The Effect of Underwater Explosion on the Kinetics of Alkaline Leaching of Roasted Tungsten Carbide Scraps for Recycling

Seung Woo Baik*, Atsushi Shibayama**, Kenji Murata*** and Toyohisa Fujita****

*Researcher of Satellite Venture Business Laboratory, Akita University, 1‐1
Tegata Gakuen, Akita, 010‐8502, Japan
***Department of Material-process Engineering & Applied Chemistry for Environment,
Faculty of Engineering and Resource Science, Akita University
***NOF Corporation, Japan
****RACE, Department of Geosystem Engineering, Graduate School of Engineering,
The University of Tokyo, Japan

E-mail : swbaik@ms.svbl.akita-u.ac.jp, sibayama@ipc.akita-u.ac.jp

Wasted tungsten scraps are important resources for recycling, however, the mechanical recycle process of tungsten has a difficulty for recycling due to its mechanical strength. Underwater explosion fracturing technique was designed for solving this problem. The kinetics for alkaline leaching of roasted tungsten alloy scraps with different size distribution prepared by two ways of crushing technique has been investigated to evaluate the effect of the underwater explosion-crushing. The merit of this technique for fracturing of waste tungsten alloy scraps can be understood by estimating of those leaching tendencies. The present work aims at the evaluation of the explosion-crushing method for efficiency of alkaline leaching from a kinetic point of view. Alkaline leaching was carried out with 10% NaOH solution in the range of 293-353K at various times. The leaching of roasted tungsten carbide scraps by NaOH was strongly dependent on temperature and leaching time, and underwater explosion accelerated the leaching ratio. The leaching mechanism was turned out to reaction controlled, and activation energy of alkaline leaching was 60-64kJ/mol.

Key Words : Tungsten Carbide Scraps, Underwater Explosion, Kinetics, Alkaline Leaching, Recycling

1. Introduction

Nowadays, the demand of valuable metal is increasing rapidly but storage of natural resources has decreased year by year. Therefore, recycling is an important factor in the world's valuable metal supply and also environmental concerns have led to a higher recycling rate. The most widely used transition metal carbide is tungsten carbide, hexagonal WC, which is employed as the hard constituent in WC-Co hard metals, which are used mainly for cutting tool bits and industrial devices. Tungsten carbide comes in many shapes and sizes from drills and end mills, to inserts, dies, and seal rings[1]. It is estimated that today some 30% is recycled. The metal tungsten is generally obtained from low grade mineral ores ($<$ 1 mass% WO_3) or concentrates ($<$ 7-60% of W), such as scheelite and wolframite, under alkaline and acidic conditions involving hydrometallurgical processes. On the other hand, the grade of the waste tungsten-bearing scrap is in the range of 40-95%. High grade of waste tungsten scraps is a first need for recycling. The second reason is a cost. The costs of WC production from primary tungsten-bearing ore are 4 times higher than those of tungsten carbide recycled from scrap, according to international estimates.

Though tungsten-bearing scrap has some valuable merits for recycling, the practical recovery process has a difficulty in crushing into adequate size of pieces which can be roasted thoroughly, because of those of mechanical properties, i.e. high hardness ($>$ 20000N/mm^{-2}), fracture toughness and high tensile strength(0.34GPa)[1]. A conventional recycling process of tungsten scraps is shown in Figure 1. At first, tungsten scraps is roasted in air atmosphere and processed scrap undergoes crushing
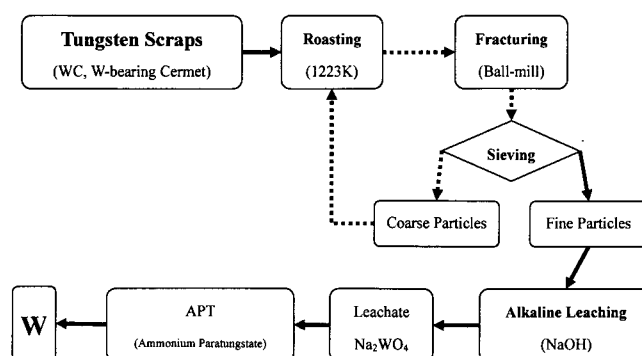

