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From scrap to product: the effect of recycled tungsten carbide and alumina content on the mechanical properties of oxide-carbide duplex ceramic composite

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ABSTRACT

With the depletion of critical raw materials (CRMs), such as tungsten (W) and cobalt (Co), the sustainable recycling of tungsten carbide-cobalt (WC-Co) hard metal scraps has become essential. This study explores a sustainable recycling method for WC-Co scraps to produce duplex ceramic composites intended for dry machining. WC-Co scrap (6% Co) was mechanically crushed, sieved to under 1 mm, leached by H_2SO_4, and then ball-milled to obtain fine WC powder with a particle size of ~1 μm. To study the effect of using recycled powder and to trace the effect of alumina content, two compositions were synthesized via spark plasma sintering (SPS) at constant pressure and holding time at temperatures ranging from 1500 °C to 1600 °C. Composites containing 46% alumina and 12% ZrO_2 were combined with either recycled or commercial WC (42% by volume), and a third composite with high-alumina content (72% Al_2O_3, 2% ZrO_2, and 26% WC) was also prepared. Microstructural analysis via a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS) showed minimal impurity in the recycled powder and material integrity. Density measurements using the Archimedes method, along with mechanical testing, were conducted to evaluate the mechanical properties. Composites produced from recycled WC exhibit mechanical properties comparable to those of commercial composites, with minimal degradation. This recycling approach offers a safe, environmentally friendly and sustainable solution, minimizing health risks (compared to other recycling methods), while effectively preserving critical materials for high-performance, wear-resistant applications in machining.

1. Introduction

The rapid industrialization and technological advancements of the 21st century have led to an unprecedented demand for critical raw materials (CRMs) such as tungsten (W) and cobalt (Co) [1,2]. In addition to hard metals, cermets, advanced ceramics and composites also rely on these elements, but they are subject to significant environmental and geopolitical constraints. The mining and refining of these materials are energy-intensive and environmentally detrimental. Recycling tungsten carbide-cobalt (WC-Co) hard metal scraps not only conserves these CRMs but also aligns with global sustainability goals by reducing the ecological footprint and dependence on primary resource extraction [3,4]. Sustainability in recycling tungsten and cobalt reduces the depletion of these CRMs, enabling more reliable production of advanced ceramic composites and reducing their environmental impact [5].

Among high-performance ceramics, duplex interpenetrating ceramic composites are distinguished by their mechanical and tribological properties. By combining different phases within a composite, these materials achieve a simultaneous enhancement in hardness (strength) and fracture toughness. Such composites are of paramount importance in extreme environments – for example, in dry machining – where traditional materials often fail due to wear and thermal degradation. Optimizing the balance between hardness and fracture toughness in composites is challenging, as improvements in one property often come at the expense of the other. The development of duplex interpenetrating structures, where one phase improves toughness and the other provides hardness, has proven to be a game-changer in addressing these limitations [6–8]. Advanced processing techniques, such as spark plasma sintering (SPS), enable precise control over microstructure and phase distribution, allowing for the creation of tailored composites that meet the rigorous demands of industrial applications [9,10].

This study focuses on leveraging sustainability in material design by incorporating recycled WC powders, obtained from recycled WC-Co cemented carbides, into duplex oxide-carbide ceramic composites. By adopting a systematic recycling methodology – including mechanical crushing, sieving, acid leaching, and ball milling – high-purity recycled WC-Co powders were obtained and incorporated into ceramic composites with varying alumina content. SPS was employed to fabricate these composites, ensuring optimal densification and microstructural integrity. Mechanical property evaluation showed that the composites fabricated from recycled particles exhibited properties comparable to their commercial counterparts, demonstrating that recycling does not significantly compromise performance. Furthermore, this approach significantly reduces environmental impact, enhances resource efficiency, and offers a viable solution for mitigating the challenges associated with the depletion of CRMs.

2. Experimental procedures

2.1. Recycling of WC-Co hard metal scraps

The scrap material used was WC-Co hard metal scraps (Sandvik H6N grade) containing 6% cobalt. The initial morphology and composition of the material were analyzed via a JEOL JSM-6460LV scanning electron microscopy (SEM) equipped with an Oxford Instruments INCA X-act Energy 350 energy dispersive spectrometer (EDS). Figure 1 demonstrates the initial scrap pieces.

