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Oxidative Dissolution of Cemented Tungsten Carbides in Molten Sodium Carbonate by Addition of Copper(I) Oxide as Oxidizing Agent for Tungsten Recycling

Kouji Yasuda[1] · Kohei Suzuki[2] · Ryotaro Uehata[2] · Rika Hagiwara[2]

Abstract

Due to the monopolized supply of tungsten resource, it is important to efficiently recycle tungsten scrap for use as a secondary resource. The recycling of tungsten from cemented carbide tools by the molten carbonate method was investigated using simulated hard and soft scrap (carbide tool tips and WC powder, respectively). The oxidative dissolution of tungsten was examined in molten Na_2CO_3 under Ar–O_2–CO_2 atmospheres at 1173 K. Based on the immersion potentials of Cu, W, Co, C, and WC–Co, Cu_2O was suggested to work as an oxidizing agent for tungsten dissolution. The oxidative dissolution rate for carbide tool tips with 12.8 mol% Cu_2O addition reached 57 mg h^{-1} for the reaction time of 2.5 h, equivalent to 0.32 mm h^{-1}. The decrease in the dissolution rate after 2.5 h was attributed to the decrease in the Cu(I) ion concentration in the melt and the inhibition of ion diffusion by the deposited metallic Cu. No violent reaction leading to explosion was observed, even for the oxidative dissolution of fine WC powder with a large surface area. Thus, this method provides significant safety improvements compared to the molten nitrate method.

Graphical Abstract
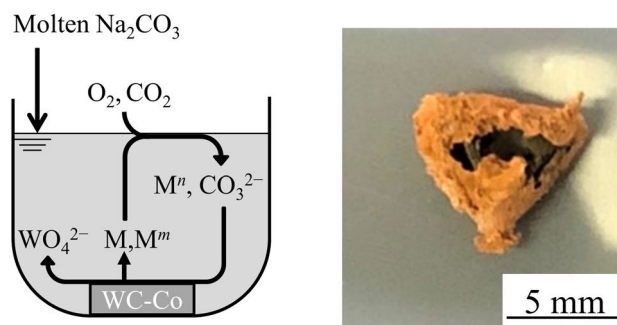
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Introduction

Tungsten is one of the critical metals with high hardness, wear resistance, and thermal resistance. It is widely used in high-speed steel, heat-resistant steel, cemented carbide tools, and processed materials (e.g., plates, wires, and bars) for lighting and electronic components. Cemented carbide tools composed of tungsten carbide (WC) particles and cobalt metal binder are utilized as cutting and abrasive tools in

diverse industrial fields, including automobile, aircraft, and civil engineering. The application for cemented carbide tools accounted for 65% in 2016 of the tungsten consumptions in the world, and 77% in 2019 in Japan [1, 2].

In terms of global supply, China is the major supplier of tungsten resources, with 51% of the world's tungsten reserves and 84% of global tungsten mining production in 2021 [3]. This monopolized situation would lead to unstable supply of tungsten resources in the event of mining accidents as well as financial and political circumstances. Tungsten is designated as a critical metal, at least in some regions including the EU, the U.S., and Japan. To prepare for supply difficulties, it is important to secure resources and achieve secondary use of tungsten scrap. However, the recycling rate of tungsten scrap in Japan was only 9.0% in 2019 [2]. Therefore, it is important to efficiently recycle cemented carbide scrap and use it as a secondary resource. Waste from cemented carbide tools is classified as hard or soft scrap. Hard scrap consists of relatively large pieces of cemented carbide, such as spent drill bits and tips from cutting and abrasive tools. Soft scrap is a fine powder generated during the powder molding process of these tools.

The commercially operated recycling methods for cemented carbide tool scrap are classified into direct and indirect [1, 4, 5]. The direct method gives a separation by either physical or chemical treatment, or a combination of both. One of the typical processes is zinc alloying method, in which WC particles are recovered by crushing cemented carbide scrap after the alloying/dealloying reaction of metallic Zn and Co, which has a difficulty of composition adjustment. Indirect method such as thermal oxidation method and molten nitrate method [6, 7] is appropriate for strict purity control. Various pyrometallurgical and hydrometallurgical processes have been reported as laboratory-level experiments. Typical processes are oxidative roasting and carbothermic reduction at high temperature [8, 9] and acid leaching and electrolysis methods near room temperature [10, 11]. In the thermal oxidation method, cemented carbide scrap is calcined in air at high temperature, then the surface oxide layer is leached in an alkali solution by a treatment known as "peeling." The surface layer formed in a thermal oxidation contains $CoWO_4$ in addition to WO_3 [12], and the oxidation stops for large scraps owing to the whole coverage with $CoWO_4$ layer [6, 7]. Then, the repeated calcination and leaching steps are necessary for large scraps. In the molten nitrate method, cemented carbide scrap is oxidatively dissolved in molten $NaNO_3$ at 973–1173 K using the oxidizing power of nitrate [6, 7, 13, 14]. The resulting Na_2WO_4 is then purified by hydrometallurgical processing. However, the reaction in molten nitrate is strong and fast with vigorous gas evolution, which poses a risk of explosions, especially for the treatment of soft scrap owing to its large specific surface area. Other molten salt methods using electrolysis

in hydroxide [15, 16] and dissolution in mixture of sulfates and hydroxides [17] have also been reported for recycling tungsten materials, which were summarized in [15].

