

APPENDIX A

Macro-hardness, micro-hardness and volume fraction of retained austenite (V_γ) of heat treatment specimens

Table A.1 Macro-hardness, micro-hardness and volume fraction of retained austenite (V_γ) of heat treatment specimens austenitized at 1050°C.

Specimen No.	Tempering temperature (°C)	Macro-hardness (HV30)	Micro-hardness (HV0.1)	Volume fraction of retained austenite (%)
No.1 (Nb-free)	As-hardened	927.1	857.6	10.3
	400°C	827.8	766.7	8.5
	450°C	839.6	791.5	7.8
	500°C	876.3	834.0	3.2
	525°C	894.6	851.5	1.6
	550°C	854.0	800.9	1.5
	600°C	704.9	660.6	1.1
No.2 (0.70%Nb)	As-hardened	913.5	841.5	15.2
	400°C	791.9	725.5	14.5
	450°C	806.8	730.1	13.5
	500°C	863.1	788.9	8.2
	525°C	873.8	818.1	2.5
	550°C	833.2	764.8	2.4
	600°C	656.4	585.0	1.4
No.3 (1.05%Nb)	As-hardened	909.5	836.5	15.9
	400°C	796.1	735.5	12.9
	450°C	804.2	742.6	12.4
	500°C	846.8	773.6	3.7
	525°C	857.2	792.9	3.3
	550°C	816.1	743.9	2.5
	600°C	668.0	608.9	2.0
No.4 (2.58%Nb)	As-hardened	960.2	878.8	18.5
	400°C	830.1	736.7	18.0
	450°C	850.8	748.0	16.1
	500°C	888.9	795.6	13.5
	525°C	907.1	817.5	5.8
	550°C	862.1	771.0	5.7
	600°C	702.5	615.8	5.2

Table A.2 Macro-hardness, micro-hardness and volume fraction of retained austenite (V_γ) of heat treatment specimens austenitized at 1100°C.

Specimen No.	Tempering temperature (°C)	Macro-hardness (HV30)	Micro-hardness (HV0.1)	Volume fraction of retained austenite (%)
No.1 (Nb-free)	As-hardened	904.8	841.5	14.7
	400°C	802.7	763.1	11.0
	450°C	821.1	790.3	10.5
	500°C	881.4	839.9	7.1
	525°C	922.1	869.6	2.8
	550°C	890.7	843.5	1.6
	600°C	760.9	720.8	1.1
No.2 (0.70%Nb)	As-hardened	885.7	799.6	22.1
	400°C	758.2	715.6	21.7
	450°C	784.7	725.5	20.4
	500°C	858.3	811.0	19.4
	525°C	911.1	848.8	8.3
	550°C	871.6	792.2	3.4
	600°C	697.5	628.1	1.6
No.3 (1.05%Nb)	As-hardened	841.7	779.3	26.8
	400°C	753.7	726.7	22.0
	450°C	766.7	743.8	20.6
	500°C	855.1	811.9	12.8
	525°C	896.6	845.1	8.5
	550°C	879.2	800.3	4.5
	600°C	744.3	680.2	2.2
No.4 (2.58%Nb)	As-hardened	872.0	811.3	28.2
	400°C	786.0	737.8	27.5
	450°C	814.7	758.0	26.5
	500°C	882.3	825.0	15.8
	525°C	927.0	854.7	9.4
	550°C	912.5	832.7	7.1
	600°C	767.1	678.8	4.9

APPENDIX B

Wear loss (W_l) and Wear Distance (W_d) for Specimens in the
Suga Abrasive Wear Test

Table B.1 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1050°C in the Suga abrasive wear test.

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 1 (Nb-free)	24	9.3	10.3	9.0	9.6
	48	16.9	17.5	15.6	16.8
	72	23.6	23.7	21.9	23.6
	96	29.8	30.6	28.1	30.5
	120	35.6	37.3	34.4	36.6
	144	41.2	43.5	40.1	43.5
	168	46.5	49.6	45.9	50.3
	192	51.9	55.5	52.1	57.2
No. 2 (0.70%Nb)	24	9.3	11.1	8.5	12.5
	48	17.0	20.3	15.6	24.2
	72	24.0	28.8	22.5	35.7
	96	30.3	37.6	29.1	47.0
	120	37.1	46.8	36.3	58.5
	144	43.9	55.5	43.3	69.7
	168	50.2	64.4	50.5	81.3
	192	57.0	73.4	57.6	92.8

Table B.1 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1050°C in the Suga abrasive wear test. (Continued)

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 3 (1.05%Nb)	24	9.6	10.9	7.7	10.9
	48	17.9	19.8	14.8	20.1
	72	25.2	27.8	22.0	28.8
	96	32.0	36.1	29.4	38.0
	120	38.8	44.3	36.8	46.4
	144	45.6	52.8	44.2	55.0
	168	52.1	61.3	51.8	64.2
	192	58.1	69.3	59.5	73.1
No. 4 (2.58%Nb)	24	7.2	10.2	9.3	10.1
	48	13.0	17.9	15.6	17.6
	72	18.9	25.0	21.5	24.9
	96	23.4	32.4	27.0	32.2
	120	29.2	39.1	32.6	39.3
	144	34.6	45.8	38.4	46.4
	168	39.8	53.0	44.1	53.7
	192	44.3	59.8	50.3	61.3

Table B.2 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1100°C in the Suga abrasive wear test.

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 1 (Nb-free)	24	8.2	7.5	8.2	7.3
	48	15.2	13.6	14.8	14.0
	72	20.9	19.6	20.4	20.6
	96	25.8	25.3	25.6	27.2
	120	30.8	30.6	31.0	33.4
	144	35.8	36.3	36.3	39.9
	168	40.2	42.6	42.0	46.4
	192	44.6	48.1	46.7	52.6
No. 2 (0.70%Nb)	24	9.0	9.7	7.8	9.5
	48	16.3	17.5	14.2	18.4
	72	23.4	24.7	20.5	27.0
	96	30.2	31.9	26.5	35.3
	120	36.5	38.9	32.7	44.1
	144	42.8	45.7	38.9	53.2
	168	49.2	52.8	45.3	62.1
	192	55.8	59.8	51.3	71.2

Table B.2 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1100°C in the Suga abrasive wear test. (Continued)

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 3 (1.05%Nb)	24	8.5	9.48	7.5	10.4
	48	15.8	16.78	14.2	18.6
	72	22.8	23.88	20.8	26.7
	96	29.9	30.48	27.3	34.9
	120	36.8	36.92	33.5	43.4
	144	43.5	43.78	40.1	51.5
	168	50.0	50.16	46.6	59.6
	192	56.2	57.10	53.1	67.9
No. 4 (2.58%Nb)	24	6.5	7.0	5.6	9.5
	48	11.8	13.3	10.7	17.1
	72	17.0	19.8	15.9	23.9
	96	22.5	25.5	20.8	30.4
	120	27.6	31.7	25.7	37.1
	144	32.9	37.4	30.5	43.5
	168	37.4	43.7	35.7	50.3
	192	42.0	49.9	40.6	57.0

APPENDIX C

Wear loss (W_l) and Wear Distance (W_d) for Specimens in the
Rubber Wheel Abrasive Wear Test

Table C.1 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1050°C in the rubber wheel abrasive wear test.

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 1 (Nb-free)	785	78.9	102.7	92.4	114.0
	1570	148.1	195.7	177.0	219.7
	2355	214.4	283.9	250.7	317.4
	3140	279.4	372.0	355.9	410.4
No. 2 (0.70%Nb)	785	77.8	92.1	79.7	102.0
	1570	142.3	175.7	151.6	197.0
	2355	203.3	260.4	221.5	288.3
	3140	262.6	336.8	289.2	377.8
No. 3 (1.05%Nb)	785	77.9	88.6	73.0	96.7
	1570	140.8	165.1	143.3	186.2
	2355	193.4	238.5	212.4	275.7
	3140	249.7	310.9	281.1	363.3
No. 4 (2.58%Nb)	785	72.3	96.2	78.6	100.4
	1570	136.2	190.8	159.9	210.5
	2355	203.0	281.2	239.9	316.3
	3140	268.6	370.0	320.2	417.9

Table C.2 Wear loss (W_l) and wear distance (W_d) of specimen austenitized at 1100°C in the rubber wheel abrasive wear test.