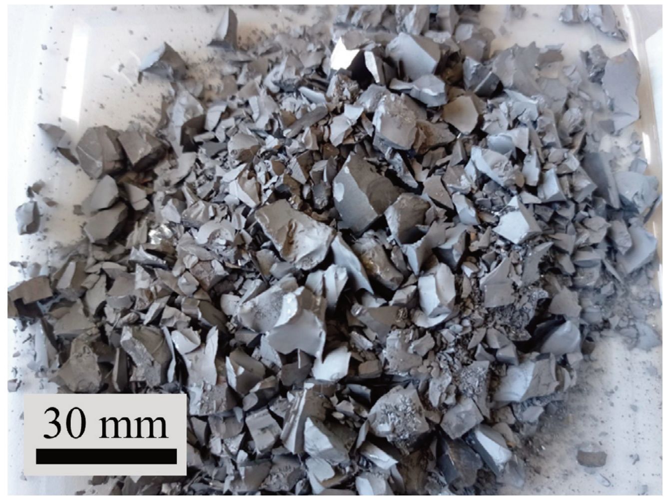


Fig. 1. Macro photograph of pre-crushed carbide pieces (maximum particle size: 10–15 mm). Photo by Piotr Klimczyk.

The WC-Co scrap was mechanically crushed using a carbide mortar and a 30-mm diameter carbide ball. A manual balancing press was employed to exert controlled pressure, reducing the scraps into smaller particles. The crushed material was sieved to isolate fractions smaller than 1 mm. This crushing and sieving process was repeated multiple times to ensure consistency and uniformity in particle size. The <1 mm WC-Co powder underwent a leaching treatment to reduce the cobalt content based on Equation (1) ($Co + H_2SO_4 \rightarrow CoSO_4 + H_2$) and to remove potential impurities.

This was carried out by immersing the powder in a 20% H_2SO_4 solution at room temperature for 240 hours under continuous mixing. The leached powder was thoroughly washed with distilled water to neutralize residual acid, followed by drying in an oven. The dried, leached powder was further processed through ball milling using a Pulverisette 6 (Fritsch) planetary mill equipped with WC-Co jars and balls. Initially, 10-mm diameter balls were used at 300 rpm for 1 hour, followed by milling with 5-mm diameter balls at 400 rpm for 2 hours. Isopropanol was employed as the milling medium to prevent oxidation. After milling, the powder was dried to remove any residual solvent.

2.2. Sintering

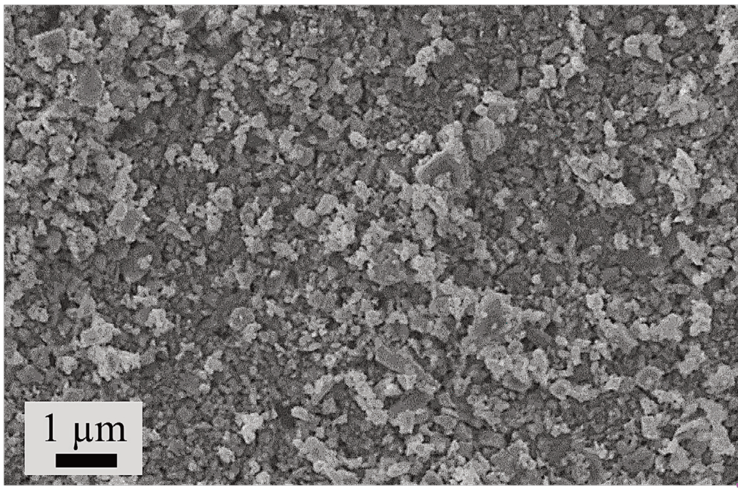
The initial materials used for the preparation of duplex oxide-carbide ceramics were two alumina powders differing in average particle size (AA-04 grade, 0.5 µm, Sumitomo, Japan, and TM-DAR grade, 100 nm, Taimei, Japan), partially stabilized zirconia powder (ZrO_2 + 3 mol% Y_2O_3, YSZ grade, 30–60 nm, Inframat, USA), and two types of tungsten carbide powders (DS 60 grade, 0.6–0.7 µm, HC Starck, Germany, and recycled WC, <1.0 µm, obtained in this work). Different compositions were prepared by ball milling, and after the preparation of mixtures, the mixed powders were sintered using SPS (HP D5, FCT, Germany) under controlled conditions. The compositions and sintering conditions are given in Table 1.

