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Microstructure characterization and effect of thermal cycling and ageing on vanadium-doped Cu–Al–Ni–Mn high-temperature shape memory alloy

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The effect of vanadium addition on the microstructure of Cu–Al–Ni–Mn high-temperature shape memory alloy (SMA) and its thermal cycling and ageing behaviour has been investigated. Using scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction analysis, the morphology, distribution and structure of secondary phase, induced by vanadium addition, have been identified. The effect of secondary phase on grain refining of Cu–Al–Ni–Mn has also been revealed. Differential scanning calorimetry measurement was used to investigate the effect of thermal cycling and ageing on the transformation temperature. It has been found that thermal cycling has a strong influence on the transformation temperature of the present Cu–Al–Ni–Mn–V high-temperature SMA. Ageing also caused an apparent change of the transformation temperature. It has been suggested that this was mainly due to the precipitation of secondary phase, because the sample was heated to a rather high temperature in both thermal cycling and the ageing process. The experiment showed that the transformation temperature could be maintained stable in the thermal cycling process by pre-ageing the sample at a suitable temperature.

1. Introduction

For a long time, tremendous effort has been made to develop shape memory alloys (SMAs) of various compositions to satisfy increasing demands of application. Among the many SMAs developed so far, Ni–Ti, Cu–Zn–Al and Cu–Al–Ni base alloys are the most popular and have been extensively studied [1]. Ni–Ti alloy exhibits excellent shape memory behaviour and good mechanical properties [2]. However, the fact that it exhibits shape memory effect normally at a temperature lower than 100 °C, and its high cost, limit its application. Cu–Zn–Al SMA is cheap, easy to manufacture and exhibits good shape memory effect, but the mechanical properties, such as fatigue and thermal stability, of this alloy are not as good as that of Ni–Ti alloy and also it cannot be used at a temperature higher than 100 °C [2]. Compared with Ni–Ti and Cu–Zn–Al alloy, Cu–Al–Ni alloys can be exploited for their shape memory effect at high temperature [3]. Therefore, Cu–Al–Ni alloy is a potential candidate for application of shape memory effect, especially at high temperature.

Two major problems restrict the practical application of Cu–Al–Ni SMA. One is the thermal stability and the other is its mechanical property. Unfortunately, the ductility of Cu–Al–Ni SMA is generally found to be poor with limited ductility [4]. Indeed, polycrystalline Cu–Al–Ni alloy always presents intergranular failure and exhibits relatively poor shape memory effect and pseudoelasticity [5, 6]. The origin of brittleness in polycrystalline Cu–Al–Ni alloy has been attributed to the presence of the brittle γ_2 phase at grain boundaries [7], high elastic aniostropy and large grain size [8]. From this point of view, much work has been undertaken on the improvement of ductility of Cu–Al–Ni alloys by refining its grain size. The refining of grain size has been achieved mainly by the addition of fourth and fifth alloying elements,

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such as titanium, manganese and boron [9]. Other methods, including rapid solidification [10] and controlled recrystallization [11], have also been applied to refine the grain size of Cu–Al–Ni alloys.

Thermal stability is another important problem of copper base SMAs. It has been found that ageing and thermal cycling cause the change of the transformation temperature of copper base SMAs [12, 13]. This is even more serious for high-temperature Cu–Al–Ni SMA, because thermal cycling and ageing are performed at a higher temperature. Experimental work on Cu–Al–Ni–Mn–B alloys shows that ageing and thermal cycling have a strong effect on the transformation temperature [14]. The variation of the transformation temperature has been attributed to change of long-range order of the parent phase caused by ageing [15–17] and crystal defects induced by thermal cycling [13]. Furthermore, a precipitation process may also take place during high-temperature ageing and results in a reduction of the shape memory effect, and even complete loss of shape memory capacity [3, 18]. Therefore, to understand and control the thermal cycling and ageing behaviour of high-temperature Cu–Al–Ni alloys is very important for their application.

