Article

Strengthening of Nanocrystalline Al with Al$_3$Zr Core-Shell Structure

Dora Janovszky

MTA-ME Materials Science Research Group, H-3515 Miskolc-Egyetemvaros, Hungary; fekd@uni-miskolc.hu

Received: 29 July 2020; Accepted: 20 August 2020; Published: 24 August 2020

Abstract: High-density Al-based composites reinforced with ten-wt.% recycled nanocrystalline CuZrAgAl particles have been fabricated by mechanical milling, cold- and hot-pressing. The microstructures, phase transformations, and mechanical properties of the mixed powder and sintered samples were investigated. After milling in a ball mill for 30 h, the microhardness of the mixed powder increases to $301 \pm 31 \text{HV}_{0.01}$ and $222 \pm 10 \text{HV}_{0.01}$ without and with ethanol milling, respectively. On account of the interdiffusion, the melting temperature of mixed powder reduces to $574 \pm 5.0 \, ^\circ\text{C}$ and $627.5 \pm 6.5 \, ^\circ\text{C}$ after 30 h milling. The study showed that the reinforcing particles are homogeneously distributed in the sintered nanocrystalline Al-based composites. During the hot-pressing, a shell zone forms at the interface of reinforcing particles during hot pressing after high energy milling with a minimum of ten hours milling time. This shell zone consists of Al$_3$Zr (D023) phase. The coarsening resistant core-shell structure and grain refinement greatly improve mechanical properties. The compression strength at room temperature varies between 650 and 800 MPa at room temperature and is 380 MPa at 400 $^\circ\text{C}$ for the composite containing ten-wt.% of the Cu-Zr-based amorphous-nanocrystalline phases. The Brinell hardness of the sintered composite is 329 HB.

Keywords: mechanical alloying; high energy milling; core-shell structure; Al-based composite; Cu-Zr-based nanocrystalline reinforcement

1. Introduction

The development of high-strength Al-based composites is proceeding with great intensity worldwide today. A variety of reinforcing phases are used in Al composites used at room temperature: ceramic particles [1,2], carbon nanotubes [3]. Intermetallic precipitates in the matrix are more favorable for high-strength Al-based alloys at elevated temperatures [4–6]. Group 3 (Sc [7], Y [8], Er [5]) and Group 4 (Ti [9,10], Zr [11,12]) transition metals are promising alloying elements for heat resistant Al alloys. Zr seems to be the most promising alloying element for high temperature use [11,13–15]. However, Zr is a very expensive raw material. The solid solubility of this transition element in Al is very limited and the diffusion is also very slow in the Al matrix. In the case of Zr, the maximum solubility limit of Zr in Al at 656 $^\circ\text{C}$ is only 0.07 at.% [16], and this limit reduces in proportion to the decrease in temperature. This element creates intermetallic phases with Al, which precipitate from the supersaturated solid solution of zirconium in aluminum. The tetragonal Al$_3$Zr phases are thermodynamically stable and provide precipitation hardening effect even after long times without decomposition up to high temperature. Although the diffusion is slow, the growth of precipitations over time is a well-known phenomenon due to Wilhelm Ostwald [17], who has proved that the total energy of the two-phase system can be decreased via an increase in the size scale of the second phase area.

Mechanical alloying (MA) is a method to produce composite metal powders with a controlled fine microstructure during high-energy ball milling. The solid solubility of Zr in Al is limited, it can be significantly increased by mechanical alloying methods, and further heat treatment can lead to precipitation hardening. Owing to the input energy of the milling process, not only the fragmentation
takes place, but mechanochemical processes can occur [18] as well. This specific energy that is transferred to the powder is influenced by the milling time, rotation speed, ball-to-powder ratio, and the filling ratio of the grinding vial. A process control agent (PCA) has a significant effect on the milling process, and it influences the interface reaction and mechanical properties of the material being milled [19,20].

Al alloy-based composites reinforced with Al$_3$Zr particles have already been manufactured by powder metallurgy using various initial materials [11,12,21]. The core-shell structure did not form in the published composites.

Cu-Zr- and Zr-based amorphous alloys have been extensively studied recently owing to ultra-high-strength and high elastic strain, high corrosion resistance [22–25]. More and more articles on the use of Cu-Zr-based amorphous and high entropy materials containing Zr as reinforcement phases in the Al matrix have been published since the 2000s [26–29]. In some cases, the Cu-Zr-based amorphous content remained amorphous even after sintering [26], while in other cases it crystallized [24]. Dutkiewicz et al. [26] prepared nanocrystalline Al matrix composites strengthened with 20–40 wt.% amorphous Cu$_{43}$Zr$_{43}$Ag$_7$Al$_7$ powder by short mechanical milling (0.5 h) and hot pressing under vacuum at the temperature of 400 °C and the pressure of 600 MPa applied for 10 min. They reached a compression strength of 530 MPa for 20 wt.% of the amorphous phase and 560 MPa for the 40 wt.% content. The Al$_3$Zr shell did not develop at the boundary of the nanocrystalline Al matrix and amorphous particles. L. Zhang et al. [24] used a ten vol% CuZrAl amorphous powder as reinforcing particle, which crystallized to Al$_3$Zr and Cu$_2$Al phases in its full volume in the nanocrystalline Al matrix during spark plasma sintering, the compression fracture strength is 408 MPa at room temperature.