2.3. Characterization

The microstructure of the sintered composites was examined using SEM equipped with EDS to evaluate phase distribution and trace impurities. Density was measured using the Archimedes method. For measuring the hardness of the sintered materials, the HV10 method was utilized (Future Tech

Table 1. Compositions and sintering conditions, with a constant holding time of 4 minutes and a sintering pressure of 64 MPa

Sample	Composition			Sintering condition
	Alumina (vol%)	Zirconia (vol%)	Tungsten carbide (vol%)	Temperature (°C)
S1	46	12	42	1500
S2	46	12	42	1550
S3	72	2	26	1550
S4	72	2	26	1600
S5	46	12	42 (recycled)	1500
S6	46	12	42 (recycled)	1550



	Weight %
C	8.5
O	3.6
Co	0.5
W	87.5
Total	100

Fig. 2. SEM image of recycled WC particles with EDS analysis.

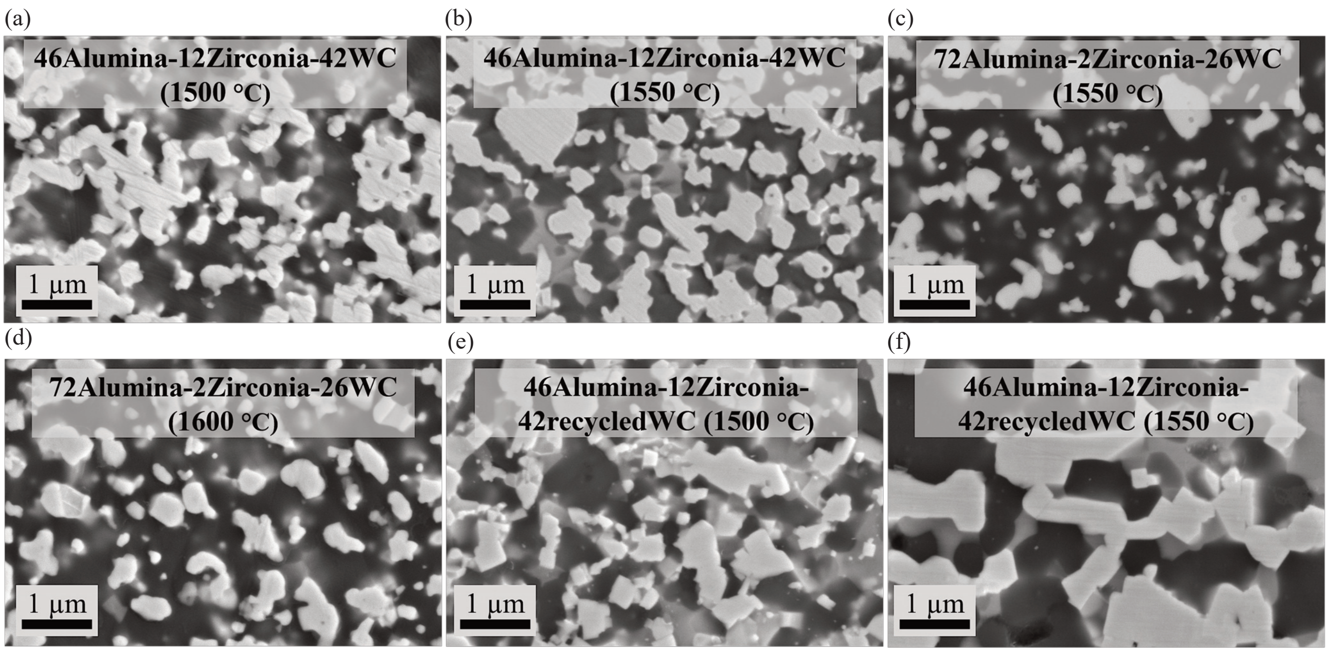


Fig. 3. SEM images of the sintered composites: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6.

