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Research Article

Effect of Cu addition on microstructure and mechanical properties of NiTi based shape memory alloy

N. Arda Tanış[a], Hakan Gökmeşe[b]*, Bülent Bostan[c]

[a]*Kırıkkale University, Faculty of Engineering, Kırıkkale,Turkey*
[b]*Konya Necmettin Erbakan University, SeydisehirAhmet Cengiz Faculty of Engineering, Dept. of Metallurgy and Materials Eng. Seydisehir-Konya, Turkey.*
[c]*Gazi University, Faculty of Technology, Dept. of Metallurgy and Materials Eng. Ankara, Turkey*

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ABSTRACT

In this research paper, pre-alloyed NiTi based shape memory alloy and 4%Cu were used as starting powder materials. Starting powder materials were blended for 60 minutes by a turbula mixer. After mix processing, microstructure and phase transformations of powders were characterized using X-ray (XRD), elemental distribution spectrometry (EDS), scanning electron microscopy (SEM). Prepared powder mixtures as NiTi and NiTi+4%Cu alloys were pressed at 785MPa in a mold and then sintering process was applied to materials at different temperatures and time. Formation of multiphase's (Ni_3Ti, NiTi, Ti_2Ni, Ni_4Ti_3 and NiTiCu) and positive effects of Cu addition were obtained by sintering at different temperatures and time. And also, stabilized NiTi phase and increasing the value of micro hardness were determined with added 4%Cu powders.

1. Introduction

Shape memory alloys (SMA) have ability to return to a taught shape when applied to a proper thermo mechanical or magnetic variations. Due to unique and outstanding features of SMA, They have been used in most commercial applications in recent years which was supported by primary and practical investigation works [1].NiTi alloys consist of near-equatomic composition, exhibit shape memory, super elastic effects, which is commonly called Nitinol alloys. These alloys transform from austenite to martensite form by temperature and pressing effects. These could also be used as an implant material due to unique biocompatibility, corrosion resistance features and these materials nowadays play an important role in research laboratories [2-7].

NiTi alloys reversible and diffusionless transformation (martensite ↔ austenite) are coming about in the temperature range 50 to 100ºC as a function of Ni content of the matrix [8].

In NiTi binary balance systems, stable Ni-Ti phases appears in the region approximately equal percentage of NiTi [9,10]. NiTi alloys have exhibited poor mechanical properties and segregation problems in their molding process. For this reason, recently powder metallurgy method has attracted much attention for porous NiTi alloys [11,12]. However, Formed impurity increase in the manufacturing process by powder metallurgy technique should not been overlooked [13]. These negative effects could be solved with optimum sintering temperature and timesin the sintering atmosphere with controlled homogeneous atmosphere conditions which has an important place in production process [14-16].

In this study, Cu powders were added to the pre-alloyed NiTi alloy powders. The obtained experiment samples were sintered at different temperature and time conditions. Multiphase microstructures and increasing of the mechanical properties depending on sintering temperature and time were obtained with distribution of Cu contents in main phase

* Corresponding author. Tel.: +90-539-8761547; Fax: +90-332-5820450.
E-mail address: hgokmese@konya.edu.tr

2. Experimental Studies

NiTi pre-alloyed powders used in the experiments were produced by gas atomization technique and were obtained from Nanoval GmbH and Co.KG Company.The average grain size of nickel-rich pre-alloyed NiTi powders was 14µm .NiTi and 4% Cu powders were blended in a turbula mixer. And then blended powders were pressed in 10mm diameter spherical mold at 785MPa.The green parts were sintered at high purity argon gas atmosphere which was refined into hot copper chip (at 450ºC) to reduce oxidation and impurities. The schematic diagram of sintering stage under high purity argon atmosphere of NiTi and NiTi+%4Cu samples is shown in Fig 1. According to sintering diagrams (Figure 1), Pressed NiTi (14 µm) powder metal samples were sintered at 900ºC for 300 minute and 1050ºC for 60 minute. NiTi-4% Cu samples were sintered at 850ºC and 1000ºC for 60 minute and at 1050ºC for 300 minute (Figure 1).

