

CHAPTER III

RESEARCH METHODOLOGY

3.1 Preparation of specimens

Raw materials including steel scrap, pig iron, ferroalloys, and high-purity metals were melted in a high-frequency induction furnace lined with alumina. The molten metal was superheated to 1580°C and held for 10 minutes to ensure compositional homogeneity. The melt was then poured into a CO₂-bonded sand mold preheated at 200°C to produce cylindrical castings with dimensions of 25 mm in diameter and 65 mm in height, as shown in Figure 3.1. To obtain the specimens for the abrasive wear test, the same melt was poured into a Y-block mold with a width and height of 50 mm and a length of 200 mm, as shown in Figure 3.2. The chemical compositions of the alloys are presented in Table 3.1. To minimize premature solidification and oxidation, the riser was immediately covered with exothermic powder upon pouring. After solidification, the riser was removed using a wire electrical discharge machine (Wire-EDM).

For alloy design, the carbon balance (C_{bal}) parameters were calculated using the equation shown in Table 3.1 to estimate the equilibrium carbon concentration in the matrix, following the methodology reported in previous studies (Inthidech & Matsubara, 2020; Matsubara et al., 1996). To facilitate optimal matrix transformation during subsequent heat treatment, the C_{bal} value of each specimen was adjusted to 0% (Inthidech & Matsubara, 2020; Matsubara et al., 1996). In the case of specimen No. 4, which contained the highest niobium addition, significant carbide formation substantially reduced the carbon content of the matrix. To compensate, the initial carbon content of this alloy was deliberately set higher than that of the other specimens in order to maintain a target C_{bal} of 0%.

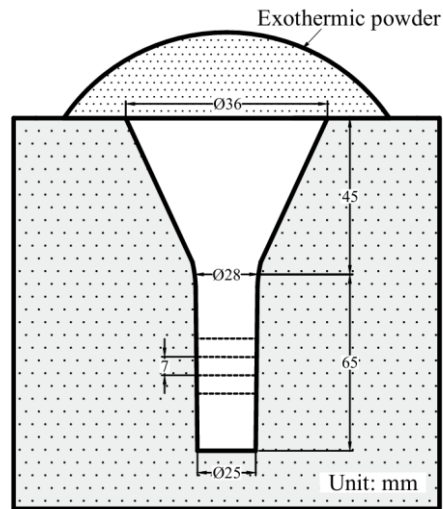


Figure 3.1 Schematic illustration of the CO₂-bonded sand mold prepared for test specimens.

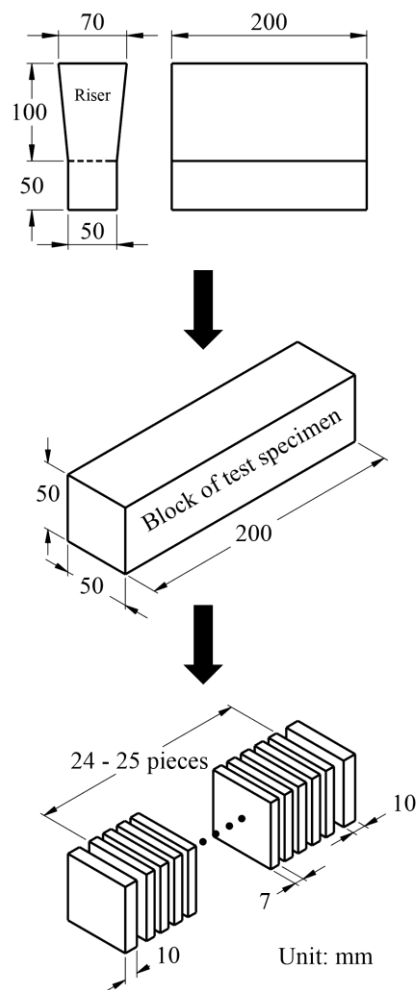


Figure 3.2 Schematic drawings of processes for making abrasive wear specimens from Y-block ingots for wear test.

