OXIDATION BEHAVIOR OF CuAlTa SHAPE MEMORY ALLOY AT HIGH TEMPERATURES

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ABSTRACT

The isothermal oxidation behavior of Cu-11Al-3Ta (in mass %) high temperature shape memory alloy (HTSMA) was investigated by using the thermogravimetric analysis (TG) method. The alloy was initially heated under standart atmospheric pressure in the range from 25ºC to 1000ºC with a heating rate 20ºC/min. The oxidation gain was linear till 600ºC, while parabolical at higher temperatures. Different isothermal oxidation temperatures (700ºC, 800ºC, 900ºC and 1000ºC) were chosen in the temperature interval investigated. The oxidation kinetics was followed by the gravimetric method at the temperature values selected. The activation energy of the process was calculated using the Arrhenius relation. The phase transformation temperatures (A_s, A_f, M_s and M_f) of the as-cast alloy were determined by the differential scanning calorimetry (DSC) method. They referred to 291ºC, 396ºC, 287ºC and 224ºC, respectively. It was found that they changed significantly in the course of oxidation. Many martensite plates were observed in the alloy's structure using Nikon Eclipse MA200 optical microscope. Grain boundaries were also detected.

Keywords: *oxidation kinetics, shape memory alloys, thermal activation energy.*

INTRODUCTION

Shape memory alloys (SMAs) are metallic alloys containing two, three or even four components of a specific content. There are two chief families of SMAs - the copper-based materials such as Cu-Al (Zn, Ni, Be, Mn, etc.), and NiTi-based alloys. They are called shape memory materials because of their property of 'remembering' when subjected to thermo-mechanical, temperature or magnetic treatment [1]. They are widely used as intelligent materials [2] in actuators and automotives production, biomedical industry, aerospace. The investigation carried out during the last decades is predominantly focused on their unique functional properties of a shape memory effect (SME) and superelasticity (SE), which are closely related to the reversible martensitic transformations [3] in their structutre. Nowadays, NiTi-based alloys are the most important SMAs, showing excellent SME and SE. Cu-based SMAs, such as Cu-Al-Ni, Cu-Zn-Al and Cu-Al-Mn alloys, etc. [4, 5 - 7] also attract great attention for engineering applications because of their cost which is lower than that of Ni-Ti-based SMAs, and SME and SE which are better than those of Fe-based SMAs. On the other hand, these SMAs have limitations at martensitic transformation temperatures higher than 100ºC. The new generation engineering aplications in areas such as automotive, robotics, and aeronautics industries require the improvement of HTSMAs behavior at higher temperatures.

The high temperature requirement for a core exhaust chevron design is resolved by identification, testing and validation of new TiNiPt HTSMA [8, 9]. But most HTSMAs are very difficult to process and treat due to their limited ductility and poor fatigue resistance at a room temperature. This makes them very expensive to manufacture. Therefore, alternative low cost materials containing copper are studied.

The purpose of this research is to investigate the oxidation behavior at standard pressure of CuAl-based alloy containing Ta (3 mass %) and determine the transformation temperatures using a differential scanning calorimeter (DSC).

EXPERIMENTAL

Cu-11Al-3Ta (in mass, %) HTSMA was fabricated using the arc-melting process under argon gas atmosphere. Then the alloy was homogenized at 900ºC for 24 h and directly quenched in saline ice water. The step of alloy homogenization at a temperaure in the β-phase field followed by rapid cooling produced microstructures formed by the metastable phases present and corresponding martensitic transformation [10]. The specimens were cut into cubes of approximate dimensions of 5.2 mm ×5.2 mm ×5.2 mm for the subsequent oxidation study. Prior to the testing all surfaces were polished by grinding and cleaning with acetone. The prepared specimens were exposed to oxidation for 1 h at the selected temperatures (700ºC, 800ºC, 900ºC and 1000ºC) using Perkin Elmer Pyris TG/DTA thermal analysis sysytem. Perkin Elmer (DSC) equipment was used for the identification of oxidation products and the transformation temperatures determination. DSC measurements were made at a heating and cooling rate of 20ºC/min. Nicon Eclipse MA200 optical microscope measurement system was used to observe the alloy microstructure. A solution containing 100 ml H_2O + 25 ml HCI + 10g FeCI was used as an etchant.

