



Development of a manufacturing process for Zr-based spacer grid materials

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ABSTRACT

A novel manufacturing process for zirconium-based alloy strips has been developed. This process consists of a prior heat-treatment under a monotectoid temperature before subsequent deformation processes. During the prior heat-treatment process at 580 °C for 10 h, β -Nb phase particles were precipitated. The second phase particles stabilized the alloy from corrosion even the subsequent annealings at high temperatures. This result enhances the manufacturability of zirconium-based alloys, especially for high strength alloys with high Nb contents. The process developed can also be applied to commercial zirconium-based spacer grid materials, which would give rise to a higher producibility of such materials.

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1. Introduction

Zirconium alloys are indispensable materials for the fuel cladding tubes and spacer grids used in pressurized water reactors. As spacer grid materials, these alloys have to endure continuous mechanical loads and corrosion. The mechanical and corrosion properties of these alloys are strongly related to their manufacturing process. The heat-treatment adopted, in particular, affects their mechanical and corrosion properties. Nowadays, most zirconium alloys contain a small percentage of Nb to improve their resistance to corrosion. However, their heat-treatment conditions are rather limited due to the solubility and precipitation of second phase particles (SPPs). It has been suggested that the optimal heat-treatment should be kept under a monotectoid temperature (T_{mono}) of about 600 °C.

Corrosion resistance is sensitive to doping concentrations as well as annealing temperatures in Nb added Zr alloys [1–5]. Additional Nb of less than 0.4 wt% enhances the corrosion properties by forming a homogeneous solid solution of a niobium-zirconium system [4,5]. Meanwhile, a precipitation of SPPs reduces the rate of corrosion when the Nb contents are higher than 1.0 wt% [3–5]. There are two major second phases, i.e. β -Nb and β -Zr, that affect the corrosion behavior. Their formation varies depending on the annealing temperature. The β -Zr phase particles are formed at a high temperature above T_{mono} ; however, β -Nb phase particles, known to be helpful for a corrosion resistance, are only stabilized if the zirconium alloys are heat-treated below T_{mono} . Jeong et al. [4] reported that the corrosion deteriorated in Zr- x Nb alloys when the samples contained β -Zr particles which were formed during an annealing at 640 °C. They also demonstrated that the precipitation of β -Nb was beneficial for corrosion resistance. Moreover, their ki-

netic observation (using beta-quenched samples) indicated that the time required for β -Nb to be formed stretched up to 10 h during annealing at 570 °C [4,6]. In the case of β -Zr, it has rarely been investigated for its nucleation rates, because β -Zr phases are generally introduced during cooling from the β phase field [7].

On the other hand, one of the drawbacks of the low temperature annealing is that it cannot give rise to a sufficient ductility of alloys during a manufacturing process. It is very difficult to increase the reduction rates of a cold-rolling process if the annealing temperature is low. The cold-rolling process should be repeated to get the final thickness with the given reduction rates. Two or three times of cold-rollings are conducted generally; however, more times of cold-rolling can be needed if the alloys have not fully restored their ductility. Therefore, as already mentioned, the increase of the annealing temperatures enhances manufacturability and still is a desirable approach as long as it won't affect the corrosion resistance. Since the precipitation process of each SPP needs incubation times for its phase transformation, the formation of undesirable (β -Zr) or desirable (β -Nb) SPPs can be controlled appropriately. In the current paper, we present a new technique to overcome the current limited manufacturing process for Nb containing Zr-based alloys. The utilized alloys for this investigation were Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr (HANA-4), Zr-0.4Nb-0.8Sn-0.35Fe-0.15Cr-0.1Cu (HANA-5), and Zr-1.1Nb-0.05Cu (HANA-6).¹

2. Experimental procedures

The starting materials with the designated compositions for HANA-4, HANA-5, and HANA-6 were melted several times in a vacuum and beta-annealed at 1020 °C for 15 min. The beta-annealed

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¹ HANA (High performance Alloy for Nuclear Application) is a trademark of the zirconium-based alloys for a high burn-up fuel cladding material developed by the Korea Atomic Energy Research Institute [8,9].

