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Research Article

Characterization of Martensitic Transformation, Microstructure and a Kinetic Study of Ti-based High Temperature Shape Memory Alloy

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Abstract: High temperature shape memory alloys (HTSMAs) are widely used in many fiels such as industry, biomedical, aerospace, etc. In order to expand the usage areas of these alloys, it is necessary to improve the materials, especially the martensitic transformation temperatures should be controlled. Third elements are often added to the material to control the martensitic transformation temperature. Ti-12V-8Al (wt. %) alloy, which is prepared for use in aircraft engines in the aviation industry, is a good choice due to its low density. In this study, Ti-12V-8Al (wt. %) alloy was prepared with the help of arc-melting technique. The martensite-austenite transformation temperatures, phase formations, microstructure of Ti-12V-8Al (wt. %) alloy were examined by differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscope (SEM) and optical microscope (OM) respectively. In the DSC test, it was determined that the martensitic transformation temperature reduced according as the heating rate of the alloy. In XRD and SEM measurements, it was observed that the alloy has α″ martensitic phases as well as some β austenite phases. Thermal activation energies of the alloy were founded by Kissinger and Ozawa techniques. It was concluded that the activation energy amounts computed by these two techniques are parallel to each other.

Key words: Activation energy, High temperature shape memory alloy, Martensitic transformation

Ti-temelli Yüksek Sıcaklık Şekil Hafızalı Alaşımının Martensitik Dönüşüm, Mikroyapı Karakterizasyonu ve Kinetik Çalışması

Öz: Yüksek sıcaklık şekil hafızalı alaşımlar (YSŞHA) endüstri, biyomedikal, havacılık vb. gibi birçok alanda yaygın olarak kullanılmaktadır. Bu alaşımların kullanım alanlarını genişletmek için malzemelerin iyileştirilmesi, özellikle martensitik dönüşüm sıcaklıklarının kontrol edilmesi gerekmektedir. Martensitik dönüşüm sıcaklığını kontrol etmek için malzemeye genellikle üçüncü elementler eklenir. Havacılık sektöründe uçak motorlarında kullanılmak üzere hazırlanan Ti-12V-8Al (ağ. %) alaşımı düşük yoğunluğu nedeniyle iyi bir seçimdir. Bu çalışmada, Ti-12V-8Al (ağ. %) alaşımı ark-eritme tekniği kullanılarak hazırlanmıştır. Ti-12V-8Al (ağ. %) alaşımının martensit-ostenit dönüşüm sıcaklıkları, faz oluşumları, mikro yapısı sırasıyla diferansiyel taramalı kalorimetri (DSC), X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM) ve optik mikroskop (OM) ile incelenmiştir. DSC testinde alaşımın ısıtma hızına bağlı olarak martensitik dönüşüm sıcaklığının azaldığı tespit edilmiştir. XRD ve SEM ölçümlerinde alaşımın α″ martensitik fazlarının yanı sıra bazı β ostenit fazlarına da sahip olduğu gözlenmiştir. Alaşımın termal aktivasyon enerjileri Kissinger ve Ozawa yöntemleri ile bulunmuştur. Bu iki yöntemle hesaplanan aktivasyon enerjisi değerlerinin birbirine yakın olduğu sonucuna varılmıştır.

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Anahtar kelimeler: Aktivasyon enerjisi, Yüksek sıcaklık şekil hafızalı alaşımlar, Martensitik dönüşüm

1. Introduction

With the rised importance on both credibility and multi-functionality in aviation field, smart materials are quickly becoming a facilitate technology that is attracting the attention of engineers and scientists around the World [1]. In aviation field, high transformation temperatures are as significant as the lightness of the material. The lightness of the materials to be used in aircraft and space vehicles will firstly supply fuel austerities. In this reason, it is crucial to manufacture and improve materials that have both light and high transformation temperature in the aviation field [2]. NiTi based alloy has been utilized as welds in the field of aviation field [3, 4]. However the comparatively high density of NiTi alloys, which is whereon 6.7 g/cm^3, is not appropriate for the growing need of weight decline of aircraft materials in aviation field [5, 6]. In addition, the transformation temperatures of NiTi-based alloys are quite low, usually below 100 degrees [7, 8].