Specimen No.	Wear distance (W_d), m	As-hardened	L- H_{Tmax}	H_{Tmax}	H- H_{Tmax}
No. 1 (Nb-free)	785	66.8	80.6	69.5	84.4
	1570	129.2	158.1	134.9	162.0
	2355	188.3	234.6	199.8	238.0
	3140	246.9	307.7	263.8	312.0
No. 2 (0.70%Nb)	785	71.0	79.2	66.8	80.4
	1570	130.4	150.1	126.3	155.2
	2355	186.3	217.5	183.7	228.3
	3140	241.1	285.4	239.0	299.8
No. 3 (1.05%Nb)	785	71.9	69.4	65.7	83.7
	1570	130.0	135.3	124.0	159.7
	2355	184.4	199.5	180.4	232.1
	3140	237.6	262.2	235.4	300.5
No. 4 (2.58%Nb)	785	73.2	88.4	67.7	89.3
	1570	141.1	175.9	136.5	175.6
	2355	205.5	264.0	202.7	258.9
	3140	270.0	349.4	268.0	340.6

APPENDIX D
List of Publication



INFLUENCE OF NIOBIUM ON HARDNESS AND MICROSTRUCTURAL EVOLUTION IN HEAT-TREATED MULTI-ALLOYED WHITE CAST IRON

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Abstract

This study investigates the influence of niobium (Nb) on the heat-treatment behavior of multi-alloyed white cast iron containing 5 wt% each of Cr, Mo, W, and V, together with 2 wt%Co and 2.00–2.40 wt%C. Alloys with Nb contents ranging from 0.00 and 2.58 wt% were produced and subjected to annealing, austenitizing at 1050 and 1100 °C, quenching in a liquid nitrogen spray and tempering at 400–600 °C. The as-cast microstructure consisted of primary austenite dendrites (γ_p), eutectic carbides. At Nb levels above 1.05 wt%, primary MC carbides (MC_p) were also observed. The eutectic ($\gamma + MC$) fraction reached a maximum at 0.70 wt%Nb and then decreased, while the eutectic ($\gamma + M_2C$) fraction decreased continuously with Nb addition. In the as-hardened state, hardness decreased to a minimum at 1.05 wt%Nb due to matrix C depletion. However, it increased again at higher Nb levels as additional C (from 2.00 to 2.40 wt%) compensated for carbide formation. The volume fraction of retained austenite (V_γ)

increased slightly with Nb content, particularly at elevated austenitizing temperatures. Upon tempering, all alloys exhibited secondary hardening associated with secondary carbide precipitation and the martensitic transformation of retained austenite. The maximum tempered hardness (H_{Tmax}) was consistently achieved at 525 °C, reaching 927 HV30 in the alloy containing 2.58 wt%Nb austenitized at 1100 °C. Overall, Nb strongly affects carbide precipitation and retained austenite stability, exerting a dominant influence on hardness evolution. Notably, hardness values approaching 930 HV30 confirm that Nb addition is critical to sustaining the high hardness of multi-alloyed white cast iron through heat treatment.

Keywords: white cast iron, niobium, carbide, heat treatment, microstructure, hardness, retained austenite

Introduction

In the steelmaking industry, hot rolling mill rolls are essential forming tools used to shape semi-finished flat and long products.¹ Similar to other forming tools, work rolls are subjected to direct contact with hot steel plates, leading

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to progressive surface degradation during operation. Once this deterioration reaches a critical level, the rolls must be replaced either to maintain product quality or to prevent catastrophic failure. Owing to their vital role in steel production, work rolls in the finishing stands of hot-strip mills are generally produced as composite components, consisting of a wear-resistant outer shell and a tough, ductile core.^{1,2}

The development of materials for hot work rolls has evolved from low-alloyed chilled cast iron to more advanced alloys such as adamite (e.g., hyper-eutectoid Ni–Cr steels), Ni-hard irons, and high-Cr cast irons.^{1,2} In particular, high-Cr cast iron has been widely adopted due to its excellent wear and thermal resistance.^{2,3} However, the high fraction of eutectic carbides in high-Cr cast iron significantly reduces fracture toughness and limits roll durability.^{3–5} With the increasing demands for higher productivity and product quality in modern steel mills, the design of advanced roll materials with superior performance has become a primary research focus.^{4–11}

Multi-alloyed white cast iron has emerged as a promising candidate for such applications, owing to its high resistance to abrasive wear.² This alloy incorporates multiple carbide-forming elements, including chromium (Cr), molybdenum (Mo), tungsten (W), and vanadium (V). These elements react with carbon (C) to form a variety of hard carbides such as MC, M₂C, M₆C and M₇C₃, which impart exceptional abrasion resistance due to their high hardness. Moreover, residual alloying elements dissolved in the matrix strengthen the alloy through the precipitation of secondary carbides and martensitic transformation during heat treatment. A typical alloy composition includes approximately 5 wt% each of Cr, Mo, W, and V, together with 2 wt% C² (hereafter the wt% is expressed as %). More recently, cobalt (Co) has been introduced to enhance thermal stability and mechanical strength at elevated temperatures.

In terms of toughness, hypoeutectic compositions of multi-alloyed white cast iron are generally preferred. Their solidification begins with the crystallization of primary austenite (γ_p), followed by multiple eutectic reactions involving austenite and carbides.^{12–14} The type, morphology, size, and volume fraction of carbides can be tailored through compositional adjustments and cooling rates.^{12–17} Furthermore, heat treatment is essential for optimizing the microstructure and resultant mechanical properties. Similar to high-Cr cast irons and tool steels, heat treatment of multi-alloyed white cast iron involves destabilizing austenite matrix at high temperatures, where secondary carbides precipitate and promote the transformation of unstable austenite into bainite or martensite. Subsequent tempering relieves residual stresses and further reduces the retained austenite fraction formed during hardening.

Previous studies by our group have investigated the solidification behaviour,^{12,14–20} heat treatment response,^{18,20–27} and abrasive wear resistance^{28–34} of multi-alloyed white cast irons with basic alloy compositions. To further improve performance, it is essential to investigate the role of individual or combined alloying elements in influencing phase transformation, heat treatment behavior, wear resistance, and fracture toughness. Earlier work has systematically clarified the effects of C,²⁴ Cr,²³ Mo,^{20,22} W,²⁷ and V²⁵ on the heat treatment response of these alloys, revealing that each element exhibits an optimal concentration that maximizes tempered hardness. Achieving hardness and wear resistance beyond these limits requires the addition of stronger carbide-forming elements capable of producing extremely hard eutectic carbides.

Niobium (Nb) is a potent carbide former that produces niobium carbide (NbC) with a hardness of 2400–3000 HV.³ NbC generally crystallizes as a primary phase during solidification. Several studies^{35–48} have reported that NbC refines the as-cast microstructure and the proper amount of Nb enhances abrasive wear resistance in white cast irons. However, the formation of primary NbC consumes a significant amount of C, potentially reducing the C content of the remaining liquid and thereby altering the solidification mode from hypereutectic to eutectic or even hypoeutectic.⁴⁷ This shift affects the liquidus and eutectic temperatures as well as the solidification sequence. Niobium also exhibits a low partition coefficient in austenite (< 0.02),^{3,47,48} indicating that most Nb is consumed in the formation of NbC or mixed MC carbides. Moreover, relatively large primary NbC particles can shield the surrounding matrix, thereby improving wear resistance.^{39,47,49,50}

In centrifugal casting (CF), which is widely used for roll manufacturing, MC carbides with a low specific gravity tend to segregate toward the inner surface of the shell under centrifugal force. To counter this, the Nb addition has been shown to promote the formation of (V, Nb)C complex carbides with a specific gravity closer to that of the molten metal, thereby reducing segregation during CF processing.^{4,6–8,47}

Given these attributes, Nb is considered a promising alloying element for multi-alloyed white cast irons. Nevertheless, its influence on heat treatment behavior, particularly regarding hardness evolution and the volume fraction of retained austenite ($V\gamma$), has not been systematically addressed. Therefore, the present study investigates the effect of Nb additions on the heat-treatment response of multi-alloyed white cast iron.

Experimental Procedure

Preparation of Test Specimens

Raw materials including steel scrap, pig iron, ferroalloys, and high-purity metals were melted in an alumina-lined high-frequency induction furnace. The molten metal was superheated to 1580 °C and held for 10 min to ensure compositional homogeneity. The melt was then poured into a CO₂-bonded sand mold preheated at 200 °C to produce cylindrical castings measuring 25 mm in diameter and 65 mm in height, as shown in Figure 1. The chemical compositions of the alloys are presented in Table 1. To prevent premature solidification and oxidation, the riser

was immediately covered with exothermic powder (Noo-tex, Japan) upon pouring. After solidification, the riser was removed using wire electrical discharge machining (Wire-EDM).

For alloy design, the carbon balance (C_{bal}) parameters were calculated using the equation shown in Table 1 to estimate the equilibrium C concentration in the matrix, following the methodology reported in previous studies.^{2,26} To facilitate optimal matrix transformation during subsequent heat treatment, the C_{bal} value for all specimens was adjusted to 0%.^{2,26} For specimen No. 4, which contained the highest Nb addition, significant carbide formation substantially reduced the C content of the matrix. To compensate, the initial C content of this alloy was deliberately set higher than that of the other specimens to maintain a target C_{bal} of 0%.

