

RESEARCH ARTICLE

Effect of copper addition on solidification behavior, microstructure and hardness of modified low-Ni ductile Ni-resist alloy

M. Aminuddin, M. Mohd Rashidi*

Faculty of Mechanical and Automotive Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, 26600 Pekan, Pahang, Malaysia

Abstract – Because of their excellent thermal properties and stable austenitic matrix, ductile Ni-resist alloys are widely used in corrosion-resistant and high-temperature applications. However, the high nickel content required to produce traditional Ni-resistant alloys considerably increases production costs. To assess the impact of Cu substitution on the solidification behavior, microstructural evolution, segregation characteristics, and hardness response, modified ductile Ni-resist alloys with a reduced Ni content (18 wt.% Ni) and varying Cu additions (6–10 wt.% Cu) were prepared. Induction melting, in-mold nodularization, and inoculation were used to create the alloy specimens. X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM–EDS), and dendritic arm spacing analysis were used to characterize the microstructure. The dendritic arm spacing (DAS) increased from approximately 240 to 250 μm , and the secondary dendritic arm spacing increased from 20 to 24 μm , indicating that the increased Cu content promoted interdendritic segregation and coarsening of dendrites. With increasing Cu addition, graphite nodularity gradually dropped from $75.1 \pm 0.3\%$ to $71.3 \pm 0.1\%$, and nodule count dropped from 213.0 ± 1.0 to 201.7 ± 0.6 nodules/ mm^2 . Cu enrichment in the interdendritic and grain boundary regions was confirmed by SEM-EDS analysis, whereas Ni remained comparatively evenly distributed within the γ -austenitic matrix. With a γ -Fe content of approximately 94.61%, XRD analysis confirmed that the FCC austenitic phase was stable in all compositions. Owing to solid-solution strengthening and solute segregation, the macro-hardness in the Cu-rich interdendritic regions increased from 160.0 ± 8.7 HB to 194.3 ± 5.1 HB, whereas the micro-hardness increased from approximately 215.7 ± 7.4 HV to 298.3 ± 1.5 HV. The results show that partial substitution of Cu for Ni can preserve a stable austenitic structure while altering the morphology and hardness behavior of graphite, offering valuable information for the creation of less expensive ductile Ni-resist alloys with regulated microstructural performance.

Article History

Received : 30 January 2026

Revised : 17 May 2026

Accepted : 22 July 2026

Published : 30 September 2026

Keywords

Ductile Ni-resist

Copper addition

Nickel substitution

Solidification

Microsegregation

Graphite nodularity

Dendritic arm spacing

Hardness

1. Introduction

Because of their superior castability, affordable manufacturing costs, favorable wear resistance, and ease of machining, cast irons are among the most popular engineering materials. Automobile parts, pumps, pipes, machine bases, and thermal systems are only a few of their many industrial applications. However, the shape of the graphite generated during solidification significantly affects the mechanical performance of cast irons. Gray cast iron has a comparatively low tensile strength, ductility, and fatigue resistance because graphite forms linked flakes that act as stress concentrators. While maintaining the superior casting properties of traditional cast iron, magnesium treatment converts flake graphite into spheroidal graphite, greatly enhancing the strength, toughness, and resistance to crack initiation [1]–[4]. Despite these advances, phase changes and oxidation cause microstructural instability in typical ductile iron at high temperatures, limiting its use under harsh thermal and corrosive conditions. Consequently, alloy modification has emerged as a successful strategy for improving the service capacity of ductile cast iron under challenging operating conditions [5]–[6]. Austenitic ductile Ni-resist alloys have garnered significant interest among alloyed cast irons because of their superior mechanical performance, thermal stability, dimensional stability, corrosion resistance, and oxidation resistance across a broad temperature range. These improved properties are achieved mainly by adding nickel, which stabilizes the γ -austenitic matrix and suppresses the ferrite formation during cooling [6]. To maximize the microstructure and service performance, ductile Ni-resist alloys typically contain 18–36 wt.% Ni, along with alloying elements such as Cr, Mn, and Cu [7]–[8]. Consequently, ductile Ni-resist alloys have been widely used in applications where superior thermal stability and corrosion resistance are crucial, such as in exhaust manifolds, turbocharger housings, heat-resistant pumps, furnace components, marine systems, and chemical processing equipment [7], [9].

Nickel is one of the costliest alloying elements in ductile Ni-resist cast irons, despite its superior austenite stability and corrosion resistance. Therefore, researchers have made considerable efforts to develop lower-Ni austenitic ductile irons without compromising their microstructural stability and mechanical performance, given the rising cost and variable availability of Ni. Partially replacing Ni with Cu is a viable strategy because Cu also enhances austenite stability and provides solid-solution strengthening at a significantly lower material cost [5], [10]. However, Cu substitution cannot be considered solely from a compositional perspective. Cu partitions during solidification, promoting enrichment in late-to-freeze (LTF) and interdendritic regions and altering the final microstructure, local chemical homogeneity, dendritic evolution, and graphite nucleation. Therefore, creating economically viable low-Ni ductile Ni-resist alloys requires an understanding of how Cu affects the solidification behavior. Earlier studies have shown that Cu strongly influences the

*CORRESPONDING AUTHOR | M. M. Rashidi | ✉ mrashidi@ump.edu.my

microstructural evolution and solidification behavior of ductile cast irons. While preserving the stability of the γ -austenitic matrix, moderate Cu additions strengthen the matrix through solid-solution strengthening. However, a higher Cu content also promotes micro-segregation during solidification, enriching the LTF and interdendritic regions, where the local chemical composition differs from that of the dendritic cores [11]. Cu redistribution during solidification affects dendritic arm spacing (DAS/SDAS), graphite growth kinetics, carbide formation tendencies and localized hardness. Owing to alterations in the local solidification path and solute redistribution, excessive Cu addition has also been shown in several experiments to reduce graphite nodularity and promote graphite degeneration [12]. These results imply that the metallurgical function of Cu goes beyond simple alloy substitution and should be assessed alongside the solidification mechanisms controlling microstructural development.

Cu-containing ductile irons have been the subject of several investigations; however, most of them have focused on mechanical characteristics, corrosion resistance, oxidation behavior, or general microstructural findings [7]–[9]. In austenitic ductile irons, recent studies have examined phase evolution, carbide morphology, and thermal stability [5]–[6]. Nevertheless, few investigations on reduced-Ni ductile Ni-resist alloys have consistently linked Cu-induced micro-segregation with dendritic development, graphite shape, and hardness. Determining the metallurgical linkages between solidification behavior, interdendritic segregation, graphite formation, and mechanical response is also challenging because prior studies have frequently assessed these features separately. While Bork et al. [5] emphasized the significance of alloy chemistry in regulating austenitic stability and carbide morphology, a recent study by Shin et al. [12] showed that Cu segregation during solidification greatly affects the final microstructure of ductile iron. However, the quantitative relationships among the Cu content, dendritic arm spacing, graphite nodularity, and localized hardness in modified low-Ni ductile cast iron alloys remain poorly understood.

