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The Effect of Grinding Time on the Mechanical Activation of the Mixture of Al-B_2O_3 Powders

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In this study, the characterization of the product obtained after the mechanical activation of B_2O_3 powders with aluminium metal powders, which is the first stage of elementary boron production by aluminothermic method, was investigated. For this purpose, B_2O_3 powders mixed with metallic aluminium powders in different Al/B_2O_3 ratios with a ball/ore ratio of 20/1 were activated in a high energy mill for various times. It has been observed that the energy transferred to the environment during activation causes a decrease in the amount of B_2O_3 as well as its size. After the mechanical activation process, an increasing rate of amorphization was observed in the samples depending on the grinding time in the XRD images of the samples. When the peaks of these samples were compared with the peaks in the literature, it was also seen that they corresponded to some Al-B compounds. It was observed that amorphization decreased as the amount of aluminium in the mixture increased. it was thought that the reason for the decrease in amorphization was the elastic collisions of the steel balls and aluminium, which is a ductile metal, during the grinding in the mill.

Keywords: *Elemental Boron, Spex Milling, Mechanical Alloying*

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1. Introduction

Although elemental boron was first isolated over 150 years ago, many of its properties are still unknown. This is probably related to the relative difficulty of obtaining pure boron and the fact that it exists in amorphous form and in at least four crystalline modifications. In recent years considerable interest has developed in the potential use of boron in semiconductor devices, high-energy fuels, structural materials, and high-melting hard materials [1]. The boron can be used in abrasives as it is the second hardest element after diamond [2]. Elemental boron production is carried out by metallothermic reduction, mechanochemical synthesis, molten salt electrolysis and gas phase reduction [3].

Mechanical alloying(MA) is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill. It frequently leads to the formation of metastable phases of different types. The raw materials used for MA are widely available commercially pure powders that have particle sizes in the range of 1±200 mm. But, the powder particle size is not very critical, except that it should be smaller than the grinding ball size. This is because the powder particle size decreases exponentially

with time and reaches a small value of a few microns only after a few minutes of milling. The raw powders fall into the broad categories of pure metals, master alloys, prealloyed powders, and refractory compounds [4,5].

Mechanical alloying process is a nonequilibrium processing technology which arouses great interest due to its proven ability to alloy the immiscible elements [6]. During milling process, the heavy deformation induces a circulation of deforming, welding, and fracturing on particles. The specific schematic figures representing the milling states of mechanical alloying are shown in Figure 1. In particular, when two milling balls collide, a number of powders are trapped between them. The powders will be plastically flattened, welded, and fractured due to the impact energy. The powder features can be described in three series, depending on whether the types of the treated powders are ductile–ductile, ductile–brittle, or brittle–brittle combinations [6].

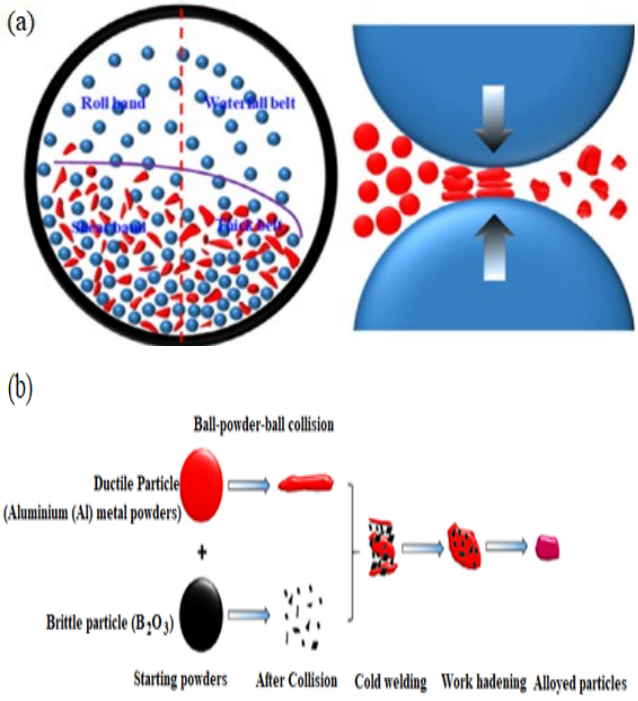

Fig. 1. a) Schematic diagrams depict ball–powder–ball collision during mechanical alloying. b) Deformation processes of initial particles after collision [6].