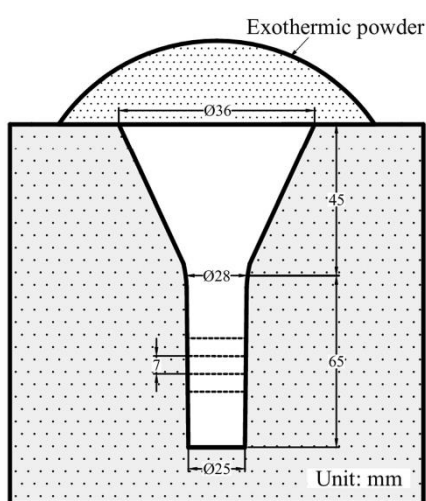


Figure 1. Schematic illustration of the CO₂-bonded sand mold prepared for test specimens.

Heat Treatment Procedures

The heat treatment sequence consisted of annealing, austenitizing, hardening and tempering, as schematically illustrated in Figure 2. Prior to heat treatment, all specimens were coated with an anti-oxidation solution (C-PRO, Japan) to minimize surface oxidation. The ingots were first annealed in an electric furnace at 950 °C for 5 h to reduce micro-segregation during solidification and homogenize the microstructure. After annealing, they were sectioned into 7 mm thick specimens using Wire-EDM.

The specimens were subsequently austenitized in a vacuum furnace at austenitizing temperatures of 1050 °C and 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 to 600 °C in 50 °C intervals. Each tempering treatment was maintained for 200 min, followed by air cooling (AC) to room temperature.

Table 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

$$\%C_{bal} = \%C - \%C_{stoch}^{3,18}$$

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

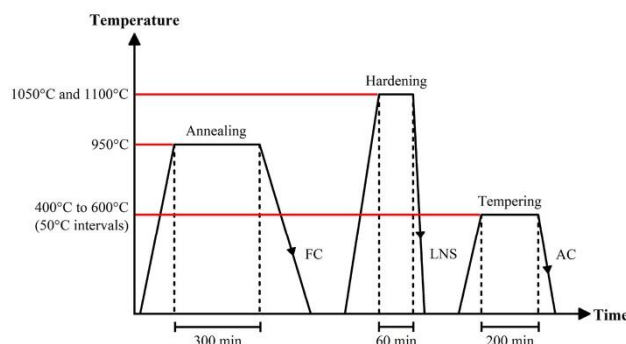


Figure 2. Schematic illustration showing the heat treatment processes.

Microstructure Examination

Optical microscopy (OM) and scanning electron microscopy (SEM) were employed to evaluate the microstructures of the test specimens. Prior to examination, the specimens were ground using silicon carbide (SiC) papers with grit sizes ranging from 180 to 1200, followed by polishing with a 0.1 μm alumina suspension to achieve a mirror-like surface finish. For microstructural analysis, the polished specimens were etched with Groesbeck's reagent (4 g. of KMnO_4 , 4 g. of NaOH and 100 ml of water) to reveal carbide morphologies and types, while Vilella's reagent (1 g. of Picric acid, 5 ml of HCl and 100 ml of Ethanol) was used to highlight the matrix structure.

Measurement of Hardness and Volume Fraction of Retained Austenite (V_γ)

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 micro-hardness 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.

The volume fraction of retained austenite (V_γ) was quantified by X-ray diffraction (XRD) following the method in accordance with the method proposed by Kim.⁵¹ A goniometer equipped with an automatic rotating and swinging sample stage was employed to minimize the influence of preferred crystallographic orientation. $\text{Mo-K}\alpha$ radiation ($\lambda = 0.0711 \text{ nm}$), filtered through a Zr foil, was used as the X-ray source, and scans were conducted over a 2θ range of 27° – 43° . An example of the XRD pattern for specimen No. 1, austenitized at 1050°C and containing 15% V_γ , is presented in Figure 3.

For quantitative analysis, the diffraction peaks from 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 XRD 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.

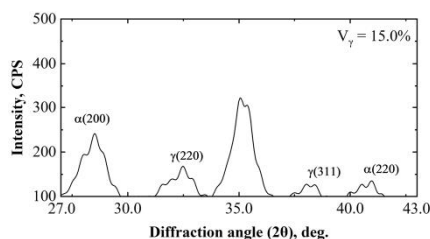


Figure 3. X-ray diffraction pattern of specimen No. 1 (Nb-free) in the as-hardened state with 15% V_γ (austenitizing temperature: 1050°C).

Experimental Results and Discussions

As-Cast Microstructure

The as-cast microstructures of the specimens are shown in Figure 4. In the Nb-free alloy and the specimen containing 0.70%Nb, the microstructures exhibited a hypoeutectic morphology, consisting of primary austenitic dendrites (γ_p) and eutectic colonies of austenite with carbides. The eutectic carbides were identified as MC and M_2C types, consistent with previous reports by Wu et al.^{15–18} and Hashimoto et al.¹⁹ for multi-alloyed white cast irons of

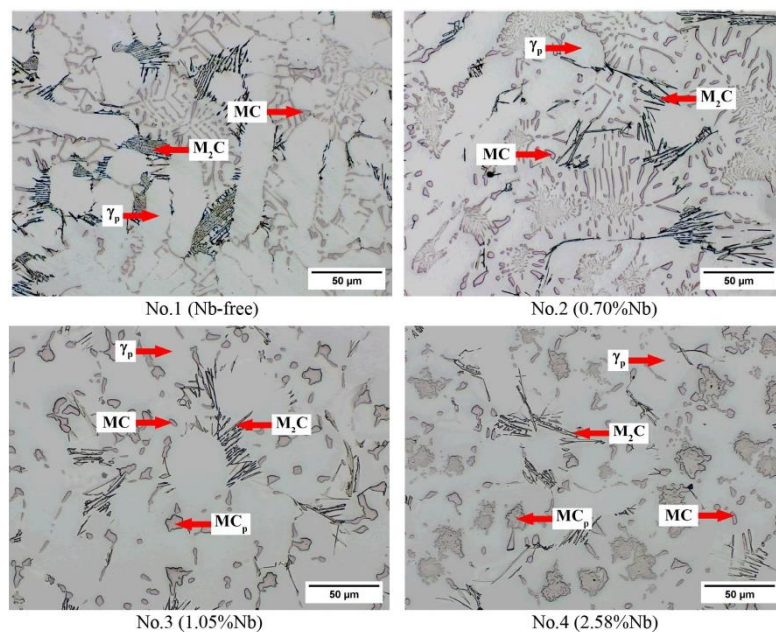


Figure 4. Microstructural features of as-cast specimens with different Nb contents.

similar composition. Morphologically, eutectic MC carbides exhibited a petal-like structure, whereas M_2C carbides displayed a plate-like morphology. Although the overall microstructures of the two specimens were comparable, notable differences were observed in dendrite size and eutectic MC morphology. In particular, the specimen containing 0.70%Nb exhibited finer dendritic structures and eutectic MC carbides with irregular, roughened boundaries.

By contrast, the specimens containing 1.05% and 2.58%Nb exhibited hypereutectic compositions characterized by the coexistence of primary carbides with eutectic ($\gamma + MC$) and ($\gamma + M_2C$) structures. The primary carbides were predominantly of the MC type (MC_p), reflecting the strong carbide-forming tendencies of Nb and V. Owing to its high affinity for carbon, Nb promoted the early precipitation of (V, Nb)-rich MC carbides during solidification. Increasing Nb content resulted in larger MC_p carbides, increased fraction of these carbides, and a more pronounced granular (or block angular) shaped morphology. The occurrence of austenite dendrites in the hypereutectic alloys can be rationalized by the faceted-nonfaceted growth imbalance.⁴⁷ In this system, austenite (nonfaceted phase) and MC carbides (faceted phase) grow competitively; the composition

and temperature fields are biased toward the faceted phase, enabling the nucleation and growth of austenite dendrites immediately after the crystallization of primary MC carbides but prior to cooperative eutectic solidification.

