Green and Sustainable Technologies for Materials Manufacturing and Processing
"COMMONIZATION" OF MATERIALS: GUILTY BY ASSOCIATION

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ABSTRACT
As transparency efforts driven by green building requirements move the evaluation of “green” materials and chemicals into the offices of architects and designers and away from scientists, it is important to understand that common, generic terms may not necessarily represent the hazards and risks associated with specific chemicals or materials. Such terms, and the perceptions they create, may negatively exaggerate the actual health-based risks associated with the exposure to a specific product, often via a “guilty by association” mindset. This paper will review requirements that encourage material selection based on chemical content, and will provide examples of common building materials and how generic chemical terms influence market-place decisions.

INTRODUCTION
In 2014, the construction industry accounted for 4% of US GDP, according to a recent report by McGraw Hill Construction, nearly 50% of all buildings in the US are being built to be “green.” Therefore, trends in this industry segment will have a large impact on the materials science community, which ultimately provides the materials and finishes used in buildings.

In the green building community, there is a growing belief that sustainable buildings should enhance the health and well-being of occupants, resulting in a desire to construct them using “non-toxic” materials. These factors have driven a movement to have manufacturers publically share the content of construction materials and finishes to levels as low as 1000 or even 100 ppm, with the presumption that such transparency will eliminate all harmful chemicals from the building. For example, Version 4 of the United States Green Building Council’s (USGBC) Leadership in Energy and Environmental Design (LEED) Building Rating System, which is arguably the most influential green building rating system in the world, offers credit for selecting products that identify material ingredients to 1000 ppm. Common sense and science dictate that the mere presence of a chemical in a product does not necessarily make that product a health risk. Even the most regulated drinking water will contain trace amounts of lead and other heavy metals.

Credits such as the LEED v4 Material Ingredient Credit can inadvertently create fear in the marketplace. The intent of this LEED credit is “to encourage the use of products and materials for which life-cycle information is available and that have environmentally, economically, and socially preferable life-cycle impacts.” Yet, most people in the building industry are not scientists and likely do not understand that the mere presence of a chemical in a product does equate to a product health risk. Before jumping on this bandwagon, it is important to remember that chemical risk is a function of toxicity, exposure, hazard, dose and time, and is specific to each compound. Toxicity indicates what health problems are associated with various doses or concentrations, and is estimated using two sources of information: 1) any available data on effects on humans, and 2) bioassay experiments. Exposure is an estimate of how much of the chemical a person is likely to eat, drink, or absorb from water, air, or other sources.
Many decisions made to comply with the green ratings systems and requirements are based solely on the potential hazard a chemical poses rather than the actual risk a chemical poses or the risk that is created if the chemical is not utilized. OSHA has stated that hazard determination does not involve an estimation of risk and that the difference between the terms hazard and risk is often poorly understood. OSHA goes on to say that considerable differences may exist in the risk posed by a substance depending on conditions that result in or limit exposure.

An easily grasped example of hazard versus risk involves the hand-held hair dryer. If “hazard” is broadly assumed to be anything that can cause harm, then these devices clearly have inherent hazards associated with their use. If “risk” is considered to be the chance that someone will actually suffer harm, then an example of risk associated with a hand-held dryer would be the risk of being electrocuted if one uses it in standing water, such as a bathtub.

In an effort to simplify the identification of potentially “harmful” chemicals for non-technical specifiers, so-called listings of “chemicals of concerns” (COC’s) have been developed by a wide variety of groups. Such lists are commonly being used by the promoters of healthy buildings. Unfortunately, many of these groups have overly simplified risk and hazard and rely instead on simple lists of broad groups of chemicals that should be avoided. Generally, the worst-case hazard, or “hazard endpoint,” such as “reproductive toxin” or “potential carcinogen” is given, without including information about exposure, dose or toxicity levels. In addition, these COC groupings often link materials together based on a “worst player,” and ultimately target not only problematic chemicals, but ones that are perfectly safe. This “commonization” of materials through the use of generic terms and broad classes can create negative perceptions of whole groups of materials that are not based on sound science, and can ultimately create fear and frustration on the part of end-users and manufacturers.

Generic terms for chemical compounds can be extremely misleading. It is not uncommon for non-scientists to refer to an entire class of related, or even non-related, compounds using a common name. Examples of these include “chlorine,” “antimicrobials,” and “phthalates.” To a scientist, such terms are vague, and often refer to a part of a compound or even a material’s function. However, by using such common, non-exact terms, whole classes of materials are being lumped together and are presumed to be equally dangerous to human health; this phenomenon unfairly targets many safe materials. For instance sodium chloride (table salt) and chlorine gas are two extremely different compounds, but both could be listed as chlorine-containing substances; only the latter is generally considered to be dangerous.

In 2008, the United States passed legislation prohibiting the manufacture, sale, distribution, or import of any children’s toy or child care article that contains concentrations of more than 0.1 percent of three (3) specific phthalate-based plasticizers due to concerns about their toxicity and ability to bioaccumulate. Although parts of the ban apply only to items that can be placed in the mouth and be sucked or chewed, the details are often overlooked. This lack of addressing the specific risk associated with exposure via oral ingestion, combined with the use of the generic term “phthalate” has penalized other products which contain other phthalate-based chemicals, since opponents assume that all phthalates are harmful via any route of exposure or contact. Although the use of these chemicals in building materials does not pose a health risk since there is no route for ingestion-based exposure, by using the common term “phthalate,” all chemicals in the family become suspect.

By focusing too narrowly on a presumed health risk and a specific product function, it is possible that other benefits to building occupants or consumers are not being considered. For example, some green building schemes, including LEED V4, frown upon the addition of all antimicrobial compounds out of fears that we are unnecessarily using chemicals that will result in
microbes that are resistant to modern medicines. While specific antimicrobial agents have been linked to such resistance, the use of a common term based on a material’s function has created the perception that all antimicrobial substances are problematic and should be avoided. However, when these compounds are eliminated, the risks of mold and bacteria growing on materials greatly increases, the material life span can be reduced, and germs and harmful bacteria may be more easily spread. In general, the effort to eliminate a few “dangerous” compounds is not accounting for such holistic trade-offs.

Finally, titanium dioxide is an example of a commonly used material that is simultaneously considered “dangerous” by some and beneficial by others. The fine dust forms of titanium dioxide have been listed as possible carcinogens by IARC, yet other forms are approved for use in cosmetics, food and other products due to its low risk to human health. It is a well-known UV-blocking substance widely used in sunscreens, and has documented antimicrobial properties, both of which enhance human health. It has other beneficial uses in sustainable buildings as well, but none of these can be realized if the material is avoided due to a specific, narrowly defined health risk associated with only one form.

Although these trends towards transparency and simplifying chemical risks are global, the examples discussed here will pertain to the US market. The impacts of commonization by chemical family, function and form will be addressed.

**GUILTY BY CHEMICAL FAMILY: “PHTHALATES”**

One example where an entire family of chemicals is now perceived by some to be unsafe based on the issues of a few specific chemicals is the case of phthalate esters or “phthalates.” “Phthalates” are a class of synthetic chemicals with a broad spectrum of uses including softeners in plastics, solvents in perfumes, and additives to nail polish, as well as in lubricants and insect repellents. Polyethylene terephthalate (PET) is one of the most commonly used polymers in the world, used to make polyester fibers and clear plastic bottles, among other things. However, when people use the generic term “phthalate,” they not generally referring to terephthalates but to dialkyl ortho-phthalates, which are a class of about 30 commercial chemicals; these ortho-phthalates are used primarily as plasticizers for polyvinyl chloride (PVC) and as solvents.

In February 2009, three types of ortho-phthalates were permanently banned from use in children’s toys and child care articles in the US: di (2-ethylhexyl) phthalate (DEHP); dibutyl phthalate (DBP); and butyl benzyl phthala te (BBP). The US Consumer Product Safety Improvement Act (“CPSIA”) of 2008 prohibits the manufacture, sale, distributions, or import into the United States any children’s toy or child care article used for feeding or teething that contains concentrations of more than 0.1 percent of DEHP, DBP, or BBP. Three additional phthalates were “interim banned:” diisononyl phthalate (DINP); diisodecyl phthalate (DIDP); and di-n-octylphthalate (DnOP). The permanent CPSIA ban applies to children’s toys and to child care items that can be brought to the mouth by a child so that it can be sucked and chewed. The interim ban applies only if the toy or toy part can be placed in the mouth; if it can only be licked, then it is not considered as being able to be “placed in mouth.”

Yet, the later part of this requirement – must be able to be sucked and chewed – is usually not mentioned.

Furthermore, to assume that because these chemicals are harmful in children’s toys they must be harmful in all products is not accurate. For example, for a child to be exposed to DEHP in a toy they must chew or suck on it for lengthy periods of time. In fact, the CSPC specifically states that the ban does not apply to components of children’s toys that are inaccessible, nor to children’s socks, shoes, and packaging for toys or feeding items. These same chemicals used in building materials, such as carpets or floors, do not pose a risk, because there is no route for oral exposure. However, many manufacturers have moved away from the use of ortho-phthalates due.
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to market demand. Other chemically different members of the phthalate family, such as PET, have been widely tested and are generally considered to be safe for human use.

But, for many people, the fact that a few specific phthalates have been banned from being used in a limited number of specific types of products has translated into a belief that all phthalates should be universally banned. As a result, products which contain other chemicals in this family are penalized because of the negative association with the term “phthalate,” even though they are not part of the ban. The CPSC even states that children’s items may contain other non-banned phthalates, which should suggest that other phthalates are safe to use. Thus, by using a generic chemical term, an entire family of chemicals has been given a “bad reputation,” even though the hazards are associated with a limited number of specific compounds.

GUILTY BY FUNCTION: “ANTIMICROBIAL” COMPOUNDS

So-called “antimicrobial” compounds are another example whereby a large number of materials have been lumped together as being dangerous. In this case, the determination has been made based on the function of the material, i.e., the ability to inhibit the growth of microbes, rather than by chemical classification. Indeed, antimicrobial products make use of a wide variety of organic and inorganic compounds, some of which are man-made, and some of which are naturally occurring. Discouraging, or even banning, the use of all “antimicrobials” without consideration of their actual chemistry in an effort to reduce the potential for drug-resistant microbes is reactionary and is frequently not based on good science.

Many of the concerns and issues surrounding antimicrobials may again be attributed to not understanding the complete risk assessment of specific chemicals. Antimicrobial use has increased dramatically, with at least 275 chemicals now registered with the US EPA. As an example, Triclosan is a synthetic broad-spectrum antimicrobial that was first registered with the EPA as a pesticide in 1969. In recent years, evidence of Triclosan (and other antimicrobials) has been found throughout our environment including in water, soil, breast milk, and urine. Due to the amount of Triclosan in the environment and its ability to bioaccumulate, there have been many questions raised regarding the impacts Triclosan and other antimicrobials may have on the environment and human health. These questions have resulted in the discouragement or even banning of numerous antimicrobials in green buildings without an understanding the risk or benefit of the specific chemicals, presuming that all are “guilty” simply based on their ability to kill microbes.

In many cases there is no proven benefit to adding antimicrobials to consumer goods or building products. However, for many years this was deemed to be a best practice for controlling microbial growth, and was an attribute requested by customers; as a result, in many cases antimicrobials were overused. Now the pendulum is beginning to swing the other way, and there is a movement to ban all use of antimicrobials, even though there is currently no true scientific understanding of the actual environmental and health impacts of many members of this broad group of unrelated materials.

However, there are cases in which there truly is a need for antimicrobials, such as in healthcare facilities treating individuals with compromised immune systems. And although many consumer products lack clear evidence that antimicrobial addition is beneficial, in 1997 the FDA studied Triclosan in toothpaste and found that it was effective in preventing gingivitis. This is an example of an instance where we may cause more harm by NOT using antimicrobials.

Perhaps the most glaring example of harm that could occur by not using antimicrobials is in hospital settings. A report based on hospital infections in Pennsylvania estimates that in the US in 2006 there were approximately 720,000 hospital acquired infections, resulting in 74,000
And yet, motivated by legitimate fears of creating anti-bacterial resistant microbes, some hospitals and the USGBC are now encouraging the elimination of antimicrobials from buildings. However, the use of antimicrobial compounds in materials that are frequently touched and that are difficult to clean is known to be an effective means of reducing the transmission of infectious disease.

In addition to organic substances, including Triclosan, inorganic materials have also been shown to have antimicrobial properties. These include copper and silver, both of which have been used for over a century to control microbial growth. Copper alloys, such as brass and bronze, have also been shown to prevent the spread of microbes in healthcare facilities.

Initial research indicates that clean, uncoated copper surfaces are perpetually able to kill certain microbes that come in contact with the metal surface; thus, copper appears to be a "self-sanitizing" compound. For example, the use of copper in hospitals on specific surfaces such as toilet seats, faucet handles and door plates has been shown to reduce the amount of three specific types of microbes by 90 -100% as compared to the control fixtures, made of plastic, chrome-plated metals, or aluminum. In another study, a consulting room was retrofitted with copper in areas of high patient contact. Over six months, 71% of the bacterial load was reduced. A study from 1983 showed that the use of copper and bronze doorknobs prevented the spread of microbes in hospitals. However, the use of copper fixtures is banned from LEED V4. This is despite any firm evidence showing that copper leads to the development of drug-resistant microbes.

Silver has also been shown to be highly effective at killing microbes. There is a long history of applying silver compounds directly to wounds; this practice is being resurrected to avoid the use of antibiotics, which have clearly been linked to the rise of so-called "super bugs." Other recent research suggests that the addition of small amounts of silver to other drugs can greatly enhance the efficacy of those drugs in killing microbes, increasing the number of bacteria killed by 10 to 1000 times. Silver does have some documented toxicity issues: there have been documented cases of silver-resistant bacteria, and silver coatings were shown to be toxic to heart tissue when used in heart valves. It can also cause the skin to permanently turn blue-gray. However, outright bans of antimicrobials do not address the potential benefits in reducing the number of fatal infections in healthcare facilities.

Beyond the control of infectious disease, there are reasons to use materials containing antimicrobials in healthcare settings, specifically in porous substances used for sound control. Numerous studies have shown that modern hospitals are extremely noisy, and that this noise has a negative impact on patients, as well as staff. For example, studies have shown that the addition of sound absorbing materials to healthcare spaces can dramatically improve the acoustical quality of the space, directly resulting in reduced patient pain and stress, improved sleep, and reduced medical errors. Ultimately, all of these contribute to improved patient recovery rates.

However, many of the best materials for correcting ambient noise issues are open, porous materials. Because mold and bacteria can grow in these materials, due to their inability to be easily cleaned, they cannot be considered for use in healthcare settings unless they are treated. But guidelines put out by several healthcare organizations limit the use of antimicrobials in building products. By limiting the ability of manufacturers to add antimicrobial agents to porous products, it becomes even more difficult to justify the use of these acoustical absorbers in healthcare settings, potentially causing documented, negative impacts on patients due to increased noise.

Moving beyond applications in healthcare, there are valid uses for antimicrobial substances in other arenas that may not be immediately obvious to non-technical end users. For example, manufacturers may add these substances to enhance processability, for example
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extending the time during which a paint or binder is able to be used before it is attacked by microbes (i.e., spoils) and needs to be disposed of. Thus the use of small amounts of specific antimicrobials can avoid the generation of unnecessary waste, and the associated environmental impacts.

Manufacturers may also add specific antimicrobials to give final products particular functions. Again, the addition of small amounts to paints helps to ensure the long-term stability and durability of the paint and the surfaces below.17 However, adding these substances to items that are cleaned regularly, such as clothing or flooring, is not functionally necessary, and could cause more harm than good. In such cases, responsible manufacturers should be assessing all the potential risks associated with the use of antimicrobial agents and using them only when the benefits outweigh the risks.

Research is also being conducted into ways of incorporating antimicrobials into coatings in such a way that they continue to inhibit the growth of microbes, but remain safe for humans. Examples include the addition of silver to zeolites, glass, epoxies and other materials.17

Understanding all of the risks should naturally lead to a discussion of the potential trade-offs involved with using or avoiding specific antimicrobials. However, banning entire classes of materials solely due to function is not a holistic perspective, and can result in harm being done, or benefits not being realized. It also avoids addressing the risks associated with specific chemicals, instead broadly implying that all members of the category are problematic simply based on one of the functions.

GUILTY BY FORM: TITANIUM DIOXIDE

A specific example of the importance of understanding the entire risk equation is titanium dioxide. Titanium dioxide is used to whiten many products, from food to building materials. The US Centers for Disease Control lists respirable titanium dioxide particles, i.e. dust, as an occupational carcinogen and IARC lists the powdered form as possibly carcinogenic to humans. Yet at the same time, the US FDA allows the use of titanium dioxide in cosmetics and in food products, in quantities up to 1% by weight of the food.18 The EPA Safer Choices (formerly Design for the Environment) program considers titanium dioxide to be a “material of verified low concern.”19 So without an understanding of the entire risk equation, including the chemical form, it is easy to understand the confusion that arises when one is told in one instance that the substance is a carcinogen and in another, it is safe.

To clarify the carcinogen classification, it is important to understand that the IARC listing is related specifically to findings that fine and ultrafine powders were found to cause respiratory cancers in rats. This led to concern that workers exposed to high levels of dust could be at risk, and the subsequent listing as a possible carcinogen.20 When used in foods, cosmetics and other products, in the appropriate amounts, the dose and routes of exposure are not ones by which humans can be harmed. Thus the form of this chemical is key to its safety or risks.