Despite major advances in the development of Cu-containing ductile and Ni-resistant cast irons, several significant scientific questions remain unanswered. The combined impact of Cu addition on solidification-induced microsegregation, dendritic evolution, graphite morphology, and localized mechanical responses has received relatively little attention. Simultaneously, previous research has mostly focused on individual properties, such as hardness, corrosion resistance, oxidation performance, and phase stability. Specifically, with a stable reduced Ni concentration of 18 weight percent, the formation of interdendritic and late-to-freeze (LTF) areas has not been thoroughly studied. Furthermore, knowledge remains limited on the simultaneous effects of increasing Cu content on dendritic arm spacing (DAS/SDAS), graphite nodularity, nodule count, γ -austenite stability, macrohardness, and microhardness. Optimizing the alloy composition while balancing the production cost, microstructural integrity, and mechanical performance requires addressing these interactions. This study is novel because it establishes a comprehensive understanding of the relationship between Cu addition, solidification-induced micro-segregation, dendritic evolution, graphite morphology, phase stability, and hardness response in modified low-Ni ductile Ni-resist alloys with a fixed Ni content of 18 wt percent. In contrast to earlier studies that mainly focused on individual properties, this study uses optical microscopy, SEM-EDS, XRD, dendritic arm spacing analysis, and macro- and microhardness measurements to explain the metallurgical mechanisms governing microstructural evolution during solidification. By demonstrating how Cu substitution can reduce Ni consumption while preserving a stable γ -austenitic matrix and appropriate graphite shape, the results provide useful information for alloy design. This knowledge supports the development of more affordable and ductile Ni-resist alloys for corrosive and high-temperature industrial applications. Thus, the purpose of this study is to examine how the microstructural evolution, dendritic structure (DAS/SDAS), micro-segregation behavior, graphite morphology, phase stability, and hardness response of modified ductile Fe-Cr-Si-Ni alloys are affected by increasing the Cu content from 6 to 10 wt. %, while keeping the Ni content fixed at 18 wt. %. To provide a metallurgical basis for improving the alloy composition in low-Ni ductile Ni-resist systems, this study also attempts to determine the correlations between Cu-induced interdendritic segregation, graphite nodularity, nodule count, and macro- and microhardness.

2. Materials and Methods

2.1 Alloy Preparation and Castings Process

Steel scrap, pig iron, electrolytic nickel, and pure copper were used as the main charge materials in an induction melting furnace to create modified ductile Ni-resist alloys with different Ni contents. The target alloy compositions were 6Cu–18Ni, 7Cu–18Ni, 8Cu–18Ni, 9Cu–18Ni, and 10Cu–18Ni, with a fixed nickel content of 18 wt.% and variable copper additions of 6, 7, 8, 9, and 10 wt. %. This compositional design was intended to assess the effects of progressive Cu substitution on the microstructural evolution, segregation properties, and solidification behavior while preserving a stable austenitic matrix. To guarantee the total dissolution and homogenization of the alloying elements, the melting process was conducted in an induction furnace at approximately 1500 ± 20 °C. To improve the chemical homogeneity and reduce compositional segregation, we periodically stirred the molten metal during melting. We superheated the molten alloy before casting to improve its fluidity and encourage the dissolution of any remaining inclusions. We poured the molten alloy at a controlled temperature of 1400 ± 20 °C into the green sand molds. Bentonite, water, and silica sand were used to make the molds. To reduce the differences in solidification behavior between the compositions, all the castings were made under the same molding and cooling conditions. For the microstructural and mechanical analyses, we prepared cylindrical cast samples measuring approximately 25 mm in diameter and 100 mm in length. To promote graphite spheroidization, we used inoculation and in-mold modularization methods in this study. In a specially constructed reaction chamber inside the runner system, a FeSiMg nodularizer containing approximately 5 wt.% Mg with particle sizes ranging from 1 to 4 mm was added at a dosage greater than 1.1 wt.% of the molten metal. To improve graphite nucleation and

reduce carbide formation during solidification, we concurrently added an FeSi-based inoculant. Table 1 summarizes the chemical compositions of the alloying additions and raw materials used.

2.2 Metallographic Preparation

The specimens were separated from the cast samples for metallographic analysis after they solidified and cooled to room temperature. To achieve a mirror-like surface finish suitable for optical microscopy, scanning electron microscopy (SEM), and hardness testing, the specimens were sequentially ground on SiC abrasive papers ranging from 240 to 2000 grit and then polished with a 0.3 μm alumina suspension. The selected samples were etched using a 2% nital solution for microstructural observation, revealing the matrix components, graphite morphology, and dendritic structure. Using optical microscopy, we assessed the graphite morphology, nodularity, and nodule count in compliance with ASTM A247 and A439 standards. To obtain representative average values, we examined at least five distinct observation fields for each composition.

2.3 Microstructural Characterization

Scanning electron microscopy and optical microscopy were used for microstructural analysis. We used a field-emission scanning electron microscope with energy-dispersive spectroscopy for elemental analysis and segregation assessment. We conducted SEM analysis in the secondary electron imaging mode at an accelerating voltage of 15–20 kV. The representative regions examined included dendritic cores, interdendritic regions, graphite nodules, and late-to-freeze (LTF) zones. To ascertain the distribution of Fe, Ni, Cu, Si, and Mg within the microstructure, elemental mapping and compositional analyses were performed using SEM–EDS. Special attention was given to identifying the Cu segregation behavior in the interdendritic and grain boundary regions.

2.4 Dendritic Arm Spacing (DAS and SDAS Measurement)

Image analysis software was used to measure the primary dendritic arm spacing (DAS) and secondary dendritic arm spacing (SDAS) from the SEM micrographs. The linear intercept method was used to measure the well-developed dendritic regions. To guarantee statistical reliability, at least 20 separate measurements were taken from several micrographs for each alloy composition. The average distance between neighboring primary dendritic trunks was used to calculate the DAS values, whereas the distance between secondary dendritic arms was used to calculate the SDAS values. To assess the impact of Cu addition on dendritic coarsening behavior during solidification, the average values were computed and reported.

2.5 X-ray Diffraction (XRD) Analysis

XRD analysis with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) was used to identify the phases. Diffraction patterns were captured over a 2θ scanning range of 20° – 100° with a step size of 0.02° . To determine whether γ -austenite and secondary phases were present, the obtained diffraction peaks were indexed and compared with the standard diffraction data. To assess the stability of the austenitic matrix with increasing Cu addition, the relative γ -Fe content was calculated from the dominant face-centered cubic (FCC) austenitic diffraction peaks.

2.6 Hardness Measurement

The Brinell hardness method was used to measure the macro-hardness in compliance with the ASTM E10 guidelines. For each measurement, a standard tungsten carbide ball indenter with the appropriate test load and dwell time was used. Each sample surface had at least five indentations made at various points, and the average hardness value was recorded for each sample. To assess the localized hardness differences between the dendritic and interdendritic regions, microhardness testing was performed using a Vickers microhardness tester. The measurements were performed with a controlled dwell time and fixed load. To evaluate the impact of Cu segregation on the local hardness distribution, multiple indentations were made across the dendritic cores, interdendritic regions, and late-to-freeze zones.

2.7 Solidification and Microstructure Analysis

The dendritic morphology, segregation traits, graphite nodularity, and late-to-freeze regions were analyzed to assess the solidification behavior. To determine the impact of alloy modification on the microstructural evolution of low-Ni ductile Ni-resist alloys, the relationship between Cu addition, segregation tendency, dendritic coarsening, and graphite degeneration was systematically examined.