Recently, we proposed a molten carbonate method for recycling tungsten from hard cemented tool scrap [18]. This method involves the oxidative dissolution of cemented carbide scrap in molten Na_2CO_3 under an $Ar–O_2–CO_2$ atmosphere. The resulting Na_2WO_4 is then treated using the same wet processing and hydrogen reduction of WO_3 as in the molten nitrate method. The reaction is easy to control by changing the partial pressures of O_2 and CO_2, which are the parameters for oxidation and basicity, respectively. Importantly, this provides significant safety improvements compared to the molten nitrate method. In our previous study [18], tungsten metal was selected as a model sample for the fundamental study of this process, and the thermodynamics and kinetics of the oxidative dissolution of tungsten metal into molten Na_2CO_3 at 1173 K were investigated. Oxidative dissolution and Na_2WO_4 formation were confirmed in an $Ar–O_2–CO_2$ atmosphere at various partial pressures of CO_2 (pCO_2), and the results verified that oxidative dissolution proceeds via two types of oxidation mechanisms involving O_2^{2-}/O_2^- and CO_3^{2-} ions as oxidizing agents.

In the present study, we propose a revised recycling process of tungsten from cemented tool scrap using metal ions as a mediator for oxidative dissolution. We explore the use of oxidizing agents for tungsten dissolution with reference to the principles of oxidizing agents used in aqueous solutions. Table 1 compares the characteristics of various oxidizing agents in molten Na_2CO_3 with those in aqueous solutions. In aqueous solutions, physically-dissolved oxygen gas is one of the typical oxidizing agents such as for metal corrosion. While chemically-dissolved and physically-dissolved species have different dissolution forms, the O_2^{2-}/O_2^- ions in molten Na_2CO_3 belong to this category because they are oxygen species chemically-dissolved by reaction with O^{2-} ions. In addition, H^+ ions, which are the constituent ions of the electrolyte in aqueous solution, also serve as oxidizing agents such as in the dissolution of the Al and Zn metals in acids. The CO_3^{2-} ions in molten Na_2CO_3 are oxidizing agents in this classification. However, these oxidizing agents lack either oxidizing power or solubility as indicated in the table. Therefore, metal oxides (MO_x) were considered as candidates of oxidizing agents with improved oxidizing power and solubility, with reference to the use of oxidizing agents such as $KMnO_4$ in aqueous solution systems. In this method, the oxidation power and solubility can be controlled by changing the metal oxide and gas atmosphere.

The flowchart of the proposed process is shown in Fig. 1a, and the principles are schematically shown in Fig. 1 (b). Hard tool scraps are added into molten Na_2CO_3 with an addition of MO_x as oxidizing agents. The added MO_x is dissolved in molten carbonate to form M^n ions (Reactions (1) and (2)).

Table 1 Characteristics of various oxidizing agents in molten Na_2CO_3 and their corresponding oxidizing agents in aqueous solution

Oxidant in molten Na_2CO_3	Half reaction(s)	Oxidizing power	Solubility	Corresponding oxidant in aqueous solution
O_2^{2-}/O_2^{-}	$O_2^{2-} + 2e^- \to 2O^{2-}$ $O_2^- + 3e^- \to 2O^{2-}$	High[a]	Low[c]	Dissolved oxygen
CO_3^{2-}	$CO_3^{2-} + 2e^- \to CO_2^{2-} + O^{2-}$	Low[b]	High[d]	H^+
Bubbled O_2 gas	$O_2 + 4e^- \to 2O^{2-}$	High[a]	Mixed reaction of direct contact and dissolved ion	Bubbled gas (e.g., Cl_2, O_2)
MO_x	$M^{n+} + ne^- \to M$ $M^{n+} + me^- \to M^{n-m}$	M-dependent	M-dependent	Additive (e.g., $KMnO_4$)