In the production of elementary boron by mechanochemical method, high purity B_2O_3 powders are ground in a grinder and brought to the desired content, microstructure and grain size as a result of a mechanical effect. The desired product is obtained by chemical or reduction reactions during grinding. Next, the obtained product is purified by leaching processes [7-10].

In this study, we investigated the characterization of the product obtained after the mechanical activation of B2O3 powders with aluminium metal powders, which is the first stage of elementary boron production by aluminothermic method.

2. Experimental

Boron oxide (B_2O_3) powder used; It is 98% min purity (SO_4:500 ppm max, Cl:10 ppm max, Fe:15ppm max) and +315µm (75%min) grain size (in granules) and was obtained from Eti Maden Operations. Aluminium powders (Alfa Aesar) with 99.5% purity and -150+45µm grain size were used as reducers. A high-energy spex mill was used for the mechanical activation process (Fig. 2(a)). The spex chamber where mechanical activation is performed (Figure 2. (b)) is a specially produced tungsten carbide material with a depth of 56 mm, an inner diameter of 48 mm and a wall thickness of 7 mm. Steel balls with a diameter of 4.75 mm were used in the spex mill for mechanical alloying experiments. SEM and EDX analyses of the samples obtained as a result of the studies were performed by the Zeiss EVO MA10 brand SEM device shown in Figure 2(c). XRD patterns of the samples after mechanical grinding were taken on the Bruker D8 Advance brand X-Ray diffractometer seen in Figure 2(d).

(a) Speks Mill

(b) Mill Jar

(c)SEM Device (Zeiss EVO MA10)

(d) Bruker D8 Advance X-Ray Diffractometer.

Fig 2. Equipment used in experimental studies.

$B_2O_3 + 2Al = 2B + Al_2O_3$ (1)

According to equation (1), aluminium metal powders and B_2O_3 powders were mixed at 1, 2, 3 and 4 times of the aluminium stoichiometric ratio, and after the Ball / Powder (B_2O_3 + Al) ratio was adjusted to 20/1, and they were subjected to the mechanical activation in the spex mill for different times.

While making stoichiometric calculations, the amount of material to be placed in the spex chamber was calculated to fill 1/3 of the chamber. The mechanical activation process was carried out for 15, 30, 45, 90, 720 and 960 minutes for each mixture. After the mechanical activation process, the spex chamber was opened in a nitrogen gas atmosphere in a glove box, and the mixture of powder and balls was placed in lidded containers containing 25 ml of alcohol to prevent the reaction of powders with oxygen. Then, the alcohol in these containers was evaporated in an argon gas atmosphere in the oven. After the alcohol was evaporated, the SEM and XRD analysis of the remaining solid were examined.

3. Results and Discussion

After the samples are numbered from A1 to A24, the mechanical activation process conditions of these samples are given in Table 1. SEM images of from A1 to A10, A16, A18, A20, A22 and A24 samples after mechanical activation are given in Figure 3, Figure 4 and Figure 5.

Table 1. Test conditions of the samples.

No.	St.	Grinding Time (Min.)	Ball /Powder B_2O_3+Al	No.	St.	Grinding Time (Min.)	Ball /Powder) B_2O_3+Al
A1	1	15	20/1	**A13**	4	15	20/1
A2	1	30	20/1	**A14**	4	30	20/1
A3	1	45	20/1	**A15**	4	45	20/1
A4	1	90	20/1	**A16**	4	90	20/1
A5	2	15	20/1	**A17**	1	720	20/1
A6	2	30	20/1	**A18**	1	960	20/1
A7	2	45	20/1	**A19**	2	720	20/1
A8	2	90	20/1	**A20**	2	960	20/1
A9	3	15	20/1	**A21**	3	720	20/1
A10	3	30	20/1	**A22**	3	960	20/1
A11	3	45	20/1	**A23**	4	720	20/1
A12	3	90	20/1	**A24**	4	960	20/1

St.: Stoichiometric Ratio of Al., No.: Simple Number.

