Vickers Hardness Evaluation of a High-Entropy Alloy after Melting in a Boron Nitride-Coated Crucible and Subsequent Pack Carburizing

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Abstract - High-Entropy Alloys (HEAs) belong to a group of materials featuring combinations of at least five elements in equimolar proportions, enabling the formation of body-centered cubic (BCC) structures with high-temperature resistance, wear resistance, and high hardness. This research developed a seven-element HEA designed to achieve a BCC structure, prepared via induction furnace melting. After melting the alloy designated as L5.7, Vickers hardness was measured; subsequently, a pack carburizing heat treatment was performed to increase hardness. Two melts were conducted: the first in a high-density graphite crucible and the second in a hexagonal boron nitride (h-BN) crucible. The average hardness result for the melt performed in the BN crucible was 19.57% higher compared to the other. For this same melting condition, after carburizing, an average hardness of 1783 HV was obtained—49.71% higher than the carburized sample melted in the uncoated crucible. Based on the results, it is concluded that boron nitride (h-BN) contributed to the increase in Vickers hardness both before and after the thermochemical treatment.

Keywords: High-Entropy Alloy; melting; boron nitride; pack carburizing; Vickers hardness.

I. INTRODUCTION

High-Entropy Alloys (HEAs) and Refractory High-Entropy Alloys (RHEAs) are composed of multiple elements, including refractory metals. These alloys exhibit high melting points and excellent microstructural stability, coupled with superior mechanical properties. The addition of elements such as Al, Cr, Si, Ti, and Zr improves properties such as oxidation resistance while reducing density, thereby expanding their applications in high-temperature environments [1]; [2] and [3].

Metallic alloys began to be utilized following the discovery of bronze alloys, as the resulting material exhibited superior mechanical strength compared to pure metals. With the evolution of materials (Fig. 1), metallic alloys were implemented across diverse fields, replacing the original metals [4].
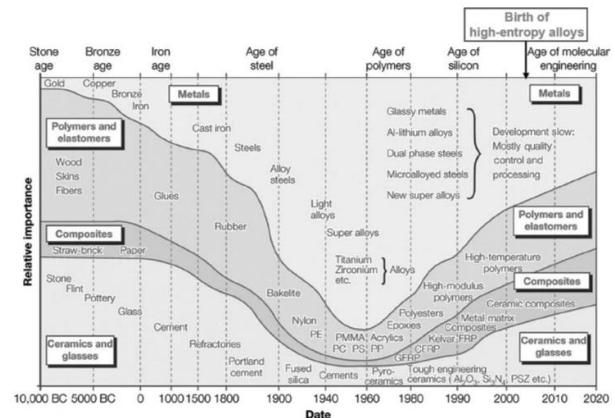

Figure 1. Historical evolution of engineering materials, highlighting the emergence of HEAs, published in Advanced Engineering Materials [5].

Most metallic alloys are composed of a single primary element, chosen for its properties, with other elements added in smaller quantities to contribute specific characteristics [6]. Thus, the combination within the metallic alloy's composition provides the desired properties, making them widely used across various industrial sectors. A classic example is steel, obtained from an alloy of iron—the base and primary element—and carbon, which is essential for providing the steel with its hardness and strength properties [7].

In addition to high mechanical strength and wear resistance, High-Entropy Alloys exhibit high thermal stability and oxidation resistance. These are related to the core effects that the high-entropy system promotes within the crystal structure [1]: the high-entropy effect, the lattice distortion effect, the sluggish diffusion effect, and the cocktail effect [8].

Currently, HEAs compete with conventional materials due to their properties and versatility, primarily driven by the

aforementioned characteristics. Other features under study include plastic deformation and various hardening mechanisms (work hardening, solid solution strengthening, or precipitation hardening). One of the sectors utilizing HEAs is the manufacturing of tools and components that require high performance in terms of durability and safety, derived from their mechanical properties [9; 10]. These alloys have significant applications in the metal-mechanical industry and, through heat treatments, achieve the desired mechanical properties.

Thermochemical treatments are used to promote surface hardening of a part or alloy through chemical changes on the exposed surface when another chemical element is added [11]. Carbon is the most commonly used element, although nitrogen and boron may also be utilized. Among existing heat treatments, the most common is pack carburizing, which promotes the formation of a surface layer with high carbon content to maintain a tough core through diffusion [12].