button-type ingots were quenched and then heat-treated at 580 °C for 10 h in a vacuum to stabilize the β -Nb second phase. For a comparison, this prior heat-treatment wasn't performed for certain selected samples. The sample ingots were then hot-rolled and cold-rolled to strips with a thickness of 1.0 mm. The hot-rolling was done at about 620 °C within 15 min, and the subsequent annealing process for every cold-rolling treatment was conducted below and/or above T_{mono} . The annealing temperature after each cold-rolling used to be determined within 570–600 °C in order not to degrade the corrosion resistance in the conventional manufacturing of the strips. The temperatures and times for the annealing are presented in Table 1. The annealing was done in a vacuum furnace to minimize the specimen oxidation.

For the tensile mechanical test, sub-sized plate specimens with a gage length of 12.5 mm were prepared. The specimens were loaded under a constant strain rate according to ASTM E8. The strain rate was initially $5.0 \times 10^{-3} \text{ min}^{-1}$ until a yielding appeared and was then increased ten times. For the corrosion test, samples with dimensions of 25 mm \times 20 mm were cut from the strips. The specimens were ground up to 1200 grit emery paper, and then pickled in a 5HF–45HNO₃–50H₂O (vol.%) solution. The final thickness of the samples after pickling was 0.56 mm. The corrosion test was performed by using autoclaves in 400 °C steam at 10 MPa. The weight gains of the corroded samples were measured periodically.

For the transmission electron microscopy (TEM) observation, the samples were mechanically polished to 70 μm and then jet-polished with a 90C₂H₅OH–10HClO₄ (vol.%) solution under –45 °C and 15 V conditions. The microstructures, including the SPPs of the samples, were analyzed by using a TEM equipped with an energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows the microstructural changes of the HANA-4 prior to the deformation processes of hot and cold rolling. After being beta-quenched from 1020 °C, martensite structures were observed throughout the samples (Fig. 1(a)). SPPs were over-saturated into the zirconium matrix during the martensitic transformation. If the samples were heat-treated at elevated temperatures, the SPPs would be precipitated depending on the annealing times. A heat-treatment at 580 °C for 10 h induced a nucleation of the β -Nb SPPs in the matrix as shown in Fig. 1(b). These results are consistent with previous research by Kim et al. for a Zr–xNb binary alloy system [4,6].

The HANA-4 with and without prior heat-treated ingots were hot-rolled and cold-rolled into strips. In general, hot-rolling is performed above T_{mono} , while the annealing temperature after cold-rolling is limited to below T_{mono} . Fig. 2 shows the microstructures

