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## MICROSTRUCTURAL EVOLUTION OF AlCuFeMnTi-0.75Si HIGH ENTROPY ALLOY PROCESSED BY MECHANICAL ALLOYING AND SPARK PLASMA SINTERING

In this work, we have designed a new high entropy alloy containing lightweight elements, e.g., Al, Fe, Mn, Ti, Cu, Si by high energy ball milling and spark plasma sintering. The composition of Si was kept at 0.75 at% in this study. The results showed that the produced $AlCuFeMnTiSi_{0.75}$ high entropy alloy was BCC structured. The evolution of BCC1 and BCC2 phases was observed with increasing the milling time up to 60 h. The spark plasma sintering treatment of milled compacts from 650-950°C showed the phase separation of BCC into BCC1 and BCC2. The density and strength of these developed high entropy alloys (95-98%, and 1000 HV) improved with milling time and were maximum at 850°C sintering temperature. The current work demonstrated desirable possibilities of Al-Si based high entropy alloys for substitution of traditional cast components at intermediate temperature applications.

*Keywords:* high entropy alloy, powder metallurgy, mechanical alloying, spark plasma sintering, high energy ball milling

## 1. Introduction

High entropy alloys (HEAs) as defined by Yeh et al. [1], are a new class of metallic alloys which are prepared by mixing five or more metallic elements in the range of 5-35 at.%. HEAs have excellent mechanical properties because elements of various atomic sizes are dissolved, and thus, research continues to search for an emerging alloy that can be used in various industrial fields [2]. Most of the high entropy alloys are prepared by adding heavy elements such as Co, Cr, and Ni for phase stabilization [3,4]. However, these elements are quite expensive to be mass-produced. Therefore, most of the researchers are moving away from the Cantor based composition to explore this field from a different perspective. Lightweight high entropy alloys have also been developed in the past [5]. Researchers have also tried to develop a balance in properties by tuning BCC and FCC composition to produce precipitation strengthened HEAs [6]. However, the addition of high amounts of secondary phases can be harmful to the mechanical performance of these alloys in structural applications. Various lightweight HEAs have been developed to reduce the weight of the final structural parts. However, additional weight reduction of the HEAs components

can improve the competitiveness among the lightweight HEAs. Various suitable lightweight (Li, Mg, Be, Sc, etc.) elements have been already added in the past but they are are highly expensive or contain toxic materials [7,8]. Therefore, addition of lightweight elements which are non-toxic and cheaper, such as Al, Ti, and Si can be a good approach. Si is a popular element in aluminum structural parts and its addition improves the fluidity of cast components [5,9]. Therefore, Si can be chosen as one of the potential candidates to produce lightweight HEAs. Also, to produce lightweight and strong HEAs, the selection of fabrication methodology is equally important. HEAs fabricated by casting and melting methods are not desirable due to the inherent shrinkage defects and porosity [10]. In contrast, HEAs produced through advanced powder metallurgy process constitutes the novel high energy milling procedures combined with consolidation by SPS [11]. Therefore, in this study, $AlCuFeMnTiSi_{0.75}$ HEAs were fabricated by choosing lightweight Ti and Si. We have avoided expensive or scarce elements such as Co, Cr, and Ni. The alloying behavior of $AlCuFeMnTiSi_{0.75}$ HEAs was studied by mechanical alloying for various times and different SPS temperatures. Finally, we evaluated the relative sintered density and strength of the developed HEAs and correlated the results.

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## 2. Experimental

AlCuFeMnTiSi$_{0.75}$ (in mole fraction) HEAs were prepared by 5, 15, 30, 45, and 60 h milling of six elemental powders (purity ≥99.5%) and average particle size 45 μm with 0.3 wt% stearic acid as PCA. The mechanical alloying process was carried out in a stainless steel vial and Ø20 mm balls under an Ar atmosphere and ball to powder mass ratio of 10:1. The sealed vials were then fitted in a high energy ball mill (RETSCH, PM400, Germany) at 300 rpm.