After sintering process of samples, sanding, polishing and etching processes for metallographic investigations were applied to the sintered samples respectively. Etched samples were examined by optical microscope (LEICA) and scanning electron microscope (SEM). Also, electron distribution spectrometer (EDS) analyses were performed. XRD analyses was applied to the pre-alloyed powders and sintered parts for determine of phase transformations by APD 2000PRO version X-ray Diffractometer device. Hardness measurements (HV 0.5) of samples were performed by Shimadzu model micro hardnessdevice.

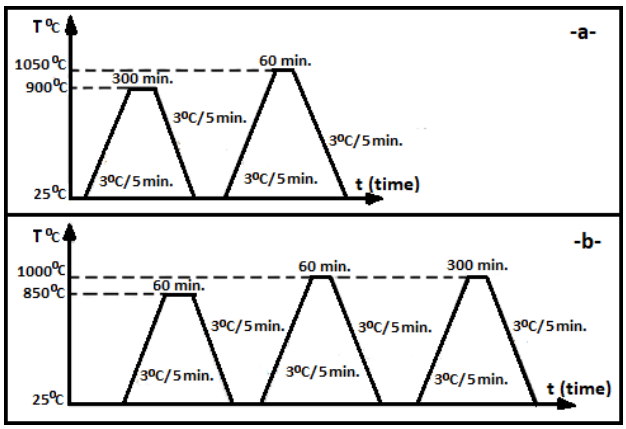


Figure 1. Sintering diagrams; a- NiTi samples, b- NiTi-4%Cu samples

3. Results and Discussion

Figure 2 shows SEM images of pre-alloyed NiTi powders (particle size-14µm) used in experiments. It could be identified to be uniform, spherical, pure and smooth surface structure of powders in Figure 2-a and b. This condition could be good affects on pressing ability and sintering behavior, as known [17]. The element distribution of powders (%55Ti, 45Ni and 49,9Ti, 50, 1%) is shown in Table 1 as weight and atomic ratio respectively.

DSC analysis was applied to pre-alloyed NiTi powders to determine of powder transformation temperatures (Figure 3). According to the DSC analysis in Figure 3, start and finish temperatures of powder austenitic transformations were determined at -15ºC and 4ºC respectively. XRD analysis of NiTi powders is given in Figure 4. According to X-ray diffraction (Figure 4), it was observed to exhibit only austenitic phase at ambient conditions of powders. When nickel intent increased above 50 at. %, the Af transformation temperature could be seen to decreased until - 40°C for 51 at. % nickel [18].

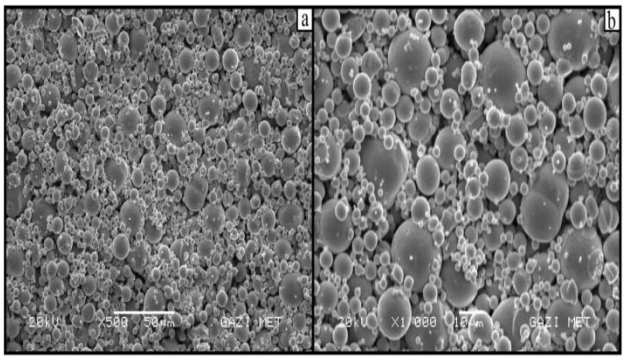


Figure 2. SEM images of pre-alloyed NiTi powders (particle size-14µm)

