



Thermal cycle stability of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ high-temperature shape memory alloy



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ABSTRACT

The microstructure, martensitic transformation and thermal cycle stability of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ high-temperature shape memory alloy were studied. The results show that the martensite transformation of $\text{L}_{21}/\text{D}_{022}$ occurred in the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy. In the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy, the transformation temperatures of forward transformation and reverse transformation are pretty high, reaching 589.6 °C and 649.1 °C, respectively. The temperatures of the martensitic transformation and the transformation heat show a neglectable difference after 200 thermal cycles in the alloy. This alloy exhibits good thermal stability during 200 thermal cycles between room temperature and 850 °C, in which the microstructure and martensitic transformation behavior have no obvious change.

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1. Introduction

High-temperature shape memory alloys (HTSMAs) with the martensite transformation temperatures above 100 °C, have been studied in motor industries, aerospace industries and chemical industries [1]. In the past decades, many alloying systems have been developed, such as Ni-Ti-based [2,3], Ni-Mn-based [4,5] and Co-based [6–10] HTSMAs. Moreover, much work also has been done experimentally [11,12] and computationally [13,14] to study the phase stability of martensite. Thermal stability has been achieved for several Ni-Ti-base HTSMA material systems [2,3]. However, these alloys have relatively low martensitic transformation temperatures. It is difficult to obtain good thermal cycling performance at high temperature because of the diffusion effect and phase instability. It noted that the Co-based alloys had received some attention in high-temperature alloys, because of their high strength, high curie temperature and excellent corrosion resistance [15]. Recently, more cobalt-based high-temperature shape memory alloys, such as Co-Cr-Ga-Si [6], Co-Cr-Al-Si [7], Co-V-Si(-Ga) [8,9] and Co-V-Ga [10] alloy systems have been reported for exhibiting high temperature martensitic transformations.

Our previous work reported an off-stoichiometric Co_2VSi Heusler-typed HTSMA that experienced $\text{L}_{21}/\text{D}_{022}$ martensitic transformation about 700 °C, showing considerable recovery strain and good mechanics performance [8]. However, the precipitated phase of $\text{Co}_5\text{V}_3\text{Si}_2$ and the ageing effect at high transformation temperature led to terrible thermal cycle stability of the alloy, which is also investigated in CoCrAlSi alloy [7]. Furthermore, due to the complex phase relation of the Co-V-Si ternary alloy system [8] and the high sensitivity of martensite transition temperature to the composition of the alloy, it is hard to enhance the performance of the alloy through simple ageing treatment or composition control. In order to improve the thermal cycling stability of Co-V-Si HTSMAs, the alloying elements Ga, Al and In with low melting points are considered, which are also the Heusler-type structure (L_{21}) forming elements of Co_2VZ . The effects of alloying Ga on Co_2VSi alloy have been experimentally investigated [9]. The results showed that as the Ga content increases, the R phase precipitated from martensite and the martensite phase transition temperature decreased. The specific attention to phase stability can be expected by further studying on Co-V-Si system. It is also concluded that the In element has a slight solubility limit in cobalt [16]. Hence, Al was selected as the alloying element to replace Si partially in the work. This work intends to investigate crystal structure, microstructure evolution and thermal cycle stability of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy during thermal cycles.

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2. Experimental procedures

The polycrystalline $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy was prepared by arc melting of high purity cobalt (99.9 wt%), vanadium (99.7 wt%), silicon (99.999 wt%) and aluminum (99.999 wt%) in an argon atmosphere. The ingot weighing 30 g is re-melted five times to achieve uniformity. Prior to heat treatment, the ingot was manufactured as plate-shaped specimens by wire cut electrical discharge machining. Then, the samples were prepared by the vacuum quartz tube containing an argon atmosphere to avoid the oxidation of specimens.