Subsequently, the as-milled powder was sintered by spark plasma sintering machine (Model Dr. Sinter Lab SPS-211lx, Fuji Electronic Industrial Co., Japan) in a 15mm-inner-diameter graphite mold at 650, 750, 850, and 950°C for 8 min. Sintering was performed under Ar atmosphere with a constant pressure of 30 MPa and a heating rate of 100°C/min.

The crystal structure of the AlCuFeMnTiSi$_{0.75}$ high entropy alloy as-milled powders and as-sintered specimens was analyzed by X-ray diffraction (XRD, Rigaku Miniflex 600, Benchtop) with CuK$_\alpha$ radiation. The scanning speed was 2°/min and the scanning angle (2θ) was from 35° to 55°. The refinement in the crystalline size of solid solution phases in powder particles was examined by the Scherer equation [12]. The microstructure of the SPSed specimens was observed using scanning electron microscopy (SEM, JSM IT500HR, JEOL, Japan) with energy-dispersive X-ray spectroscopy (EDS) detector. The relative sintered density and microhardness of HEAs were calculated by Archimedes principle and Micro-Vickers hardness tester (Mitutoyo HM-200, Japan) at a load of 1960 mN for 5s, respectively.

## 3. Results and discussion

Figure 1 shows the powder XRD pattern of AlCuFeMn-TiSi$_{0.75}$ HEA with milling time. The XRD pattern analysis results showed that HEA had a BCC structure as seen from the BCC1
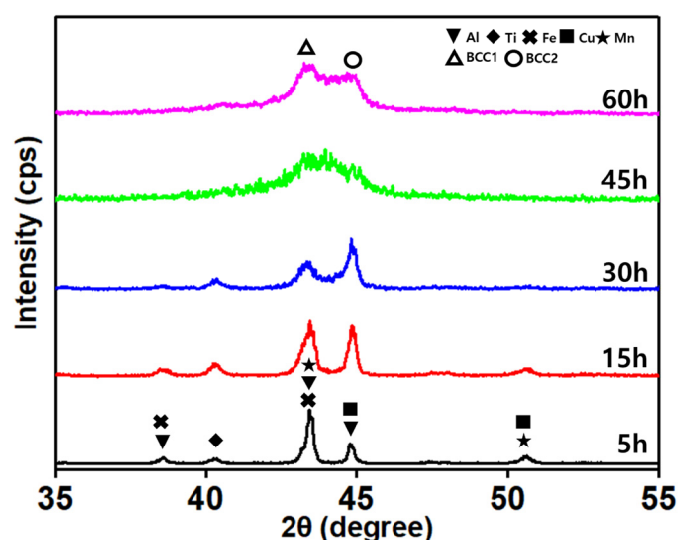


Fig. 1. XRD patterns of milled AlCuFeMnTiSi$_{0.75}$ HEA powder for different hours

and BCC2 peaks. When the milling time was increased, each constituent element peak alloyed and disappeared after 30 h.

Initially at 15 h, the alloying of the HEA powder was very poor which was manifested by the additional peaks of Ti in the XRD patterns. It can be seen that after 45 h, Ti began to alloy and phase separation occurred as BCC1 and BCC2. As the milling time approached 60 h, the alloying behavior improved, and the BCC1 and BCC2 phase separation occured as shown. In addition, the refinement of the powder particles can be confirmed from the reduction in the crystalline size of the BCC1 and BCC2 phases presented in Table 1. It can be due to the high energy ball milling of the HEA powder for a longer duration and a change in entropy of the system [13].