The distribution of alloying elements was further characterized using electron probe microanalysis with characteristic X-ray mapping, as shown in Figure 5. The elemental maps revealed that Cr, Mo, and W were predominantly concentrated in the M_2C carbides, whereas V and Nb were enriched within the MC carbides. In the case of eutectic MC carbide, V acted as the primary alloying element in all specimens. As the Nb content increased, the eutectic MC carbides exhibited a corresponding increase in Nb concentration, and no clear alloy segregation was observed within the carbides. For the MC_p carbides, EDS line scans of representative MC_p particles from the 1.05% and 2.58%Nb specimens are shown in Figure 6. In the alloy with 1.05%Nb, the MC_p carbides were predominantly V-rich with minor Nb enrichment. Conversely, in the 2.58%Nb specimen, the MC_p exhibited a Nb-rich core surrounded by a V-rich eutectic MC rim. These findings are consistent with the results reported by Bacalini et al.⁴⁷, who reported that Nb-rich primary carbides act as effective nucleation sites for the subsequent growth of eutectic MC

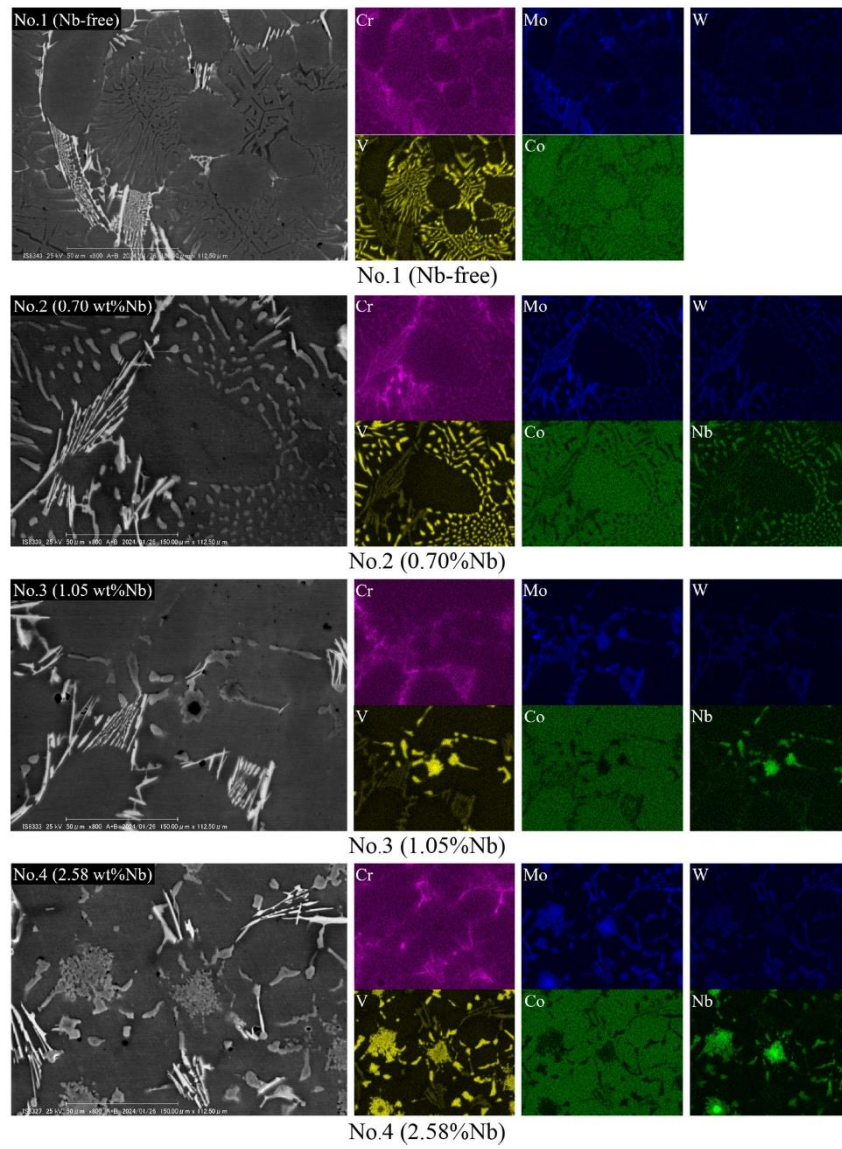


Figure 5. EDS mapping analysis results of as-cast specimens with different Nb content.

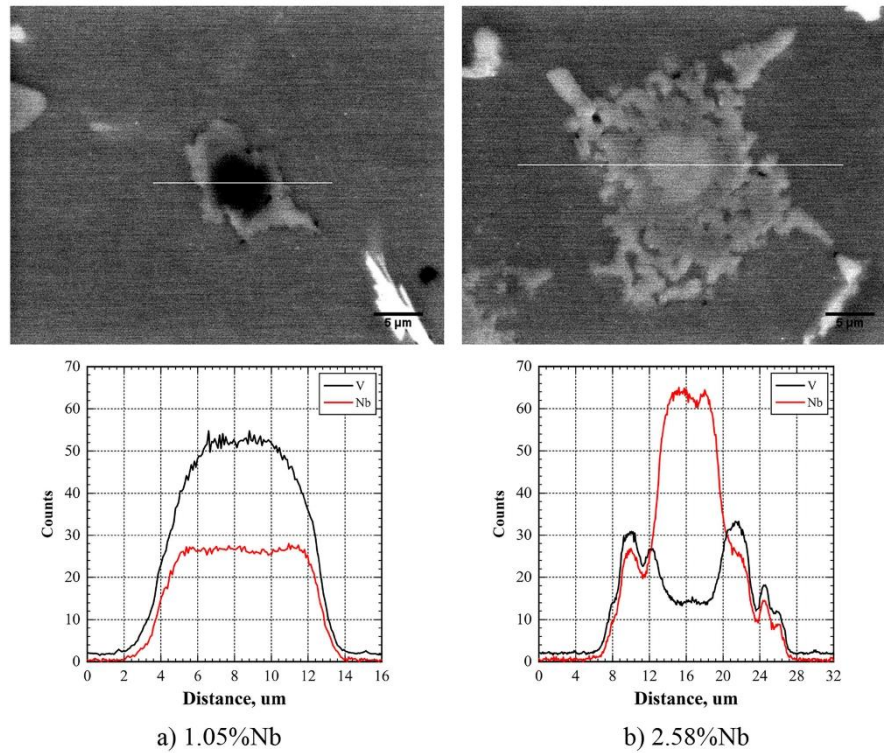


Figure 6. EDS line scanned profile of primary MC carbide (MC_p) in specimen with 1.05% Nb (a) and 2.58% Nb (b).

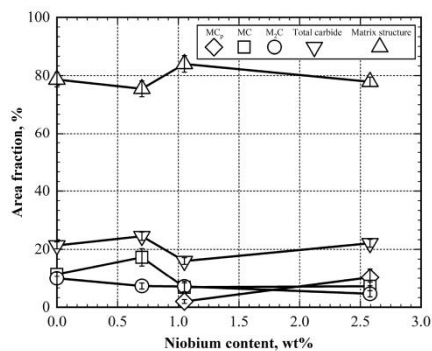


Figure 7. Effect of Nb content on the area fractions of the matrix and carbide phases in as-cast specimens.

carbides during solidification. Moreover, a progressive reduction in the V content of MC_p carbides was observed with increasing Nb concentration. This trend is attributed to the higher carbide affinity of Nb relative to V, which promotes the formation of NbC (MC-type) carbides during the early stages of solidification, thereby limiting the incorporation of V into the MC_p phase.

To further elucidate the influence of Nb on solidification behavior and phase evolution. Quantitative image analysis was employed to determine the area fraction of carbides and matrix phases. The results were calculated from 5 micrographs for each specimen at a magnification of 50 $\times$, as summarized in Figure 7. The MC_p carbides were first detected at 1.05%Nb and their fraction increased progressively with further Nb additions. The area fraction of eutectic MC carbides initially increased, reaching a maximum at 0.70%Nb, followed by a sharp decline at 1.05%Nb, and then exhibited a slight increase at 2.58%Nb. The initial

increase is attributed to the enhanced nucleation of the (γ + MC) eutectic facilitated by Nb addition. At 1.05%Nb, however, the formation of MC_p carbides consumed substantial amounts of Nb, V, and C from the liquid, thereby promoting the growth of austenite dendrites and suppressing eutectic formation. This finding is consistent with the results of Ibrahim et al.,^{52,53} who reported that when Nb was added to high chromium cast iron, the precipitation of NbC consumed C from the liquid melt, leading to a depletion of C available for the formation of eutectic M_7C_3 carbides. At 2.58%Nb, the C enrichment in the melt was sufficient to sustain eutectic (γ + MC) formation despite the earlier precipitation of MC_p carbides.

In contrast, the area fraction of eutectic M_2C carbides decreased continuously with increasing Nb content. This trend suggests that Nb additions preferentially stabilize MC carbides while suppressing the (γ + M_2C) eutectic reaction, most likely due to competitive carbon consumption. These observations agree with the findings of Boccalini et al.⁴⁷ Overall, the total carbide fraction increased up to 0.70%Nb, decreased sharply at 1.05%Nb, and subsequently exhibited a slight increase at higher Nb concentrations, whereas the matrix fraction displayed an inverse trend. The emergence of primary MC carbides significantly influences the alloy's properties. While the carbide fraction governs hardness, the presence and distribution of these carbides are critical for enhancing structural integrity and abrasive wear resistance.