Table 3.1 Chemical composition and C_{bal} value of test specimens.

Specimen	Elements (wt%)									C_{bal}
	%C	%Si	%Mn	%Cr	%Mo	%W	%V	%Co	%Nb	
No. 1	1.97	0.50	0.50	4.98	5.02	4.98	5.07	1.99	0.00	0.00
No. 2	2.07	0.50	0.50	5.26	4.65	5.13	5.18	1.93	0.70	- 0.02
No. 3	2.00	0.50	0.50	5.37	5.02	5.09	4.38	1.98	1.05	+ 0.03
No. 4	2.39	0.50	0.50	5.96	5.02	4.99	5.45	1.96	2.58	- 0.06

$$\%C_{bal} = \%C - \%C_{stoich} \text{ (Hashimoto et al., 2004b; Laird et al., 2000)}$$

$$\%C_{stoich} = (0.060)\%Cr + (0.063)\%Mo + (0.033)\%W + (0.235)\%V + (0.129)\%Nb$$

3.2 Heat treatment processes

3.2.1 Heat treatment condition to investigate heat treatment behavior

The heat treatment sequence consisted of annealing, austenitizing, hardening, and tempering, as schematically illustrated in Table 3.2 and Figure 3.3. Prior to heat treatment, all specimens were coated with an anti-oxidation solution to minimize surface oxidation. The ingots were first annealed in an electric furnace at 950°C for 5 hours to reduce micro-segregation during solidification and homogenize the microstructure. After annealing, they were sectioned by wire electrical discharge machining (Wire-EDM) into specimens with a thickness of 7 mm.

The specimens were subsequently austenitized in a vacuum furnace at either 1050°C or 1100°C for 60 min. Immediately after austenitizing, they were hardened by liquid nitrogen spray (LNS) quenching to induce martensitic transformation. The as-hardened specimens were then tempered in an electric furnace at temperatures ranging from 400°C to 600°C in 50°C increments. Each tempering treatment was maintained for 200 min, followed by air cooling (AC) to room temperature.

Table 3.2 Heat treatment conditions to investigate heat treatment behavior.

Heat treatment	Annealing	Hardening	Tempering
			400
			450
		1050	500
		1100	525
			550
			600
Holding time (min)	300	60	200
Cooling condition	Furnace cooling (FC)	Liquid N ₂ spray (LNS)	Air cooling (AC)