At present, most investigations on grain-refined Cu–Al–Ni SMA were on titanium, manganese and boron-doped alloys. The purpose of the present work was two-fold: first to understand the effect of vanadium addition on the microstructure of Cu–Al–Ni alloy, and second to investigate the effect of ageing and thermal cycling on the Cu–Al–Ni–Mn–V alloy.

2. Experimental procedure

Alloy with nominal composition of Cu–15%Al–7% Ni–0.5%Mn–0.5%V (wt %) was prepared by induction melting of pure copper, aluminium, nickel, manganese and vanadium metals of 99.9% purity in a graphite crucible. The ingot was homogenized at 1073 K for 48 h then hot rolled to a plate of 2 mm thickness. Annealing was done by heating samples to 873 K for 1 h and cooling inside the furnace. The samples to be investigated were heated to 1200 K for 10 min, then quenched into water. Ageing of the quenched samples was performed at different temperatures for different times. The quenched samples were etched using $FeCl_3$, CH_3CH_2OH and H_2O solution. To identify the dispersed secondary phase, electrolysis was applied to extract it, and the electrolyte was a 50% phosphoric acid aqueous solution. Microstructure observation and phase identification were performed using a JSM-820 scanning electron microscope (SEM) and a Rigaku D/Max-RC X-ray diffractometer. Transformation temperatures were measured using a PE DSC 7 with scan rate of 20 K min^{-1}.

3. Result and discussion

3.1. Microstructure evaluation of as-quenched Cu–Al–Ni–Mn–V alloy

Chemical composition analysis of the alloy was done using EDX analysis, and the result showed that the composition of the alloy was Cu–15.1%Al–6.8% Ni–1.2%Mn–0.5%V–0.2%Si (wt %), which is in good agreement with the nominal composition of the alloy, despite the presence of a small amount of silicon. No silicon had been added to the raw material to be melted. However, a refining agent containing mainly SiO_2 had been used in the melting. It is believed that silicon was induced in this way. Fig. 1a shows a typical morphology of the microstructure of the as-quenched sample observed under SEM. It can be seen that the quenched structure is fully martensitic and there is a dispersed fine secondary phase in the matrix of the martensite. Fig. 1b shows the magnified morphology of the as-quenched microstructure obtained in SEM. It clearly shows that the secondary phase is needle-shaped with a length of about 5–10 μm and width about 1 μm. Fig. 1c and d show the morphology of secondary phase and the corresponding elemental mapping of vanadium. It clearly indicates that the secondary phase is a vanadium-rich phase. The grain size of the sample obtained by quenching from 1200 K is about 100–300 μm. This result shows that the addition of vanadium into the alloy has the apparent effect on refining the grain size of the Cu–Al–Ni–Mn alloy, considering that the temperature of solution treatment is high, up to 1200 K. The refining of grain size by vanadium addition is believed to be due to the grain growth being inhibited by the dispersed fine secondary phase. In comparison with the grain size of titanium-doped Cu–Al–Ni–Mn alloy, however, the grain-refining effect of vanadium addition is not as strong as that of titanium addition.

As identified by Adachi *et al.* [18], the dispersed fine secondary phase in titanium-doped Cu–Al–Ni SMA is titanium-rich Heusler-type ordered structure, and either semi- or good coherency with the β matrix. It was claimed that the shape memory recovery of titanium-doped Cu–Al–Ni alloy was not significantly affected [9]. The vanadium-rich secondary phase in vanadium-doped Cu–Al–Ni alloy has been identified in this work. Table I gives the composition of vanadium-rich secondary phase by EDX analysis.

This result proves that most of the vanadium added existed in the secondary phase and the secondary phase contains mainly vanadium and silicon. Fig. 2 is an X-ray diffractogram of the secondary-phase power electrolyte extracted. The indexing of this diffractogram shows that most of the peak can be indexed in accordance with V_5Si_3 phase (JCPDS 8-379). The strong diffraction peak of copper was due to copper deposited and mixed together with the secondary phase particles in the electrolytic extraction process.