From the year 2000, more than 2100 articles were published in Scopus on the subject Cu-Zr- and Zr-based bulk metallic glasses (BMGs). The high-volume of amorphous materials will certainly be utilized worldwide. Recycling of the Cu-Zr- and Zr-based bulk metallic glasses and devitrified alloys due to mechanical stress or heat treatment is also expected to be required in the future. However, its reuse through the casting process is expensive due to the strict purity requirements. The high energy milling process could be an alternative technical route for the reuse of these expensively produced up-cycled materials.

In this work, the goal was to present that it is a possibility to realize the recycling of a Cu-Zr-based nanocrystalline alloy with elevating the mechanical strength parameters of aluminum. The created microstructural core-shell structure provides a new opportunity for the strengthening effect of the Al$_3$Zr phase. A dedicated industrial application could be the aeronautical or airplane industry where the Al strength mainly important (joinings and wing cover construction). The homogenous and continuous distribution of the reinforcement particles is ensured by the powder metallurgy route. Nanocrystalline-amorphous Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ (at.%) powder was chosen as a reinforcement. A weight fraction of ten percent of the CuZrAgAl powders was selected in this study for test measurements.

2. Materials and Methods

The aluminum powder of size 4–51 µm and purity 99.5% was supplied by Alfa Aesar, Haverhill, MA, USA. The melting temperature from differential scanning calorimetry (DSC, Netzsch Ltd., Selb, Germany) tests was found to be 657.7 °C. The master alloy ingots with the atomic composition Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ were prepared by arc-melting from a mixture of pure metals under a purified argon atmosphere (minimum 99.9 wt.%) with a Ti-getter. The ingots were re-melted by induction melting in a quartz crucible under the argon atmosphere. The cast rod was prepared by centrifugal casting with 30 mm in length and 3 mm in diameter under purified argon atmosphere. Centrifugal cast rods were ground after compression test and fractionated to a particle size below 320 µm for ball-milling. The mode of the Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ particle size distribution by laser diffraction particle size analyzer is 21.3 µm. The amorphous content of Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ powder is 12 wt.%. A more detailed description of the materials can be found in the previously published work [30].
Al powder with 10 wt.% Cu₃₆Zr₄₈Ag₈Al₈ particles was milled at room temperature in a Pulverisette 5 high-energy ball-mill (Fritsch, Idar-Oberstein, Germany) at 200 rpm under a protective argon atmosphere using a stainless-steel grinding bowl and steel balls of different diameters, which were used together. The diameters of the hardened balls were 20, 12, and 10 mm. The weight ratio of the ball to the powder (BPR) was 10:1. The maximal milling process lasted 30 h to assure that the milling has proceeded short enough to avoid excessive contamination (Fe) from the milling media. Two series of experiments were employed to make the nanocrystalline composite powders.

A1 experiment: No process control agent was used during the milling process.

A2 experiment: 1 cm³ was used as a process control agent to reduce adhesion to the surface of the crucible and balls.

In order to avoid overheating in the vials, the milling procedure was interrupted every 60 min and halted for 60 min in both experiments. To study the effect of the milling time, samples were taken after 15 h by interrupting the milling cycle. The microstructure of the powders was examined by a Hitachi S-4800 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) equipped with a BRUKER AXS type energy-dispersive X-ray spectrometer (EDS). Cs-corrected S/TEM Themis transmission electron microscope (ThermoFisher, Hillsboro, MA, USA) was used to investigate the core-shell structure. The particle size distribution of the ground material was determined by a Horiba LA-950 V2 type laser diffraction particle size analyzer (Horiba Ltd., Kyoto, Japan) in distilled water.

Thermal analysis was performed in a Netzsch STA 449 F1 Jupiter Simultaneous TG-DTA/DSC (Netzsch Ltd., Selb, Germany) apparatus at a heating rate of 0.66 °C/s. The samples for these measurements were kept in closed Al₂O₃ crucibles and were under a continuous purified Ar flow.