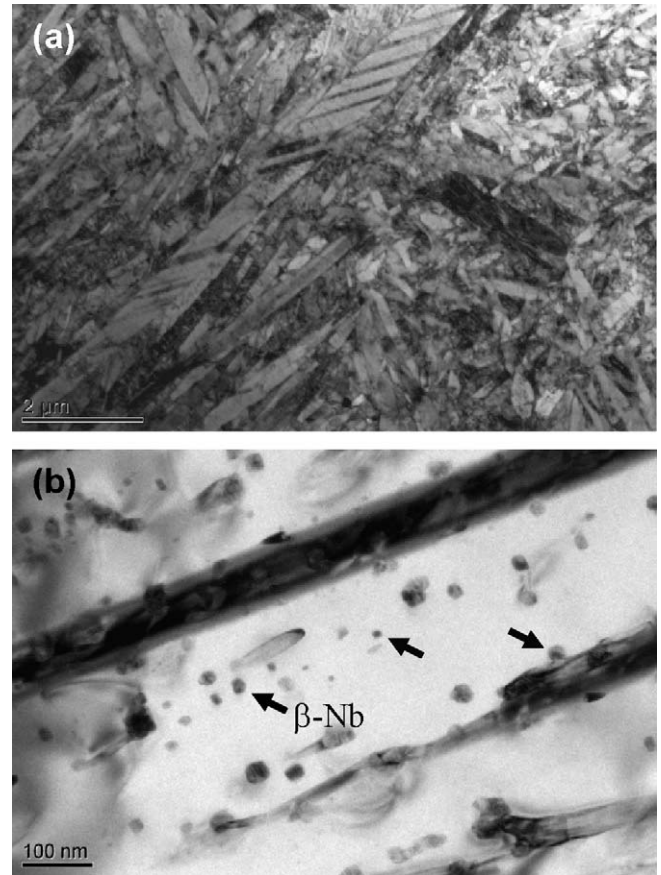


Fig. 1. TEM microstructures of the HANA-4 strips (a) beta-quenched and then (b) prior heat-treated at 580 °C for 10 h. The arrows indicate the β -Nb second phase particles.

of the samples without being prior heat-treated and then annealed above and below T_{mono} . The samples annealed below T_{mono} during the cold-rolling processes (H4E) revealed the absence of β -Zr phase particles as presented in Fig. 2(a). In the commercial manufacturing process, the prior heat-treatment cannot be found and the annealing temperature does not exceed T_{mono} . In this case, manufacturing conditions coincide with the commercial ones. On the other hand, the samples annealed above T_{mono} (H4G) contained β -Zr SPPs as shown in Fig. 2(b). It is noted that the β -Zr phase was precipitated during three 620 °C \times 1 h annealings. This detrimental β -Zr phase should be prevented from forming. Thus, this annealing condition is not applicable to the manufacturing process of zirconium-based alloy strips.

Table 1
Manufacturing conditions for HANA-4, HANA-5, and HANA-6 alloy strips.

ID	Prior heat-treatment	Annealing after 1st cold-rolling	Annealing after 2nd cold-rolling	Final annealing	Remarks
H4A	○	570 °C \times 3 h	600 °C \times 1 h	600 °C \times 1 h	HANA-4
H4B	○		620 °C \times 1 h	580 °C \times 1 h	
H4C	○			600 °C \times 1 h	
H4D	○			620 °C \times 1 h	
H4E	×		580 °C \times 4 h	580 °C \times 10 min	HANA-5
H4F	×			640 °C \times 10 min	
H4G	×	620 °C \times 1 h	620 °C \times 1 h	620 °C \times 1 h	
H4H	○			620 °C \times 1 h	
H5A	○	570 °C \times 3 h	600 °C \times 1 h	580 °C \times 1 h	HANA-6
H5B	○			600 °C \times 1 h	
H5C	○		620 °C \times 1 h	600 °C \times 1 h	
H6A	○	570 °C \times 3 h	580 °C \times 1 h	580 °C \times 10 min	HANA-6
H6B	○		600 °C \times 1 h	580 °C \times 10 min	
H6C	○			600 °C \times 10 min	

