

V 과 Sb 첨가가 Zr-0.84Sn 합금의 $\beta \rightarrow \alpha$ 상변태 특성에 미치는 영향

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Effect of V and Sb on the Characteristics of β to α Transformation in Zr-0.84Sn Alloy

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Abstract Effect of V and Sb content on characteristics of β to α phase transformation in Zr-0.84Sn alloy has been studied using optical microscopy and transmission electron microscopy. As V content increased, the $\beta \rightarrow \beta + \alpha$ transformation temperature was lowered, thus allowing the width of α -lath in air-cooled Zr-0.86Sn-0.40V alloy to be fine. The width of α -lath in air-cooled Zr-0.84Sn-xSb, however, was rarely changed with Sb content. The β to α transformed microstructures of water-quenched Zr-0.84Sn, Zr-0.84Sn-0.10V and Zr-0.84Sn-0.19V alloys were mainly slipped martensite. On the other hand, those of water-quenched Zr-0.86Sn-0.40V and Zr-0.85Sn-0.05Sb alloys were predominantly twinned martensite. In case of water-quenched Zr-0.85Sn-0.12Sb and Zr-0.84Sn-0.17Sb alloys, basketweave structure was observed. The transition of slipped martensite to twinned martensite in Zr-0.84Sn-xV alloys and the transition of twinned martensite to basketweave structure in Zr-0.84Sn-xSb alloys were due to the decrease of M_s temperature.

Key words: Zirconium, Phase Transformation, Martensite

1. Introduction

Zirconium alloys, extensively used as fuel cladding and core structural material in light water reactors, are faced with limitation for service because nuclear industry tends toward extended burn-up and increased coolant temperature. Therefore, recently there has been significant interest in development of advanced zirconium alloy for nuclear fuel claddings.

Many researchers have examined the effect of alloying elements and adequate heat treatment for given alloying composition on the size and distribution of precipitates which could affect the corrosion resistance as well as mechanical properties of zirconium alloy used as nuclear fuel cladding materials.^{1~5)}

Comparatively, little attention has been paid to the effect of alloying elements on the characteristics of β -quenching which was one of important steps in the fabrication process of nuclear fuel claddings. There is still a controversy with regard to whether diffusion is in-

involved in the β to α transformation during quenching of zirconium alloy.^{6,7)} Furthermore, it has been a subject of considerable research and controversy whether alloying elements have a measurable effect on the formation of slip and twin in case of martensitic transformation occurring in zirconium alloy.⁸⁾

The purpose of present work is to investigate the effect of V and Sb addition on the characteristics of β to α transformation and microstructural changes in air-cooled and water-quenched Zr-0.84Sn-base alloy. The effect of microstructural changes with alloying element on microhardness was checked in water-quenched Zr-0.84Sn-base alloy.

2. Experimental procedures

Seven different Zr-base alloys were made from high purity sheet-type pure zirconium and alloying elements by arc melting and re-melted five times for homogenization. The quantity of impurities in these alloys was rarely changed from that in pure zirconium

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Table 1. Chemical composition of Zr-0.84Sn-base alloy.
Unit : at.%

Alloys	Zr	Nominal			Analyzed		
		Sn	V	Sb	Sn	V	Sb
0	bal	0.80	-	-	0.86	-	-
1	bal	0.80	0.10	-	0.84	0.10	-
2	bal	0.80	0.20	-	0.84	0.19	-
3	bal	0.80	0.40	-	0.86	0.40	-
4	bal	0.80	-	0.10	0.85	-	0.05
5	bal	0.80	-	0.20	0.85	-	0.12
6	bal	0.80	-	0.30	0.84	-	0.17

from Cezus. The alloy composition was given in Table 1. The ingots were solution-treated at 1050°C for 20min and then water-quenched. The buttons were fabricated into sheet with the dimension of 50mm (L) × 10mm (W) × 1mm (t) through repetitive process of hot-rolling, cold-rolling and annealing. This was followed by annealing at 610°C for 2 hours to remove stored energy.