X-ray diffraction (XRD) phase analysis was performed by a Bruker D8 Advance diffractometer (XRD, Bruker Gmbh, Berlin, Germany) using Cu Kα radiation (40 kV, 40 mA), in parallel beam geometry obtained with a Göbel mirror equipped with a Vantec-1 position sensitive detector (1° window opening), measured in the 2–100° (2θ) angular range, at a speed of 0.007° (2θ)/29 s. The specimens were rotated in the sample plane during the measurement to obtain data from the whole surface and to reduce in-plane preferred orientation effects. The crystalline fraction was determined by XRD analysis using peak area determination in TOPAS4 (amorphous hump method). Quantitative results were obtained by the combined use of Rietveld refinement and peak area calculation (Pawley fit). Small amount phases were identified from the peaks on the difference curve of the Rietveld refinement.

The MA powders produced experimentally at 30 h were consolidated into bulk compacts. Samples of 8 mm in diameter and height of ~12 mm were cold compacted in a steel die with 1.4 GPa and after all samples were subjected to hot compaction, followed by air-cooling. The hot compaction was carried out at pressures of 0.4 GPa and temperature of 400 °C for 0.5 h in a pressing die filled with alumina. To clarify whether the layer around the reinforcement is formed only due to hot-pressing, the powders were milled with ethanol for 0.5 h (that is, only preparation of homogeneous mixture) and for 10 h. Compression tests were carried out by an Instron 5982 electromechanical universal material testing equipment with a strain rate of 1 × 10⁻²¹/s at room temperature and 400 °C as well. The compression tests were continued until the first crack appeared. The microhardness measurements were performed by Instron Tukon 2100B equipment (Instron, Grove, PA, USA), applying a load of 10 g for 15 s for milled powders. The powder samples were embedded in acrylic resin and polished to produce a surface suitable for micro indenting. Only symmetric indenting marks were used to calculate HV₀.₀₁ values to avoid misleading results from the indenting of aggregates. Brinell hardness measurements were performed by a Wolpert UH 930 equipment (Instron, Grove, PA, USA) applying 1 mm diameter ball and a load of 187.5 kg and 31.25 kg for 15 s for hot-pressed samples. The mean and standard deviation was calculated from 10 measurements in the case of Vickers hardness and 5 measurements in the case of Brinell hardness.
3. Results and Discussion

3.1. Morphology of the Milled Al-CuZrAgAl Composite Powder Particles

The morphological variations of Al-CuZrAgAl composite powder during the milling process is investigated by SEM, shown in Figure 1. The dark-grey particles in all the backscattered SEM images correspond to Al particles (Figure 1). Whereas the brighter objects represent Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ particles. It has been observed that without a PCA, a more spherical composite powder can be obtained after 15 h and 30 h milling time, thanks to the fact that there is no obstacle to cold-welding (Figure 1a–d). Al particles are stuck to and surround the reinforcing particles. The presence of ethanol as a PCA modified the surface properties of the milling material, diminished the cold-welding between particles, and the particle size reduced faster (Figure 1e,f). Many of the Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy particles larger than a few microns are only partially connected with Al particles after 15 h milling (Figure 1e,f). Al particles consisted of cold-welded thin sheets due to the shearing effect of the milling media.

![Figure 1](image1.png)

**Figure 1.** Backscattered SEM images of as-milled composite powders after 15 h (a,b,e,f) and 30 h (c,d,g,h) milled without (a–d) and with ethanol (e–h).

The mode of the size distribution curve of the initial Al powder and the reinforcing material is 14.2 μm and 21.3 μm, respectively. As shown in Figure 2a without a PCA, the mode of composite powder size distribution increased substantially to 63 μm after 15 h of milling time. Al particles are stuck to and surround the reinforcing particles. By contrast, when using ethanol as a PCA, the mode decreased to 10.8 μm after 15 h of milling time. The particle size distribution is symmetric after 30 h milling using ethanol (Figure 2b). Ninety percent of the particle based on the volume distribution is below 94 μm without using ethanol and 20 μm in the case of using ethanol.

![Figure 2](image2.png)

**Figure 2.** Particle size distributions of milled powders with different milling parameter: (a) milled without ethanol, (b) milled with 1 cm$^3$ ethanol.
3.2. Microstructure of the Al-Based Composite Powder Particles

New phases have developed due to the mechanical alloying of the energy introduced by milling. The phase transformations were monitored by X-ray examination. According to Rietveld refinement and Pawley fit peak area calculation, the formed phases are influenced by the amount of ethanol and milling time during mechanical alloying (Figure 3 and Table 1).

![Figure 3](image)

**Figure 3.** X-ray diffraction (XRD) patterns of the composite powders after 30 h of milling time: (a) milling without ethanol; (b) milling with 1 cm$^3$ ethanol.

