

Article

Coupling Effect of Mn Addition and Deformation on Mechanical and Electrical Properties of Al-Zr Alloys

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Abstract: In order to increase the strength of Al-Zr alloys, which are promisingly used for heat-resistant conductors, the coupling effect of Mn addition (0.16 wt.% and 0.88 wt.%) and deformation on the precipitation, mechanical, and electrical properties of an Al-0.18wt.% Zr alloy was studied using transmission electron microscopy (TEM), atom probe tomography (APT), hardness testing, and electrical conductivity measurement, respectively. Results showed that the Mn addition fully suppresses the Al₃Zr precipitation in both hot-deformed and undeformed cases, which is mainly due to a strong Mn-vacancy bonding, in which Mn atoms seize vacancies and hence reduce the available vacancies for Al₃Zr nucleation. Minor 0.16 wt.% Mn addition causes a simultaneous decrease in hardness and electrical conductivity, regardless of whether there is deformation. The higher 0.88 wt.% Mn addition, however, significantly increases the hardness by over 40%, especially in combination with deformation. Possible influencing factors such as grain size, dislocations, intergranular/intragranular precipitation, and solute clusters are comparatively discussed in terms of microstructural features and mechanical/electrical properties that are tuned by Mn addition and/or deformation. It is found that the Mn addition can make remarkable contributions to the hardness and thermal stability of the Al-Zr alloys when coupled with deformation.

Keywords: Al-Zr alloy; Mn addition; precipitation; mechanical properties; electrical conductivity



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1. Introduction

Heat-treatable aluminum (Al) alloys are widely used in many fields as structural materials, owing to their advantages including high strength, low density, and good corrosion resistance [1,2]. The high strength of Al alloys is mainly derived from precipitation hardening, which depends closely on the homogeneous distribution of nanosized precipitates within the grain interior [3–5]. Besides their structural applications, Al alloys are also promising candidates for applications in electrical engineering, where high strength and good electrical conductivity are simultaneously required. Unfortunately, a significant number of nanosized precipitates, although contributing to a high strength, will lead to a low electrical conductivity due to the unfavorable scattering effect. A minor addition of alloying elements, especially immiscible elements, is preferred in Al alloy conductors that can reach an optimized combination of strength and electrical conductivity.

Al alloys with the addition of minor immiscible Zr (0.1–0.4 wt.%) are considered prospective materials for conductors [6]. The dilute Al-Zr alloys have a high heat resistance and excellent capacity-expansion characteristics [7], which can improve the transmission capacity when used as high-voltage transmission lines. Basically, nanosized Al₃Zr metastable precipitates with an L1₂ structure are artificially produced in the Al-Zr alloys [8–10], which are used to hinder the grain growth and provide good thermal stability at elevated temperatures up to 150–210 °C [11]. Moreover, formation of the Al₃Zr precipitates is accompanied by a significant decrease in the Zr concentration within the Al matrix [6,8], which ensures

an electrical conductivity level close to that of pure Al. For the precipitation purpose, a long period of annealing (up to 300 h) at 300–450 °C is usually applied to the Al-Zr alloys, because the Zr diffusivity in Al matrix is quite slow [12]. Apart from the long aging time, another drawback is that the Zr solid solubility in Al is limited [13]. This means the Al₃Zr precipitates that could be formed in the Al-Zr alloys have a very low volume fraction. The strength of the Al-Zr alloys is thus relatively low, even compared to the commercial electrotechnical Al-Mg-Si alloys. Determining how to increase the strength has attracted extensive attention in the development of Al-Zr alloy conductors.

This work is aimed at studying the aging response and resultant mechanical/electrical properties of Al-Zr alloys with different minor Mn additions. The choice of Mn addition is based on the following considerations: (i) The formation of the Al₆Mn phase has been experimentally found to occur as the temperature is raised beyond 460 °C for 4 h [14]. It is reasonably believed that some Mn-rich dispersoids could be additionally precipitated to further impede the grain boundary movement, which will suppress the recrystallization and also enhance the thermal stability. (ii) The Mn-rich dispersoids and strengthening of the Mn solution make more contributions to the strength [15], which may increase the strength of Al-Zr alloy conductors to some degree. In order to reveal the intrinsic Mn addition effect and its coupling effect with the dislocations that are induced by deformation, both the cast Al-Zr-Mn alloys and their deformed Al-Zr-Mn counterparts (analogous to conductors) were exposed to aging treatments for comparison.

2. Materials and Methods

Al-0.18 wt.% Zr (abbreviated as AlZr), Al-0.18 wt.% Zr-0.16 wt.% Mn (AlZrMn-1), and Al-0.18 wt.% Zr-0.88 wt.% Mn (AlZrMn-2) alloys were used in the present work. Note that 0.16 wt.% and 0.88 wt.% Mn additions are measured concentrations after casting; the nominal additions are 0.20 wt.% and 1.00 wt.%, respectively, which represent a low addition (the former) and a high addition (the latter) for comparison. The chemical composition of the three alloys is shown in Table 1. All the alloys were melted and cast in a stream of argon, using 99.7 wt.% industry pure Al, Al-5.0 wt.% Zr master alloy, and Al-10.0 wt.% Mn master alloy. The casting temperature was 740 °C and a copper mold was used with a cooling rate evaluated as 60–100 K/s. The cast ingots (20 mm × 20 mm × 150 mm in size) were subjected to solution treatment at 600 °C for 4 h (with cold-water quenching); thereafter, the samples were divided into two parts. One part of the solution-treated samples was directly aged at 350 °C for different times from 5 h to 70 h. The other part was hot-rolled into deformed samples in a diameter of ~9.5 mm, followed by aging treatments the same as their undeformed counterparts. The hot rolling was performed at 520 °C and the degree of deformation was about 77% (from 20 mm down to $\varnothing$ 9.5 mm).

Table 1. Chemical composition of the cast alloys.

Alloys	Al	Zr	Mn	Si	Fe
AlZr	Bal.	0.18	-	0.04	0.09
AlZrMn-1	Bal.	0.17	0.16	0.05	0.14
AlZrMn-2	Bal.	0.18	0.88	0.05	0.13

Microstructures of the alloys were characterized using scanning electron microscopy (SEM, JSM-6700E with EDX detector, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM). The TEM examinations were performed on a JEOL-2100 microscope (JEOL Ltd., Tokyo, Japan) operating at 200 kV. The TEM foils were prepared following the standard electro-polishing techniques for Al alloys [16,17]. Cross-sectional TEM examinations were carried out to measure average grain size (d) of the hot-deformed alloys using a linear intercept method, for which at least 150 grains were examined to obtain an average value. In measuring the size of precipitates, the smallest size l_1 and the largest size l_2 were first measured, and the precipitate size was determined as $l = \sqrt{l_1 \times l_2}$ [18,19]. At least 200 precipitates were examined to obtain the average precipitate size. The pre-

precipitate number density (ρ) was evaluated in term of the measured inter-particle spacing λ : $\rho = \lambda^{-3}$ [18,19]. Similarly, at least 200 precipitates were measured to determine the average inter-particle spacing. More details about the measurements of precipitates are provided in previous publications [16,17,20]. Image analysis was performed by geometrical phase analysis (GPA) [21], where the reference area used in the digital processing as a strain-free area was chosen in the matrix as far as possible from the precipitate under study, as a general procedure. On the images the standard deviation was never allowed to exceed 0.2%, which was then considered the maximum error on the measurements.

Dislocation density was measured by performing X-ray diffraction (XRD) experiments. Each sample was tested at least six times to obtain a set of diffraction profiles. The evaluation of these profiles was performed following the Multiple Whole Profile (MWP)-fit method developed by Ungar and co-workers [22,23], where simulated profiles are fitted to the recorded profiles. This is undertaken for all reflections simultaneously with *ab initio* theoretical functions for the strain- and size-induced profile broadening. The reader can refer to reference [24] for experimental details.