RESULTS AND DISCUSSION

Fig. 1 shows the plots of mass gain per unit area as a function of the temperature applied. They are obtained on the ground of the continuous thermo-gravimetric analyzis of Cu-11Al-3Ta alloy oxidized in air at temperatures in the range of 25ºC - 1000ºC. According to Fig. 1a the alloy oxidation follows a varied path. At the beginning the mass gain increases linearly. In this region As = 281ºC (Austenit start) and Af = 413ºC (Austenit finish). They are defined in the course of the transition of austenite phase to that of martensite. Then, the mass

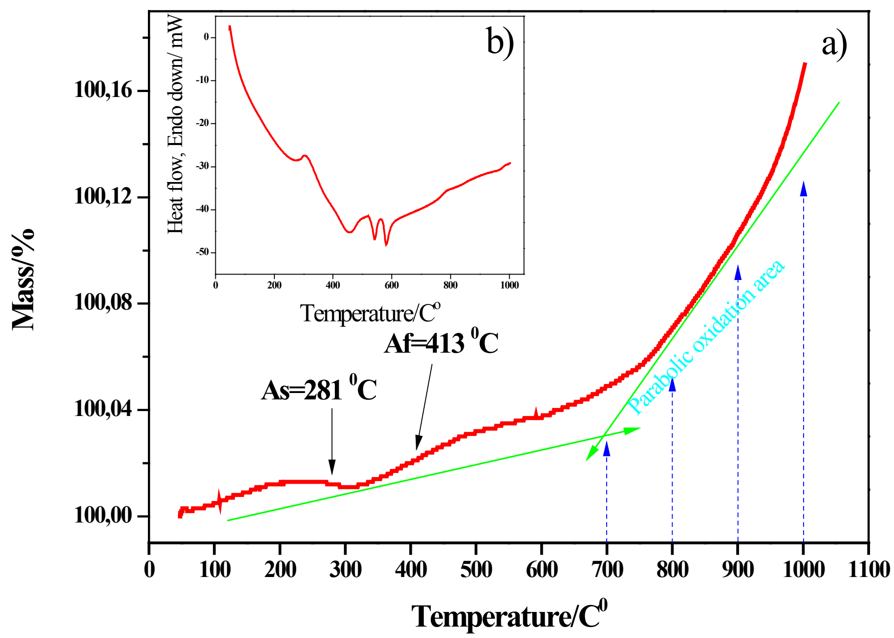

Fig. 1. a) Non-isothermal TG/DTA measurement of Cu-11Al-3Ta HTSMA from room temperature to 1000ºC in air atmosphere; b) DTA curve of Cu-11Al-3Ta alloy sample between room temperature and 1000ºC.

Table 1. The oxidation rate constants and the transformation temperature values of the CuAlTa HTSMA after isothermally oxidation between 700 to 1000ºC for 1 h.

Oxidation Temperature	A_s (ºC)	A_f(ºC)	M_s(ºC)	M_f(ºC)	k_p $mg.cm^{-4}s^{-1}$
As-cast	291	396	287	224	-
700 ºC	364	414	308	214	0.1921
800 ºC	362	416	295	223	0.0020
900 ºC	342	416	287	209	0.1031
1000 ºC	366	446	303	189	0.1071

growth follows a parabolic rate law [11].

Four different isothermal temperatures are selected in the region of parabolic mass increase. The TG mass gain curves referring to isothermal oxidation for 1 h under standard pressure are shown in Fig. 2. The oxidation rate constant k_p is expressed [11] by:

$$(\Delta W/A)2 = k_p\, t \quad (1)$$

where (ΔW/A) is the mass gain per unit area of the sample, t is the oxidation time. k_p can be calculated from the slope of the linear regression line of $(\Delta W/A)^2$ vs. t plot. The values of k_p calculated on the ground of Eq. 1 are shown in Table 1. It is seen that k_p at 700ºC is remarkably higher than the corresponding values obtained at the other oxidation temperatures. The DTA curve of the alloy is shown in Fig. 1b. It includes some endothermic peaks. That close to 700ºC refers to Al_3Ta phase precipitate. The latter is thought to cause the abnormal mass gain observed at 700ºC.