Air-cooling and water-quenching of specimens were performed after heat-treatment at 990°C for 2 hours in a vertical vacuum furnace. The cooling rate during air-cooling and water-quenching was measured in the temperature range from 990°C to about 100°C using thermocouples attached to the surfaces of specimens, and they were about 6.8°C/s and 1400°C/s, respectively.

The microstructural examination of air-cooled specimens was conducted by optical microscopy. Prior to optical microscopy, specimens were ground on silicon carbide paper and etched using a mixed solution of 5% HF, 45% HNO₃ and 50% distilled H₂O.

Microstructures of water-quenched specimens were observed by transmission electron microscopy. Thin foils for transmission electron microscopy were prepared from the middle part of water-quenched specimen by mechanical thinning to about 100µm thickness. Disks of 3mm in diameter were punched out from these thin foils, and electropolishing was done in a solution of 90% ethanol, 10% perchloric acid below -40°C. Hardness of water-quenched specimens was measured using Vickers microhardness (VMH) test equipment at the load of 500g.

3. Results and discussion

Fig. 1 shows optical microstructures of the β to α transformed Zr-0.84Sn, Zr-0.84Sn-0.10V and Zr-0.85Sn-0.05Sb alloys which are air-cooled from 990°C with the cooling rate of 6.8°C/s. The basketweave

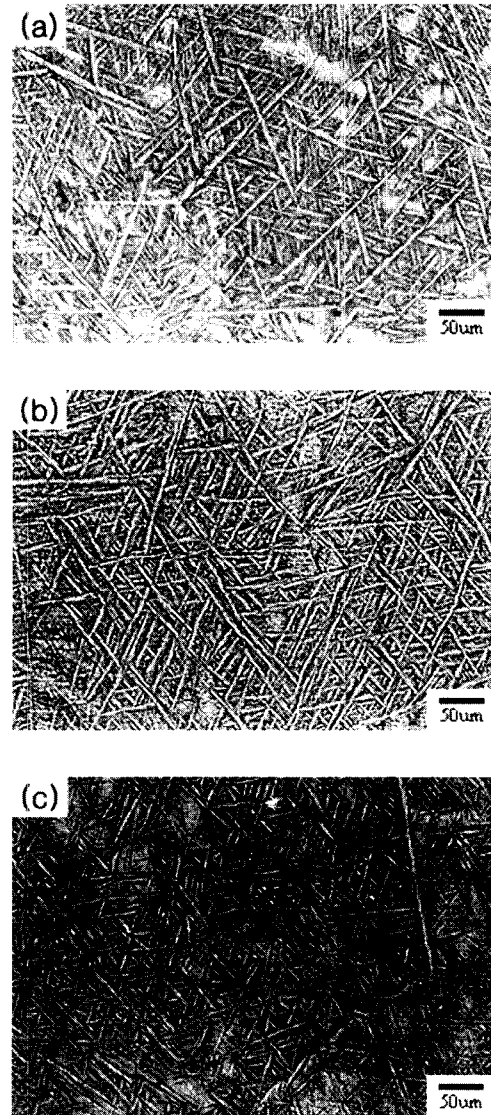


Fig. 1. Optical micrographs of air-cooled (a)Zr-0.84Sn, (b)Zr-0.84Sn-0.10V and (c)Zr-0.85Sn-0.05Sb alloys after heat treatment at 990°C for 2 hrs.

structure consisted of fine α-laths with 1~3µm width was observed in all the specimens and seemed to be triangular. It was considered that crystallography of transformation was <1120> governed by direction invariant during the transformation process.⁹ The microstructure appeared to have developed through the partitioning of prior β grain by primary laths and the transformation continued by successive generation of even smaller laths. Although the length of α-lath in Zr-0.85Sn-0.05sb alloy slightly decreased compared to others, there was little difference in the transformation characteristics of Zr-0.84Sn alloy by adding 0.10at.% V and 0.05at.% Sb.