3.2. Effect of ageing and thermal cycling on the transformation temperature of Cu–Al–Ni–Mn–V alloy

Fig. 3 shows the curve obtained from the DSC scan of the as-quenched sample. The M_s, M_f, A_s and A_f temperature are 365, 410, 382 and 423 K, respectively, as determined from the DSC curve. Hence, the present alloy is a possible candidate for high-temperature usage. As pointed out by many previous workers,

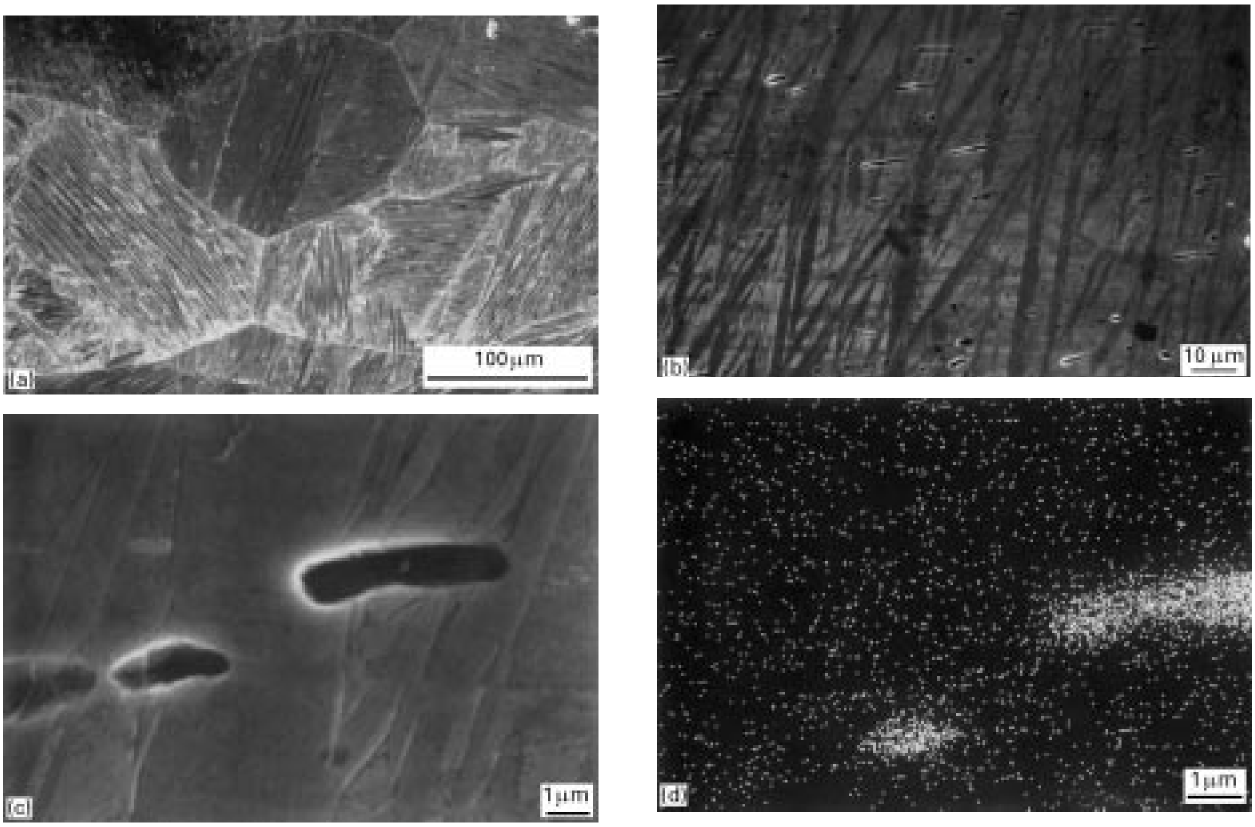

Figure 1 Morphology and distribution of secondary phase inside the matrix of martensite in an as-quenched sample: (a) general morphology of the as-quenched sample, (b) SEM image of martensite and secondary phase, (c) high magnification SEM image of secondary phase, and (d) elemental mapping of vanadium of the secondary phase corresponding to (c).