Behavior of Hardness and Volume Fraction of Retained Austenite (V_γ) in As-hardened State

It is well established that the type and morphology of carbides in multi-alloyed white cast irons undergo minimal changes during heat treatment, as reported by several studies.^{18,22–27} In contrast, the matrix phase exhibits pronounced microstructural transformations depending on the specific heat treatment conditions. The matrix structures in the as-hardened state, characterized via scanning electron microscopy (SEM), are presented in Figure 8. All specimens were found to consist of secondary carbides (Sc), martensite (M), and retained austenite (γ_R). Consistent with the findings of Hashimoto et al.,¹⁸ the secondary carbides were identified primarily as MC, M_6C and M_7C_3 . These results indicate that austenite destabilization occurs during austenitizing through the precipitation of secondary carbides, which subsequently facilitates the martensitic transformation upon quenching.

The area fraction of secondary carbides was quantified via back-scattered electron imaging combined with image analysis software. For each specimen, 5 micrographs at 6000 $\times$ magnification were analyzed, with the results summarized in Figure 9. The fraction of secondary carbides was found to decrease with increasing Nb content up to

1.05%, before increasing again at higher Nb levels. The initial decrease in secondary carbide fraction can be attributed to the increased formation of MC eutectic carbides and MC_p carbides. Preferential consumption of C and V by Nb reduces the availability of C and V in the matrix for the formation of secondary carbides. In contrast, the higher fraction of secondary carbides in the 2.58%Nb specimen is due to its higher C than other conditions. This excess C facilitates the formation of both primary and eutectic carbides, while simultaneously enriching the matrix, thereby enhancing the precipitation of secondary carbides during austenitizing. Furthermore, specimens subjected to higher austenitizing temperatures exhibited an increased fraction of retained austenite and a reduced fraction of secondary carbides. This trend can be attributed to the enhanced solubility of alloying elements in austenite at elevated temperatures, which suppresses secondary carbide precipitation and thereby stabilizes the retained austenite.

The influence of Nb content on macro-hardness and the V_γ in the as-hardened state is shown in Figure 10. As Nb content increased, the macro-hardness initially decreased, reaching a minimum at 1.05%Nb, before increasing again with further Nb addition, regardless of the austenitizing temperature. At a fixed Nb level, higher austenitizing temperatures consistently resulted in lower hardness values. The highest macro-hardness was obtained in the alloy containing 2.58%Nb, achieving 960 and 872 HV30 after austenitizing at 1050 °C and 1100 °C, respectively. In contrast, V_γ increased steadily with increasing Nb content. The underlying reasons can be explained as follows,

The increase in the V_γ with rising Nb content can be attributed to the reduced precipitation of secondary carbides in the matrix (Figure 9). In addition, the suppression of M_2C eutectic carbide formation with increasing Nb content enhances the solubility of Mo, W, and Cr in austenite, which lowers the martensite start (M_s) temperature and thereby promotes the stabilization of austenite. Thus, although Nb itself is not regarded as a strong austenite stabilizer, its indirect role through the modification of carbide chemistry markedly increases the retained austenite fraction after quenching. This effect becomes more pronounced at elevated austenitizing temperatures, where the enhanced solubility of alloying elements in austenite promotes further stabilization during quenching, ultimately resulting in an increased V_γ value.

With respect to the variation in hardness, the initial decline in hardness with Nb addition up to 1.05% can be attributed to two simultaneous factors: (i) the increase in the V_γ and (ii) the reduction in the overall carbide fraction. As the Nb content increases, although more MC eutectic carbides are formed, the reduced precipitation of secondary carbides in the matrix combined with the higher V_γ leads to a decrease in hardness. At 1.05%Nb, where MC_p carbides begin to

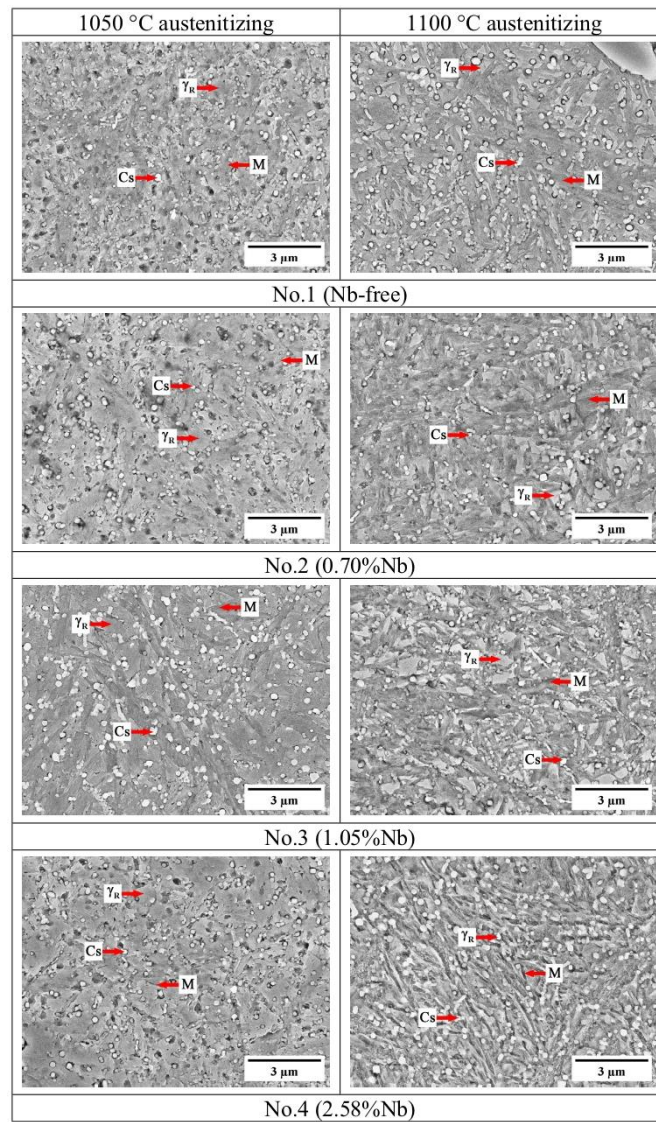


Figure 8. Typical matrix microstructures of as-hardened specimens with different Nb content.

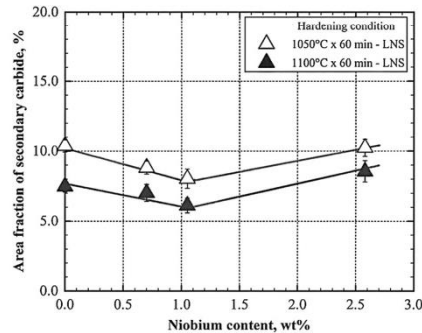


Figure 9. Relationship between Nb content and area fraction of secondary carbide precipitated in the as-hardened specimens.

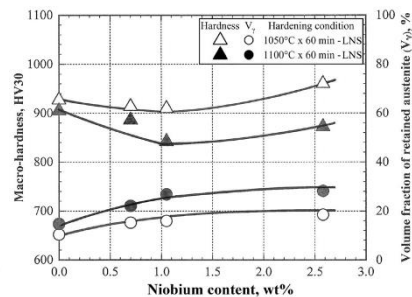


Figure 10. Relationship between macro-hardness, volume fraction of retained austenite (V_γ) and Nb content in as-hardened state.

crystallize, a significant amount of V, Nb, and C is consumed to form MC_p , thereby suppressing the formation of both MC and M_2C eutectic carbides and greatly reducing the precipitation of secondary carbides. Although MC_p carbides are intrinsically hard, their strengthening effect is outweighed by the pronounced reduction in the total carbide fraction, together with the higher V_γ , resulting in decreased hardness. In addition, the hardness of martensite itself is reduced due to the diminished carbon content in the matrix. These results are consistent with the findings of Kim et al.,³⁹ who reported that the crystallization of MC_p reduces the dissolution of carbide forming elements in the matrix, thereby lowering matrix hardness.

At higher Nb content (2.58%Nb), by contrast, a distinct increase in hardness was observed. This improvement can be explained by the additional C required to compensate for the formation of MC_p carbides during solidification.

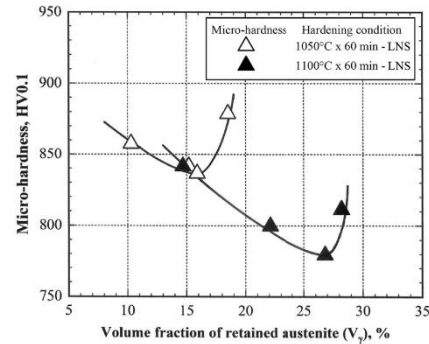


Figure 11. Relationship between micro-hardness and volume fraction of retained austenite (V_γ) in as-hardened state.