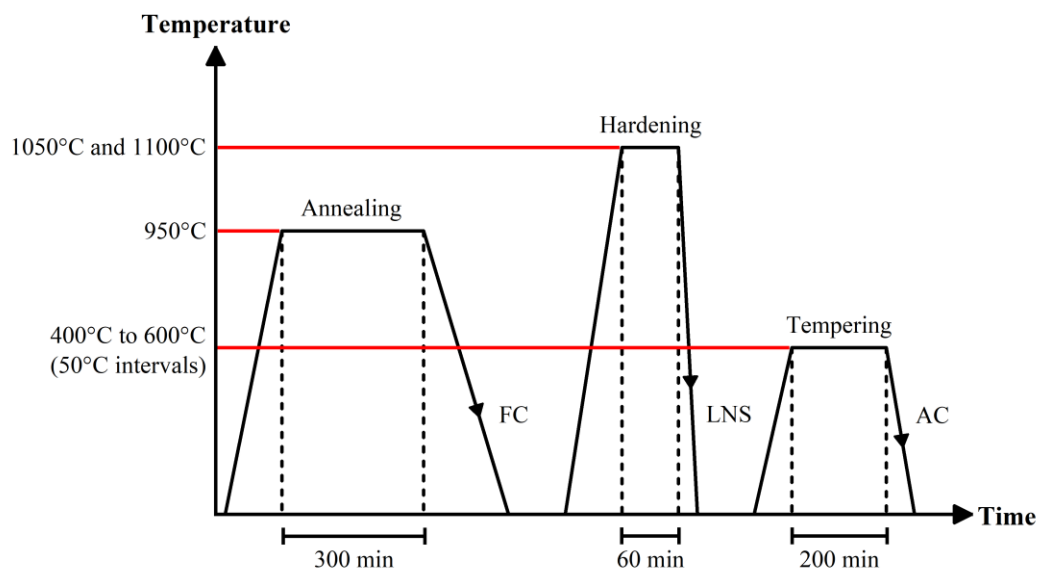


Figure 3.3 Schematic illustration showing the heat treatment processes.

3.2.2 Heat treatment condition of test piece to perform carry out abrasive wear test

The specimens for abrasive wear test are heat-treated under conditions of heat treatment as summarized in Table 3.3. As-hardened specimens (As-H) are tempered at 3 levels between 400 to 600°C. The three temperatures are determined from the tempered hardness curve of each specimen which is made by the previous

section. The selected temperatures are a temperature at which the maximum tempered hardness is obtained ($H_{T_{max}}$), the lower and higher temperature than $H_{T_{max}}$ ($L-H_{T_{max}}$ and $H-H_{T_{max}}$), respectively. The method is schematically illustrated in Figure 3.4. In this method, there are reasonable differences among matrix microstructures of three specimens, especially in the V_γ . It can be understood that under the similar hardness in $L-H_{T_{max}}$ and $H-H_{T_{max}}$ specimens, the V_γ value differs greatly between both specimens. Using these three test specimens of $L-H_{T_{max}}$, $H_{T_{max}}$ and $H-H_{T_{max}}$, the effects of hardness and V_γ on the abrasive wear behaviors are evaluated, and additionally those results will be related to the niobium content of specimens.

Table 3.3 Heat treatment for abrasive wear specimens.

Heat treatment	Annealing	Hardening	Tempering
Temperature (°C)	950	1050 1100	3 levels between 400 and 600°C
Holding time (min)	300	60	200
Cooling condition	Furnace cooling (FC)	Liquid N ₂ spray (LNS)	Air cooling (AC)

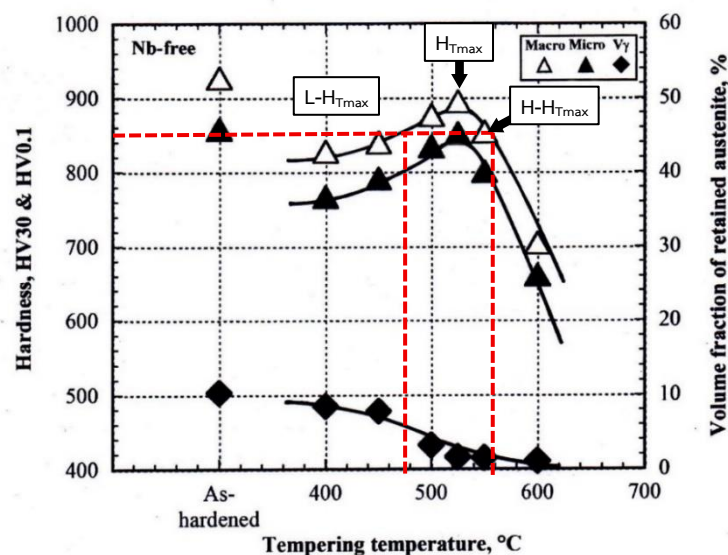


Figure 3.4 Schematic illustration showing how to determine three tempering temperatures from tempered hardness curves.

3.3 Microstructural Examination

Optical microscopy (OM) and scanning electron microscopy (SEM) were employed to characterize the microstructures of the test specimens. Prior to examination, the specimens were ground using silicon carbide (SiC) abrasive papers and subsequently polished with 0.1 μm alumina suspension to obtain a mirror-like surface finish. For microstructural analysis, the polished specimens were etched with Groesbeck's reagent to reveal carbide morphologies and types, while Vilella's reagent was used to highlight the matrix structure. The components of etchants, etching method and observation point are summarized in Table 3.4.