The alloy was further characterized by quenching in ice water after six hours of heat treatment at 1200 °C. The microstructure of the alloy was observed by metalloscope (Leica DMI 5000 M) etched with 10 g FeCl_3 + 25 ml HCl + 100 ml H_2O solution. The backscattered electron (BSE) image was performed on each phase using electron probe microanalysis (EPMA, JXA-8100, JEOL, Japan), with the acceleration voltage of 20 kV and the probe current of 1.0×10^{-8} A. The crystal structure was measured using a transmission electron microscopy (TEM) and an X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation. The thin films were processed using the Precision Ion Polishing System (PIPS) for the TEM observation. Phase change behavior and thermal cycling process at 10 °C/min heating and cooling rates were investigated by differential scanning calorimetry (DSC, TA Instrument 2920).

3. Results and discussion

Fig. 1(a) indicates the optical microstructure after heat-treated at 1200 for six hours of the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy. There is no second phase and exhibit typical single martensite in this alloy. Fig. 1 (b) shows the X-ray diffraction patterns obtained from the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy at room temperature. All the diffraction peaks can be matched by D0_{22} structure, where $a = b = 0.3847$ nm, $c = 0.6209$ nm, and $c/a = 1.614$. Comparing with the previous off-stoichiometric Co_2VSi ($\text{Co}_{63.5}\text{V}_{17}\text{Si}_{19.5}$) alloy [8], the alloying of

the Al element gives rise to the enlargement of lattice volume and the decrease of the valence electron concentration. The decrease of electronic concentration and the deformation of the D0_{22} structure lead to the decrease of the martensitic transition temperature, but the martensitic structure is still present at room temperature. The TEM bright-field (BF) image and corresponding selected area diffraction patterns (SADPs) obtained from the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy shows in Fig. 1 (c, d). Combining with X-ray diffraction patterns and the SADPs from $[1\ 1\ 0]$ matrix zone axis in Fig. 1 (d), it indicates that the martensite of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy still shows a D0_{22} structure. In summary, the XRD and TEM results demonstrate that the martensite phase changes from the L2_1 structure to the D0_{22} structure, which is the same as previous studies on Co-Cr-Al-Si, Co-Cr-Ga-Si and Co-V-Si (-Ga) alloys [6–9].

The previous work reported that the Co_2VSi alloy with ordered BCC structure phase is labile at temperature higher than 820 and changes into the A12 phase during annealing process [8]. The phase transition properties of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy measured by DSC are shown in Fig. 2. It shows that the alloying of the Al element in Co_2VSi alloys decreased the temperature of martensitic transformation. In order to study the thermal cycling stability of martensite in $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy, DSC measurements were repeated 200 times from room temperature to 850 . The $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy with the single martensitic phase shown in Fig. 2(a), almost no change in all endothermic peaks and exothermic peaks during the thermal cycles. In addition, the martensite transformation temperatures and enthalpy values during heating and cooling show negligible differences, which are summarized in Table 1 (M_p : the peak temperature of forward martensitic transition; A_p : the peak temperature of the forward austenite transition; Hysteresis: the temperature interval between A_p and M_p). As the thermal cycles go on, the A_s , M_s and the transformation heat ($H_{M \rightarrow A}$ and $H_{A \rightarrow M}$) almost keep the same, which shows in Fig. 2(b) ($H_{M \rightarrow A}$: the transformation heat of martensite transforms into austenite; $H_{A \rightarrow M}$: the transformation heat of austenite transforms into martensite). It means in $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy, the reverse and forward martensitic phase transformations show excellent thermodynamic stability at