To reveal the solute distribution at the atomic level, atom probe tomography (APT) examinations were performed using an Image Scientific Instruments 3000HR local electrode atom probe (LEAP, Image Scientific Instruments Inc., Staten Island, NY, USA). The APT sample blanks with a square cross-sectional area of approximately $300 \times 300 \mu\text{m}^2$ and length of 1 cm were prepared by a combination of slicing and mechanical grinding. A two-step electropolishing was used for making tips from these blanks [25]. A 10.0 vol% perchloric acid in methanol solution was used for coarse polishing, and the final polishing was performed using a solution of 2.0 vol% perchloric acid in butoxyethanol. APT data collection using the electrical pulsing mode was performed at a specimen temperature of $30 \pm 0.3 \text{ K}$, with a voltage pulse fraction (pulse voltage/steady-state DC voltage) of 20%, a pulse repetition rate of 200 kHz, and a background gauge pressure of $<6.7 \times 10^{-8} \text{ Pa}$ ($5 \times 10^{-10} \text{ torr}$).

Vickers hardness (HV) was tested on a LECO Hardness Tester (LV700AT, LECO, St. Joseph, MI, USA) under a weight of 5 kg and with a dwelling time of 10 s. Data provided in the following sections are an average of at least 9 measurements. Electrical resistivity of samples (gauge 1200 mm, standard measurement length 1000 mm) was measured by a double direct current electric bridge at room temperature, with the resistivity converted into %IACS (IACS: International Annealed Copper Standard). The following relation was used to express this in IACS units: $\text{IACS} = w_{\text{Al}}/w_{\text{Cu}} \times 100\%$, where w_{Al} is the conductivity of the studied Al alloy in MS/m and w_{Cu} is the conductivity of copper (58.0 Ms/m).

3. Results

3.1. The Effect of Mn Addition on Grain Evolution

Figure 1 shows optical microscope (OM) images to compare the grain size among the three alloys without deformation. The cast and solutionized AlZr alloy (free of Mn addition) has very coarse grains with size reaching a millimeter (Figure 1a). Grains in the AlZrMn-1 alloy have an average size of about $800 \mu\text{m}$ (Figure 1b), close to observations in the AlZr alloy. This indicates that 0.16 wt.% Mn addition should be too little to affect the grain nucleation. As the Mn addition increased to 0.88 wt.%, a remarkable grain refining effect is evident, in which the average grain size reduces to about $200 \mu\text{m}$ in the AlZrMn-2 alloy (Figure 1c). The variation of the average grain size with Mn addition in the cast alloys, as shown in Figure 1d, clearly demonstrates that the grain refinement is strongly dependent on the Mn content.

Figure 2a–c present representative TEM images showing the cross-sectional grain structure in the three as-deformed alloys, respectively. One can see that the grains were highly refined after deformation. Figure 2d–f are statistical results of the grain size distribution, correspondingly. The average grain size is quantitatively measured to be $0.5 \mu\text{m}$ in the AlZr alloy, $0.5 \mu\text{m}$ in the AlZrMn-1 alloy, and $0.3 \mu\text{m}$ in the AlZrMn-2 alloy. The grain refinement induced by Mn addition in the hot-deformed alloys is not so noticeable as in the cast alloys. This is reasonable because the severe deformation makes a predominant

contribution to the grain refinement, and the Mn effect mainly lies in the formation of Mn-rich dispersoids that could inhibit the grain boundary movement. At this point, it should be especially mentioned that the grains in the hot-deformed alloys (shown by TEM images as in Figure 2 and subsequent figures) are actually sub-grains [26]. In this paper, we call them grains for simplicity.

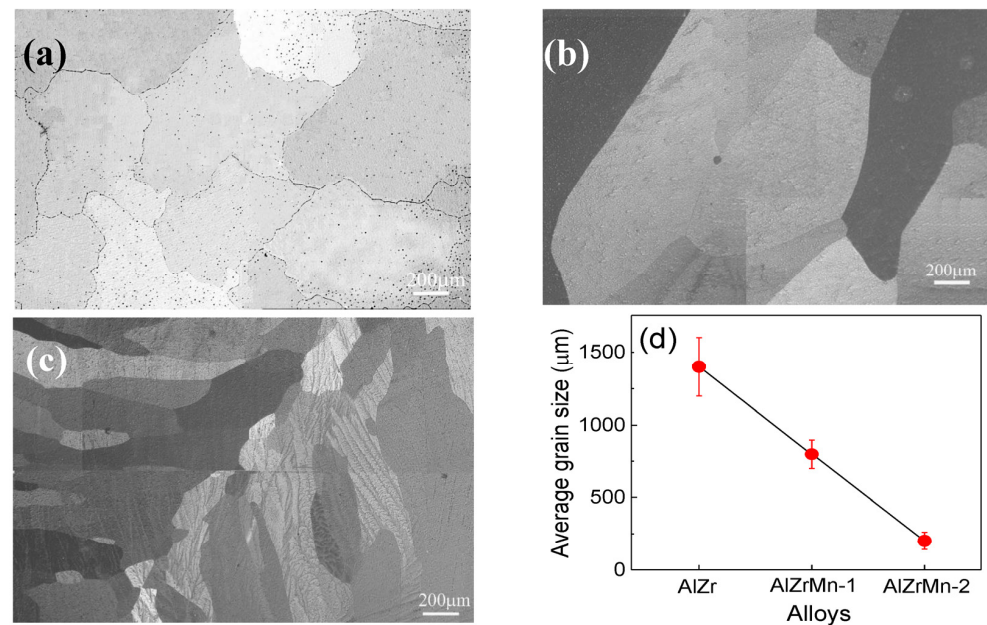


Figure 1. Representative OM images to show the grains in cast and solutionized AlZr (a), AlZrMn-1 (b), and AlZrMn-2 (c) alloys. The average grain sizes of the three alloys are compared in (d).

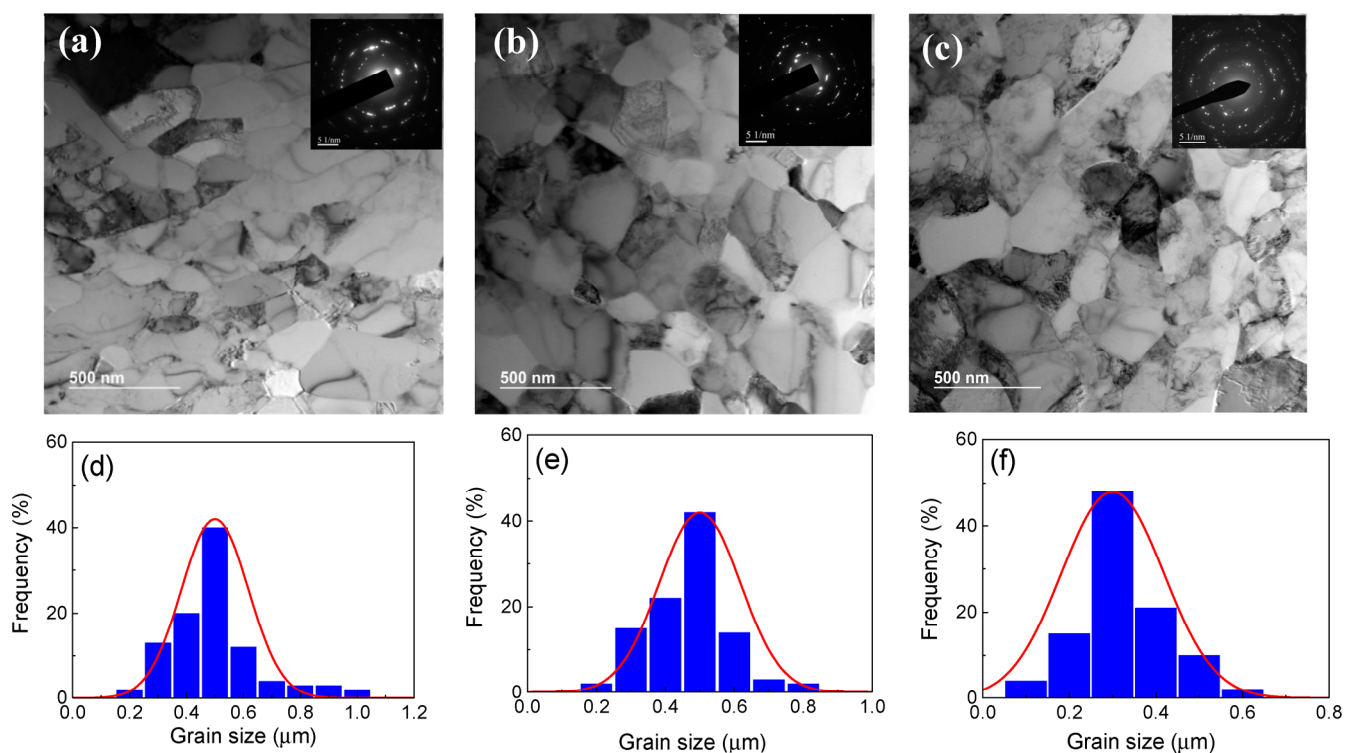


Figure 2. Representative TEM images to show grains in the hot-deformed AlZr (a), AlZrMn-1 (b), and AlZrMn-2 (c) alloys, and statistical results of their grain size distribution accordingly (d–f). Insets in (a–c) show corresponding selected area electron diffraction.

