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Oxidation kinetics and oxygen permeability of the NiTiCu biomaterials

N. Ozdemir
Department of Metal Education, Faculty of Technical Education, Firat University 23169 Elazig, Turkey

The oxidation kinetics of NiTiCu alloys were investigated by thermogravimetric analysis (TGA). The oxidation kinetics followed a linear dependence of weight gain when indicated a diffusion controlled mechanism with various activation energies ranging from 157.569 to 25.123 kJ/mol. It is observed in SEM micrographs that TiO_2 oxides are formed between grain boundaries and inside of the grains. The morphology of the oxides is non-uniformly distributed into the grain boundaries. The oxygen permeability dependence of temperature of the alloys was also investigated. The increase in Ti content in the alloys leads to significant enhancement of the oxygen permeability and the oxygen transport increases in the sequence S1 < S2 < S3 <S4.

Key words: Alloys, Thermogravimetric analysis, microstructure, oxidation

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Corresponding authors: nozdemir@firat.edu.tr

1. Introduction

Titanium and its alloys are attractive material due to their superior strength –weight ratio and their corrosion resistance. The application of Ti-based alloys is concentrated mainly in aerospace military and chemical industries [1]. Shape memory and superelasticity of nearly equiatomic Ni–Ti alloys are widely employed in various medical devices. NiTi alloys combine their shape memory effect and superelasticity with excellent oxidation and mechanical properties and good biocompatibility. In orthodontic applications, superelasticity is especially useful, because constant force can be transmitted to the dentition over a long activation period resulting in a desirable biological response [2-5].

On the other hand, in order to improve the oxidation resistance of Ti-based alloys is used many methods. The silicon has been extensively used on oxidation behavior of these alloys and it is found that the addition of Si increases the high temperature oxidation resistance [6-9].

The oxidation and corrosion characteristic of an alloy in the various environments which it is likely to encounter during use in an important factor affecting the choice of material for a particular purpose. The oxidation behavior of a material is decided by numerous factors such as the composition of alloy, the distribution of particles size in the matrix and production techniques and environmental effects on oxidation behavior of alloys are important factors to prevent some negative effects such as oxidation, wear, etc. Even a very small change in one of these factors can seriously affect the oxidation behavior of the material [10-11]. In view of considering such effects, it may be worth investigating more closely the oxidation behavior of an alloy under different conditions. Hence, the evaluation and characterization of the oxidation behavior of a material is important.

In this connection, we have investigated oxidation behavior, oxygen permeability and microstructure of NiTiCu alloys with different composition.

2. Experimental

2.1. The preparation of the alloys,

In this study, Ti (purity 99.5%, grain size, 150 μm), Ni (purity 99.9%, grain size, 10 μm) and Cu (purity 99.9%, grain size, 60 μm) powders were used. The chemical composition of the alloys is shown in Table 1. The powders were mixed with each other in conical flask using a mechanical stirrer of 1500 cycle/min for 20 min. Four various mixtures were used cold compacted in a floating die using hydraulic press at compaction pressure of 20 MPa. The alloys were sintered in a furnace at 560 ^oC in argon atmosphere.

2.2. Measurements

The chemical composition in weight percentage of NiTiCu alloys are given in Table 1. and the alloys were named as S1, S2, S3 and S4. (see Table 1). The surface of the alloys was polished to 3 μm finish with diamond paste before subjected to oxidation. The oxidation kinetics was performed in non-isothermal condition using by a computer-controlled Shimadzu TGA-50 instrument at 10 ^{o}C/min heating rate. The thermogravimetric (TGA) thermograms were obtained in an open crucible from room temperature and 500 ^{o}C. Microstructures of the alloys were investigated by using a scanning electron microscopy (SEM).