**Table 1.** Features of the amorphous phase and the crystallites based on the X-ray examination of raw and mixed powders.

| Phases                | Experiment | A1 BPR:10/1 | A2 BPR:10/1 | Sintered |
|-----------------------|------------|-------------|-------------|----------|
|                       | Volume of Ethanol | 0 | 15 | 30 | 15 | 30 | |
| Al Fm$_3$m             | Milling Time, h | wt.% | 90.00 | 82.24 | 83.84 | 83.4 | 87.68 | 75.5 |
| CuZr$_2$ I4/mmm        |            | wt.% | 7.06 | 8.61 | 7.46 | - | 0.28 | 3.8 |
| CuZr(Ag, Al) Fm$_3$m   |            | wt.% | 0.74 | 1.92 | 2.10 | 0.30 | 0.34 | - |
| CuZr Fm$_3$m           |            | wt.% | - | - | - | 0.3 | 0.35 | 0.6 |
| Al$_{0.8}$Ag$_{3.2}$ Fm$_3$m |            | wt.% | 0.85 | 5.17 | 4.93 | 3.7 | 0.35 | 2.4 |
| Al$_2$Zr I4/mmm        |            | wt.% | - | - | - | 1.8 | - | 2.4 |
| AgO                   |            | wt.% | - | - | - | 0.1 | - | 0.8 |
| Al$_2$FeO$_4$ I4_1/amd |            | wt.% | - | - | - | 0.1 | - | - |
| γ-Al$_2$O$_3$ Fd$_3$m  |            | wt.% | - | - | - | 0.3 | - | 1.2 |
| α-Iron Im$_3$m         |            | wt.% | 0.15 | 2.07 | 1.67 | - | - | - |
| CuAl$_2$              |            | wt.% | - | - | - | - | 2.3 | - |
| amorphous              |            | wt.% | 0.12 | - | - | 10.00 | 11.00 | 11.0 |
| Rwp                   |            | - | - | - | 39.07 | - | 13.49 | 20.07 |
| GOF                   |            | - | - | - | 3.33 | - | 1.15 | 1.07 |

In the case of without ethanol milling, the amorphous content of nanocrystalline-amorphous Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ alloy transforms into nanocrystalline phases after 15 h milling time (Table 1) and its presence cannot be detected even after 30 h. The amount of the CuZr$_2$ phase is roughly constant during the milling process (Table 1).
The weight fraction of Al decreases from 90 wt.% to 82 wt.% and 84 wt.% after 15 and 30 h milling, respectively. Naturally, this is only possible if the amount of Al integrates into the crystalline phases. Indeed, the quantity of the aluminum-containing phases (the Al$_{0.8}$Ag$_{3.2}$ and CuZr(Ag,Al) strongly increases after 15 h milling time (Table 1). There is no significant difference between the weight fraction of phases after 15 and 30 h of milling. The maximal content of α-Fe contamination from milling medium that evolved in our experiments was approximately 2 wt.%, according to XRD.

Using ethanol, four new phases appear after ball milling process, which lasted 15 h (Table 1). Table 1 clearly shows the Al phase is only 83.4 wt.% after 15 h milling. Dislocations are able to create channels to diffuse the atoms and thus an intensive mechanochemical process could start. Owing to the development of new active surfaces and the dislocations created by the impact of the milling balls, the Al atoms react with Zr and a new phase—Al$_3$Zr—forms “in-situ”. Furthermore, a small amount (0.3 wt.%) of the γ-Al$_2$O$_3$ phase is detected. Impure Fe atoms also react with this Al$_2$O$_3$ phase and form an Al$_2$FeO$_4$ complex phase. The quantity of the alloyed CuZr(Ag, Al) phase and the Al$_{0.8}$Ag$_{3.2}$ phase decreases, also a small amount of new CuZr and AgO phases has appeared. Summarizing the phase transformation during the milling process, it can be stated that an intensive mechanochemical process takes place during high-energy milling when using ethanol.

The thin oxide layer with nanometer-size normally existing on Cu-Zr-based alloy surface [31,32] has such a strong effect that prevents further amorphization, despite the high input energy during the milling process. The effect of ethanol on the creation of the amorphous structure has been investigated in the previous study [30]. Using 1 cm$^3$ ethanol as a PCA, the “X-ray amorphous” fraction based on XRD increases up to 10 wt.% after 15 h milling. The reason for this, on the one hand, the crystalline phases of CuZrAgAl particles have become amorphous structure again, and, on the other hand, the XRD diffraction detects very small nanograin (<5 nm) as an amorphous phase. The maximum position of initial Cu$_{36}$Zr$_{48}$Ag$_8$Al$_8$ amorphous halo is 0.2182 nm, but this position of the amorphous structure formed during milling is 0.2848 nm. This proves that the composition of the “X-ray amorphous” phase is changed.

With an increase in milling time of up to 30 h, the newly developed phases disappear, except the CuZr phase. The CuZr$_2$ phase appears again appears in very small amounts (Figure 3 and Table 1). This means that a new stage developed in the mechanochemical process. The weight fraction of pure the Al phase increases to almost its initial value after 30 h milling time. The weight fraction of the Al$_{0.8}$Ag$_{3.2}$ phase decreases to one-tenth. The pure α-Fe contamination content is not detectable after both 15 and 30 h milling time. The weight fraction of the Zr content phases decreased from 7.8 to 1 wt.%, so the amorphous structure and the Al matrix are further enriched with Zr. The maximum position of the amorphous halo continues to increase up to 0.3203 nm.