Table 3.4 Etchant, etching method and observation point.

Etchant	Etching method	Observation
<u>Groesbeck's reagent</u> - KmnO_4 4 g. - NaOH 4 g. - Water 100 mL	Immersion at room temperature	Types of carbide
<u>Vilella's reagent</u> - Picric acid 1 g. - HCl 5 cc. - Ethanol 100 cc.	Immersion at room temperature	Carbide and matrix structures
<u>Nital reagent</u> - HNO_3 5 mL - Ethanol 95 mL	Immersion at room temperature	Matrix structure

3.4 Hardness measurement

The macro-hardness of the specimens was determined using a Vickers hardness tester under a load of 294.2 N (30 kgf), whereas the matrix microhardness was measured with a Micro-Vickers tester under a load of 0.98 N (100 gf). For each condition, measurements were taken at five randomly selected locations, and the average value was reported.

3.5 Measurement of volume fraction of austenite

The volume fraction of retained austenite (V_γ) was quantified by X-ray diffraction (XRD) following the method described by Kim (1979). A goniometer equipped with an automatic rotating and swinging sample stage was employed to minimize the influence of preferred crystallographic orientation. The measurement condition is shown in Table 3.5. The Mo-K α radiation ($\lambda = 0.0711$ nm), filtered through a Zr foil, was used as the X-ray source, and scans were conducted over a 2θ range of 27° – 43° .

The basic equation of quantitative measurements of the volume fraction of retained austenite is expressed by equation as

$$I_{hkl} = K(FF^*)(LPF)me^{-2M}[A(\theta)](V_i/v_i^2) \quad (3.1)$$

where I_{hkl} = integrated intensity per angular diffraction peak (hkl).

K = proportionality constant.

FF^* = structure factor of the unit cell of interested phase, it equal to $4f^2$ and $16f^2$ in diffraction line of α (ferrite or martensite) and γ (austenite), respectively.

LPF = Lorenz Polarization Factor which equal to $(1+\cos^2 2\theta)/\sin^2 \theta \cos \theta$.

M = multiplicity factor of the (hkl) plane reflection.

e^{-2M} = Debye-Waller or temperature factor which is function of θ , where $M = (B \sin^2 \theta)$ and B is material constant.

$A(\theta)$ = absorption factor which independent from θ if sample is flat.

V_i = volume fraction of the interested phase.

v_i = volume fraction of unit cell.

$$\text{Assume, } K' = K * A(\theta) \quad (3.2)$$

$$\text{and } R_{hkl} = [(FF^*)(LPF)me^{-2M}]/v_i^2 \quad (3.3)$$

Substitutes equation (3.2) and (3.3) in the equation (3.1), then

$$I_{hkl} = K'(R_{hkl})(V_i) \quad (3.4)$$

The calculation of numerous peaks in the diffraction pattern, equation 3.4 becomes

$$\Sigma I_{hkl} = K'(\Sigma R_{hkl})(V_i) \quad (3.5)$$

Therefore, peaks of ferrite or martensite (α) and austenite (γ) are considered. The integrated intensity equation is expressed as

$$\Sigma I_{\alpha} = K'(\Sigma R_{\alpha})(V_{\alpha}) \quad (3.6)$$

$$\Sigma I_{\gamma} = K'(\Sigma R_{\gamma})(V_{\gamma}) \quad (3.7)$$

Then, the pair of ferrite or martensite and austenite can be written as

$$\Sigma I_{\alpha} / \Sigma I_{\gamma} = (\Sigma R_{\alpha} / \Sigma R_{\gamma})(V_{\alpha} / V_{\gamma}) \quad (3.8)$$