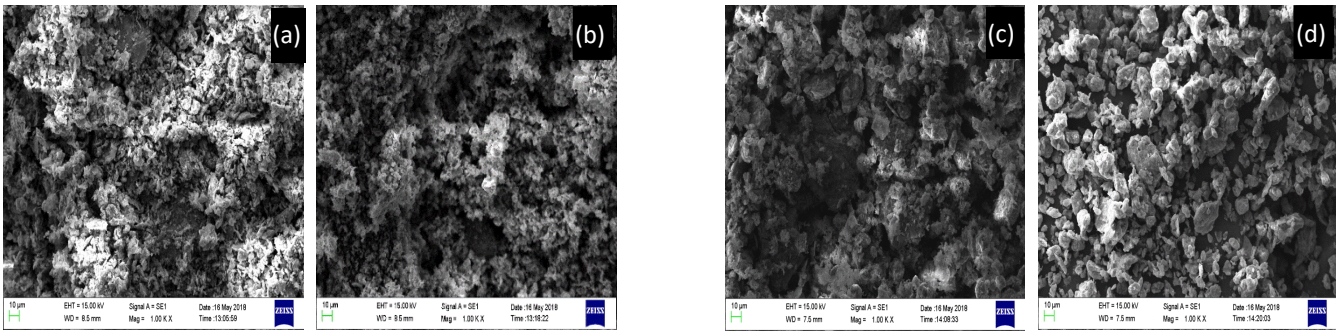

Fig 3. SEM images of samples A1(a), A2(b), A3(c), and A4(d) (1000X)
A1(St:1, G.T. =15′), A2(St:1, G.T. =30′), A3(St:1, G.T. =45′), A4(St:1, G.T. =90′)

When the images of the samples, which are taken as stoichiometric ratio 1 and subjected to mechanical activation for 15, 30, 45 and 90 minutes, are examined, it is seen that the grains first agglomerate after 15 minutes of grinding (Figure 3 (a), and after 90 minutes of grinding, these lumps break up and the grains are separated from each other. This situation can be explained as that after 15 minutes of grinding, the samples clump together due to static electricity caused by friction, and as the grinding time increases, these lumps are separated from each other again due to the increase in their temperature. The images in Figure 3 (c) and (d) and Figure 4 (c), (d) and (f) also support this situation.

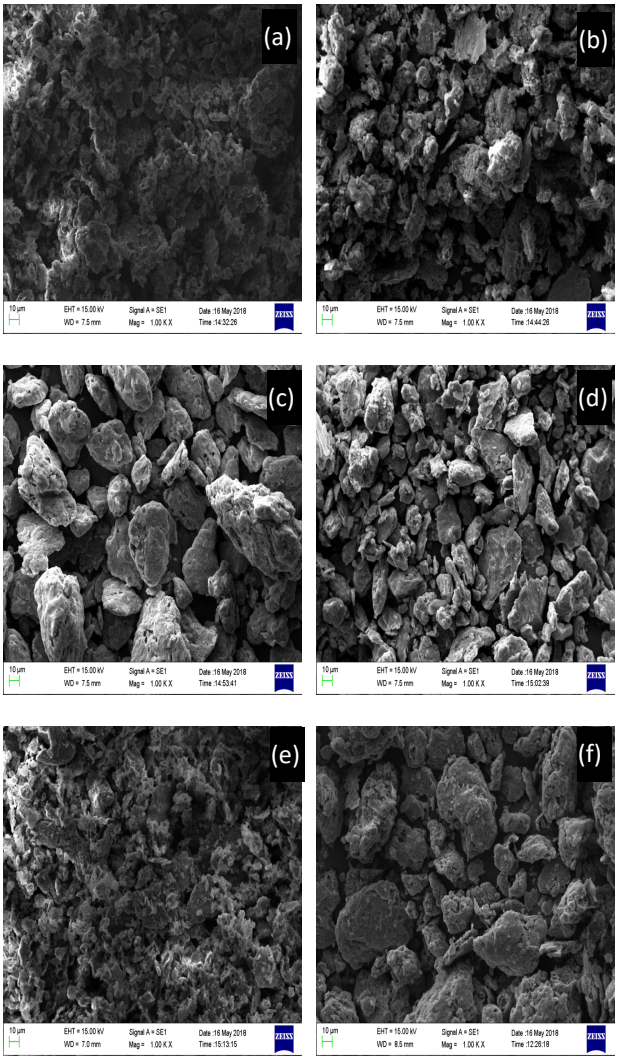

Fig 4. SEM images of samples A5(a), A6(b), A7(c), A8(d), A9(e) and A10(f) (1000X)
A5(St:2, G.T. =15´), A6(St:2, G.T. =30´), A7(St:2, G.T. =45´), A8(St:2, G.T. =90´), A9(St:3, G.T. =15´), A10(St:3, G.T. =30´).