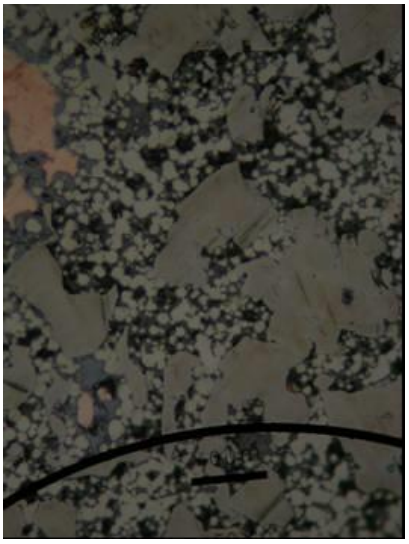
Table 1. Chemical composition in weight percentage of NiTiCu alloys

Alloy	%Ni	%Ti	%Cu
S1	45.1±0.1	48.9±0.1	6.0±0.1
S2	45.2±0.1	49.1±0.2	5.7±0.2
S3	45.0±0.2	49.5±0.1	5.5±0.1
S4	45.0±0.2	49.6±0.1	5.4±0.2

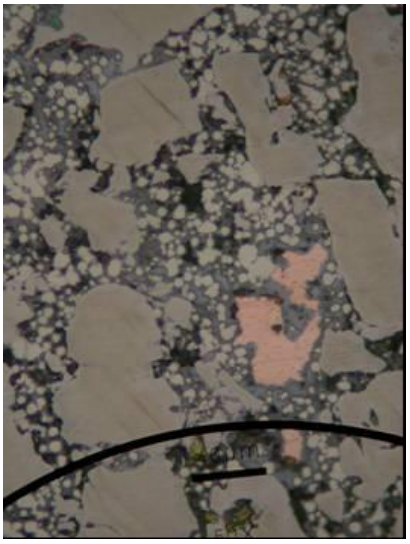
3. Results and discussion

3.1. Microstructure

The micrographs of the alloys are shown in Fig 1(a-d). The results obtained from SEM on the oxidized alloys revealed various morphologies depending upon the alloy composition.



(a)



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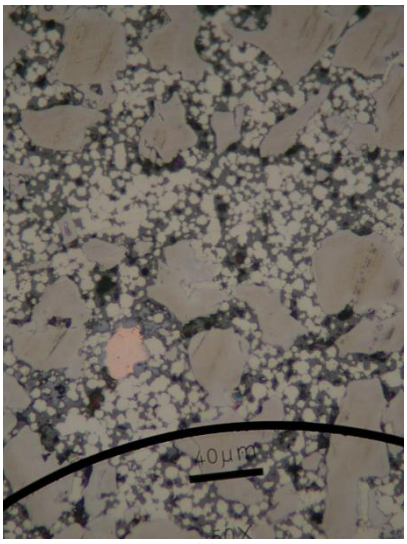

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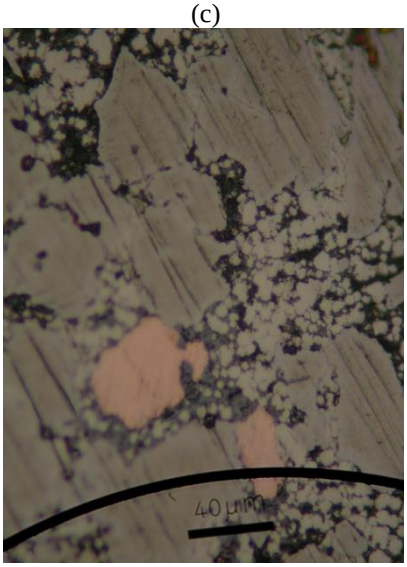

(d)

Fig.1. The micrographs of the alloys a) S1 b) S2 c) S3 d) S4

It is observed in the figure that TiO_2 oxides are formed between grain boundaries and inside of the grains, where the dark phases are TiO_2 scales. It can be noted that the morphology of oxides is non-uniformly distributed into the grain boundaries. This type of structure shows the formation of oxides at the grain boundary. It is evaluated that the morphology is formed by inward oxygen transport through grains and grain boundaries. The microstructure formation of oxidation is associated with the construction of shapeless oxides in main matrix.

3.2. Oxidation kinetics

Oxidation kinetics of the alloys was carried out by thermogravimetry analysis performed in the temperature range of 25-500 ºC. TGA curves are plotted as a percentage change from the initial mass of the alloys. Fig. 2 shows the relationship between weight gain and time for the alloys. It is seen that oxidation is proportional to weight gain. From