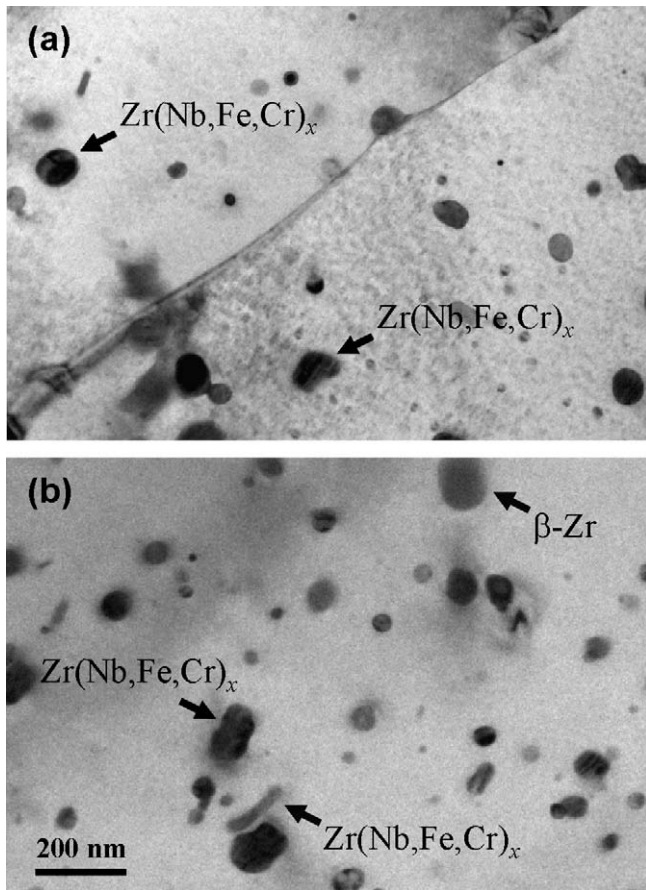


Fig. 2. TEM microstructures of the HANA-4 strips without prior heat-treatment depending on the annealing (a) below the monotectoid temperature (H4E) and (b) above the monotectoid temperature (H4G). The arrows indicate various second phase particles.

However, the samples with prior heat-treatment revealed quite different aspects as shown in Fig. 3. The β -Zr SPPs were not observed in the samples annealed at 620 °C for 1 h after second and final cold-rolling (H4D). Moreover, even a high temperature annealing (above T_{mono}) could not induce a dissolution of β -Nb SPPs as shown in the selected area diffraction patterns in Fig. 3. A precipitation process is dependent on temperature and time. According to a previous report by Kim et al. [6], at least 2 h are necessary for the formation of β -Zr SPPs at 620 °C in beta-quenched samples. In the absence of prior heat-treatment, it was possible for the β -Zr phase to precipitate during a repeated annealing at a high temperature of 620 °C as shown in Fig. 2(b). However, it would hardly occur in samples that had been pre-heat-treated. Once the β -Nb precipitates were stabilized during the prior heat-treatment process, both the phase transformation of β -Nb and the nucleation of β -Zr would be restricted due to kinetic reasons. First, the driving force for a nucleation of β -Zr is different for the two heat-treatment conditions [10]. Second, the nucleation and growth process of β -Zr SPPs is interfered with by the existence of β -Nb SPPs. In fact, Robson [11] proposed that the retained β -Zr has an apparent effect on the kinetics of a subsequent β -Nb evolution. The incubation times for the nucleation of β -Zr SPPs can therefore be affected by the prior heat-treatment process. Consequently, a microstructural difference between the with and without prior heat-treated samples was observed.

Fig. 4 shows the tensile mechanical properties for the investigated HANA-4 strips, whose annealing conditions were identified according to the ID in Table 1. The tensile strength and elongation

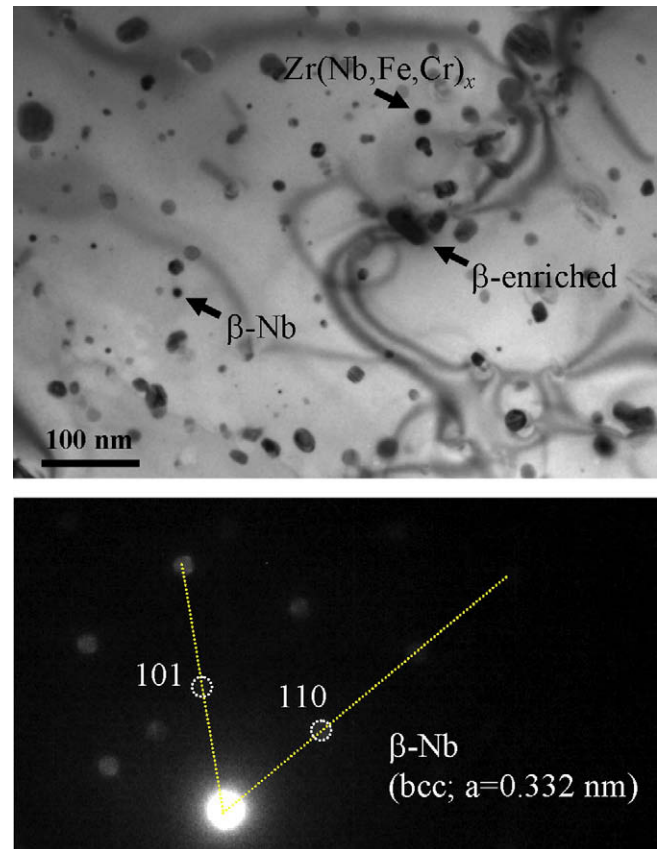


Fig. 3. TEM microstructures of the HANA-4 strips with prior heat-treatment which were annealed above the monotectoid temperature (H4D). The arrows indicate various second phase particles.