Table 1. The chemical composition of powders

Elements	Ti	Ni
Weight %	55	45
Atomic %	49.9	50.1

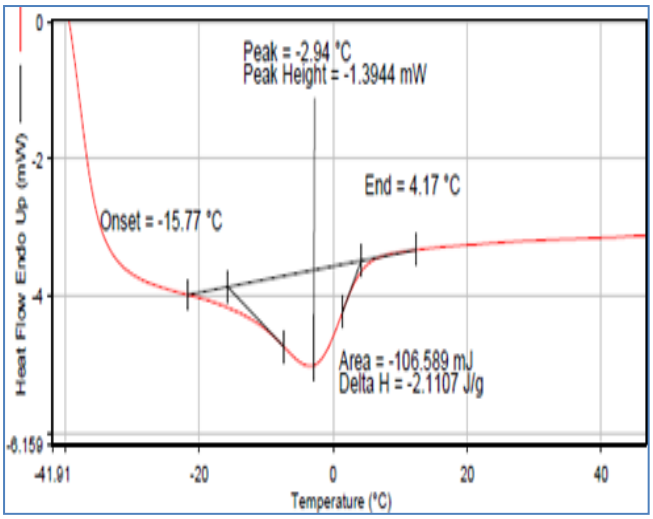


Figure 3. DSC analysis of powders

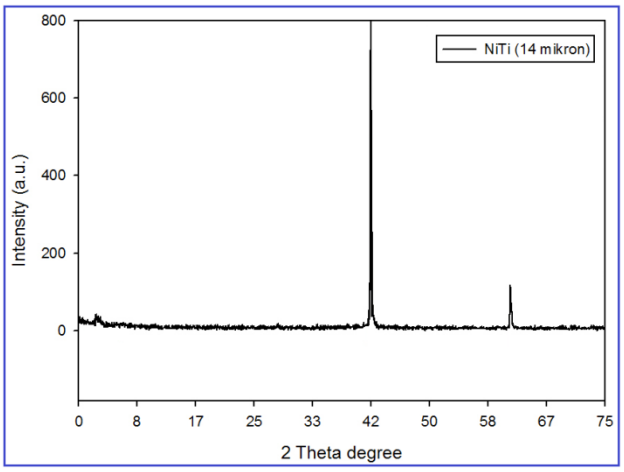


Figure 4. XRD analysis of NiTi powders

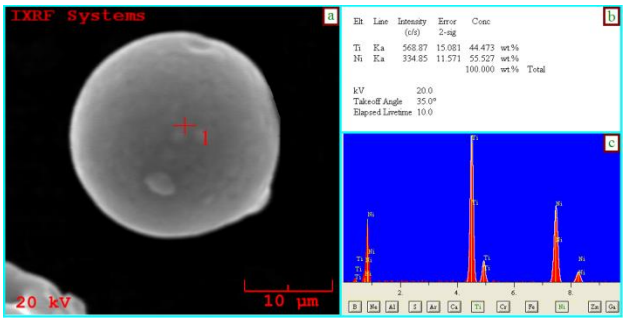


Figure 5.EDS analysis of NiTi powders; a-SEM image, b- wt.% elements dispersions, c- Ni and Ti peaks

In the present study, Ni content was only 50.1at. % (Table 1) and so the onset temperature could be decreased until -15ºC (Figure 3). The point EDS analysis on the SEM image of NiTi powder is given in Fig.5. According to EDS result in Fig.5, it was observed to be having only Ni and Ti content of powders with spherical and smooth surface characteristic. EDS analysis applied to powders supports XRD analysis and shows only austenitic phases in structure (Figure 5.b). Only Ti and Ni peaks were identified by EDS analyses in Figure 5-c. It was determined to belong to NiTi alloy of this peaks which define to B2austenitic phase (110, 200 and 211) [17].

Bulk density of pressed samples (NiTi powder) was measured approximately as 5 g/cm^3. Bulk density of NiTi samples added wt.4%Cu was measured as 5.21 g/cm^3. Density of NiTi samples added wt.4%Cu after sintering (850ºC-60 min.) was measured as 4.73 g/cm^3 (Figure 6). The value of increased density was measured as 5.063 g/cm^3 with increasing of the sintering temperature (1000ºC-60 min.). The value of density was determined as 5.235g/cm^3 after sintering process applied at 1000ºC for 300min in an another sample. The cause of the increased density value in samples could be considered as Cu powder content which affected to density of the structure with swelling effects at this temperature and then damping effects on the structure [19]. After sintering at 850ºC for 60 min., the hardness value of samples was measured as 532 HV, but increased with sintering temperature (1000ºC-60 min.) decreased hardness value and was measured as 523 HV, because of Cu contents swelling and damping effects. Increasing of the sintering time, increased the hardness value was measured as 730HVat 1000ºC for 300min. (Figure 6).