Figure 1　Conventional recycling process of tungsten waste scraps.

by ball mill and sieving to adjust particle size of scrap for favorable condition of chemical leaching. Fine particle moves on the succeeding chemical process, otherwise coarse particles turn back to former process. This repetition of process is owing to unavoidable mechanical property of tungsten carbide. Mechanical destruction of hard alloy ware is a laborious task. At present, it is performed with the help of conventional ball mills, which requires tens or even hundreds hours of milling. Using steel equipment for that purpose results in contamination of the processed material with iron up to 10%, whereas iron content should not exceed 0.1%. Therefore, expensive equipment made from WC alloy is used, and it becomes worn out in a few hundred hours of milling and after that must be replaced.

Accordingly, a new technique has been developed for promoting the intended effect on the adjusting their size and size distribution in the NOF Corporation in Japan, which performs explosives & propulsion business. This technique is underwater explosion crushing which is a technique of being exploded of scraps with some explosives under water in a water-tank. It is not clear, however, what is occurred except crushing, but at least, it would be expected that a lot of defects are produced during severe condition as like explosion, which will enhance oxidation of scrap in subsequent roasting process.

In view of these considerations, the aim of the present work is at the comparison of leaching rates of tungsten alloy scrap prepared by different crushing method, and also a better understanding of the leaching kinetics.

2. Experimental

Three kinds of roasted tungsten alloy scraps with different particle size distribution were provided by Japan New Metal Co and NOF Corporation. These were prepared by explosion technique and by conventional fracturing method, followed by roasting at 1173K in air. The particle size distribution was examined using sieving test with #6, #10, #20, #32, #100, #150 and #200 standard sieves. Apparent density of sample was measured by pycnometry method with specific gravity glass flask for several times and mean value of density was calculated. The tungsten grade of raw sample was examined from solutions prepared from aqua regia leaching and cinchonine precipitation from W solution manufactured by melting with alkaline reagent (Na_2CO_3) and oxidizer (Na_2O_2, H_2O_2) at 1073K. Alkaline
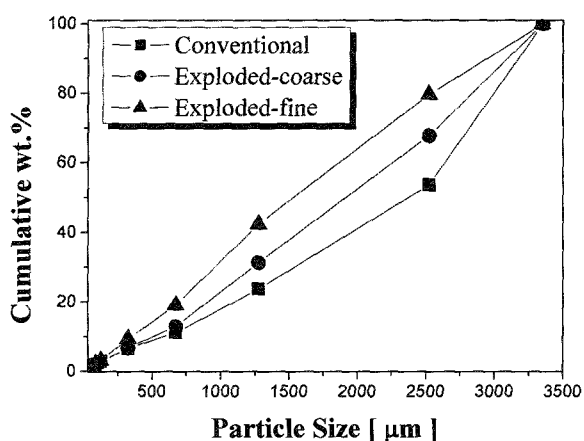
leaching was carried out under the following operating conditions : 10 g of sample, 10% NaOH, ratio of solid to liquid $(S/L) = 5\%$, stirring speed = 200rpm and temperature range 293-353K. All experiments were conducted in a glass flask (0.5L) with a mechanical stirrer in air atmosphere. Chemical analysis of the solution was performed by ICP, SPS3000 (Japan).

3. Results and discussion

The grade of sample by ICP analysis was 76.6% of W in this study. Figure 2 shows the particle size distribution of three kinds of samples. Particle size of exploded-sample is finer than that of conventional one. In the conventional sample, a percentage of oversize 10 mesh (nominal aperture size = 1700μm) was 76 mass%, while two exploded-samples, i.e. exploded-coarse and exploded-fine samples were 69 mass% and 58 mass%, respectively. It is well known that the rate of dissolution of solid in aqueous solution is a function of specific surface area, thus it can be expected that exploded-sample, especially exploded-fine sample, may dissolved much faster than conventional one. As shown in Figure 3, these were well distinguished as amounts of each sample according to particle size distribution. The sample was presented irregular shape, and large particle, in particular, had a cylindrical form which seems to reflect a history-effect of original one.