In addition, any assumptions that all forms of titanium dioxide are dangerous fail to acknowledge many known benefits for this common material. Beyond its ability to whiten cosmetics, titanium dioxide is a well-known, effective UV-blocking additive used in many sunscreens21 and other sun-blocking cosmetics. Thus, while the loose particulate form of TiO₂ is considered a carcinogen, it is also a key ingredient in a product known to reduce the instances of skin cancers.

Within the building products industry, titanium dioxide has traditionally been used as a filler in many architectural materials due to its very high light refractive index (2.7 for the rutile form); the addition of titanium dioxide can consequently increase the light reflectance of the finish. This is turn has been shown to increase the effectiveness of natural light within a space,
lowering the need for lighting, thereby reducing energy usage.\textsuperscript{22,23,24} Many of the sustainable building schemes recognize the use of highly reflective surfaces as a strategy for enhancing daylighting and lowering energy costs and the associated environmental impacts. Increased regulation of greenhouse gases emitted from power plants will likely increase the desire for products that contribute to reductions in energy usage, making the use of highly reflective surfaces that incorporate TiO\textsubscript{2} even more desirable.

Newer uses for titanium dioxide in construction products include self-cleaning surfaces, which take advantage of the super-hydrophilic properties of the material;\textsuperscript{25} the use of these in architectural finishes would lower or negate the use of cleaners, potentially reducing exposure of occupants to these chemicals. In exterior applications, it could be used to help keep daylight harvesting surfaces, such as solar cells and windows, clean.

In addition, titanium dioxide has beneficial photo-catalytic properties that are being exploited in a number of ways to improve the built environment.\textsuperscript{25} ALCOA and others have developed architectural coatings which oxidize harmful nitrous oxide (NO\textsubscript{x}) fumes and turn them into nitrides;\textsuperscript{26,27} others have used the same principles to create “smog-eating” roof tiles and other surfaces.\textsuperscript{28,29} These products have the potential to use existing surfaces to reduce the generation of harmful smog in the environment.

Finally, the anatase form of titanium dioxide has been shown to be an anti-bacterial substance that is activated by UV light, creating the potential for surfaces that can sterilize themselves in the presence of light.\textsuperscript{25,30} The use of this property in medical facilities and other areas is being investigated.

Thus, while titanium dioxide can be a potential carcinogen in certain situations related primarily to the generation of dust during manufacturing, it can also be used with minimal risk to humans, as evidenced by its approval for use in food and cosmetics. Furthermore, it can actually be used to improve the indoor environmental quality of buildings and the health of humans. It can also reduce the environmental impacts of buildings through various mechanisms, including energy reduction. Thus, although different forms of this material have different hazards, there are some who are assuming that all forms are problematic based on the listing of the dust.

Indeed in many of the new transparency requirements and lists of chemicals of concern, only the hazard end-point of “potential carcinogen” would be listed, despite the fact that this classification, in this case, is for a narrowly defined form of titanium dioxide. Again such broad groupings, in this case ignoring form, can ignore the potential benefits associated with other, non-hazardous forms.

TRADE-OFFS

Trade-offs such as those associated with antimicrobials and titanium dioxide are frequently not being addressed by those advocating the elimination of chemicals to improve the health of building occupants. Instead, it is likely that a non-scientist would see that LEED credits that encourage the avoidance of antimicrobials are “proof” that any material that can kill microbes should be avoided. Similarly, they might see that TiO\textsubscript{2} is a possible carcinogen and leap to the conclusion that it should be avoided as a “toxic” chemical. Indeed, the internet is full of articles and blogs asking such questions as whether one’s lipstick, hand wash, toothpaste or sunscreen is causing health issues due to the presence of titanium dioxide or antimicrobial chemicals.

In addition to balancing the trade-offs between a material’s beneficial properties and potential hazards and risks, manufacturers face other trade-offs. These include costs, both in using alternate materials, including things such as capital investment and availability of materials, and productivity losses, due for example to spoiled paint. There can also be a lack of
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non-toxic alternatives; even the US EPA’s Safer Choice program recognizes that in some cases there may be hazards associated with some of the chemicals that are currently “best options.”

However, by referring to generic lists of potentially problematic materials, commonization is resulting in a situation whereby these trade-offs are generally not considered. As a consequence, some beneficial and safe products can be overlooked or omitted from use in buildings and other products.

MARKETPLACE FRUSTRATIONS

Today’s climate for increasing transparency, while well intended, is creating frustration for manufactures and consumers alike. For manufacturers, much of this frustration can be linked to the difficulty in obtaining and then conveying highly technical information around chemical content and risk to their customers and stakeholders. For consumers, much of the frustration can be linked to a lack of easy-to-understand information, resulting in difficulties in assessing risks and comparing products.

Efforts to simplify such information for non-technical audiences have been made. In some cases, the use of generic terms, such as “antimicrobial” or “phthalate” have helped lead to these cases of “commonization” and have allowed perfectly safe chemicals to be assumed to be health hazards. Indeed, several of the earliest influential “red lists” of so-called toxic chemicals were primarily lists of generic families or functions, helping to propagate the issues associated with commonization. Updated programs tend to have summary lists which contain generic terms, but these are generally now expandable into more detailed lists that include specific CAS numbers, etc. However, if someone merely scans the summary lists, the commonization effect is still applicable. Additionally, the ability to thoroughly comprehend the chemical and toxicity information associated with each chemical requires a reasonably scientific background, and most consumers do not have this skill set.

While manufacturers and consumers would both like easy-to-understand ways to assess the true risks associated with products, there is currently no easy solution. And the current trend of requiring chemical transparency to lower and lower trace levels is likely to only add to the confusion and resulting frustration.

CONCLUSIONS:

As transparency requirements in building products becomes more widespread and stringent, manufacturers and consumers alike will continue to face issues related to the evaluation and understanding of a material’s true risk. Efforts to simplify the transparency process have resulted in the misuse of generic terms for chemicals and materials. This commonization often oversimplifies or takes the place of a complete and thorough chemical evaluation and may misrepresent a chemical.

True risk assessments for chemicals should be based on the end-use and include consideration of exposure route, duration of exposure, and dose. Exposure is rarely being considered by the current schemes for evaluating chemicals, but it plays a vital role in understanding risk. These assessments should also compare costs, benefits and hazards of using the material. For building materials, such cost-value assessments should include the impact on the total indoor environmental quality and health of the occupants, the impact on the building’s environmental profile, and other pertinent factors, such as manufacturability and availability of alternatives.

This commonization of materials based on chemical family, function or form has resulted in many safe materials being perceived by the public as potentially toxic. In some instances, this
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misconception has resulted in the green building schemes avoiding or banning whole groups of materials. These decisions tend not to have addressed a holistic, scientific assessment of the benefits and risks associated with specific materials and finished goods.

Attempts to simplify transparency have led to many misinformed decisions regarding the appropriate use of a specific chemical or products containing these chemicals. Just as the industry has adopted comprehensive life cycle analyses, ultimately allowing for the creation of environmental product declarations that attempt to address all of the environmental impacts and phases of a product, there needs to be a clear way to perform a similar assessment of a product’s true impact on human health and well-being. Such systems need to be chemical and product specific, and consider the holistic impacts rather than use common terms for chemical family, function or form. They need to be based on internationally recognized, consensus-based standards that give guidance on how to evaluate the hazards, risks and benefits of specific materials, similar to the ISO suite of standards that were developed to for creating life cycle assessments.

In short, scientists need to actively steer the industry away from a system that utilizes over-simplified lists to one that assesses the true, holistic risk associated with the use of a specific chemical in a specific product. Only then will we move away from a market in which products can be guilty merely by association to one in which well-informed, science-based decisions can be made.

REFERENCES:
3USGBC, LEED V4 for Building Design and Construction, 1 July 2015.
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18US Food and Drug Administration Department of Health and Human Services, “Title 21–Food and Drugs, 21CFR Part 73.”
19US Environmental Protection Agency Safer Choice Program, http://www2.epa.gov/saferchoice
EXPERIMENTAL RESEARCH AND APPLICATION OF COPPER OXIDE FLOTATION USING THE COMBINED COLLECTORS OF BENZOHYDROXAMIC ACID AND BUTYL XANTHATE

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ABSTRACT

Benzohydroxamic acid with double dentate can combine with copper and form cyclic hydroxyl oxime acid copper chelate, so it has good recovering capability and selectivity for copper oxide minerals, especially for malachite. The flotation results of the pure mineral malachite show that the strongest synergistic collecting effect between hydroximic acid and xanthate can be generated with the highest malachite recovery of 95.5% when certain sodium sulphide is used as vulcanizing agent in the optimal pH range and the best ratio of hydroximic acid to xanthate is 3.5:1. In the refractory real ore flotation experiments, due to the synergistic collecting effect, the flotation recovery of malachite can reach to over 92% under the condition of optimum proportion, increasing 12% compared with the conventional collectors. In industrial production, the flotation indexes of the copper grade are high, and the copper oxide resource is utilized with high efficiency.

INTRODUCTION

Beneficiation of copper oxide ore is one of the recognized puzzles in mineral processing industry, and it is also the important research field for dressing workers. Copper oxide ore is the vital component of copper resource in the world, which has abundant reserves. Majority of sulphide deposits have oxidized zone on the top, and some oxidation deposits are oxidized to become the large and medium-sized oxidation deposits [1]. However, most copper oxide ores have the problems such as high slime, poor floatability, complex ore property and low flotation recovery, so it is of great significance in beneficiation of copper oxide ore to develop an efficient collector for copper oxide ore especially for malachite[2~4]. At present, sulfuration-xanthate...
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flotation is the most important method for treating copper oxide ore. In recent years, due to the decrease of mining grade, the utilization of refractory copper oxide ore draws more and more attention [5], except for sulfuration-xanthate method, chelating flotation method [6], chemical beneficiation method [7], microwave irradiation flotation method, hydrothermal sulfuration-floatation method [8] and ammonia leaching of sulfide precipitation-floatation method [9] have been occurred.

1 MATERIAL PREPARATION OF SINGLE MINERAL FLOTATION EXPERIMENTS, REAGENTS AND RESEARCH METHODS

The pure malachite samples were taken from a mine in Congo, and the purity was 98%. It was peacock green with well crystallization, and the copper content was 54.8%. The samples were crushed, handpicked, ground in porcelain mill and then sieved with a 0.074mm sieve, the through product was used in experiments.

Reagents used in this reseach are as follows: sodium sulfide (Na₂S·9H₂O), analytically pure, colorless cubic crystal, soluble in water; butyl xanthate (C₄H₉OCSSNa), industrial quality, pungent pale yellow powder; benzohydroxamic acid (C₃H₇NO₂), industrial quality with 70% purity, pink powder.

Single mineral flotation tests were conducted on a XFG-76 flotation machine with 50 ml volume, and the impeller speed was 1500 rpm. For each test, 2g of samples and moderate distilled water were added in the cell, and stirred 2 min to adjust the pulp, in order to examine the flotation behavior of malachite under different conditions. The flotation time was 3 min, after flotation, the froth product and the unfloated product were dried under natural conditions and weighed, and the percentage of the froth product weight to the total weight was calculated, that is the recovery, the experiment process is shown in Fig.1.
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2 RESULTS AND DISCUSSIONS

2.1 CONDITION EXPERIMENTS OF SODIUM SULFIDE CONCENTRATION

The concentration of butyl xanthate and pine oil was fixed at 220mg/L and 72mg/L, respectively. The relationship between sodium sulfide concentration and malachite recovery is shown in Fig.2.

Fig.2 The relationship between sodium sulfide concentration and malachite recovery
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The results showed that the recovery of malachite was extremely low when butyl xanthate was used as the collector without sodium sulfide. When sodium sulfide was used as vulcanizing agent and its concentration was in the range of 0~300mg/L, malachite recovery increased with the increase of sodium sulfide concentration, while the recovery had a decrease as the concentration was more than 300 mg/L.

Sodium sulfide, as a vulcanizing agent, can vulcanize malachite surface, mainly because sodium sulphide solution shows strong alkaline, adding sodium sulphide solution means adding OH⁻, HS⁻ and S²⁻ in the pulp, these three ions can react with malachite according to the following reactions:

\[ x\text{CuCO}_3\cdot y\text{Cu(OH)}_2 + 2\text{OH}^- = (x-1)\text{CuCO}_3\cdot y\text{Cu(OH)}_2\cdot \text{Cu(OH)}_2 + \text{CO}_3^{2-} \]

\[ (x-1)\text{CuCO}_3\cdot y\text{Cu(OH)}_2\cdot \text{Cu(OH)}_2 + \text{HS}^- = (x-1)\text{CuCO}_3\cdot y\text{Cu(OH)}_2\cdot \text{CuS} + \text{OH}^- + \text{H}_2\text{O} \]

In the case of the presence of OH⁻ ions, part of mineral surface can achieve hydroxylation, the HS⁻ ions change the hydroxylation area into sulfide area, at the same time part of the carbonate dissolves, leading to the formation of new hydroxylation area[4]. The reaction will not stay on the mineral surface, but go deep into the mineral internal, and form the CuS thin films with different thickness, finally strengthened the hydrophobicity of mineral surface, and improved the adsorption rate of collector. At last, depending on the different initial concentrations of the sodium sulfide, CuS thin films of different thickness were formed[6].

The uneven surface of malachite made its surface exist different areas of complete sulfidation, incomplete sulfidation and non sulfuration, when butyl xanthate was used as the collector, it can adsorb on the complete sulfidation area of malachite surface, so some malachite can be recovered.

### 2.2 CONDITION EXPERIMENTS OF BUTYL XANTHATE CONCENTRATION

The concentration of sodium sulfide and pine oil was fixed at 300mg/L and 72mg/L, respectively. Butyl xanthate was used as the collector, and the relationship between its concentration and malachite recovery is shown in Fig.3.
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Fig. 3 The relationship between butyl xanthate concentration and malachite recovery

After the sulfuration of malachite, the area of complete sulfuration can be considered as copper sulfide ore, in the redox system formed by the CuS thin film, dissolved oxygen and butyl xanthate, the dissolved oxygen took place reduction reaction in the cathode, and the oxidation reaction between CuS and butyl xanthate took place in the anode. Due to the two independent and interdependent electrode reaction processes of CuS thin film on malachite surface, xanthate can adsorb on CuS film successfully, and xanthate copper was formed, making malachite surface hydrophobic, and the specific reaction process equation are as follows:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]
\[ \text{CuS} + 2\text{C}_4\text{H}_6\text{OCS}^- \rightarrow \text{Cu}(\text{C}_4\text{H}_6\text{OCS})_2^- + \text{S} + 2\text{e}^- \]
\[ 2\text{CuS} + 4\text{C}_4\text{H}_6\text{OCS}^- + 3\text{H}_2\text{O} \rightarrow 2\text{Cu}(\text{C}_4\text{H}_6\text{OCS})_2^- + 2\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 8\text{e}^- \]

Because of the different surface activities of malachite surface, the optimal sodium sulfide concentrate for the formation of sulfide film is different, at the best concentration of sodium sulfide, only part of malachite surface formed complete sulfuration area, malachite of incomplete sulfuration area and non sulfuration area is difficult to adsorb butyl xanthate, at the same time, the adsorption of butyl xanthate on sulfide film of malachite surface was dynamic adsorption - desorption process, so it is difficult to achieve the complete recovery of malachite using single butyl xanthate.

Owing to the adsorption characteristics of butyl xanthate on malachite surface, the recovery
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of malachite increased with the increase of butyl xanthate concentration, when the concentration was more than 120 mg/L, the malachite recovery was basically constant, which was only 76.8% at the concentration of 160 mg/L.

2.3 Condition experiments of benzohydroxamic acid concentration

The concentration of pine oil was 72 mg/L, benzohydroxamic acid was used as the collector without sulfuration, and the effect of benzohydroxamic acid concentration on malachite recovery is shown in Fig.4.

![Graph showing the effect of benzohydroxamic acid concentration on malachite recovery](image)

Fig.4 The effect of benzohydroxamic acid concentration on malachite recovery

The results showed that part of malachite can be recovered using benzohydroxamic acid as the collector without sulfuration, mainly because benzohydroxamic acid can occur chemical adsorption on malachite surface, the bidentate on the one side can chelate with Cu²⁺ and form stable penta cyclic chelate, and the hydrocarbon chain on the other side was hydrophobic, thus making malachite floated, the main chemical equation is as follows:

\[
2 \left( \text{O} \quad \text{N} \quad \text{O} \right) + \text{Cu}^{2+} \rightarrow \left( \text{O} \quad \text{Cu} \quad \text{O} \right) \quad + 2\text{H}^+ \]

Since the activity of copper ions on malachite surface is different, only part copper ions can form stable chelate with benzohydroxamic acid, so the malachite can not be recovered completely even if the concentration of benzohydroxamic acid has a great increase.
2.5 CONDITION EXPERIMENTS OF DIFFERENT RATIOS OF BENZOHYDROXAMIC ACID TO BUTYL XANTHATE

The concentration of sodium sulfide and pine oil was 300 mg/L and 72 mg/L, respectively. Benzohydroxamic acid and butyl xanthate were used as the combined collector, and the total concentration was 180 mg/L, the effect of the ratio of benzohydroxamic acid to butyl xanthate on malachite recovery is shown in Fig.5.

