

EFFECTS OF SOLUTE ELEMENTS AND CERAMIC PARTICLE REINFORCEMENT ON GRAIN GROWTH AND HARDNESS OF NANOCRYSTALLINE 304L STAINLESS STEEL¹Gizem AYDIN, ²Cantekin KAYKILARLI, ²Hasan KOTAN¹Bursa Technical University, Graduate School, Department of Metallurgical & Materials Engineering, Bursa, 16310, Türkiye, gizem.aydinn01@gmail.com²Bursa Technical University, Department of Metallurgical & Materials Engineering, Bursa, 16310, Türkiye, cantekin.kaykilarli@btu.edu.tr, hasan.kotan@btu.edu.tr<https://doi.org/10.37904/metal.2026.5244>**Abstract**

In this study, an AISI 304L stainless steel was produced with a nanocrystalline structure using a high-energy mechanical alloying technique with Y-element and nanoscale B₄C additions and annealed at 900 °C for 1h. Structural changes and mechanical properties were investigated using X-ray diffraction analysis, Archimedes density and microhardness test, respectively. The results showed that the crystal structure of 304L stainless steel, which has a face-centered cubic (fcc) lattice at equilibrium, transforms into martensite with a body-centered cubic (bcc) lattice due to the severe plastic deformation induced by high-energy mechanical alloying. Upon thermal exposure, a reverse martensite-to-austenite phase transformation was triggered. The relative density of 304L steel improved with the addition of Y and B₄C. A significant increase in hardness was observed after mechanical alloying and attributed to the formation of a nanocrystalline structure and deformation-induced martensite. However, annealing led to a decrease in hardness, which was associated with grain growth. This reduction in hardness was less pronounced in 304L containing solute elements and ceramic particle additions. Evaluation of the hardness changes together with XRD peak broadening results indicated that solute addition and ceramic particle reinforcement play an important role in restricting grain growth.

Keywords: Stainless steels, mechanical alloying, thermal stability, martensitic transformation**1. INTRODUCTION**

Nanocrystalline materials consist of single- or multi-phase polycrystalline structures with grain sizes smaller than 100 nm [1]. Due to their ultrafine grain sizes, they exhibit superior physical and mechanical properties compared to traditional microstructures. In particular, hardness and high strength make these materials suitable for advanced engineering applications [2]. The relationship between the nano-scale grain structure of nanocrystalline materials and the material's mechanical properties is expressed by the Hall-Petch equation given in Equation (1). The Hall-Petch equation describes how dislocation movement becomes more difficult as grain size decreases due to the increased number of grain boundaries, thereby increasing the material's strength [3].

$$\sigma_y = \sigma_0 + kd^{-1/2} \quad (1)$$

where:

 σ_y – the yield strength σ_0 – the resistance of the lattice to dislocation motion (a constant)

k - strengthening coefficient (a constant unique to each material)

d - the grain diameter

Grade 304L stainless steel, an austenitic stainless steel, is well known for its excellent formability and corrosion resistance. The production of this alloy in a nanocrystalline form offers the potential for enhancement of mechanical properties [4]. However, certain inherent limitations of the nanocrystalline structure restrict the practical application of these materials [5]. One of the primary limitations is their low thermal stability, which arises from the high grain boundary volume fraction. In nanocrystalline materials, a significant portion of the free energy is associated with grain boundaries, creating a strong driving force for grain growth at elevated temperatures. Consequently, the microstructure can rapidly evolve into a coarser-grained state. This transformation leads to a deterioration in mechanical properties, thereby limiting their suitability for structural engineering applications [6, 7]. Therefore, controlling grain growth is essential to ensure that nanocrystalline stainless steels maintain their mechanical integrity under high-temperature conditions. Various approaches to limiting grain growth have been reported in the literature. Fundamentally, these approaches are based on kinetic and thermodynamic stabilization mechanisms, both of which play a significant role in preserving microstructural stability at elevated temperatures. It is widely accepted that solute atoms segregate to grain boundaries, thereby reducing grain boundary energy and mobility [8, 9]. Li et al. studied [10] Hf-added Fe-Cr alloy produced via mechanical alloying method and reported a stable microstructure under high-temperature conditions. This phenomenon was similarly explained by solute drag and thermodynamic stabilization.