The effect of leaching time and particle size distribution on the dissolution of tungsten is shown in Figure 4. It is shown that the tungsten extraction increases with leaching time and exploded-sample shows higher rate of extraction than that of conventional sample, which means extraction of W is accelerated by explosion-crushing. It is thought that this tendency stems from small particle size and large surface area by explosion-crushing. At low temperature (293K), in Figure 4(a), the results show a linear behavior, indicating that the process of alkaline leaching is completely reaction-controlled. With increasing leaching temperature, in Figure 4(b, c and d), the leaching rate decreases in the subsequent stage and levels off. Neither of conventional sample nor exploded-fine and coarse sample, however, show maximum W extracted rate stays below 55%. This result seems to be caused by a condition of raw sample, being not clear presently,
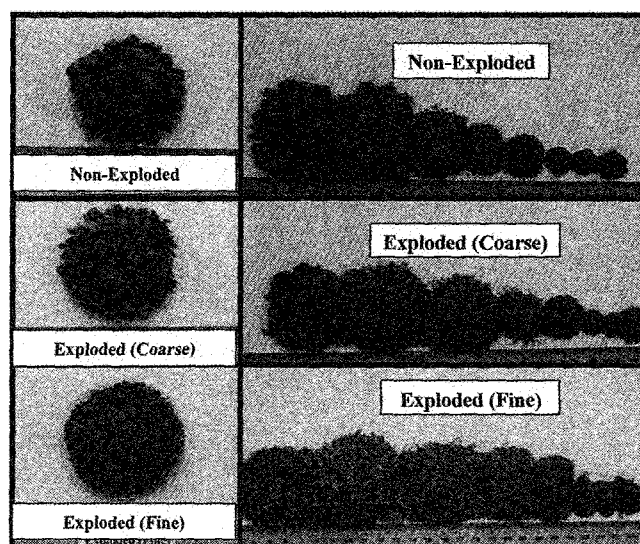

Figure 2   Particle size distributions of three kinds of samples.

Figure 3   The shape and size distribution of three kinds of samples.

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influences on tungsten leaching and two expected factors can be nominated in this case. One is low grade of sample though ICP result shows 76.6% of W, which can be explained that WC is not fully oxidized enough to form state of W^{3+} in the roasting process and remains as mixed-valence oxides or WC as it is. The other is a possibility of inhibition by rapid equilibrium between Na_2WO_4 and NaOH solution from following reaction.

$$WO_3(S) + 2NaOH \ (aq) \rightarrow Na_2WO_4(aq) + H_2O(aq)$$
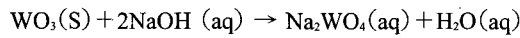
Many researchers reported that shrinking core model could well explain kinetics of alkaline/acidic leaching. Amer[6] assumed first-order dependence on C_{Na} in the reaction of mechanically activated wolframite concentrate with sodium hydroxide and showed reaction mechanism changed to zero-order in high NaOH concentration. Martins[7-8] considered shrinking core model, that is the evolution of the unreacted core with time for first to zero reaction orders, respectively, to the leaching agent and to the scheelite in soda ash leaching of low-grade scheelite. A mixed reaction control model was applied by Conradt[9] and Kuhn[10] to explain the leaching behavior of nuclear waste glasses.

Figure 5 shows the relation of $-\ln \ln(1-\alpha)$ vs $\ln$ t of conventional sample (a) and exploded-sample (b and c), respectively.

Hancock and Sharp[5] suggested that reaction mechanism can be distinguished by different m-values from following relation. The reaction mechanism according to m-value is presented in Table 1.[2-5].