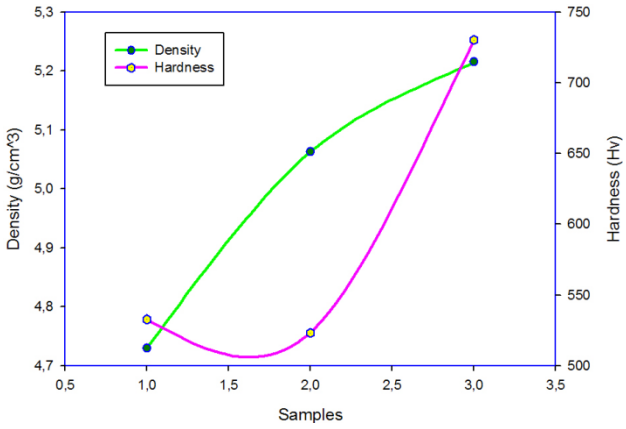


Figure 6. Density and hardness values of NiTi + 4%Cu samples after sintering; 1-850ºC-60 min., 2- 1000ºC-60 min., 3- 1000ºC-300 min.

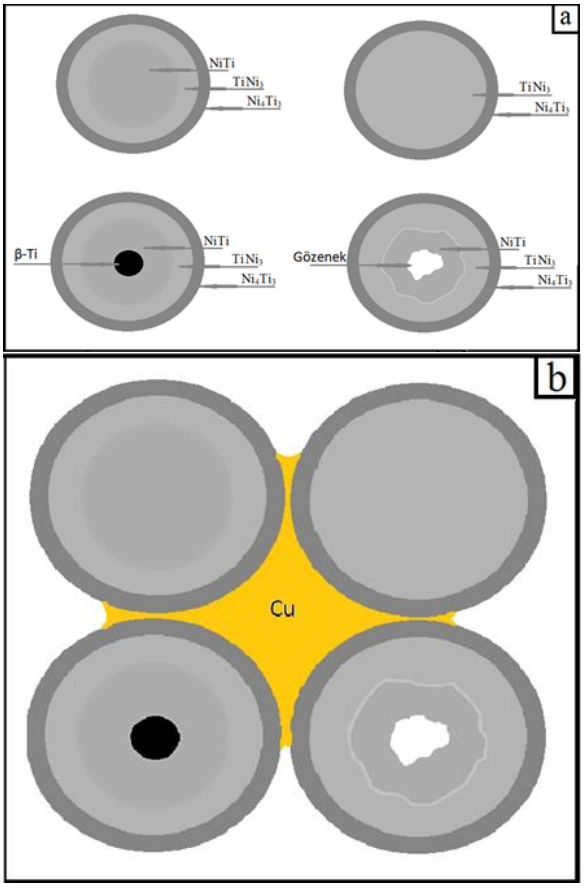


Figure 7. Illustration of the schematic phase occurred after sinter; a- Compounds, b- Shapes

Figure 7 shows schematic illustration of sintering process. When the schematic illustration was investigated, different multiphase structure was obtained with sintering process (as NiTi, $TiNi_3$, Ni_4Ti_3 and NiTiCu). Obtained phases in NiTi systems are recently illustrated with this type of schematic representation for clear expression [20,21].