Optical microstructures of Zr-0.84Sn alloys containing 0.40at.% V and 0.17at.% Sb were presented in Fig. 2. In case of Zr-0.86Sn-0.40V alloy, the width of

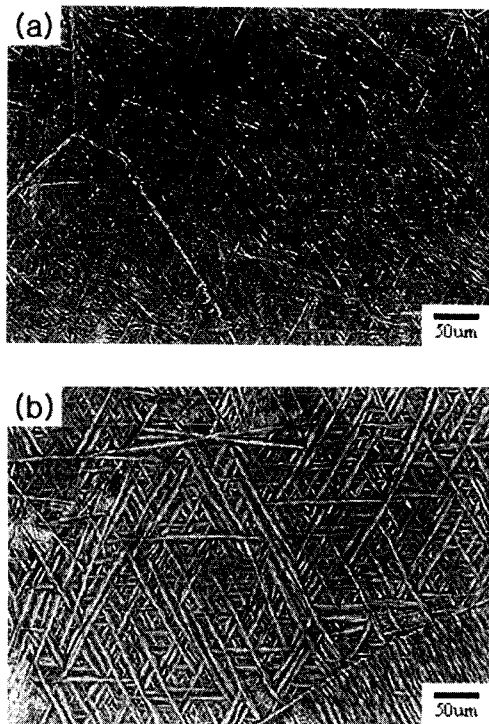


Fig. 2. Optical micrographs of air-cooled (a)Zr-0.86Sn-0.40V and (b)Zr-0.84Sn-0.17Sb alloys after heat treatment at 990°C for 2 hrs.

α -lath decreased to a few μm . The width and length of α -lath, on the other hand, rarely changed in case of Zr-0.84Sn-0.17Sb alloy.

According to Woo et al., as the oxygen content increases, the $\beta \rightarrow \alpha + \beta$ transformation temperature increased allowing diffusion to occur at an enhanced rate and the width of α -lath in Zircaloy-4 becomes larger with increasing oxygen content.¹⁰ On the contrary, from Kallstrom's report, the length of α -lath in Zircaloy decreased with increasing C content because the nucleation sites for α -lath were supplied sufficiently through the formation of precipitates.¹¹ However, the effect of impurities such as oxygen and nitrogen on the transformation temperature of Zr-base alloy might be ignored as the alloys used this study showed no appreciable change in the quantity of impurities before and after melting process. In this study, therefore, microstructural change due to the transformation temperature change was mainly dependent on the content of V and Sb.

The solubility of V in α -zirconium was nearly zero and that of Sb was about 1.0at.%.¹² The fine α -lath structure of Zr-0.86Sn-0.40V alloy might be occurred as the $\beta \rightarrow \alpha + \beta$ transformation temperature decreased and the nucleation site increased through the formation



Fig. 3. TEM micrographs of water-quenched Zr-0.84Sn alloy after heat treatment at 990°C for 2 hrs.

of precipitates with increasing V content. On the other hand, the width of α -lath in Zr-0.84Sn-0.17Sb alloy rarely changed because the addition of Sb was not considered to affect the $\beta \rightarrow \beta + \alpha$ transformation temperature. The effect of V and Sb addition in Zr-0.84Sn alloy on the air-cooled microstructure was considered to be similar with that of binary alloy where the $\beta \rightarrow \beta + \alpha$ transformation temperature decreased with increasing V content and rarely changed with increasing Sb content.¹²

Fig. 3 shows TEM micrograph of the β to α transformed microstructure in water-quenched Zr-0.84Sn alloy from 990°C with the cooling rate of 1400°C/s. It was worth noting that martensitic transformation would accompany inhomogeneous shear leading to the formation of twinned martensite or slipped martensite caused by the motion of either partial or perfect dislocations, respectively.¹³ From Fig. 3, one could notice numerous dislocations within twin free α -laths and boundaries consisted of tangled dislocations between the α -laths. This was in agreement with the tendency that the inhomogeneous shear was satisfied by dislocations.

Microstructural changes with V content in water-quenched Zr-0.84Sn alloy from 990°C are shown in Fig. 4. Zr-0.84Sn alloy containing up to 0.19at.% V showed a slipped martensite that could be observed in Zr-0.84Sn alloy of Fig. 3. This slipped martensite, however, changed gradually to twinned martensite with increasing V content.

