from avoiding injuries, and negative human health impacts, e.g. from life cycle production emissions, occupational accidents as well as impacts from the conflict in the DRC. No such wider study has been conducted for a product containing WC-Co, leading to the third knowledge gap identified:

Knowledge gap 3: Net impacts of a WC-Co product have not been assessed.

1.3 Research Questions

The overarching research question for this licentiate thesis is: What are the environmental, resource and health impacts of hard materials? The point of departure is that an environmental systems perspective is required in order to avoid sub-optimization and the exclusion of important processes when answering this question. Therefore, the environmental systems analysis methods of material flow analysis (MFA) and life cycle assessment (LCA) are applied (Finnveden and Moberg, 2005). Tungsten carbide with cobalt (WC-Co), representing the typical hard material being used within manufacturing today, is applied as a case study. Some specific research questions in the assessment of WC-Co that are addressed in this licentiate thesis are:

1) What is the LCI data of non-Chinese WC-Co production?
2) What is the dissipation rate of tungsten in a specific product?
3) What is the net impacts of the use of a WC-Co product?

These questions correspond to the three knowledge gaps identified in Section 1.2 and are addressed in Paper I, Paper II and Paper III, respectively (Table 2).

<table>
<thead>
<tr>
<th>Paper</th>
<th>Object of study</th>
<th>Main concern</th>
<th>Method applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Cemented tungsten carbide with cobalt</td>
<td>Environmental impacts</td>
<td>LCA</td>
</tr>
<tr>
<td>II</td>
<td>Tungsten in tire studs’</td>
<td>Resource impacts</td>
<td>MFA</td>
</tr>
<tr>
<td>III</td>
<td>The tire studs’ of a studded passenger car</td>
<td>Net (human health) impacts</td>
<td>LCA</td>
</tr>
</tbody>
</table>

Tire stud pins are made from cemented tungsten carbide with cobalt.
2 METHODS

2.1 Life Cycle Assessment

Environmental management have historically been focused on direct emissions from industrial facilities. A shift in focus, away from end-of-pipe strategies limited to single industrial facilities, towards a wider life cycle perspective on products paved the way for LCA within environmental work in industry (Baumann and Tillman, 2004). LCA is a method for assessing life cycle environmental impacts related to products and services, which often involves the whole life cycle of products or services (cradle-to-grave) (Baumann and Tillman, 2004; ISO, 2006). Studies can also be conducted for certain parts of the life cycle, such as from extraction to production (cradle-to-gate) (Baumann and Tillman, 2004). LCA studies are either of the attributional or consequential type (Finnveden et al., 2009). In an attributional LCA, the environmental impacts associated with whole product systems are assessed, while environmental impacts of changes in product systems are assessed in a consequential LCA. All the applications of LCA aim at change or improvement (Tillman, 2000). LCA is typically applied to assess and improve product systems and for the support in decision making within a company, including process optimizations, marketing and strategic decisions (Hellweg and Canals, 2014).

The LCA framework consists of four steps (Figure 1) (ISO, 2006). First, the goal and scope of the study are defined. In this step, the purpose and object of study, e.g. a specific product, is decided upon and the intended audience is specified. The types of environmental impacts to be assessed are also identified. Importantly, a relevant functional unit of the study, describing the function of the studied product, is defined and should allow for fair comparison to other products. Some examples of functional units are 1 kg of steel, 1 person-kilometer and 1 liter of water. Methodological choices in subsequent steps are guided by the decisions made in the goal and scope step (Tillman, 2000). Choices made in this step, for example, determine what type of LCA that should be conducted, i.e. attributional or consequential, the choice of system boundary, e.g. which processes to include in the study, allocation procedure, e.g. how to allocate environmental impacts to multiple outputs from a process and how to handle recycled products, and the level of detail, e.g. whether general or specific data should be selected. Second, in the inventory analysis step, a flowchart is constructed to illustrate the included processes. Data on material and energy inputs, byproducts and outputs in the form of emissions and waste are then gathered for these processes. This data is finally related to the functional unit via calculations applying mass and energy balances, resulting in a set of life cycle inventory (LCI) data for the studied system. There exists different methods for LCI data compilation (Suh and Huppes, 2005). The most common method for compiling LCI data is the application of a process-flow diagram and algebra to link data on amounts of inputs and outputs to the functional unit. Other methods for compiling LCI data include a matrix representation of the product system and input-output analysis. Third, impacts associated with the inventory data are quantified in the impact assessment step. The categories representing the environmental impacts of the product system need to be defined and inventory data is classified to its relevant impact category. Global warming, ozone depletion, acidification and eutrophication are examples of commonly included impact categories. Then, inventory data on inputs and outputs for the processes in the studied system are characterized into impact categories, which are in turn linked to damage on the three main areas of protection considered in LCA: the natural environment, natural resources and human health (Finnveden et al., 2009). Characterization factors (CF) are applied for the translation from inputs and outputs to impacts on areas of protection according to (Hauschild and Huijbregts, 2015):