The deformation also promotes high-density dislocations formation in the hot-deformed alloys. Figure 3a,b are representative longitudinal-section TEM images of the hot-deformed AlZr alloy and AlZrMn-2 alloy, respectively. Abundant dislocations are visibly observed in both the two alloys, but it is hard to quantitatively determine the dislocation density from TEM examinations. XRD-based measurements were performed to quantify the dislocation density (ρ) of the hot-deformed alloys. Figure 3c shows the evolution of dislocation density with average grain size in the three hot-deformed alloys. It is evident that the dislocation density increases with reducing grain size. In other words, more Mn addition leads to higher dislocation density, which is mostly associated with a pinning effect on dislocations exerted by the Mn solute atoms.

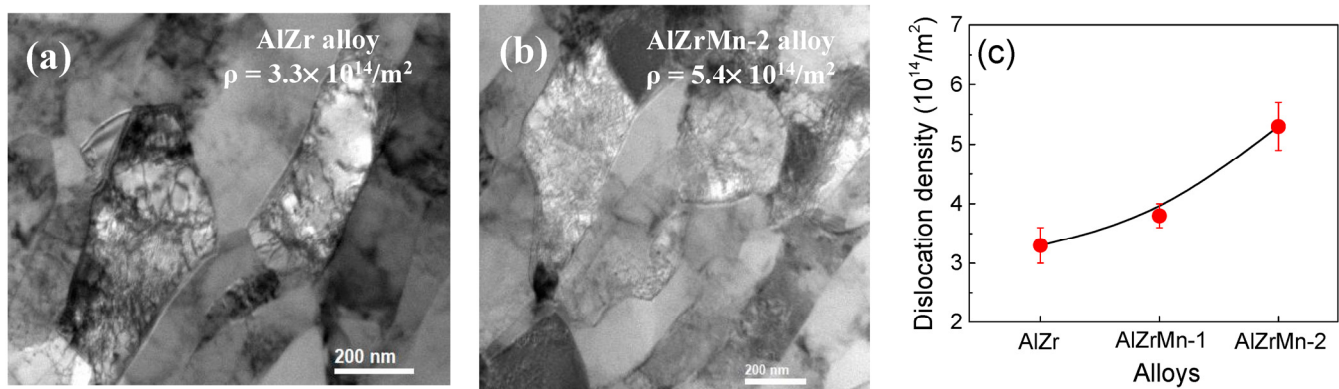


Figure 3. Representative longitudinal-section TEM images to show high-density dislocations in the deformed AlZr (a) and AlZrMn-2 (b) alloys. (c) Experimental measurements on the dislocation number density of the three hot-deformed alloys.

3.2. The Effect of Mn Addition on Aging Precipitations

Figure 4 shows representative TEM images of the three cast alloys aged at 350 °C for 75 h. Some nanosized intragranular second-phase particles are clearly found in the AlZr alloy, as typically marked by arrows in Figure 4a. Unsurprisingly, these fine particles are characterized to be $L1_2$ -structured Al_3Zr precipitates (see lattice parameters inserted in Figure 4a and the FFT image inserted in Figure 4b), whereas in the aged AlZrMn-1 (Figure 4c) and AlZrMn-2 alloys (Figure 4d), Al_3Zr precipitates are not detected within the grain interior. Note that there are a few “black dots” in Figure 4c,d. These “black dots”, after careful examination, are found not to be the Al_3Zr precipitates. Instead, the “black dots” have a crystal structure close to that of the Al matrix but in a distorted manner. The TEM results indicate a possibility that Zr atoms assemble into atomic clusters rather than form Al_3Zr precipitates. The local Zr segregation induces distortion in crystal lattice, which should be responsible for the visible contrast or “black dots”, as shown in Figure 4c,d. APT examinations were performed to verify the Zr clusters. Figure 5 presents representative APT images of the AlZr, AlZrMn-1, and AlZrMn-2 alloys aged at 350 °C for 75 h, where only Zr atoms are shown for clear demonstration. Al_3Zr nanoprecipitates are detected in the AlZr alloy, which are highlighted in green using a 25 at.% Zr isoconcentration surface (see Figure 5a), whereas in the AlZrMn-1 and AlZrMn-2 alloys, no Al_3Zr nanoprecipitates are found but Zr clusters are evident (see Figure 5b,c). In comparison, the AlZrMn-1 alloy (Figure 5b) contains much fewer Zr clusters than the AlZrMn-2 alloy (Figure 5c). Note that no Mn clusters are detected in the AlZrMn-1 and AlZrMn-2 alloys.

The above experimental results manifest an unexpected Mn suppressing effect on the Al_3Zr precipitation. The most likely reason is that the Mn atoms capture vacancies more strongly than the Zr atoms, and hence decrease the available vacancies for Al_3Zr precipitation. It is generally recognized that the vacancies play a critical role in the aging precipitation [27,28]. A well-known example is that a small addition of In, Sn, or Cd to Al-Cu alloys suppresses natural aging while promoting precipitation at elevated

temperatures [29]. The suppression of natural aging is related to a strong binding of the microalloying element (In, Sn, or Cd) with vacancies. Such a strong binding effectively traps the quenched vacancies and hence remarkably retards the Cu diffusion [29]. However, the vacancies are released at elevated temperatures, which accelerates the precipitation of θ' -Al₂Cu precipitates. Similar precipitation behaviors with the same mechanisms were also reported in Al-Mg-Si alloys microalloyed by Sn [30]. Coming back to the present work, the quenched vacancies are ready to aid the Zr diffusion and finally advance the Al₃Zr precipitation in the AlZr alloy, as experimentally observed in Figure 5a,b, whereas in the case of Mn addition, the stronger Mn-vacancy binding [31] makes vacancies preferentially combine with Mn atoms. The vacancy-mediated Zr diffusion is cut down, and the vacancy-stimulated Al₃Zr precipitation is also blocked. As a result, only Zr clusters are formed in the AlZrMn alloys even after a long period of aging. The greater the Mn addition, the slower the Zr diffusion. This explains why the Zr clusters are more in the aged AlZrMn-1 alloy than in the aged AlZrMn-2 alloy.