Table 1. Chemical composition of iron, alloyed materials, nodularizer, inoculant, and Cu (wt %)

	Elements							
	C	Si	Mn	P	Mg	Ni	Cu	Fe
Pig iron	2.91	2.27	0.12	0.07	-	0.02	-	Balance
Steel	0.20	0.15	0.60	0.03	-	-	-	Balance
Nickel	-	-	-	-	-	99.00	-	Balance
Nodularizer	-	44.00	-	-	5	-	-	-
Inoculant	-	70.00						Balance
Copper	-	-	-	-	-	-	99.00	-

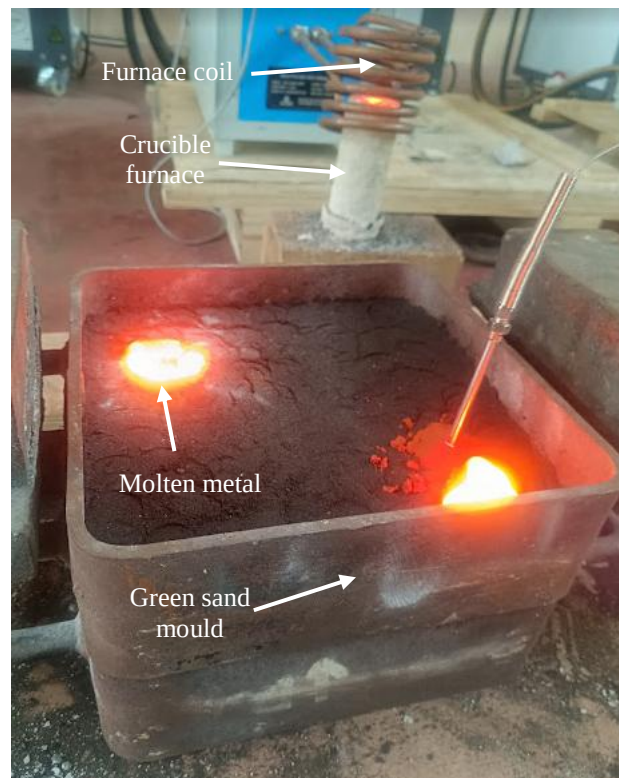


Figure 1. Setup of molten metal consist of induction furnace, ladle, mould and solidification sample

3. Results and Discussion

3.1 Graphite Morphology and Nodularity

Successful modularization during casting was indicated by the microstructures of the modified ductile Ni-resist alloys, which showed spheroidal graphite nodules dispersed within a predominantly γ -austenitic matrix. Figures 2-4 display representative optical and SEM micrographs. At lower Cu compositions, the graphite nodules appeared uniform; however, as Cu increased from 6 wt percent to 10 wt percent, graphite spheroidization gradually deteriorated. According to the quantitative results compiled in Table 3, the graphite nodularity gradually decreased from $75.1 \pm 0.3\%$ for the 6Cu–18Ni alloy to $71.3 \pm 0.1\%$ for the 10Cu–18Ni alloy. Similarly, as the Cu addition increased, the graphite nodule count decreased from 213.0 ± 1.0 to 201.7 ± 0.6 nodules/mm². The results show that a higher Cu content slightly inhibited graphite spheroidization and encouraged less uniform graphite growth, despite the moderate reduction. The cast sample contained nodules (Figure 4). The formation of these graphite nodules as distinct structures inside the sample suggests that graphite was formed during solidification or casting. These nodules contribute to the overall microstructure of the material and may differ in size, shape, and distribution. The graphite nodules most likely result from the separation of carbon in the molten metal and crystallization into graphite structures during solidification [10]. A semi-spheroidal form, on the other hand, suggests that some of these graphite nodules are incomplete growths. This suggests that either the growth of these graphite structures stopped during solidification or that the graphite development process was incomplete. The polished surface of the alloy formed during casting (Figure 2) revealed a hypoeutectic composition with multiple components, including Fe, C, Si, Cu, Ni, and other elements, as indicated in Table 2. Austenite matrix, eutectic austenite, graphite aggregate, carbides, and impurity inclusions are the several phases that make up this alloyed iron. Generally, the outer portion of the alloyed iron grain, such as the last-to-freeze (LTF) area, is abundant in positive segregation elements such as Mn, whereas the core portion is rich in Ni and Si [8].

Phase formation, element solubility, and solute segregation are interrelated metallurgical processes that occur during solidification. In the ductile Ni-resist alloy, Ni and Cu show markedly different partitioning behaviors. The austenitic phase was stabilized during solidification because nickel, which has a partition coefficient near unity in austenitic iron, preferentially remained dissolved within the γ -austenite matrix (Table 2). Phase formation, element solubility, and solute segregation significantly affected the final microstructure and mechanical behavior of the modified ductile Ni-resist alloy during solidification. Deliberately reducing the Ni content to at least 10 weight percent preserved the stability of the austenitic matrix, while gradually adding Cu up to 10 weight percent caused notable changes in the microstructural evolution and solidification dynamics. Tables 3 and 4 summarize the γ -Fe content, Late to Freeze (LTF), nodularity, and nodule count of the 6Cu–18Ni to 10Cu–18Ni ductile iron castings. XRD confirmed that the as-cast structures comprised austenite and multiple additional constituents. The γ -Fe fraction was nearly constant at $94.61 \pm 0.1\%$ across all compositions, suggesting a stable austenitic matrix. This finding aligns with earlier research showing that, despite slight alloying changes, a high Ni content stabilizes the austenitic phase and preserves the matrix composition [13]. Alloyed LTF parameters were balanced, indicating that increasing the Cu content had little effect on the relative proportion of the

secondary constituents. This is consistent with previous studies, which have shown that the addition of Cu mainly affects the graphite morphology rather than dramatically changing the austenite-to-secondary-phase ratio [9].

Cu-induced segregation during solidification may explain the observed decrease in the nodularity. As the Cu concentration increased, carbon diffusion and graphite growth kinetics were locally altered owing to preferential solute enrichment in the interdendritic and late-to-freeze (LTF) regions. Excessive Cu accumulation near grain boundaries may reduce the efficiency of Mg-assisted graphite spheroidization, resulting in partially degenerated or semi-spheroidal graphite structures. All alloys retained nodularity values above 70%, which is generally considered acceptable for maintaining the mechanical advantages of ductile austenitic cast iron, despite the gradual decrease. This implies that the reduced Ni system with up to 10 wt.% Cu still maintained a stable austenitic matrix and primarily spheroidal graphite morphology. Similar findings have been documented in earlier studies on Cu-containing ductile irons, where segregation-induced solidification heterogeneity led to a decreased nodule density and increased graphite degeneration with increasing Cu content [14]. However, the current study also shows that this behavior is largely controlled even at lower Ni contents, suggesting that partial Ni substitution by Cu in ductile Ni-resist alloys may be feasible.