$$\text{Beside, } V_{\alpha} + V_{\gamma} + V_c = 1 \quad (3.9)$$

where V_c is the volume fraction of carbides. Assuming only ferrite or martensite and austenite exist in the microstructure, the equation becomes

$$V_{\alpha} + V_{\gamma} = 1 \quad (3.10)$$

The volume fraction of austenite (V_{γ}) which relates to integrated intensity of ferrite as austenite peak to R-value is

$$V_{\gamma} = 1 / [1 + (\Sigma I_{\alpha} \Sigma R_{\gamma} / \Sigma I_{\gamma} \Sigma R_{\alpha})] \quad (3.11)$$

For quantitative analysis, the diffraction peaks of the (200) and (220) planes of ferrite (α) or martensite (M), together with the (220) and (311) planes of austenite (γ), were employed. The V_{γ} was calculated from the integrated intensities of these selected peaks using image analysis software. Specifically, three intensity ratios were evaluated: (i) $\alpha(200)/\gamma(311)$, (ii) $\alpha(200)/[\gamma(220) + \gamma(311)]$, and (iii) $[\alpha(200) + \alpha(220)]/\gamma(311)$. The reported V_{γ} value corresponds to the average of these three calculated results. The example of the XRD pattern for specimen No. 1, austenitized at 1050 °C and containing 15% V_{γ} , is presented in Figure 3.5.

Table 3.5 X-ray diffraction conditions for measurement the volume fraction of retained austenite (V_{γ}).

Parameter	Details
Target metal	Mo
Tube voltage / current	50 kV / 30 mA
Slits	Divergence slit : 1°, Receiving slit : 1.5 mm, Scattering slit : 1°
Filter	Zr
Scanning rang (2θ)	27-43 degree
Scanning speed	0.5 degrees / min
Step / sampling	0.01 degree

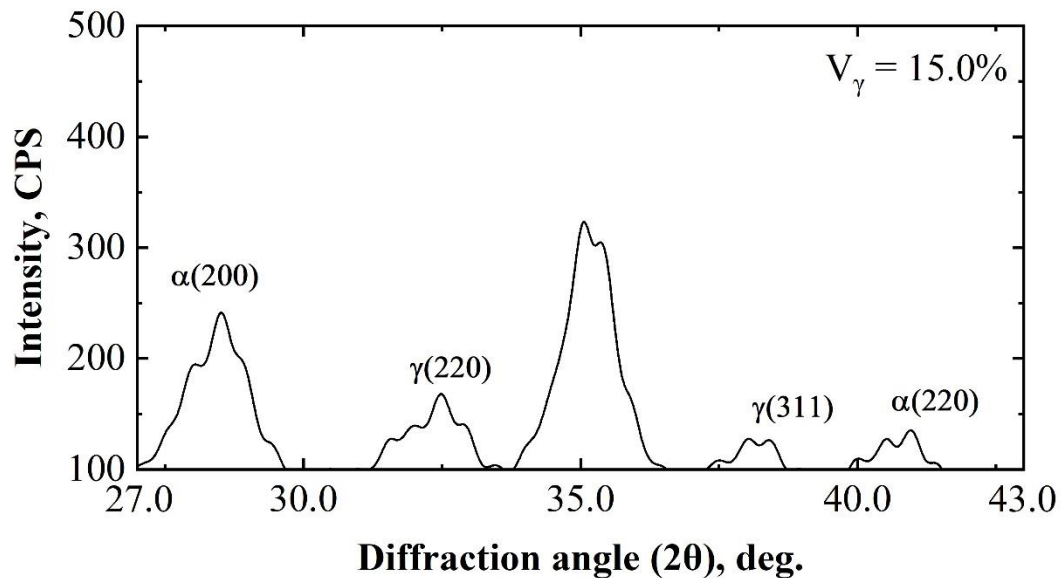


Figure 3.5 X-ray diffraction pattern of specimen No. 1 (Nb-free) in the as-hardened state with 15%V_γ (austenitizing temperature: 1050°C).