The crystallite size of the crystalline phases is calculated by the Rietveld method. The crystallite size of the initial Al powder is 635 ± 199.4 nm decreases significantly after 15 h milling time during both milling processes: 90.0 ± 28.3 nm and 82 ± 26.2 nm without and with ethanol milling, respectively. The effect of ethanol is noticeable after 30 h of milling, the crystallite size is almost half the size that of milling without ethanol (Figure 4). The crystallite size of the phases in the reinforcing particles is smaller than 10 nm after 30 h in the case of both milling, except the CuZr phase.
3.3. Thermal Analysis of the Al-Based Composite Powder Material

Thermal analysis of the composite powder provided information about the thermal properties of the amorphous structure and the alloying of the Al matrix. The melting temperature of the Al matrix decreases to 575.6 and 633.0 °C after 30 h milling time based on the DSC measurements, which confirms an intensive interdiffusion between Al and the reinforcing particles (Figure 5). The amorphous fraction is 15 wt.% after 30 h of milling. The peak position of crystallization changed from 512 °C to 495.5 °C after 30 h milling, which means that the composition of the amorphous content changed (Figure 5b). The thermal properties of the amorphous phase are in accordance with the XRD results.

Summarizing the effect of different milling parameters, it can be stated that the particle size and the crystallite size are the finest after 30 h of milling using 1 cm$^3$ ethanol. More intense mechanical alloying occurs without ethanol. The use of ethanol, in turn, promoted an increase in the “X-ray amorphous” content.

![Figure 4](image-url)

**Figure 4.** The crystallite size of the Al matrix in composite powders milled with different milling times and different amounts of ethanol.

3.4. Microstructure of the Hot-Pressed Composites

The microstructure of the hot-pressed sample after the compression test is investigated by SEM, the results are shown in Figure 6. The reinforcing particles are homogeneously distributed in the Al matrix. The porosity of all hot-pressed samples is below 5% based on density measurement. Although the powders milled for 30 h differ in several properties a micron-sized shell was observed in each sample regardless of the PCA in all the hot-pressed samples milled for 30 h (Figures 6 and 7). Energy dispersive X-ray (SEM-EDX) maps feature the pure Al matrix around the particle in red (Figure 7). Ag (blue) is particularly concentrated in the reinforcing particle. Cu (yellow) can also be detected.
outside the shell. Observing the line scan (line marked with green color in Figure 6b,c), it can be stated that the shell is mainly composed of Zr and Al and this shell contains a few Cu. The SEM-EDX line scan shows that the atomic ratio of Al-to-Zr is approximately 3:1, which corresponds to the Al$_3$Zr intermetallic phase. Although the diffusion of Cu and Ag into the Al matrix could be expected based on the diffusion coefficients, in contrast, the interdiffusion between Zr and Al dominates.

**Figure 6.** Backscattered SEM image of the fracture surface after compression test (a) and the magnified part marked with a square (b) with the results of line scan of Al matrix reinforced with Cu$_{36}$Zr$_{48}$Ag$_{8}$Al$_{8}$ particle (A1 experiment-milling without ethanol) (c).

**Figure 7.** Microstructure of the hot-pressed composite. Backscattered SEM micrograph and the results of SEM-EDX mapping Al matrix reinforced with CuZrAgAl particles (A2 experiment-30 h milled with 1 cm$^3$ ethanol).
The interface layer is continuous between the Al matrix and the Al-Zr shell. This shell-structure, which developed owing to the interdiffusion, can indicate that a very strong interfacial bonding formed between the reinforcement and the matrix.

To clarify whether this layer is formed only due to hot-pressing, the powders were milled for 0.5 h (like Dutkiewicz et al. [26]) and 10 h as was mentioned in the Materials and Methods section. A2 experiment process was chosen because the milling with the addition of ethanol is less effective in the mechanical alloying. After the cold- and hot-pressing with the same conditions of these composite powders, the microstructure of the bulk samples is also investigated by SEM. The near-spherical reinforcing particle milled 0.5 h is embedded in the Al matrix (Figure 8).

Figure 8. Microstructure of the hot-pressed composite, in which the initial powders were only mixed. Backscattered SEM micrograph and the results of line scan of Al matrix reinforced with Cu36Zr48Ag8Al8 particle (0.5 h milled without ethanol).

Around the CuZrAgAl particles, the micron-sized shells are not visible and the result of the line scan does not show a diffusion layer around the reinforcing particle. In the case when the milling time is 10 h, then the micron-sized shell has developed based on the SEM investigation. Due to the high energy milling, the vacancy concentration is high, and a defect lattice would account for the unusually large diffusion rates observed. Therefore, the combination of prolonged milling process (at least 10 h in the case of the examined experiments), the temperature, and the pressure are necessary for the formation of the micron-sized shells.