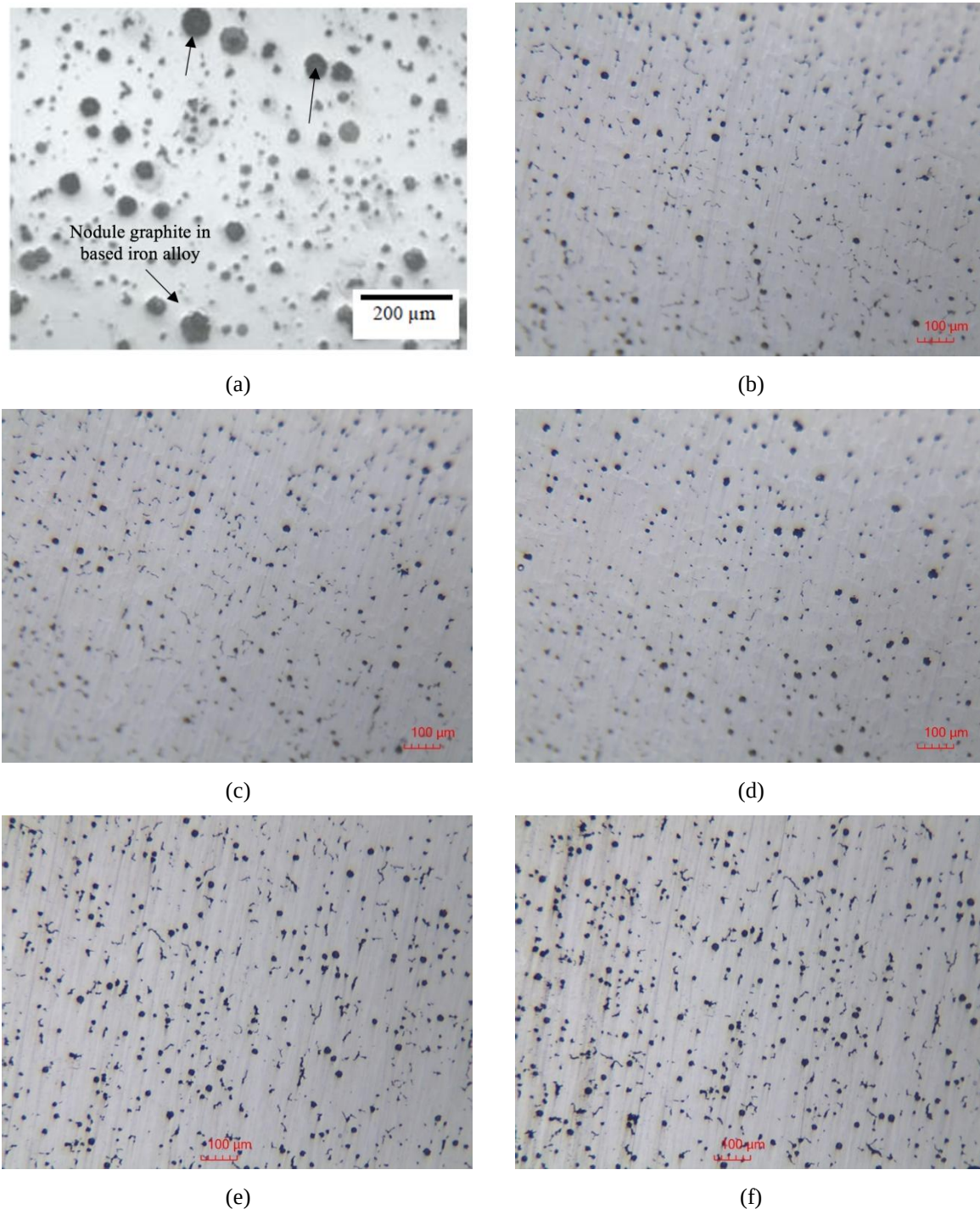


Figure 2. (a) Micrograph shows distribution of graphite (arrow) in based alloy, (b) 10Cu-18Ni, (c) 9Cu-18Ni, (d) 8Cu-18Ni, (e) 7Cu-18Ni, and (f) 6Cu-18Ni

Table 2. Compositional analysis of the matrix and interdendritic regions in a ductile Ni-resist alloy with Cu additions using representative SEM–EDS

Region	Ni (wt.%)	Cu (wt.%)	Fe + Others (wt.%)	Microstructural Implication
Austenitic matrix	~9–11	~2–4	Balance	Stable γ -austenite, uniform phase
Interdendritic/ outer region	~7–9	~8–12	Balance	Cu-rich segregation, graphite degeneration
Grain boundary vicinity	~8–10	~6–10	Balance	Local solute enrichment, stress concentration

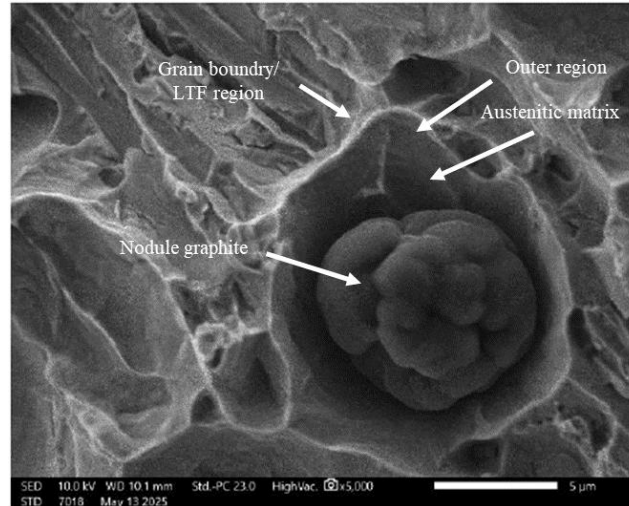


Figure 3. Micrograph of SEM revealing grain boundary of fractured surface

Table 3. Sample of chemical composition of alloy iron composition (wt %) based on spectrometer

Pig iron	Elements							
	C	Si	Mn	Cr	Mg	Ni	Cu	Fe
	3.30	2.27	0.14	0.45	0.015	17.10	>2.50	Balance

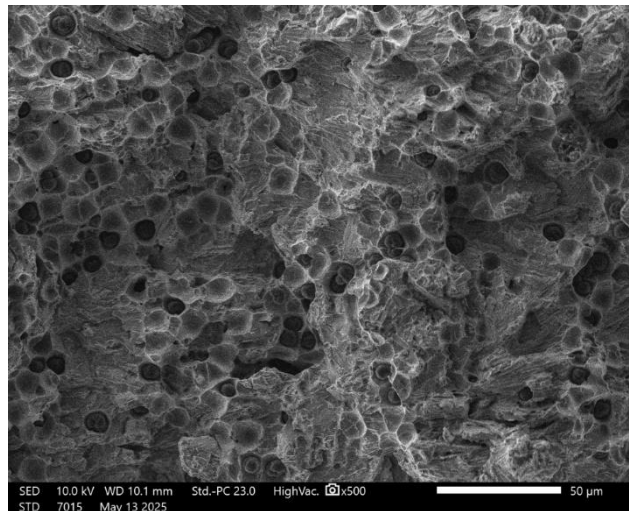


Figure 4. Micrograph of SEM showing nodule graphite and its shell distributed in macro area of fractured surface

Table 4. Amounts of constituent in the microstructure and its properties

Materials	Y-Fe	Late to Freeze LTF	Nodularity	Nodule count (No./mm ²)
6Cu-18Ni	94.61 $\pm$ 0.1	Balance	75.1 $\pm$ 0.3	213.0 $\pm$ 1.0
7Cu-18Ni	94.61 $\pm$ 0.1	Balance	73.1 $\pm$ 0.1	211.3 $\pm$ 0.6
8Cu-18Ni	94.61 $\pm$ 0.1	Balance	72.4 $\pm$ 0.2	207.7 $\pm$ 0.6
9Cu-18Ni	94.61 $\pm$ 0.1	Balance	71.7 $\pm$ 0.3	204.0 $\pm$ 1.0
10Cu-18Ni	94.61 $\pm$ 0.1	Balance	71.3 $\pm$ 0.1	201.7 $\pm$ 0.6

3.2 Dendritic Structure and Solidification Behavior

Alloy compositions exhibited a well-developed austenitic dendritic structure, according to SEM observations. Figures 5(a) and 5(b) show representative micrographs of the primary dendritic arm spacing (DAS) and secondary dendritic arm spacing (SDAS), respectively. As is typical of non-equilibrium solidification in highly alloyed cast irons, the dendritic morphology included coarse primary dendritic trunks accompanied by secondary and tertiary arms. Quantitative measurements demonstrated that progressive dendritic coarsening was encouraged by increasing Cu addition. As shown in Figure 6, the SDAS increased from 20 to 24 μm , whereas the DAS increased from approximately 240 μm in the 6Cu–18Ni alloy to approximately 250 μm in the 10Cu–18Ni alloy. A larger solidification range and slower interface advancement during solidification were indicated by the increase in dendritic arm spacing. This behavior is mainly related to the partitioning properties of Cu during solidification. Cu is rejected into the residual liquid during dendritic growth because its partition coefficient is less than unity, resulting in interdendritic solute enrichment and constitutional supercooling. Consequently, the liquidus temperature decreased locally, lowering the thermal gradients and encouraging dendritic arm coarsening via Ostwald ripening. By prolonging the austenite phase field and preventing ferrite formation during cooling, nickel also substantially contributed to the stabilization of the γ -austenitic phase. The combined Ni–Cu alloying system increased dendritic coarsening at higher Cu concentrations while producing a stable austenitic dendritic network.