Fig.5 The effect of the ratio of benzohydroxamic acid to butyl xanthate on malachite recovery

When benzohydroxamic acid and butyl xanthate were combined used, the malachite recovery increased gradually with the increase of benzohydroxamic acid ratio, and the malachite recovery was up to 95.6% at the ratio of 3.5:1, while the malachite recovery had a slight decrease when the ratio of benzohydroxamic acid was more than 3.5:1. It is showed that the combined use of benzohydroxamic acid and butyl xanthate can greatly increase the flotation recovery of malachite compared with single benzohydroxamic acid or butyl xanthate, and the main reasons are as follows:

(1) Synergistic effect between reagents. Benzohydroxamic acid and butyl xanthate have different activities, benzohydroxamic acid with higher activity first forms stable cyclic chelate with Cu\textsuperscript{2+} on malachite surface, van der waals force between the hydrocarbon chains strengthens the alternative adsorption of butyl xanthate on CuS points formed by sulfuration, moreover, the adsorption of butyl xanthate on malachite surface increases with the increase of...
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benzohydroxamic acid adsorption, synergistic effect are created between benzohydroxamic acid and butyl xanthate, increasing the malachite recovery.

(2) The inhomogeneity of malachite surface activity. The bonding orbital is filled with electrons and the antibonding orbital is empty inside malachite, and the crystal is in stable condition. In the crushing and grinding process of large malachite, the specific surface area increases, and more atoms on mineral surface are produced, in their original plate the neighbour atom bonding with these atoms on mineral surface “lost”, lattice plane are truncated, which produces excess charge and causes upper state of mineral surface, so it is required the atoms on mineral surface restructure or adsorb foreign molecules or ions in order to reduce the surface energy. Due to the randomness of crushing and grinding process, the surface activity of malachite is different, inevitably making the sulfuration degree of each surface different, and the sulfuration area of malachite surface is divided into: complete sulfuration area, incomplete sulfuration area and non sulfuration area.

(3) The complete sulfuration area on mineral surface can be seen as copper sulfide ore, according to the valence bond theory, the electronegativity of sulfur in copper sulfide is less, and the covalent radius is larger. From the hard and soft acids and bases theory, it can be seen that the electronegativity of sulfur is low, the polarizability is high, and it is easy to be oxidized, the constraints of valence electrons is relatively loose, belonging to the soft base, so it affects the coupling atoms, increases the softness of the linked atom, that is, the copper ion in copper sulfide is soft acid. However, the incomplete sulfuration area and the nonsulfuration area can be considered as copper oxide ore or close to copper oxide ore, while the electronegativity of oxygen in copper oxide is high, the polarizability is low, being difficult to be oxidized, and the constraints of its valence electrons is relatively close, its negative inductive effect makes the copper ions in the copper oxide become a hard acid. According to the hard and soft acids and bases theory, hard acids preferentially coordinate with hard bases, and soft acids preferentially coordinate with soft bases. In full sulfuration area, xanthate type soft base (electronegativity is about 2.7) is easy to adsorb in the complete sulfuration area; while in incomplete sulfuration area and nonsulfuration area, the electronegativity of benzohydroxamic acid is larger (about 3.8),
which contains large hardness O and N atoms, so it is easy to chelate with copper ion and adsorb on malachite surface, thus making malachite floated. Therefore, the combined use of benzohydroxamic acid and butyl xanthate can make the collector completely covered on malachite surface, achieving the goal of efficient recovery of malachite.

3 EXPERIMENTAL RESEARCH ON REAL ORE

The copper grade of a copper oxide ore in Congo was 2.35%, and the oxidation rate of copper minerals was 95.4%, the multielement analysis results of the raw ore is shown in table 1, and the phase analysis of copper is shown in table 2.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The multielement analysis results of the raw ore/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Cu</td>
</tr>
<tr>
<td>Content</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The phase analysis results of copper/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper phase</td>
<td>Free copper oxide</td>
</tr>
<tr>
<td>Content</td>
<td>2.45</td>
</tr>
<tr>
<td>Distribution rate</td>
<td>91.18</td>
</tr>
</tbody>
</table>

The copper oxide of the sample accounted for 97.51%, the binding rate and the oxidation rate were low, and the copper oxide mineral is mainly in the presence of malachite. From single mineral flotation experiments, it can be seen malachite have the highest recovery when benzohydroxamic acid and butyl xanthate are used as the combined collector with the ratio of 3.5:1. In order to verify the feasibility of the combined collector, the comparative tests of different collector were first conducted, the process is shown in Fig.6, and the results are shown in table 3.
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Table 3 The comparative test results of different collector of a copper oxide ore in Congo /%

<table>
<thead>
<tr>
<th>Products</th>
<th>Yield</th>
<th>Cu grade</th>
<th>Cu recovery</th>
<th>Collectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper oxide rough concentrate</td>
<td>18.06</td>
<td>12.05</td>
<td>80.10</td>
<td>benzohydroxamic acid : butyl xanthate =3.5:1</td>
</tr>
<tr>
<td>Tailings</td>
<td>81.94</td>
<td>0.66</td>
<td>19.90</td>
<td>butyl xanthate</td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.00</td>
<td>2.72</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Copper oxide rough concentrate</td>
<td>15.31</td>
<td>11.94</td>
<td>67.48</td>
<td>butyl xanthate</td>
</tr>
<tr>
<td>Tailings</td>
<td>84.69</td>
<td>1.04</td>
<td>32.52</td>
<td></td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.00</td>
<td>2.71</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Copper oxide rough concentrate</td>
<td>17.44</td>
<td>11.62</td>
<td>74.73</td>
<td>benzohydroxamic acid</td>
</tr>
<tr>
<td>Tailings</td>
<td>82.56</td>
<td>0.83</td>
<td>25.27</td>
<td></td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.00</td>
<td>2.71</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Copper oxide rough concentrate</td>
<td>18.42</td>
<td>10.03</td>
<td>68.74</td>
<td>pentyl xanthate</td>
</tr>
<tr>
<td>Tailings</td>
<td>81.58</td>
<td>1.03</td>
<td>31.26</td>
<td></td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.00</td>
<td>2.68</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

The results showed that the grade and recovery of copper oxide rough concentrate were highest using the combined collector developed by single mineral flotation experiments, and the
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recovery had a great increase compared with other collectors. So the combined collector had good feasibility to real ore.

According to the process and reagent system of Fig.7, the closed circle experiment was conducted using the combined collector of benzohydroxamic acid and butyl xanthate at the ratio of condition test, and the results are shown in table 4.

<table>
<thead>
<tr>
<th>Products</th>
<th>Yield</th>
<th>Cu grade</th>
<th>Cu recovery</th>
<th>Malachite content</th>
<th>Malachite recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper oxide concentrate</td>
<td>7.41</td>
<td>32.12</td>
<td>88.02</td>
<td>52.11</td>
<td>92.67</td>
</tr>
<tr>
<td>Tailings</td>
<td>92.5</td>
<td>0.35</td>
<td>11.98</td>
<td>0.33</td>
<td>7.33</td>
</tr>
<tr>
<td>Raw ore</td>
<td>100.0</td>
<td>2.70</td>
<td>100.00</td>
<td>4.17</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The results showed that the concentrate with the grade and recovery of 32.12% and 88.02% was obtained using sodium carbonate as regulator, sodium sulfide as vulcanizing agent, and benzohydroxamic acid and butyl xanthate as the collector, the malachite recovery reached to 92.67%. Under the same experimental condition, the comparative test was carried out using butyl xanthate as the collector, the grade of the obtained copper oxide concentrate was 28.04%, and the recovery was 75.61%. Therefore, malachite mineral can be effectively recovered using the combined collector developed by single mineral flotation experiments at a appropriate ratio, and the recovery of copper oxide increased 12%.
4. CONCLUSION

(1) In order to weaken the hydrophilicity of minerals and decrease the collector dosage, it is necessary to vulcanize malachite properly.

(2) The nonuniformity of malachite surface caused the nonuniformity of malachite surface after sulfuration, dividing into complete sulfuration area, incomplete sulfuration area and non sulfuration area, and corresponding to soft acid, solid acid and acid between soft acid and solid acid, respectively. According to the soft and hard copper, the softer alkali like butyl xanthate and the harder alkali like benzohydroxamic acid can be used as the combined collector, and synergistic effect can be created between different collectors.

(3) There is a best ration between collectors, in the range of best ratio, the collector can
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maximize the collecting capability, which can save reagent and realize efficient collecting. The combined collector of benzohydroxamic acid and butyl xanthate developed in this research can ensure the full play of synergistic effect at the ratio of 3.5:1, and the malachite recovery is more than 95%. Furthermore, the combined collector of benzohydroxamic acid and butyl xanthate has good feasibility to real ore, effectively increasing the recovery of copper oxide ore.

REFERENCES
INVESTIGATION OF THE MICROSTRUCTURAL EVOLUTION BETWEEN PELLET AND SINTER UNDER THE CONDITIONS OF AN OXYGEN BLAST FURNACE

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State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083 PR China.

ABSTRACT

Oxygen blast furnace is a new iron-making technology for carbon saving and emission reduction. The softening process of burden was investigated under the conditions of oxygen blast furnace (OBF) and traditional blast furnace (TBF) using the softening and melting device. The results showed that the slag matrix and myrmekitic metallic iron formed at the edge of the TBF, and the slag matrix and island wustite were in the center. However, the slag matrix and myrmekitic metallic iron formed both at the edge and the center in OBF. Compared to that in TBF, the distribution of the slag and metallic iron showed that the slag was winded or separated in the metallic iron phase in OBF after the melting of burden, increasing the slag-iron separation temperature and the interaction starting temperature and improving the softening and melting properties.

1 INTRODUCTION

At present, the energy consumption of iron making in blast furnace accounts for nearly 70% of the entire steel-making process, and under the circumstances of energy conservation and emissions reduction, this process requires higher efficiency and energy conservation technology. Top gas circulation - full oxygen blast furnace (full oxygen blast furnace) can significantly cut the coke rate, reducing CO₂ emissions and having highly efficient production. In recent years, more than 10 processes have been proposed by scholars at home and abroad to answer two key questions about upper cold and down heat. The biggest advantages of OBF is that the reduction potential was improved substantially, and the indirect reduction degree reached 90%, which means that the direct reduction degree reduced significantly. It benefits the reduction of heat output in the high-temperature region and the carbon emission. Meanwhile, the improvement of indirect reduction will certainly influence the size and position of cohesive zone, which will ultimately affect the production efficiency and energy utilize situation. The softening and melting experiment under the condition of OBF proved that the softening interval will broaden, but the melting interval will narrow down, the temperament of dripping will improve, and the permeability index will significantly reduce when the reduction degree increased, the metal iron phase area increased simultaneously, and the melting point of slag phase, the viscosity, the interfacial tension also changed, which leaded the change of microstructure of burden during the softening and melting process, and the softening and melting performance was improved. C. E. Loo et al. The interaction between sinter and lump could restrain the untimely deformation of the burden layer and improve the softening and melting performance of mixed burden. Research about the change in ore phase structure during softening and melting, the evolution rule of burden properties, and the interaction between different ferric burdens is still relatively scarce. The revelation of the OBF softening and melting
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mechanism has significance for the determination of OBF process parameters. Using a self-designed experimental apparatus for load softening, this research studied the microstructural evolution of pellets and sinter pre-reduced in the OBF and T-BF gas atmosphere. The interaction effect between different ores in the mixed burden was also investigated. Comparing the microstructure of the OBF case with that of the T-BF case, the microstructural evolution mechanism of ferric burden in the OBF atmosphere was studied, and the softening and melting behavior of ferric burden in the OBF atmosphere was revealed.

2. EXPERIMENT

2.1. EXPERIMENT MATERIALS

The chemical composition of the pellets and sinter used in this research is showed in the Table 1. The granular size is 14-15 mm.

<table>
<thead>
<tr>
<th></th>
<th>TFe</th>
<th>FeO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>61.32</td>
<td>3.27</td>
<td>8.83</td>
<td>1.18</td>
<td>0.84</td>
<td>0.7</td>
<td>0.01</td>
</tr>
<tr>
<td>Sinter</td>
<td>54.44</td>
<td>8.69</td>
<td>5.75</td>
<td>2.6</td>
<td>10.76</td>
<td>2.48</td>
<td>1.87</td>
</tr>
</tbody>
</table>

2.2. EXPERIMENTAL METHOD

The flow charts of OBF and T-BF process were shown in the Fig 1. Among them, the mixed ore was mixed base in binary basicity as 1.3. The experimental atmospheres were from the computing results of blast furnace mathematical model. Drying 500 g samples at 100 degrees Celsius for 3 hours, then placed the samples into a high temperature alloy reaction tube sizes ø75 mm×800 mm.

![Experimental conditions](image)

(a) BF (b) OBF

Fig 1. Experimental conditions.

The experimental apparatus for softening and melting under load is shown schematically in Fig 2: it mainly consists of an electric furnace, graphite crucible, silicon carbon tube, displacement meter, differential pressure gauge and auxiliary equipment. The ferrous burden was charged into the graphite crucible, and over and under which coke (20±0.1 g) was placed. Several holes existed in the bottom of the graphite crucible, contributing to the dripping of slag and iron, and the top of the graphite crucible was connected to the graphite pusher. The height of
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The sample in the reaction tube was 65±5 mm. A load of 1 kg/cm² was added in the experimental process. The heating process was protected by N₂ before 473 K, and the reductive gas mixture with a flow of 12 L/min was introduced into the reaction tube. When the first iron dripped, the reductive gas mixture was switched to N₂, and the sample was cooled to room temperature. The vertical shrinkage, pressure drop and temperature of the burden layer were all recorded automatically by a computer.

Fig. 2 Experimental apparatus.

T₁₀% and T₄₀% were defined as the softening start temperature and softening finish temperature, respectively. The softening interval was defined by \( \Delta T_R = (T_{40\%} - T_{10\%}) \). T₅₇ is the softening finishing temperature, at which the pressure drop of the burden layer reached 490 Pa. Tₜₘ is also defined as the melting starting temperature; T₆ is the dripping temperature, which is recorded manually when the first iron drips. For research of evolution of the burden microstructure, the experiments were interrupted when the Temperature reached T₁₀%, T₄₀%, or T₅₇, respectively, and cooled to room temperature with a 12 L/min N₂ gas flow inlet. Then, the samples were inlaid with ethoxyline resin and cut along the direction of the load press. The microstructure was obtained by SEM, and the distribution of elements was obtained by EDS.

3. EXPERIMENT RESULTS

3.1 THE EVOLUTION OF THE BURDEN BED MACROSTRUCTURE DURING THE SOFTENING AND MELTING PROCESS

The evolution of the burden bed macrostructure during the softening and melting process under T-BF and OBF is shown in Fig. 3. In the OBF case, the reduction degree of the burden particle increased because of the greatly improved reduction potential, the wustite cores in the burden particles were almost distinguished, and the non-deformability was strengthened. The T₁₀% is 1167 °C, which is 29 °C higher than that in the T-BF case. With the increasing temperature, the reduction degree increased continually, and compared to the TBF case, the shrinking speed of the burden bed slowed down. The T₁₀% is 1333 °C, higher than that in the TBF case by 66 °C. The \( \Delta T_R \) is 166 °C, which is 37 °C higher than that in the T-BF case. Because
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of the significant reduction of the wustite amount, the proportion of slag phase in OBF case is decreased and the melting point is lowered. The gas permeability of burden bed is also improved; the $T_m$ and $T_d$ are 1415°C and 1430°C, which are higher than that those in the T-BF case, at 92°C and 16°C, respectively. The softening and melting behavior of burden in the OBF case decreases the position of the cohesive zone in the blast furnace and reduces the gas resistance in the burden bed.

Fig. 3 The evolution of the burden bed macrostructure during the softening and melting process under T-BF and OBF.