Earlier work by Krauss has shown that alloying



Fig. 4. TEM micrographs of water-quenched (a)Zr-0.84Sn-0.10V and (b)Zr-0.8Sn-0.19V and (c)Zr-0.86Sn-0.40V alloys after heat treatment at 990°C for 2 hrs.

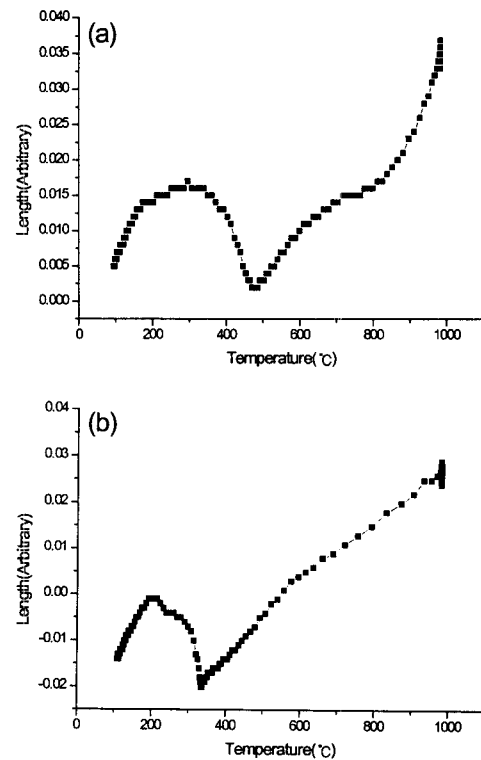


Fig. 5. The change of length (a)Zr-0.84Sn-0.10V and (b)Zr-0.86Sn-0.40V alloys cooled from 990°C with the cooling rate of 100°C/s

elements strengthened austenite by solid solution hardening and then the strengthened austenite caused the M_s temperature to be lower.¹⁴⁾ Consequently, a greater thermodynamic driving force is initiated to generate the shear that will produce martensite. Thus, if resolved shear stresses for slip of various types and twinning are determined by the austenite composition and strength, the most favorable processes are activated. Banerjee has suggested that the transition from the slipped to the twinned martensite in Zr-Nb alloy might be related with the M_s temperature.⁹⁾ As the transformation temperature decreases with increasing addition of Nb in zirconium, twinning, which is a more favorable mode of deformation at relatively lower temperature, will take place predominantly and the fraction of twinned martensite will increase.

In order to estimate the transformation temperature of Zr-0.84Sn-xV alloys, the variation of length in the specimens was examined with temperature using LVDT (Linear Variable Displacement Transducer), which was shown Fig. 5. The specimen was heat-treated at 990°C for 2 hours followed by gas-quenching, and the cooling rate was 100°C/s which was the limit of the apparatus. The temperature which corresponds to the tangential point in curve, meant that the phase trans-