The energy transferred to the environment through the balls in the spex mill caused a decrease in the amount of B_2O_3 as well as its size. According to equation (1), local alloying occurred in the powders placed in the mill as multiples of the stoichiometric ratio, with the local temperatures reaching 10000 ºC at the contact points of the balls and particles, resulting in a decrease in the amount of B_2O_3.

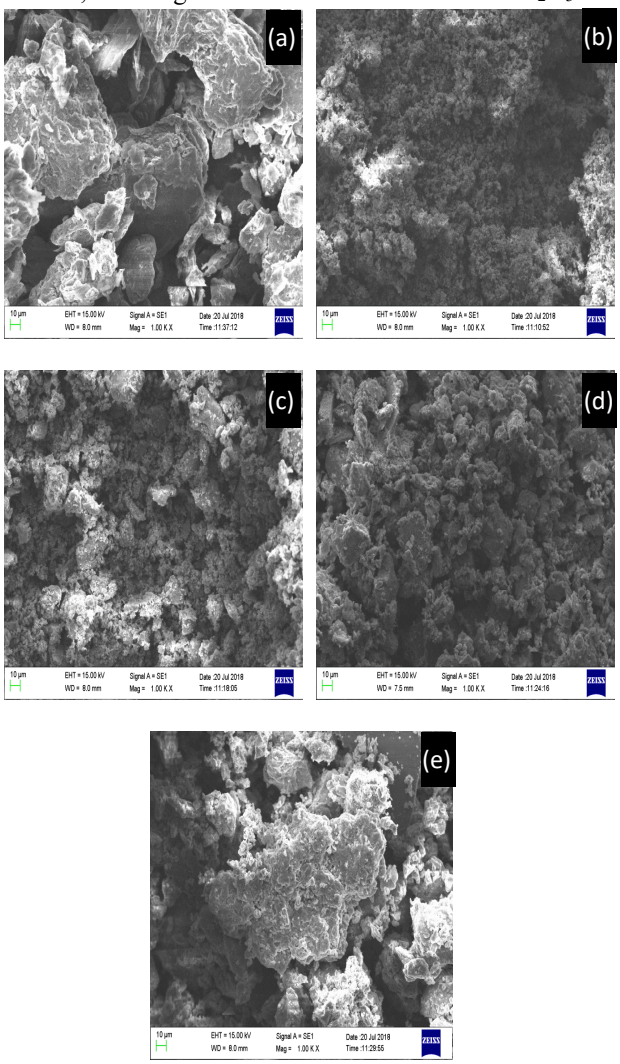

Fig 5. SEM images of samples A16(a), A18(b), A20(c), A22(d) and A24(e) (1000X)
A16(St:4, G.T. =90´), A18(St:1, G.T. =960´), A20(St:2, G.T. =960´), A22(St:3, G.T. =960´), A24(St:4, G.T. =960´)

As schematized in Figure 1(b), in the first stage of grinding, the powder size first decreased and then agglomerations formed. It was observed that these lumps were fragmented and dispersed at the later stage of grinding. however, it was observed that agglomeration started again, structural errors occurred, and amorphous phases emerged with increasing grinding time. The SEM images given in Figure 5 are in agreement with the schematic view given in Figure 1(b).

After the mechanical activation process, XRD images of all samples between A1-A24 were taken and given in Figure 6, Figure 7, Figure 8 and Figure 9.