The coarsening behavior observed in the current study is consistent with earlier findings on Cu-containing ductile irons, where higher Cu additions led to coarser dendritic structures and broader freezing ranges under comparable cooling conditions [3]. However, the comparatively mild rise in DAS and SDAS indicates that the alloy maintained metallurgical stability despite increasing Cu enrichment. The Late-To-Freeze (LTF) zone formation was also affected by the growth of coarse dendritic regions. During the final stages of solidification, these interdendritic areas became increasingly enriched with Cu, Ni, Mn, and residual solute elements. Because LTF regions are frequently linked to carbide formation, localized hardness increases, decreased graphite nodularity, and stress concentration sites, this segregation behavior is metallurgically significant. The dendritic solidification behavior is the direct source of the LTF regions. Alloying elements (Ni, Cu, and Mn) with partition coefficients less than unity are rejected from the residual liquid as dendrites expand. Consequently, the interdendritic liquid solidifies last and becomes more solute-rich. These LTF regions are frequently linked to elements such as microsegregation, carbide precipitation, shrinkage porosity, and decreased nodularity; therefore, they are metallurgically significant.

Research has verified that interdendritic enrichment and deteriorated local mechanical properties are strongly correlated with LTF zones in Ni-Resist alloys. Higher Ni contents (>18 wt. %) may reduce the LTF effects because of improved austenite stability. Nevertheless, segregation-induced defects are not completely eliminated by this mitigation, which is composition sensitive. During the final stages of solidification, the carbon concentration peaks in the interdendritic regions, where graphite nodules preferentially nucleate. Graphite spheroidization requires a dendritic framework; however, excessive dendritic coarsening can be harmful. Several factors can be emphasized, including high nodularity and fine, uniform dendrites leading to a uniform distribution of graphite nodules. In contrast, graphite degeneration, decreased nodule count, and nodule clustering are caused by coarse and irregular dendrites. This idea explains why, according to experimental ductile Ni-resist alloy studies, increases in the LTF fraction are often accompanied by decreases in nodularity and nodule count. Research has shown that dendritic refinement enhances the stability of graphite morphology in ductile irons, such as ductile Ni-resist alloys [4]. Cu is rejected into the liquid during dendritic growth because its partition coefficient k is less than 1. This results in slower interface advancement, a decreased local thermal gradient, and solute enrichment in the interdendritic liquid. Consequently, the arms thicken and coarsen, increasing the dendritic size, while the dendritic tips grow more slowly. Cu additions also lower the interfacial energy between liquid Fe and γ -Fe. The dendritic arms eventually thickened and rounded. Subsequently, the arm breakup was suppressed. As a result, the dendritic morphology became smoother and coarser.

A highly developed austenitic dendritic network, which is a distinguishing microstructural characteristic of ductile Ni-Resist alloys, is visible in the SEM micrograph. Dendrites form a continuous solidification skeleton with irregular primary trunks and well-developed secondary and tertiary arms. This morphology is indicative of solidification under non-equilibrium conditions, where high concentrations of Ni and Cu cause constitutional supercooling. It was hypothesized that Ni extends the austenitic phase field and inhibits the formation of ferrite and pearlite during cooling by acting as a potent γ -Fe stabilizer. Consequently, γ -Fe dominates dendritic growth, and the extended solidification range of Ni-Resist alloys promotes dendritic-arm thickening. By decreasing the liquidus temperature and boosting solute partitioning into the liquid phase, Cu further intensifies dendritic coarsening. Higher Ni and Cu contents resulted in coarser dendritic structures because they shortened the thermal gradients and lengthened the solute diffusion times. Effective inoculation or rapid cooling can prevent excessive dendritic coarsening. This implies that compositional effects may be partially overridden by the processing conditions. Ni enrichment promotes a low solid-liquid interfacial energy, as indicated by the rounded dendritic arm tips. The estimated dendritic arm spacing (DAS) of several tens of micrometers is consistent with the moderate cooling rates that are typical of investment casting or sand. A chemically diverse microstructure is created by the dendrites, where Ni, Cu, Mn, and residual elements are enriched in the interdendritic regions, whereas the dendritic cores are comparatively lean in solute. Additionally, this spatial distribution is essential for understanding the formation of late-to-freeze (LTF) regions.

In ductile Ni-Resist alloys, Cu typically coarsens the dendrites by increasing their size, particularly when the cooling conditions remain constant [15], [16]. According to the SEM micrograph, as the Cu addition increased, the dendritic DAS grew larger. When 10Cu-18Ni is used, the dendritic size increases to approximately 250 μm from 240 μm at 6Cu-18Ni.

The same pattern was found in dendritic arm spacing SDAS, which ranged from 20 to 24 μm (Figure 6). There are several theories regarding this. Cu is an austenite stabilizer in ductile Ni-resist alloys, comparable to Ni but weaker because of its impact on the solidification range. Cu causes the freezing range to expand, whereas the liquidus and solidus temperatures decrease. This resulted in a broader solidification range, which permitted increased dendritic arm coarsening (Ostwald ripening) and longer dendritic growth times. This resulted in larger primary and secondary dendritic arm spacings (DAS)

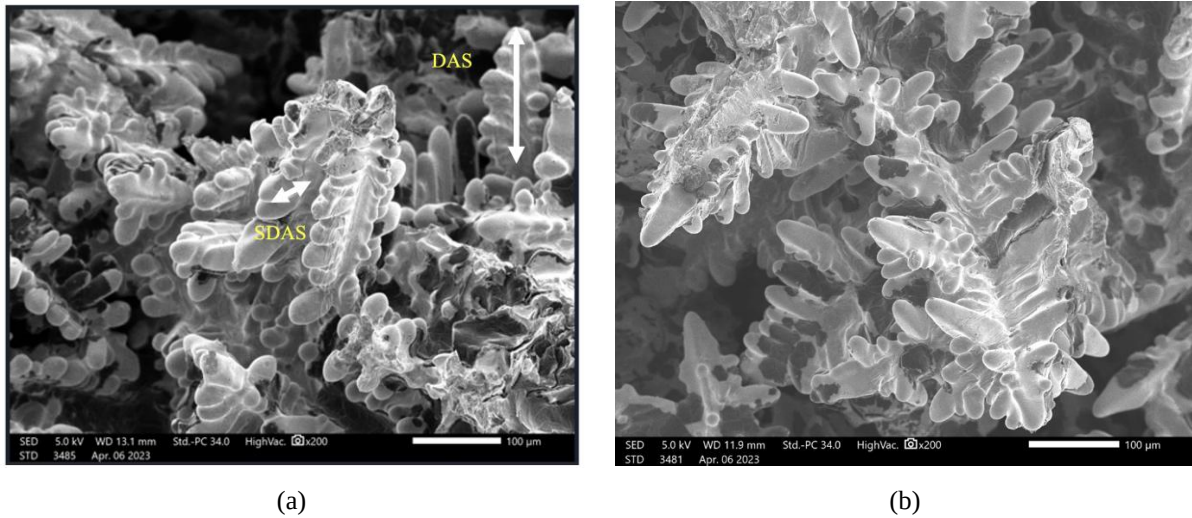


Figure 5. Micrograph shows DAS and SDAS revealed by fractured surface of (a) (6Cu-18Ni) and (b) 10Cu-18Ni.