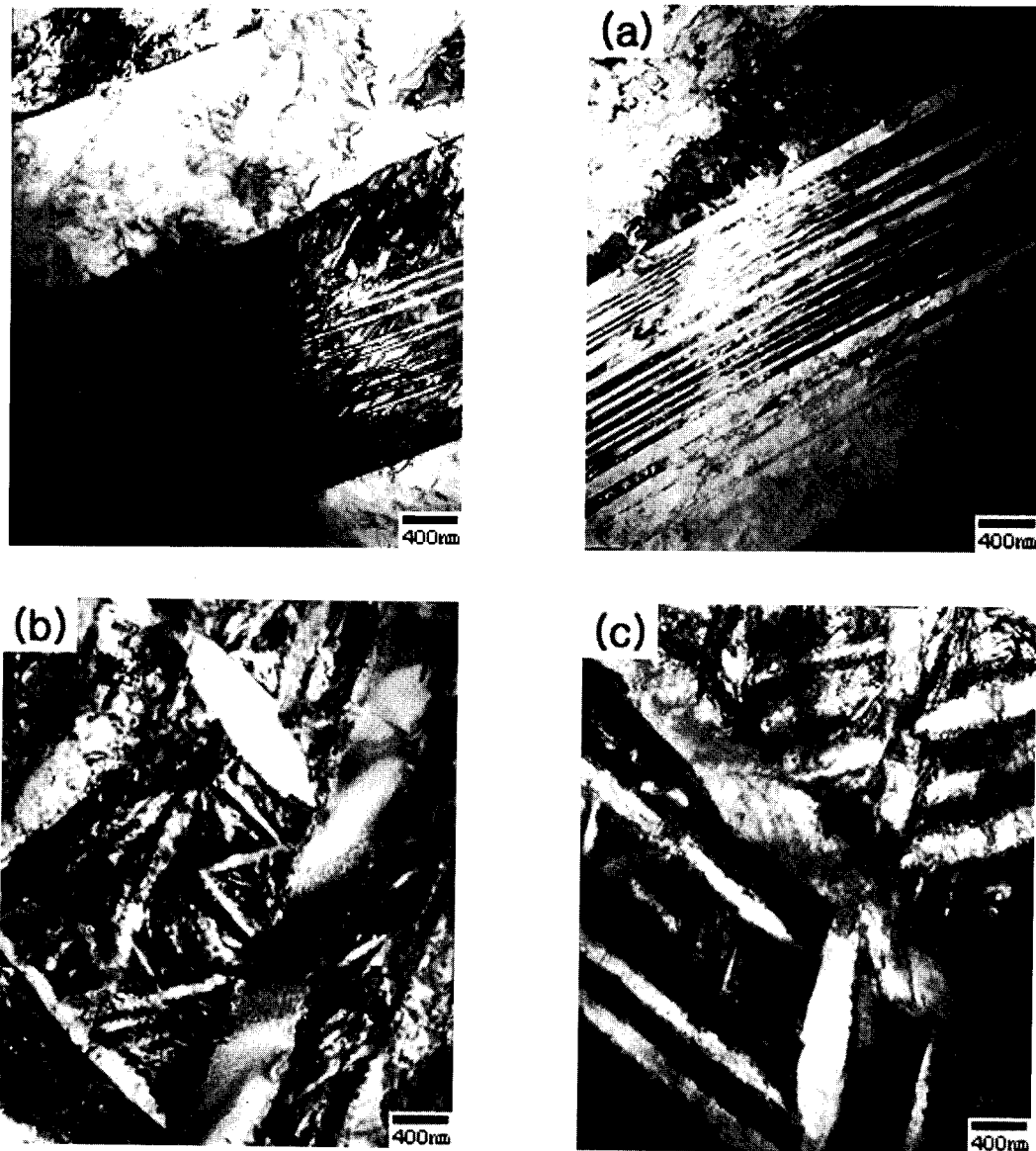


Fig. 6. TEM micrographs of water-quenched (a)Zr-0.85Sn-0.05Sb, (b)Zr-0.85Sn-0.12Sb and (c)Zr-0.84Sn-0.17Sb alloys after heat treatment at 990°C for 2 hrs.

formation was occurred in metals¹⁵⁾, and the curves showed that the transformation temperature decreased from about 470°C to about 330°C with the increase of V. Considering that the $\beta \rightarrow \beta + \alpha$ transformation temperature is above 800°C in Zr-Sn alloy, the decrease of transformation temperature might be related the martensite transformation.

From the investigation of microstructures in Zr-0.84Sn-xV alloys which were water-quenched from 990°C, the transition from slipped martensite to twinned martensite in Zr-0.84Sn-xV alloys was strongly dependent on the decrease of M_s temperature with V content. As a result, the formation of twinned martensite could be observed in Zr-0.84Sn alloy with 0.40at.% V.

Fig. 6 shows TEM micrographs of the β to α transformed microstructures in water-quenched Zr-0.84Sn alloy with Sb addition. Twinned martensite was observed only in Zr-0.84Sn alloy containing 0.05at.% Sb. Above 0.12at.% Sb, basketweave structure consisted of very fine α -lath was observed in Zr-0.84Sn alloy. The transition from twinned martensite to basketweave structure in these alloys appeared to be related with the change of M_s temperature.