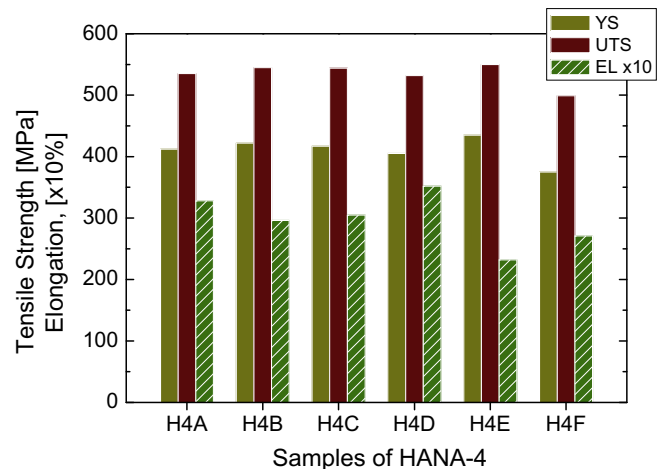


Fig. 4. Tensile mechanical properties for the manufactured HANA-4 strips.

is mainly dependent on the final annealing temperatures and times. As the annealing temperature increased, the ultimate tensile strength (UTS) and yield strength (YS) were decreased and the elongation (EL) was increased. The UTS and YS of all the samples were considered to be acceptable for their application to a spacer grid.² In the case of EL, a larger EL is better for such an application.

² Although the required mechanical properties for a spacer grid can be varied depending on the manufacturers, tensile strength of >379 MPa, yield strength of >296 MPa, and minimum elongation of 24% correspond to the material specifications in South Korea.

The increased elongation indicates an increased ductility and manufacturability. The pre-heat-treated samples (H4A, H4B, H4C, and H4D) exhibited a high EL when compared to the samples without a prior heat-treatment (H4E and H4F). Depending on the annealing conditions, the EL varied from 30% to 35% in the case of the prior heat-treated samples. The increased EL resulted from the annealing at high temperatures since it gave rise to a full recrystallization after each cold-rolling deformation. In fact, in the HANA-4, dislocations as well as deformed microstructures were observed in the conventionally manufactured strips [12,13]. In order for them to be applied to a spacer grid, the conventionally manufactured strips should be annealed at higher temperatures to achieve recrystallized microstructures.

Fig. 5 illustrates the corrosion properties of the investigated HANA-4 strips. In contrast to the largest oxidation of the high temperature-annealed samples (H4G), the prior heat-treated samples showed relatively low corrosion rates. For corrosion of 150 days, the prior heat-treated samples of H4A and H4B showed oxide weight gains of ~ 140 mg/dm², which are similar to that of H4E – the sample H4E underwent annealing at the lowest temperature. The corrosion rates of the samples with a prior heat-treatment (H4B, H4C, and H4D) increased as the final annealing temperature increased; however, the rates were still lower than those for the samples without a prior-treatment (H4F and H4G). In the case of those without a prior heat-treatment, the final annealing was critical for the corrosion resistance. Annealing at 640 °C for 10 min worsened the corrosion resistance (H4F), even though the samples were previously manufactured at low temperatures. The oxide weight gain was very large amounting to 187 mg/dm² in 150 days, compared to 155 mg/dm² for the 580 °C for 10 min annealed sample (H4E). It is considered that the worsened corrosion behavior of H4F and H4G is due to a formation of the β -Zr phase as shown in Fig. 2.