Pack carburizing employs alloy-steel or alumina boxes to hold the parts, filling the container with carburizing material (coke, graphite, carbonates, among others). The advantages of pack carburizing include the possibility of using different furnaces for the process, making it cost-effective; however, disadvantages include the difficulty in achieving surface carbon uniformity and the challenging control over the variables involved, particularly time and temperature [11].

For this study, the HEA 5.7 alloy was melted in an induction furnace using graphite and boron nitride (h-BN) crucibles. Subsequently, pack carburizing was performed using a carburizing compound consisting of 60% coke and 40% calcium carbonate ($CaCO_3$).

The use of an h-BN crucible was adopted as it is a common practice in the melting process of High-Entropy Alloys, particularly those containing refractory elements (Mo, Nb, Ta, and W). It provides a barrier that ensures alloy purity, as certain elements in the composition react with the BN, thereby increasing the alloy's hardness [13; 14].

Boron nitride (BN) is a binary chemical compound composed of boron and nitrogen atoms, exhibiting properties similar to those of carbon-based compounds. Notably, the B-N bond is isoelectronic to the C-C bond; furthermore, the size and electronegativity of the carbon atom are intermediate between those of boron and nitrogen [15].

The boron nitride utilized in this study possesses a hexagonal crystal structure (h-BN) and is considered an advanced ceramic—white in color and featuring a layered structure similar to that of graphite (Fig. 2) [16; 17]. Its standout properties include thermal and chemical stability, high thermal conductivity, and lubricating properties, which lead to its use as high-temperature coatings [19; 20].

Each layer demonstrates that boron and nitrogen atoms form covalent bonds, which provide h-BN with good mechanical strength and a Vickers hardness of approximately 1.5 GPa. Compared to graphite, the material is thermally stable, featuring a high melting point and low density [17; 19].
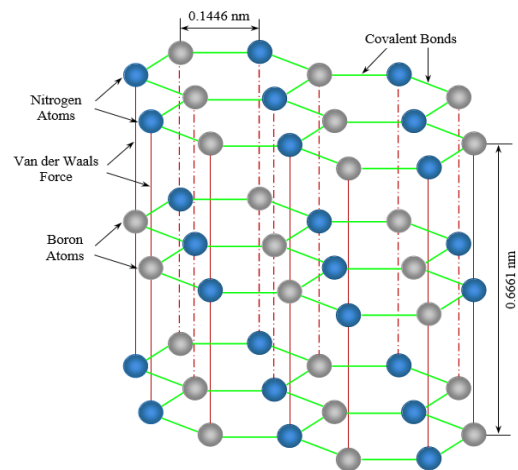

Figure 2. Crystal structure of h-BN (Adapted from [21]).

II. METHODOLOGY

The experimental development and execution were carried out at the Thermophysical Properties Laboratory – Protolab, at the University of Sorocaba/SP (UNISO). The High-Entropy Alloy, designated as L 5.7, was developed based on metallurgical principles, with its composition defined to meet the δ, γ and VEC parameters [22]. Hardness properties were obtained under as-cast, annealed, and thermochemical treatment conditions, with final hardening achieved through the pack carburizing process (Table 1).

Table 1. Composition and calculation of L 5.7 parameters.

Composition	Cr$_{eq}$ (%)	ΔR	δ	γ	VEC	Δχ	T (ºC)
CrFeMoNbTaTiV	141.94	14.29	0.059	1.182	6.221	0.222	2011

Cr – Equivalent chromium coefficient; Δr – Difference in atomic radii; δ - Difference in the size of atomic radii; γ - Represents the formation of phases; VEC – Valence electron concentration; Δχ - Difference in electronegativity; T – Melting temperature of the alloy.

After determining the composition of the L 5.7 alloy, two induction furnace melts were conducted, and the alloy was subsequently subjected to a pack carburizing thermochemical process. The melting procedures consisted of a first melt in a graphite casting crucible and a second melt in a hexagonal boron nitride (h-BN) crucible.

For the pack carburizing, the process conditions were kept identical: a temperature of 900°C, a dwell time of 4 hours, and a carburizing mixture composed of 60% coke and 40% calcium carbonate ($CaCO_3$). The process was carried out in a heat-resistant alumina (Al_2O_3) crucible [23].

Samples from each melt (1 and 2) were carburized in a muffle furnace with a maximum temperature capacity of 1200°C, followed by Vickers hardness measurements. It is important to note that after the 4-hour treatment period, the crucible was removed from the furnace to undergo a 24-hour cooling process (Fig. 3).