Various production methods are used to obtain nanocrystalline structures. Depending on the technique used, the final microstructure and consequently the material properties may vary. Among these production methods, the high-energy mechanical alloying technique stands out for its ability to produce materials with a very fine grain structure through a plastic deformation process occurring in the solid state [11]. Due to the high deformation energy generated at this stage, martensitic transformations may occur in austenitic stainless steels [12]. Subsequent heat treatments promote the reverse transformation of deformation-induced martensite into austenite, leading to the development of a transformation process within the microstructure that is governed by alloying and temperature. Forouzan et al. [13] reported a deformation-induced martensitic transformation and the subsequent reversion upon heat treatment in AISI 304L austenitic stainless steel.

Despite existing studies, further investigation is required into the effects of solute elements and nanoscale ceramic additives on phase transformations and microstructural stability under annealing conditions. In this study, nanocrystalline 304L stainless steels, with and without Y and B₄C additions, were produced via high-energy mechanical alloying. The alloys were annealed at 900 °C to investigate structural evolution as a function of composition and temperature. Microstructural stability was further assessed through hardness measurements, enabling correlation between grain size and mechanical properties.

2. EXPERIMENTAL PROCEDURE

In this study, a commercially purchased, high-purity AISI 304L stainless steel powders with a composition of Fe-19Cr-11Ni (wt%) was used as the base material. High-purity Y and B₄C powders, each at a weight percentage of 1 %, were added to the base material. The alloy compositions were prepared in a glove box system under a protective argon atmosphere. The ball-to-powder mass ratio for mechanical alloying was set at 10:1. A high-energy ball mill was used for mechanical alloying. The powders were placed in a hardened steel vial with 440C stainless steel balls, and the mechanical alloying process was carried out at room temperature for 20 hours. The powders, following the completion of the mechanical alloying process, were consolidated at room temperature using a single-axis hydraulic pressing. Each sample was compacted under a load of 3 tons for 3 min., resulting in cylindrical green compacts with a diameter of 5 mm. A sintering process was applied to investigate the structural changes and mechanical properties of nanocrystalline stainless steels with and without Y and B₄C additions. The samples were sintered at 900 °C for 1 h at a heating and cooling

rate of 5 °C/min under a protective argon atmosphere in a tube furnace. XRD analysis was performed using a Bruker/D8 Advance after the grinding and polishing processes were completed. XRD scans were conducted in the 35-95° range at a scanning rate of 1°/min. The sintered samples' density was obtained according to Archimedes' method in an ethanol medium. Microhardness tests were performed using a QNE5S hardness tester to investigate the mechanical properties of the stainless-steel alloy in relation to the additives and sintering temperature. The hardness tests were conducted under conditions of a 20 g load and a 10-second dwell time. Measurements were taken from six different regions of each sample, and the standard deviation was calculated.

3. RESULT AND DISCUSSION

3.1 Structural Characterization

Figure 1a shows the XRD patterns for 304L and 304L+1Y+1B₄C stainless steels powders obtained after the mechanical alloying process. AISI 304L, which belongs to the austenitic stainless-steel group, is known to have a face-centered cubic (fcc) crystal structure at equilibrium. As seen in **Figure 1**, both alloys produced after the mechanical alloying process are solid solutions with a body-centered cubic (bcc) crystal structure. In austenitic stainless steels, phase transformations may occur due to the severe plastic deformation that takes place during mechanical alloying [14, 15]. That is, if the stress exceeds a critical value during severe plastic deformation induced by high energy mechanical alloying and the material is subjected to deformation at a temperature below the martensite transformation temperature (M_d), a deformation-induced martensitic phase transformation may occur. This phase transformation depends on the stacking fault energy and, consequently, the material's chemical composition, and occurs due to the increased difficulty of dislocation movement [16]. **Figure 1b** clearly reflects the structural evolution after sintering and the reverse transformation behavior. The XRD patterns show a clear reappearance and sharpening of fcc austenite peaks, indicating that a significant portion of the deformation-induced martensite has reverted back to the stable austenitic phase. This martensite-to-austenite reverse transformation is thermodynamically driven and promoted by atomic diffusion during heat treatment. Importantly, the extent of this reverse transformation appears to be more pronounced in the Y and B₄C added alloy. This suggests that these additions not only influence phase stability but also affect transformation kinetics. Yttrium (Y), known for its strong affinity for segregating to defects such as grain boundaries and interfaces, can reduce defect energy and modify diffusion pathways. Meanwhile, B₄C-related reactions or dispersed ceramic particles may act as effective pinning sites, refining the microstructure [17]. Together, these effects likely promote a more complete martensite reversion compared to the base 304L alloy.