\[ IS = \sum_i CF_i \times q_i \]  

(1)

where IS is the final impact score [e.g. CO₂ eq], CFᵢ is the midpoint characterization factor for impact category i [e.g. kg CO₂ eq/kg substance] and qᵢ is the quantity of an input or output [e.g. kg substance]. Characterization factors can also be applied to go from a midpoint impact indicator to damage on areas of protection (endpoint characterization factors such as DALY/kg CO₂ eq, see Section 2.1.1). The characterization factors are based on environmental models (modelling environmental mechanisms including fate, exposure and effects of substances) aimed at the provision of best estimates for impacts.
given limited knowledge (Hauschild, 2005). Consequently, life cycle impact assessment (LCIA) results describe potential impacts and not real effects (Hauschild, 2005). An example of a ready-made LCIA method is the ReCiPe method (Goedkoop et al., 2013). The impact assessment results can further be weighted into a final score for total environmental and resource impact based on economic values or other bases. Fourth, the results are interpreted in the light of the study’s goal and scope in order to draw relevant conclusions. The dominant life cycle processes can be identified for various impact categories (dominance analysis) and the inputs and outputs responsible for the largest contribution to various impact categories can be highlighted (contribution analysis) (Heijungs and Kleijn, 2001). Sensitivity and uncertainty analysis is also conducted in this step.

Over the last three decades, substantial development of LCA has taken place (Guinée et al., 2011). The focus on environmental impacts has been widened into also considering economic and social impacts in the methods of life cycle costing (LCC) and social life cycle assessment (SLCA).

![Figure 1. Steps in the LCA framework (ISO, 2006).](image)

### 2.1.1 Disability-adjusted life years

The disability-adjusted life years (DALY) indicator can for example be applied to quantify the burden of disease in a population and is commonly used for this purpose, e.g. in the global burden of disease studies (Abajobir et al., 2017). The indicator can also be applied to convert LCIA data into an aggregated measure for human health impacts. Since DALY was applied in Paper III, it is described in more detail in this section. An early use of DALY in LCA was in the impact assessment model Ecoindicator99 (Goedkoop and Spriensma, 2001) and later in the ReCiPe method (Goedkoop et al., 2013). DALY was developed in the 1990s for the World Health Organization and the World Bank (Murray and Lopez, 1996) and provide a measure for the number of years lost due to disability and/or premature death (Murray, 1994; Devleesschauwer et al., 2014):

\[
\text{DALY} = \text{YLL} + \text{YLD} \quad (2)
\]

\[
\text{YLL} = N \times L_{\text{death}} \quad (3)
\]

\[
\text{YLD} = I \times D \times L \quad (4)
\]

where \(YLL\) is the years lost due to premature death [year], \(YLD\) is the years lost due to disability [year], \(N\) is the number of deaths [-], \(L_{\text{death}}\) is the standardized life time at the age of death and a measure of the number of years that the person could have lived [year], \(I\) is the number of incidents [-], \(D\) is the disability
weight [\cdot] and \( L \) is the average time spent with a disability until the severity of the disease is changed or the person dies [year].