TABLE I Composition of matrix and secondary phase of Cu–15.1%Al–6.8%Ni–1.2%Mn–0.5%V–0.2%Si alloy determined by EDX analysis

	Al	Ni	Mn	V	Si	Cu
Secondary phase (at %)	0.52	0.45	1.5	63.4	25.5	Bal.
Matrix (at %)	29.32	5.83	1.13	0.14	0.32	Bal.

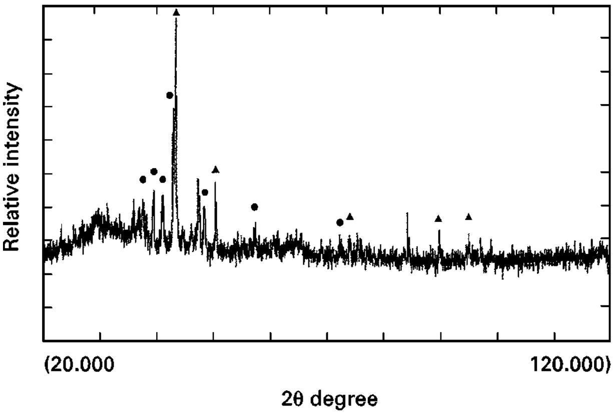

Figure 2 X-ray diffractogram of secondary phase powder obtained by electrolytic extraction: (●) V_5Si_3, (▲) Cu.

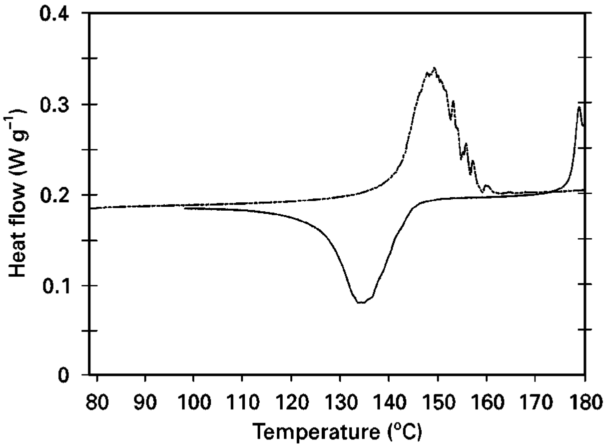

Figure 3 (– – –) Heating and (—) cooling DSC curves of as-quenched sample (normalized).

there is a severe ageing effect when copper-base SMA is used at high temperature [3, 17]. Therefore, it is necessary to clarify the ageing behaviour of the Cu–Al–Ni–Mn–V SMA prepared in this research. Fig. 4 shows the transformation temperature in accordance with the numbers of thermal cycles. The thermal cycle was made in the temperature range from 303–453 K. It can be seen that the transformation temperature increases with increasing number of cycles. The increment was rather large, about 23 and 18 K for A_s and M_s, respectively, after 50 cycles, as compared with that of copper base SMA for which transformation cycling was performed at a temperature below 373 K (referred to here as low-temperature SMA). In the case of low-temperature SMA, e.g. Cu–Zn–Al alloy, the change of transformation temperature caused by thermal cycling is only several degrees [13]. Furthermore, the variation of

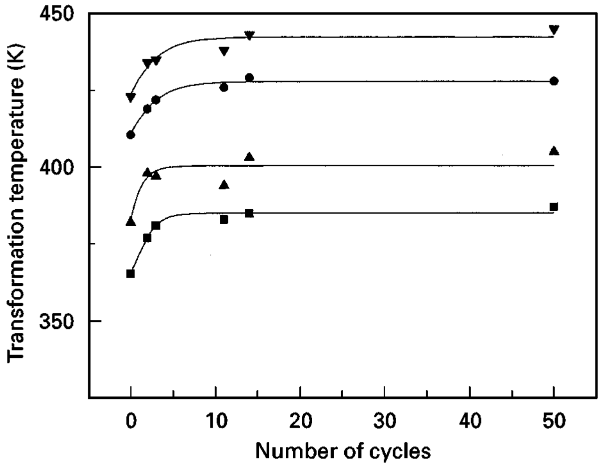

Figure 4 The dependence of the transformation temperature on the number of thermal cycles made on the as-quenched sample. (■) M_f, (●) M_s, (▲) A_s, (▼) A_f.