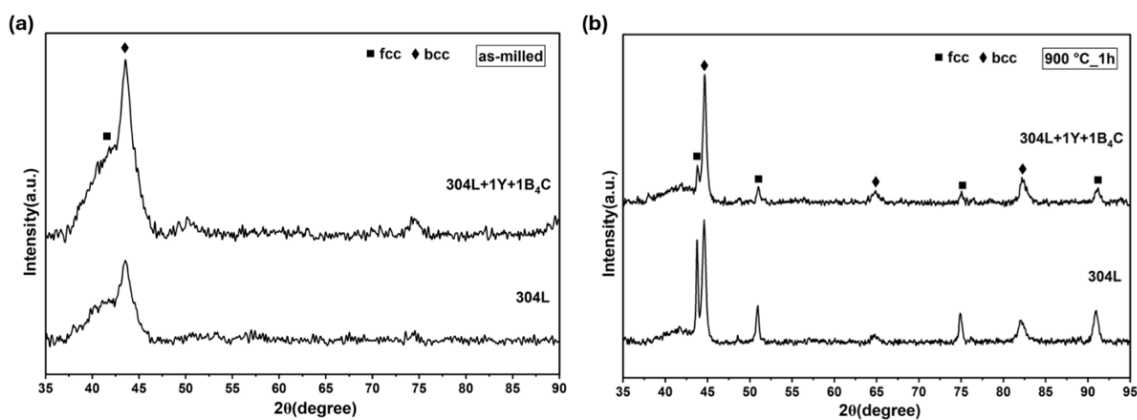


Figure 1 XRD patterns of (a) as-milled and (b) annealed 304L and 304L+1Y+1B₄C stainless steels

The fcc/bcc phase ratios were calculated after annealing at 900 °C. For the 304L alloy, the crystal structure consisted of 0.717/0.283 fcc/bcc, respectively. In contrast, the 1Y + 1B₄C-added stainless steel exhibited an fcc/bcc ratio of 0.364/0.636, indicating a significantly higher fraction of the bcc phase. This pronounced difference suggests that the addition of Y and B₄C alters both phase stability and transformation kinetics during annealing. The higher retained bcc fraction in the modified alloy implies that the reverse transformation from deformation-induced martensite (bcc) to austenite (fcc) is partially suppressed. This behavior can be attributed to several factors. Y tends to segregate at lattice defects such as dislocations and grain boundaries, reducing atomic mobility and thereby hindering the diffusion-controlled martensite-to-austenite reversion during annealing at 900 °C. Additionally, both Y and B₄C can modify the local chemical composition and effectively reduce the stacking fault energy, which favors the stabilization of bcc martensite over fcc austenite. As a result, compared to the base 304L alloy, the Y and B₄C-added material retains a larger fraction of the bcc phase after annealing, indicating a slower or less complete reverse transformation and enhanced martensite stability.

3.2 Relative Density and Hardness Results

After sintering at 900 °C, the relative density of the 304L steel was measured as 82.2 %, whereas 304L + 1Y + 1B₄C steel exhibited a higher value of 88.3 %, as indicated in **Figure 2a**. This difference indicates that the addition of Y and B₄C positively influences densification under the applied sintering conditions. The improved relative density in the modified alloy can be primarily attributed to its finer initial particle size after mechanical alloying, which enhances particle packing and promotes diffusion during sintering. Although the presence of hard B₄C particles could potentially hinder densification, this effect appears to be outweighed by the benefits of refined powder structure. As a result, the Y and B₄C-added steel achieves a higher densification level. Nevertheless, while this difference contributes to the overall mechanical response, the observed improvements in hardness, as given in **Figure 2b**, are still predominantly governed by phase composition and microstructural factors. First, in the as-milled state, the hardness values were significantly high for both steels, measured as 879.5 ± 28.6 HV for 304L and 1124.5 ± 40.9 HV for the 304L + 1Y + 1B₄C alloy. After sintering under the same conditions, the hardness decreased to 533.8 ± 38.4 HV for 304L and 883.7 ± 42.2 HV for the Y and B₄C - added stainless steel. This reduction in hardness in both steels after sintering is associated with recovery processes, grain growth, and the partial reverse transformation of deformation-induced martensite to austenite.