$$-\ln \ln(1-\alpha) = \ln k + m\ln t,$$

where, α = fraction of reaction,
k = rate constant
t = reaction time

They showed that m-value of diffusion-controlled reaction is in the range of 0.5-0.6 and reaction-controlled reaction shows around 1.0 of m-value. According to this relation, tungsten dissolution seems to be controlled by reaction on the surface of tungsten oxide in NaOH solution, i.e., the rate seems to be limited by the concentration of hydroxide adsorbed on the surface. This indicates that reaction between WO_3 and Na^+ holds the key to proceed in the whole reaction and therefore, leaching rate increases with increase in temperature and NaOH %, on the other hand, other factors, such as S/L(solid/liquid ratio) affect insignificantly. Furthermore m-value was increased with increasing leaching temperature from 0.9 to 1.5. This indicates that mechanism of reaction changes from 1_{st} order reaction to 0_{th} order reaction with temperature. This
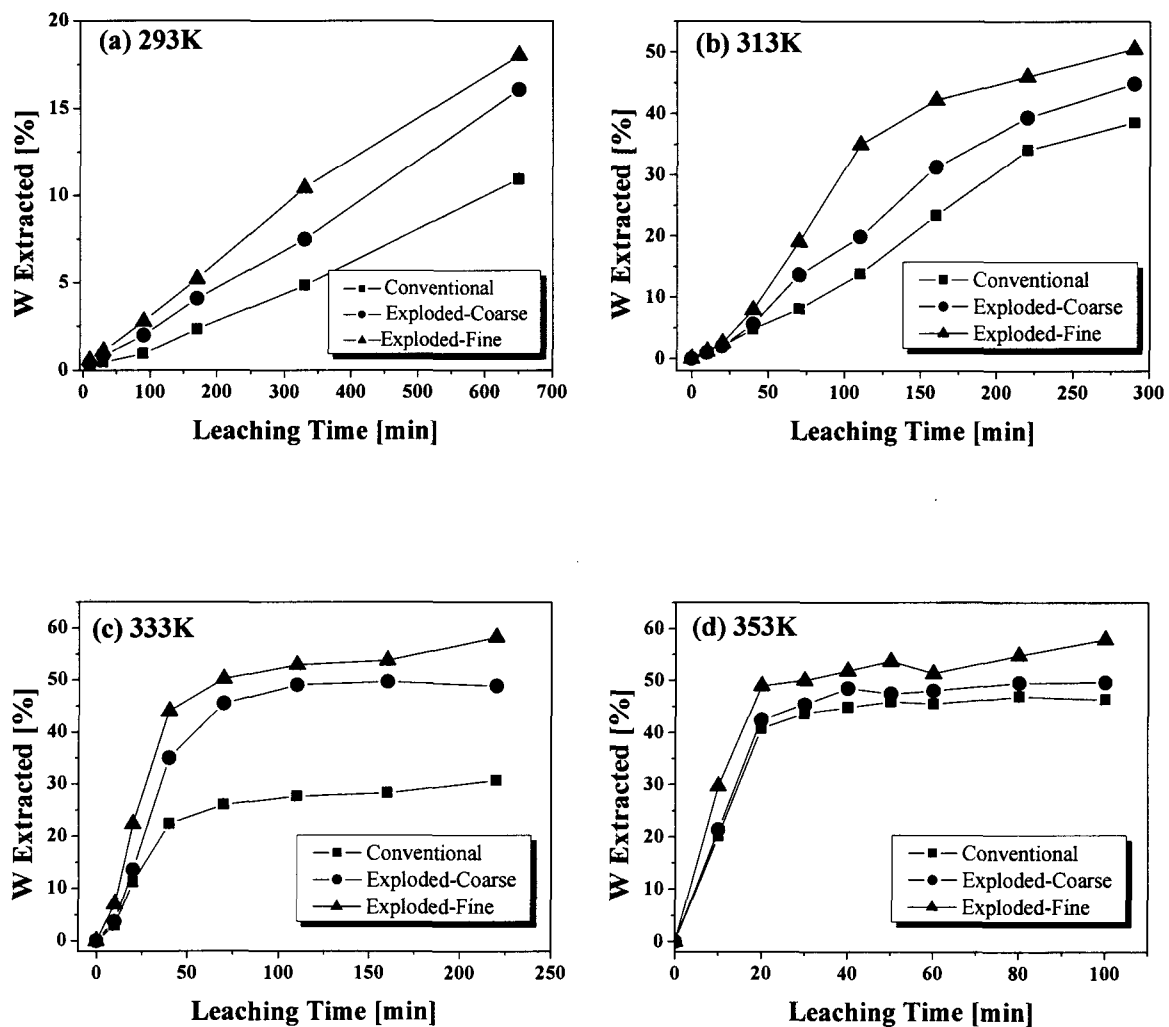

Figure 4   Effect of leaching time on the tungsten dissolution for three samples with different particle size distribution, (a) 293K,
(b) 313K, (c) 333K and (d) 353K, respectively.

reaction order tendency is similar with results of Amer and
Martins by shrinking core model.