[a]0 V vs. O_2/O^{2-}, [b]-1.31 V vs. O_2/O^{2-} for 1 atm-CO/CO_3^{2-} at 600 ppm-CO_2 [18], [c]the order of 10^{-7} mol cm^{-3} [19], [d]1.84×10^{-2} mol cm^{-3}
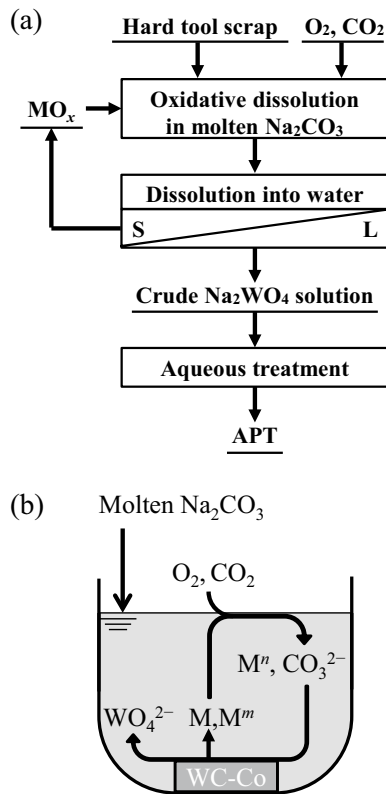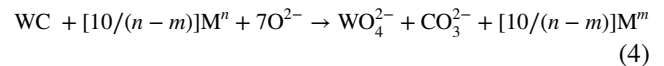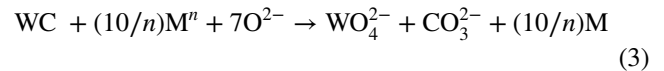

Fig. 1 **a** Flowchart of molten carbonate method for recycling of tungsten and **b** schematic drawing of the reaction scheme of oxidative dissolution of hard tool scrap by utilizing metal ions as a reaction mediator proposed in this study. The produced M metal and M^m ions are oxidized to M^n ions by O_2 gas injection to be recycled and utilized

Here, M^n denotes ions of metal M with oxidation state n, that is, cation M^{n+} or complex oxoanion $M_aO_b^{(2b-an)-}$.

$$MO_x \to M^{n+} + xO^{2-} \tag{1}$$

$$aMO_x + (b - ax)O^{2-} \to M_aO_b^{(2b-an)-} \tag{2}$$
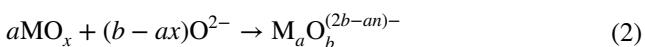
The dissolved M^n ions function as an oxidizing agent by their reduction to M metal or M^m ions (where $n > m$) with a lower oxidation state. Tungsten in the carbide tool is therefore oxidized and dissolved in the melt as WO_4^{2-} ions. Carbon in the carbide tool can be also oxidized and dissolved depending on the oxidizing power of the agent.

$$WC + (10/n)M^n + 7O^{2-} \to WO_4^{2-} + CO_3^{2-} + (10/n)M \tag{3}$$

$$WC + [10/(n-m)]M^n + 7O^{2-} \to WO_4^{2-} + CO_3^{2-} + [10/(n-m)]M^m \tag{4}$$

The formed M metal and M^m ions are oxidized by oxygen gas to be recycled into M^n ions.

$$(10/n)M + 5/2O_2 \to (10/n)M^n + 5O^{2-} \tag{5}$$

$$[10/(n-m)]M^m + 5/2O_2 \to [10/(n-m)]M^n + 5O^{2-} \tag{6}$$
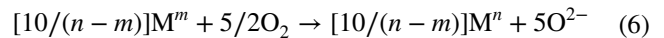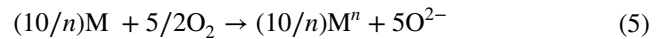
Here, the concentration of O^{2-} ions can be adjusted based on the partial pressure of CO_2 in the system in equilibrium with CO_3^{2-} ions.

$$CO_3^{2-} = CO_2 + O^{2-} \tag{7}$$

Thus, a constant O^{2-} concentration can be maintained, regardless of the formation or consumption of O^{2-} ions during the reaction. In total, M^n ions are not consumed and work as a mediator of the oxidative dissolution since oxygen gas is the oxidizing agent. The obtained salt is dissolved into water to recover the tungsten component as ammonium paratungstate (APT, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$).

In this study, we selected Cu_2O as an example of oxidizing agent and experimentally verified the concept of the function of an oxidizing agent for the oxidative dissolution of simulated scrap (WC–Co cemented carbide tips and WC powder) using the molten carbonate method at 1173 K. Previously, Na_2CO_3 slag has been widely investigated for copper smelting to eliminate impurities in crude copper [20–26]. However, to the best of our knowledge, there are no reports on the utilization of Cu_2O as an oxidizing agent in molten Na_2CO_3. Therefore, the first contribution of this study is to present the potential of Cu_2O as an oxidizing

agent in molten Na_2CO_3. High oxidizing power and high solubility in molten carbonate are both necessary for Cu_2O to function as an oxidizing agent. We investigated the oxidizing power based on the immersion potential of Cu metal and discussed its solubility based on literature. The second contribution of this study is to demonstrate the feasibility of the oxidative dissolution of tungsten using Cu_2O as an oxidizing agent based on experiments with simulated hard and soft scrap (cemented carbide tips and WC powder, respectively). Finally, the rate and characteristics of the reaction system are evaluated.