TABLE 1

Crystalline size of BCC1 and BCC2 in AlCuFeMnTiSi$_{0.75}$ HEA powder for different milling times

| Milling time (h) | Crystalline size (nm) | |
| --- | --- | --- |
| | BCC1 | BCC2 |
| 5 | — | — |
| 15 | 18.62 | 29.94 |
| 30 | 17.19 | 22.93 |
| 45 | 14.64 | 17.97 |
| 60 | 11.76 | 12.23 |

Figure 2 shows the XRD patterns of AlCuFeMnTiSi$_{0.75}$ HEAs milled at different times and subsequently SPSed at different temperatures. The HEAs evolved into a BCC structured alloy (the single BCC or BCC1/BCC2) with increasing milling time and densification. This was because of the higher sintering energy supplied to the alloy which caused a rapid dissolution of the residual elements (Ti or Fe) into the HEA matrix. In addition, the BCC2 peak increased with milling time and subsequent densification for all the compositions (Fig. 2a-d). This was because the phase transformation proceeded from the BCC1 phase to the BCC2 phase to stabilize the existing phase when Ti was dissolved [13]. At 650°C, XRD pattern showed an unalloyed peak indicating a poor alloying behavior at lower SPS temperature (Fig. 2a). The unalloyed peaks disappeared, and the densification improved considerably when the SPS temperature increased from 650-850°C (Fig. 2a-c). At 950°C, the XRD pattern showed re-appearance of several peaks that were not noticed at 750°C and 850°C. This can be correlated to the elution of low melting point Al and Cu from the HEA matrix [14]. Therefore, it was judged that 650°C and 950°C were not suitable processing conditions for the HEA.

Figure 3 shows the SEM image of the milled samples for various times and SPSed at 850°C. At lower milling times (a) and (b), it is difficult to judge whether alloying occurs or not. The big chunks of Ti-particles were found randomly in the HEA matrix. The constituent particles did not mix up completely up to 15 h. This was also confirmed from the XRD investigations where the harder Ti particles were present up to 15 h. The alloying improved reasonably up to some extent beyond 15 h. Phase separation of BCC1 and BCC2 was noticed with a Ti-rich
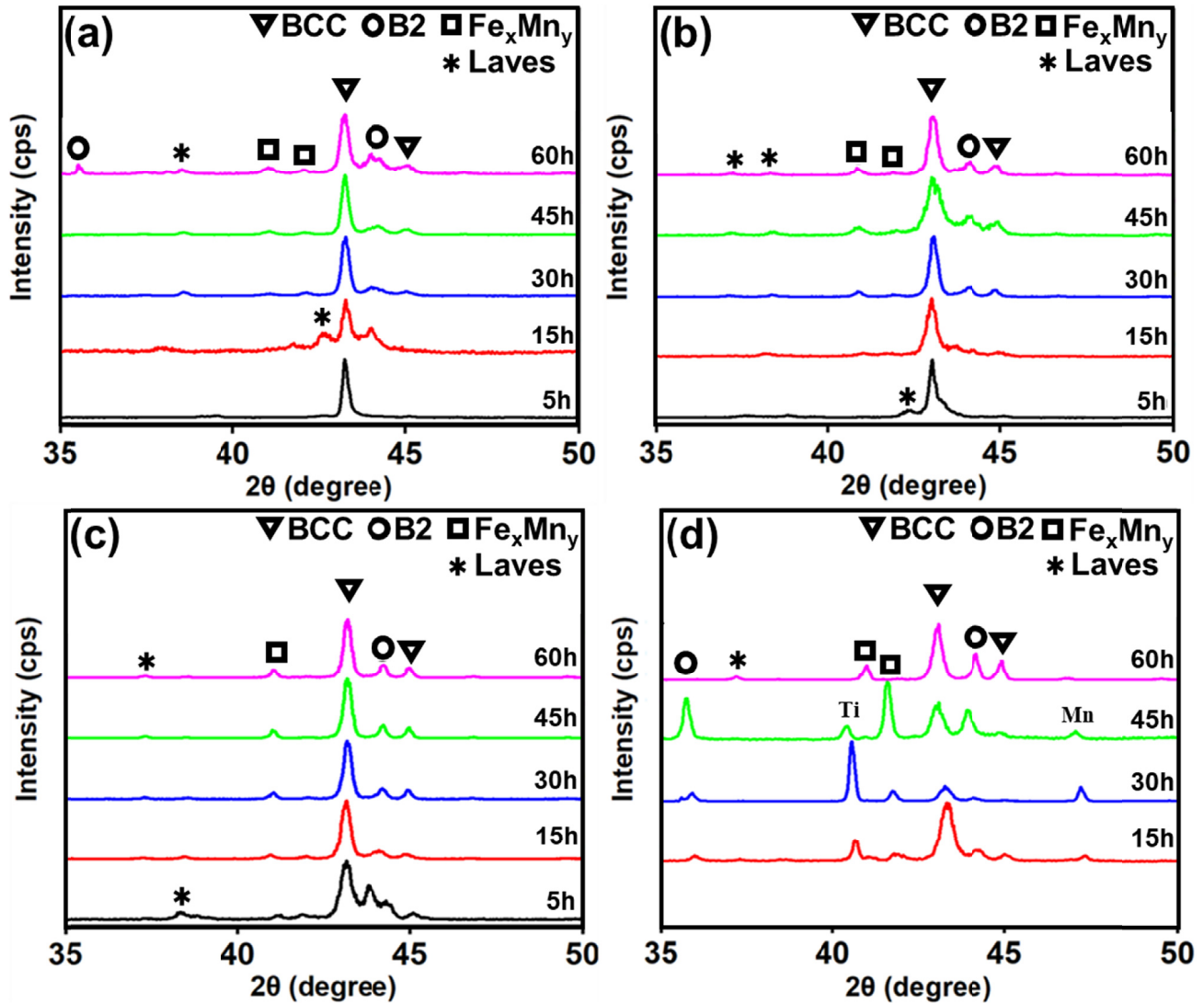
Fig. 2. XRD patterns of AlCuFeMnTiSi$_{0.75}$ HEA powder SPSed at various temperatures. (a) 650, (b) 750, (c) 850, and (e) 950°C