According to Figs. 4 and 5, the ductility of the strips along with their corrosion resistance was enhanced when the strips were prior heat-treated and then annealed at high temperatures. The prior heat-treatment at 580 °C for 10 h induced a precipitation of the β -Nb SPPs and stabilized the alloy, and further, hindered a dissolution of the β -Nb SPPs and the formation of the β -Zr phase. The microstructures were expected to bring about excellent corrosion resistance; indeed, the corrosion behavior shown in Fig. 5 agrees well with the microstructures shown in Figs. 2 and 3. Thus, it was possible to enhance the ductility of the strips while not worsening the corrosion resistance by executing a high temperature

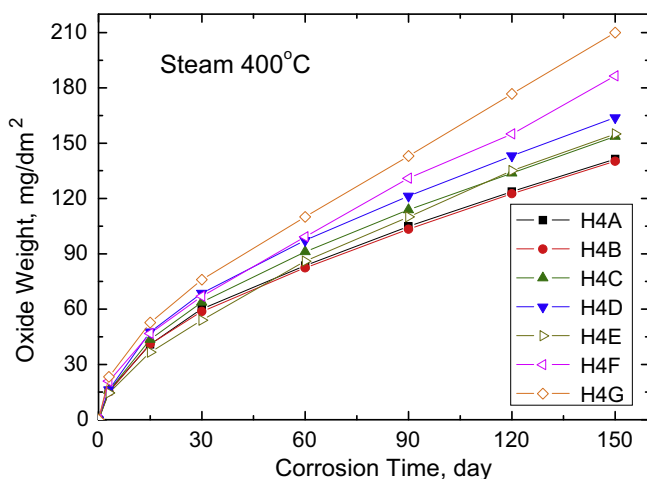


Fig. 5. Variations in oxide weight gains during corrosion in 400 °C steam for 150 days.

annealing above T_{mono} . The manufactured strips with a prior heat-treatment (H4A, H4B, H4C, and H4D) actually showed higher elongation than the conventionally manufactured strips (H4E) as shown in Fig. 4.

Fig. 6 shows the microstructures for the HANA-5 annealed above T_{mono} (H5C) and for the HANA-6 annealed at about T_{mono} (H6C). In both cases, β -Zr SPPs were not detected in the microstructures. This would be favourable for the corrosion resistance as observed in the prior heat-treated HANA-4 strips (Fig. 5). The tensile properties for HANA-5 and HANA-6 are presented in Fig. 7. The UTS and YS of the HANA-5 strips are higher than those of HANA-6. The elongation is opposed to that. All the manufactured strips were satisfactory for a commercial application. Among the three alloys (HANA-4, HANA-5, and HANA-6), HANA-4 is the hardest and HANA-6 is the softest.

Sufficient ductility is necessary for a reliable deformation during the manufacturing of zirconium-based alloy strips. Reduction rates can also be increased as the strips become more ductile. In the respect of the microstructures, ductility corresponds to recrystallized microstructures. As a spacer grid material, the recrystallization of the strips should be achieved for an irradiation creep resistance, a proper spring force, etc. From these points, annealing at higher temperatures has advantages for the manufacturability and mechanical properties of zirconium-based alloys. According to our recent study on the recrystallization of HANA-4 and HANA-6 [13], a final annealing for fully recrystallized microstructures requires annealing at high temperatures and/or long times in the case of HANA-4. In contrast to HANA-6 showing an ease of recrystallization, HANA-4 can be exposed to a degradation of its