3.6 Abrasive wear test

3.6.1 Preparation of surface of wear test specimens

The surface of the abrasive wear test specimens was prepared using a grinding machine to achieve a maximum average roughness (Ra-max) of less than 1 μm.

3.6.2 Suga abrasive wear test

The Suga abrasive wear tester is used to evaluate two-body type abrasive wear resistance in accordance with the ASTM D6037 and ISO 7784-3 standards. The schematic drawing of the Suga tester and the experimental conditions are presented in Figure 3.6 and Table 3.6, respectively. An abrading wheel, 44 mm in diameter and 12 mm in thickness, is covered with 180-mesh emery paper. An abrasive load of 9.8 N (1 kgf) is applied to the surface of the test specimen. During the test, the abrading wheel rotates intermittently, synchronizing with the back-and-forth movement of the test specimen over a 30 mm stroke distance on the same surface area. After 400 strokes (24 m), the specimen is cleaned in an ultrasonic acetone bath and dried. The weight loss is measured using a high-precision digital balance with 0.1 mg accuracy. The wear loss per test is determined by the weight difference before and

after the procedure. This test is repeated eight times on the same worn area, resulting in a total sliding distance of 192 m.

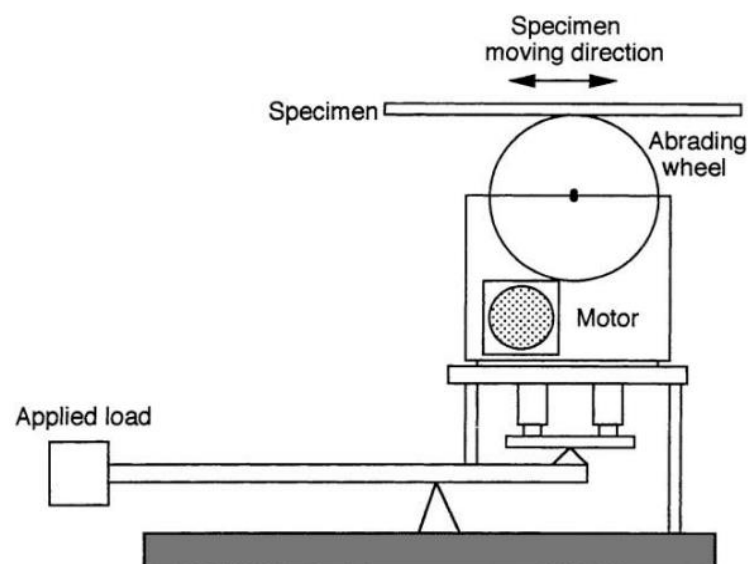
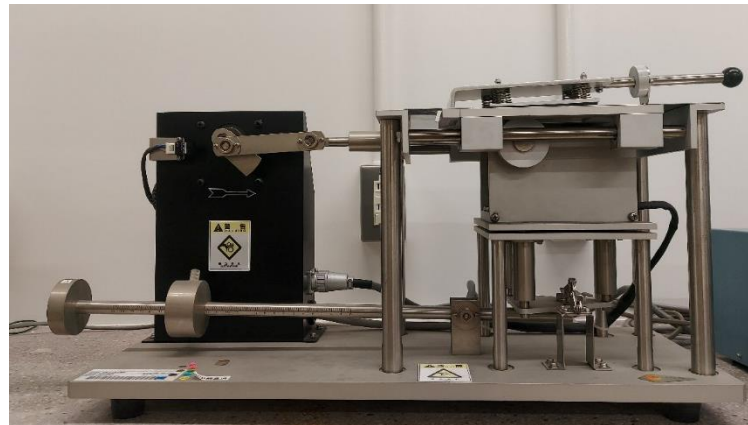


Figure 3.6 Schematic drawing of Suga abrasive wear tester.

Table 3.6 Experimental conditions for the Suga abrasive wear test.