FLC-50VX hardness tester), and measurements were performed at least five times for each sample. Fracture toughness (K_{IC}) was calculated based on the length of cracks propagated along the Vickers indent by Niihara's equation [11], and the Young's modulus was computed using the method described in [12].

3. Results and discussion

The crushed and milled powders exhibited minimal impurities, as confirmed through SEM and EDS analyses. Figure 2 illustrates the morphology of the recycled WC powder with a fine particle size distribution (~1 µm), which is essential for uniform sintering and optimal mechanical properties. The EDS analysis (Fig. 2) confirmed the removal of cobalt impurities during leaching and highlighted the high purity of the recycled powders. The composition of the recycled WC matches that of commercial-grade powders, ensuring its suitability for composite fabrication. The results underscore the effectiveness of the recycling process in providing a sustainable alternative to commercial materials, contributing to environmental conservation without compromising on quality.

The sintered composites exhibited distinct microstructural features based on their composition and the source of WC powders. SEM imaging (Fig. 3) revealed that samples S1 and S2, which utilized commercial WC, displayed a well-distributed interpenetrating microstructure with consistent phase interfaces. This structure significantly contributes to the mechanical performance of the composites. Samples S5 and S6, synthesized using recycled WC powders, also demonstrated interpenetrating microstructures with uniform phase distribution (for S5, see Fig. 4). However, the phases in these samples were slightly larger, with less bending and sharper corners compared to S1 and S2. Samples S3 and S4, with higher alumina content, did not exhibit interpenetrating structures but presented homogenous grain distribution.

The density and mechanical properties of the sintered composites are represented in Fig. 5. The relative density of all samples exceeded 99.4%, indicating near-complete densi-