Al3Zr phase was detectable in all samples according to the X-ray measurements of the hot-pressed samples after 30 h of milling (Figure 9 and Table 1). The lattice parameters of Al3Zr are a = 0.400745 nm and c = 1.72891 nm. Compared to the values found in the literature, these values are in harmony with Kematick and Frantzen’s experimental results [33]. Based on these parameters, this phase is a fully relaxed (D023) Al3Zr phase, which is the most stable Al3Zr phase. This result proves that the shell may be the Al3Zr phase. A new CuAl2 phase also formed during the hot-pressing (Figure 9 and Table 1). The crystallite size of the phases in the sintered sample remained nearly the same during the hot-pressing. The amount of “X-ray amorphous content” did not change during the hot-pressing. The maximum position of the amorphous halo increased from 0.3203 to 0.3238 nm, that is, the composition of the amorphous content remained nearly the same.

Figure 10 displays a bright-field transmission electron microscopy (BF TEM) image of the hot-pressed composites. The shell structure around the reinforcing particle appears clearly in the BF TEM image (Figure 10a-white arrows indicate). The reinforcing particle consists of crystals with a size of 3–9 nm based on the high-resolution transmission electron microscopy (HRTEM) image (Figure 10b).
The results of line scan of Al matrix reinforced with phases. This intermetallic phase has high strength and can enhance the interface bonding between the reinforcing particle and matrix.

Figure 9. XRD pattern of the hot-pressed sample (milling without ethanol and 30 h of milling time before the hot pressing).

Figure 10. TEM microstructure of the hot-pressed composites: BF TEM image of the composite. (a) HRTEM image of the reinforcing particle; (b) HAADF image and STEM-EDX mapping of the composite (c).
The Al content of this particle is higher than in the initial state, increased from 8 at.% to 16.6 at.% to 16.6% based on scanning transmission electron microscope with Energy-dispersive X-ray spectroscopy (STEM-EDX) analysis. The high-angle annular dark-field image (HAADF) shows that the shell is composed of particles of 20–300 nm in size (Figure 10c). The composition of the layer is 73.67 ± 18.82 Al, 25.71 ± 5.56 Zr, 0.57 ± 0.12 Cu and 0.05 ± 0.01 Ag (at.%) that is, indeed, the interdiffusion of Al and Zr occurred primarily. STEM-EDX analysis confirmed that the layer atomic ratio of Al-to-Zr is approximately 3:1. The selected area diffraction (SAED) pattern was recorded that the reflections of Al also appeared in the diffraction in order to accurate calibration (Figure 11). Based on the SAED pattern, the shell consists of Al₃Zr particles with no detectable presence of any other phase. This intermetallic phase has high strength and can enhance the interface bonding between the reinforcing particle and matrix.

Considering the thermodynamic aspects of the research, the heat of the mixings between Al and Ag, Cu, Zr are −4, −1 and −44 kJ/mol, respectively. Between Al and Zr there is the strongest tendency to form intermetallic phases, ten stable intermetallic phases are in the Al-Zr system. Amongst these equilibrium phases, Zr₂Al₃ has the most negative free energy of formation. Calculated data using Kaptay equation [34] of the enthalpy of formation for the Al₃Zr and Zr₂Al₃ intermetallic compound is −41.389 kJ/mol and −44.909 kJ/mol, respectively [35]. Therefore, thermodynamically it is expected to form this phase at the Zr–Al interface owing to the interdiffusion during the hot-compaction. But the nucleation and growth of a phase are influenced not only by energy but also by kinetics. Laik et al. found that Zr₂Al₃ layer forms at the Zr/Zr₁₂Al₃ interface above 600 °C [36]. Ag atoms have nearly the same radius as Al, and Zr atom has the largest atomic radius in this system (Table 2). The concentration and the diffusion coefficient together influence the diffusion flux according to Fick’s law in microcrystalline alloys. The diffusion coefficient in Fick’s first and second law determines the rate of the diffusion:

\[ D = D_0 \exp \left( -\frac{E}{RT} \right) \]  

where \( D \) diffusion coefficient [m²/s], \( D_0 \) pre-exponential [m²/s], \( E \) activation energy [J/mol or eV/atom], \( R \) gas constant [8.314 J/molK], \( T \) absolute temperature [K]. Pre-exponential depends on mechanisms (e.g., the interstitial diffusion mechanism and solute-vacancy complex mechanism) [37], on diffusion direction [38], and the size of atoms [39]. Based on the calculations, it is expected that Cu will diffuse most into the Al matrix (Table 2). The Cu atom is smaller than the Al atom, so lattice diffusion is rapid. In the reverse position, the larger Al atoms can jump in a vacancy of the Cu lattice, the Al diffusion in Cu is four orders of magnitude smaller than the diffusion of Cu in Al (Table 2). However, in addition