Figure 3. After cementation, the crucible is removed from the muffle furnace to cool slowly.

After cooling, the samples were ultrasonically cleaned, dried, weighed, embedded, and polished to 1200 grit sandpaper, and the Vickers Hardness was determined (Fig. 4). The measurement was performed by means of the resistance to penetration of the indenter, a diamond-tipped pyramid-shaped indenter, which imprints a mark on the sample where diagonal measurements are obtained for hardness calculation.
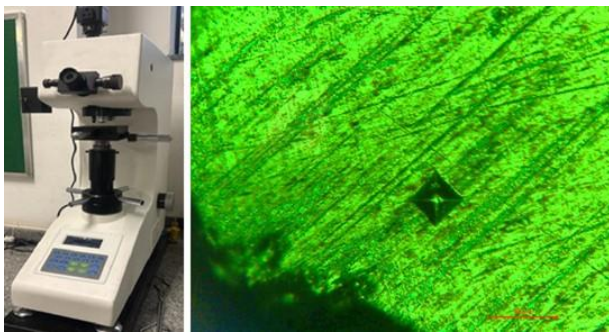

Figure 4. Equipment for measuring Vickers hardness and Indentation imprinted on the molten sample in a crucible lined with BN after solid carburization at 900ºC for 1h, with a calculated hardness of 1783 HV.

III. RESULTS AND DISCUSSION

The highest measured hardness value was observed for the sample melted in the h-BN crucible, reaching 1869 HV, with an overall average reading of 1783 HV. This indicates that a reaction occurred between the alloying elements—CrFeMoNbTaTiV—and the h-BN, contributing to the significant increase in hardness (Table 2).

Table 2. Vickers' hardness measured on samples of the High Entropy Alloy after melting and solid carburization.

High Entropy Alloy – L 5.7 – Vickers Hardness (HV)			
I. Crucible melting without BN - reference	*II. Cementation ref. I 900ºC/4h*	*III. Melting crucible with BN - reference*	*IV. Cementation ref. III 900ºC/4h*
1103	1131	1319	1628
1131	1173	1336	1628
1145	1174	1355	1756
1159	1174	1373	1783
1174	1181	1392	1783
1186	1189	1411	1783
1204	1204	1431	1864
1209	1212	1431	1864

High Entropy Alloy – L 5.7 – Vickers Hardness (HV)			
I. Crucible melting without BN - reference	*II. Cementation ref. I 900ºC/4h*	*III. Melting crucible with BN - reference*	*IV. Cementation ref. III 900ºC/4h*
1219	1219	1492	1869
1224	1251	1514	1869
1175	**1191**	**1405**	**1783**

The results demonstrate that the evaluated cast samples exhibit high Vickers hardness. The low density and high strength properties of High-Entropy Alloys are achieved through the inclusion of refractory and low-density elements in their composition, such as vanadium (V), zirconium (Zr), chromium (Cr), niobium (Nb), and titanium (Ti), as noted by [24].

The composition of L 5.7, comprising seven elements (CrFeMoNbTaTiV), yielded promising results, with average values ranging from 1175 to 1783 HV. These results may be attributed to the constituent refractory elements and the alloy's BCC (body-centered cubic) packing microstructure [21] (Fig. 5).
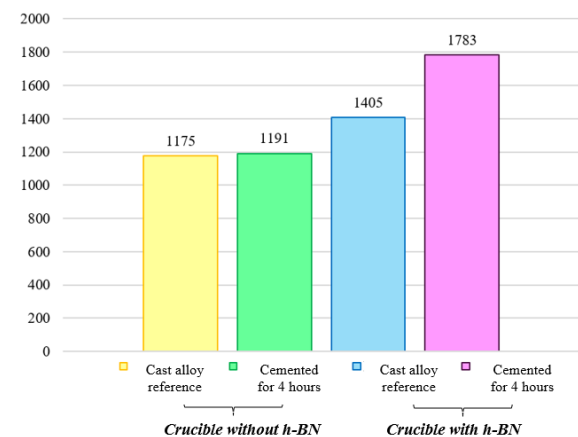

Figure 5. Vickers hardness of L 5.7 samples after melting in a crucible with and without h-BN coating and subsequent solid carburization (T = 900ºC).