Materials and Methods

Measurement of Immersion Potential in Na_2CO_3 Molten Salt

Na_2CO_3 (Fujifilm Wako Pure Chemical Corp., 99.8%, 300 g) was placed in an alumina crucible (As One Corp., > 99%, outer diameter: 90 mm, inner diameter: 80 mm, height: 140 mm) and dried under vacuum at 453 K for more than 12 h to remove moisture. The crucible was placed at the bottom of a quartz vessel in an airtight quartz container and heated in a vertical furnace. The flow rate of the mixed $Ar–O_2–CO_2$ gas was controlled using a mass flow controller (Horiba STEC Co. Ltd., SEC-E40 or PE-D20). The flow rate was fixed to 50 mL min^{-1} as sccm (standard cubic centimeter per minute) and the partial pressure was controlled by each flow rate; a CO_2 partial pressure of 6×10^{-4} atm (60 Pa) was attained at a flow rate of 0.03 mL min^{-1}. The measurements were conducted in an $Ar–O_2–CO_2$ atmosphere (pO_2: 0.2 atm (2×10^4 Pa), pCO_2: 6×10^{-4} atm) at 1173 K by a three-electrode method using an electrochemical measurement system (Hokuto Denko Corp., HZ-7000). The working electrodes were W plate (Nilaco Corp., $4 \times 5 \times 0.1$ mm, 99.95%), Co plate (Nilaco Corp., $4 \times 5 \times 0.1$ mm, 99.95%), C plate (Nilaco Corp., $4 \times 5 \times 2$ mm, 99.5%), WC–Co tip (Big Daishowa Seiki Co., Ltd., TPGD070202FN), and Cu plate (Nilaco Corp., $4 \times 5 \times 0.1$ mm, 99.6%). Au wire (Japan Metal Service, Ltd., 99.99%, diameter: 0.5 mm) was immersed in the molten Na_2CO_3 as a quasi-reference electrode (QRE). Because the atmosphere and molten salt contain O_2 gas and O^{2-} ions, respectively, the potential of the QRE corresponds to the O_2/O^{2-} equilibrium at a given O_2 partial pressure, and the activity of O^{2-} ions determined by the CO_2 partial pressure [18].

Oxidative Dissolution in $Na_2CO_3–Cu_2O$ Molten Salt

Figure 2 illustrates the experimental setup used for oxidative dissolution experiments. An outline of the experimental setup is described elsewhere [18]. Powdered Na_2CO_3
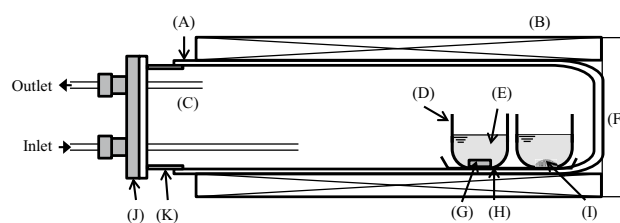

Fig. 2 Schematic of oxidative dissolution experiment of carbide tool tip and WC powder at 1173 K with the addition of metal oxide. (A) Alumina reaction tube, (B) electric furnace, (C) alumina tube, (D) alumina crucible, (E) molten Na_2CO_3 with/without addition of Cu_2O, (F) heat insulator, (G) carbide tool tip, (H) Au plate, (I) WC powder, (J) stainless-steel lid, and (K) stainless-steel flange