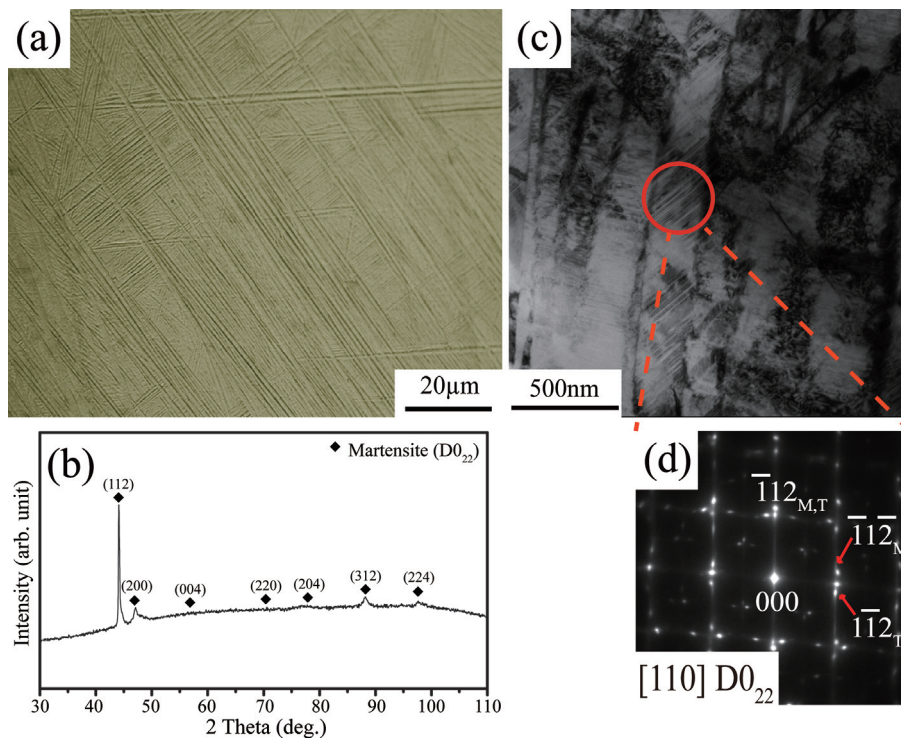


Fig. 1. Microstructure of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy (a) Optical micrograph, (b) XRD pattern, (c) BF image, (d) SADPs.

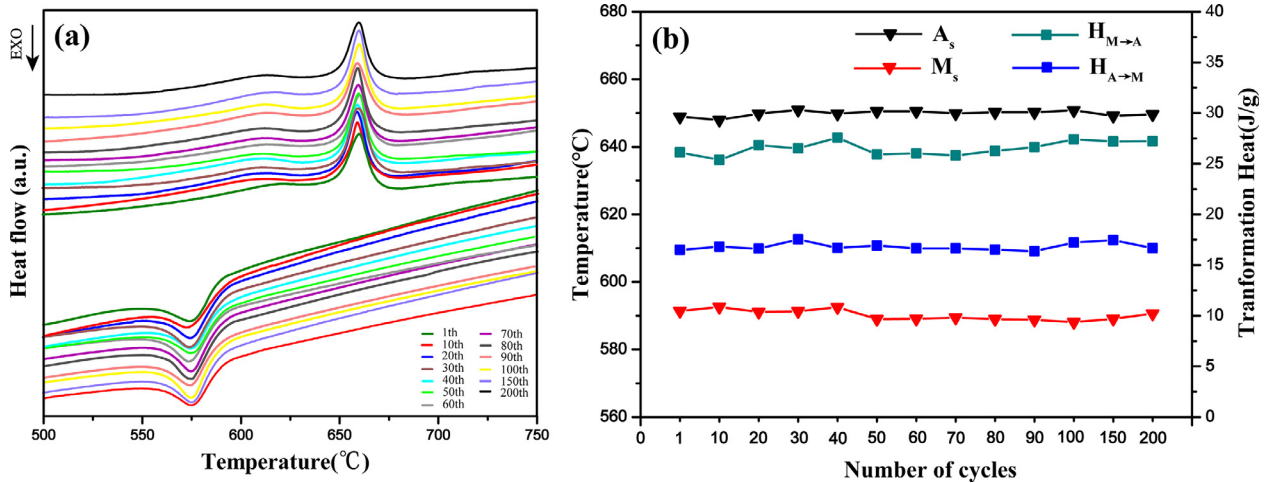


Fig. 2. DSC cycle curves of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy (a) and corresponding transformation temperatures and transformation heats (b).