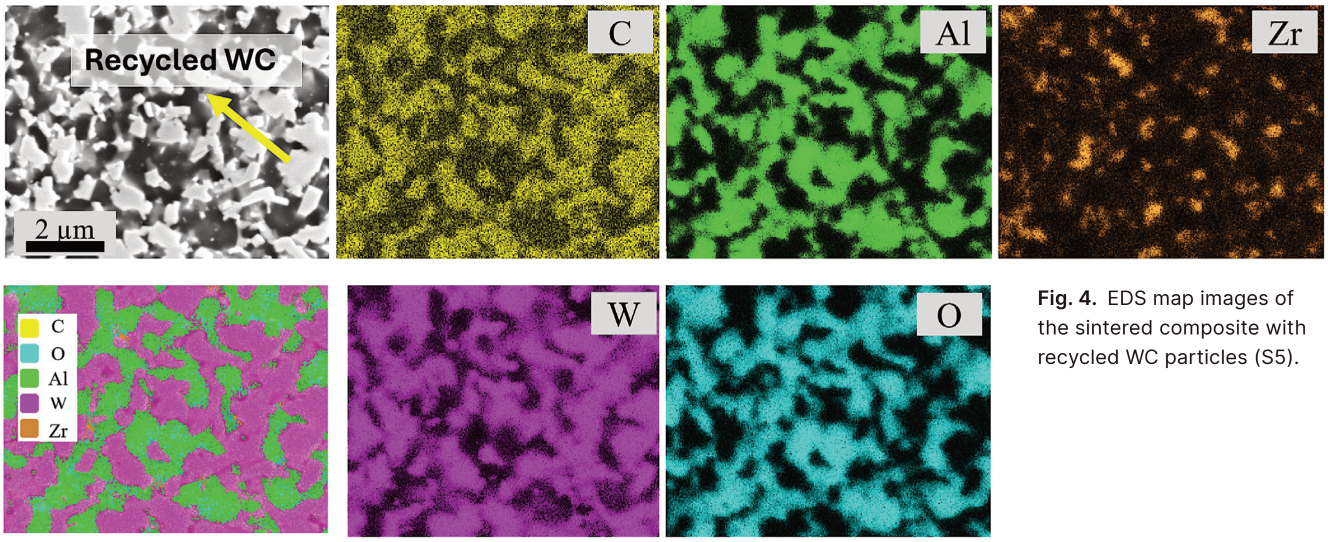
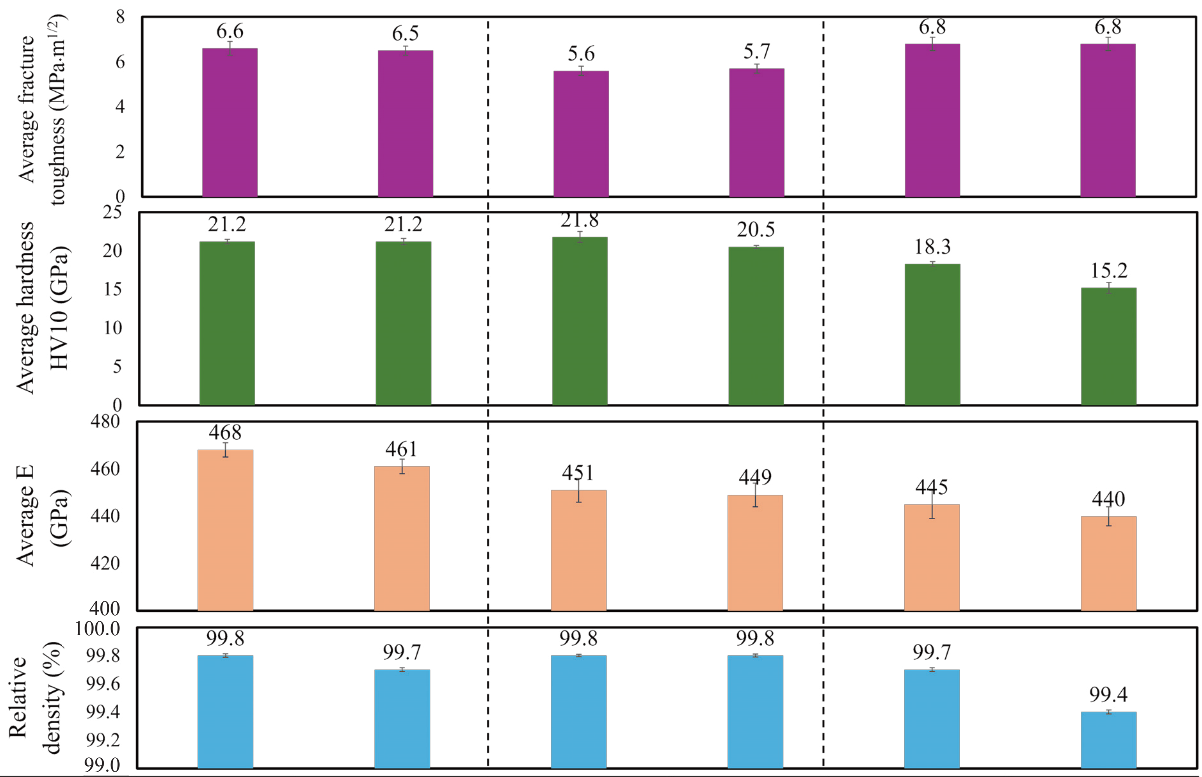


Fig. 4. EDS map images of the sintered composite with recycled WC particles (S5).



Sample	S1	S2	S3	S4	S5	S6
Sintering temperature (°C)	1500	1550	1550	1600	1500	1550
Composition	46%Alumina-12%Zirconia-42%WC		72%Alumina-2%Zirconia-26%WC		46%Alumina-12%Zirconia-42%recycledWC	

Fig. 5. Relative density and mechanical properties of the sintered composites.

fication achieved through SPS. Notably, samples S1, S3 and S4, fabricated using commercial WC powders, achieved the highest relative densities of 99.8%.