---

**Figure 11.** The collected 2D SAED pattern (a) of shell and the 1D distribution (b) calculated from panel (a).
where we find \( \Delta \) (99.2 wt.%). Based on their investigation, very rapid, leading to the structures of the lattices of Al and Al

It should be noted that the diffusion along the grain boundaries and in amorphous structure can be many orders of magnitude higher than in the bulk [39]. In nanocrystalline materials, where the grain size is about 10 nm, the number of atoms being in grain boundaries can be higher than 20%. Moreover, the diffusion at the interface between the amorphous and crystalline phases is even greater.

The interdiffusion through the resulting Al\(_3\)Zr layer is very rapid, leading to the structures of the lattices of Al and Al\(_3\)Zr are similar, therefore, the nucleation of Al\(_3\)Zr takes place easily as explained by Kidson and Miller [41]. The growth of the Al\(_3\)Zr shell is a diffusion-controlled process. In the case of binary interdiffusion and reaction, the thickness of a growing phase can be described by a parabolic relationship [42]:

\[
k_p = \frac{\Delta x^2}{2t}
\]

where \( \Delta x \) represents the thickness of the intermetallic phase developed during interdiffusion after time \( t \). Parabolic growth constant \( (k_p) \) of the phase varies with the composition of the neighboring phases.

If the average thickness of Al\(_3\)Zr shell is taken to be 500 nm and the mean square displacement is equal to half of the thickness, the parabolic growth constant is:

\[
k_p = \frac{\Delta x^2}{2t} = \frac{0.5 \times 0.5 \times 10^{-9}}{2 \times 1800} = 1.7 \times 10^{-17} \text{ m}^2/\text{s}
\]

Mehta et al. [43] determined the parabolic growth constant from diffusion couples of Al versus Zr (99.2 wt.%). Based on their investigation, \( k_p \) is 2.50 (0.08) \( \times 10^{-15} \) \( \text{m}^2/\text{s} \) at 425 °C. There are four types of atoms and different phases in the investigated system, so this approximation is strong, yet the two results show an approximately good agreement. The interdiffusion through the resulting Al\(_3\)Zr layer is very rapid, leading to the structures of the lattices of Al and Al\(_3\)Zr are similar, therefore, the nucleation of Al\(_3\)Zr takes place easily as explained by Kidson and Miller [41]. The width of the diffusion layer as a function of time and temperature according to Arrhenius type relation is:

\[
\Delta x = k_0 \exp\left(\frac{-Q_A}{RT}\right)\sqrt{t}
\]

where \( k_0 \) is the rate constant, \( t \) is the time of annealing. The values of \( Q_A \) and \( k_0 \) are 188.2 ± 2.5 kJ/mol and 2.9\(^{+0.35}_{-0.35}\) \( \times 10^4 \) m/s\(^{1/2} \), respectively reported by [36]. Inserting 400 °C and 0.5 h values in Equation (4) we find \( \Delta x \approx 3.15 \) nm. This value is much less than the layer thickness produced in our case, which is due to faster diffusion due to the long milling process. The explanation for unusually rapid diffusion is likely to be the high vacancy concentration and lattice defects due to long high energy milling.
3.5. Mechanical Properties of the Hot-Pressed Composites

The microhardness (HV$_{0.01}$) of initial and mixed powder is displayed in Figure 12a. The Vickers hardness of initial Al and Cu$_{36}$Zr$_{18}$Ag$_{8}$Al$_{8}$ powder is 45 and 421 HV$_{0.01}$, respectively (Figure 12a). The hardness of the mixing powders increased significantly owing to the milling process, particularly in the case of milling without ethanol (Figure 12a). On the one hand, the crystallite size of the Al matrix is greatly reduced below 100 nm, and on the other hand, due to the presence of the reinforcing particles. The different rate of hardness increase proves that the mechanical alloying took place to a greater extent without ethanol milling. The mixed powder with 30 h milling without ethanol especially has the highest microhardness reaching 272 HV, which is about six times larger than that of the pure Al (45 HV$_{0.01}$).

![Figure 12. Microhardness of initial and mixed powders with different milling time (a) and Brinell hardness of the hot-pressed samples (b).](image)

Considering the Brinell hardness of the hot-pressed samples using a short milling time (0.5 h) before compaction increases from 15 HB of pure Al to 53 ± 1 HB/312.5 owing to the reinforcing particles (Figure 12b). However, a larger-scale hardness increase has been detected in the case when the powder was milled for a long time before pressing when the shell-core structure is formed (Figure 12b). The Brinell hardness of bulk pressed samples after 10 and 30 h milling are in the range of 275 and 329 HB/1875, which is a typical level for non-alloy steels.