phase (Fig. 3c-d). It can be seen that when Ti remained in the milling process, Ti-rich phase was formed even after the SPS process.

Further milling of the powder up to 60 h and SPS resulted only in the formation of BCC1 and BCC2 phases (Fig. 3e). The phase fraction of BCC2 increased from 45 to 60 h of milling. The dissolution of Ti in the matrix enhanced the phase fraction of Ti-rich BCC2 phase in order to stabilize BCC1 phase. The resultant two phases BCC1 and BCC2 were analyzed by EDS mapping as shown in Figure 3f. The BCC1 phase was Ti-Si-rich while the BCC2 phase was Al-Cu rich. Therefore, the phase separation of BCC1 and BCC2 occurred due to limited solubility of Al-Cu in Ti-rich phase. Besides, there was no segregation of specific elements as found in arc melted HEAs [15], therefore, a uniform lightweight high entropy alloy can be manufactured through mechanical alloying and sintering.

Figure 4a-b shows the density and microhardness of the samples milled up to 60 h and SPSed at 750-850°C. We have ignored 950°C data due to the poor sintering behavior shown by XRD results at this condition. From Fig. 4, it can be seen that

the microhardness and density of HEAs improved with milling time and sintering temperature. The attractive microhardness value (1000.5±35HV) was noted for sample milled for 60 h and SPSed at 850°C. This was due to the increase in the degree of densification caused by the refinement of crystalline size during milling (Table 1). The sintered density