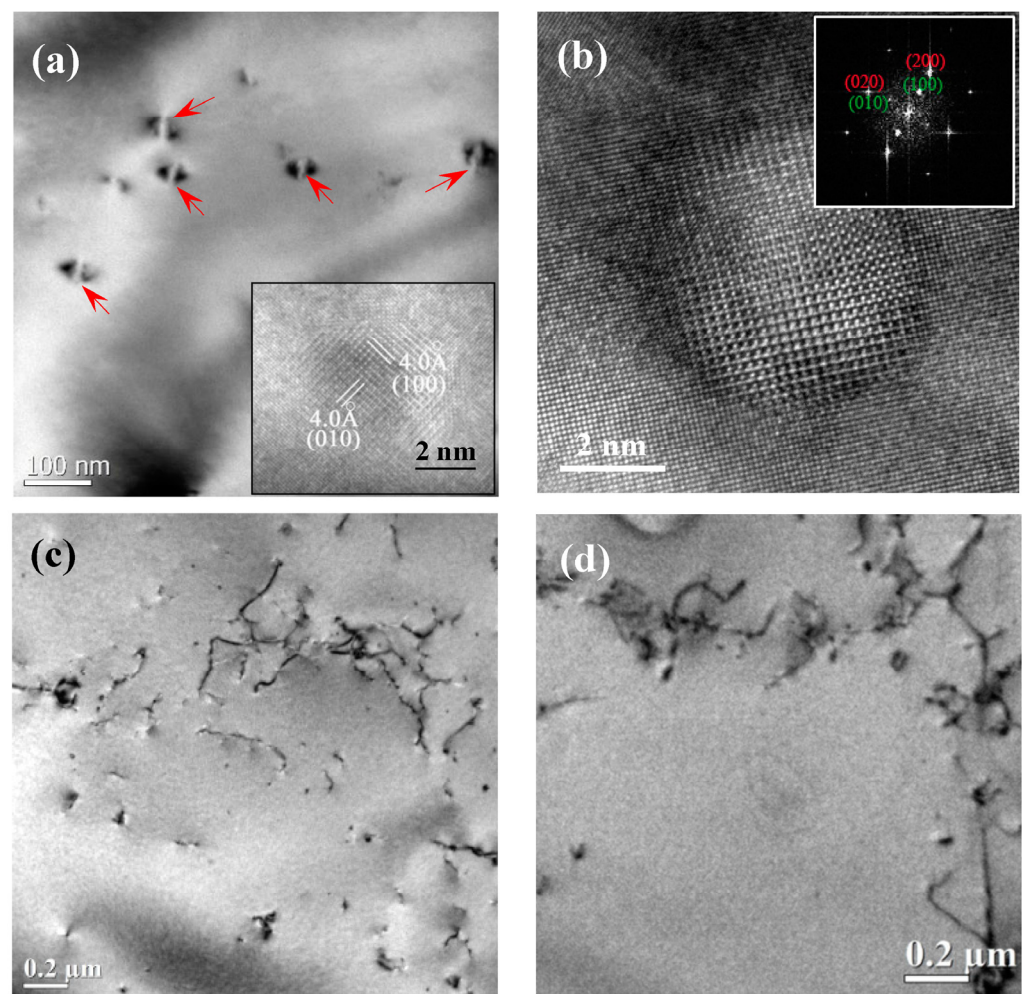


Figure 4. Representative TEM images of three cast alloys aged at 350 °C for 75 h, respectively. Nanosized intragranular second-phase particles characterized as Al₃Zr are clearly visible in the AlZr alloy, as typically marked by arrows in (a) and magnified in (b). The determined lattice parameters inserted in the bottom-right corner of (a) and the FFT image inserted in the top-right corner of (b) are used to identify the Al₃Zr precipitate with a L1₂ structure. No Al₃Zr nanoprecipitates are detected in the AlZrMn-1 (c) and AlZrMn-2 (d) alloys.

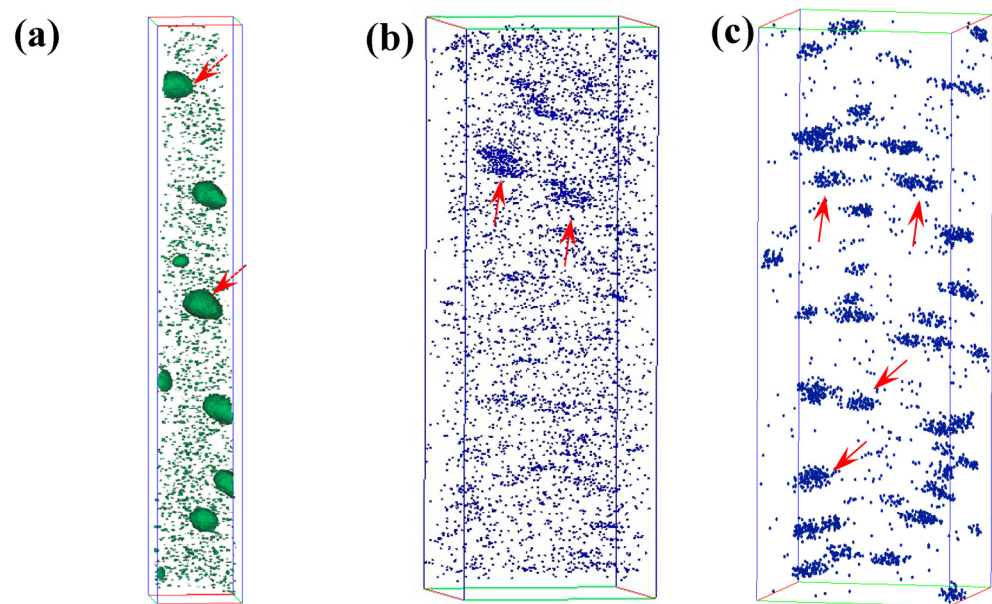


Figure 5. Representative APT images showing Zr atom distribution in the aged AlZr (a), AlZrMn-1 (b), and AlZrMn-2 alloys (c) without deformation. Dot arrows in (a) indicate Al_3Zr precipitates, while the solid arrows in (b) and (c) indicate Zr clusters. In (a), the Al_3Zr precipitates are highlighted in green using a 25 at.% Zr isoconcentration surface. Size: $30 \times 30 \times 140 \text{ nm}^3$ in (a), and $40 \times 40 \times 150 \text{ nm}^3$ in (b,c).

When the alloys are deformed to ultrafine-grained or nanograined alloys, a great number of crystalline defects are induced that will promote the solute diffusion [32]. The grain boundary energy is also raised, and solute atoms are apt to diffuse toward the large-angle grain boundaries because of energy minimization [33,34], especially in the case of a shortened diffusion distance. This scenario is similarly observed in the present hot-deformed dilute AlZr and AlZrMn alloys when subjected to artificial aging. Figure 6a–c show representative TEM images of the hot-deformed AlZr, AlZrMn-1, and AlZrMn-2 alloys after aging at 350 °C for 40 h, respectively. Intragranular nanosized precipitates are seldomly captured in all the three alloys after aging. In contrast, intergranular precipitations are frequently observed, as typically indicated by arrows in Figure 6a–c. The intergranular precipitates vary with Mn addition. The intergranular precipitate is determined to be Al_2Zr in the AlZr alloy, as revealed from the HRTEM image and corresponding fast Fourier transform (FFT) pattern (inset) of a representative intergranular precipitate indicated by a square in Figure 6a. In the AlZrMn-1 alloy, structural analyses based on HRTEM and the corresponding FFT pattern (insets in Figure 6b) point to an Al_2Zr precipitate, the same as in the AlZr alloy. No Mn-rich precipitates are detected at the grain boundaries. These results show that Zr atoms are prone to segregate at the grain boundaries and precipitate to second-phase particles once the intergranular Zr concentration reaches a critical point. Minor Mn addition such as 0.16 wt.% doping in the AlZrMn-1 alloy has no apparent effect on the intergranular precipitation, whereas in the AlZrMn-2 alloy where the Mn addition is raised up to 0.88 wt.%, intergranular Mn-rich precipitates are predominantly found, with the Al_2Zr ones much reduced. The intergranular precipitate, as typically shown in Figure 6c, is proven to be Mn-rich by EDX analysis (inset). The corresponding HRTEM image and determined lattice constant (Figure 6d) indicate the precipitate being Al_6Mn . In this case, the Mn atoms also diffuse to and segregate at the grain boundaries, precipitating the nano-sized Mn-rich particles. The SEM images and XRD results shown in Figure 7 clearly demonstrate the formation of intergranular Al_6Mn particles in the aged AlZrMn-2 alloy, while XRD results did not detect the Al_6Mn particles in the aged AlZr and AlZrMn-1 alloys. Quantitatively, the number density of intergranular nanoprecipitates is determined to be about $1.2 \pm 0.1 \times 10^{18} / \text{m}^3$ in the AlZr alloy, about $1.1 \pm 0.2 \times 10^{18} / \text{m}^3$ in the

AlZrMn-1 alloy, and about $2.2 \pm 0.2 \times 10^{18} / \text{m}^3$ in the AlZrMn-2 alloy. Intergranular precipitation promoted by the Mn addition is well validated.