(3.07 g) and Cu_2O (0.265 g or 0.529 g, Fujifilm Wako Pure Chemical Corp., 99.5%) were placed in an alumina crucible (Nikkato Corp., SSA-S, C1, volume: 30 cm^3, height: 24 mm) and dried overnight under vacuum at 453 K. The Na_2CO_3 powder was weighed such that the depth of the molten salt was 6 mm. The as-purchased WC–Co tip (Big Daishowa Seiki Co., Ltd., TPGD070202FN, 480 mg, thickness: 2.5 mm) or WC powder (0.100 g, Kojundo Chemical Laboratory Co., Ltd., 99%, average particle diameter: 150 μm) was embedded into the crucible containing the powdered Na_2CO_3 and Cu_2O. The composition of the tip, as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Hitachi Ltd., SPECTRO BLUE), was 88.5 wt% W–5.0 wt% Co. Others are carbon and minor additives. The temperature of the alumina reaction tube was raised from 293 to 1173 K at a rate of 5 K min^{-1} and maintained for a reaction time of 0–25 h. This is sufficiently above the melting temperature of Na_2CO_3 (1131 K). The 0 h experiment was conducted by raising the temperature to 1173 K and then immediately lowering the temperature at a rate of 5 K min^{-1}. The flow rate was fixed at 50 mL min^{-1}, and the partial pressure of CO_2 was 6×10^{-4} or 0.8 atm (60 or 8×10^4 Pa). The recovered tip was analyzed using X-ray diffraction (XRD, Rigaku Corp., MiniFlex, Cu Kα line, 30 kV, 10 mA). The recovered salts were crushed in a mortar and dissolved in deionized water using a sodium tartrate chelating agent to avoid the precipitation of WO_3 in acidic solution. After filtration, the solution was adjusted to pH = 1 using HNO_3 solution. The amount of tungsten dissolved in the molten carbonate was determined using ICP-AES.

Results and Discussion

Potential of Cu_2O as an Oxidizing Agent

The oxidizing power of Cu(I) ions was estimated from the immersion potential. In the same way that the immersion potential in an aqueous solution correlates with the

ionization tendency, the immersion potential of a metal in molten Na_2CO_3 corresponds to the M^n/M potential. Therefore, to proceed with the dissolution of W by using MO_x as an oxidizing agent for WC–Co tips according to Reactions (3) and (4), the immersion potential of metal M should be more positive than that of W. The immersion potentials of Cu (as the metallic component of the additive); W, Co, and C (as components of the cemented carbide tip); and the WC–Co tip itself were measured in molten Na_2CO_3 in Ar–O_2–CO_2 (pO_2: 0.2 atm, pCO_2: 6×10^{-4} atm) at 1173 K. The measured immersion potentials are listed in Table 2. While the immersion potentials for the components of the cemented carbide tip and the tip itself were in the range of -0.6 to -1.0 V vs. Au QRE, the value for Cu was -0.39 V. The fact that Cu has a more positive immersion potential than W and WC in molten Na_2CO_3 at 1173 K suggests Cu_2O will function as an oxidizing agent. The details of the electrochemical behavior of Cu, such as cyclic voltammetry, will be reported in a separate paper.

Several researchers have studied the refining of crude copper in molten Na_2CO_3-based slag in different atmospheres. Takeda et al. [23] confirmed the phase separation of Cu_2O–Na_2O slag (> 50 wt% Cu) and molten Na_2CO_3 with low solubility of Cu_2O (< 1 wt% Cu) in the presence of molten Cu metal at 1523 K in an Ar atmosphere. Kojo et al. [21] and Fukuyama [27] reported that the solubility of Cu_2O in molten Na_2CO_3 coexisting with molten Cu in a CO_2 atmosphere was dependent on the oxygen partial pressure. Thus, Cu_2O has low solubility in molten Na_2CO_3 in both CO_2 and Ar atmospheres, with representative values of 1 wt% solubility of Cu at $pCO_2 = 0.01$ MPa and $pO_2 = 0.1$ Pa at 1523 K. Claes et al. [28] investigated the solubility of Cu_2O in molten Na_2CO_3–K_2CO_3 at a lower temperature (1073 K) in a pure CO_2 atmosphere, and found a value of > 10.5 g L^{-1}. According to these reports except for the study by Claes et al., the solubility of Cu_2O in molten Na_2CO_3 is expected to be smaller than 1 wt% at 1173 K. When a larger amount of Cu_2O is added, Cu_2O–Na_2O liquid phase is expected to

form via release of CO_2 gas in addition to the Na_2CO_3–Cu_2O sat. (< 1 wt% Cu) phase (reaction (8)).

$$Na_2CO_3 + Cu_2O \rightarrow Na_2CO_3 - Cu_2O \ \text{sat.} + Cu_2O\text{-}Na_2O + CO_2 \tag{8}$$
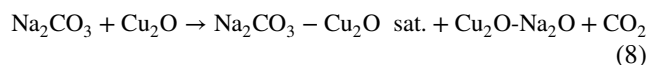
At 1173 K, the Cu_2O–Na_2O system exists as a liquid phase, with a eutectic point at 1076 K and 72 wt% Cu_2O [29]. The Cu_2O–Na_2O liquid phase is expected to have greater density than Na_2CO_3–Cu_2O, because solid Cu_2O and solid Na_2CO_3 (the main components of the respective systems) have densities of 6.0 and 2.53 g cm^{-3}, respectively, at 298 K. Therefore, the bottom side of the melt would possess high Cu_2O solubility as Cu_2O–Na_2O phase.