This superior densification is attributed to the high purity and homogeneity of commercial WC particles, which facilitated efficient particle compaction and sintering kinetics. In contrast, samples S5 and S6, prepared with recycled WC powders and sintered at 1500 °C and 1550 °C, exhibited slightly lower densities (99.7% and 99.4%). The reduced density can be linked to the influence of recycled WC particles, which, despite their high purity, may contain residual surface defects or larger particle sizes that hinder optimal packing and sintering. Samples S1 and S2 exhibited remarkable mechanical properties, including a hardness of 21.2 GPa and fracture toughness of 6.6 and 6.5 MPa·m$^{1/2}$. Recycled WC powders (S5 and S6) yielded composites with slightly lower hardness (18.3–15.2 GPa) and comparable fracture toughness (6.8 MPa·m$^{1/2}$). These results indicate that while recycled powders influence hardness, they maintain competitive fracture toughness, making them a viable option for high-performance applications. The lower hardness of S6 compared to S5 (15.2–18.3 GPa), or S4 compared to S3 (20.5–21.8 GPa), can be attributed to sintering temperatures, since the lower sintering temperatures preserved grain boundaries and finer WC grains, which enhance resistance to deformation during indentation. The Young's modulus values, ranging from 440 GPa (S6) to 468 GPa (S1), were consistent with microstructural observations. Excessive sintering temperature leads to localized grain growth that can trap voids and induce microcracking. This grain growth is clearly visible in Fig. 3 for samples with higher sintering temperature. Additionally, the slight reduction in both modulus and toughness in S3 and S4 can be attributed to the higher alumina content, as alumina inherently exhibits lower mechanical properties compared to the interpenetrating structures of WC and ZrO_2.

4. Conclusions

- WC-Co hard metal scrap was recycled into high-purity powders through mechanical crushing, leaching, and ball milling, while maintaining material integrity and suitability for composite fabrication.
- The resulting duplex ceramic composites achieved densities exceeding 99.4%, demonstrating the effectiveness of the recycling and sintering processes.
- Composites of alumina and recycled WC achieved a hardness of 15.2–18.3 GPa, fracture toughness of 6.8 ± 0.3 MPa·m$^{1/2}$, and a Young's modulus of around 443 ± 3 GPa, comparable to commercial WC composites (hardness of 21.2 GPa, toughness of 6.6 MPa·m$^{1/2}$, and Young's modulus of 468 GPa).
- Higher WC and ZrO_2 content led to better interpenetrating structures and superior mechanical properties.

Data availability statement

All research data are contained within the article and can be shared upon request from the authors.

Acknowledgments

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Jäätmetest tooteni: volframkarbiidi taaskasutamise ja alumiiniumoksiidi sisalduse mõju oksiid-karbiidi duplekskeraamilise komposiidi mehaanilistele omadustele

Arash Kariminejad, Piotr Klimczyk, Maksim Antonov ja Irina Hussainova

Tänu kriitiliste toorainete, nagu volfram (W) ja koobalt (Co), ammendumisele on volframkarbiid-koobalti (WC-Co) kõvasulamjäätmete jätkusuutlik taaskasutamine muutunud hädavajalikuks. Uuring käsitleb WC-Co jäätmete taaskasutamise jätkusuutlikku meetodit kuivlõiketöötluseks mõeldud duplekskeraamiliste komposiitide tootmiseks. WC-Co jäätmed purustati mehaaniliselt, sõeluti osakesteks, mille suurus oli väiksem kui 1 mm, leotati H_2SO_4 abil ja jahvatati kuulveskiga peenosakesteks (~1 µm). Pulbri taaskasutamise ja alumiiniumoksiidi sisalduse (WC asendamise) mõju uurimiseks paagutati kaks kompositsiooni, kasutades säde-plasma paagutamist temperatuuridel 1500–1600 °C. Esimeses kompositsioonis oli mõõdukas alumiiniumoksiidi ja ZrO_2 sisaldus koos taaskasutatud või kommertsliku (äsja sünteesitud; kasutamata) WC-ga; teises oli suurem Al_2O_3 sisaldus ja vastavalt madalam WC sisaldus. Mikrostruktuuri analüüs elektronmikroskoopia (SEM) ja energiadispersiivse röntgenspektroskoopia (EDS) abil näitas minimaalseid lisandeid taaskasutatud pulbris ning materjali terviklikkust (väike defektide sisaldus). Tihedust mõõdeti Archimedese meetodil; samuti hinnati mehaanilisi omadusi (kõvadus, Youngi moodul ja tugevus). Tulemused näitasid, et taaskasutatud pulbri komposiitide mehaanilised omadused on võrreldavad äsja sünteesitud pulbritest toodetud komposiitide omadega, minimaalsete halvenemistega. Kirjeldatud taaskasutusmeetod pakub ohutut, keskkonnasõbralikku ja jätkusuutlikku lahendust, vähendades terviseriske ning säilitades kriitilisi materjale kõrgetasemeliste kulumiskindlate masintöötlusrakenduste jaoks.