The conceptual foundation for DALY are provided by Murray (1994) and Murray and Acharya (1997). The development of DALY was from the beginning based on four different principles: 1) All health impacts that the society is willing to allocate resources to should be included in the indicator. 2) Except those features related to the disease, individuals should only be characterized by their age and sex. Other parameters such as income or education were not included based on social equality. 3) All health impacts should be treated equally in order to secure comparability between different societies and over time. 4) The unit of the indicator is time. A number of social preferences are further incorporated in DALY and these have consequences for the construction of the indicator (Murray, 1994). One social preference is connected with the amount of time that is lost due to premature death, in turn dependent on a standardized life time. The DALY indicator also incorporates social preferences in connection to the time lived at different ages through the use of an age weighting. Time lived with a disability is included through disability weighting in order to be able to compare with years lost due to premature death and a time preference incorporated through discounting also imply certain valuations. The incorporation of standard life expectancy and disability weighting are required for the calculation of DALY while the inclusion of age weighting and discounting are eligible. Anand and Hanson (1998) raise critique against the use of disability weighting. Their criticism is due to the independence of disability weighting on social context, implying that no consideration is taken on the varying ability of people to handle the same disability, and the systematic partiality against individuals with permanent disabilities. Therefore, careful consideration and transparent presentation of methodological choices in the application of DALY are important.

2.2 Material Flow Analysis

The movement of materials through the natural ecosystem can be used as a desirable metaphor for human-induced flows (Husar, 1994). The ecosystem has a capability of having a sustained development compared to many anthropogenic systems. The main difference between the flows of materials in the ecosystem (via producers, consumers and recyclers) and the anthropogenic system is that the latter lacks efficient recyclers. Furthermore, contrary to ecosystems, the physical separation of manufacturing, consumption and recycling might be large in the anthropogenic system, exemplified by global trade flows. Today, MFA is applied in many different fields to study the societal metabolism, i.e. the stocks and flows of materials and energy through the economy, including, waste handling, product design and LCA (Brunner and Rechberger, 2004). The application of MFA within the fields of resource conservation and environmental management dates back to the 1970s (Brunner and Rechberger, 2004). Later, issues of e.g. toxic combustion emissions highlighted the inability of the traditional MFA to successfully consider waste handling processes, such as in incineration or landfilling. This led to the development of a specific type of MFA called substance flow analysis (SFA), which focuses on specific substances, e.g. heavy metals and nutrients, rather than goods (Brunner and Ma, 2009). The object of study in MFA is materials, which includes both goods such as fuels, cars, and municipal solid waste as well as substances (Brunner and Rechberger, 2004).

MFA studies the flows and stocks of materials from a system perspective (Brunner and Rechberger, 2004). The method is based on the principle of mass conservation (Lavoisier, 1789), which implies that mass cannot be created nor destroyed but transformed into other forms. This principle makes MFA attractive as decision-support in environmental management, since results can be verified (Brunner and Rechberger, 2004). In the general MFA procedure, three steps can be identified (Figure 2): problem and scope definition, flows and stocks quantification, and presentation and evaluation of the results (Brunner and Rechberger, 2004; Bringezu and Moriguchi, 2002). These steps should be conducted iteratively to ensure that the objectives influence all steps and decisions made in the study. First, objectives are formulated and the scope is defined: which materials, flows and stocks as well as geographical and temporal boundaries that should be included are decided upon. Second, flows and stocks are quantified based on the mass conservation principle, where the sum of the mass \( (m_i) \) for all inputs \( i \) to a process equals the total mass
\( (m_o) \) for all outputs \( o \) from the process plus the stock \((m_{stock})\), which considers the accumulation or depletion of materials in the process, according to:

\[
\sum_i m_i = \sum_o m_o + m_{stock}
\]  

(5)

The quantification can further be done either by static or dynamic modelling. In static modelling, flows and stocks are quantified by applying steady state, while variations of stocks in time are considered in dynamic modelling (van der Voet, 2002). The third step involves an evaluation and presentation of the quantified flows and stocks. Important audiences for the presentation and evaluation are technical MFA experts and stakeholders in policy- and decision-making processes.

Figure 2. Steps in the general procedure for material flow analysis (Brunner and Rechberger, 2004; Bringezu and Moriguchi, 2002)
3 RESULTS AND DISCUSSION

The main findings in Paper I, Paper II and Paper III are summarized in Table 3 and described in more detail in Sections 3.1-3.3, followed by a discussion on potential alternatives to WC-Co in Section 3.4.