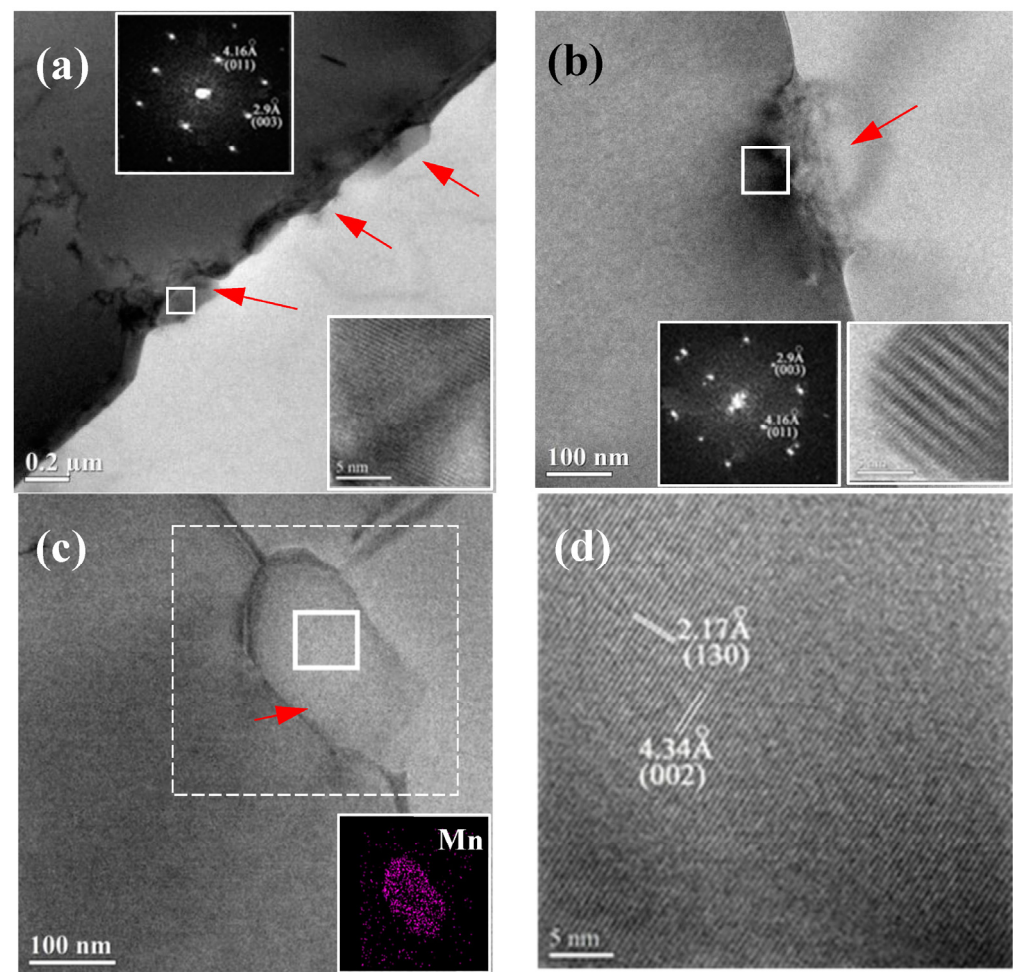


Figure 6. Representative TEM images to show the intergranular second-phase particles (marked by arrows) in the hot-deformed AlZr (a), AlZrMn-1 (b), and AlZrMn-2 (c) alloys after aging at 350 °C for 40 h, respectively. The intergranular particle typically indicated by square in (a) and (b) is determined to be Al_2Zr by structural analyses based on HRTEM and corresponding FFT pattern (see insets, respectively), whereas in the AlZrMn-2 alloy, intergranular Mn-rich precipitates are predominantly found. These Mn-rich precipitates, as typically shown in (c) (inset: Mn mapping on the region indicated by dot square), are characterized to be Al_6Mn , based on the structural analyses (d) of the part indicated by the solid square in (c).

Note that the microstructures of alloys without solid solution treatment were also examined simply. Typically, Figure 8a shows a SEM image of the AlZrMn-2 alloy free of solid solution treatment, where large constituent second-phase particles are frequently observed that were formed during casting. These particles were found to be Mn-rich and Zr-rich using line scanning analysis (Figure 8b). Since a great number of Mn and Zr atoms have been consumed in the constituents, the available Zr and Mn atoms that could be used for precipitates during aging treatment are quite limited. In this case, intergranular precipitation was hardly detected in the aged alloys.

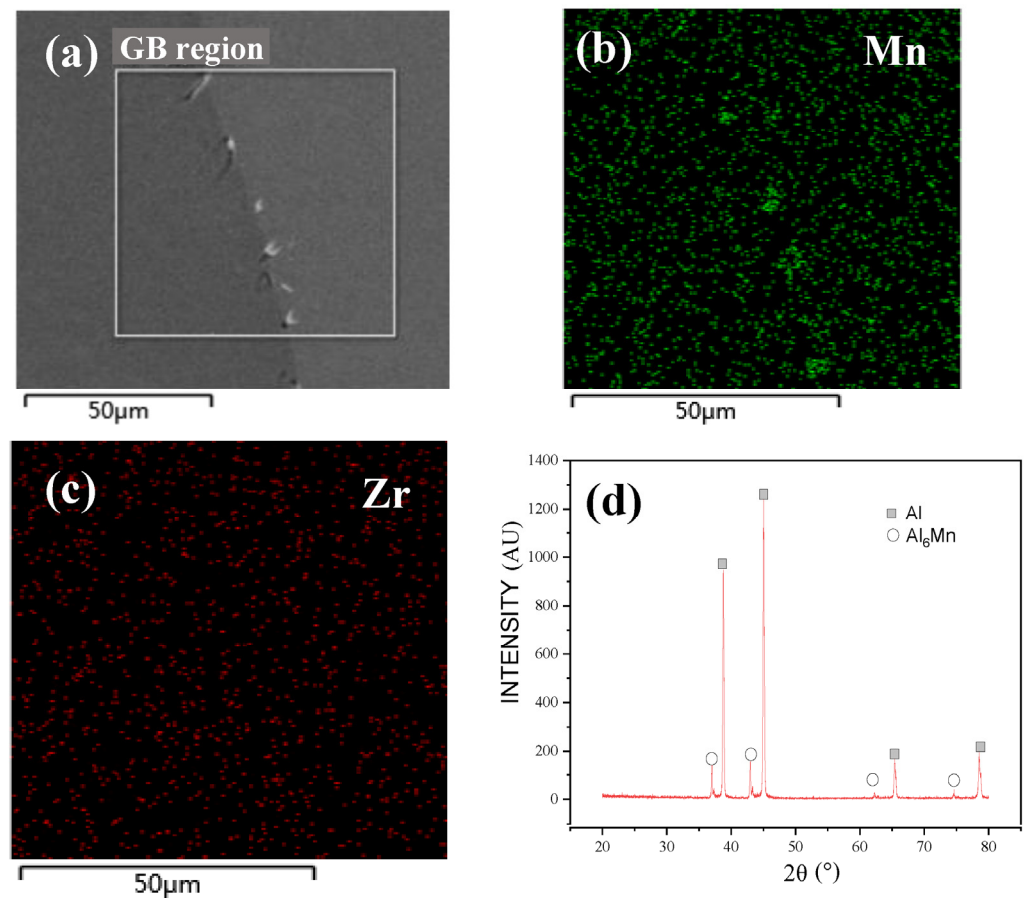


Figure 7. A representative SEM image (a) to show some Mn-rich second-phase particles at the grain boundary in the hot-deformed AlZrMn-2 alloys after aging at 350 °C for 40 h, with corresponding Mn mapping (b) and Zr mapping (c). XRD results given in (d) clearly represent the Al₆Mn phase, where the absence of Al₂Zr phase is due to its too low volume fraction.

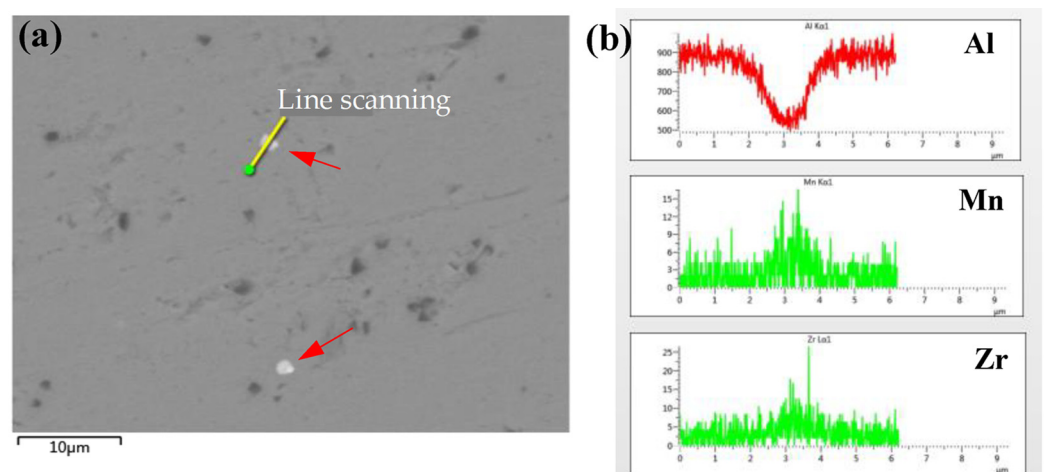


Figure 8. A representative SEM image (a) to show some large constituent second-phase particles (indicated by arrows) in the AlZrMn-2 alloy, which are determined to be Mn-rich and Zr-rich by line scanning examinations (b) corresponding to the line indicated in (a). These particles will survive in the case of no solid solution treatment, which consume many Mn and Zr atoms and highly reduce the solutes available for precipitation in aging treatment.