Oxidative Dissolution of WC–Co Tips in Na_2CO_3–Cu_2O Molten Salt

The dissolution experiments of WC–Co tip were conducted by a reaction with 6.4 mol% of Cu_2O (12.8 mol% $CuO_{0.5}$) with respect to Na_2CO_3 at 1173 K for 25 h under a CO_2 partial pressure of 6×10^{-4} or 0.8 atm (denoted as low and high pCO_2 conditions, respectively). Figure 3a–c show photographs of the tips before and after the reaction. Red-brown deposits adhered to the surface of the remaining tips under each condition. Under low pCO_2 conditions (Fig. 3b), the deposits were firmly adhered to the tip. In contrast, a brittle black layer existed between the tip and deposit under high pCO_2 conditions (Fig. 3c). Moreover, the tip and deposit peeled apart easily off, as shown in Fig. 3d. The peeled black layer was analyzed by XRD (Fig. 3e). The XRD peaks were attributed to metallic Cu and Co, which confirmed the precipitation of Cu on the tip surface and the presence of residual Co from the carbide tip. In addition, sharp and broad peaks attributed to graphite and amorphous carbon, respectively, are not observed. The cross-section of the tip after the reaction under high or low pCO_2 conditions is shown schematically in Fig. 3f.

Figure 4 compares the dissolved weight of W in molten Na_2CO_3 with and without 6.4 mol% Cu_2O, as determined by ICP-AES. At each CO_2 partial pressure, the dissolution amount drastically increased with the addition of Cu_2O. In conjunction with the XRD results, it was confirmed that dissolved Cu(I) ions acted as oxidizing agents for W and C with Cu precipitation, which is reasonable from the immersion potentials listed in Table 2. The reason for the lack of dissolution of the Co residue, despite its more negative immersion potential than Cu, is expected to the stable oxide layer in his melt.

$$WC + 10Cu(I) + 7O^{2-} \rightarrow WO_4^{2-} + CO_3^{2-} + 10Cu \tag{9}$$

Comparing the results of the reactions with added Cu_2O, the dissolution rate was higher under high pCO_2 conditions.

Table 2 Immersion potential of different electrodes in molten Na_2CO_3 in Ar–O_2–CO_2 atmosphere (pO_2: 0.2 atm, pCO_2: 6×10^{-4} atm) at 1173 K

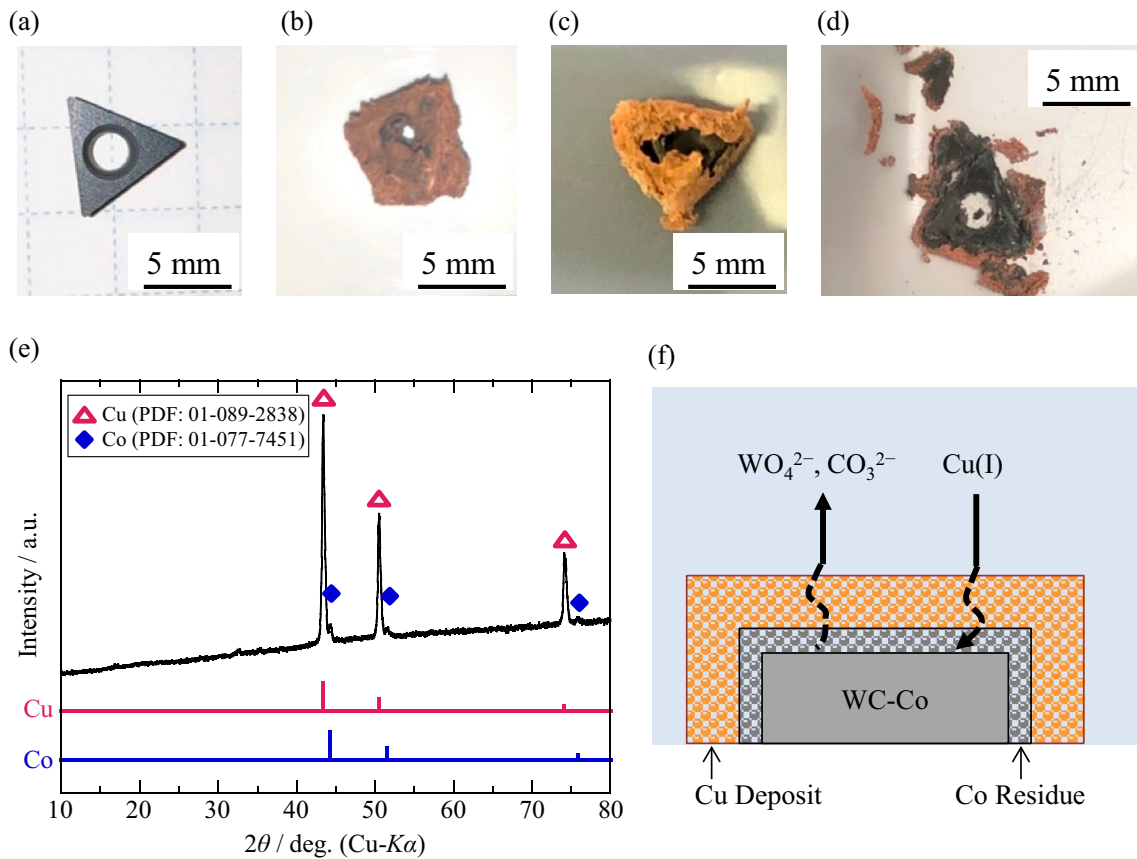| Classification	Electrode	Immersion potential vs. Au QRE (V)
Component of carbide tool tip	W	-0.94
	Co	-0.60
	C	-0.90
	WC–Co	-1.09
Metal component of candidate oxidizing agent	Cu	-0.39