Table 3. Summary of the main findings in Paper I, Paper II and Paper III.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Object of study</th>
<th>Main findings</th>
</tr>
</thead>
</table>
| I     | Cemented tungsten carbide with cobalt                | • Environmental impacts are dominated by a few inputs to and outputs from the WC-Co production processes  
• Recycling greatly reduces WC-Co environmental impacts  
• Energy requirement of non-Chinese production is lower than that of Chinese production |
| II    | Tungsten in tire studs                               | • The dissipation rate of tungsten in tire studs is 98% between manufacturing and waste management  
• There is effectively no functional recycling of tungsten in tire studs  
• Unintentional release of WC-Co nanoparticles is in the same order of magnitude as the release of some engineered nanomaterials |
| III   | The tire studs∗ of a studded passenger car           | • The purpose of tire studs to save lives is not justified from a life cycle perspective  
• Largest contributions to negative health impacts are use phase particle emissions and occupational accidents in cobalt mining  
• 16-28% of human health impacts occur outside Scandinavia |

*Tire stud pins are made from cemented tungsten carbide with cobalt.

3.1 Paper I: Environmental impacts of non-Chinese WC-Co production

Comprehensive and detailed LCI data for typical non-Chinese production, including recycling, was provided by applying a cradle-to-gate attributional LCA. In order to illustrate the applicability of the LCI data and to identify hotspots, an LCIA was also conducted. The functional unit was 1 kg WC-Co with a typical cobalt content (6-16%) and WC grain size (>0.2 μm) (Fang et al., 2014). The cobalt content and the WC grain size affect the mechanical properties of WC-Co, including hardness and toughness. The studied production system was divided into a foreground system, including the production of tungsten concentrates in the mining phase, transport of the concentrates, production of ammonium paratungstate (APT) in hydrometallurgy, WC powder in pyrometallurgy and WC-Co in powder metallurgy, and a background system, including the production of inputs and energy to the foreground system as well as the waste management of waste outputs from the foreground system. Allocation in waste treatment was conducted with the cut-off method, implying that only direct impacts associated with a product is assigned to that product (Ekvall and Tillman, 1997). The Ecoinvent database (2017) was used to model the background system. Impact categories recommended for LCAs of metals (Santero and Hendry, 2016), namely global warming, acidification potential, eutrophication potential, smog potential, ozone depletion potential, net water consumption, primary energy requirement and waste generation, were used for the LCIA. The impact assessment methods of climate change, terrestrial acidification, freshwater eutrophication, photochemical oxidant formation, ozone depletion and water depletion were modeled by the ReCiPe method (version 2008) with the hierarchist scenario, representing common policy principles regarding e.g. time frames (Goedkoop et al., 2013). The cumulative energy demand (CED) (Frischknecht et al., 2015) and EDIP2003 (Wenzel et al., 1998) methods were used for the impact categories for primary energy requirement and waste generation, respectively, since these are not provided by the ReCiPe method. Parameter uncertainty was handled by creating a baseline case as well as a low and high environmental impact case. Uncertainty in the model was assessed by creating scenarios with varying recycling rate and type of tungsten ore (i.e. scheelite and wolframite).
Comprehensive LCI data for the non-Chinese production of 1 kg WC-Co, for different scenarios varying the recycling rate and the type of tungsten ore, is provided in Paper I. The largest material inputs, added in ≥1 kg/kg WC-Co, are kerosene, sodium carbonate and water in the hydrometallurgy phase as well as water in the mining phase. The mining and powder metallurgy phases are responsible for the largest inputs of diesel and electricity, respectively. The LCIA results showed that the mining, hydrometallurgy and powder metallurgy contribute the most to the selected impact categories. For the total CED, a limited number of inputs contributed the most, including the inputs of kerosene (10-31%) and electricity (3-15%) to hydrometallurgy phase and the inputs of cobalt (1-9%) and electricity (8-51%) to the powder metallurgy phase. Inputs of diesel and tannin to the mining phase also contributed markedly in several of the scenarios. The energy requirement for the production of 1 kg WC powder in Paper I (58 MJ eq) was compared with the results from the study of Chinese WC powder production by Ma et al. (2017) (170 MJ eq), suggesting that the non-Chinese production is more energy-efficient. For the impact categories of freshwater eutrophication, water depletion and landfilling, the mining phase generally dominated. The largest contribution in general from the mining phase to freshwater eutrophication, water depletion and landfilling were the emission of nutrients from separated sulfidic tailings (93-97%), input of water (53-68%) and separated material (>98%), respectively. In general, the other included impact categories followed the total CED well and recycling significantly reduced impacts. Subsequently, the LCI data and the LCIA results can be used in cradle-to-grave LCAs of products containing WC-Co or any of its precursors.