Table 1
The martensitic transformation temperature of the studies alloy

Number of thermal cycles	A_s (°C)	A_p (°C)	A_f (°C)	M_s (°C)	M_p (°C)	M_f (°C)	Hysteresis (°C)
1st	649.1	658.2	667.5	589.6	572.1	558.2	86.1
50th	650.5	659.8	667.3	589.0	573.7	559.8	86.1
100th	650.8	659.8	667.9	588.1	574.4	560.0	85.4
150th	649.2	658.6	664.6	589.1	573.9	559.5	84.7
200th	649.6	659.1	667.0	590.6	573.1	557.5	86.0

high temperatures. These results indicate that the martensite phase transformation of the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy has good cyclic reversibility.

Fig. 3 shows the optical metallograph and corresponding BSE image of the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy during thermal cycles. After the first thermal cycle to 850 °C, a single martensite phase can still

be found in $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy. The optical metallograph after the first thermal cycle (Fig. 3(a)) is similar to the annealed specimen. Observing the microstructure after two hundred thermal cycles, it can be found that the microstructure remained the same after the first thermal cycle. It is conclusion that the microstructure stability of the alloy. The constant microstructure also confirms the stability of the thermodynamical.

4. Conclusions

In conclusion, the results show that the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy undergoes $L2_1/DO_{22}$ martensitic transformation. The alloy exhibits typical DO_{22} structure single martensite at room temperature, with the lattice constant of $a = b = 0.3847$ nm, $c = 0.6209$ nm, and $c/a = 1.614$. In the $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy, the temperatures of forward transformation and reverse transformation are very high, reaching 589.6 °C and 649.1 °C, respectively. The martensitic transformation