The excess C not only promotes the precipitation of eutectic carbides but also enriches the matrix, facilitating secondary carbide precipitation during austenitizing and enhancing martensitic hardness after quenching. These combined mechanisms account for the recovery and subsequent enhancement of hardness at elevated Nb levels.

Further evidence supporting this interpretation is provided by the correlation between micro-hardness and the volume fraction of retained austenite (V_γ), as shown in Figure 11. Specimens with higher V_γ consistently exhibited lower micro-hardness values up to approximately 27% V_γ , thereby confirming both the softening effect of retained austenite relative to martensite and the reduction in secondary carbide precipitation. Notably, an abrupt increase in micro-hardness was observed at 28% V_γ (corresponding to the 2.58%Nb specimen), which suggests the precipitation of additional secondary carbides with exceptionally high intrinsic hardness. This hardening phenomenon markedly enhanced the matrix strength despite the nearly unchanged level of retained austenite, highlighting the complex interplay among secondary carbide precipitation, retained austenite stability, and martensitic transformation.

Behavior of Hardness and Volume Fraction of Retained Austenite (V_γ) in Tempered State

Effect of Tempering Temperature on Hardness and Volume Fraction of Retained Austenite (V_γ)

During tempering, the amount of retained austenite generally decreases with increasing tempering temperature, while martensite formed during hardening undergoes tempering reactions that significantly influence the overall hardness of the cast iron. The relationships between macro-

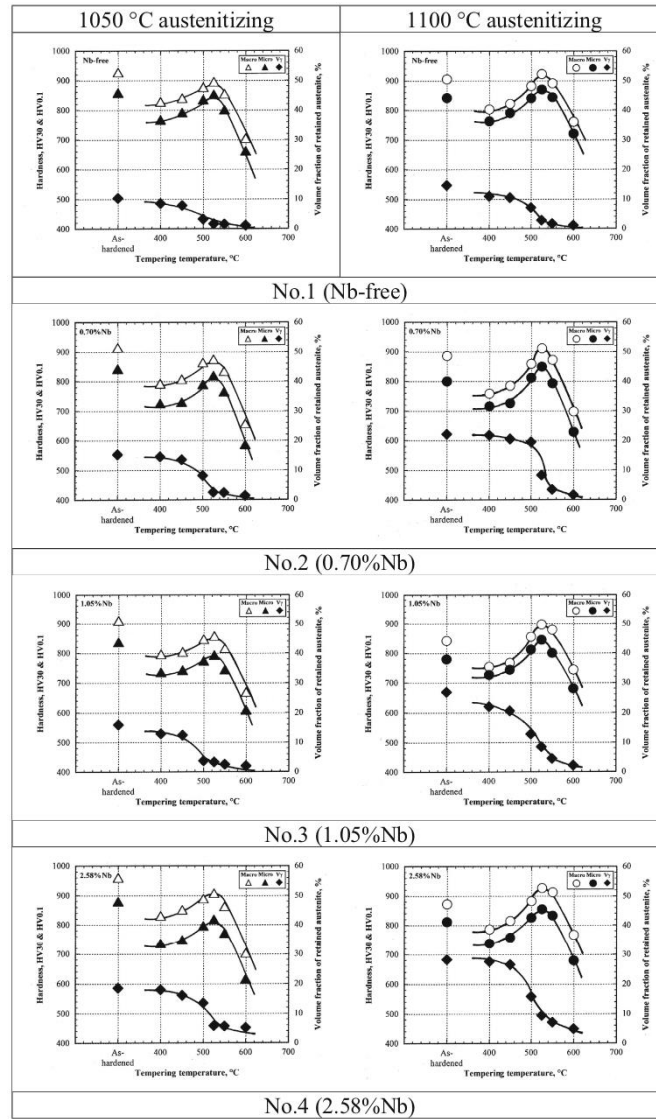


Figure 12. Effect of tempering temperature on variation of macro-hardness, micro-hardness and volume fraction of retained austenite (V_r) of specimens with different Nb content.

hardness, micro-hardness, V_γ , and tempering temperature are shown in Figure 12. For reference, hardness and V_γ values in the as-hardened condition are also included. All specimens exhibited the characteristic secondary hardening behavior, that is, an initial decrease in hardness at 400 °C, followed by an increase to a maximum value (H_{Tmax}), and a subsequent sharp decline at higher temperatures. Macro-hardness curves displayed a similar trend to micro-hardness but with consistently higher values, reflecting the fact that macro-hardness measurements incorporate both the matrix and carbide phases, whereas micro-hardness values represent only the matrix. The V_γ decreased gradually up to approximately 450–500 °C, irrespective of the austenitizing temperature. A more abrupt reduction in V_γ was observed at 525–550 °C, after which the decrease became gradual again as the temperature approached 600 °C. At H_{Tmax} , V_γ values were consistently below 10%, regardless of austenitizing temperature.

The initial hardness reduction at 400 °C relative to the as-hardened state is primarily attributed to the tempering of martensite, specifically the precipitation of very fine $M(Mo, W, V, Cr)_3C$ within the martensitic lattice.^{3,25} At this relatively low temperature, the decomposition of retained austenite is limited because the thermal energy is insufficient to destabilize the austenite phase. As the tempering temperature increases, hardness rises due to secondary carbide precipitation within the retained austenite. This process depletes carbon and alloying elements from the austenite, reducing its stability and promoting its transformation into martensite during post-tempering cooling, thereby enhancing matrix hardness. The maximum hardness was observed at 525 °C for specimens austenitized at both 1050 and 1100 °C, corresponding to the peak rate of retained austenite transformation into martensite. At this stage, additional carbide reactions within the martensite matrix produce nearly pure secondary carbides²⁵ such as MC , M_6C , and M_2C , which exhibit high hardness and significantly strengthen the alloy.^{18,20–27}

When the tempering temperature exceeds 525 °C, however, coarsening and agglomeration of secondary carbides occur via Ostwald ripening, while excessively high temperatures may also promote the transformation of retained austenite into softer phases such as pearlite or ferrite. These microstructural changes collectively lead to a pronounced reduction in matrix hardness. Furthermore, specimens hardened at higher austenitizing temperatures consistently exhibited higher H_{Tmax} compared to those treated at lower austenitizing temperatures. This behavior is attributed to the increased dissolution of C and alloying elements in austenite at elevated austenitizing temperatures, which enhances secondary hardening during tempering and results in greater hardness.

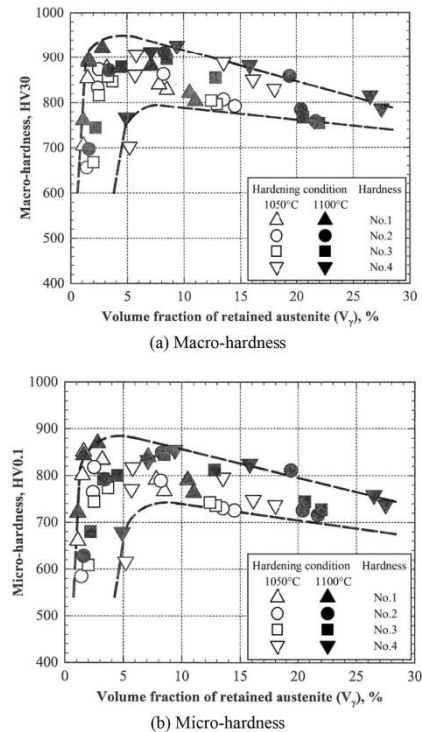


Figure 13. Relationship between hardness and volume fraction of retained austenite (V_γ) in tempered state.

Effect of Volume Fraction of Retained Austenite (V_γ) on Tempered Hardness

As discussed earlier, the hardness of cast iron is largely governed by the presence of eutectic carbides and the characteristics of the matrix microstructure. While eutectic carbides undergo minimal alteration during tempering, the matrix phases are significantly affected and play a decisive role in determining the overall hardness. Consequently, the V_γ in the tempered matrix becomes a critical factor influencing the mechanical response, particularly hardness. The relationship between macro-hardness, micro-hardness, and the volume fraction of retained austenite (V_γ) for all tempered specimens are presented in Figure 13a and b, respectively. Both macro- and micro-hardness follow similar trends, whereby, hardness increases with V_γ abruptly, reaching a maximum at approximately 2–3% V_γ , and then gradually decreases with further increases in V_γ . Although the overall variation in micro-hardness closely

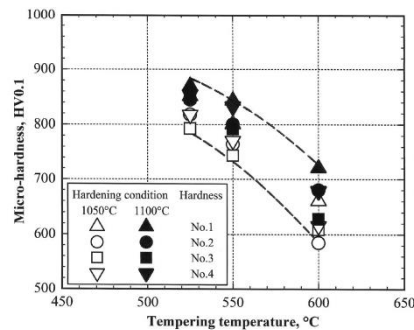


Figure 14. Relationship between micro-hardness and tempering temperature of specimens with less than 10% V_γ .

parallels that of macro-hardness, the absolute values of micro-hardness remain consistently lower. At a constant V_γ , specimens quenched from 1100 °C exhibited higher hardness than those quenched from 1050 °C. This difference can be attributed to the stronger secondary hardening effect observed at higher austenitizing temperatures. Notably, maintaining V_γ within the range of approximately 2–10% was found to be effective for achieving macro-hardness values above 900 HV30.