3.2 Paper II: Resource impacts of WC-Co in tire studs

In a number of countries, passenger cars use tire studs during winter, including Sweden, Norway, Finland, Canada, Russia and the U.S (Tuononen and Sainio, 2014) but the societal flows of tungsten in tire studs have until now not been assessed. Flows of tungsten related to the use of tire studs in Sweden from raw material extraction, production over to use and waste management of tire studs was quantified using MFA with a steady-state mass-balance flow model. The dissipation rate, functional recycling rate as well as the share of tungsten in tire studs that become hibernating stocks, i.e. a material stock no longer in use but remain unrecovered but is expected to be in the future (Daigo et al., 2015), were quantified to assess resource implications. In addition to the resource issues related to tungsten outlined in Section 1, various measurements of road dust and road-runoff have identified tungsten-rich particles at elevated levels caused by the wear of tire studs (Bäckström et al., 2003; Bourcier et al., 1980; Bučko et al., 2011; Tuoriniemi, 2013). Further, measurements have been able to confirm that a share of this release is nanoparticles (1-100 nm in at least one dimension (ISO, 2010)). The magnitude of released WC-Co nanoparticles has not been assessed in previous studies of nanoparticle release (Keller and Lazareva, 2014; Sun et al., 2016). Therefore, the WC-Co nanoparticles release from the use of tire studs was quantified and compared to releases of some engineered nanomaterials in Sweden. In order to assess the sensitivity of the results to various input parameters, a sensitivity analysis was conducted.

The results indicate that the use phase release in the form of worn particles from the tire studs, together with losses of tungsten during mining, are substantial. The dissipation from tire stud manufacturing to waste management is in total 98%. The rest become hibernating stocks and the use phase release account for 67% of the tungsten outflows. This can be compared to the global dissipation rate of >60% that is mainly in the form of losses to other material flows (Zimmermann and Gößling-Reisemann, 2013). The sensitivity analysis indicated that the tungsten release and total tungsten input are sensitive to a number of input parameters. However, the dissipation rate was notably insensitive. There is effectively no recycling of tire studs, despite the fact that almost all scrapped studded tires are collected in the waste management phase: 0% of the tungsten in tire studs is functionally recycled compared to the global functional recycling rate of 10-25% (Graedel et al., 2011). The dominating waste management type for tire studs is landfilling. Dissipation in the form of tungsten release in the use phase of tire studs is effectively unavoidable, but the development of methods for removing the tire studs before entering tire waste treatments or separating tire studs from other waste fractions could enable recovery of the tungsten.
Another alternative is to shift to non-studded winter tires, but then the same function would not be provided since studded tires reduce accidents more effectively than non-studded tires (Malmivuo et al., 2017).

The comparison of use phase WC-Co nanoparticle release with emissions of some engineered nanomaterials indicated that the WC-Co nanoparticle release is of similar magnitude, showing higher release than e.g. silver nanomaterials and carbon nanotubes. WC-Co nanoparticles have not been included in previous environmental risk assessments of nanomaterials (Arvidsson, 2015; Gottschalk et al., 2013) and ecotoxicity data is very limited (Kühnel et al., 2014), why such studies are recommended for future research.