From Fig. 7 shown the variation of the length of Zr-0.84Sn-xSb alloys with temperature, the transformation temperature decreased greatly with the addition of 0.12at.% Sb. The decrease of the transformation temperature accelerated the formation of twin in the martensitic transformation in general.¹⁶⁾ However, it

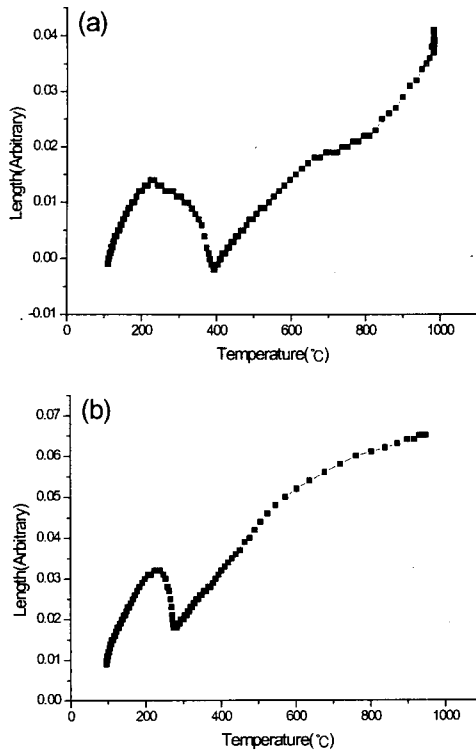


Fig. 7. The change of length (a)Zr-0.85Sn-0.05Sb and (b)Zr-0.84Sn-0.17Sb alloys cooled from 990°C with the cooling rate of 100°C/s.

caused the basketweave structure to be formed in Zr-0.84Sn-xSb alloys. Considering the α -laths in this case were much finer than those in air-cooled alloy and the transformation temperature was very low compared to that of slow cooling, this basketweave structure was very different from that in air-cooled alloy.

According to Huh's report, as the tangential point at lower temperature than M_s temperature in curve meant MF temperature¹⁵⁾, the MF temperature was rarely changed with the increase of Sb content. It was considered, therefore, that the addition of Sb resulted in the change of M_s temperature, which might be closely related to the transition from twinned martensite structure to basketweave structure in Zr-0.84Sn alloy.

These metallographic features, revealed by transmission electron microscopy, suggested that the M_s temperature might be strongly dependent on the alloying element and was an important factor in determining the morphology of the martensite such as slipped martensite, twinned martensite and basketweave structure in Zr-0.84Sn alloy which were water-quenched from 990°C.

Yang and Bangaru considered that water-quenched Zircaloy-4 had non-martensitic characteristics through observing precipitates existed between α -laths^{4,17)}, and Northwood found out the retained β phase in water-

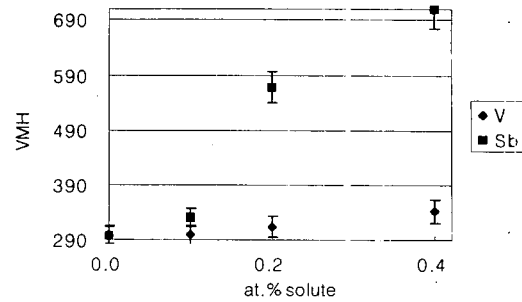


Fig. 8. Vickers microhardness of water-quenched Zr-0.84Sn-xV and Zr-0.84Sn-xSb alloys after heat treatment at 990°C for 2 hrs.

quenched Zr-Nb alloy.⁷⁾ On the contrary, Keys suggested that water-quenched Zr-Cr alloy showed martensitic characteristics⁶⁾ and Srivastava, could not detect any precipitates in rapidly cooled Zr-2.5Nb alloy.⁹⁾ In this work, no precipitates could be detected in Zr-0.84Sn alloy, even for containing 0.40at.% V. This was in conformity with diffusionless process of β to α transformation in water-quenched zirconium alloy. However, Sb-added Zr-0.84Sn alloy having basketweave structure showed water-quenched β to α transformation related to diffusion. It was considered that critical conditions for diffusionless transformation depended on composition of zirconium alloy since the M_s temperature varied with the composition.