3.3. The Effect of Mn Addition on Mechanical/Electrical Properties

3.3.1. The Cast and Solutionized Alloys

When the cast and solutionized alloys are directly subjected to artificial aging, the AlZr alloy displays a normal age-hardening curve, including three regions of under-aging, peak aging, and over-aging; see Figure 9a. This evolution is well known [3] to be associated with the nucleation, growth, and coarsening of Al_3Zr nanoprecipitates. The 0.16 wt.% Mn addition, however, induces hardness insensitive to aging time in the AlZrMn-1 alloy (Figure 9a). Within the whole aging time range studied here, hardness of the AlZrMn-1 alloy only slightly fluctuated. As the Mn addition increased to 0.88 wt.%, the AlZrMn-2 alloy shows a hardness that was almost unchanged within 30 h but gradually increased beyond 30 h. The hardness in the AlZrMn-2 alloy is greater than that in the AlZr alloy at an aging time longer than about 75 h (Figure 9a). The gradual increase in hardness over a prolonged aging time should be related to the progressive formation of Zr clusters in the AlZrMn-2 alloy (see Figure 5b). The Zr cluster strengthening, in combination with the Mn solid solution strengthening, finally yield a strength (hardness) that is superior to that of the over-aged AlZr alloy. In contrast, the AlZrMn-1 alloy, having much less Mn addition (hence little Mn solid solution strengthening), exhibits a hardness lower than that of the AlZr alloy (with Al_3Zr nanoprecipitate strengthening) and AlZrMn-2 alloy (with improved Mn solid solution strengthening and Zr cluster strengthening).

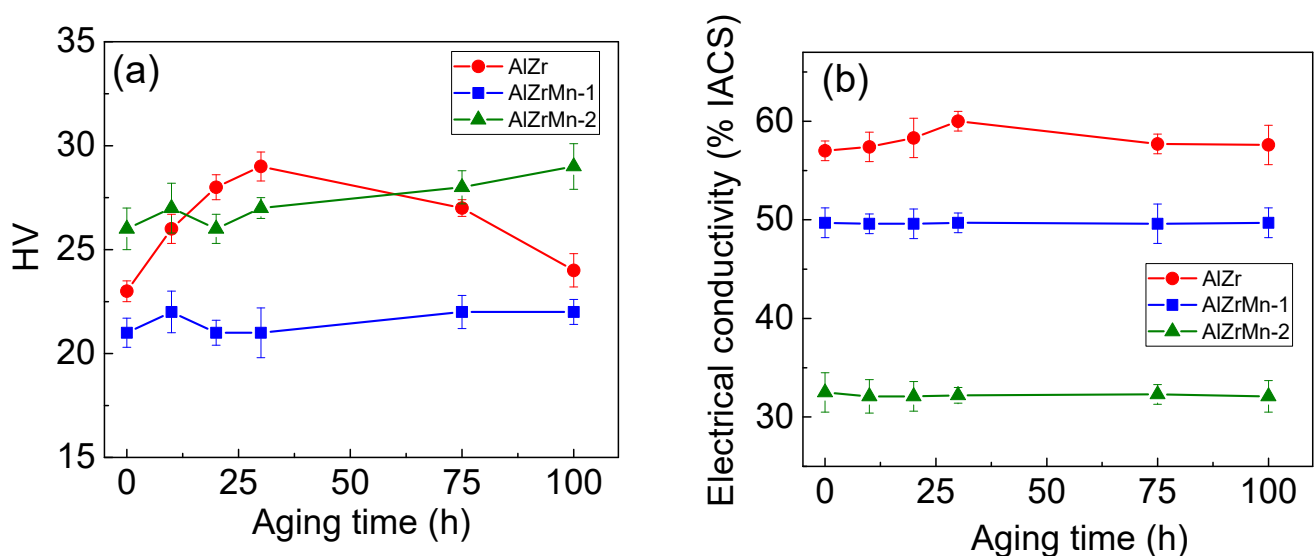


Figure 9. Variation in hardness (a) and electrical conductivity (b) with aging time of the three cast and solutionized alloys when aged at 350 °C.

In comparison, the electrical conductivity is quite insensitive to aging time in all the three alloys; see Figure 9b. Only a very small peak electrical conductivity is found in the AlZr alloy, corresponding to the peak strength at an aging time of about 30 h. The AlZrMn-1 and AlZrMn-2 alloys show electrical conductivity that hardly changes with aging time. Basically, the AlZr alloy has the greatest electrical conductivity, followed by the AlZrMn-1 alloy, and the AlZrMn-2 shows the lowest value. This trend is reasonably understood, because the Mn addition increases the solute concentration in the Al matrix, which magnifies the scattering of electron motion [35–37]. The greater the Mn addition, the lower the electrical conductivity. An interesting result revealed from Figure 9b is that the Mn solute effect on electrical conductivity predominates over the effect of Zr atom distribution, as the AlZrMn-2 samples with Zr solute atoms at the initial aging stage (for example, aged at 5 h) and the Zr clusters at the late aging stage (for example, aged at 100 h) have almost the same electrical conductivity.

It is surprising that the electrical conductivity remains almost unchanged during the aging treatment; see Figure 9b. This phenomenon can be explained as follows: (1) In the AlZrMn-1 and AlZrMn-2 alloys, no precipitates were formed and only Zr atom clusters were found. The scattering effect from atom clusters is comparable with the Zr atoms that were solid solutioned in the matrix; therefore the electrical conductivity experiences a slight change. (2) In the AlZr alloy, Al_3Zr nanoparticles were precipitated, which would significantly increase the electrical conductivity. However, a discrepancy in crystal lattice exists between the Al_3Zr and Al matrix, and the coherency between the two phases will induce a local stress/strain field at the interface. Figure 10 shows the local stress/strain field using GPA analysis. A remarkable local stress/strain field is evident even in the case of the Al_3Zr precipitate having a size of a few nanometers, which will also have a scattering effect and hence decrease the electrical conductivity. As a result, the total electrical conductivity exhibits a minor variation during the whole aging treatment.