of the prepared HEAs was 93-98% of relative sintered density. The sintered density was improved at 850°C, which was a result of a small amount of porosity and increased sintered density. We compared our results with some of the previous studies based on Si-containing HEAs produced by the powder metallurgy route. Chae et al. produced AlCuFeMnMgTi HEA milled for 60 h and densified by SPS at 600-700°C [13]. In their studies, a gradual refinement of the solid solution phases during milling was observed until 60 h. The hardness and density were slightly reduced because of the higher Mg loss at 700°C. Similarly, Sharma et al. produced dual-phase AlCuSiZnFe HEA by mechanical alloying for 45 h and densification from 600-800°C [14]. In their studies, although the hardness was higher at 800°C yet the formation of hard reaction compounds was noticed. They suggested the optimal
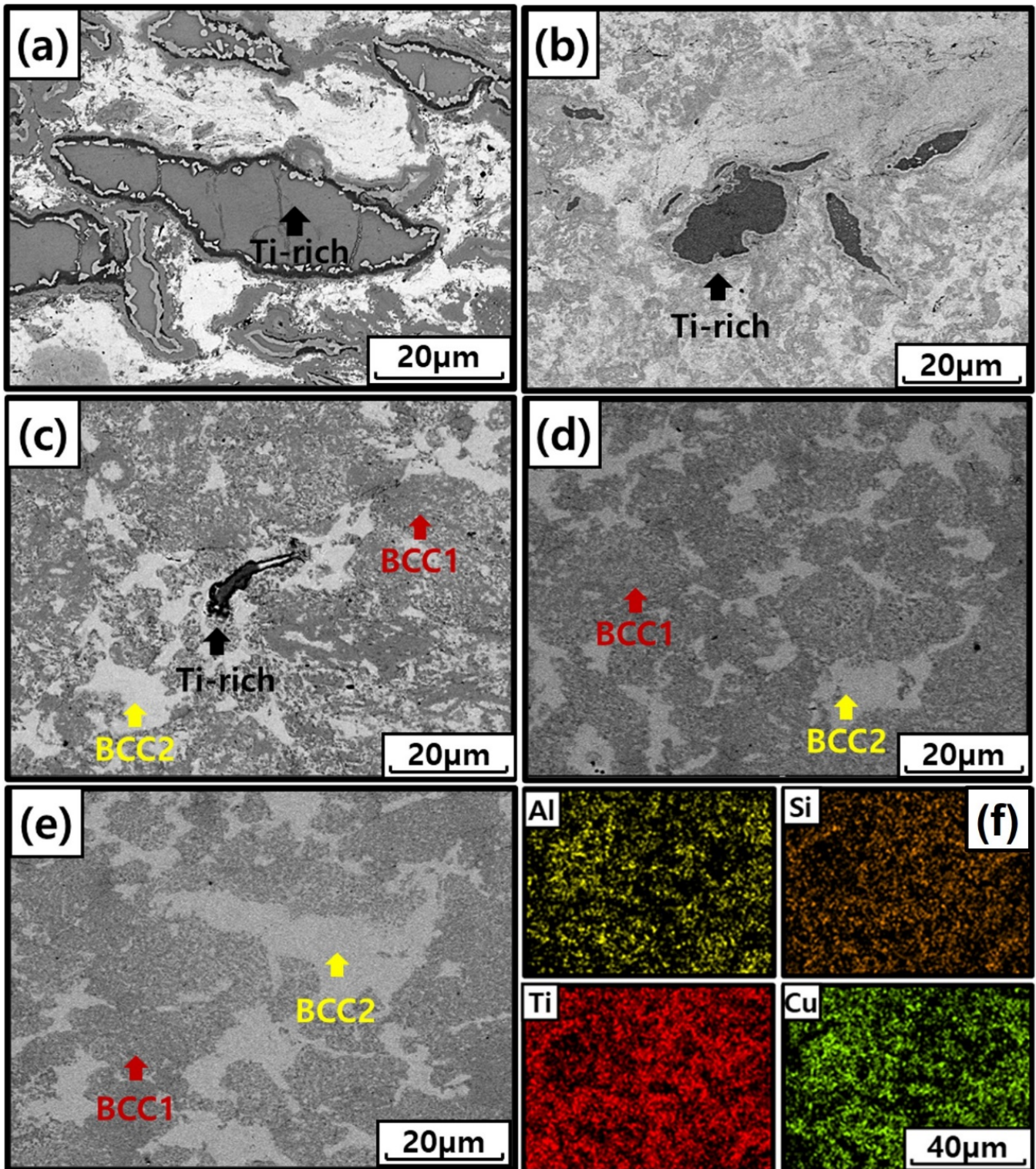
Fig. 3. SEM image of AlCuFeMnTiSi$_{0.75}$ HEA milled for (a) 5, (b) 15, (c) 30, (d) 45, and (e) 60 h and SPSed at 850°C. The EDS- mapping of (e) is shown in (f)

HEA properties at 700°C. The effect of Si in CoCrCuFeNiSix (x = 0-0.9) HEA was studied by Chopkar et al. and they also obtained an enhancement in mechanical properties but at a higher Si atomic fraction (0.9%) as compared to the present work [16]. In the present work, the milling time and SPS condition for this type of HEA should be adjusted at 60 h and 850°C for better utilization of mechanical properties.