Figure 8 shows XRD analysis of samples sintered at 1000ºC for 60 and 300 min. Intensity of Ni_3Ti phase in the XRD analysis (Figure 8) was obtained as the inner phase in NiTi phase structure with NiTi phase diagram (Figure 9). Table 2 shows phase ratio of NiTi + 4% Cu structure after sintering at 1000°C. Ni_3Ti ratio of samples sintered at 1000ºC for 60 min. and 300 min. was identified approximately 68% and 76% respectively. So it was determined that increasing Ni_3Ti ratio with increasing of sintering time (Table 2). This ratios and phases could be clearly observed in NiTi phase diagram (Figure 9) [22]. Ti_2Ni and Ni_3Ti formation were confirmed at slow cooling condition which used in this experiment. Gibbs energies of Ti_2Ni and Ni_3Ti phases are less thanNiTi phase and so it is difficult to obtain of only alone NiTi structure by solid – state diffusion [23, 24].

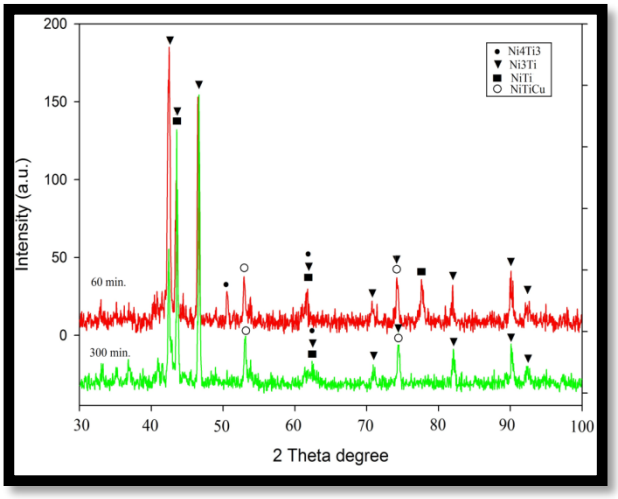


Figure 8. XRD analysis of NiTi+ 4% Cu structure after sintering at 1000°C

Table 2. Phase ratio of NiTi + 4% Cu structure after sintering at 1000°C

Sintering time (min.) at 1000°C	Phase rate (%)			
	NiTi	Ni_3Ti	Ni_4Ti_3	NiTiCu
60	20	68	10	2
300	16	76	6	2

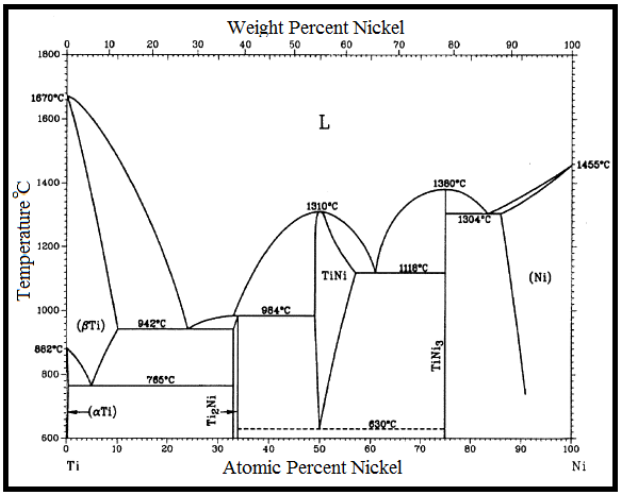


Figure 9. NiTi phase diagram (obtained of B_2 and Ti_3Ni_4phases) [25].

Figure 10-a and b illustrate microstructure of green pre-alloyed NiTi samples that sintered at 900ºC for 300 min. and 1050ºC for 60 min. When the microstructure images in Figure 10 were investigated, the change of the microstructure and phases with the effect of sintering temperature was observed. The appearance of liquid phase (Ti-$NiTi_2$ eutectic) with rising to 1050ºC of sintering temperature could be seen in Figure 9.

After sintering at 1050ºC, the appearance of liquid phase sintering (Ti-$NiTi_2$autectic) was identified with illustration of the schematic phase in Figure 7. As a result of this, It was expected to develop of a much more homogeneous microstructure with the disappearance of grain boundaries and diffusion towards the grain boundary of elements (Figure 10 b-d) [8].