In order to analyze the softening and melting process of burden under T-BF and OBF, the microstructure of burden at $T_d$ was observed to reveal the mechanism of melting temperature increase in the OBF case. Fig 4 shows the burden microstructures after slag flow out in the T-BF and OBF atmospheres. In the T-BF case, there was unreduced wustite ore at the center of burden at first, but as the temperature increased, wustite ore began melting to continuously wash the external metallic iron, and finally, low-melting-point slag broke through the metallic iron due to the load to fill the pore spaces between burdens. As shown in Fig 4(a), low-melting-point Fe$_2$SiO$_4$ phase, formed by wustite, existed among two burden particles, and the gas permeability of the burden bed would significantly decrease due to the outflow of low-melting-point slag phase. In the OBF case, due to wustite ore disappearing at the center of burden, an abundant liquid phase flow out would not exist during the melting process, as only little melting slag oozed from the burden margin. In addition, the increase in the slag melting point would lead to $T_d$ increase, which would decrease the position of the cohesive zone and decrease the thickness. Thus, the $\Delta P_{\text{max}}$ in the OBF case was lower.
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![Microstructures of T-BF and OBF atmospheres](image)

**Fig.4** The burden microstructures after slag flow out in the T-BF and OBF atmospheres.

### 3.2 THE EVOLUTION OF BURDEN MICROSTRUCTURE DURING THE SOFTENING AND MELTING PROCESS

The microstructural evolution of the interface between the sinter and pellet is shown in **Fig 5**. In the T-BF case, a 10% shrinkage rate was reached at 1138 °C. At this temperature, the original interface still can be identified clearly, and there is an aggregation of metal iron in the pellet side. A temperature of 1267 °C corresponds to a 40% shrinkage ratio, where it is difficult to distinguish the original interface. A bulky vermicular iron phase formed in the pellet side, while a relatively minor iron phase formed in the sinter side. The T_m corresponds to 1323 °C. At this temperature, the metal iron phases contacted each other and formed a structure with the sinter features of the slag phase that was winded or cut by the metal iron phase. It can be determined from the microstructure of the interface that the interaction effect was completely performed. In the OBF case, a 10% shrinkage ratio was reached at 1167 °C, and the interface structure was very similar to that in the T-BF case. At 1333 °C, the temperature corresponded to a 40% shrinkage ratio, and the initial interface still can be distinguished because the vast metal iron phase existing on both sides of the interface impeded the interaction between slag phases. The T_m corresponds to 1415 °C, when some of the iron phases of the interface area have connected and were translated to lamellar form at this time. It can be derived that the interaction was fully performed because the initial interface is already indistinguishable.
Investigation of Microstructural Evolution between Pellet and Sinter

By observing the interfacial microstructure of the pellet-sinter mixed burden, it can be concluded that the starting temperature of the interaction effect in OBF is higher than that in T-BF. The research of P. F. Nogueira\textsuperscript{14,15} revealed that the interaction between different burdens changed the interface basicity Ca. The distribution of Ca and Si in the direction perpendicular to the interface was observed by the EDS line-scanning method. The results of the ratio change rule are shown in Fig. 6. In the T-BF case, there is a mutation in Ca in the case of 10% shrinkage, which means that the interaction effect has not occurred yet. At a 40% shrinkage ratio, the Ca variation within certain limits of both sides of the interface shows a gradual trend. In the transitional zone from sinter to pellet, the Ca presents a descending trend, which indicates the appearance of the interaction effect. When the shrinkage ratio reached 60%, the Ca tends toward a stable value, which means that the interaction effect has already fully developed. Compared to the above situation, the sample with a 40% shrinkage ratio in the OBF case corresponding to 1415 °C shows that the mutation in Ca still exists in the interface, meaning that the interaction effect has not yet occurred. When the shrinkage ratio reached 60% at 1430 °C, the Ca tended toward a stable value, meaning that the interaction effect had already fully developed. Thus, it can be concluded that the decisive factor for the softening and melting behavior is the Ca change caused by the interpenetration of the slag of different burdens. The change in Ca will certainly lead to a change in the melting point, viscosity, and interfacial tension of slag.
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Fig. 6 The distribution evolution of Ca in the interface between the pellet and sinter during the softening and melting process under T-BF or OBF conditions.

4. CONCLUSIONS

Compared to the T-BF case, the furnace bed structure during the softening and melting process under the OBF atmosphere is greatly changed, the proportion of wustite in the burden particle is reduced and the amount of iron phase is increased. The non-deformability of the burden particle is strengthened, and the softening and melting properties of the burden are improved.

In the T-BF case, the iron shell of the burden particle is fractured first, followed by the flow of the liquid slag phase. In the OBF case, the liquid slag phase with a higher melting point is exuded from the iron phases, and the melting temperature is obviously increased.

The proportion of wustite in the OBF case is decreased, while the iron phase is increased, which will inhibit the interaction behavior between the pellet and sinter. In the T-BF case, the interaction has already occurred at 1267°C when the softening process is terminated, while in the OBF case, there is no distinct indication of the interaction effect when the softening process is terminated at 1333°C.

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Investigation of Microstructural Evolution between Pellet and Sinter

REFERENCES

NOVEL ENGINEERED CEMENTITIOUS MATERIALS BY USING CLASS C FLY ASH AS A CEMENTITIOUS PHASE

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ABSTRACT

This paper reports the synthesis and characterization of novel composites fabricated by using Class C Fly Ash (CFA) as the main cementitious constituent. This study demonstrates the favorable impacts of Ca(OH)\(_2\) additions, high temperature curing, and/or carbonation on enhancing the compressive strength of CFA based composites. For example, the CFA matrix had a compressive strength of \(~30\) MPa after curing under ambient conditions for 28 days. The heat treatment of CFA samples at 70°C for 3h and subsequent carbonation at 87°C for 3h enhanced the compressive strength to \(~66\) MPa. The concomitant effect of the addition of 2.8 wt% Ca(OH)\(_2\) in the FA matrix, and the heat treatment of CFA samples at 70°C for 3h and subsequent carbonation at 87°C for 3h further increased the compressive strength to \(~87\) MPa. The curing period of the CFA based composites can also be drastically reduced by high temperature curing and/or carbonation. For example, conventional curing takes 28 days under ambient conditions, whereas heat treatment and/or carbonation can reduce the curing time to 3-6 h. From thermogravimetric analysis (TGA) and SEM study of the fracture surfaces, the predominant mechanism for strength development was proposed to be enhanced hydration of the heat treated samples, and CaCO\(_3\) formation at the phase boundaries of the carbonated samples.

1. INTRODUCTION

Fly Ash (FA) is the principal by-product during the combustion of pulverized coal in thermal power plants [1-5]. FA is generally grey in color, abrasive, mostly alkaline, and refractory in nature [6, 7]. The chemical composition of FA has high percentage of silica (60–65%), alumina (25–30%), magnetite, FeO\(_x\) (6–15%) [6]. The Fly Ash can be classified into two classes – Class F fly ash (FFA) and CFA (CFA) [8]. The CFA refer to those having more than 8% CaO and are usually from lignite and subbituminous coal combustion. The FFA are from bituminous and anthracite coals and have less than 8% CaO [5].

Some of the reasons for reutilizing FA are, (a) to minimize disposal costs, (b) decreased area reserved for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements, (c) financial returns from the sale of the by-product or at least can offset the processing and disposal costs, and (d) the by-products can replace some scarce or expensive natural resources. Therefore, it is critical to find sustainable solution for its utilization rather than land disposal to minimize the environmental challenges associated with its disposal [2, 6, 7].

FA has already partly replaced Portland Cement (PC) in hardened concrete [9-11]. FA usage in structural concrete as a replacement of PC is around 30% of the binder. The resulting concrete has similar or enhanced performance compared to that of Portland cement concrete of equivalent 28 day strength is possible [11]. However, in order to promote wide scale usage of FA, it is critical to develop cementious materials mainly composed of FA.

It is well known FA can also be activated by alkali to form hardened solid by geopolymerization [12-20]. The alkali activation of waste materials is a chemical process that transforms glassy structures (partially or totally amorphous and/or metastable) into very compact well-cemented composites [12]. In general, two types of cementitious materials can be produced by alkali activation: (a) Si and Ca based, and (b) Si and Al based. The alkali activation of metakaolin or FFA is a typical example of the second situation [13]. Geopolymers has also the potential to replace Ordinary Portland Cement (OPC) [14]. Interestingly, CFA has been used
Novel Engineered Cementitious Materials using Class C Fly Ash

during most of the research studies [15-17]. A few research studies have focused on synthesizing
gelpolymer from CFA [18, 19]. Nevertheless, in all the studies, high concentration of alkali
solution is used to activate the mix.

However, the usage of large amounts of alkali activators raises several concerns due to
the, (a) the production of large amounts of alkali is an energy intensive process and can
indirectly lead to increased CO$_2$ emissions, and (b) free alkali and silicate can have deleterious
effects on concrete in poorly formulated systems. Therefore, it is critical to develop fundamental
understanding whether the FA based cementitious materials can be fabricated with low or no
alkali solutions [20].

Recently, Riyad et al. [21] proposed a “Green Cement Paradigm (GCPa)” . The main
components of this paradigm are: (a) use environmentally friendly precursors and aggregates, (b)
minimize or eliminate the usage of alkali or other harmful chemicals as an activator, (c) use of
environmentally friendly practices for example, low w/c (w-water, c- cement) ratio etc., and (d)
create a cementitious network composed of hydraulic and carbonate bonds for faster ASTM
(American Society of Testing and Materials) certification according to industry standards. In
order to validate the GCPa, CFA was chosen as a precursor. It was also shown that CFA can
have cementitious behavior if the cold pressed compacts are cured with tap water or low alkali
solutions [21, 22]. In this paper, we report for the first time, the development of CFA based
composites by engineering compositions, and performing different conditioning processes, for
example, heat treatment and/or carbonation. We will also report a comprehensive study of
mechanical behavior, microstructure analysis, and phase characterization of these composites.

2. EXPERIMENTAL

CFA powder was procured from Headwaters Resources, Sioux Falls, SD. Different
compositions were then designed by adding controlled amount of Ca(OH)$_2$ (Part number 21181,
Sigma-Aldrich Corp. St. Louis, MO, USA) in CFA (Table 1). All the compositions were mixed
with 3 g of water in a ball mill (8000 M, SPEX SamplePrep, LLC, Metuchen, NJ) for 2 minutes.
They were then cold pressed in a cylindrical steel die (~25.4 mm diameter, MTI Corp.,
Richmond, CA) by using a Carver Laboratory press (Model 3853, Carver Inc., Wabash, IN) at
~86 MPa.

The samples were fabricated by using four different processing conditions: (a) the
samples were cured in a closed chamber for 28 days (Condition A), (b) the composition A-2
(Table 1) was heat treated at 50°C, or 70°C, or 90°C, and all the other compositions listed in
Table 1 were heat treated at 70°C in a closed chamber in a heating oven for 3 h (Condition B),
(c) the samples were carbonated by following the procedure outlined in the next paragraph
(Condition C), and (d) the samples were heat treated samples at 70°C by following Condition B,
and then they were carbonated by following the procedure outlined in the next paragraph
(Condition D).

Table 1: Different compositions of CFA and Ca(OH)$_2$:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing</th>
<th>CFA (g)</th>
<th>Ca(OH)$_2$ (g)</th>
<th>Water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2</td>
<td>Cold Pressed</td>
<td>18</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>B-2</td>
<td></td>
<td>17.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>C-2</td>
<td></td>
<td>17</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>D-2</td>
<td></td>
<td>14.4</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>E-2</td>
<td></td>
<td>10.8</td>
<td>7.2</td>
<td></td>
</tr>
</tbody>
</table>

Before carbonation, all the samples were dried at 100 °C for 24 h in an oven. The dried
samples were then placed inside an autoclave chamber (Model 25 X-I, Wisconsin Aluminum
Foundry Co., INC., Manitowol, WI). Initially, the chamber was partially filled with 3 L of water,
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3. RESULTS AND DISCUSSION

3.1 EFFECT OF TEMPERATURE ON COMPRESSIVE STRENGTH

Figure 1 shows the effect of temperature on the mechanical strength of composition A-2 (Table 1) cured by conditions A and B. The compressive strength of the sample was ~30 MPa after curing at RT for 28 days (Condition A). Comparatively, the compressive strength of samples cured by condition B at 50ºC and 70ºC were similar. Interestingly, slightly higher compressive strength of ~45 MPa was observed for samples cured at 90ºC (Condition B). The potential mechanism will be discussed in Section 3.5.

3.2 EFFECT OF Ca(OH)₂ ADDITIONS ON COMPRESSIVE STRENGTH

Figure 2 shows the effect of Ca(OH)₂ additions (Table 1) on the compressive strength of the samples fabricated by Condition A. Initially, the green strength of all compositions was ~5 MPa, however, a significant enhancement in compressive strength was observed after the addition of Ca(OH)₂ in the matrix. For comparison, the samples composed of only CFA (Composition A-2, Table 1) showed a compressive strength of ~30 MPa after curing for 28 days. After the addition of 2.8 wt% Ca(OH)₂ (Composition B-2, Table 1), the compressive strength increased to ~22 MPa and ~45 MPa after curing for 7 and 28 days, respectively. Similarly, after the addition of 20 wt% Ca(OH)₂ (Composition D-2, Table 1) and 40 wt% Ca(OH)₂ (Composition E-2, Table 1), the compressive strength increased to ~38 MPa for both compositions after curing for 7 days, and to ~51 MPa and ~47 MPa after curing for 28 days, respectively. It is interesting to note that the addition of only 2.8 wt% Ca(OH)₂ can enhance the compressive of CFA matrix by 50%. The potential mechanism will be discussed in Section 3.5.
Figure 1: The plot shows the effect of curing temperature (Condition B) on the mechanical performance of A-2 composition (Table 1). For comparison, the samples studied at RT were cured for 28 days (Condition A).

Figure 2: Effect of Ca(OH)$_2$ additions (Table 1) on the compressive strength of samples cured by following Condition A.

3.3 EFFECT OF HEAT TREATMENT AND/OR CARBONATION ON THE COMPRESSIVE STRENGTH

Figure 3 shows the comparison of the compressive strength of the CFA samples treated by Conditions A-D (Table 1). As compared to condition A, all the other curing conditions resulted in the enhancement of the compressive strength; however, condition D had the most significant effect on the compressive strength. For example, Composition A-2 (Table 1) had a similar compressive strength of ~30 MPa after curing by either Condition A or B. The carbonation treatment by either Condition C or D enhanced the compressive strength to ~38 and ~66 MPa, respectively. After adding 2.8 wt% Ca(OH)$_2$ in the FA matrix (Composition B-2, Table 1), the compressive strength increased marginally to ~31 MPa and ~45 MPa by curing by Conditions A and B, respectively. However, after the carbonation treatments by Conditions C and D, the compressive strength increased to ~63 MPa and ~87 MPa, respectively.
Comparatively, after the addition of 40 wt% Ca(OH)$_2$ (Composition E-2, Table 1), the compressive strength was similar to Composition B-2 (Table 1) after the samples were cured by either Conditions A, or B, or C. However, the compressive strength increased to ~94 MPa after the samples were cured by condition D. This study also shows that the addition of as low 2.8 wt% Ca(OH)$_2$ in the FA matrix can effectively enhance the strength of CFA samples. The potential mechanism will be discussed in Section 3.5.

3.4 MICROSTRUCTURE AND PHASE ANALYSIS

Figure 4 shows TGA analysis of the CFA based compositions. The CFA powder showed only a small weight loss of ~0.5% during the entire heating cycle. In comparison, all the other compositions showed a weight loss of 2-4 wt% until 200º C (Stage I). The weight loss during Stage I was due to the loss of capillary water and/or decomposition of C-S-H (Calcium Silicate Hydrate) phases from the samples [21, 23]. The ~2 wt% weight loss between 200-600ºC is due to the decomposition of Ca(OH)$_2$ phase (Stage II) [23]. A significant amount of weight loss also occurred in the temperature range of 600 - 800ºC in the carbonated CFA (Condition C), and heat treated and carbonated CFA (Conditions D) samples (Stage III). This weight loss can be attributed to the decomposition of CaCO$_3$ from the cement matrix [23].

Figure 3: Comparison of the compressive strength of the samples treated by different conditions A-D.
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Figure 4: TGA analysis of the A-2 composition (Table 1) cured by different conditions.

Figure 5: XRD profiles of, (a) as-received CFA, and after, (b) heat treatment at 90°C (Condition B), (c) carbonated (Condition C), (d) heat treatment and carbonated (Condition D) of A-2 composition (Table 1), and carbonation of composition B-2 (Table 1) by using Condition, (e) C, and (f) D.
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Figure 6: SE SEM micrographs of carbonated CFA (Composition A-2, Table 1) by Condition C at, (a) low, and (b) high magnification.

The XRD of as received CFA (Fig. 5) showed Mullite (3Al₂O₃·2SiO₂), Quartz (SiO₂), and anhydrite (CaSO₄) are the major crystalline phases. The CFA samples fabricated by condition B also showed similar results which indicate that the hydrated phases are most probably amorphous or cannot be detected by XRD. Comparatively, XRD patterns of all the carbonated samples showed calcite phase (CaCO₃) along with other crystalline phases described above. This result shows that the Ca(OH)₂ rich phases present in CFA has reacted with the CO₂ during the carbonation experiments.

Figure 6 shows the SEM micrograph of the carbonated CFA sample at low and high magnification, respectively. Calcite (CaCO₃) was observed in the XRD analysis (Fig. 5) of all the carbonated samples. Figure 6 (b) clearly shows the deposition of calcite particles around the bigger spherical particles CFA particles. Therefore, we can conclude that Ca(OH)₂ present in the CFA has reacted with the CO₂ to form CaCO₃ during the carbonation process.

3.5 POTENTIAL MECHANISM

Rovaník [24] reported that the elevated temperature curing can enhance the compressive strength of metakaolin-based geopolymer. Bakharev et al. [25] also reported that the properties of metakaolin-based geopolymeric materials are dependent on curing conditions. More particularly, this study showed that mechanical performance of CFA is enhanced by high temperature curing (Fig. 1). For example, the samples cured at 70°C for 3 h (Condition B) had comparable strength to samples cured for 28 days in ambient conditions. TGA results showed that the samples treated at 70°C (Condition B) showed similar hydration as the samples cured at RT for 28 days (Condition A) (Fig. 4). Based on the current evidence, the mechanical performances of CFA based compositions are enhanced at high temperature due to faster hydration reaction. Nevertheless, authors agree that more studies are needed to understand the detailed mechanism of hydration reactions and concomitant strength development.

Lime-pozzolan mortars have been used by mankind for centuries [26]. Anitohos et al. [27] reported that addition of quicklime in CFA accelerated the degree of reaction of reaction throughout the curing period. The quicklime addition lead to the creation of CH bonds among ash particles, and lead to the increased solubility of SiO₂ leading to a greater release of soluble SiO₂ into the hydrating matrix. Shi [28] also used quicklime to activate the action of natural pozzolans. Shi [28] further reported that for a given CaO content, the quicklime had a higher lime consumption rate than hydrated lime before 28 days, but no difference could be observed thereafter. In addition, lime-pozzolan cements made with quicklime gave higher strengths than the cement made with hydrated lime. In this study, we have also observed strength enhancement in all the compositions containing Ca(OH)₂ as an additive as compared to only CFA based compositions. It would be interesting to explore cold pressed quick lime-CFA composition in future.