Al_3Ta phase containing Ta particles and molten aluminum is observed [12] in the structure of CuAlTa alloy. It is suggested that the parabolic change shown in Fig. 1 is determined by Al_3Ta phase. The latter is thought to cause the formation of Al_2O_3 and Ta_2O_5 structures [10]. They most probably determine the fact that k_p value at 700ºC is higher than those at the other oxidation temeperatures

The oxidation activation energy, E_o, is calculated using the following equation [11]:

$$kp = k_0 exp(-E_0/RT) \quad (2)$$

where k_0 is the pre-exponential factor, T is the temperature, while R is the gas constant. Fig. 3 displays the plot of ln k_p vs. 1000/T for the temperature range studied. The value of E_o is found equal to 12.66 kJ mol^{-1}.

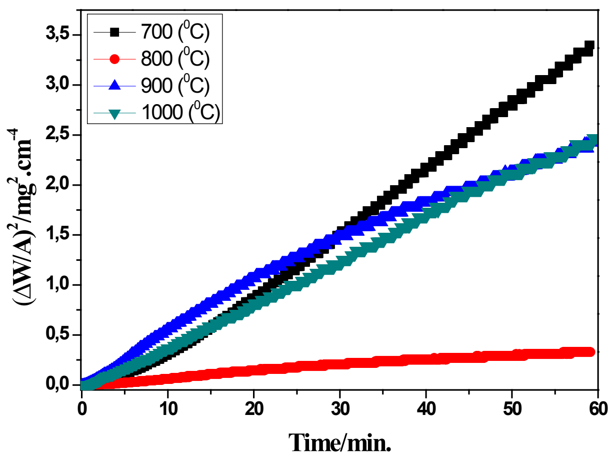

Fig. 2. Oxidation curves of Cu-11Al-3Ta HTSMA at 700 - 1000ºC for 1 h in air atmosphere.

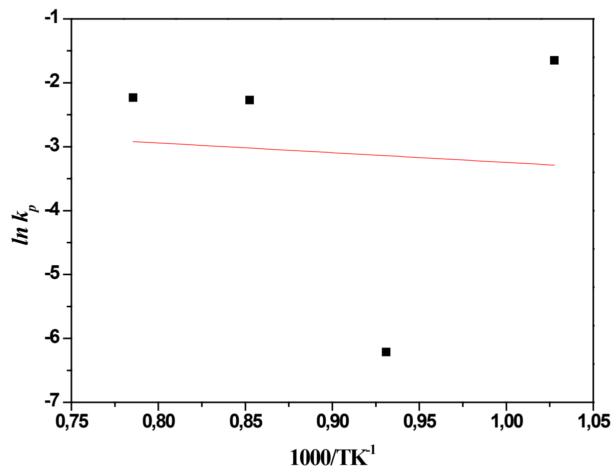

Fig. 3. Arrhenius' curve for the parabolic oxidation constant (k_p) in a temperature range of 700 - 1000ºC.

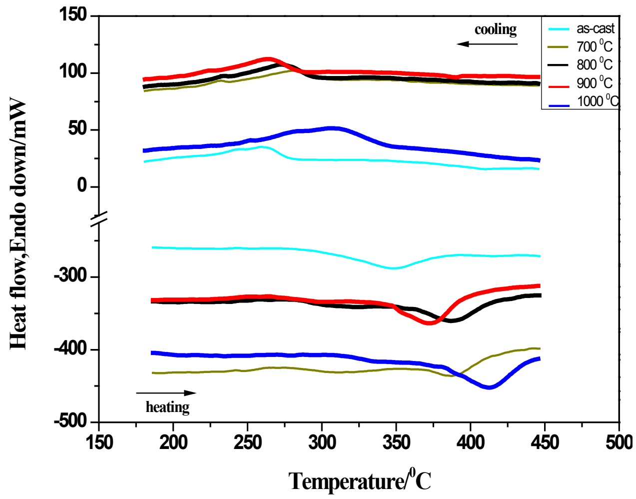

Fig. 4. The DSC curves for Cu-11Al-3Ta alloys at different temperature (DSC curves are marked by different).