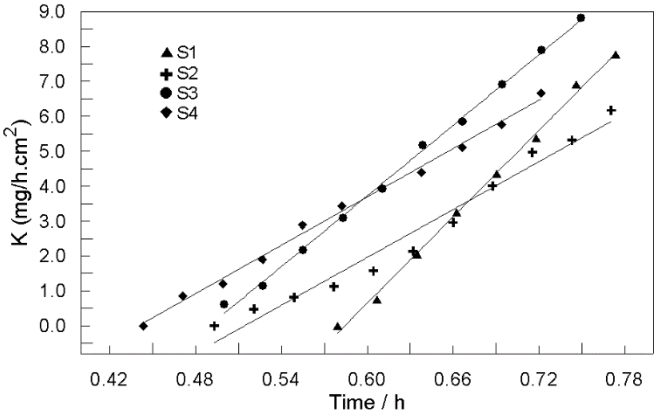

Fig. 2. Plots of K versus time for the alloys

these figures, it can be seen that the S4 alloy has a greater oxidation kinetics and oxidation kinetics of the alloys follows S1<S2<S3<S4. It is well-known that when an alloy is exposed to oxidized environments at elevated temperatures, oxidation of non-oxide alloy will occur. In oxidation mechanism of the alloys, TiO_2 scales can be formed on surface and grain boundaries according to the reaction,

$$Ti+O_2 \rightarrow TiO_2$$

The oxidation kinetics at a given temperature can be expressed by the linear rate, parabolic and logarithmic laws. The oxidation rate constants of the alloys were calculated and shown as a function of time. Plots of the oxidation rates with time were found to be linear (Fig. 2). This shows that the oxidation rates of alloys linearly increases with time. Thus, it is suggested that the oxidation process is controlled by the interfacial reaction between oxygen gas and Ti metal. In this process, diffusion controls the oxidation of alloys. In the studied temperature range, linear oxidation law is determined using the generic oxidation relationship,

$$(\Delta w / A) = Kt \qquad (1)$$

where $\Delta w / A$ is the weight gain per geometric area, K is the oxidation rate and C is a constant.

The temperature dependence of oxidation rate of the alloys follows the usual Arrhenius relationship [12],

$$K = K_o \, exp\left[-\frac{E}{RT}\right] \qquad (2)$$

where K_o is the pre-exponential constant, E is the activation energy, R is the gas constant and T is the temperature. Arrhenius diagram where K values are plotted versus the inverse of temperature. Thus, linearity is expected when logarithmic of K, determined from the Eq(2), is plotted versus 1000/T in Fig. 3. From these figures, the oxidation behavior was classified into two ranges with a rapid oxidation in the initial stage followed by a slower oxidation (see ranges I and II). It is evaluated that the oxidation at lower temperature is controlled by the diffusion of Ti ion through the grain boundaries. At high temperature, the oxidation is controlled by the diffusion of oxygen ion through the grain boundaries. The plots exhibited two distinct activation energy values. These are termed by E^{1st} and E^{2nd} , respectively (see in Fig. 3, E^{1st} for range I and E^{2nd} for range II) and these values were calculated from the slope of Fig. 3 and are given in Table 2. Oxidation mechanism shows two activation energy values having E^{1st} and E^{2nd} due to a change in the kinetic of the oxidation formation. It can also be evaluated that the difference between activation energy values indicates different oxidation mechanisms and oxidation kinetics with increasing temperature. The first range, the oxidation rates are controlled by the surface reaction of oxygen with active sites on the surfaces of the specimens, while at higher temperatures (range II), oxidation is controlled by the chemical reaction, but also by the diffusion of oxygen through the boundary layer on the oxidized. We note to discussion that there is a significance of the activation energy. This energy changes during the oxidation of the alloys and the dominant oxidation mechanism changes during the oxidation process. In the investigated temperature range, there are two oxidation stages, in which the oxidation mechanism controlled by various mechanisms. In these mechanisms, oxygen gas chemically reacts with surface appearing due to oxide formed at the alloy surface and grain boundary.