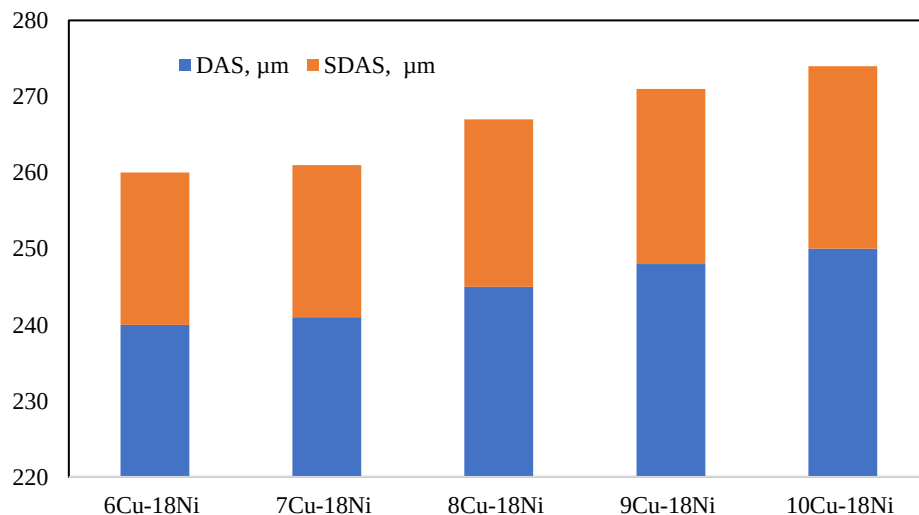


Figure 6. DAS and SDAS dimension of varying Ni-Resist composition percentage

3.3 Segregation Behavior and SEM-EDS Analysis

SEM-EDS analysis was used to examine the segregation properties of the modified ductile Ni-resist alloys. Table 2 summarizes the representative compositional analysis of the dendritic and interdendritic regions. The findings showed that Ni and Cu were partitioned differently during solidification. Owing to its strong austenite-stabilizing effect and a partition coefficient close to unity, nickel remained relatively uniformly distributed within the γ -austenitic matrix. In contrast, Cu showed strong segregation toward the grain boundaries and interdendritic areas. The austenitic matrix contained only approximately 2-4 weight percent Cu, whereas the interdendritic regions contained approximately 8–12 wt. % Cu. This Cu enrichment changes the local solidification chemistry and increases the microstructural heterogeneity. Localized Cu buildup in interdendritic areas altered graphite nucleation conditions and postponed eutectic transformation, which in turn encouraged partial graphite degeneration and decreased nodularity. Furthermore, Cu segregation in the LTF regions caused localized compositional gradients and increased stress-concentration sites within the microstructure. These results align with the solidification theory of solute redistribution in multicomponent alloy systems[17], which states that during dendritic growth, elements with partition coefficients less than unity preferentially segregate into the remaining liquid. The current findings are also consistent with earlier research that found Cu-rich interdendritic segregation in ductile irons with Cu additions above the solubility limit[18]. By directly linking segregation behavior to DAS/SDAS evolution, graphite morphology degradation, and localized hardness variation in reduced-Ni ductile Ni-resist alloys, this study builds on earlier findings.

3.4 Phase Stability and XRD Analysis

According to XRD analysis, all the alloy compositions maintained a predominantly γ -austenitic structure after solidification. The (111), (200), (220), and (311) crystal planes produced distinctive FCC austenitic peaks in the diffraction patterns, as shown in Figure 7. Across all alloy compositions, the calculated γ -Fe content remained roughly constant at $94.61 \pm 0.1\%$, suggesting that the austenitic matrix could still be stabilized by reducing the Ni content to 18 wt percent and adding Cu up to 10 wt percent. The identification of the austenitic structure phase was confirmed by the appearance of distinctive peaks from the FCC phase (austenite) at particular 2θ values using XRD. Other peaks were observed, suggesting that alloying caused a slight phase change in the material. XRD provides important information on the crystal structure, phase identification, grain size, stress analysis, and texture of austenitic iron [19]. The FCC crystal structure at room temperature and under typical conditions serves as the basis for phase analysis-based crystal structure identification [24]. The FCC lattice planes are represented by separate peaks in the XRD pattern of the austenitic material (Figure 7). At $43.5^\circ 2\theta$, $50.5^\circ 2\theta$, $74^\circ 2\theta$, and $90^\circ 2\theta$, these peaks usually contain reflections from planes such as (111), (200), (220), (311), and (222) in the FCC crystal structure. The FCC structure is confirmed by the distinct and crisp peaks of the austenitic phase in the diffraction pattern. The strong austenite-stabilizing effect of Ni is the main reason for the stability of the γ -austenitic phase at high temperatures. Although its impact was less than that of nickel, copper also helped stabilize austenite. The combined Ni–Cu alloying system maintained the FCC matrix structure at room temperature and stopped the ferritic transformation during cooling. The XRD patterns showed no discernible secondary phase transformation, indicating that the investigated Cu additions did not destabilize the austenitic phase within the examined composition range. Despite the overall matrix stability, the localized Cu segregation observed in the SEM–EDS analysis suggests that microstructural heterogeneity continued to develop during non-equilibrium solidification.

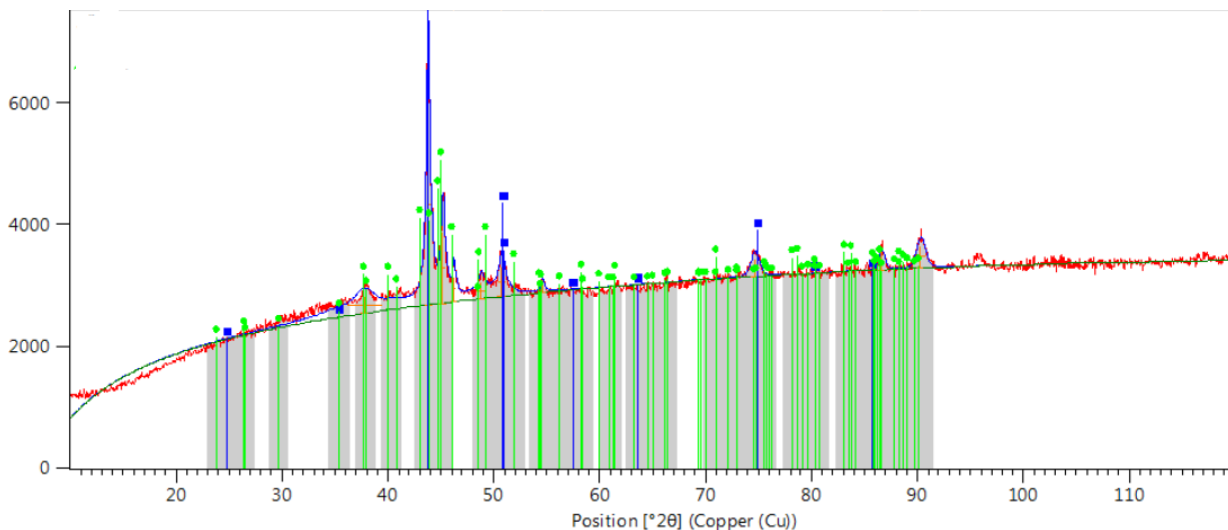


Figure 7. XRD pattern of alloyed iron

Figure 8 shows the SEM-EDS spectrum of the ductile Ni-Resist alloy sample, confirming the distribution and presence of the main alloying and treatment elements in the sample. Strong peaks for Fe, Ni, and Cu dominated the spectrum, suggesting that the alloy was mainly an iron-based matrix alloyed with notable nickel and copper contents, in line with the desired 6Cu–18Ni to 10Cu–18Ni (wt.%) compositions [20]. The highest intensities appear in the iron (Fe) peaks (Fe $L\alpha$, Fe $K\alpha$, and Fe $K\beta$), indicating that Fe is the base element forming the alloy matrix. Ni $L\alpha$, Ni $K\alpha$, and Ni $K\beta$ peaks clearly show the presence of nickel (Ni) and confirm its function as a potent austenite stabilizer in Ni-Resist alloys. Copper (Cu) peaks (Cu $L\alpha$, Cu $K\alpha$, and Cu $K\beta$) are also visible, confirming that Cu was successfully added and dissolved in the alloy system. The coexistence of Fe, Ni, and Cu peaks supports the formation of a Ni-stabilized austenitic γ -Fe matrix, which is typical of ductile Ni-Resist alloys. The remaining magnesium from the in-mold FeSiMg nodularization treatment is indicated by a clear Mg $K\alpha$ peak. Although magnesium is mostly consumed during graphite spheroidization, traces usually remain, indicating successful nodularization. The FeSiMg nodularizer and inoculant additions, along with the potential contributions from the silica-based molding material, caused a prominent Si $K\alpha$ peak. Silicon is essential for stabilizing the ductile iron microstructure and promoting graphite formation. The SEM-EDS spectrum confirmed the successful incorporation of all the target alloying elements into the Ni-Resist alloy. Within the measurement sensitivity, no unanticipated or harmful impurities were detected. The presence of Mg and Si confirmed the effectiveness of the in-mold modularization and inoculation procedures. The Fe–Ni–Cu elemental combination supports the austenitic dendritic matrices, solute-enriched interdendritic regions, and stable spheroidal graphite morphology. Although EDS provides qualitative to semi-quantitative elemental identification, it cannot resolve nanoscale microsegregation issues. Nonetheless, the identified elemental peaks fit well with the microstructural analysis of dendritic solidification and segregation behavior.

