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

Y. GAO, M. ZHU*
Department of Mechano-Electronic Engineering, South China University of Technology, Guangzhou 510641, People’s Republic of China
E-mail: memzhu@scut.edu.cn

J. K. L. LAI
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong

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. © 1998 Kluwer Academic Publishers

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 γs phase at grain boundaries [7], high elastic anisotropy 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.

* Author to whom all correspondence should be addressed.
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–15.1%Al–6.8% Ni–1.2%Mn–0.5%V–0.2%Si (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 FeCl₃, CH₂C₂OH and H₂O 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 EDAX 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 SiO₂ 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, 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 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 EDAX 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 V₅Si₃ 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 Mₛ, Mₐ, Aₛ and Aₐ 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,