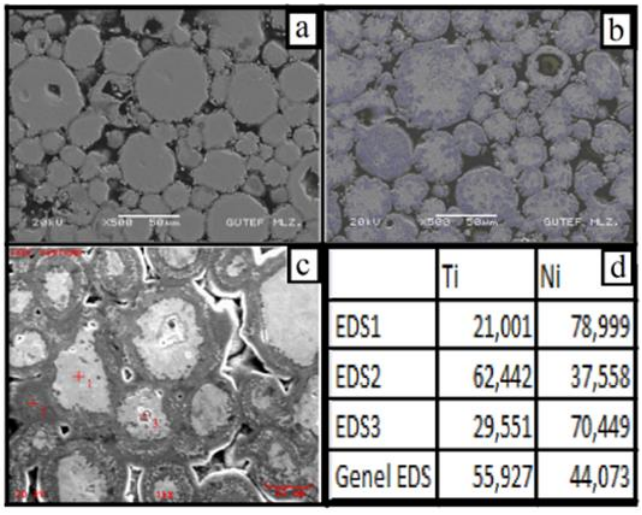


Figure 10. SEM images of pre-alloyed NiTi samples after sintering; a- 900°C-300 min., b- 1050°-60 min., c- EDS image (1050°C-60min.), d- Ni and Ti amounts

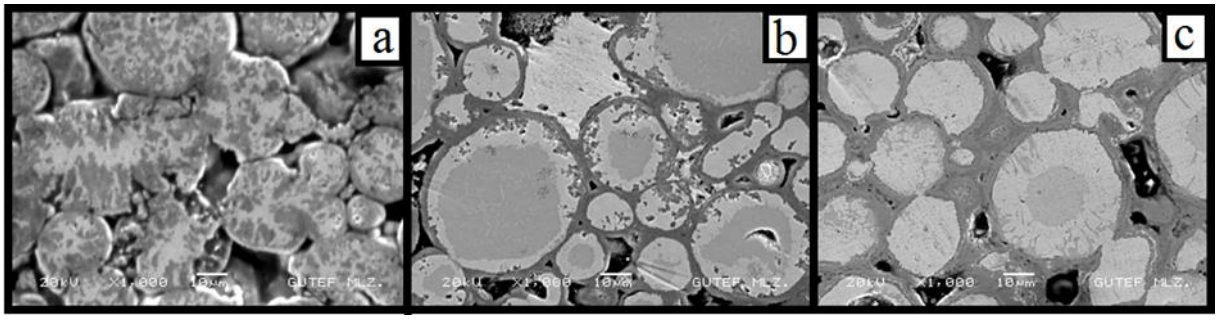


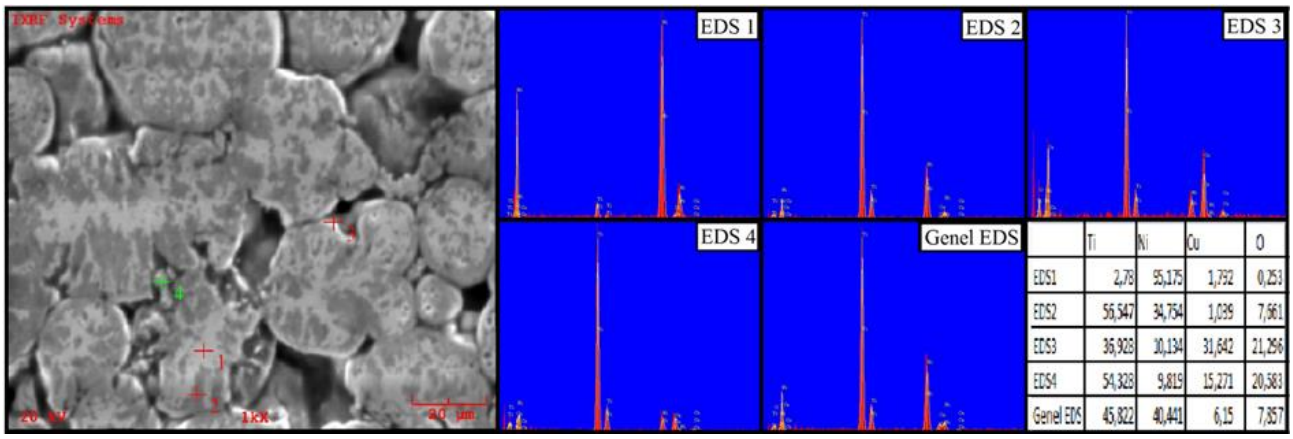
Figure 11. SEM images of sintered TiNi+%4Cu samples; a- 850°C-60min., b- 1000°C-60min., c- 1000°C-300min.