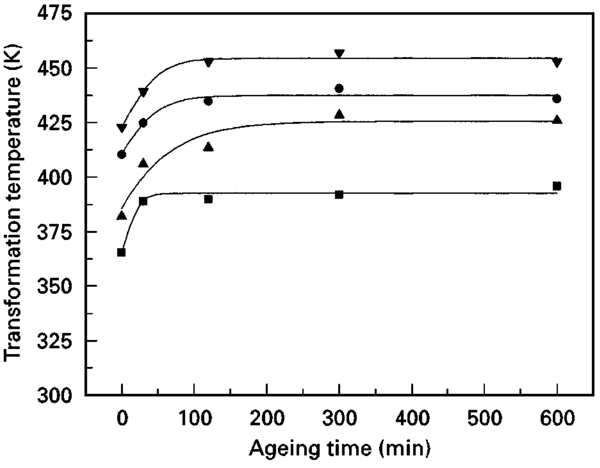

Figure 5 The dependence of the transformation temperature on time of ageing at 453 K after quenching. (●) M_s, (■) M_f, (▲) A_s, (▼) A_f.

transformation temperature reached a steady state after about 10 cycles for low-temperature SMA. In the present case, however, the transformation temperature varied even after 50 thermal cycles. These results indicate that the effect of thermal cycling on-high temperature SMA and low-temperature SMA is different.

Several mechanisms have been proposed for the change of transformation temperature induced by thermal cycles. It has been proved that thermal cycling results in the formation of defects such as dislocations in SMA and the presence of the dislocation is favourable to nucleation of martensite, which causes a rise of several degrees in the M_s point [13]. The change in the degree of order of the parent phase in thermal cycling is another reason for the change of the transformation temperature [19]. Furthermore, a secondary phase may precipitate if the temperature of thermal cycling is high enough and results in a large change of transformation temperature [3]. Precipitation of secondary phase causes a chemical composition change in the matrix. Therefore, the martensitic transformation temperature changed, and the variation of the transformation temperature is rather large due to the fact that the transformation temperature is very sensitive to the chemical composition. The fact that the temperature of thermal cycling reached 453 K and the transformation temperatures of high temperature SMA exhibited a great change during thermal cycling, implied that precipitation of secondary phase was an important reason for the change of the transformation temperature in the thermal cycling process of the Cu–Al–Ni–Mn–V high-temperature SMA and this was proved by microstructure observation.

It is very important that SMAs maintain a steady transformation temperature during cycling for the purpose of practical application. As discussed above, the transformation temperature continually changed during the thermal cycling process, because cycling reached temperatures high enough for the secondary phase to precipitate. It was proposed, therefore, that the transformation temperature could be maintained stable if the microstructure could be kept steady during the thermal cycling process. From this point of view, it was considered that if Cu–Al–Ni–Mn–V alloy was aged prior to thermal cycling at temperatures higher than the highest temperature reached during thermal cycling, then a secondary phase may not precipitate further and the transformation temperature could be maintained stable in the thermal cycling process. Thus, Cu–Al–Ni–Mn–V alloy was aged at different temperatures of the parent phase range, and then thermal cycling was performed to determine how the transformation temperatures varies.