Fig. 8 shows the changes of Vickers microhardness with content of V and Sb for Zr-0.84Sn alloy that were water-quenched after heat treatment at 990°C for 2 hours. The hardness of Zr-0.84Sn alloy was about 290VMH and slightly increased up to 342VMH with 0.40at.% V. In case of Zr-0.84Sn-xSb alloys, the hardness greatly increased up to about 710VMH by addition of 0.40at.% Sb, where the transition of slipped martensite to basketweave structure was occurred. Therefore, it was considered that the hardness of zirconium alloy was dependent on the microstructural changes varied with alloying elements.

4. Conclusions

1) The fine α -lath structure of air-cooled Zr-0.84Sn-xV alloys was formed as a result of decreased diffusion rate due to the decreased $\beta \rightarrow \beta + \alpha$ transformation temperature. However, the addition of Sb had little effect on the change of the width of α -lath in Zr-0.84Sn alloy.

2) The transition from slipped to twinned martensite was occurred in water-quenched Zr-0.84Sn alloy with increasing V content. On the other hand, the structure

of twinned martensite was changed to basketweave structure in water-quenched Zr-0.84Sn alloy with increasing Sb content.

3) Critical condition for diffusionless transformation depended on the composition in water-quenched Zr-0.84Sn alloy since M_s temperature was strongly dependent on the addition of V and Sb.

4) Hardness of Zr-0.84Sn alloy greatly increased with Sb content, which is due to change from twinned martensite to basketweave structure.

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References

1. P. Chemelle, D.B. Knorr, J.B. Van der Sande and R.M. Pelloux, *J. of Nucl. Mater.*, **113**, 58 (1983).
2. T. Kudo, Y. Wakashima, H. Imahashi and M. Vagai, *J. of Nucl. Mater.*, **132**, 126 (1985).
3. K.U. Huang, *J. of Nucl. Mater.*, **136**, 16 (1985).
4. W.J.S. Yang and R.B. Adamson, *Proc. 8th Int. Symp. on Zirconium in the Nuclear Industry ASTM-STP 1023*, California, CA, 1988, 451 (ASTM, Philadelphia, 1989).
5. K. Loif, R. Borrelly and P. Merle, *J. of Nucl. Mater.*, **210**, 84 (1994).
6. L.H. Keys, G. Johanson and A.S. Malin, *J. of Nucl. Mater.*, Vol. **59**, 137 (1976).
7. D.O. Northwood and K. Dosen, *Metallography*, **13**, 249 (1980).
8. S. Banerjee and R. Krishan, *Met. Trans. A*, Vol. **4**, 1811 (1973).
9. D. Srivastava, Madangopa K., S. Banerjee and S. Ranganathan, *Acta Metall. Mater.* Vol. **41**, No.12, 3445 (1993).
10. O.T. Woo and K. Tangri, *J. of Nucl. Mater.*, **79**, 82 (1979).
11. G. Okvist and K. Kallstrom, *J. of Nucl. Mater.*, **35**, 316 (1970).
12. T.B. Massalski et al., *Binary alloy phase diagrams*, Vol. **2**, 2030, 2157 (ASM, Ohio, 1986).
13. C.M. Wayman, *Proc. Int. Conf. On Solid-to-Solid Transformation*, Pittsburgh, Pennsylvania, USA Aug. **10-14**, 1981 (AIME, New York, 1982).
14. G. Krauss and A.R. Marder, *Metallurgical Transactions*, Vol. **2**, 2343 (1971).
15. I.S. Chung, K.C. Park and J.R. Huh, *J. of the Korean Inst. of Metals*, Vol. **26**, No. 9, 895 (1988).
16. S. Banerjee and R. Krishan, *Acta Metallurgica*, Vol. **19**, 1317 (1971).
17. N.V. Bangaru, *J. of Nucl. Mater.*, **131**, 280 (1985).