## 4. Conclusions

In this study, an AlCuFeMnTiSi$_{0.75}$ high entropy alloy was prepared by mechanical alloying and SPS methods. The results showed the formation of various phases BCC1 and BCC2 up to a milling time of up to 60 h. In addition, after the SPS treatment at 750°C and 850°C, the BCC1 and BCC2 phases were separated,
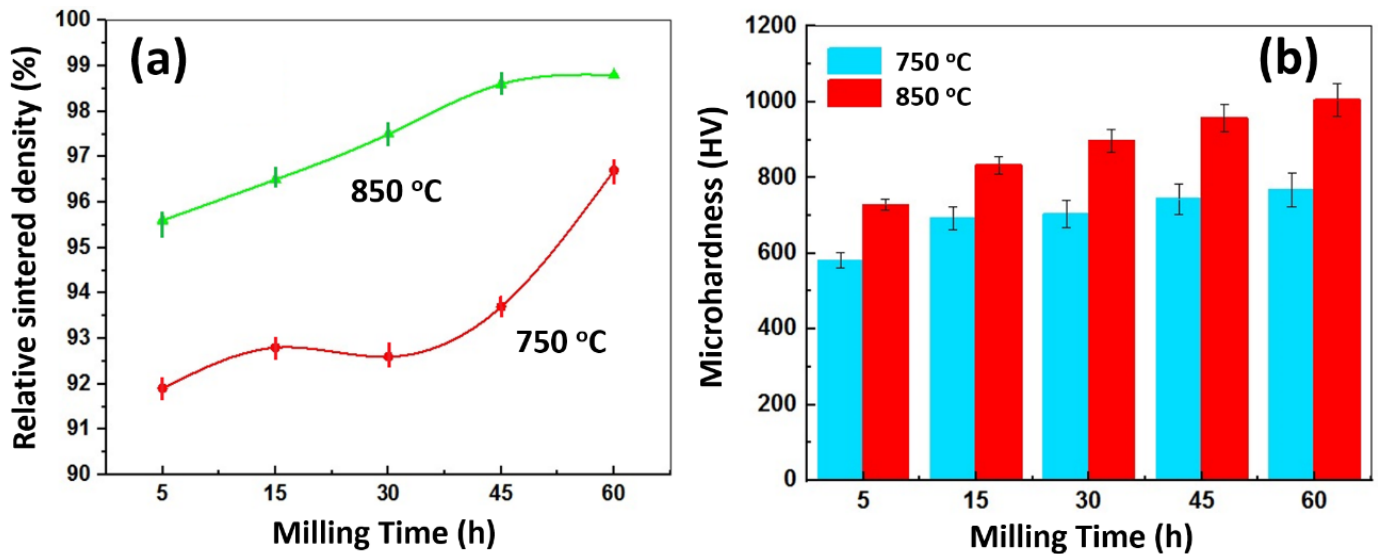
Fig. 4. (a) Relative sintered density and (b) microhardness of the milled AlCuFeMnTiSi$_{0.75}$ HEAs for different hours and SPS treatment

as confirmed in the SEM images, the phase distribution was uniformly observed. It can be seen that increasing the SPS temperature to 850°C significantly improves the density. The density and hardness values increased with milling time and higher SPS temperature up to 850°C. In this study, it was concluded that the optimal treatment conditions for AlCuFeMnTiSi$_{0.75}$ HEA were 60 h and 850°C for better realization of microstructure properties.

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