Table 2. Oxidation parameters of the alloys

Alloy	E^{1st}(kJ/mol)	E^{2nd}(kJ/mol)
S1	157.569	54.577
S2	69.454	47.777
S3	76.844	33.155
S4	69.008	25.123

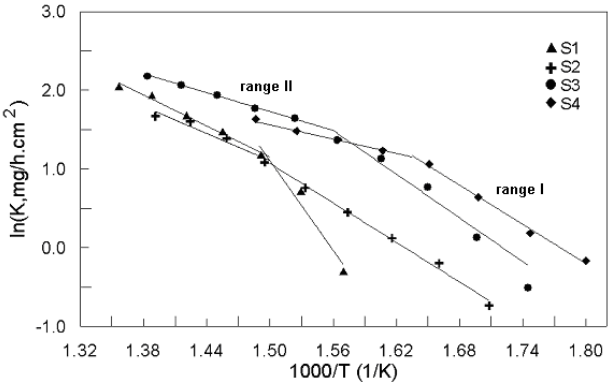

Fig. 3. Plots of lnK versus 1000/T for the alloys

The activation energy values of the oxidation are changed with composition of the alloys. This indicates that Ti content increases amount of oxidation. Thus, it seems more likely that the diffusion of Ti becomes the dominant process for the oxidation of alloys studied. The difference in the activation energy values in the two cases may be understood in view of the fact that the alloy investigated is a homogeneous structure and oxides particles is a formed contain main oxide TiO_2. We suggest that the diffusion of oxygen is the dominant for oxidation of these alloys. It is evaluated that the activation energy values are close to required for oxygen molecules diffusion through the oxide layer during the oxidation process. Two oxidation modes take place in the alloys. In the fist mode, oxidation is slow which occurs by diffusion of oxygen in matrix, while the second mode is fast in matrix.

In order to indicate effect of Ti content on oxidation behavior of the alloys, Fig. 4 was plotted using slopes of Fig.3. It is seen that the content has a important effect on oxidation behavior. The increase in Ti content cause the fact that the oxidation mechanism changes.

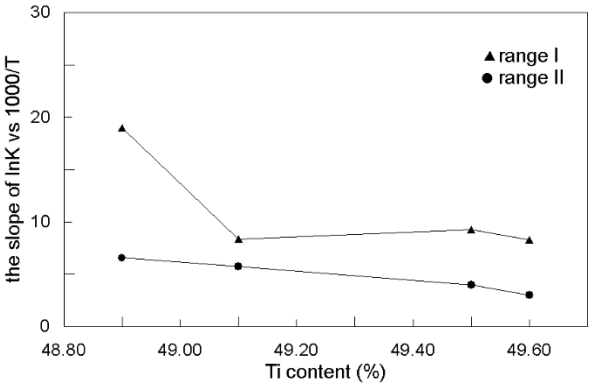

Fig. 4. The variation of slopes of lnK vs 1000/T with Ti content.

The oxygen permeability of the alloys by means of TGA is also expressed as follows,

$$O_{per} = \frac{m.d}{A.(\Delta T / \beta).\Delta P} \quad (3)$$

where m is the mass of oxidized surface with thickness of d, A is the area measured temperature range, ΔT is the temperature range, β is the heating rate, ΔP is the difference pressure between two sides of the alloys. The oxygen permeability of the alloys was determined using Eq. (3) via TGA curves and is given as a function of temperature (Fig. 5). It is clearly seen in the figure that oxygen permeability of the alloys increases depending of alloy composition. The increase in Ti content leads to enhancement of the oxygen permeability and oxygen transport increases in the sequence S1<S2<S3<S4.

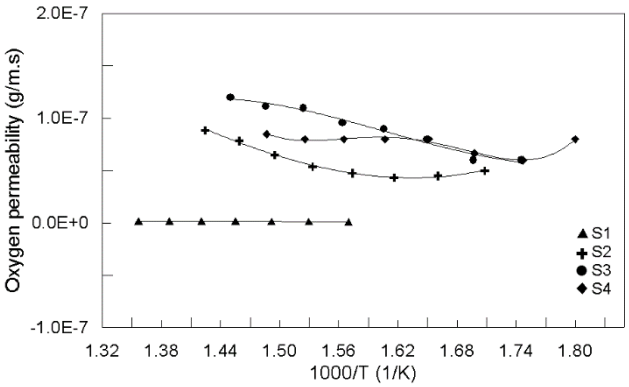

Fig. 5. Plots of oxygen permeability versus 1000/T for the alloys

4. Conclusions

It is found that the oxidation kinetics of alloys studied follows a linear dependence of weight gain In microstructure, TiO_2 oxides are formed between grain boundaries and inside of the grains and the morphology of the oxides is non-uniformly distributed into the grain boundaries. The oxygen permeability dependence of temperature for the composites was also investigated. The oxygen transport increases in the sequence S1 < S2 < S3 <S4.

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