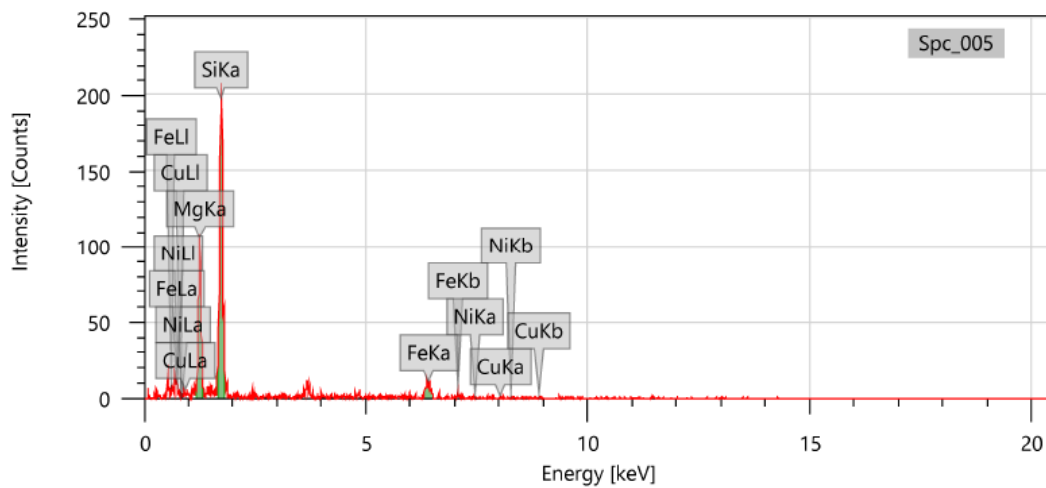


Figure 8. The ductile Ni-Resist alloy's SEM-EDS spectrum confirms the successful alloying and processing process by displaying dominant Fe, Ni, and Cu peaks along with residual Mg and Si from in-mold nodularization and inoculation treatments

3.5 Hardness Behavior

Macro-hardness and micro-hardness measurements were used to assess the influence of Cu addition on the mechanical response of the modified ductile Ni-resist alloys. The average macro-hardness increased progressively from 160.0 $\pm$ 8.7 HB for the 6Cu–18Ni alloy to 194.3 $\pm$ 5.1 HB for the 10Cu–18Ni alloy (Table 5). This increase in hardness is primarily attributed to the solid-solution strengthening of the γ -austenitic matrix resulting from Cu dissolution within the Fe-based lattice. Microhardness measurements further revealed localized hardness variations within the microstructure. The dendritic cores exhibited an average hardness of 215.7 $\pm$ 7.4 HV, whereas the Cu-rich interdendritic and late-to-freeze (LTF) regions exhibited significantly higher hardness values of 298.3 $\pm$ 1.5 HV. The higher hardness observed in the interdendritic regions is associated with Cu segregation and localized solute enrichment during solidification, which increases lattice distortion and resistance to plastic deformation. Cu segregation and localized solute enrichment during solidification increased the microhardness in the interdendritic areas. The localized lattice distortion caused by the buildup of Cu and Ni in these areas limited dislocation motion and strengthened the resistance to plastic deformation. Additionally, coarse dendritic structures and reduced graphite nodularity caused a heterogeneous hardness distribution and localized stress concentrations. The addition of Cu increased the hardness; however, the increased microstructural heterogeneity may have caused excessive segregation, which can detrimentally affect the ductility and toughness. Therefore, in reduced-Ni ductile Ni-resist alloys, the Cu content must be optimized to balance the hardness enhancement with the graphite stability and segregation control. The observed strengthening behavior aligns with earlier research on Cu-alloyed ductile irons, where Cu serves as a solid-solution strengthening element and an austenite stabilizer. In low-Ni austenitic ductile iron systems, the current study also shows a strong correlation between Cu segregation, dendritic evolution, and localized hardness variation.

Table 5 Macro-hardness and micro-hardness measurements

Materials	Brinell Hardness (HB)	Microhardness (HV)
6Cu-18Ni	160.0 $\pm$ 8.7	215.7 $\pm$ 7.4
7Cu-18Ni	168.7 $\pm$ 4.0	239.0 $\pm$ 12.8
8Cu-18Ni	176.3 $\pm$ 6.4	275.3 $\pm$ 4.5
9Cu-18Ni	189.0 $\pm$ 6.2	290.7 $\pm$ 5.9
10Cu-18Ni	194.3 $\pm$ 5.1	298.3 $\pm$ 1.5

4. Conclusions

The summary of findings is as follows

- XRD analysis revealed that a stable γ -austenitic matrix with approximately 94.61% γ -Fe content was maintained when the Cu content was increased from 6 wt.% to 10 wt.% in modified ductile Ni-resist alloys containing 18 wt.% Ni. However, the addition of Cu encouraged interdendritic segregation during solidification, increasing the microstructural heterogeneity and affecting the graphite growth behavior.
- As the Cu content increased, graphite nodularity gradually dropped from 75.1 $\pm$ 0.3% to 71.3 $\pm$ 0.1%, and nodule count dropped from 213.0 $\pm$ 1.0 to 201.7 $\pm$ 0.6 nodules/mm². All alloys maintained a nodularity value above 70% despite graphite degeneration, indicating the preservation of primarily spheroidal graphite morphology.
- Increasing Cu addition promoted dendritic coarsening; DAS increased from approximately 240 to 250 μ m, and SDAS increased from 20 to 24 μ m. SEM-EDS analysis confirmed Cu segregation during the last stages of solidification and showed Cu enrichment in the interdendritic and late-to-freeze (LTF) regions.

- iv) In contrast to graphite precipitation, the LTF regions exhibited a stronger propensity for carbide formation and localized enrichment of alloying elements. These distinct areas increased the microstructural heterogeneity and localized hardness.
- v) As the Cu content increased, the macro-hardness increased from 160.0 ± 8.7 HB to 194.3 ± 5.1 HB, and the micro-hardness increased from 215.7 ± 7.4 HV to 298.3 ± 1.5 HV. The main causes of the hardness improvement are the Cu-induced solid-solution strengthening and segregation strengthening within the interdendritic regions.
- vi) The results show that, in addition to nominal alloy composition, designers of low-Ni ductile Ni-resist systems should consider micro-segregation behavior, dendritic evolution, and graphite morphology during solidification. Therefore, achieving a balance between austenitic phase stability, graphite quality, hardness enhancement, and overall microstructural uniformity requires the optimization of Cu content.

Acknowledgements

The authors sincerely thank the Faculty of Mechanical and Automotive Engineering Technology, Automotive Excellence Center (AEC), Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA), and the Ministry of Higher Education (Malaysia) for providing the laboratory facilities and financial assistance.

Funding

This study received financial support from FRGS grants and university grants under project no. RDU220135 and RDU220305, respectively.