Fig. 3 Photographs of **a** as-received carbide tool tip and **b, c** after the reaction in molten Na_2CO_3 at 1173 K for 25 h with the addition of 6.4 mol% Cu_2O in **b** Ar–CO_2 (pCO_2: 6.0×10^{-4} atm) and **c** Ar–CO_2 (pCO_2: 0.8 atm) atmospheres. **d** Photograph of the carbide tool tip after removing deposit shown in (**c**). **e** XRD pattern of the deposit on the carbide tool tip shown in (**d**). **f** Schematic of the cross-section of the tip in (**b**) and (**c**) after the reaction
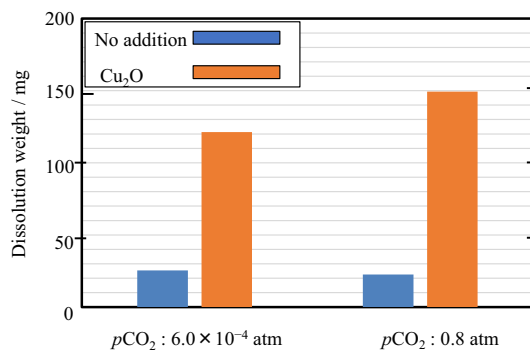
Fig. 4 Dissolution weight of W from carbide tool tip in the condition with and without 6.4 mol% Cu_2O at each CO_2 partial pressure

This was ascribed to the higher solubility of Cu_2O in molten Na_2CO_3 at higher pCO_2 [21, 27].

Since all the Cu(I) ions were likely to be consumed before the end of the 25 h reaction time, oxidative dissolution experiments were conducted with shorter reaction time to investigate the rate of oxidative dissolution.

In these experiments, the amount of Cu_2O was doubled to 12.8 mol% (25.6 mol% $CuO_{0.5}$), and the pCO_2 partial pressure was fixed at 6.0×10^{-4} atm. The amount of W that dissolved in the absence of Cu_2O was also measured for comparison. Figure 5 shows the amount of dissolved W with respect to the reaction time. The arrow indicates the equivalent amount of W dissolution for 12.8 mol% Cu_2O according to Reaction (9). The plot for the reaction with 12.8 mol% of Cu_2O shows that the reaction is mostly complete after 2.5 h, after which the extent of reaction increases gradually toward the equivalent value. The reaction rate after 2.5 h was 57 mg h^{-1}. Since the rate of weight loss is affected by the shape of the carbide tool, the reaction rate was evaluated as a one-dimensional value under a simplified assumption. From the initial thickness of 2.5 mm, initial weight of 480 mg, and W ratio of 88.5 wt% contained in the tip, this rate is equivalent to 0.32 mm h^{-1} under the assumption that the dissolution reaction only proceeded from the upper surface of the tip with a reaction area of 0.55 cm^2, as shown in the photographs in Fig. 3.
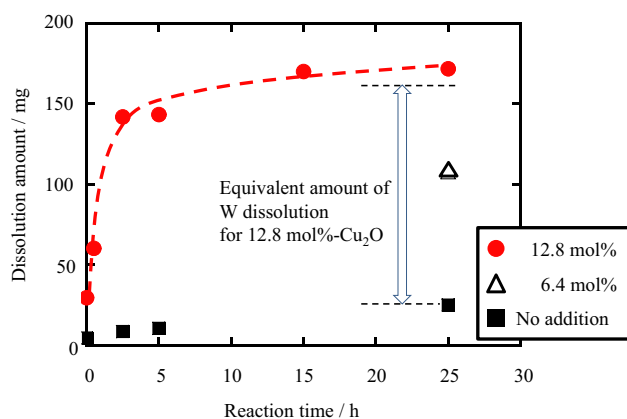
Fig. 5 Dependence of dissolution thickness of carbide tool tip on reaction time in molten Na_2CO_3 at 1173 K in Ar–CO_2 (pCO_2: 6.0×10^{-4} atm) atmosphere with and without the addition of Cu_2O