In the range below 5% V_γ , both macro- and micro-hardness values exhibited considerable scatter. Beyond this threshold, however, the variation in hardness decreased progressively with increasing V_γ . This trend can be explained by the increased V_γ and the corresponding reduction in the martensite fraction. The large scatter in hardness values at less than 5% V_γ is primarily attributed to variations in the matrix structure among specimens. Specimens showing relatively low hardness values were typically associated with over-tempering, which softened the matrix. Conversely, specimens with higher hardness values possessed matrices composed predominantly of martensite, together with a uniform distribution of fine secondary carbides, both of which contributed significantly to enhanced hardness.

To further clarify this behavior, the relationship between matrix hardness (micro-hardness) and tempering temperature was examined for specimens with V_γ below 5%, as illustrated in Figure 14. Despite the limited variation in V_γ , micro-hardness decreased progressively with increasing tempering temperature from 525 to 600 °C, although some data scattering was observed. At a tempering temperature of 525 °C, the micro-hardness exceeded 800 HV0.1, representing the peak hardness (H_{Tmax}) in the present study. This high hardness can be attributed to a matrix predominantly composed of tempered martensite and finely dispersed secondary carbides. The subsequent reduction in

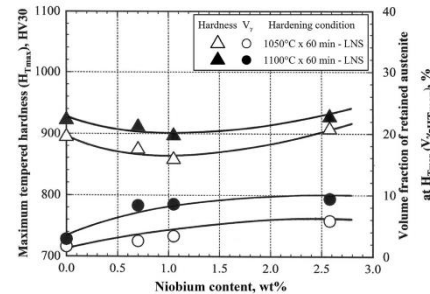


Figure 15. Relationship between maximum tempered hardness (H_{Tmax}) volume fraction of retained austenite (V_γ) at H_{Tmax} and Nb content.

hardness at higher tempering temperatures is likely due to the coarsening of secondary carbides and the transformation of retained austenite into softer phases, such as pearlite or ferrite. Notably, specimens tempered at 600 °C exhibited a pronounced decline in micro-hardness, indicating that both carbide coarsening and phase transformation processes were largely completed at this stage.

Effect of Nb Content on the Maximum Tempered Hardness (H_{Tmax})

The relationship between H_{Tmax} , the V_γ at H_{Tmax} , and Nb content is presented in Figure 15. Overall, all specimens exhibited H_{Tmax} values exceeding 850 HV30. The H_{Tmax} decreased with Nb up to 1.05% and subsequently increased gradually with further Nb additions. This trend was observed consistently regardless of the austenitizing temperatures. For a given Nb content, the H_{Tmax} values obtained after austenitizing at 1100 °C were higher than those at 1050 °C. The maximum H_{Tmax} was achieved at 2.58%Nb, reaching 907 and 927 HV30 for the 1050 and 1100 °C austenitizing conditions, respectively.

The initial decrease in H_{Tmax} up to 1.05%Nb can be rationalized as follows: although the retained austenite fraction in the as-hardened state increased slightly with rising Nb content, the extent of secondary hardening, arising from both secondary carbide precipitation and the transformation of retained austenite to martensite, was insufficient to counteract the softening effect. In addition, the crystallization of primary MC_p carbides consumed significant amounts of C and carbide-forming elements, thereby restricting the precipitation of fine secondary carbides within the martensitic matrix, which is a key mechanism of secondary hardening. In other words, the MC_p carbides, despite their intrinsic hardness, effectively reduce overall hardness by suppressing secondary carbide precipitation in the matrix. At higher Nb contents (> 1.05%),

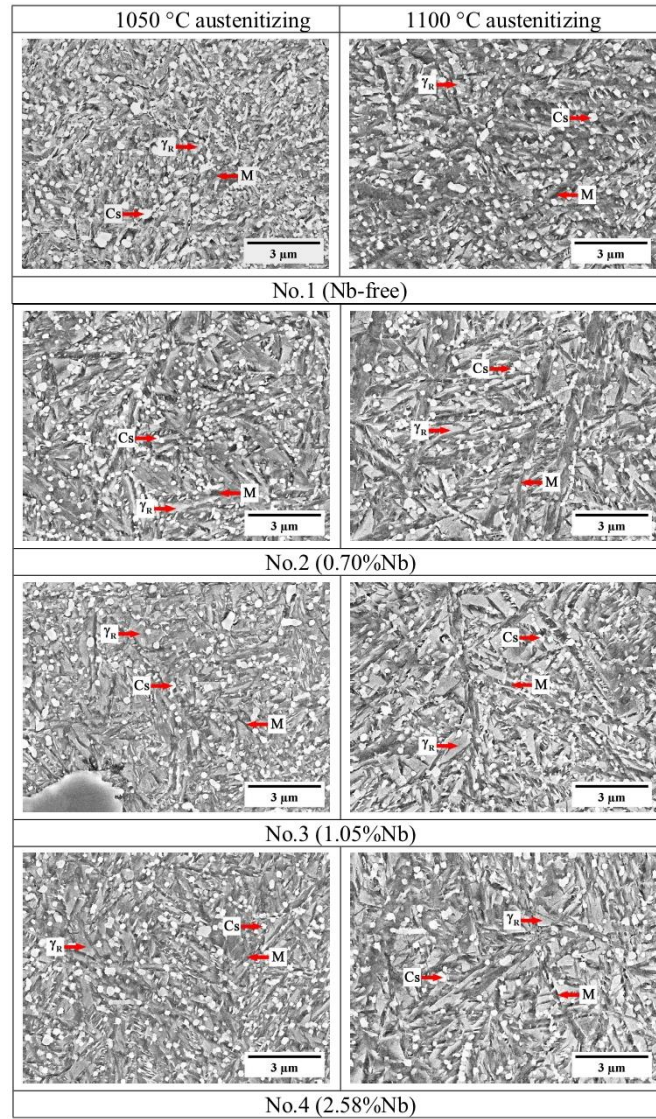


Figure 16. Matrix structures of H_{Tmax} specimens with different Nb content.

by contrast, H_{Tmax} increased gradually. This improvement can be attributed to enhanced secondary hardening, as the additional C in cast iron provides a sufficient supply for the

formation of both primary MC_p and eutectic carbides, while still retaining enough C dissolved in the matrix to promote secondary hardening.

The residual $V\gamma$ values at H_{Tmax} was less than 5% in the Nb-free specimen and remained below 10% in the Nb-bearing specimens. This indicates that even at the maximum hardness achieved through tempering, a certain fraction of austenite was retained in the microstructure. The $V\gamma$ at H_{Tmax} was higher in specimens hardened from the higher austenitizing temperature of 1100 °C, due to the greater amount of retained austenite generated in the as-hardened state. Consequently, under identical tempering conditions, a higher fraction of austenite persisted in the matrix when hardening was performed at the higher austenitizing temperature.

From the above results, it is evident that Nb exerts a pronounced influence on H_{Tmax} . To further clarify this effect, the matrix microstructures of specimens tempered to H_{Tmax} were characterized by SEM, with representative micrographs shown in Figure 16. The matrices of all specimens consisted of martensite (M), retained austenite (γ_R) and secondary carbides (Sc). While the amount of retained austenite could not be clearly distinguished from SEM observations, notable differences in the size and distribution of secondary carbides were observed as a function of Nb content. The amount of secondary carbides appeared to decrease with increasing Nb content up to 1.05%. In contrast, the specimen containing 2.58%Nb exhibited a larger size of secondary carbides relative to the other specimens. The relationship between Nb content and area fraction of secondary carbide precipitated in the H_{Tmax} specimens is shown in Figure 17. As the Nb content increased, the area fraction of secondary carbide decreased to a minimum at 1.05%Nb and subsequently increased, regardless of the austenitizing temperatures. The initial reduction in secondary carbide fraction can be attributed to the formation of eutectic MC and MC_p carbides, which deplete C and V available in the matrix for secondary carbide precipitation during heat treatment. As Nb increased from 1.05 to 2.58%

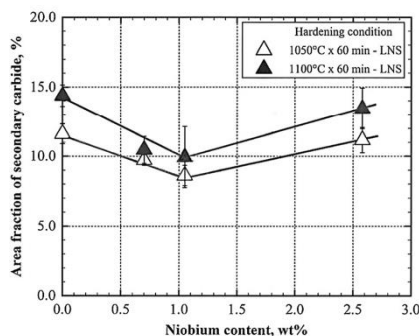


Figure 17. Relationship between Nb content and area fraction of secondary carbide precipitated in the H_{Tmax} specimens.