Nevertheless, the Y and B₄C-added steel maintains higher hardness after sintering. This substantial increase in hardness can be directly correlated with the differences in fcc/bcc phase ratios as well as the microstructural effects introduced by Y and B₄C additions [18, 19]. As previously determined, the base 304L steel predominantly consists of the fcc (austenitic) phase after annealing, whereas the modified steel retains a much higher fraction of the bcc phase, which corresponds to deformation-induced martensite. Since bcc martensite is inherently harder and stronger than fcc austenite due to its lower atomic packing factor and higher resistance to dislocation motion, the increased bcc fraction in the Y and B₄C-added steel significantly contributes to the observed hardness enhancement.

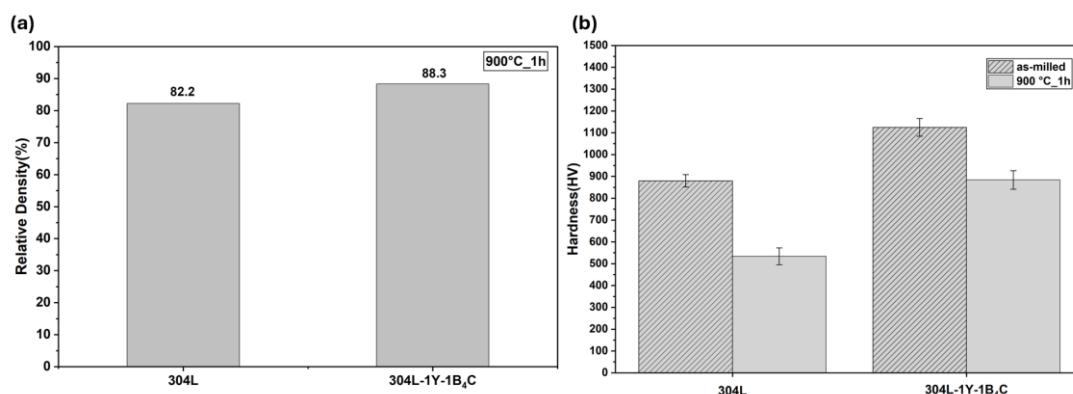


Figure 2 (a) Relative density and (b) hardness results of 304L and 304L+1Y+1B₄C stainless steels

In addition, the role of Y and B₄C as thermal stabilizers further explains the hardness difference. Y is known to segregate at defects such as grain boundaries and dislocations, where it reduces boundary energy and suppresses atomic diffusion during annealing. This effect limits recovery and recrystallization processes, thereby preserving a high defect density and stabilizing the microstructure. Similarly, B₄C can act as strong obstacles to dislocation movement (dispersion strengthening) and also serve as pinning sites that inhibit grain growth [20]. Moreover, the combined presence of Y and B₄C contributes to microstructural refinement, resulting in smaller grain sizes. According to the Hall–Petch relationship, a decrease in grain size leads to an increase in hardness due to the increased resistance to dislocation motion at grain boundaries. The pinning effect of B₄C particles and the segregation behavior of Y both contribute to maintaining this refined structure during heat treatment.

Overall, the significantly higher hardness of the Y and B₄C-added stainless steel can be attributed to (i) the higher retained fraction of hard bcc martensite, (ii) dispersion strengthening from B₄C-related phases, and (iii) grain refinement induced by Y and B₄C additions. These combined mechanisms result in a microstructure that is more resistant to plastic deformation compared to the base 304L alloy.

4. CONCLUSION

In this study, the effects of Y and B₄C additions on the phase evolution and mechanical properties of mechanically alloyed 304L stainless steel were investigated. Y and B₄C additions significantly influenced the phase evolution and mechanical properties of mechanically alloyed 304L stainless steel. While annealing promoted partial reversion to fcc austenite, the modified steel with Y and B₄C additions retained a higher fraction of bcc martensite, indicating enhanced phase stability. This, combined with dispersion strengthening and microstructural refinement, resulted in a substantial increase in hardness compared to the base 304L steel.

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