In relation to the sample melted in the uncoated graphite crucible, there was no significant increase in hardness—approximately 1.36% after the pack carburizing thermochemical treatment (T = 900°C; t = 4 hours) - compared to the hardness of the reference as-cast alloy. This marginal increase in hardness may have occurred due to several factors, as noted by [11; 12]:

- *Complex Crystal Structure*: High-Entropy Alloys possess complex crystal structures with the potential formation of multiple phases, which may hinder the accumulation of carbides that would typically increase surface hardness.

- *Temperature Sensitivity*: The carburizing process is heavily influenced by the temperature used; this generally affects the formation and stabilization of hard phases and may reduce carbide formation.

- *Limited Carbon Diffusion*: Carbon diffusion may have been limited by the high number of elements present in the L 5.7 alloy (sluggish diffusion effect), thereby affecting the efficiency of the thermochemical treatment.

The results for the melt conducted in the h-BN-coated graphite crucible demonstrate its significant influence on the increase of the alloy's Vickers hardness, both for the as-cast reference and the subsequently carburized samples. The difference in hardness increase was 26.90%, significantly higher than that obtained in the first melt using the uncoated graphite crucible. The comparison between the as-cast references from the two distinct crucibles showed a 19.57% difference, while the samples after pack carburizing exhibited a substantial difference of 49.71%.

Figures 6, 7, 8, and 9, obtained via Scanning Electron Microscopy (SEM), display concentrations of calcium oxide (CaO) resulting from the reaction of the carburizing material (coke with $CaCO_3$) and carbon.
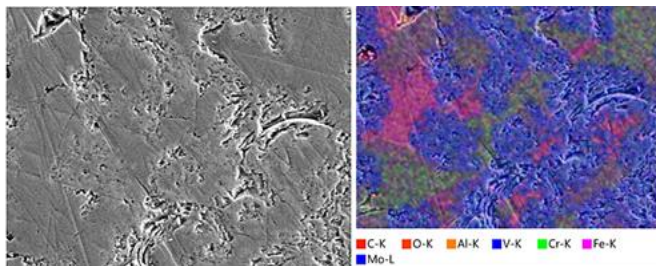

Figure 6. L 5.7 alloy melted in a graphite crucible and carburized, showing segregation of certain alloying elements, specifically Fe and Cr. This segregation may have contributed to the marginal increase in surface hardness after the thermochemical process compared to the non-carburized alloy.
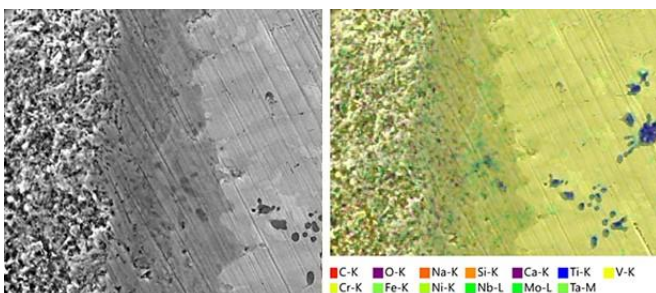

Figure 7. L 5.7 alloy melted in a boron nitride (BN) crucible after the pack carburizing thermochemical process. The image reveals dendrites and dark Ti-rich precipitates within the dark surface layer.
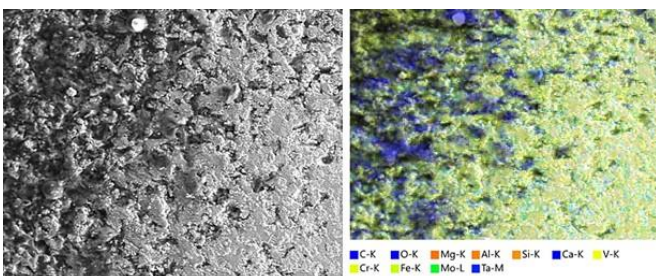

Figure 8. Energy Dispersive Spectroscopy (EDS) of the dark edge of the L 5.7 alloy sample melted in a BN crucible, showing carbon

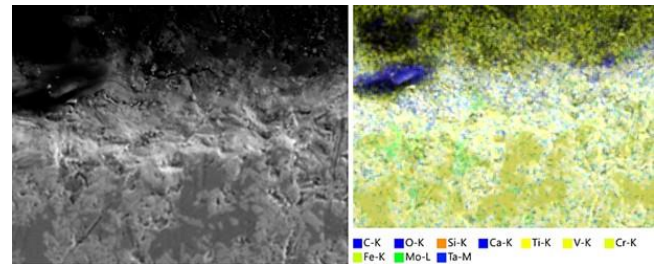incorporation on the surface and the presence of CaO after the pack carburizing process.