3.3 Paper III: Human health impacts from the use of tire studs

The function of tire studs is to reduce the number of accidents and thus save lives by increasing the friction between the tires and the winter road. However, the use of tire studs is controversial and debated since it causes an increased release of worn road particles, which are in turn associated with negative impacts on human health (Elvik et al., 2013). Thus, tire studs are associated with both positive and negative human health impacts in the use phase, but the net impact has not been assessed. The net life cycle human health impacts of the use of tire studs in a studded passenger car in Scandinavia was studied by conducting a cradle-to-grave LCA. The functional unit was set equal to the number of tire studs in a studded passenger car, corresponding to 0.07-0.3 kg WC-Co in the tire stud pins and 0.31-0.65 kg aluminum in the tire stud bodies. Impact assessment was conducted based on the method for assessing life cycle human health impacts in terms of DALY developed by Arvidsson et al. (2018). Three system boundaries were applied and five different types of health impacts were quantified. In system boundary 1, impacts saved in the use phase and negative impacts from use phase particle emissions were assessed. DALY saved in the use phase were mainly based on accident reduction rates from using studded tires compared with other tires, see e.g. Elvik (1999). Use phase emissions from road wear and tire stud wear, calculated in Paper II, were translated into impacts by applying the endpoint characterization factor for particulate matter from Goedkoop et al. (2013). Within system boundary 2, a life cycle perspective was applied including impacts from life cycle production emissions and occupational accidents. Life cycle production emissions were calculated based on the LCI data in Paper I for WC-Co, based on EcoInvent database (2017) for aluminum and applying endpoint characterization factors from the ReCiPe method (Goedkoop et al., 2013). Occupational accidents were quantified based on the approach and work environment characterization factors provided by Scanlon et al. (2014). With the application of system boundary 3, direct impacts from revenues in cobalt mining causing fatalities in the conflict, based on Furberg et al. (2018), were assessed. A low and high impact scenario were constructed in order to consider parameter uncertainties.

The use of tire studs in a studded passenger car is not justified from a life cycle perspective since the DALY saved in the low and high impact scenarios (2.1×10⁵-2.5×10⁴) is lower than the negative human health impacts (2.5×10⁴-1.1×10³). The DALY lost is thus generally higher than DALY saved, with a small overlap in the HS of the use phase saves and the LS of impacts from use phase emissions. As much as 72-84% of the total negative human health impacts occur at system boundary 1. The contribution to impacts from use phase emissions are dominated by road wear particles (93-100%). System boundary 2 is responsible for 16-27% of the total negative human health impacts. The production of the tire stud aluminum bodies has the largest contribution to life cycle production emissions in the LS (91%) while the production of WC-Co pins has the largest contribution in the HS (66%). Occupational accidents are dominated by impacts in artisanal cobalt mining (87-90%). System boundary 3 only covers 0.4-1% of the total negative health impacts. A number of other contributions to positive or negative human health impacts could have been included in this study as well, e.g. human health improvements from increased income in a population (Feschet et al., 2013), impacts from noise caused by studded tires (Johnsson and Nykänen, 2013), inclusion of occupational accidents related to construction of capital goods (Scanlon et al., 2014) and indirect deaths associated with the conflict in the DRC (Checchi et al., 2017). However, their
inclusion would not change the results of the study, either because the contributions are inapplicable for this case (in the case of the income effect, see Paper III) or simply because they would only increase the negative human health impacts, which are already dominating. Alternatives to studded tires have been posed, e.g. electronic stability control in cars, but this solution does not seem to provide the same accident reduction as studded tires (Elvik, 2015).

3.4 Alternatives to WC-Co
These findings (Section 3.1-3.3) suggest the question whether there are any alternatives to WC-Co that can provide the same function but with less environmental, resource and human health impacts. Relating back to Section 1, there do exist a number of alternative hard materials available on the market although their use has so far been limited. Suggestions for the substitution of tungsten carbides (WC) in WC-Co have been posed, including molybdenum carbides, tantalum carbides and silicon-containing cermet (EC, 2017; Prakash, 2014). Marginal substitutes for WC-Co such as aluminum-containing cermet as well as superhard materials including diamond and cubic-boron-nitride have also been identified by the EC (2017). However, the substitution potential is limited in many cases due to high costs or reduced performance (EC, 2017). Some of these suggested alternatives, rely on scarce metals with a very low concentration in the earth’s crust, such as molybdenum (1.1 ppm) and tantalum (1.1 ppm) (Wedepohl, 1995). Furthermore, tantalum is considered to be a conflict mineral (Young, 2015). From a resource perspective, the saying “out of the ashes and into the fire” seems highly fitting to describe some of these suggested substitutions, or at least “into another fire”. The shift from one scarce metal to another might provide a short-term solution in some cases, but it does not provide solutions with the potential to be successful in the longer run.