Fig. 5 shows the variation of the transformation temperature with time of ageing at 453 K. It can be seen that the transformation temperatures increase with the time of ageing and gradually reach stable values after being aged for about 120 min. On comparing the increment of transformation temperature caused by ageing at 453 K with that caused by thermal cycling, it was found that the former was much higher than the latter. Thus, if the thermal cycling is made without pre-ageing, the transformation temperature will continue to change for many cycles, as the samples were heated at a temperature near to 453 K for a very short time in each of the thermal cycles. The experimental result showed that the ageing temperature had marked influence on the variation of transformation temperature. Fig. 6 shows the dependence of transformation temperature on ageing time at 513 K. The increment of transformation temperature caused by ageing at 513 K is much higher than that caused by ageing at 453 K, and the time to reach a steady value is much shorter. It should be mentioned here, however, that thermoelastic martensitic transformation did not take place when the ageing temperature was too high. For the alloy investigated here, thermoelastic martensitic transformation did not take place after samples were aged at 543 and 573 K for 120 and 45 min, respectively. This was due to the metastable β′ phase being decomposed to equilibrium phase.

Fig. 7 shows the dependence of transformation temperature on the number of thermal cycles obtained on a sample pre-aged at 513 K for 5 min. It can be seen that the transformation temperature becomes steady

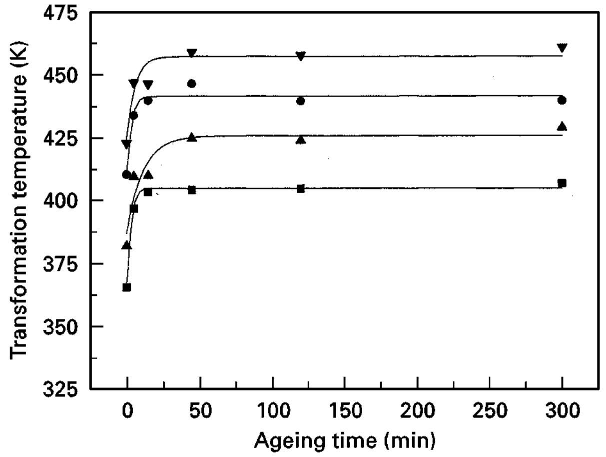

Figure 6 The dependence of the transformation temperature on time of ageing at 513 K after quenching. (■) M_f, (●) M_s, (▲) A_s, (▼) A_f.

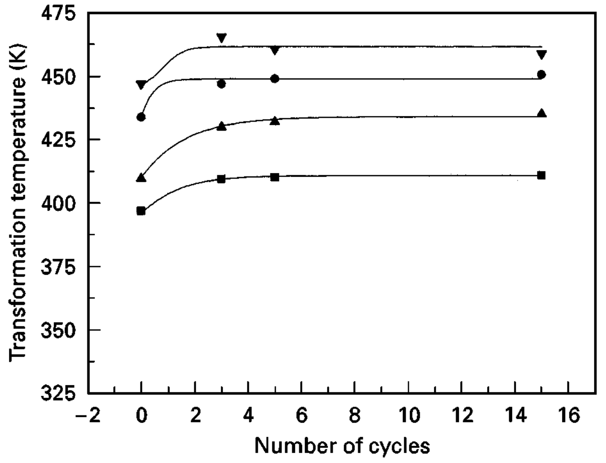

Figure 7 The variation of transformation temperature with the number of thermal cycles on the sample pre-aged at 513 K for 5 min after quenching. (■) M_f, (●) M_s, (▲) A_s, (▼) A_f.

after less than 10 cycles. This result proves that it is effective to maintain a stable transformation temperature by pre-ageing. However, there was still a rather large increment in transformation temperature in the initial several thermal cycles of the pre-aged samples. Because the sample had been pre-aged at 513 K, the change in transformation temperature should not mainly result from the precipitation of a secondary phase, but for other reasons, such as introduction of dislocations [13] and changing degree of order [19].

The fact that the variation of transformation temperature was seriously influenced by ageing temperature implies that the ageing process of vanadium-doped Cu–Al–Ni–Mn alloy at high temperature was a thermal activation process. When the variation of the transformation temperature was used as the measurement of this process. The activation energy of the ageing process could be determined by plotting the change of transformation temperature against temperature in an Arrhenius equation relation. Table II gives M_s and A_s points of samples aged at different temperatures for 15 min.