Ti-based alloys are a very good example of high temperature shape memory alloys. High temperature shape memory alloys occur solid-to-solid phase transformations excited by suitable temperature and/or stress changes and during which they can recover in appearance sustained strains [9]. Ti-based alloys are the most preferred alloys because of their low density (4.5 g/cm^3), useful mechanical qualities, low elastic modulus, high corrosion resistance, admissible biocompatibility and anti-magnetic features [10]. Secondly, Ti–V–Al alloy has an excellent cold workability. In the course of cold rolling, a depletion in thickness over 90 % can be simply achieved [11].

In titanium alloys, Al acts as efficient solution-strengthening component and rises the critical slip stress [12]. A high strength will obstruct dislocation movement along invalidity and increase the shape memory effect in high temperature shape memory alloys. In this way, the supplement of Al may have an useful influence on the shape memory effect of Ti–V–Al alloy [13].

In addition to these, thermal activation energy is an extremely useful property for shape memory alloys. The energy needed while phase transformation occurs in alloys is called thermal activation energy [14, 15]. This energy has a great effect on the activation of solid-solid transformation in the alloy. Kissenger and Ozawa have formerly improved a computational method for this energy [16, 17].

In our previous research, some properties of Ti–12V-xAl (x = 2, 4 and 6 wt. %) alloys designed for use in aircraft engine parts in the aviation industry were investigated [17]. Our aim is to examine what kind of changes will occur in the alloys as the Al contribution increases. This study is a continuation of that article and the transformation temperatures, phase transformation, microstructure and thermal activation energy properties of Ti-12V-8Al (wt. %) alloy were investigated. Transformation temperatures, phase formation, microstructure and chemical composition were researched by DSC, XRD, SEM and OM. Thermal activation energies were determined using the Kissinger and Ozawa method.

2. Material and Method

The Ti-12V-8Al (wt. %) alloy was produced by arc-melting system under argon atmosphere in water-cooled copper crucible. In the sample production, pure titanium, vanadium and aluminum (99.9 %, 99.99 % and 99.99 % respectively) were used. The

alloy was melted at least four times to ensure homogenization. The arc-melted alloy was cut in plate form in the cutting device for analyses. Leaf-shaped ingots were sealed into a quartz tube under vacuum. After homogenizing at 900 °C for 8 hours, rapid cooling was done by dropping into ice water. The transformation temperatures of the alloy were examined by DSC (Seteram; France) at different heating rates in the temperature range 70- 350 ^{o}C. Thermal cycles were taken at 20 ^{o}C/min, 30 ^{o}C/min and 40 ^{o}C/min heating rates. Thermal activation energies were calculated with the Kissinger and Osawa techniques using peak temperatures (T_p) acquired from DSC graph. X-ray diffraction (Pixcel3D) was used to determine of the phase structure of the Ti–12V-8Al (wt. %) alloy at room temperature. The microstructure and chemical composition of alloy with scanning electron microscopy (Quanta 200 FEG) and optical microscope (Simadzu DUH-W201S) were examined.

3. Results and Discussion

Figure 1 appears the DSC graph enrolled at three different heating rates of Ti–12V-8Al (wt. %) alloy. According to the DSC curves, the reverse martensitic transformation temperatures were determined based on the tangent technique. In the Figure 1, the endothermic peak on the heating curves displays the reverse martensitic transformation from orthorhombic martensite to cubic austenite. It is seen that the endothermic peak, which shows the reverse martensitic transformation temperatures in the alloy, decreases with the heating rate. It is also seen from the DSC curves that the endothermic peaks are weak. The reason for this is thought to be due to the partial transformation of the α″ martensite phases as a result of the heterogeneous dispertion of the precipitates at the grain boundaries [18, 19, 20]. The reverse martensitic transformation A_s starting and A_f finishing temperatures of alloy are 171 °C and 256 °C respectively at a heating rate of 20 ^{o}C/min (Table 1). Exothermic peak representing martensitic transformation was not observed during cooling. This is ascribed to the partial transformation of the β phase to the α″ phase, to the fact that some β phase remains unchanged in the structure or the DSC can not be detected due to the low level of enthalpy of the transformation [17, 21]. The A_s austenite start and A_f austenite finish values of the reverse martensitic temperatures related to the heating rate are given in Table 1.