Parameter	Details
Testing Machine	Suga abrasive wear tester (Two-body type) (ASTM D6037 and ISO 7784-3)
Abrading Wheel	Ø 44 mm, Thickness 12 mm
Abrasive Paper	180-mesh emery paper
Applied Load	9.8 N (1 kgf)
Stroke Length	30 mm
Test Cycles per Run	400 Strokes
Number of Repetitions	8 times (on the same area)
Total Sliding Distance	192 m
Total worn area	0.012 m x 192 m = 2.304 m ²
Cleaning Method	Ultrasonic acetone bath
Measurement Device	Digital balance (0.1 mg accuracy)

3.6.3 Rubber wheel abrasive wear test

The rubber wheel abrasive wear test is used to evaluate three-body type abrasive wear resistance in accordance with the ASTM G65 standard. The schematic drawing of the equipment is shown in Figure 3.7. ASTM 60 grade silica sand was used as the abrasive material. The rubber wheel measures 250 mm in diameter and 15 mm in thickness. The test conditions are summarized in Table 3.7. The abrasives are fed through a nozzle to the contact interface between the rotating rubber wheel and the specimen. The sand feeding rate is 250-300 g/min under a load of 85.3 N (8.7 kgf). The test is conducted for 1,000 revolutions per cycle at a rotating speed of 120 rpm. After cleaning the specimen in an ultrasonic acetone bath and dried. The weight of the specimen before and after the test is measured using a high-precision digital balance with 0.1 mg accuracy. The test is repeated four times on the same worn area.

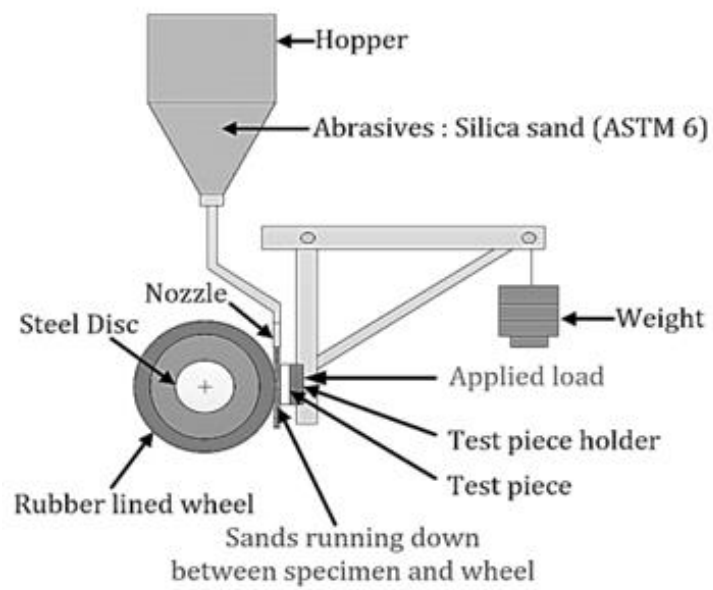


Figure 3.7 Schematic drawing of rubber wheel abrasion tester.

Table 3.7 Experimental conditions for the Rubber wheel abrasive wear test.

Parameter	Details
Testing Machine	Rubber wheel abrasive wear tester (Three-body type) (ASTM G65)
Rubber Wheel	Ø 250 mm, Thickness 15 mm
Abrasive material	ASTM 60 grade silica sand
Applied Load	85.3 N (8.7 kgf)
Sand Feeding Rate	250-300 g/min
Rotating Speed	120 rpm
Total Revolutions	1,000 revolutions/cycle
Number of Repetitions	4 times (on the same area)
Total wear distance	3140 m
Total worn area	$0.015 \text{ m} \times 3140 \text{ m} = 47.12 \text{ m}^2$
Cleaning Method	Ultrasonic acetone bath
Measurement Device	Digital balance (0.1 mg accuracy)