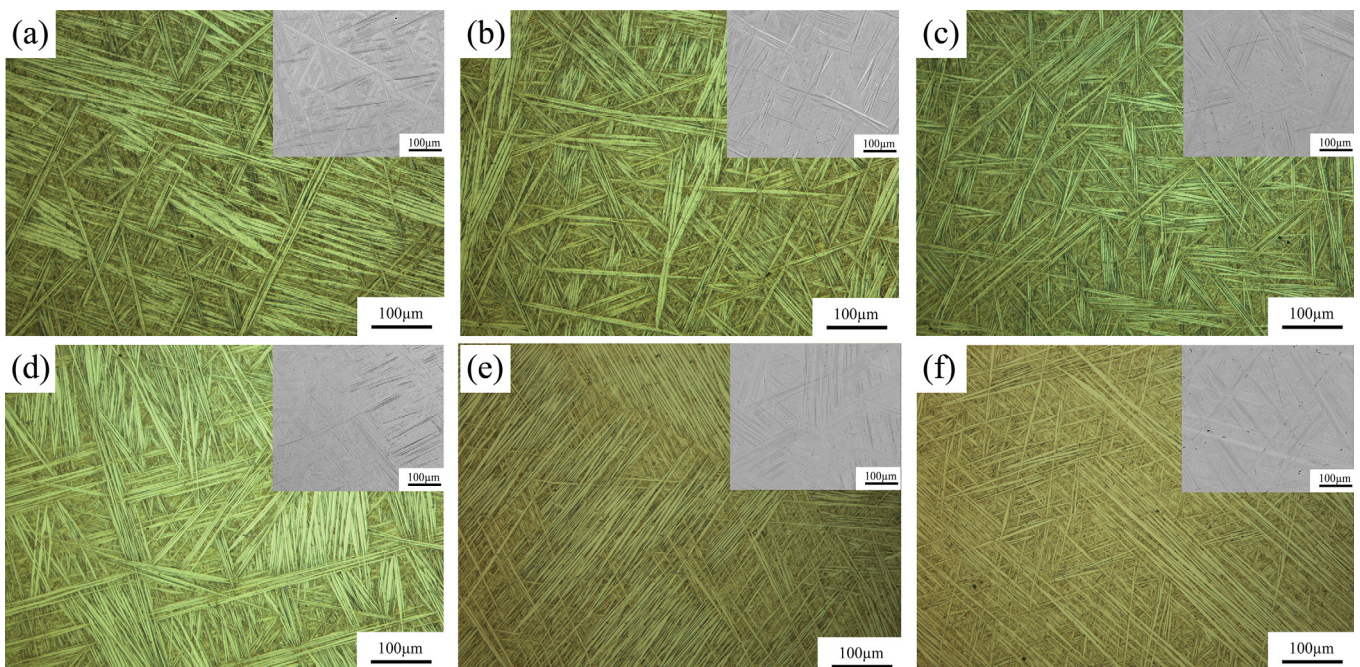


Fig. 3. Optical metallograph and BSE image (inset) of the of $\text{Co}_{64}\text{V}_{15}\text{Si}_{17}\text{Al}_4$ alloy during thermal cycles. (1st(a), 10th(b), 50th(c), 100th(d), 150th(e), 200th(f)).

temperatures and the transformation heat show a neglectable difference. The alloy shows excellent thermal stability after 200 thermal cycles between room temperature and 850 °C. There is no significant difference in the microstructure and martensitic phase transformation behavior during the whole thermal cycles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] G.S. Firstov, J. Van Humbeeck, Y.N. Koval, *Mater. Sci. Eng. A.* 378 (2004) 2–10.
- [2] O. Benafan, R.D. Noebe, T.J. Halsmer, S.A. Padula, G.S. Bigelow, D.J. Gaydos, A. Garg, *Shape Mem. Superelasticity.* 2 (2016) 218–227.
- [3] H.H. Saygili, H.O. Tugrul, B. Kockar, *Shape Mem. Superelasticity.* 5 (2019) 32–41.
- [4] Y. Xin, Y. Li, *Microstructure, Mater. Sci. Eng. A.* 649 (2016) 254–262.
- [5] J. Yao, B. Cui, X. Zheng, Y. Wu, J. Sui, W. Cai, *Vacuum* 147 (2018) 78–81.
- [6] X. Xu, T. Omori, M. Nagasako, A. Okubo, R.Y. Umetsu, T. Kanomata, K. Ishida, R. Kainuma, *C. Appl. Phys. Lett.* 103 (2013).
- [7] K. Hirata, X. Xu, T. Omori, M. Nagasako, R. Kainuma, *J. Alloys Compd.* 642 (2015) 200–203.
- [8] H. Jiang, X. Xu, T. Omori, M. Nagasako, J. Ruan, S. Yang, C. Wang, X. Liu, R. Kainuma, *Mater. Sci. Eng. A.* 676 (2016) 191–196.
- [9] H. Jiang, C. Wang, W. Xu, X. Xu, S. Yang, R. Kainuma, X. Liu, *Mater. Des.* 116 (2017) 300–308.
- [10] X. Xu, A. Nagashima, M. Nagasako, T. Omori, T. Kanomata, R. Kainuma, *Appl. Phys. Lett.* 110 (2017) 12–16.
- [11] X.L. Meng, W. Cai, F. Chen, L.C. Zhao, *Scr. Mater.* 54 (2006) 1599–1604.
- [12] R. Santamarta, E. Cesari, J. Muntasell, J. Font, J. Pons, P. Ochin, *Intermetallics.* 18 (2010) 977–983.
- [13] H.-B. Luo, Q.-M. Hu, C.-M. Li, R. Yang, B. Johansson, L. Vitos, *Phys. Rev. B.* 86 (2012) 1–8.
- [14] Z. Gao, B. Chen, X. Meng, W. Cai, *J. Alloys Compd.* 575 (2013) 297–300.
- [15] J. Ma, I. Karaman, R.D. Noebe, *Int. Mater. Rev.* 55 (2010) 257–315.
- [16] J.P. Bros, M. Gaune-Escard, D. El Allam, R. Haddad, E. Hayer, *J. Alloys Compd.* 233 (1996) 264–271.