Figure 9. Energy Dispersive Spectroscopy (EDS) of the light-colored edge of the L 5.7 alloy sample melted in a BN crucible, showing another aspect of the carburized layer.

Boron nitride is widely used for melting crucibles due to its high thermal stability. However, it may not be entirely inert when in contact with the reactive elements that compose the L 5.7 alloy, such as titanium, niobium, and tantalum [15; 19]. The following interactions may have occurred during the melting of the alloy in the hexagonal boron nitride (h-BN) crucible:

- *High-Temperature Melting and Decomposition:* The melting of the L 5.7 alloy occurs at high temperatures due to the refractory elements in its composition (Mo, Nb, Ta, and V). At these temperatures, the h-BN material may undergo decomposition or an interfacial reaction with the liquid metal. This reaction releases boron and nitrogen into the alloy matrix [25; 26].

- *Interstitial Solid Solution:* Boron and nitrogen have small atomic radii and dissolve into the interstitial sites of the refractory metal structures. This hinders dislocation movement, thereby causing an increase in the initial hardness [27].

- *Formation of Hard Phases and Dispersion Hardening:* According to [25; 28], the elements Mo, Nb, Ta, and V act as formers of stable and hard borides (TiB2, NbB2) and nitrides (TiN, NbN). Consequently, an interfacial reaction occurs, generating precipitates within the microstructure. This process promotes enrichment through the dispersion of these ceramic particles.

IV. CONCLUSIONS

The study of High-Entropy Alloys (HEAs) involves diverse compositions that lead to varying properties. Accordingly, the objective of this study was to develop a seven-element HEA with equimolar concentrations in its composition to crystallize into a BCC structure. Following the melting process, the study aimed to evaluate the influence of hexagonal boron nitride (h-BN) usage and pack carburizing on the increase of Vickers hardness.

For L 5.7 alloy, the analysis of the results and discussions allows for the following conclusions:

- *Influence of Crucible Material:* Two separate melts were performed to produce the L 5.7 alloy—the first in a standard graphite casting crucible and the second in a graphite crucible coated with hexagonal boron nitride (h-BN). The results

demonstrate that h-BN has a significant influence on the measured hardness values.

- *Hardness Enhancement with h-BN:* The average Vickers hardness results show a substantial increase both for the as-cast alloy produced in the coated crucible (1405 HV) and for the same sample after the pack carburizing process (1783 HV).

- *Uncoated Crucible Limitations:* The average Vickers hardness for the alloy melted in the uncoated graphite crucible was 1175 HV, rising to only 1191 HV after pack carburizing. This marginal increase suggests that the 4-hour treatment time may have been insufficient or led to surface carbon loss, hindering effective hardening in the absence of the h-BN coating.

- *Ceramic Reinforcement via Nitrides:* The use of h-BN as a crucible coating for alloy melting significantly contributed to the hardness increase. This is attributed to the formation of nitrides (such as TiN and NbN) resulting from the reaction of nitrogen with titanium and niobium. These hard compounds act as ceramic reinforcements within the metallic matrix.

- *Boride Incorporation:* Another occurring reaction is the formation of high-hardness borides, which are incorporated into the alloy due to the presence of boron. Specifically, the reaction with titanium and niobium yields TiB_2 and NbB_2.

- *Synergistic Hardening Mechanisms:* The use of h-BN promoted the hardness increase through three distinct phenomena:

  A. Dispersion Hardening: The formation of nitrides and borides creates physical barriers to dislocation movement [28].

  B. Grain Refinement: The presence of these particles during the solidification process acts as nucleating agents, contributing to a finer microstructure.

  C. Solid Solution Strengthening: A portion of the boron and nitrogen atoms occupies the interstitial sites of the crystal lattice, further increasing its mechanical strength.

Therefore, it is concluded that the Vickers hardness of the alloy increases as a function of the enrichment provided by the hexagonal boron nitride (h-BN) and the subsequent formation of metallic borides and nitrides. However, this reaction may lead to embrittlement, causing the alloy to exhibit ceramic-like behavior.

ACKNOWLEDGMENT

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