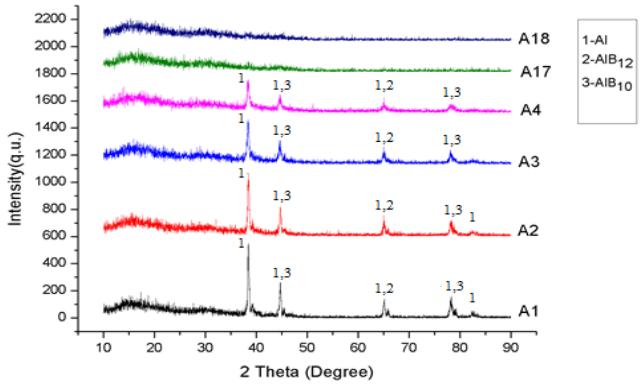

Fig 6. XRD images of samples containing stoichiometric aluminium powder after grinding.
A1(St:1, G.T =15′), A2 (St:1, G.T =30′), A3 (St:1, G.T =45′), A4 (St:1, G.T =90′), A17 (St:1, G.T =720′), A18 (St:1, G.T =960′).

Especially in the XRD images given in Figure 6, the change in the crystal structure of the sample can be seen very clearly depending on the grinding time. An increasing rate of amorphization is observed in samples numbered A1, A2, A3, A4, A17 and A18. The X-ray pattern of amorphous compounds does not contain any significant peaks. When the peaks of these samples were compared with the peaks in the literature, it was observed that they corresponded to some Al-B compounds. It is known that local temperatures rise to 10000ºC during the grinding process. The occurrence of partial reductions and some Al-B alloys at these temperatures is to be expected.

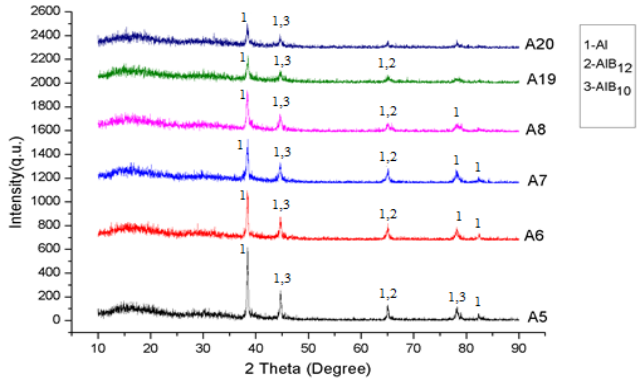

Fig 7. XRD images of samples containing 2 times the stoichiometric ratio of aluminium after grinding.
A5(St:2, G.T =15′), A6(St:2, G.T =30′), A7(St:2, G.T =45′), A8(St:2, G.T =90′), A19(St:2, G.T =720′), A20(St:2, G.T =960′).

In the XRD images given in Figure 7, the change in the crystal structure of the samples, again depending on the grinding time, is clearly seen. It is observed that as the grinding time increases in samples numbered A5, A6, A7, A8, A19 and A20, there is amorphization in the crystal structure, and the intensity of the Al peak decreases gradually. Again, when these peaks were compared with the literature peaks, it was observed that some peaks thought to correspond to Al-B compounds occurred due to the local temperature increases in the grinding process.

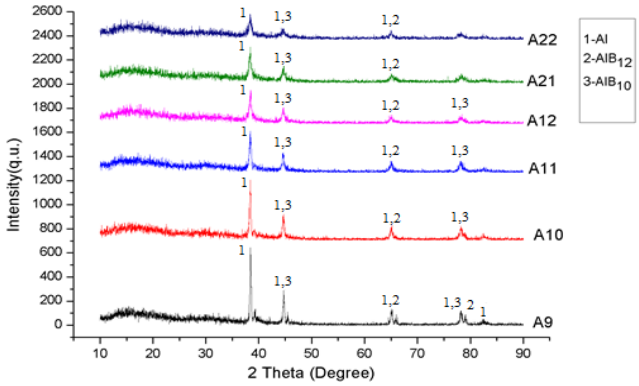

Fig 8. XRD images of samples containing 3 times the stoichiometric ratio of aluminium after grinding.
A9 (St:3, G.T=15′), A10 (St:3, G.T =30′), A11 (St:3, G.T =45′), A12 (St:3, G.T =90′), A21 (St:3, G.T =720′), A22 (St:3, G.T =960′).