The formed multiphase structures ($TiNi_3$, NiTi, Ti_2Ni, Ni_4Ti_3) were determined after sintering at 1050ºC (Figure 10 c and d) [13]. The porosity was reduced with increasing of the sintering temperature to over of 1000ºC but was not removed under this temperature.

The reason for this situation, NiTi alloy exhibits an endothermic reaction at about 950°C (for ~ 49% NiTi alloy). Because of liquid phase sintering mechanism occur after 1020°C, endothermic reaction can become active (Figure 10 and 11) [26, 27]. In NiTi alloys, sintering temperature play an active role [28-31]. Sintering temperature after a certain point affects enhancing the mechanical properties and also could be seen to reduce the porosity[32]. Positive effects increased mechanical properties were obtained by multiphase structures of NiTiintermetallics formed by the addition of wt.4%Cu content [33]. Multiphase structures (as Ni_4Ti_3 phases) were obtained by Cu addition to sintered samples (NiTi) which was seen in figure 10 c and d. The obtained NiTi-4%Cu samples were sintered at 850ºC for 60 minute, 1000ºC for 60 and 300 minutes respectively (Figure 11 a-c).

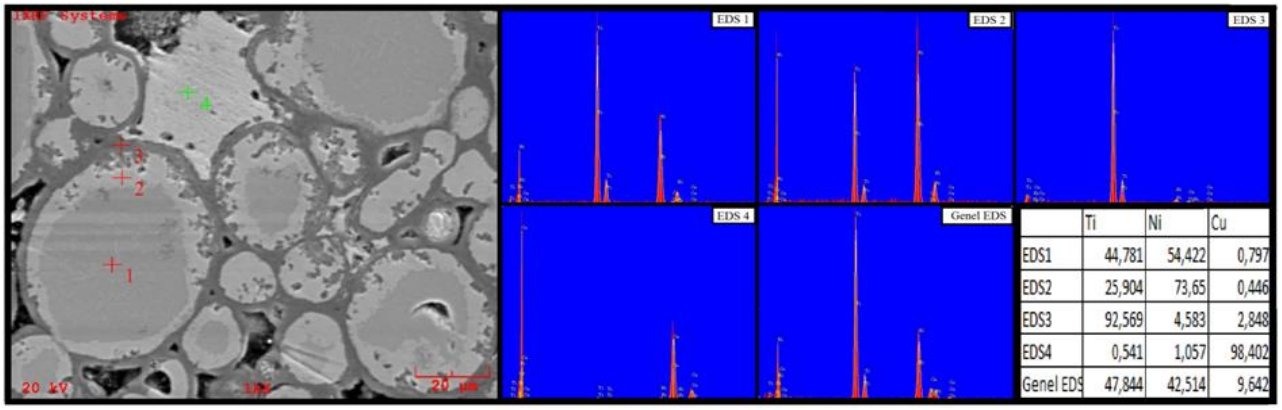
The homogeneous and purity microstructure with increasing of sintering time in Figure 11-c were achieved. The dissolution of Cu in microstructure was affected directly by sintering time which could be seen in Figure 11 b, c and other literature investigations [34]. For determining the element distribution amount of the resultant multiphase structure, EDS analyses were applied to sintered parts at 850ºC and 1000ºC for 60 minutes and at 1000ºC for 300 minutes (Figure 12, 13 and 14).