Declaration of Competing Interest

The authors declare no conflict of interest.

Credit Authorship Contribution Statement

M. Aminuddin: Conceptualization; Methodology; Investigation; Writing original draft

M. Mohd Rashidi: Project administration; Writing-review & revise; Validation; Supervision

Availability of Data and Materials

The data supporting the findings of this study are available upon request from the corresponding author.

Ethics Declarations

This study did not involve human participants or animal subjects. Therefore, ethical approval was not required.

Generative Artificial Intelligence Declarations

The authors claim that artificial intelligence-assisted technologies, such as generative AI, were not used to generate content, ideas, or theories. We have used AI to enhance readability and refine the language. This was used with extreme human control and supervision. The authors take full responsibility for reviewing and approving the content of this manuscript.

References

- [1] N. Fatahalla, A. AbuElEzz, and M. Semeida, "C, Si and Ni as alloying elements to vary carbon equivalent of austenitic ductile cast iron: Microstructure and mechanical properties," *Materials Science and Engineering: A*, vol. 504, no. 1–2, pp. 81–89, 2009, <https://doi.org/10.1016/j.msea.2008.10.019>.
- [2] J. O. Choi, J. Y. Kim, C. O. Choi, J. K. Kim, and P. K. Rohatgi, "Effect of rare earth element on microstructure formation and mechanical properties of thin wall ductile iron castings," *Materials Science and Engineering: A*, vol. 383, no. 2, pp. 323–333, 2004, <https://doi.org/10.1016/j.msea.2004.04.060>.
- [3] W. Xu, W. Zhang, X. Liu, *et al.*, "Effect of austenitizing temperatures on microstructure and exceptional strength-plasticity synergy in heavy-section pearlitic ductile iron," *Materials Characterization*, vol. 230, Art. no. 115811, 2025, <https://doi.org/10.1016/j.matchar.2025.115811>.
- [4] C. Pittel, C. Bleicher, K. Lipp, and A. Merten, "Production of efficient nodular cast iron gears—Considering the fatigue strength and rolling contact fatigue strength based on the local microstructure," *International Journal of Metalcasting*, vol. 19, pp. 3107–3126, 2025, <https://doi.org/10.1007/s40962-024-01525-z>.
- [5] M. Bork, R. Chulist, M. Górny, M. Kowalczyk, and J. Marosz, "The influence of nickel content on the structure parameters and magnetic properties of austenitic ductile iron castings," *Archives of Civil and Mechanical Engineering*, vol. 25, no. 3, Art. no. 117, 2025, <https://doi.org/10.1007/s43452-025-01173-y>.
- [6] M. Bork, M. Górny, Ł. Gondek, J. Morgiel, and K. Morgiel, "The evaluation of thermal stability, electric conductivity and carbide morphology of austenitic ductile iron castings," *Materials*, vol. 18, no. 20, Art. no. 4734, 2025, <https://doi.org/10.3390/ma18204734>.
- [7] K. I. Yaakob, M. R. Maarof, and M. A. Rosnizan, "Evaluation of elevated temperature oxidation of higher manganese Ni-resist alloy," *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, vol. 122, no. 2, pp. 52–61, 2024, <https://doi.org/10.37934/arfmts.122.2.5261>.

- [8] A. Vaško, V. Zatkalíková, M. Uhrčík, and V. Kaňa, “Corrosion resistance of austenitic NiMn-nodular cast iron in NaCl solution,” *Archives of Metallurgy and Materials*, vol. 69, no. 3, pp. 1115–1122, 2024, <https://doi.org/10.24425/amm.2024.150932>.
- [9] S. Xiang, S. Jonsson, R. P. Babu, B. Zhu, and J. Odqvist, “Influence of tension and compression dwell on the creep-fatigue properties of the austenitic cast iron Ni-resist D5S,” *Materials Science and Engineering: A*, vol. 814, Art. no. 141179, 2021, <https://doi.org/10.1016/j.msea.2021.141179>.
- [10] X. Wang, B. Jiang, C. Yang, et al., “Effects of Ni addition on the microstructure and low-temperature impact behavior of ductile iron after ferritization treatment,” *Materials Today Communications*, vol. 50, Art. no. 114513, 2026, <https://doi.org/10.1016/j.mtcomm.2025.114513>.
- [11] G. A. Çelik, M.-I. T. Tzini, Ş. Polat, Ş. H. Atapek, and G. N. Haidemenopoulos, “Thermal and microstructural characterization of a novel ductile cast iron modified by aluminum addition,” *International Journal of Minerals, Metallurgy and Materials*, vol. 27, no. 2, pp. 190–199, 2020, <https://doi.org/10.1007/s12613-019-1876-8>.
- [12] S.-Y. Shin, S.-H. Ha, D.-H. Kim, and J. Choi, “Effect of Cu addition above the solubility limit on microstructure formation and Cu segregation in 800 MPa grade ductile cast iron during solidification,” *Archives of Metallurgy and Materials*, vol. 69, no. 2, pp. 425–428, 2024, <https://doi.org/10.24425/amm.2024.149759>.
- [13] M. M. Rashidi and M. H. Idris, “The effects of solidification on the microstructure and mechanical properties of modified ductile Ni-resist iron with a high manganese content,” *Materials Science and Engineering: A*, vol. 597, pp. 395–407, 2014, <https://doi.org/10.1016/j.msea.2013.12.070>.
- [14] J. Tlatlik, J. Hohe, and I. Varfolomeev, “Composite descriptors for cast iron microstructures: A data-driven approach to understanding microstructure–property relationships,” *Engineering Fracture Mechanics*, vol. 330, Art. no. 111655, 2025, <https://doi.org/10.1016/j.engfracmech.2025.111655>.
- [15] C. Öberg, R. Rablbauer, B. Zhu, and S. Jonsson, “Monotonic and cyclic creep of cast materials for exhaust manifolds,” *SAE International Journal of Materials and Manufacturing*, vol. 12, no. 2, pp. 149–162, 2019, <https://doi.org/10.4271/05-12-02-0012>.
- [16] G. Di Egidio, P. Ferro, and A. Morri, “Microstructure in non-standard heavy section ductile iron castings: Influence of solidification time and casting size,” *Journal of Iron and Steel Research International*, vol. 32, no. 12, pp. 4249–4263, 2025, <https://doi.org/10.1007/s42243-025-01598-y>.
- [17] Y. Xu, Y. Xu, W. Cao, X. Meng, F. Zhang, and X. Lv, “Effect of solute elements (B, C, N, O) on γ -Fe $\Sigma 5$ (210)[001] grain boundary: A first-principles study,” *Journal of Iron and Steel Research International*, vol. 32, no. 6, pp. 1716–1724, 2025, <https://doi.org/10.1007/s42243-025-01436-1>.
- [18] S. N. Lekakh, M. Li, and L. Godlewski, “High-temperature performance of alloyed cast irons and Cr/Ni austenitic steels—An overview and discussion,” *International Journal of Metalcasting*, vol. 20, no. 4, pp. 2114–2132, 2026, <https://doi.org/10.1007/s40962-025-01775-5>.
- [19] M. Górný, G. Angella, K. Jalava, Ł. Gondek, J. Marosz, and B. Cygan, “The effect of austenitization on ausferrite stability and section sensitivity of Ni and Cu alloyed austempered ductile iron,” *Materials Today Communications*, vol. 54, Art. no. 115606, 2026, <https://doi.org/10.1016/j.mtcomm.2026.115606>.
- [20] M. Lanchas, D. O. Fernandino, J. Massone, and R. Boeri, “Revealing, modification and influence of the austenitic grain size on the solid-state transformations in ductile iron,” *International Journal of Metalcasting*, vol. 19, no. 6, pp. 3378–3391, 2025, <https://doi.org/10.1007/s40962-025-01547-1>.