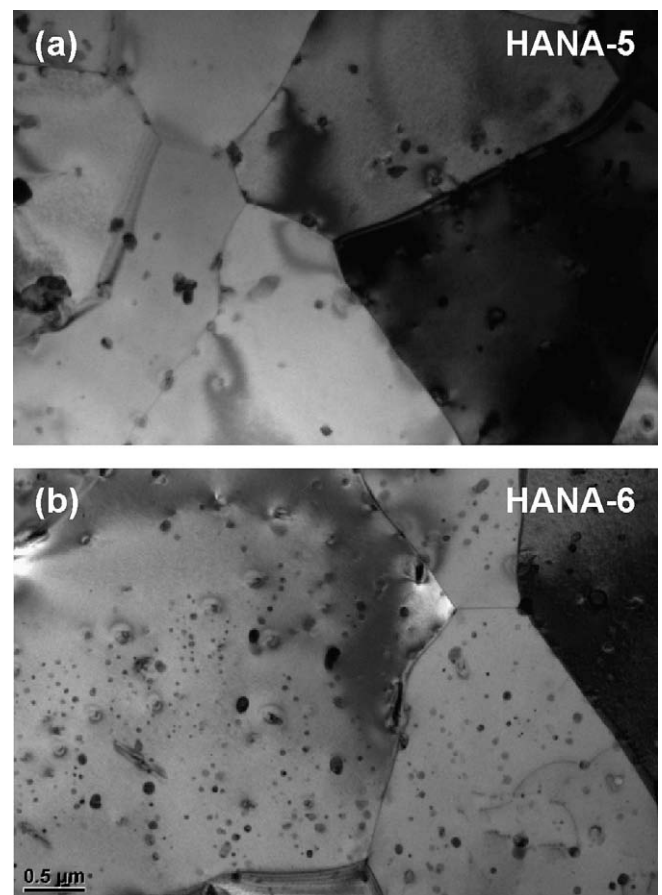


Fig. 6. TEM microstructures of the (a) HANA-5 (H5C) and (b) HANA-6 (H6C) strips which were prior heat-treated and then annealed above the monotectoid temperature.

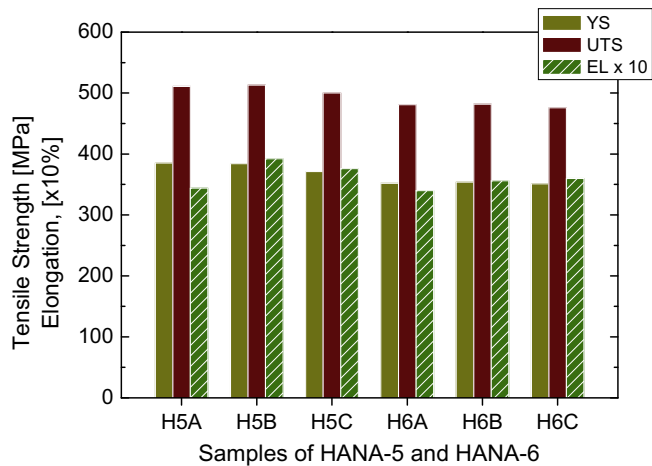


Fig. 7. Tensile mechanical properties for the manufactured HANA-5 and HANA-6 strips.

corrosion properties during annealing at highly restricted conditions. However, this difficulty was resolved successfully by introducing a prior heat-treatment. During the prior heat-treatment process β -Nb SPPs were precipitated and maintained stable during further annealing even at high temperatures. The prior heat-treatment can be applicable to various Nb-contained zirconium alloys, and it is expected to be profitable for manufacturing strips by overcoming the limited processing variables.

4. Conclusion

Zirconium-based alloys of HANA-4, HANA-5, and HANA-6 were manufactured as strips with different annealing conditions. We introduced a prior heat-treatment process, which was performed at 580 °C for 10 h, to precipitate the β -Nb phases. The retained β -Nb second phase particles desensitized the alloys from corrosion

and enabled a high temperature annealing at above the monotectoid temperature. The high temperature process is advantageous for manufacturing zirconium-based alloy strips by providing a sufficient ductility of the strips; however, it can be detrimental to their corrosion resistance since harmful β -Zr phases can be formed. According to our investigation, a prior heat-treatment did not deteriorate the corrosion resistance even in the case of a high temperature annealing. The proposed manufacturing process, which consisted of a prior heat-treatment below T_{mono} before the subsequent deformation processes, enhanced the manufacturability of the Zr-based alloys especially for the high strength alloys with high Nb contents.

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