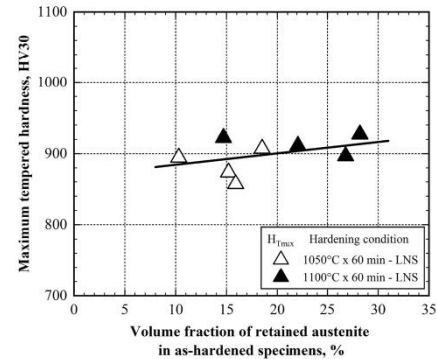


Figure 18. Relationship between maximum tempered hardness (H_{Tmax}) and volume fraction of retained austenite ($V\gamma$) in as-hardened state.

(with a corresponding increase in C from 2.0 to 2.4%), the area fraction of secondary carbides increased. This is due to the higher total C in the alloy, which leads to higher C concentration dissolved into the matrix during hardening. Consequently, this promotes greater precipitation of secondary carbides during tempering. Regarding the austenitizing temperature, specimens hardened from higher austenitizing temperature resulted in a higher area fraction of secondary carbide regardless of Nb. This is attributed to the fact that at high austenitizing temperature, alloying elements can easily dissolve into the matrix and result in a higher amount of secondary carbide precipitated during tempering. The $V\gamma$ in the as-hardened state must be carefully considered to achieve the desired target hardness after tempering. As shown in Figure 18, the H_{Tmax} is directly correlated with $V\gamma$ in the as-hardened state. With increasing $V\gamma$ from 10 to 28%, H_{Tmax} rises proportionally, indicating that retained austenite contributes indirectly yet significantly to secondary hardening. This effect arises from two mechanisms: (i) the precipitation of secondary carbides and (ii) the transformation of retained austenite into martensite during tempering. Notably, a minimum of $\sim 10\%V\gamma$ in the as-hardened state is required to achieve an H_{Tmax} above 900 HV30. However, excessive retained austenite becomes detrimental, as a considerable fraction may remain untransformed after tempering. In such cases, the softening effect of retained austenite on the matrix outweighs the strengthening effect provided by secondary carbide precipitation and martensitic transformation, thereby lowering the overall hardness.

Degree of the Secondary Hardening

In the tempered hardness curves of each specimen (Figure 12), secondary hardening is clearly observed. This

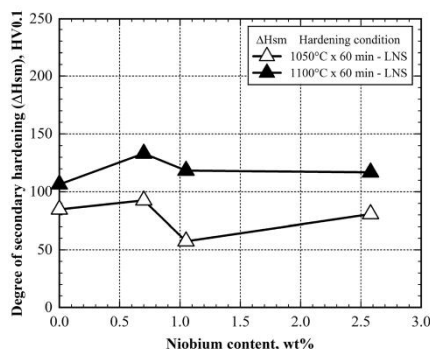


Figure 19. Effect of Nb content on degree of secondary hardening of matrix (ΔH_{sm}).

phenomenon, which occurs during tempering, is primarily attributed to the precipitation of alloy carbides within the tempered martensitic matrix through carbide reactions, as well as the transformation of retained austenite into martensite.^{18,20–27} These mechanisms govern the variation in matrix hardness. The influence of Nb content on the degree of secondary hardening of the matrix (ΔH_{sm}), defined as the difference in micro-hardness between H_{Tmax} and the micro-hardness at the onset of secondary hardening, is presented in Figure 19. Irrespective of austenitizing temperature, the ΔH_{sm} value increases with Nb content up to 0.70%, beyond which it decreases sharply at 1.07%Nb, followed by a gradual increase with further Nb addition. The maximum ΔH_{sm} values, 92.6 HV0.1 for specimens austenitized at 1050 °C and 133.2 HV0.1 for those austenitized at 1100 °C, are obtained at 0.7%Nb. At the same Nb content, specimens hardened from 1100 °C exhibit a greater ΔH_{sm} than those hardened from 1050 °C, indicating that higher austenitizing temperatures enhance secondary hardening. In other words, specimens containing a larger fraction of retained austenite in the as-hardened state yield higher ΔH_{sm} values.

It can be said that the extent of secondary hardening depends on both the type and quantity of secondary carbides precipitated, as well as on the martensite formed from retained austenite during tempering. The increase in ΔH_{sm} up to 0.70%Nb arises from the larger fraction of retained austenite in the as-hardened state, which transforms into martensite during tempering. Beyond 0.70%Nb, however, ΔH_{sm} decreases abruptly due to the depletion of Nb, V, and C in the matrix, which suppresses secondary carbide precipitation, as corroborated by the microstructural evidence shown in Figure 16.

From the present results, it can be concluded that the addition of Nb has a pronounced effect on the hardness of

the alloy by influencing both carbide precipitation and the stability of retained austenite. At moderate levels ($\sim 0.70\%Nb$), the formation of fine MC-type eutectic carbides is promoted. However, no significant improvement in overall hardness is achieved by heat treatment. When the Nb content exceeds 0.70%, hardness decreases sharply due to the excessive consumption of Nb, V, and C in the formation of primary carbides, which suppresses both eutectic reactions during solidification and secondary carbide precipitation during hardening–tempering treatments. With further Nb addition, compensating for C depletion becomes necessary, requiring an additional C supply in the cast iron. Overall, Nb contributes to hardness enhancement, but its effect is strongly dependent on concentration and on maintaining an appropriate balance between primary and secondary carbide formation. The degree of secondary hardening induced by Nb is relatively limited compared with other strong carbide forming elements such as Mo^{20,22} or V.²⁵ Nevertheless, hardness approaching ~ 930 HV30 are achieved with Nb addition, demonstrating that Nb plays a crucial role in sustaining the high hardness of cast iron through heat treatment.

Conclusions

This study systematically investigated the influence of Nb on the microstructural evolution and hardness behavior of multi-alloyed white cast iron subjected to heat treatment. Cast irons with varying Nb from 0.00 to 2.58% were produced and the cast irons were annealed, hardened and tempered under various conditions. The results obtained are summarized as follows:

- The as-cast microstructure consisted of primary austenite dendrites, eutectic carbides and at Nb levels above 1.05%, primary MC carbides (MC_p). The eutectic ($\gamma + MC$) fraction reached its maximum at 0.70%Nb, decreased at 1.05%Nb, and slightly increased again at 2.58%Nb, whereas the eutectic ($\gamma + M_2C$) fraction decreased continuously with Nb addition.
- In the as-hardened state, the matrix was composed of martensite, secondary carbides, and retained austenite. Hardness initially decreased with increasing Nb up to 1.05%, due to the reduced C content of the matrix, and subsequently increased at higher Nb levels due to additional C supplied for carbide formation. Specimens austenitized at 1050 °C consistently exhibited higher hardness than those treated at 1100 °C. The volume fraction of retained austenite ($V\gamma$) increased with Nb content and was higher at elevated austenitizing temperatures.
- Upon tempering, all alloys displayed characteristic secondary hardening, caused by the precipitation of fine secondary carbides and the

transformation of retained austenite into martensite. The maximum tempered hardness (H_{Tmax}) was obtained at 525 °C for both austenitizing conditions. H_{Tmax} decreased to a minimum at 1.05%Nb, then increased gradually, reaching maximum values of 907 HV30 and 927 HV30 at 2.58%Nb for 1050 °C and 1100 °C austenitizing, respectively. Maintaining $V\gamma$ in the range of 2–10% was found to be effective for achieving macro-hardness above 900 HV30.

- The degree of secondary hardening of matrix (ΔH_{sm}) increased with Nb addition up to 0.70%, declined sharply at 1.05%Nb, and then increased again with further Nb addition, with higher values consistently obtained at 1100 °C.
- Overall, Nb addition strongly affects both carbide precipitation and retained austenite stability, thereby exerting a dominant influence on hardness evolution. An optimal Nb content near 0.70% promotes fine MC eutectic carbides and pronounced secondary hardening, while higher Nb levels (> 1.05%) require additional C to offset matrix depletion.
- Hardness approaching 930 HV30 were achieved with Nb addition, confirming that Nb is a key element in sustaining the high hardness of multi-alloyed white cast iron through heat treatment.

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Conflict of interest We declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

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