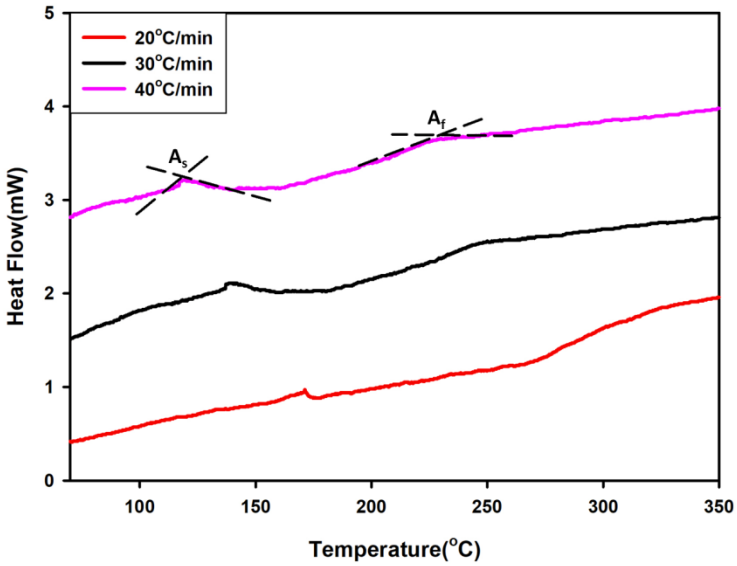

Figure 1. The DSC graph of Ti–12V-8Al (wt. %) alloy

Thermal activation energy can be obtained by finding utilization of thermal cycling curves with different heating rates, and this can be realized with the help of the techniques suggested by Kissinger and Ozawa [16, 22]. The thermal activation energy values were estimated from the slopes of Figure 2. In the Kissinger and Ozawa techniques, the formula in Equation 1 and Equation 2 are used, respectively.

$$\frac{d\left(\ln\left(\frac{\beta}{T_p^2}\right)\right)}{d\left(\frac{1000}{T_p}\right)} = -\frac{E_A}{R} \tag{1}$$

$$\frac{d(\ln(\beta))}{d\left(\frac{1000}{T_p}\right)} = 2.19 \times -\frac{E_A}{R} \tag{2}$$

In these equations, maximum peak temperatures T_p are acquired straight from the output of DSC curves recorded at 20 ºC, 30 ºC and 40 ºC. For these temperatures are 174 ºC, 162 ºC and 146 ºC respectively. R is the universal gas constant (8.314 J/ mol K), β is the heating rate and E_A is the thermal activation energy.