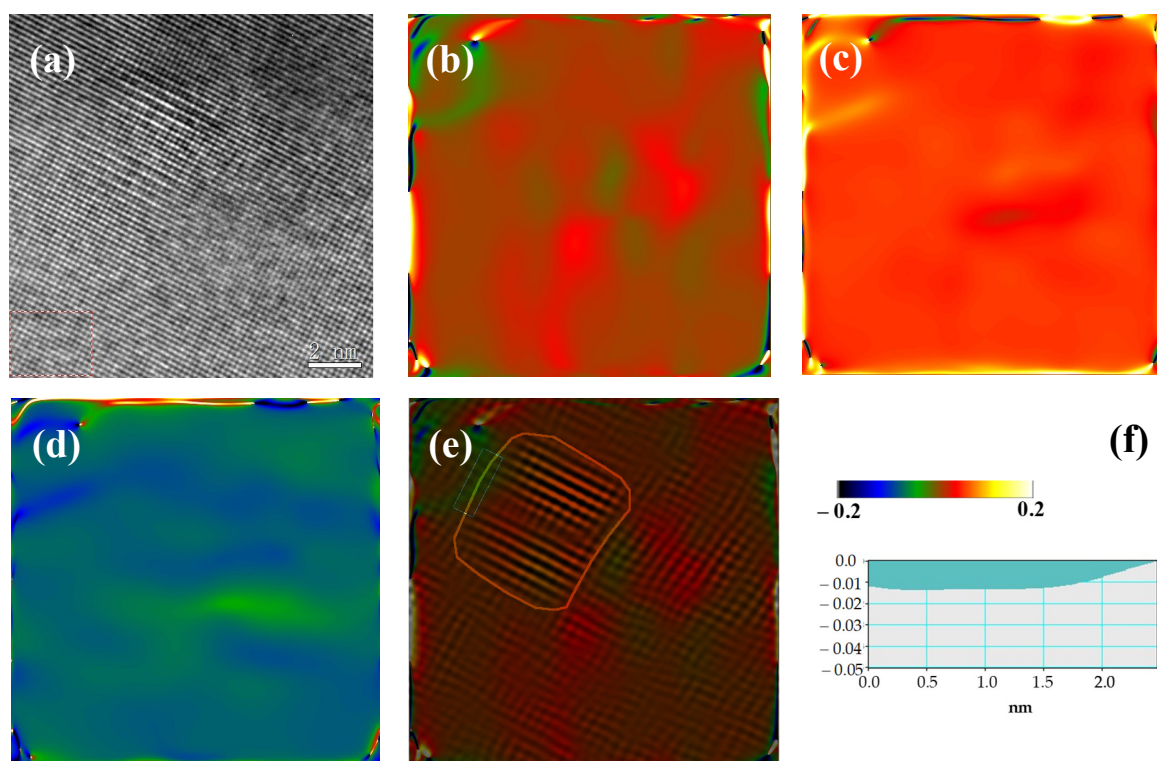


Figure 10. Geometrical phase analysis (GPA) of a coherent Al_3Zr precipitate in the cast AlZr alloy after aging. (a) A representative HRTEM image to show a coherent Al_3Zr precipitate. Corresponding GPA results demonstrating the local ε_{xx} strain field (b), ε_{yy} strain field (c), and ε_{xy} strain field (d). (e) is a picture overlapping the GPA ε_{xx} strain field with the HRTEM image, where the Al_3Zr precipitate/matrix interface is highlighted by a loop line. (f) shows the distribution of ε_{xx} in a profile that is measured along a segment (as marked by green box in (e)) of the Al_3Zr precipitate/matrix interface.

3.3.2. The Hot-Deformed Alloys

When the hot-deformed alloys are subjected to artificial aging, the variation in hardness with aging time is quite different from that in the deformation-free counterparts; see Figure 11a. All the three alloys show significantly reduced hardness within 12 h when aged at 350 °C. Thereafter, the hardness reaches a plateau that remains almost stable. Two reasons are responsible for the hardness drop at the initial aging stage: one is the grain coarsening and the other is dislocation annihilation. Figure 12 typically shows a representative TEM image of grains in the hot-deformed AlZrMn-1 alloy after aging for 40 h and corresponding grain size distribution. The average grain size increases to about 1.1 μm , from 0.5 μm before aging, whereas in the AlZrMn-2 alloy after aging, no apparent grain coarsening is

observed, mainly due to a strong pinning effect of the intergranular nanoprecipitates on the grain boundary movement. The initial hardness drop in the AlZrMn-2 alloy seems to be mostly caused by the dislocation annihilation, whereas in the AlZr and AlZrMn-1 alloys, the hardness drop is induced by the combination of grain coarsening and dislocation annihilation. After the hardness drop, grains and dislocations become relatively stable, which is represented by the hardness plateau.

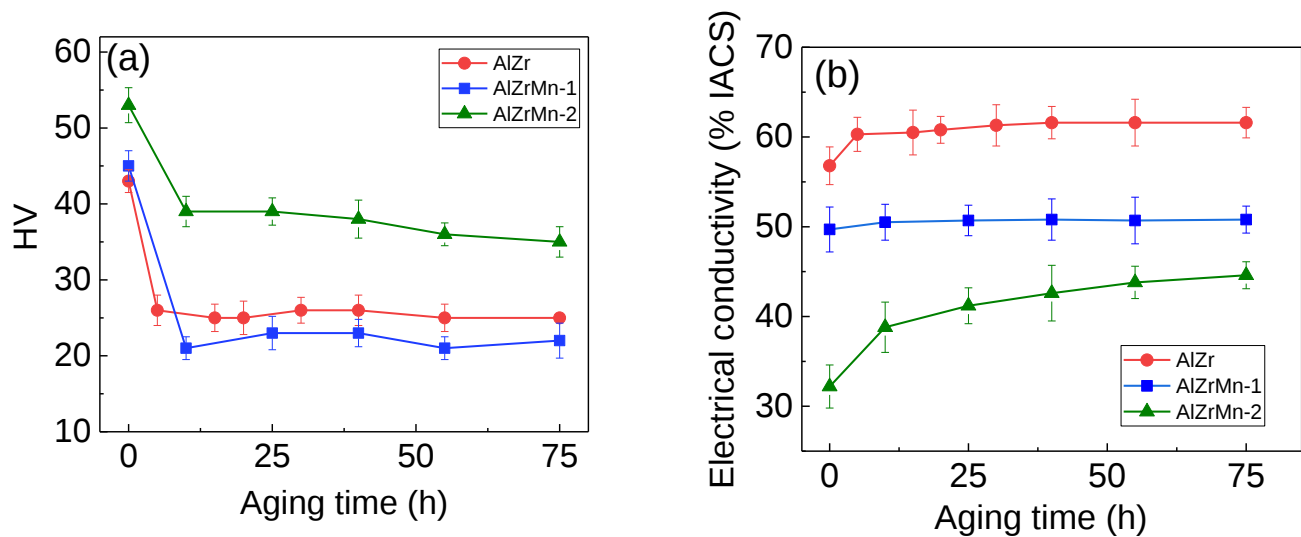


Figure 11. Variation in hardness (a) and electrical conductivity (b) with aging time of the three hot-deformed alloys when aged at 350 °C.

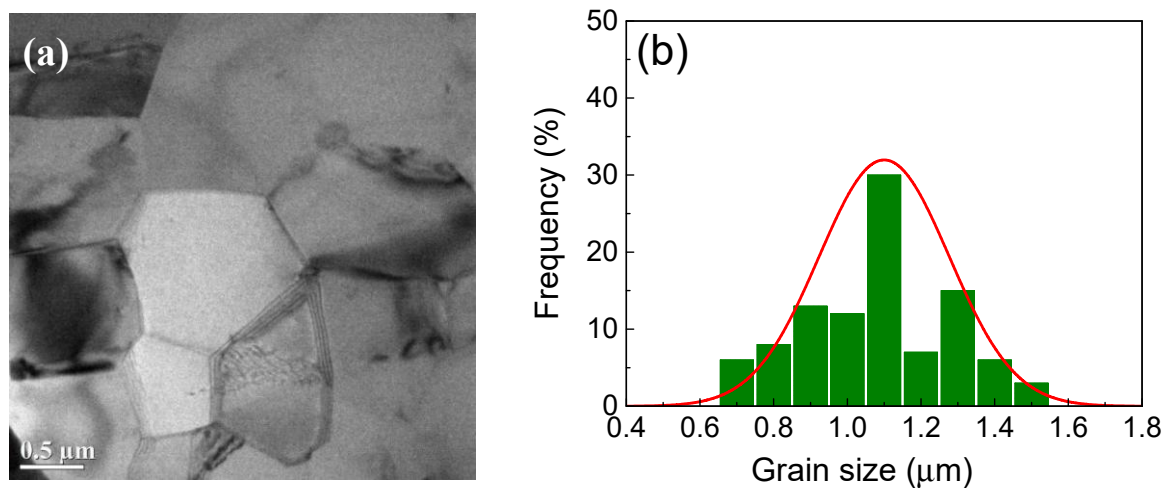


Figure 12. A representative TEM image (a) showing grains in the hot-deformed AlZrMn-1 alloy after aging for 40 h and corresponding grain size distribution (b).

The hot-deformed AlZr and AlZrMn-1 alloys both show that electrical conductivity is insensitive to aging time, similar to that in their cast counterparts; see Figure 11b in comparison with Figure 9b. However, the hot-deformed AlZrMn-2 alloy shows a difference, namely, that the electrical conductivity increases gradually within the whole aging time range studied. This aging time dependence of electrical conductivity can be explained as follows: since the ultrafine grains in the AlZrMn-2 alloy are retained during the aging treatment, the preferential segregation of solute atoms at high-energy grain boundaries is always in progress. The solute atoms dissolved in the Al matrix and their scattering to electron motions decrease gradually [38], which leads to a continuous increase in electrical conductivity.