Haq et al. [29] reported that the carbonation of FA based Geopolymers resulted in
improved mechanical properties due to uniformity, presence of strong silica network, and higher
gelopolymization. In our studies, we also observed carbonation significantly enhanced the
compressive strength (Fig. 3). Furthermore, the combined effect of high temperature curing and
carbonation (Condition D) gave the best possible result. More studies are needed to optimize the
Ca(OH)₂ content and curing conditions to further explore CFA based cementitious compositions.

4. CONCLUSIONS
CFA can be used solely as a cementitious phase. The mechanical performance of CFA
compacts can be enhanced by using Ca(OH)₂ as a particulate additive. For example, the addition
of 2.8 wt% Ca(OH)₂ in the CFA matrix can enhance the compressive strength by 50% by curing
under ambient conditions at RT (Condition A). In addition, high temperature curing and/or
carbonation can also significantly enhance the compressive strength of the samples. For example,
the CFA matrix (Composition A-2, Table 1) had a similar compressive strength of ~30 MPa after
curing by either Condition A or B. The carbonation treatment by either Condition C or D further
enhanced the compressive strength to ~38 and ~66 MPa, respectively. The concomitant effect of
the addition of 2.8 wt% Ca(OH)₂ in the FA matrix (Composition B-2, Table 1) and curing by
Conditions C or D can increase the compressive strength to ~63 MPa and ~87 MPa, respectively.
The curing period of the CFA based cementitous compositions can be drastically reduced by high
temperature curing and/or carbonation to 3-6 h as compared to curing for 28 days required
for conventional curing under ambient conditions.

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in this material are those of the author(s) and do not necessarily reflect the views of the National
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Novel Engineered Cementitious Materials using Class C Fly Ash


EFFECTS OF COMPOSITION CHANGES ON THE SINTERING PROPERTIES OF NOVEL STEEL SLAG CERAMICS

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ABSTRACT

Pyroxene ceramics are designed based on CaO-MgO-SiO2-FeO system, composing of pyroxene group minerals as main crystal phases. Steel slag, which is rich in component of CaO and FeO(or Fe2O3), could be used as a kind of main raw materials in such novel ceramics and the prepared ceramics have good mechanical properties. In this paper, steel slag in combination with quartz, talcum, clay and feldspar was converted to novel ceramics by traditional preparing process. Effect of composition changes on the properties of the production was studied by scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques coupled with the tests of physical and mechanical properties of the samples. The results revealed that the sintering temperature and flexural strength decreased with increasing calcium and iron and decreasing magnesium content. Part of the iron oxide or RO involved in crystal phase formation, while the rest were unchanged in the sample.

INTRODUCTION

Around one hundred million tons steel slag is produced every year in China, but the utilization ratio of steel slag is lower than 30%1. The ways of utilization of steel slag usually include internal recycling within the steel industry, such as reuse as raw materials in sintering, and external recycling in other industries, such as being used as raw materials of cement, concrete and road bed, being applied to agriculture as soil amendment as well as being used in wastewater treatment by virtue of its absorptivity2-8. However, none of these means could help to improve the utilization level of steel slag both in quantity and quality at present. In recent years there have been many reports on producing ceramics from steel slag. HE et al9. produced glass-ceramics by using steel slag as main raw materials; Daqiang Cang et al10. produced novel ceramics with high flexural strength of 143MPa and low water absorption of 0.02% from Ca-rich and Fe-rich steel slag and the main crystalline phases were detected as diopside, augite and some other pyroxene minerals. The CaO-MgO-SiO2-FeO system ceramics are a compromising route for the commercial use of steel slag due to the fact that traditional ceramics can’t reuse large amounts of iron-rich and calcium-rich slag as main raw materials for the strictly limitation on less composition of
Effects of Composition Changes on Sintering Properties of Novel Steel Slag Ceramics

CaO and Fe₂O₃ than about 3% and 1%, respectively.

The structural formula of pyroxene is $\text{M}_2\text{M}_1\text{T}_2\text{O}_6$, where $\text{T}$ stands for $\text{Si}^{4+}$, while there are many alternatives for $\text{M}_1$ and $\text{M}_2$. In the CaO-MgO-SiO₂-FeO system ceramics, $\text{M}_1$ could be iron or magnesium and $\text{M}_2$ could be iron, calcium or magnesium. Xianbin Ai et al. have studied how MgO in raw materials influences the sintering properties as well as the characteristic of the ceramics; Lihua Zhao et al. have studied how the changes of raw materials influences the crystal phases in the ceramics; but there haven’t been any reports on how the fluctuation of elements influences the sintering properties and characteristics of the ceramics. In fact, it is pretty important to know the regular pattern because different elements may form different crystal phases in composition or distribution in ceramics, which then influences the characteristics of the products. Therefore this paper focuses on influences of the elements composition changes on the sintering properties.

2 EXPERIMENT

The steel slag was obtained from SHANDONG steel and iron plant (China), and other materials were from SHANDONG Provence. All materials were dried at 105°C for 24h and then crashed.

A total of six mixtures were prepared on the same ratio of (CaO+MgO+FeO)/SiO₂ closed to 1 to guarantee the composition of as-mixed samples in the range of pyroxene component, in the proportions summarized in Table 1.

300g of the test samples were milled for 30min with 300ml water, using an alumina ball mill and spheres, at 300 cycles/min. The slurry were sieved through an 180μm sieve and then dried at 105°C for 24h. 6-10 wt% water was added in the dried powder and then pressed in a laboratory uniaxial press at 80MPa into rectangular (50mm*100mm*10mm) specimens.

Specimens were sintered in an electric muffle in air atmosphere in the thermal interval 900-1200°C. The heating rate was 7°C/min and the holding period was 60min. Finally, the fired samples were subjected to physical and mechanical tests such as linear shrinkage, water absorption and flexural strength. The crystallized samples obtained from the heat treatment were then studied by XRD using a Rigaku DMax-RB powder diffractometer. The microstructure characterization was performed in the scanning electron microscope (SEM) in MLA-250(FEI) operating at 25 KV. Right before SEM test, the samples were etched with 0.5vol. % HF for 1.5 minutes at room temperature and coated with carbon to be analyzed.
Effects of Composition Changes on Sintering Properties of Novel Steel Slag Ceramics

Table 1 The Main Chemical Composition of the Six Mixtures

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>($\text{CaO+MgO+FeO}/\text{SiO}_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>21.78</td>
<td>46.57</td>
<td>7.55</td>
<td>6.82</td>
<td>12.55</td>
<td>1.03</td>
</tr>
<tr>
<td>J2</td>
<td>22.68</td>
<td>45.78</td>
<td>7.97</td>
<td>7.58</td>
<td>10.84</td>
<td>1.02</td>
</tr>
<tr>
<td>J3</td>
<td>23.63</td>
<td>44.89</td>
<td>8.37</td>
<td>7.96</td>
<td>9.74</td>
<td>1.03</td>
</tr>
<tr>
<td>J4</td>
<td>25.00</td>
<td>43.65</td>
<td>8.99</td>
<td>8.91</td>
<td>7.48</td>
<td>1.03</td>
</tr>
<tr>
<td>J5</td>
<td>27.32</td>
<td>41.53</td>
<td>10.01</td>
<td>10.25</td>
<td>4.12</td>
<td>1.03</td>
</tr>
<tr>
<td>J6</td>
<td>27.75</td>
<td>41.18</td>
<td>10.23</td>
<td>10.82</td>
<td>2.96</td>
<td>1.02</td>
</tr>
</tbody>
</table>

3 RESULTS
3.1 PHYSICAL AND MECHANICAL PROPERTIES

Figure 1 shows the linear shrinkage of sintered samples. As expected, firing shrinkage values increased with higher sintering temperature but then decreased because of over-fired. Increasing CaO, FeO and decreasing MgO content didn’t result in the change of the maximum of linear shrinkage but for the corresponding temperature of the maximum values. The maximum values of linear shrinkage is up to nearly 14%.
The results of water absorption and flexural strength versus sintering temperature are shown in Fig. 2 and Fig. 3, respectively. The trends of water absorption are consistent with the flexural strength. Figure 3 indicates that flexural strength decreased with increasing calcium and iron and decreasing magnesium content, although the flexural strength of J1-J3 didn’t change significantly. The sintering temperature of the maximum of flexural strength decreased with increasing calcium and iron and decreasing magnesium content. Table 2 shows the maximum flexural strength and the corresponding sintering temperature of the six samples. Sintering temperatures decreased and flexural strength decreased first and then increased with the increasing calcium and iron and decreasing magnesium content. This may due to the differences of low-melting-point and the types of the crystals.
Table 2 The Maximum Flexural Strength and the Corresponding Sintering Temperature of the Six Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>J1</th>
<th>J2</th>
<th>J3</th>
<th>J4</th>
<th>J5</th>
<th>J6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering temperature (°C)</td>
<td>1180</td>
<td>1180</td>
<td>1180</td>
<td>1160</td>
<td>1140</td>
<td>1120</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>122.67</td>
<td>111.87</td>
<td>115.67</td>
<td>90.6</td>
<td>57.34</td>
<td>98.59</td>
</tr>
</tbody>
</table>

3.2 X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY

Fig. 4 XRD patterns of the samples fired at their optimum sintering temperatures

XRD analysis of the six fired samples at their optimum sintering temperatures (shown in Table 2) are given in Fig. 4. XRD results pointed out the diopside and augite as the major phases in sample J1-J3. Phases developed in J4 are diopside ferrian, almandine and quartz. Diopside ferrian, andradite and quartz are the major phases in J5, while the dominated phases in J6 are diopside ferrian, quartz and wollastonite. This suggests that the main phases tends to change from pyroxene or augite to iron diopside, andradite and quartz as the increase of calcium and iron content and reduction of magnesium.

SEM images of six samples fired at their optimum sintering temperature (shown in Table 2) are shown in Fig. 5. Back scattered electron detector (BESD) was used in this research. SEM and BESD showed little difference among J1-J3 from the appearance; J4 has larger crystal grains and pore size, this might be responsible for its low flexural strength; pores in J5 connect to form channels, and the crystal grains in J5 have irregular shapes and are distributed disorderly; J6 is relatively denser than J5. According to the XRD results, it
Effects of Composition Changes on Sintering Properties of Novel Steel Slag Ceramics

is the type along with the shape of crystals that determines the mechanical strength of the samples. It is also notable that the white dots and lumps in all samples have been identified by EDS as iron oxides or FeO-MgO (i.e. RO phase) which came from steel slag. This means that not all the iron have been converted to form crystals. That is to say there's still some iron left in the form of RO or free iron.

![SEM images of samples fired at their optimum sintering temperatures](image)

**CONCLUSIONS**

Under the premise of (CaO+MgO+FeO)/SiO2=1 the optimum sintering temperature of samples decreased, while the flexural strength firstly decreased and then increased with the increase of iron and calcium content and the reduction of magnesium content. The main crystal phases transformed from pyroxene and diopside to hedenbergite, andradite and quartz.

**ACKNOWLEDGEMENTS**

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**REFERENCE**

2. Baciocchi, R., Costa, G., Di Bartolomeo, E., Polettini, A. & Pomi, R. Carbonation of
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ABSTRACT

Powertrain components play a crucial role in the efficiency and performance of vehicles and machines. These components should not only last under the prevailing severe loading conditions but also consume as little as possible energy by themselves during production and operation. Typically these components are being fabricated from special steels involving additional heat treatments. Increased demands by either downsizing in the vehicle industry or high and erratic loading as occurring in heavy equipment such as windmills have been pushing existing alloys to their limits. The powertrain of a windmill accounts for approximately 25 percent of the total equipment cost and is a major cause for downtime. Recent developments demonstrated that by dedicated alloying of molybdenum to existing special steels considerable performance improvements and efficiency gains could be achieved. The paper explains the underlying metallurgical reasons and demonstrates examples of gear and bearing steels.

INTRODUCTION

Increasingly stringent demands by authorities to reduce vehicle exhaust emissions have forced the automotive industry to take a variety of measures for lowering fuel consumption (Table 1). Much in focus has been the reduction of vehicle weight by using high strength steel (HSS) and therefore lower gage or by incorporating low-density materials such as aluminum, magnesium or carbon fiber reinforced plastics. Steel clearly has the smallest carbon footprint in generating these materials and is the only means of reducing weight and cost simultaneously. The intensive use of such advanced materials, often being applied in a mix, has led to weight savings of several ten kilograms in smaller cars to several hundred kilograms in larger vehicles. An often quoted value states that vehicle weight reduction of 100 kg results in an average reduction of fuel consumption by 0.5 liters per 100 km. Weight reduction is particularly relevant in stop-and-go traffic where the vehicle mass has to be accelerated frequently. However, aerodynamics (drag coefficient) becomes the more relevant influencing factor during cruising at more constant speeds.

Increasing efforts are being done for optimizing the powertrain. A major trend is that of downsizing the engine and incorporating one or several turbochargers. The characteristic of such engines is an almost instantly high torque at low revolutions (Figure 1) putting rather sudden and high loads on the gearbox. Gearboxes have also evolved to 8 or even 9 transmission ratios allowing operating the engine in the optimum rpm range under nearly all conditions. Another mega trend in the automotive industry is the partial or full electrification of the powertrain. However, despite of officially low CO₂ emission values emanating from artificial driving cycles, the real CO₂ emission value of an electric vehicle much depends on the energy mix fed into the electric grid. Effectively low CO₂ values can only be achieved when the electric energy used for battery charging mainly originates from wind, solar or hydro power plants. Any vehicle, irrespective of the applied propulsion method, involves rotating parts that are prone to frictional power losses. Reducing friction in bearings, gears and drive shafts can achieve further fuel savings in the order of a few percent.

Lightweight strategies increase the contact stresses above \( P_{\text{max}} \) of 2.14 GPa (or FZG load stage 14) due to the reduction of component sizes. Such high contact pressure requires advanced technical solutions particularly in terms of materials and treatments. Steels with improved
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

mechanical properties offering a reduced coefficient of friction, resistance to high contact pressure and potential to apply a low friction surface coating represents a viable alternative to conventional gear and bearing steels in this respect.

The present paper focuses on optimizing special steel alloys used in powertrain applications. A modification of the well-established gear steel 20MnCr5 capable of accepting substantially higher loads will be presented. The steel also has the potential for depositing a low-friction coating after carburizing treatment. Furthermore, the slip-rolling resistance, friction and wear behavior of steels such as 36NiCrMoV1-5-7, Cronidur 30 (AMS 5898), 20MnCr5 (SAE 4820 or 5120) and 100Cr6H (SAE E52100) was analyzed with regard to the application in high-pressure contacts.

Table 1: Typical measures of reducing fuel consumption of cars.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Weight</th>
<th>Fuel Economy</th>
<th>Cost</th>
<th>Cost per 1% FE improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light weighting (HSS)</td>
<td>-140kg</td>
<td>5%</td>
<td>-100</td>
<td>-€20</td>
</tr>
<tr>
<td>Turbo charged gasoline engine</td>
<td>-20kg</td>
<td>10%</td>
<td>€200</td>
<td>€20</td>
</tr>
<tr>
<td>(down-sized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbo charged Diesel engine</td>
<td>+100kg</td>
<td>30%</td>
<td>€1000</td>
<td>€33</td>
</tr>
<tr>
<td>(vs. gasoline)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Advanced stop-start system</td>
<td>+5kg</td>
<td>5%</td>
<td>€200</td>
<td>€40</td>
</tr>
<tr>
<td>Light weighting (Al/Mg)</td>
<td>-280kg</td>
<td>10%</td>
<td>€750-1250</td>
<td>€75-125</td>
</tr>
</tbody>
</table>

Figure 1: Power and torque characteristics of naturally aspirated 3.0l, 2.5l and downsized turbocharged engines (2.0l) (data by BMW AG).