Taking a longer-term perspective on WC-Co substitution, potential alternatives may be found among synthetically produced diamond and nanomaterials made out of the abundant element of carbon. Arvidsson and Sandén (2017) explored the idea that carbon nanomaterials might substitute scarce metals in various applications. Cemented carbide is mentioned as one potential material that could be replaced by other materials having high strength and toughness. Monocryalline graphene, which is known as the strongest material ever measured (Lee et al., 2008), is mentioned as one such alternative. Diamond is another carbon-based alternative, with combinations of WC-Co and diamond being used in industry already, e.g. as inserts of WC-Co substrates coated with diamond (Konstanty, 2015). In this case, however, issues associated with the use of WC-Co are not entirely resolved. Further, nano-diamond has been suggested as a promising material, for example in the form of coatings used in hard material applications (Mochalin et al., 2012; Hu et al., 2007; Kharisov et al., 2010). Both natural and synthetic diamond are used within industry today, but synthetically produced diamond is dominating since this allows tailoring of the diamond properties and the production of large quantities (USGS, 2018b). Application of nanofabrication techniques in this field is of particular interest, with its relations to other carbon-based materials like graphene. However, compared with other hard and abrasive materials, the use of industrial diamond is currently limited due to its high unit cost (Konstanty, 2005). The global production of 4.46 billion carats industrial diamond in 2014 (USGS, 2018b), equivalent to 890 metric tonnes, is indeed small in comparison with the global cemented carbide production of 49 000 metric tonnes in 2010 (Leal-Ayala et al., 2015). From a resource perspective, the use of the abundant carbon in synthetically produced diamonds is advantageous in comparison with the use of the scarce tungsten metal in cemented carbides. From an environmental perspective, the study by Mendoza et al. (2014) indicates that the use of diamond tools in sawing of granite is beneficial by for example saving energy, but differences in life cycle impacts from producing conventional and diamond sawing tools was not investigated. Diamond used in hard material applications has so far not been evaluated from a life cycle perspective, which is important in order to avoid burden-shifting between phases.
4 CONCLUSIONS

The use of WC-Co, representing the currently dominating hard material for manufacturing tools, is associated with environmental, resource and human health impacts. Environmental impacts have been presented as ready-to-use cradle-to-gate LCI data and LCIA results for the typical non-Chinese production of WC-Co, and a number of its precursors. The results indicate that the typical non-Chinese WC-Co production is less energy-intensive compared with Chinese production. The mining, hydrometallurgy and powder metallurgy phases contribute the most to the cradle-to-gate life cycle impacts and a large part of the impact is caused by a limited number of inputs and outputs. The impacts were greatly reduced by recycling. Regarding resource impacts, the MFA case study on tire studs concluded that the use of tungsten in this product is disadvantageous. The high tungsten dissipation rate of 98%, implying a negligible functional recycling of tungsten, is dominated by the use phase particle release from wear that is effectively unavoidable. Implementation of tungsten recovery in waste management together with research on alternatives to WC-Co in tire studs and environmental risk assessments on WC-Co nanoparticle release are recommended. The case study on net human health impacts of tire studs concluded that the purpose of tire studs to prevent injuries is not justified, since negative human health impacts outweigh the benefits of the use of tire studs in a studded Scandinavian passenger car. The DALY lost are larger already in the use phase and even more so when a life cycle perspective is applied. Impacts from use phase emissions and occupational accidents in artisanal cobalt mining have the largest contribution to the DALY lost with 72-84% and 7-16%, respectively. In total, 16-28% of the DALY lost occur outside Scandinavia, where the benefits occur, indicating a partly unfair distribution of health impacts over the life cycle. These results indicate that assessments, applying a life cycle perspective, of alternatives to tire studs are required. A number of alternatives to WC-Co with varying substitution potential have been suggested in literature, such as tantalum carbides, cermets and diamond. However, questions remain to be answered regarding these alternatives: Can they provide the same function as WC-Co and perform better from an environmental, resource and health perspective? Are there any trade-offs in a substitution with such materials? These questions are suggested as points of departure for future research on sustainable alternatives to WC-Co.
5 REFERENCES

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