In Figure 2 and 3, it is evident that explosion-crushing is
more efficient to fracture wasted scraps, with comparing the
results obtained from sieving test. Considering that the sample is
roasted, it is not possible to oxidized completely in large particles,
because large sample sustains its original shape after roasting
though large volumetric expansion is occurred in transformation
from WC to WO_3. Both samples have over 10 mesh sized particles,
so it is thought that it does not show homogeneous dissolution
but corrosion of oxide ceramics. The corrosion process primarily
consists of a dissolution reaction and diffusion-controlled mass
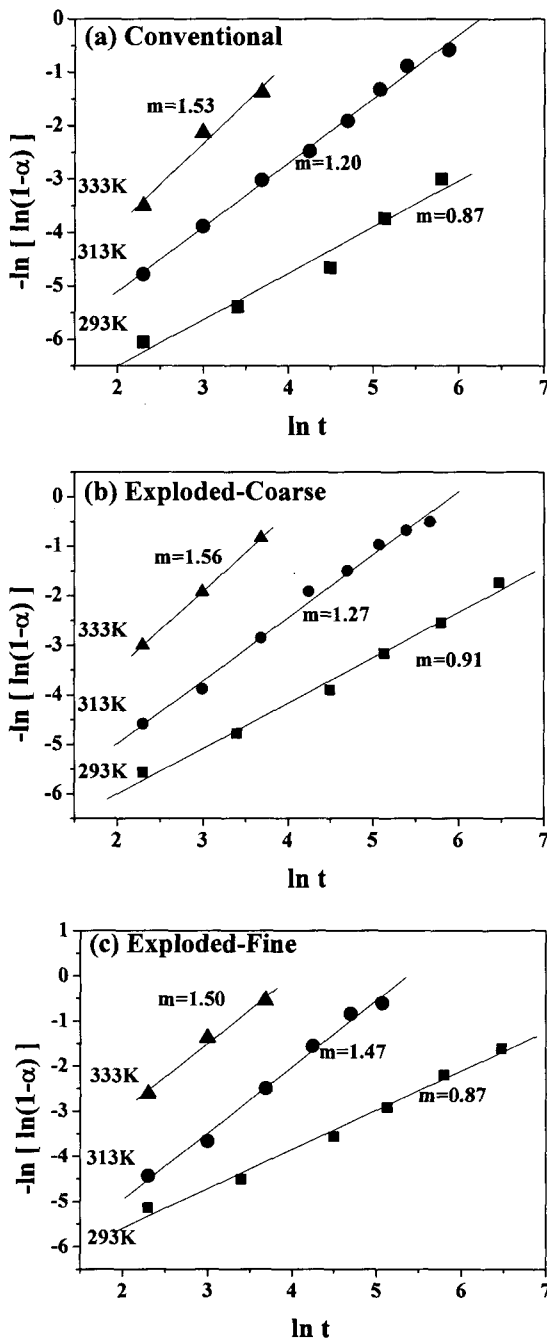transport through the corrosion layer. It is well described in Figure

Table 1   Reaction mechanism according to m-value calculated from $-\ln$
$[\ln(1-\alpha)]$ vs ln t plot

Reaction Mechanism	Kinetic Equation	m
Diffusion(D1)	$\alpha^2 = kt$	0.62
Diffusion(D2)	$(1-\alpha)\ln(1-\alpha)+\alpha =kt$	0.57
Diffusion(D3)	$(1-(1-\alpha)^{1/3})^2=kt$	0.54
Diffusion(D4)	$1-3/2\,\alpha -(1-\alpha)^{2/3}=kt$	0.57
1$_{st}$ order reaction	$\ln(1-\alpha)=kt$	1.00
Interfacial reaction	$-(1-\alpha)^{1/2}=kt$	1.07-1.11
0$_{th}$ order reaction	$\alpha =kt$	1.24
Nucleation and growth	$(-\ln(1-\alpha))^{1/2}=kt$	2.0
	$(-\ln(1-\alpha))^{1/3}=kt$	3.0