HIGH PERFORMANCE GEAR STEELS

The general requirements for high performance gear components are a hard case providing wear resistance and a tough core preventing brittle failure under high impact loads [1]. Accordingly, various alloy concepts and thermo-mechanical treatments have been developed to achieve this property combination. Alloy concepts for gear applications significantly vary in different markets due to historical drivers (e.g. automotive, machine building, military), practical experiences as well as local availability of alloying elements (Table 2).
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Table 2: Common carburizing steel grades for gear in various geographical markets.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Standard</th>
<th>Region</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>20MnCr5</td>
<td>EN 10084 (1.7147) min. 0.17 - 1.10 - - 1.00 - 1.00</td>
<td>Germany</td>
<td>0.22</td>
<td>0.40</td>
<td>1.40</td>
<td>0.035</td>
<td>0.035</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18CrNiMo7-6</td>
<td>EN 10084 (1.6587) min. 0.15 - 0.50 - - 1.50</td>
<td>France</td>
<td>1.00</td>
<td></td>
<td>0.25</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.40</td>
<td>0.90</td>
<td>0.025</td>
<td>0.035</td>
<td>1.80</td>
<td>0.35</td>
<td>1.70</td>
</tr>
<tr>
<td>15CrNi6</td>
<td>EN 10084 (1.5919) min. 0.14 - 0.40 - - 1.40</td>
<td>France</td>
<td>0.21</td>
<td>0.40</td>
<td>0.60</td>
<td>0.035</td>
<td>0.035</td>
<td>1.70</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.40</td>
<td>0.90</td>
<td>0.025</td>
<td>0.035</td>
<td>1.70</td>
<td>0.35</td>
<td>1.70</td>
</tr>
<tr>
<td>17NiCrMo6-5</td>
<td>EN 10084 (1.6566) min. 0.14 - 0.60 - - 0.80</td>
<td>Italy, France</td>
<td>0.15</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.20</td>
<td>0.40</td>
<td>0.90</td>
<td>0.025</td>
<td>0.035</td>
<td>1.10</td>
<td>0.25</td>
</tr>
<tr>
<td>SAE 8620</td>
<td>SAE J1249</td>
<td>North America</td>
<td>0.18</td>
<td>0.15</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>0.40</td>
<td>0.15</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>min.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.23</td>
<td>0.35</td>
<td>0.90</td>
<td>0.030</td>
<td>0.040</td>
<td>0.60</td>
<td>0.25</td>
</tr>
<tr>
<td>SAE 9310</td>
<td>SAE J1249</td>
<td>North America</td>
<td>0.08</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>0.08</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>min.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.13</td>
<td>0.45</td>
<td>0.95</td>
<td>0.025</td>
<td>0.040</td>
<td>1.40</td>
<td>0.15</td>
</tr>
<tr>
<td>20CrMnTi</td>
<td>GB T 3077 - 999 min. 0.17 0.17 0.80</td>
<td>China</td>
<td>0.17</td>
<td>0.17</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.23</td>
<td>0.37</td>
<td>1.10</td>
<td>0.035</td>
<td>0.035</td>
<td>1.30</td>
<td>0.15</td>
</tr>
<tr>
<td>20CrMoMo</td>
<td>GB T 3077 - 999 min. 0.17 0.17 0.90</td>
<td>China</td>
<td>0.17</td>
<td>0.17</td>
<td>0.90</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
<td>0.20</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>max.</td>
<td>0.23</td>
<td>0.37</td>
<td>1.20</td>
<td>0.025</td>
<td>0.035</td>
<td>1.40</td>
<td>0.30</td>
</tr>
<tr>
<td>SCM420</td>
<td>JIS</td>
<td>Japan</td>
<td>0.18</td>
<td>0.15</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Carburizing steel must comply with the following key requirements in view of component properties and durability:

- Chemical composition / hardenability
- Homogeneity / microscopic and macroscopic cleanliness
- Mechanical properties (strength, fatigue strength and toughness)
- Wear resistance, rolling strength and vibration resistance
- High and uniform dimensional stability [2].

A performance map (Figure 2) relates an easily measurable property like in this case surface hardness to a complex system property such as the tooth root endurance strength. The fact that for a given surface hardness a rather wide range of tooth root endurance strength levels can be obtained suggests that alloy composition, microstructure and thermo-mechanical treatment have an extremely high impact on the actual gear performance. Another system property of high importance for gear durability is the resistance to gear tooth flank micro pitting. High contact pressure, the status of lubrication, material properties, microstructure and chemical composition influence this system property. For case carburizing steels three quality levels can be distinguished: grade ML stands for the minimum requirement; grade MQ represents requirements which can be met by experienced manufacturers at moderate cost; grade ME represents requirements which must be aimed at when higher allowable stresses are desirable.

The approach practiced is to design alloying concepts taking the entire processing route into consideration including modified or innovative heat treatments. A fundamental way of dealing with these demands is to adjust the chemical composition of carburizing steels. In this respect one can principally define two approaches. An economically driven approach aims achieving a defined performance spectrum with a cost reduced alloy concept whereas a performance driven approach targets superior properties at equal or moderately increased cost. The current work considers both approaches focusing on modified molybdenum-based alloy concepts including niobium microalloying. Thereby innovative heat treatment conditions have also been tested.
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Optimization concept for carburizing steels

As performance reference, grade 18CrNiMo7-6 (1.6587) has been selected since this grade currently is being widely used for demanding gear applications in Europe. The task was to modify the main alloying elements in a way to achieve either the same performance at lower alloy cost or better performance at similar alloy cost. The following approach is considered to be relevant in this respect:

- Improving hardenability
- Increasing core tensile strength and toughness
- Increasing fatigue strength in both core and case
- Reducing quench distortion and thus residual stresses
- Improving microstructural stability to withstand elevated temperatures during service.

Considering the stress state at the gear tooth root [4], the most critical area appears to be below the surface, whereas the surface-near region is less critical. In case hardenability is insufficient and core strength is too low, the applied stress can locally exceed the material strength. This will result in poor tooth root fatigue endurance. Residual tensile stress due to quench distortion can add to the applied stress and worsen the situation, while shot peening introducing compressive residual stress has a beneficial effect. Degradation of the microstructure during service due to tempering effects (hot running) leads to softening which is detrimental. This also applies for retained austenite present in the outer quench layer.

Additionally, a typical surface near defect in a carburized layer, the intergranular oxidation layer has to be avoided because it acts as a fatigue fracture initiation site and reduces the fatigue strength of the tooth. The soft zone caused by intergranular oxidation results in surface softening in the carburized layer [5]. Elimination of surface structure anomalies is thus an important aspect in the development of high fatigue strength gears. Improving toughness can effectively be achieved by raising the tempering temperature. However, this requires reinforcing the tempering resistance in order not to lose strength. A fundamental way to deal with these issues is to adjust the chemical composition of the carburizing steel. Accordingly, the chemical composition of carburizing steels can be further developed to achieve the above goals using the following guidelines:

- Prevent intergranular oxidation → reduce Si, Mn, and Cr.
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

- Prevent MnS inclusions → reduce S, limit Mn
- Prevent TiN inclusions → control Ti / N wt.% ratio close to 3.4
- Improve hardenability → increase Mo.
- Improve toughness → increase Ni and Mo.
- Refine and homogenize grain size → balance Nb, Ti, Al and N microalloying addition.
- Strengthen grain boundaries → reduce P and S, add Mo and Nb.

Increasing base hardness and core hardenability

Several alloying elements, besides carbon, contribute to hardenability as such: molybdenum, manganese, chromium, nickel as well as boron microalloying. For cost reduction reasons alloys using higher manganese and chromium additions, eventually combined with boron microalloying have been favored for many gear applications. However, such cost reduced alloy concepts, although providing good hardenability, have limitation in terms of toughness and tempering resistance. Besides, the prevention of intergranular oxidation requires Mn, Cr and also Si levels to be reduced. In the other extreme alloy producers have developed richly alloyed steels for those applications where transmission failure causes high replacement and outage costs. An example is 15NiMoCr10-4 (C:0.15%, Si:1.1%, Cr:1%, Mo:2% and Ni:2.5%), which is used in high end applications e.g. in aerospace or Formula-1 gear. However such steel requires special melting technology and is not widely available. Comparing this steel to another high-Ni steel (14NiCrMo13-4) the increase of the molybdenum content from 0.25% to 2.0% brings about a significant improvement of hardenability, surface hardness and also tempering resistance [6] (Figure 3). The high tempering resistance of the material bears two important advantages. Firstly, it allows performing duplex treatments, i.e., the case hardened surface obtains a second treatment such as PVD coating or plasma nitriding (PN) to further increase surface hardness. These treatments are usually performed in a temperature window of 300 to 500°C. It is thus prerequisite that the hardness obtained in the underlying material after quenching from the carburizing temperature is not degraded by the second heat cycle. Secondly, many conventional case carburizing steel grades are restricted to a maximum operating temperature of 120 to 160°C. A steel grade with high tempering resistance can be operated hotter without degrading. Elevated operating temperatures may occur for instance by frictional heating when the transmission experiences lubrication problems.

Good tempering resistance in a typical gear steel base alloy can also achieved with lower molybdenum additions as indicated in Figure 4. Already a Mo addition of 0.5 to 0.7% provides good resistance against softening for tempering parameters up to around 16x10^3. Resistance against softening under a tempering parameter of 16x10^3 means that a secondary treatment at a temperature of 450°C for up to 10 hours should be possible. This condition is typical for plasma nitriding. Microalloying of Nb further enhances the tempering resistance, obviously as a synergy effect with Mo. Molybdenum and niobium have to some extend similar metallurgical effects. Both exert strong solute drag on grain boundaries as well as dislocations [7] and also lower the activity of carbon [8]. These fundamental effects are noticed by delayed recovery or recrystallization as well as a reduced rate of pearlite growth thus increased hardenability. The solubility of both elements in austenite is however very different. Molybdenum has a good solubility [9] whereas that of niobium is low [10]. Therefore niobium precipitates as NbC particles at rather high temperature. Manganese, chromium and particularly molybdenum increase the solubility of niobium in austenite [11]. Accordingly, more niobium will be in solution after quenching from austenitizing temperature, which is then available for fine precipitation during tempering treatment acting against softening.
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Figure 3: Surface hardness of the carburized layer in relation to tempering temperature and effect of increased molybdenum content.

Figure 4: Effect of tempering resistance in function of the molybdenum content and synergy effect with niobium (HP = T x (20 + log t) x 10^{-3} [T in K, t in h]).

Adding niobium in combination with titanium to carburizing steel has a marked effect on the grain size distribution [12-19] as shown in Figure 5 for grade 18CrNiMo7-6. Not only is the grain size generally much finer but also the scatter range is narrower. The microalloyed variant safely avoids prohibited grain sizes despite the high carburizing temperature (1030°C) and the long duration (25 hours). Similar good results of grain size stability have been obtained with modified variants of 25MoCr4 and 20CrMo5 grades Figure 6. The Nb and Ti dual microalloyed 25MoCr4 variant reveals resistance to coarsening up to 1050°C carburizing temperature whereas the Nb-only microalloyed 20CrMo5 variant is stable up to 1000°C. The latter alloy indicates that for very high carburizing temperatures indeed addition of multiple microalloy elements appears to increase the temperature stability of pinning precipitates. However, at standard carburizing conditions below 1000°C also the Nb-only microalloyed concept exhibits very fine austenite grain size with rather narrow scattering.

Developed gear steel for high temperature carburizing and subsequent surface treatment

Based on the individual and synergetic effects of alloying elements described before, the intended processing route and the desired property profile a modified alloy concept has been designed (Table 3) for a full scale production trial including gear running tests. The developed alloy design can be considered as a modified 20MnCr5 grade. It is aiming for higher performance than that of 18CrNiMo7-6 at similar alloy cost. The content of carbon is increased for higher maximum hardness while Mo and Ni are added for increased hardenability and tempering resistance. Niobium microalloying is applied for austenite grain size control. The achieved mechanical properties of the developed case-carburizing steel obtained after heat treatment indeed corresponds to the postulated expectations (Figure 10 and Table 3). The toughness of the developed steel is lower than that of 18CrNiMo7-6 due to the reduced nickel alloy content, yet remains still on a level clearly above the minimum requirement.
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Figure 5: Grain size distribution of a Nb+Ti microalloyed 18CrNiMo7-6 (1.6587) heat compared to a conventional analysis (carburizing conditions: 1030°C / 25 h).

Figure 6: Grain size stability under various carburizing conditions for Nb microalloyed 20CrMo5 (1.7264) and 25CrMo4 (1.7325).

Table 3: Chemical composition of the modified carburizing steel 20MnCr5.

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>20MnCr5 mod.</td>
<td>0.26</td>
<td>0.12</td>
<td>1.46</td>
<td>1.23</td>
<td>0.54</td>
<td>0.91</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4: Mechanical properties of developed case-carburizing steel (hardened at 880°C/2h + oil/180°C/2h) vs. reference grade 18CrNiMo7-6.

<table>
<thead>
<tr>
<th>Property</th>
<th>20MnCr5 mod.</th>
<th>18CrNiMo7-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, Rm (MPa)</td>
<td>1758</td>
<td>1182</td>
</tr>
<tr>
<td>Impact energy, A, (J)</td>
<td>47</td>
<td>80</td>
</tr>
<tr>
<td>Rotating fatigue limit @50% @N=10^7 (MPa)</td>
<td>722</td>
<td>510</td>
</tr>
<tr>
<td>Hardenability@11 mm (HRc)</td>
<td>51</td>
<td>41</td>
</tr>
<tr>
<td>Hardenability@25 mm (HRc)</td>
<td>50</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 5: Hardness characteristics after various heat treatments.

<table>
<thead>
<tr>
<th>Treatment after carburizing at 1030°C</th>
<th>20MnCr5 mod.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface (HV1)</td>
</tr>
<tr>
<td>As quenched</td>
<td>769</td>
</tr>
<tr>
<td>Freezing -70°C/2h - Tempering 200°C/2h</td>
<td>717</td>
</tr>
<tr>
<td>Plasma nitriding at 400°C</td>
<td>994</td>
</tr>
<tr>
<td>Plasma nitriding at 440°C</td>
<td>1009</td>
</tr>
</tbody>
</table>

The heat treatment behavior of the developed alloy has been tested by a carburizing process operated at 1030°C to a nominal case depth range of 0.95 to 1.2 mm. For determining the depth of the case layer a limit hardness of 550HV was defined according to ISO 6336-5. The targeted
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Surface hardness was set to 680-700 HV. Additionally a secondary plasma nitriding treatment has been also performed at 400 and 440°C, respectively. Table 4 summarizes the hardness data for the various pilot heat treatments. Due to its increased tempering resistance the developed steel shows very high surface hardness of around 1000HV after plasma nitriding whereas the core hardness is being reduced. Nevertheless a core hardness of more than 400HV is still a high value. With some further optimization this steel has potential of fulfilling the case depth requirements at secondary treatment temperatures up to 440°C.

Operational performance of the developed carburizing steel was tested and benchmarked at FZG TU Munich, Germany. The tooth root load-carrying capacity was tested in a pulsator rig. Investigations on the flank load carrying capacity were performed by running tests on a back-to-back gear test rig according to DIN ISO 14635-1 as described in [20, 21]. The test gears for these investigations were case hardened after the gear milling. Subsequent to case carburizing the test gears were mechanically cleaned by shot blasting. The flanks as well as the tooth roots of the test gears for the investigations on the tooth root bending strength were not ground. For the running tests gear wheels with a module of 5 mm and a gear ratio of 17/18 were used. This test gear is typical for the examination of the pitting load capacity.

A performance benchmark for the gear tooth root fatigue strength (DIN3990) of the developed steel against established case carburizing alloys is shown in Figure 12. In this graphic the grey shaded area indicates the typical performance range of state-of-the-art carburizing grades established in Europe. Additionally some non-European grades are indicated. The developed steel is situated above the quality level ME and thus performing better than established steel grades.

In order to determine the flank pitting load capacity repeated gear running tests in the high cycle as well as low cycle fatigue range were carried out as described in [21]. The test rig was driven with a constant speed of 3000 rpm and all test runs were performed under oil spray lubrication (approx. 2 l/min into the tooth mesh) with FVA 3 + 4% Anglamol 99 (S-P-additive), a mineral oil of viscosity class ISO VG 100, and an oil temperature of 60°C. Figure 14 represents a benchmark comparison of the obtained data against established case carburizing grades. The developed steel (20MnCr5 mod.) exhibits a very high pitting endurance limit, outperforming the leading established alloys of quality level ME.

---

**Figure 7**: Benchmarking of gear tooth root fatigue of developed case-carburizing steel vs. established alloys (DIN3990).

**Figure 8**: Benchmarking of gear tooth flank micropitting of developed case-carburizing steels vs. established alloys (DIN3990).
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The current results suggest that the developed steel 20MnCr5 mod. has the potential of providing an economically viable solution for highly loaded gear in heavy machinery and vehicles. Its use in vehicle transmission could enable downsizing of components reducing weight. In larger transmissions such as used in trucks and heavy machinery its use can help avoiding unexpected failure and extending warranty periods.

STEELS WITH IMPROVED SLIP ROLLING RESISTANCE

Energy dissipated in gears and bearings by rolling friction gives rise to power loss and hence contributes to reduced efficiency as well as increased emissions. The energy dissipation is related to micro-slip and friction at the contact interface, inelastic properties of the material and roughness of the rolling surfaces. Friction can be lowered by lubrication as well as by low-friction coatings on the surfaces of the mating rolling bodies. With increasing contact pressure due to lightweight design of bearing elements inelastic deformation of the material becomes larger leading to hysteresis losses. Furthermore, surface degradation related to rolling fatigue increases roughness and can cause hard low-friction coatings to spall off. Furthermore, increased torques or contact pressures raises oil film temperatures on the gear tooth flanks towards 200°C, leading to in-situ tempering and thus hardness loss of many state-of-the-art steels.

In previous investigations on the slip-rolling resistance of thin film coatings [22-25], the substrates were mainly made of the well-known bearing steels 100Cr6H (SAE E52100) and Cronidur 30 (AMS 5998, 1.4108). Cronidur 30 is a martensitic cold working steel melted under pressurized nitrogen. The use of pressurized electro slag re-melting in combination with sophisticated rolling technology, extremely high cleanliness and a homogeneous microstructure can achieve high durability values at a maximum hardness of 60 HRC. An important aspect of this steel grade is its high temper resistance up to 500°C making it also compatible to typical thin film coating processes. Both steels 100Cr6H and Cronidur 30 are widely used in the bearing industry. However, nitrogen alloyed steels, like Cronidur 30 are not widely available and are expensive. The steel grade 36NiCrMoV1-5-7 can be a lower cost alternative having good availability. Other advantages of this steel are:

- High tempering resistance allowing the application of thin film coatings
- Uncomplicated heat treatment
- Reduced friction as uncoated steel under mixed/boundary conditions
- High load carrying capacity
- Low wear as uncoated steel
- Tribological compatibility with state-of-the-art lubricants

The three steels, of which the chemical composition is given in Table 6, have been benchmarked by slip rolling testing using the Optimol 2-disc tribometer equipment and procedures described in [22]. The mechanical properties of these steels after heat treatment are summarized in Table 7. The hardness of grade 36NiCrMoV1-5-7 is clearly lower than that of 100Cr6H and Cronidur 30 yet its toughness is particularly good allowing operations up to 510°C without significant hardness loss.