The XRD images in Figure 9 and Figure 10 show the change in the crystal structure of the samples due to the mechanical activation process. The images in Figures 6 and 7 are similar to Figures 8 (samples A9, A10, A11, A12, A21 and A22) and Figure 9 (samples A13, A14, A15, A16, A23 and A24). It has been observed that deformations depending on the dislocation density occur in the high-energy grinding process in the spex.

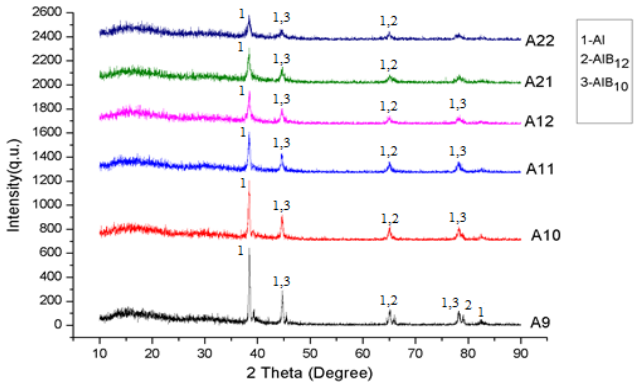

Fig 9. XRD images of samples containing 4 times the stoichiometric ratio of aluminium after grinding.
A13 (St:4, G.T=15′), A14 (St:4, G.T =30′), A15 (St:4, G.T =45′), A16 (St:4, G.T =90′), A23 (St:4, G.T =720′), A24 (St:4, G.T =960′).

When the XRD analyses given in Figures 6, 7, 8, and 9 are examined, it is seen that there is a decrease in the degree of amorphization due to the stoichiometric increase of the aluminium amount. This decrease in the degree of amorphization is more clearly seen, especially in mixtures that are milled for 720 and 960 minutes. The fact that aluminium is a malleable material causes the amorphization rate of the mixture to slow down or even stop as the grinding time increases. Because during ball-mix collisions, aluminium exhibits ductile behavior,

causing most of the energy consumed for grinding to be used for sound, heat and flatten by striking processes. When the SEM images of the samples, which were milled for 960 minutes in figure 5, are examined, it can be seen that this idea is proven. In addition, in the SEM images, it is seen that the small particles clump together and turn into large particles due to the heat generated during the ball mixture collisions due to the increase in the amount of aluminium.

It has been determined that this formation is caused by aluminium, which is a ductile material. Because aluminium shows ductile behaviour during the collision of the balls and therefore reduces the energy and grinding efficiency of the balls. This result can also be understood by looking at the SEM images of the samples that have been subjected to a 960-minute grinding process in Figure 5. In addition, when we looked at the SEM images, it was seen that small grains fused and turned into large grains due to the heat generated during grinding due to the increase in the amount of aluminium.

In addition, it was determined that the various Al-B alloys occurred when the amount of aluminum and the grinding time increased. This can be clearly seen from the XRD images of the A18, A20, A22 and A24 samples.

4. Results

In this study, the characterization of the product obtained after the mechanical activation of B_2O_3 powders with aluminum metal powders, which is the first stage of elementary boron production by aluminothermic method, was investigated. For this purpose, aluminium metal powders and B_2O_3 powders were mixed at 1,2, 3 and 4 times of the stoichiometric ratio, and after the Ball / Powder (B_2O_3 + Al) ratio was adjusted to 20 /1, and they were subjected to the mechanical activation in the spex mill for 15, 30, 45, 90, 720 and 960 minutes.

When the SEM images of the samples, it is seen that the grains first agglomerate after 15 minutes of grinding, and after 90 minutes of grinding, these lumps break up and the grains are separated from each other. This situation can be explained as that after 15 minutes of grinding, the samples clump together due to static electricity caused by friction, and as the grinding time increases, these lumps are separated from each other again due to the increase in their surface temperature. The energy transferred to the environment through the balls in the spex mill caused a decrease in the amount of B_2O_3 as well as its size.

After the mechanical activation process, XRD images of all samples between A1-A24 were taken. In the XRD images, the change in the crystal structure of the sample was seen very clearly depending on the grinding time. An increasing rate of amorphization is observed in samples numbered A1, A2, A3, A4, A17 and A18. When the peaks of these samples were compared with the peaks in the literature, it was observed that they corresponded to some Al-B compounds.

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