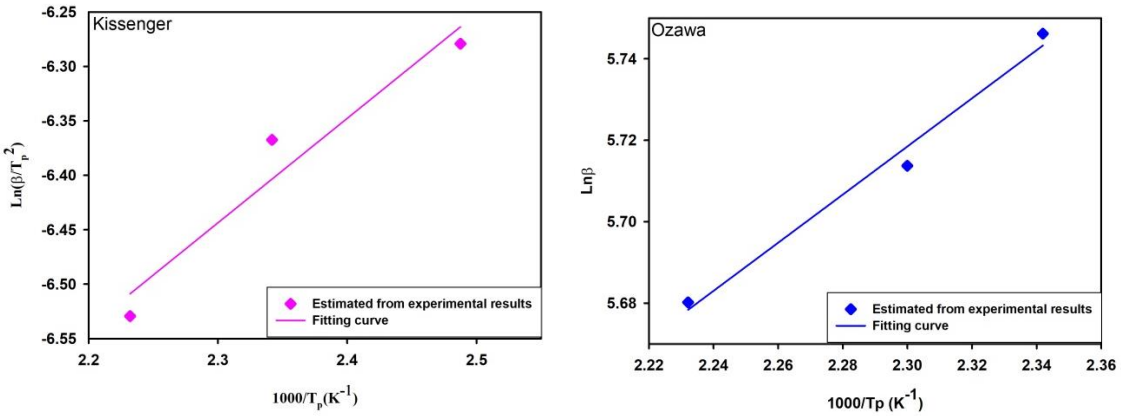

Figure 2. The Kissinger and Ozawa plots from which the activation energy for Ti–12V-8Al (wt. %) alloy is obtained

Table 1. A_s and A_f temperatures of the reverse martensitic transformation and thermal activation energy values

Heating Rate (ºC/min)	A_s (ºC)	A_f (ºC)	$E_{Kissenger}$ (kJ/mol)	E_{Ozawa} (kJ/mol)
20	171	256		
30	138	243	7.126	5.281
40	118	224		

The thermal activation energy found by Kissenger technique for Ti-12V-8Al (wt. %) is 7.126 kJ/ mol. In accordance with the Ozawa technique, this value was found to be 5.281 kJ/ mol. It is observed that these amounts are inferior than the thermal activation energy of the Ni-Ti. Therefore, activating Ti-V-Al alloy is easy than Ni-Ti alloy [23, 24, 25].

The XRD graph of the Ti-12V-8Al (wt. %) alloy at room temperature is given in the Figure 3. It was seemed that the alloy has an orthorhombic α″ martensite phase and

some β phase rested stable in the structure. The highest peak at 41.29 degrees indexed by (111) seen in 6 Al-added sample in our other article [17] is also seen in this sample. Furthermore, with the increase of aluminum contribution in the alloy, a new β phase emerged.

Figure 4 shows SEM surface morphologies of the alloy at 2500 and 5000 magnification. In the microstructure of the alloy, it is seen that it contains β phase as well as α″ martensite phase. This result is in agreement with XRD analysis. The acicular martensite structures and β phase are indicated by arrows in Figure 4. In the microstructure analysis, it was determined that the alloy did not have a completely α″ martensite structure at room temperature and that some β phase remained unchanged in the structure.