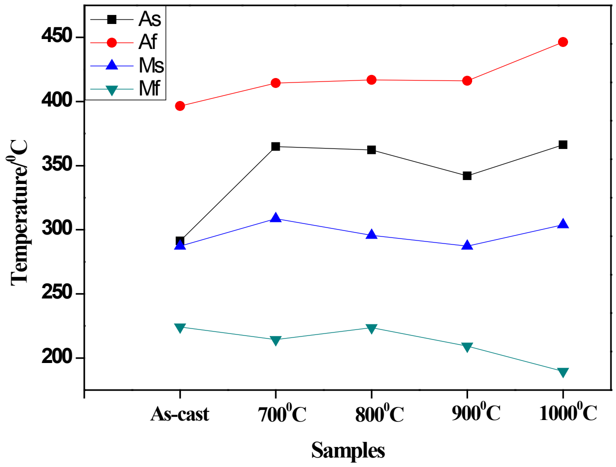

Fig. 5. The changes of transformation temperature of Cu-11Al-3Ta by oxidation temperature.

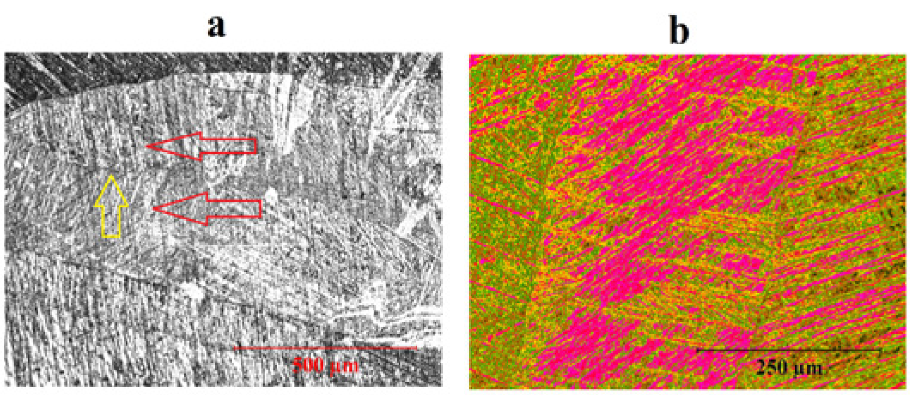

Fig. 6. Optical micrographs image of Cu-11Al-3Ta alloy taken from the different region: a) 500µm; b) 250µm.

DSC measurements are carried out to investigate the effect of the oxidition behavior on the shape memory effect of CuAlTa HTSMA. The heat flow curves of as-cast and oxidized samples are shown in Fig. 4, while the changes of the transformation temperatures are summarized in Table 1. The comparison of the transformation temperature values shows that they increase (Fig. 5). This is because they are significantly effected by the oxidation [11].

Fig. 6a,b shows the optical micrograph images of CuAlTa alloy at a room temperature. Martensit plates and grain boundaries are seen. Fig. 6a shows twisted martensite plates at places indicated by a red arrow. The sides of the plane marked by an yellow arrow are in a twin relationship. It is seen in Fig. 6b that these martensite plates are separated by grain boundaries.

CONCLUSIONS

The following observations are obtained in the course of the thermal oxidation and micro-structure analysis of CuAlTa alloy:

● Cu-11Al-3Ta is a high temperature shape memory alloy having a martensitic transformation temperature higher than 200ºC;

● The transformation temperatures of the alloy increase as a result of the oxidation;

● The rate constant k_p at 700ºC is remarkably higher than those obtained at the other oxidation temperatures studied. Al_2O_3 phase originating at the melting temperature of Al at 660°C is believed to determine this effect.

The micrographs obtained show twisted martensite plates and grain boundaries between them in the alloy's structure.

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