Table 2   Apparent density and presumed oxidation ratio

Sample	Non-Oxide	Oxide					Apparent Oxidation Ratio[%]
	Non-oxide [mass %]	Apparent Density[kg/m³]					Total[%] where, WO₃=100%
		+ #10	#10/#32	- #32	Mean density [kg/m³]	oxide	
Conventional	9.05	8.46	7.41	7.15	8.19	82.0	74.58
Ex-Coarse	9.24	7.23	7.20	7.13	7.11	96.7	87.74
Ex-Fine	2.39	7.07	7.12	7.12	7.08	95.7	93.38

4 and 5. This made clear simply by checking the density of
sample. The presumed oxidation ratio from density data is shown
in Table 2. The non-oxide mass % is calculated by pick-up
method with naked eye from soft-crushed powder and apparent
density is calculated from crushed powder of sample. The
apparent oxidation ratio of conventional sample is 74.58%, while
exploded-coarse and exploded-fine sample is 87.7 and 93.4%,
respectively.

The activation energies for the dissolution of the tungsten were
determined from time-dependent results at various temperatures.
The activation energy was calculated from the slope of Arrhenius
plot and are presented in Figure 6. To calculate the kinetic
constant (k) at each temperature the equation α (t) $=kt$ was used.
The kinetic constant was determined by least square fits and R^2
value obtained for linear fitting analysis are usually greater than
0.98. his is a strong indication that dissolution of W in NaOH is
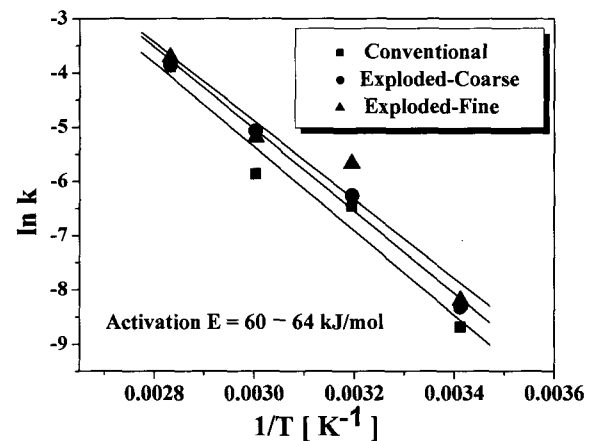reaction-controlled. The kinetic constant k is higher in exploded

Figure 5 $-\ln[\ln(1-\alpha)]$ vs ln t plot for estimation of mechanism of disso-
lution of tungsten in NaOH solution.

Figure 6   Activation energy for the dissolution process of the tungsten
calculated from equation, α (t) $=kt$.

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sample than that of conventional sample. The values of the activation energies range from 60 to 64 kJ/mol. It is difficult, however, to clarify the actual mechanism of tungsten leaching experimentally because of the diversity of the factors influencing dissolving behavior of tungsten. But, It is too unwarrantable to jump to the conclusion that samples are in different oxidation state from oxidation ratio, because powders being regard as oxides, actual samples may contain a few non-oxides. Now, It is also unsure whether oxidation state affects to W leaching in NaOH solution or not. Further researches are necessary on this topic.

4. Conclusions

The kinetics for alkaline leaching of roasted tungsten alloy scraps with different size distribution prepared by two way of crushing methods has been investigated to evaluate of the effect of explosion-crushing. The results obtained in the present study yielded the following conclusions.

The leaching rate of roasted tungsten carbide scraps by NaOH is strongly dependent on temperature. The underwater explosion-crushing sample was leached much faster than the conventional sample. It seems to be concerned with particle size distribution macroscopically and presence of micro-crack and/or different oxidation ratio during roasting process microscopically. It can be concluded that explosion-crushing is more effective in recovery of tungsten by alkaline leaching. In the relation of $-\ln[\ln(1-\alpha)]$ vs $\ln t$, it is reasonable to think that tungsten dissolution seems to be controlled by reaction between Na^+ and WO_3 on the surface of tungsten oxide. The value of the activation energy ranges between 60 and 64 kJ/mol.

Acknowledgments

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