4. Discussion

4.1. Strengthening Mechanisms of the Alloys with and without Deformation

4.1.1. The Alloys without Deformation

Quantitatively, the increase in strength (σ_{ss}^{Mn}) contributed by the Mn solid solution strengthening is expressed by [39]:

$$\sigma_{ss}^{Mn} = k_{Mn} C_{Mn}^{2/3}, \quad (1)$$

where C_{Mn} is the Mn concentration dissolved in the matrix (in wt.%) and k_{Mn} is a scaling factor ($\sim 32.0 \text{ MPa (wt.\%)}^{-2/3}$ [40]). The difference in Mn concentration between the AlZrMn-1 and AlZrMn-2 alloys is about 0.72 wt.%, Equation (1) estimates a difference in σ_{ss}^{Mn} , $\Delta \sigma_{ss}^{Mn}$, to be $\sim 25.0 \text{ MPa}$. This value agrees well with the difference in measured hardness between the AlZrMn-1 and AlZrMn-2 alloys, especially at the initial aging stage, considering the strength–hardness relationship of $\sigma \approx 3 \times Hv$ generally recognized in bulk Al alloys [4,6]. Regarding the Zr cluster strengthening in the AlZrMn-2 alloy at the prolonged aging time, a quantitative expression proposed by Marceau et al. [41] is simply used here:

$$\sigma_{cluster}^{Zr} = \frac{1.8MT}{b \cdot L_{cluster}^{Zr}} \cos^{3/2} \left(\frac{\phi_{cluster}^{Zr}}{2} \right) \left(1 - \frac{\cos^5(\phi_{cluster}^{Zr}/2)}{6} \right), \quad (2)$$

$$L_{cluster}^{Zr} = \bar{r}_{Zr} \cdot (2 \cdot \pi / 3 \cdot f_{Zr})^{1/2}, \quad (3)$$

where M is the Taylor factor (~ 3.1 [3]); $\bar{r}_{Zr}$ and f_{Zr} are the average Guinier radius and volume fraction of the Zr clusters, respectively, which are determined from the APT results; $L_{cluster}^{Zr}$ is the average spacing of Zr clusters on the glide plane; $\phi_{cluster}^{Zr}$ is the dislocation breaking angle for shearing of the Zr clusters; and T is the line tension, which is equal to $0.5 \cdot G \cdot b^2$ [7]; G and b are the shear modulus (28 GPa [7]) and Burgers vector (0.286 nm [7]) of Al. Using the APT-derived $\bar{r}_{Zr}$ and f_{Zr} (0.5 nm and 1.2 vol.%, respectively), the Zr cluster strengthening, evaluated to be $\sim 36 \text{ MPa}$, contributed to the strength. This evaluation is in reasonable agreement with the hardness results in AlZrMn-2 alloy, where the 100 h-aged sample has a hardness 10 HV more than the initially aged sample.

4.1.2. The Alloys with Deformation

As the hardness drop in the AlZrMn-2 alloy is merely related to the dislocation annihilation, it is possible to quantify the dislocation strengthening by following the expression below [42]:

$$\sigma_d = M\alpha Gb\sqrt{\rho}, \quad (4)$$

where σ_d is the dislocation strengthening contribution; α is a constant with the value of approximately 0.14; ρ is the dislocation density; and M , G , and b have been defined above. The hardness drop (or strength drop $\Delta \sigma_d$) in the AlZrMn-2 alloy is approximately written by:

$$\Delta \sigma_d = M\alpha Gb \left(\sqrt{\rho_i} - \sqrt{\rho_{aged}} \right), \quad (5)$$

where ρ_i and ρ_{aged} are the dislocation density before and after aging, respectively. Using the experimentally measured values of $\rho_i \sim 5.3 \times 10^{14} \text{ m}^{-2}$ and $\rho_{aged} \sim 9.3 \times 10^{13} \text{ m}^{-2}$ (aged for 40 h), $\Delta \sigma_d$ is calculated to be about 45 MPa. The hardness drop is measured to be about $HV = 17$, corresponding to a drop in strength of about 52 MPa. The calculation is basically consistent with the measurement.

4.2. Coupling Effect of the Mn Addition with Deformation

The influence of Mn addition on grain evolution, aging precipitation, and mechanical/electrical properties of undeformed vs. hot-deformed Al-Zr alloys provides a possibility to understand the coupling effect of Mn addition with deformation. Comparing Figure 11

with Figure 9, and also referring to Figure 13 showing the summary of hardness vs. electrical conductivity of the alloys aged for 75 h, one can clearly see the following: (i) The AlZrMn-1 alloy shows hardness and electrical conductivity that are almost unchanged with prolonging aging time, in both hot-deformed and undeformed cases. This hints that solute atoms, including Zr and Mn, are predominantly dissolved in the Al matrix. No precipitation leads to the aging-time-independent hardness and electrical properties. (ii) The hot-deformed AlZrMn-1 alloy after aging has hardness and electrical conductivity that are basically the same as those of the undeformed alloy. Considering their grain size and dislocation density are much different, it is concluded that the grain size and dislocations make much smaller contributions than the solute atoms. (iii) The hot-deformed AlZr alloy after aging displays hardness and electrical conductivity that are both slightly increased when compared with its undeformed counterpart. This is mainly attributed to the solute segregation or precipitation at grain boundaries (rather than within grain interior), which reduces the scattering effect on electron motion and the refined grain size, as well as increased dislocations that contribute to strength. (iv) Deformation yields the best benefit in the AlZrMn-2 alloy. After aging, this alloy with deformation achieves an increase of above 30% in hardness, and simultaneously an increase of above 40% in electrical conductivity, compared to its undeformed counterpart. A positive coupling between the Mn microalloying and deformation is reached as the Mn addition increased to 0.88 wt.%. Compared with the commercial Al-Zr wires (ultrafine-grained materials with electrical conductivity of 55~60% IACS and ultimate tensile strength of 160~230 MPa), the present AlZr alloys, either hot-rolled or rolling-free, exhibit comparable or even higher electrical conductivity but inferior strength (or hardness). The results revealed in Figure 13 signify that, using Mn alloying in combination with severe plastic deformation, it is possible to achieve an optimized electrical conductivity–strength/hardness synergy that is superior to that of commercial Al-Zr wires.

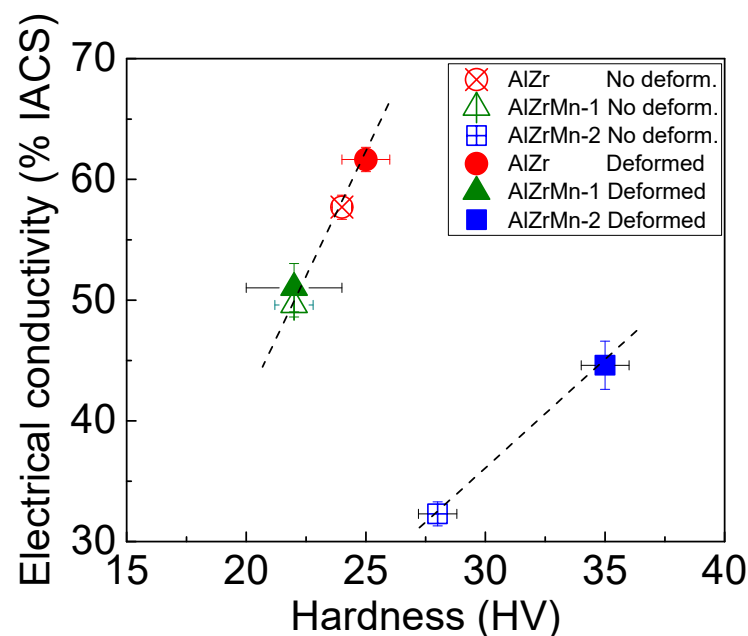


Figure 13. Hardness vs. electrical conductivity: comparison among the alloys aged at 350 °C for 75 h. The lines are guide to the eyes.

5. Conclusions

- (1) The addition of Mn to Al-Zr alloys significantly reduces the grain size in the cast condition while having a negligible grain-refining effect in the hot-rolling condition. The Mn addition completely suppresses the Al_3Zr precipitation, but promotes the intergranular Al_2Zr precipitation and Mn-rich particle precipitation in the deformation case.

- (2) A 0.16 wt.% Mn addition causes an apparent decrease in both hardness and electrical conductivity in the Al-Zr alloy, in both hot-deformed and undeformed cases. With a higher 0.88 wt.% Mn addition, however, the hardness of Al-Zr alloy is significantly increased, by over 40%.
- (3) A positive coupling of Mn addition and deformation is only realized in the case of higher Mn added. With no Mn addition, deformation slightly increases both the hardness and the electrical conductivity in the Al-Zr alloy.

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