Table 6: Chemical composition of steel grades tested for slip rolling resistance.

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>N</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6H</td>
<td>1.0</td>
<td>0.25</td>
<td>0.35</td>
<td></td>
<td></td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cronidur 30</td>
<td>0.25-0.35</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>14.0-16.0</td>
<td>0.85-1.1</td>
<td>&lt;0.5</td>
<td>0.3-0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36NiCrMoV1-5-7</td>
<td>0.30</td>
<td>0.25</td>
<td>0.2</td>
<td>0.002</td>
<td>0.002</td>
<td>1.50</td>
<td>0.8</td>
<td>3.0</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

Table 7: Mechanical properties (heat treated condition) of steel grades tested for slip rolling resistance.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>100Cr6H (SAE E52100)</th>
<th>Cronidur 30 (AMS 5890)</th>
<th>36NiCrMoV1-5-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness [HRC]</td>
<td>65.6</td>
<td>62.2</td>
<td>~ 54</td>
</tr>
<tr>
<td>Ultimate Strength $R_m$ [MPa]</td>
<td>~ 2300</td>
<td>~ 2300</td>
<td>1474</td>
</tr>
<tr>
<td>Fracture Toughness $K_{IC}$ [MPa m$^{1/2}$]</td>
<td>~ 16.5</td>
<td>~ 21</td>
<td>120</td>
</tr>
<tr>
<td>Charpy Toughness $K_V$ [J]</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Maximum ServiceTemperature [$^\circ$C]</td>
<td>150</td>
<td>475</td>
<td>510</td>
</tr>
</tbody>
</table>

Friction behavior under slip rolling conditions

Slip rolling tests were executed over 10 million cycles (132 km) at three different contact pressures with self-mating tribo-couples having the geometry shown in Figure 9. BMW factory fill engine oil SAE 0W-30 VP1 was used as lubricant at an operating temperature of 120$^\circ$C. The slip rate was adjusted to 10 percent corresponding to a sliding speed of 0.08 m/s. For the steel grade 36NiCrMoV1-5-7 five runs were repeated (min.-max. range indicated in Figure 9) and compared to statistical reference data of the two other steel grades.

Generally, all data (Figure 9) indicate a decreasing evolution of friction over the duration of the test. That means power losses reduce over run time. It is also apparent that steel grade 36NiCrMoV1-5-7 reveals a lower coefficient of friction (COF) over the entire run time at all three contact pressures. Most distinguished is the difference in COF at the mean contact pressure of 1.5 GPa where the COF of 36NiCrMoV1-5-7 is approximately 30 percent lower than for the established steel grades. Under this condition the COF of the 36NiCrMoV1-5-7 self-mating tribo-couple approaches the low level that is characteristic for steel coated with low-friction DLC thin films. With increasing contact pressure, the COF of the three steel grades assimilate. Those of grades 100Cr6H and Cronidur 30 slightly reduce whereas the COF of grade 36NiCrMoV1-5-7 slightly increases. It is thus evident that grade 36NiCrMoV1-5-7 has the potential of reducing friction even without low-friction coating at contact pressures above FZG 14.

Wear behavior under slip rolling conditions

Wear resistance in slip rolling tribo-contacts is an essential aspect as neither raceway nor ball should show significant damage over lifetime. As an evaluation criterion in the current tests it was specified that the surface damage should be not larger than 1 mm$^2$ over at least 10 million load cycles. Evaluation of the wear behavior indicated that grade 36NiCrMoV1-5-7 clearly has the potential of fulfilling the requirements for slip rolling wear resistance under all three contact pressure levels (Figure 10). The wear rate of grade 36NiCrMoV1-5-7 despite its comparably lower hardness is comparable to that of 100Cr6H and Cronidur 30. However, the wear rate of DLC coated steels is one order of magnitude lower. However, some individual samples of grade 36NiCrMoV1-5-7 showed premature failure (Figure 11). More detailed analysis could identify that the origin of premature failure was related to sub-surface non-metallic inclusions in the steel such as calcium sulfide (CaS) as well as aluminum oxide (Al2O3) and magnesium oxide (MgO) inclusions. Non-metallic inclusions acts as crack initiators, especially when they are locally agglomerated directly beneath the cyclically stressed surface. Thus, techniques such as vacuum induction melting (VIM) and vacuum arc re-melting (VAR) are necessary to improve steel cleanliness avoiding avoid rolling contact fatigue. Furthermore, refinement and homogenization of the microstructure is advisable for optimum toughness and fatigue resistance. This can be achieved by niobium microalloying, which has not yet been applied in the current commercially available grade 36NiCrMoV1-5-7.
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A recent study [26] demonstrated the significance of frictional losses in the vehicle powertrain. A total reduction of friction by 30 percent could reduce fuel consumption by around 12 percent. Grade 36NiCrMoV1-5-7 provides such a reduction in tribo-contacts subjected to 1.5 GPa mean pressure. Alternatively, DLC coated steels offer even lower friction. However, sufficient tempering resistance of the steel is prerequisite for the coating deposition. Both
molybdenum alloyed steels, Cronidur 30 as well as 36NiCrMoV1-5-7 provide the required tempering resistance for such surface treatment.

CONCLUSIONS
It has been demonstrated that significant improvements of steel properties relevant to powertrain applications are possible without applying expensive metallurgy or sophisticated treatments. In gear applications the optimized steel 22MnCr5 mod. showed much higher pitting resistance than the existing state-of-the-art steels. In bearing applications the existing steel 36NiCrMoV1-5-7 revealed a surprisingly low coefficient of friction under slip rolling conditions. In both steels molybdenum is a key alloying element. Molybdenum not only provides excellent hardenability but also severely raises the tempering resistance. The latter is crucial when operating temperature is high or when an additional surface treatment such as plasma nitriding or thin film deposition is desired. Niobium as a microalloying element controls and homogenizes the steel microstructure thus improving toughness and fatigue resistance. It also enhances the molybdenum-based tempering resistance. Detailed understanding of molybdenum-niobium based alloying concepts gained in the presented studies allows further optimizing and tailoring properties of special steel grades for powertrain applications. The envisaged benefits in terms of better efficiencies and reliability in powertrain applications as well as simplified production routes in making these steels will clearly outweigh alloy costs associated with molybdenum and niobium additions.

ACKNOWLEDGEMENT
The experimental benchmarking tests on both molybdenum-alloyed steels were financially supported by the International Molybdenum Association, London (www.imoa.info). The Gear Research Centre (FZG) of the Technical University Munich and the Federal Institute for Materials Research and Testing (BAM), Berlin are gratefully acknowledged for executing the experimental tests. Dr. Frank Hippenstiel of BGH Siegen kindly provided the tested steel materials.

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Efficiency Gains in Powertrain Components by Molybdenum-Alloyed Special Steels

NIOBIUM CARBIDE – AN INNOVATIVE AND SUSTAINABLE HIGH-PERFORMANCE MATERIAL FOR TOOLING, FRICTION AND WEAR APPLICATIONS

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ABSTRACT

Transition metals IVB to VIB in the periodic table of elements are strong carbide formers. Most prominent is tungsten carbide, which is typically consolidated with cobalt binder and is used for tooling, mineral processing and wear applications. Surprisingly little information was available about niobium carbide (NbC). Recently, pure NbC was synthesized from Nb2O5 and its properties were characterized in detail. Furthermore NbC hardmetal grades were synthesized using various metallic binders. Based on its tribological characteristics NbC appears to have great potential in tooling, friction and wear applications. Niobium carbide is largely available, efficient to produce, provides comparably low friction in many relevant tribo-contacts and shows low wear. NbC and Nb2O5 have so far no REACH classification related to human toxicology. Neither are these listed as substances of very high concern contrary to WO3 and Co3O4. The paper demonstrates the key characteristics of NbC and discusses its sustainability and reliable value chain.

INTRODUCTION

Carbides of the transition metals represented by groups IVB to VIB in the periodic table of elements are typically used as hard phases in technical alloys. The hardness of these transition metal carbides is superior to that of most minerals (Figure 1). Metals with high melting point such as cobalt, nickel or molybdenum are serving as ductile binder for hardmetals and cermets. Casting alloys containing dispersed hard phase particles provide the platform for a wide variety of metal-matrix composites.

In the arena of hardmetals, tungsten carbide has been the dominating hard phase since decades. Other transition metal carbides such as those of chromium, vanadium and titanium are also well established. Surprising little attention has been paid to niobium carbide, however. Nevertheless, niobium carbide has been occasionally used as minority phase in hardmetals, castings and tool steels. In these applications it serves either as grain refiner or as hard phase helping to enhance wear resistance, limits grain growth and enhances hot hardness. While some data on the fundamental properties of pure niobium carbide have been reported [1] reliable information on its tribological performance was not readily available. Recently it was shown however, that pure NbC as well as metal bonded NbC have a pronounced wear resistance under dry sliding versus other monolithic ceramics and carbides [2].

Hardmetals based on tungsten carbide are mainly produced by a powder metallurgy (PM) based sintering process due to the high solubility of the hard phase in alloys and in their melts as well as the mismatch in density between molten binder alloys and hard phase.
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Cobalt and nickel primarily serve as binder phase. The powder metallurgical route, however, limits the size of components, whereas castings would allow the fabrication of much bigger components. Alternatively hardmetals can be deposited as clad layers or thermally sprayed coatings onto a softer substrate material. Two well-known properties of NbC are its similar density to and its low solubility in iron. The density of NbC is very close to that of iron so that the mismatch in densities, depending on the carbide stoichiometry, and iron alloy composition is less than 10 percent. Its solubility in iron-based alloys as well as in nickel and cobalt is particularly small. Utilizing these two properties makes alternative production routes feasible for producing components as compared to PM-based processing routes.

Material health and safety issues with established hardmetals recently caused significant concerns. The European “Registration, Evaluation, Authorization and Restriction of Chemical substances program”, also known under the acronym REACH [3], currently classifies cobalt as very toxic for the human health. Furthermore tungsten carbide-cobalt hard metal dust was shown to be more toxic in combination than either pure cobalt or tungsten carbide alone [4]. So far, Ni powders do not have the same hazardous classification as Co powders. Niobium, on the contrary, is known to be one of the most biocompatible metal. No particular hazards or critical notifications for its oxide (Nb$_2$O$_5$) and carbide (NbC) were filed in the framework of REACH (Table 1). Biocompatibility evaluation using cell viability tests indicated no significant difference of NbC over a wide range of stoichiometry as compared to the established human body implant alloy Ti-6Al-4V [5].

The explored global tungsten reserves are estimated to around 3.10 million tons metal content or 6.384 million tons of tungsten as “reserves and resources” [6]. The reserves of the currently operating niobium mines, including the known deposits and secondary resources, largely exceed those of tungsten. In addition, significant new deposits have been discovered. Approximately 90 percent of the refined niobium (FeNb) is used as microalloy addition in the world steel

![Figure 1: Hardness comparison between mineral species and technical alloys; definition of hard metal and MMC materials.](image-url)
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industry. The current production capacity of FeNb and purified Nb$_2$O$_5$ is far bigger than its consumption. Both products can be precursor of niobium carbide.

### Table 1: Summary of health & safety classification and labeling (extract)

<table>
<thead>
<tr>
<th>Substance</th>
<th>[CAS]</th>
<th>[EINECS]</th>
<th>Hazard Class and Classification Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$</td>
<td>[1308-06-1]</td>
<td>[215-157-2]</td>
<td>Mutagenic category 2, Carcerogenic category 1A, Reproductive toxicity category 1B</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>[1314-35-8]</td>
<td>[215-231-4]</td>
<td>Mutagenic category 2, Carcerogenic category 1A</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>[1313-96-8]</td>
<td>[215-213-6]</td>
<td>Carcerogenic category 1A</td>
</tr>
</tbody>
</table>

Yet, the use of niobium carbide as a hard material is much less established than that of tungsten carbide. Nevertheless, its physical and chemical properties indicate an outstanding potential of niobium carbide for applications where currently tungsten carbide is being the standard material.

### METHODS OF NI OBIUM CARBIDE SYNTHESIS

Niobium carbide can be synthesized by various practical methods of which two are being considered here. One method is the direct carbo-thermal reduction of pure niobium oxide (Nb$_2$O$_5$) at elevated temperature (>800 °C) by the solid-state reaction:

\[
\text{Nb}_2\text{O}_5 + 7\text{C} \rightarrow 2\text{NbC} + 5\text{CO}(g) \quad (1)
\]

Reaction (1) does not represent the actual steady state reaction, since the reduction process is controlled by a gas-solid phase reaction (2) involving the so-called Boudouard reaction (3) as an intermediate step:

\[
\text{Nb}_2\text{O}_5 + 9\text{CO}(g) = 2\text{NbC} + 7\text{CO}_2(g) \quad (2)
\]

\[
7\text{CO}_2(g) + 7\text{C} = 14\text{CO}(g) \quad (3)
\]

Thermodynamic data indicate that reaction (2) is feasible at temperatures higher than 1000 °C. However, experiments indicated that for a complete conversion of Nb$_2$O$_5$ to oxide-free NbC reaction temperatures of at least 1200 °C must be applied. Since NbC oxidizes rapidly at temperatures above 480 °C the reaction atmosphere must be oxygen-free. An inert and reducing atmosphere of 95%N$_2$ + 5%H$_2$ was found to be practicable.

Representative NbC powders synthesized from Nb$_2$O$_5$ powder using the carbo-thermal reduction process show primary grain sizes in the sub-micron range (100 – 600 nm) reflecting the original oxide crystallite size (Figure 2). The NbC crystallites are agglomerated to larger particles (Figure 3), which can be broken down by an appropriate milling process after carbo-thermal reduction. XRD analysis indicated that these powders consist of pure niobium carbide, i.e., without traces of residual oxides or free carbon.

An alternative product developed by the Brazilian niobium mining company Companhia Brasileira de Metallurgia e Mineração (CBMM) is an innovative ferroalloy containing a high amount of primary NbC comprising controlled size and compact morphology. The production process is based on the standard alumino-thermic reduction utilized for ferro-niobium production. Yet, by adding a carbon source directly to this process primary precipitation of NbC occurs into an iron matrix instead of forming FeNb intermetallic phases (Figure 4). The carbide particles being formed in this process have sizes in the range of 10 to 50 μm and are of cubic morphology.
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(Figure 5). At the current development stage, the volume share of NbC phase embedded in an iron matrix is around 60 percent. This ferroalloy can be directly added to an iron melt for producing iron-based alloys containing a lower volume fraction of dispersed carbide particles. On the other hand, the Fe-NbC ferroalloy, in particular after further increasing the carbide volume share, can serve as a source of pure carbide supply (melt grown NbC). In this process, the iron matrix is dissolved from the ferroalloy by a leaching process using either hydrochloric or sulphuric acid (Figure 5).

![Figure 2: Morphology of NbC₁₀ crystallites obtained by carbo-thermal reduction of CBMM’s high purity Nb₂O₅ powder (de-agglomerated)](image1)

![Figure 3: Agglomerated NbC₀.₉₆ crystallites after carbo-thermal reduction of CBMM’s high purity Nb₂O₅ (used for “H1”)](image2)

![Figure 4: NbC₀.₉₄ particles formed by primary precipitation in a carbon-alloyed iron melt.](image3)

![Figure 5: NbC₀.₉₅ particles precipitated in liquid iron after chemical leaching by sulphuric acid.](image4)

BASIC PROPERTIES OF NIOBIUM CARBIDE

Table 2 resumes some of the key physical properties referring to room temperature measurements of stoichiometric niobium carbide in comparison to those of tungsten carbide published in literature [1]. The melting temperature of NbC is particularly high, which is expected to limit thermal softening as well as the tendency to adhesive wear. Data by Kelly et al. [7] indicated that the yield strength of NbC at temperatures above 1000°C is substantially higher than that of WC. The density of NbC is only about half of that of WC. This means that for producing a given component half the mass of NbC is needed, making the use of NbC economically
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Attractive. In dynamic applications where high accelerations and speeds are involved, the reduced mass results in lower inertia and kinetic energy, respectively. Since the density of NbC is very close to that of iron, gravity segregation should be rather low when dispersing solid NbC particles in melts of iron-based alloys. This likewise applies for spin casting processes where higher density particles segregate outwards and lighter density particles segregate inwards. The Young’s modulus of NbC is one of the highest amongst the refractory metal carbides, yet lower than for WC. Hence, components made from NbC will show a somewhat higher elastic deflection under mechanical loading compared to WC. On the other hand, contact stresses under a given load will be lower in NbC. Thermal stresses induced between NbC and metallic binder alloys are expected to be lower than for WC. This is reasoned by the larger coefficient of thermal expansion that is closer to that of typical metallic binders as well as to the lower Young’s modulus of NbC. Due to its metallic character niobium carbide has a relatively good thermal and electrical conductivity. Its thermal conductivity substantially increases at elevated temperature. Frictional heat generated in tribological contacts can thus be efficiently evacuated. The reasonably good electrical conductivity allows processing of NbC by for instance electrical discharge machining (EDM). It also helps avoiding the build-up of substantial static electricity in tribo-contacts with electrical isolators such as for instance polymer-based composites.