Three factors contribute to the decrease in reaction rate after 2.5 h: (1) the decrease in the driving force of the oxidation reaction owing to the decrease in the Cu(I) ion concentration, resulting in a shift of the Cu(I)/Cu equilibrium potential to a negative value; (2) the decrease in diffusion rate of Cu(I) ions with decreasing Cu(I) ion concentration; and (3) the inhibition of ion diffusion by the Cu deposited on the tip surface, as shown in Fig. 3f. Based on the above discussion, faster reactions are expected by adding Cu_2O during the reaction (against factors (1) and (2)) and by stripping and removing deposited Cu (against factor (3)). It would also be effective to construct a M^n/M^m reaction system for the oxidizing agent, whereby the reduction products are not metal but ions with a lower oxidation state; this would prevent metal from depositing on the tip surface (factor (3)). The recycle of Cu(I) ion by O_2 gas injection to the melt and product is a future effective challenge.

$$4Cu + O_2 \rightarrow 4Cu(I) + 2O^{2-} \qquad (10)$$
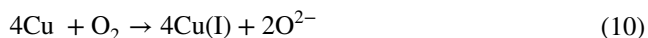
Oxidative Dissolution of WC Powder in Na_2CO_3–Cu_2O Molten Salt

Oxidative dissolution experiments were also conducted using WC powder to elucidate the applicability of the molten carbonate method with Cu_2O oxidant for recycling soft scrap. The dissolution of 76.5 mg of W from a 100 mg WC sample was confirmed through the reaction in molten Na_2CO_3 at 1173 K for 2.5 h with the addition of 12.8 mol% Cu_2O in an Ar–CO_2 (pCO_2: 6.0×10^{-4} atm) atmosphere. Notably, no salt splash was observed in the crucible after the reaction (see Fig. 6). Therefore, safe and efficient processing is expected not only for hard scrap but also for soft scrap. This is particularly valuable given the risk of explosions in
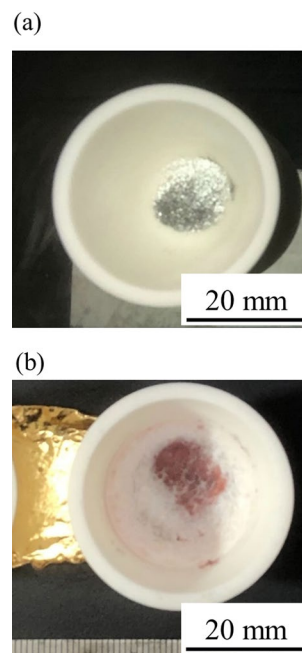

Fig. 6 Photographs of WC powder (**a**) before and (**b**) after the reaction in molten Na_2CO_3 at 1173 K for 2.5 h with the addition of 12.8 mol% Cu_2O in Ar–CO_2 (pCO_2: 6.0×10^{-4} atm) atmosphere

the molten nitrate method owing to vigorous NO_x gas evolution for samples with a high specific surface area, such as soft scrap.

Conclusions

This study investigated and experimentally verified the oxidative dissolution of cemented carbide tips and WC powder as simulated scraps by utilizing metal ions as a reaction mediator in molten Na_2CO_3 in an Ar–CO_2 atmosphere at 1173 K. A significantly higher reaction rate was achieved compared to that in a previous study by adding Cu_2O as an oxidizing agent to oxidize W component. Cu metal has a more positive immersion potential than W metal and WC–Co tips, providing it with high oxidizing power. During the reaction, Cu metal was deposited and W was oxidatively dissolved from the carbide tips, whereas Co metal remained as a residue. A high oxidative dissolution rate of 57 mg h^{-1} or 0.32 mm h^{-1} was achieved. The removal of deposits and establishment of a reaction system in which the reduction products become ions are desirable to improve the reaction rate. W was also oxidatively dissolved from WC powder with the Cu_2O oxidizing agent. Recycle of Cu into Cu(I) ions by O_2 gas injection and dissolution reaction at different CO_2 partial pressure need to be investigated. In addition, although Cu_2O was selected as the oxidizing agent to demonstrate the concept, its low solubility is undesirable. Exploration of

better oxidizing agent with both of high solubility and oxidizing power and effective redox M^n/M^m ion pair are future challenges to establish the proposed process.

Author Contributions KY: Conceptualization, methodology, writing—original draft, supervision, project administration, funding acquisition. KS: Validation, investigation, writing—review and editing. RU: Validation, investigation, writing—review and editing. RH: Writing—review and editing, supervision.

Declarations Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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