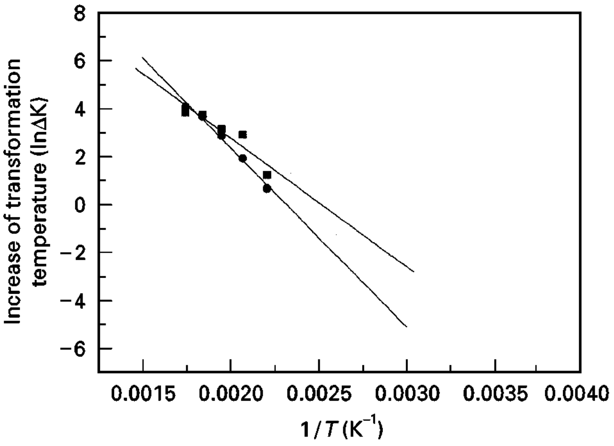

Figure 8 The correlation between increments of transformation temperature and the ageing temperature. The ageing was made on the as-quenched sample and the ageing time was 15 min. (■) M_s, (●) A_s.

TABLE II M_s and A_s points of samples aged at different temperatures for 15 min

	Ageing temperature (K)					
	Not aged	453	483	513	543	573
M_s(K)	410.5	420	435	440	460	464
A_s(K)	382	398	399	410	432	453

The activation energy of the ageing process deduced using the variation of M_s and A_s obtained in Table II was 28 and 29 kJ mol^{-1}, respectively. This value of activation energy is much lower than that obtained for the ageing process of Cu–Zn–Al and Cu–Al–Ni alloys (60–80 kJ mol^{-1} [3]). This was probably due to the inadequate selection of the variation of the transformation temperature as a measurement of the ageing process. In fact, it should be realized that the sample experienced one cycle of transformation after the ageing process was completed for the sample was heated above the A_f point and then cooled below the M_f point, which was the first transformation cycle after quenching. Thus, another mechanism, such as introduction of dislocations and changing degree of order, as discussed before, also contributed to the change of transformation temperature. Taking this into account, the increment of transformation temperature caused by the first cycle of transformation should be deducted, if the variation of transformation resulting from ageing (as listed in Table II) was used as a measurement of the ageing process. According to Fig. 7, the change of M_s and A_s caused by the first cycle was about 6 and 10 K, respectively. By incorporating this modification, the natural logarithm of increment of the transformation temperature was plotted against reciprocal ageing temperature as shown in Fig. 8. The activation energy of the ageing process was determined to be 45 and 62 kJ mol^{-1} by taking the change of M_s and A_s as measured respectively, which is close to the value obtained in the Cu–Zn–Al and Cu–Al–Ni alloy.

4. Conclusions

From the above X-ray diffraction, SEM and DSC investigation, the microstructure, thermal cycling and ageing behaviour of vanadium-doped Cu–Al–Ni–Mn shape memory alloy has been revealed. The main results are as follows.

1. The vanadium added to Cu–Al–Ni–Mn alloy reacted with silicon in the refining agent used in the melting process, and needle-shaped V_5Si_3 phase was formed and distributed homogeneously in the matrix of the alloy. The presence of the V_5Si_3 phase was beneficial to the refining of coarse grains of Cu–Al–Ni alloy.

2. Transformation cycling of this high-temperature SMA causes an increase of the transformation temperature, and the change is about 20 K, which is much bigger compared with SMAs thermally cycled at lower temperature.

3. Ageing of the alloy in the temperature range of the parent phase state, resulted in an increase in the transformation temperature. The ageing process satisfies an Arrhenius equation. The activation energy of the ageing process was estimated to be 45–62 kJ mol^{-1} approximately.

4. The transformation temperature can be maintained stable in the thermal cycling process by a pre-ageing treatment for a short time at a temperature a little higher than the highest temperature reached in thermal cycling.

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