Table 1: Comparison of basic physical properties of niobium and tungsten carbide.

<table>
<thead>
<tr>
<th></th>
<th>Melting point (°C)</th>
<th>Density (kg/m³)</th>
<th>Young’s modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Vickers hardness (GPa)</th>
<th>CTE (ppm/K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Specific heat (J/g.K)</th>
<th>Electrical resistivity (μΩ.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbC</td>
<td>3520</td>
<td>7780</td>
<td>380-480</td>
<td>214</td>
<td>17-22</td>
<td>6.6</td>
<td>14</td>
<td>0.351</td>
<td>35</td>
</tr>
<tr>
<td>WC</td>
<td>2870</td>
<td>156-30</td>
<td>620-720</td>
<td>262</td>
<td>24-30</td>
<td>5.5</td>
<td>84</td>
<td>0.203</td>
<td>20</td>
</tr>
</tbody>
</table>

One of the most crucial properties with respect to wear resistant applications is the material hardness. From literature data and current experiments it is evident that the hardness of stoichiometric niobium carbide is below that of tungsten carbide (Table 1). Yet, its hardness is still far superior to most minerals and technical alloys (Figure 1) so that sufficient resistance against abrasive wear in tribo-contacts should be given. On the other hand, finishing efforts when manufacturing niobium carbide tools are expected to be lower than those for tungsten carbide tools.

The exact hardness value of these carbides is influenced by several parameters such as the level of porosity, indentation load [8] and temperature [9,10]. An increase in each of these parameters results in a decrease of the measured hardness value. Considering the temperature dependence of hardness, a two-stage behavior can be observed. In the lower temperature range, hardness decreases moderately with increasing temperature. In the higher temperature range this decrease becomes significantly steeper. The transition between the two regimes (drop in hardness) occurs in the temperature interval of 500-800°C for WC [9]. Niobium carbide exhibits this transition at a higher temperature interval around 900°C [11]. This implies a higher hot-hardness of NbC as compared to WC, which is of relevance for metal cutting operations. Recent hot-hardness measurements on NbC- and WC-based materials confirm this trend [12].

Contrary to WC, NbC is forming sub-carbides, like Nb6C5 or Nb4C3, over a wide range of carbon stoichiometry according to the Nb-C binary phase diagram shown in Figure 6 [13]. Carbon deficiency in the range of NbC to NbC0.8 has a significant influence on physical properties of the material. With increasing carbon deficiency in that range elastic moduli [14], lattice constant [15], density [15], heat capacity [16] and magnetic susceptibility [17] decrease. Yet, hardness strongly increases with increasing carbon deficiency in NbC as shown in Figure 7 [18].
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exceeding the level of WC. In summary, properties of niobium carbide can be tailored by adjusting the carbon deficiency in the compound.

The solubility of a carbide compound in a contacting metal at high temperature is a very important property with respect to the processing and wear performance of the carbide in hot tribo-contacts with metal. The solubility of niobium carbide metals such as iron, cobalt or nickel has been reported to be very low in contrast to the rather good solubility of tungsten carbides in these metals [19,20]. The solubility of NbC in austenite is shown in Figure 8 based on an established solubility product [21]. In this plot equilibrium solubility isotherms of niobium and carbon are indicated for various temperatures. Only when the carbon content is extremely low, niobium has a reasonably good solubility. In the area of micro-asperities of hot tribo-contacts, NbC should dissociate into solute niobium and carbon according to the stoichiometric ratio. The intersection of the stoichiometry line with the solubility isotherm defines the maximum solubility of NbC in a tribo-contact at that specific temperature. Carbon already present in an iron-based alloy further limits the solubility of NbC to extremely low values. The solubility of tungsten carbide in austenite is several orders of magnitude larger than that of niobium carbide [22] and responsible for high crater wear. Accordingly, WC-based components bear the risk of efficiently dissolving into iron-based alloys in hot tribo-contacts or during cutting/machining operations whereas NbC-based tools will suffer very limited material loss by dissolution into the chips under the same condition. Consequently a protective coating preventing the dissolution is not necessary on niobium carbide components.

Due to its low solubility, solid NbC particles can be readily dispersed into liquid cast iron preserving its original morphology and without significantly disturbing the carbon balance in the alloy. Because of the close match of densities between liquid iron and NbC the tendency to segregation by either gravity or centrifugal force is relatively small. This allows manufacturing of near net-shape components by either static or spin casting. NbC particles contained in used components can be easily recycled by re-melting corresponding scrap together with fresh alloy.
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Figure 8: Solubility of NbC in austenite based on the solubility product \( \log[Nb]C=3.4–7920/T \) where \( T \) is the absolute temperature; \( [Nb] \) and \( [C] \) are concentrations in wt.% [21].

METAL BINDERS AND SECONDARY CARBIDE ADDITION

Metal binders have the important function of consolidating the hard carbide phase leading to an acceptable combination of hardness and toughness with regard to the final application. In hardmetals or cermets the metallic binder is the minority phase whereas it becomes the dominating phase in a metal matrix composite (MMC) as indicated in Figure 1. The standard binders for WC are cobalt and nickel, which can also used to consolidate NbC particles. Due to its particularly low solubility in iron, carbon steel, stainless steel or cast iron can also used as binders for NbC. Another possible binder is the intermetallic phase of iron aluminide (Fe₃Al). Iron aluminide is a low cost alternative to stainless steel, also comprising a better ductility, lower density and excellent oxidation resistance up to 1,200°C.

Previous work revealed significant NbC grain growth in NbC-Co based cermets during pressureless sintering for 1 h at 1360°C [23]. NbC grain growth, however, can be effectively suppressed when consolidating NbC-Co cermets in the solid state by hot pressing or spark plasma sintering (SPS) [23,24].

Small additions of NbC to WC-based hard metal result in efficient grain size control. Likewise, the addition of other secondary carbides has the potential of suppressing grain growth in NbC-based hard metal or cermets.

Compared to pure NbC-Ni, limited NbC grain growth and homogeneous grain size distribution could be obtained upon adding secondary phase carbides or Al metal. In that respect WC and Mo₂C were found to significantly enhance hardness and toughness of NbC-Ni cermets. Figure 9 demonstrates several examples of these approaches highlighting the grain size controlling effect on NbC by aluminum additions to iron and nickel binders as well as Cr₃C₂ and especially Mo₂C secondary carbide additions. Accordingly, NbC as hard phase offers a wide variety of possibilities for tailoring hard metal and cermet combinations to the exact needs of an application.
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Figure 9: Back scattering electron micrographs of NbC cermets vacuum sintered at 1420°C.
(a): NbC-12 vol% Co → (b): NbC-12 vol% Co + 0.9 vol% Cr2C2
(c): NbC-12 vol% Fe → (d): NbC-12 vol% (Fe + 25 at% Al)
(e): NbC-12 vol% Ni → (f): NbC-12 vol% (Ni + 25 at% Al)
(g): NbC-15 vol% Ni → (h): NbC-15 vol% Ni + 5 vol% Mo2C
The Vickers hardness (HV) and fracture toughness (KIC) of various NbC cermet prepared under exactly the same sintering conditions are being related to each other in Figure 10. Generally, the hardness of the cerments can be divided into four categories. The Co bonded WC-NbC-VC/Cr$_3$C$_2$ cemented carbides have the highest hardness, followed by the Ni bonded NbC-MeC cerments and the NbC-Ni and -Fe cerments which have a lower hardness. The NbC-Co cerments prepared by conventional sintering exhibited the lowest hardness level. Since all grades have a comparable binder content, the difference in hardness of the NbC matrix cerments can be directly attributed to the nature of the binder and the constituent components, i.e., the binder composition and the NbC grain size. Based on the microstructural analysis, the refinement of the NbC grain size in the Al-doped Fe/Ni binder NbC cerments improved the hardness. The hardness of the Fe-Al, Ni-Al, Co and Ni binders are difficult to compare directly since they exhibit different grain sizes. Considering the pure metal binder, the Fe bonded NbC cerments had the highest hardness of 1,294 kg/mm$^2$, followed by the Ni and Co bonded cerments. For cobalt bonded WC-NbC-VC/Cr$_3$C$_2$ cemented carbides, hardness rises with increasing content of grain growth inhibitor.

Figure 10: Vickers hardness and fracture toughness of NbC cerments and WC-NbC-Co cemented carbides.

Regarding the fracture toughness, there is an antagonistic correlation to the hardness of NbC matrix materials. The hardness increases and fracture toughness decreases with decreasing NbC grain size for a given binder type and binder content. The binder plays a crucial role in shielding the stress field in front of a crack tip and as such improving the toughness [25]. Ductile failure of the Co, Ni or Fe binder is usually found on fractured NbC-Co/Ni/Fe interfaces. Since intermetallic phases such as Fe-Al and Ni-Al have an intrinsically low room temperature ductility, the Al doped cerments have accordingly a lower fracture toughness. For a given low hardness value around 1,250 kg/mm$^2$, the Ni bonded NbC cerments had the highest toughness of 12 MPa m$^{1/2}$, whereas the Fe and Co bonded cerments exhibited toughness values of only 6-7 MPa m$^{1/2}$. When hardness was increased to 1,500 kg/mm$^2$, the transition metal carbide (MeC) added NbC-Ni cerments still had the highest toughness of 8.5 MPa m$^{1/2}$, whereas the corresponding NbC-12 vol% (Fe-25 at% Al) cermet had a toughness of only 5 MPa m$^{1/2}$. Analysis of the microstructures and mechanical properties (Figure 9) reveals that the addition of Al and secondary carbides have a great impact on the final NbC grain size and microstructure as well as the concomitant increased hardness and reduced toughness.
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TRIBOLOGICAL BEHAVIOR OF NbC-BASED HARD MATERIALS

Friction and wear are system dependent attributes of interacting surfaces. Therefore the tribological performance of carbides can only be reliably judged using specific tests simulating a defined tribo-contact condition under a wide range of operating conditions. Such simulations have been performed for many hard materials. Yet, for niobium carbide no reliable tribological data could be found in literature. Consequently an extensive test program in a wide range of operating conditions has been set-up to benchmark pure niobium carbide as well as NbC-based hardmetals and MMCs against established other hard materials.

The tribometers used for unidirectional sliding are proprietary developments of BAM and the details are disclosed elsewhere [26]. They comply with ASTM G99 (DIN 50324) and with DIN EN 1071-13:2010. The wear volumes of stationary and rotating specimen were calculated from stylus profilometry and the wear scar diameters were determined by using ASTM D7755-11 or DIN 51834-3. The wear rate \( k_w \) is defined as the ratio of volumetric wear to the product of normal load \( F_N \) and the sliding distance \( s \). The coefficient of friction (CoF) and the total linear wear of both tribo-partners were recorded continuously. One test per combination of parameters was performed, because the testing philosophy at BAM is to screen over a wide range of operating conditions rather than doing repeated tests. Repetitions can be done, however, for specific test conditions. The tribological data of WC-, \( \text{Cr}_2\text{C}_3 \)- and \((\text{Ti,Mo})(\text{C,N})\)-based materials elaborated under the same test conditions were available from references [27,29,30] for benchmarking.

The frictional level of different NbC grades and the Fe₃Al-NbC MMC displayed in Figure 11 compares well with different WC-based or \( \text{Cr}_2\text{C}_3 \)-based hardmetals or monolithic alumina [27]. At room temperature (RT), the friction of binderless HP-NbC₁ increased with increasing sliding speed having values of around 0.3 at low sliding speed and reaching a level of 0.8 at high sliding speed similar to monolithic alumina, whereas all metal bonded NbCs presented an opposite trend. Friction decreased with increasing sliding speed. It thus qualifies NbC for traction and frictional applications such as clutches or brake rotors rather than for low friction bearings (Figure 11). Metal bonded NbC grades showed an opposite trend to pure HP-NbC as the coefficient of friction decreased with increasing sliding speed at RT (Figure 11) [31]. At low sliding speed the value can reach unity while at high sliding speed it drops to a level of 0.4. This behavior is quite similar to that of \( \text{Cr}_2\text{C}_3 \)-based hardmetals. The friction behavior of the Fe₃Al-NbC MMC is very similar to that of the NbC-based hardmetals.

At 400°C friction of all NbC and hard metal grades decreased with increasing sliding speed but were on average lower as compared to WC grades. The friction of NbC grades at high sliding speeds was lowest at 400°C. Low friction at high sliding speed is a favorable property for cutting tools reducing cutting forces thus achieving a given cutting performance at reduced machine power.

In comparison to other hardmetals, binderless HP-NbC comprised a particularly high wear resistance especially at RT, which is more or less independent from sliding velocity (Figure 12) [27]. The wear resistance of HP-NbC as well as of Co- and Fe₃Al-bonded NbC hardmetals is highest at RT and high sliding velocities.

At RT the metal-bonded NbC grades displayed a rather constant evolution of the wear rate with increasing sliding speed (Figure 12) [2]. The RT wear rates of the MMC Fe₃Al-NbC₀.₉₄ are slightly higher than those of the NbC-bearing hardmetals and for all NbC grades the wear rates decreased with increasing sliding speed, what is beneficial for cutting applications. It is also apparent, that metallurgically synthesized or sintered NbC bearing materials tribologically compete with WC and \( \text{Cr}_2\text{C}_3 \)-bearing hardmetals or cermets. At 400°C, the cobalt bonded NbCs presented lower wear rates than the NbCs bonded with Fe₃Al or having such a matrix, because of the well-known effect of Co₃O₄ formed by tribo-oxidation lowering the wear rate. It was recently shown, that reduced Nb₁₂O₂₉ contributes to the wear resistance of NbC [32], especially under...
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Figure 11: Coefficient of friction of NbC-based hardmetals and Fe₃Al-NbC (MMC) compared to different ceramics and hardmetals under dry friction at RT and 400°C

Figure 12: Total wear coefficients of NbC-based hardmetals and Fe₃Al-NbC (MMC) compared to different ceramics and hardmetals under dry friction at RT and 400°C
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high sliding speeds at RT, where the wear rate of \( \text{Nb}_2\text{O}_5 \) at 7 m/s of \( k_r = 4.9 \times 10^{-6} \text{mm}^3/\text{N}\cdot\text{m} \) is close to that of NbC-based cermets.

SUSTAINABILITY CONSIDERATIONS

The data and knowledge on niobium carbide generated during recent years have indicated that this innovative but not yet very well known material has a large spectrum of possible applications. Niobium carbide is in many properties competitive to the established tungsten carbide and in some particular features clearly superior to it. More important, niobium carbide based materials offer sustainable solutions with regard to several aspects as follows:

Economic sustainability

Due to its comparably low density a given component manufactured from NbC has approximately half the mass in comparison to WC. That mass reduction is larger than the price difference between NbC and WC resulting in an effective cost saving when using NbC.

Niobium based raw materials (oxide, ferroalloys) are not noted on the London Metal Exchange and are not exposed to noteworthy price volatility. This price stability facilitates raw material budget planning and allows reliable cost calculation for finished products.

Niobium based raw materials mainly originate from mines in Brazil and Canada. The supply is stable and not exposed to political uncertainties or embargos. The available capacities and known reserves are large enough to cover expected future demands for NbC without constraints. The supply chain situation, the historical governance indicators and the explored global availability including the long-term geological availability (mined deposits and confirmed reserves) do not justify the inclusion of niobium in the list of critical raw materials.

Environmental sustainability

Mining operations at the premier niobium producer CBMM in Brazil, which stands for approximately 80 percent of the global niobium supply, fulfill the highest environmental standards. The mine was ISO 14001 certified in 1997 covering mining operations as well as production of all relevant niobium-based alloys and oxides.

No particular hazards or critical notifications for its oxide (\( \text{Nb}_2\text{O}_5 \)) and carbide (NbC) were filed in the framework of REACH. Niobium carbide over a wide range of stoichiometric compositions appeared to have a biocompatibility comparable to Ti-6Al-4V, a widely used material for human body implants.

Niobium carbide allows the application of a large variety of binder metals. When the use of cobalt or nickel in particular application causes concerns, it is possible to deviate to uncritical iron-based binder metals such as for instance stainless steel.

Technical sustainability

Niobium carbide can be easily generated from standard grade niobium oxide by one-step direct reduction with carbon using the same equipment as for tungsten carbide production. Hence, no specific investment will be necessary at established powder manufacturers.

The low solubility of niobium carbide in binder metals and particularly iron facilitates manufacturing. In applications where iron-based materials have to be machined, NbC-based tools do not require a protective coating to diminish crater wear. This reduces cost and carbon footprint as compared to manufacturing WC-based tools, which do require a coating.

The close match of densities between NbC and iron-based alloys as well as its low solubility allow efficient production of NbC reinforced materials by casting. Used components of
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that material can be easily recycled by re-melting. Thus, wear resistant components in any size and shape with a very high content of hard phase can be economically produced.

CONCLUSIONS
Research and development of niobium carbide-based hard materials started only recently, yet showing already a very high potential for many technical applications. Industrial pilots of these new materials are in progress, especially in areas where established tungsten carbide-based materials are causing economic, environmental or technical concerns. First results of NbC reinforced castings demonstrated already substantial lifetime improvements for components used in the mining industry. Recent benchmark trials with cobalt-bonded NbC hardmetals indicated favorable performance in high-speed machining of steel components.

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