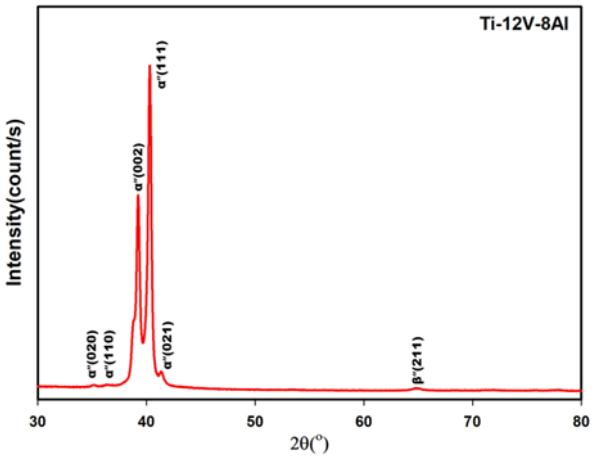

Figure 3. The XRD result of Ti–12V-8Al (wt. %) alloy

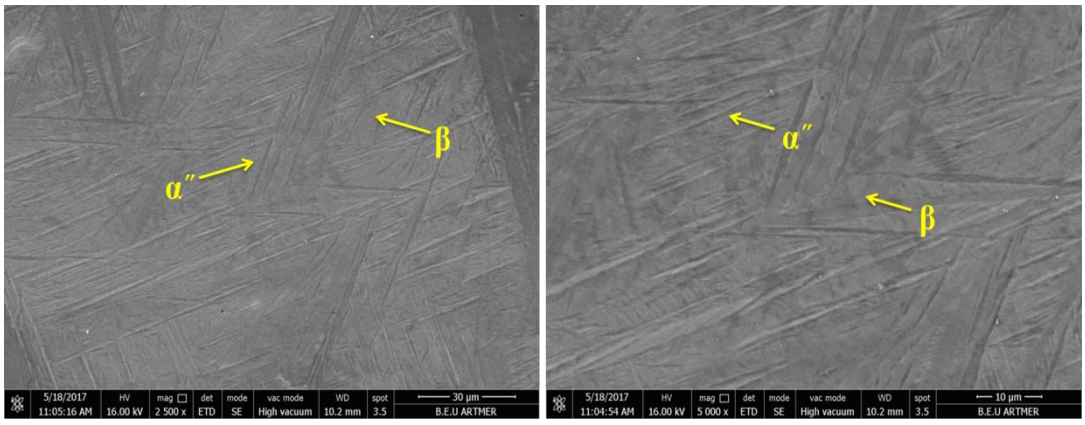

Figure 4. SEM images of the Ti-12V-8Al (wt. %) alloy at 2500 and 5000 magnification

Figure 5 represents the typical optical morphologies of the Ti-12V-8Al (wt. %) master alloy. As in the SEM images, the acicular martensite structures can be seen and contain many planar faults in Figure 5. The β phase cannot be seen very clearly.

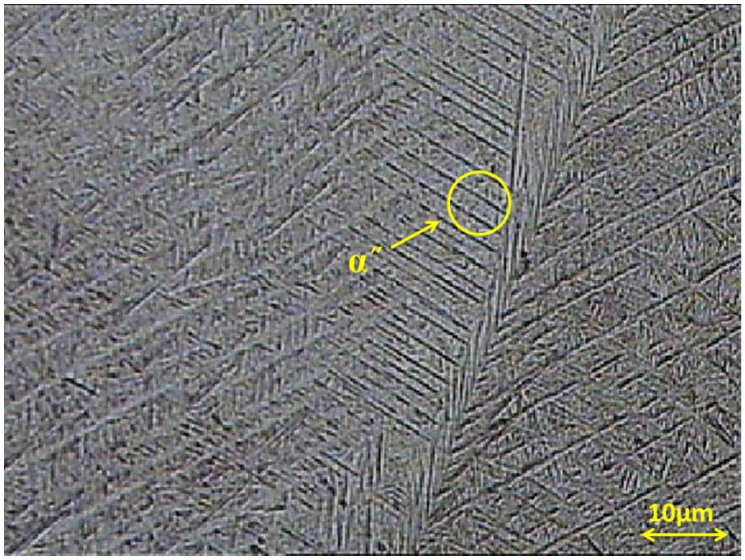

Figure 5. Optical image of Ti-12V-8Al (wt. %) alloy

4. Conclusion

In this research, phase transformation, microstructure and thermal activation energy of Ti-12V-8Al (wt. %) alloy were studied. The results are summarized below.

1. While the heating rate rises, the reverse martensitic transformation temperature of the alloy decreased in DSC analysis. The A_s and A_f reverse martensitic transformation temperatures were determined to be 171 °C and 256 °C at heating rate of 20 °C/min, respectively. No exothermic pike was found for the alloy while being cooled from 350 °C to room temperature.

2. The XRD graph at room temperature showed that there was some β phase and orthorhombic α″ martensite phase in the Ti-12V-8Al (wt. %) alloy. The martensitic structure with a lath-like or acicular shape was seen from SEM and OM, which is coherent with XRD analysis.

3. It has been identified that the thermal activation energy amounts obtained by both techniques are small rates than Ni-Ti alloy, as in our previous article [17]. It is thought that if researches are deepened by making different doping on Ti-V-Al high temperature shape memory alloys, lighter and more effective structures that can replace Ni-Ti alloys in the aviation field in the future.

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Author Statement

Öznur BAĞ: Drafted and wrote the manuscript, Investigation, Performed the experiments process, analytical and result analysis**.**

Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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