When EDS analyses were examined, same compounds ($TiNi_3$, NiTi, Ti_2Ni, Ni_4Ti_3 and NiTiCu) and elements distribution ratio could be seen in XRD analyses (Figure 8). Obtained multiphase structures were directly affected the phase transformations. Previously several studies on NiTi alloys (wt. 49-51% Ni) show B2—B19 phase transformation after dissolution treatment. Added Cu content effects not only transformation temperature but also hysteresis interval [35]. Moreover, the effect increased hardness value with high corrosion resistance, narrow transformation intervals and increasing of the resistance provide with protection of the precipitates such as $TiNi_2$ after addition of copper [36,37].



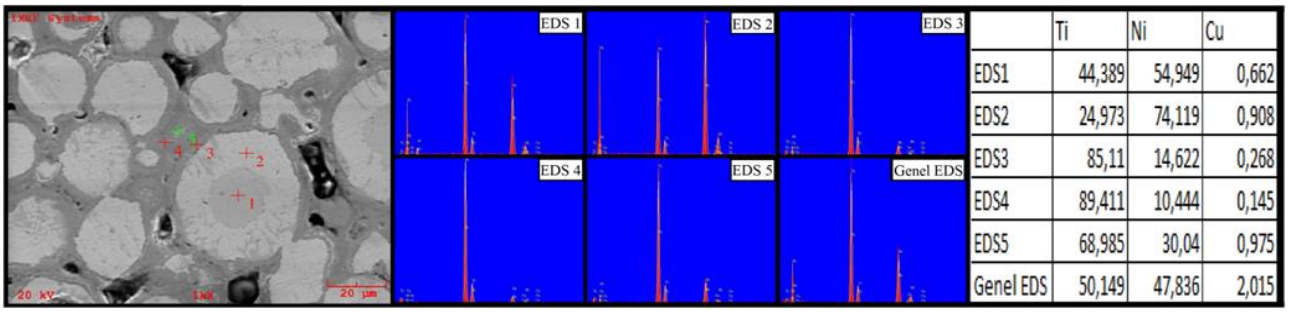
	Ti	Ni	Cu	O
EDS1	2,78	55,175	1,792	0,253
EDS2	56,547	34,754	1,039	7,661
EDS3	36,928	10,134	31,642	21,296
EDS4	54,328	9,819	15,271	20,583
Genel EDS	45,822	40,441	6,15	7,857

Figure 12. EDSanalyses of TiNi+Cu samples after sintering at 850ºC for 60 min.



	Ti	Ni	Cu
EDS1	44,781	54,422	0,797
EDS2	25,904	73,65	0,446
EDS3	92,569	4,583	2,848
EDS4	0,541	1,057	98,402
Genel EDS	47,844	42,514	9,642

Figure 13. EDSanalyses of TiNi+Cu samples after sintering at 1000ºC for 60 min



	Ti	Ni	Cu
EDS1	44,389	54,949	0,662
EDS2	24,973	74,119	0,908
EDS3	85,11	14,622	0,268
EDS4	89,411	10,444	0,145
EDS5	68,985	30,04	0,975
Genel EDS	50,149	47,836	2,015

Figure 14. EDS analyses of TiNi+Cu samples after sintering at 1000ºC for 300 min.

3. Conclusions

In this research paper, a homogeneous microstructure in the green powder metals (NiTi alloy) was confirmed with liquid phase sintering occurred with increasing temperature. Optimize sintering temperature and time of NiTi alloy + 4%Cu samples were obtained at 1000°C for 300 minute (5.235 g / cm^3). Hardness value was measured as 730 HV and an important significant increase in the hardness value was determined with multiphase structures ($TiNi_3$, NiTi, Ti_2Ni, Ni_4Ti_3 and NiTiCu) formed depending on the sintering temperature and time. It was determined that could be achieved of low porosity and good corrosion resistance, a homogeneous microstructure and martensitic transformation structures by the addition of wt.4%Cu content.

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