In order to further evaluate the mechanical properties of the hot-pressed samples, compression tests were conducted at room temperature and 400 °C. Figure 13a,b show the compression parameters of the MA powder consolidated into cylindrical samples. The sample of mixed powder (0.5 h milling time) without the core-shell structure exhibits 7% ductility, the engineering compressive stress reaches 224 ± 10 MPa. The composites with 10 and 30 h milling time before the compaction with the core-shell structure exhibit 317 ± 25 MPa and 694 ± 112 MPa high compression strength, respectively.

However, the compressive strain values of the tested composites with reinforcements are low (1.72 ± 0.5%). The fracture micrograph morphology at the room temperature displays a brittle surface (Figure 13c,d). These rods suffer from sudden brittle failure. The debonding is not observed around the reinforcing particles possibly due to good bonding between the particles and the matrix. Besides, some particles are broken after deformation, confirming the presence of a strong interface. The shell is the Al$_2$Zr intermetallic, which has high strength, but this phase may also decrease the ductility of the composites due to their inherent brittleness mainly due to the strong directional covalent bonding between Zr and Al atoms [44]. The compression properties evidently are in accordance with the hardness measurements, in which some hardness increase was observed with the increased milling time before the pressing. The higher strength and hardness are closely related to the second phase strengthening mode and the formation of the Al$_2$Zr phase. In terms of the location of the Al$_2$Zr
phase, it is more advantageous if the phase is located at the interface of nanocrystalline-amorphous particles. For its formation, first, surface activity has to be caused by a high energy milling process with longer milling time. Second, the combination of elevated temperature and pressure ensures higher interdiffusion during hot-pressing.

![Figure 12. Microhardness of initial and mixed powders with different milling time (a) and Brinell hardness of the hot-pressed samples (b).](image)

**Figure 12.** Microhardness of initial and mixed powders with different milling time (a) and Brinell hardness of the hot-pressed samples (b).

Considering the Brinell hardness of the hot-pressed samples using a short milling time (0.5 h) before compaction increases from 15 HB of pure Al to 53 ± 1 HB/312.5 owing to the reinforcing particles (Figure 12b). However, a large-scale hardness increase has been detected in the case when the powder was milled for a long time before pressing when the shell-core structure is formed (Figure 12b). The Brinell hardness of bulk pressed samples after 10 and 30 h milling are in the range of 275 and 329 HB/1875, which is a typical level for non-alloy steels.

In order to further evaluate the mechanical properties of the hot-pressed samples, compression tests were conducted at room temperature and 400 °C. Figure 13a, b show the compression parameters of the MA powder consolidated into cylindrical samples. The sample of mixed powder (0.5 h milling time) without the core-shell structure exhibits 7% ductility, the engineering compressive stress reaches 224 ± 10 MPa. The composites with 10 and 30 h milling time before the compaction with the core-shell structure exhibit 317 ± 25 MPa and 694 ± 112 MPa high compression strength, respectively.

![Figure 13. Compression property parameters of the Al matrix composites at room temperature (a), and high-temperature compressive curves of parallel samples (b), fracture morphology (c) and backscattered SEM image of the polished surface after compression test (d).](image)

**Figure 13.** Compression property parameters of the Al matrix composites at room temperature (a), and high-temperature compressive curves of parallel samples (b), fracture morphology (c) and backscattered SEM image of the polished surface after compression test (d).

Commercial precipitation-strengthened aluminum alloys rapidly lose their strength above ~250–300 °C, due to the coarsening of their strengthening precipitates [45,46]. The maximal compressive strength of heat resistant Al alloys is below 150–200 MPa at 400 °C [47,48]. The advantage of the core-shell structure was particularly evident in high-temperature compression tests. It can be found that the value of the engineering compression strength at 400 °C is 381 ± 2 MPa (Figure 13b). Then its value becomes constant and decreases significantly owing to the onset of cracking. Although the deformation is very small, the strength is very high. However, the recycling of Zr-based alloy by powder metallurgy route offers a new possibility to produce a strengthened aluminum alloy. The core-shell structure is coarsening resistant because the shell is connected to the core.

### 4. Conclusions

Aluminum matrix composites reinforced with recycled Cu-Zr-based nanocrystalline particles were synthesized by the powder metallurgy route. The CuZrAgAl reinforcement with Al₃Zr shell uniformly distributes in the Al matrix. The main conclusions that can be drawn are as follows:

- A core-shell structure has been developed by the surface interdiffusion between Al and Zr, during the hot-pressing independently of the PCA use. The shell consists of tetragonal Al₃Zr phase based on TEM investigation. However, the formation of the core-shell structure requires long-term high-energy milling before the pressing. A prolonged milling process provides good surface activity for its formation.
• The increased mechanical properties are ascribed to the homogeneously distributed particles with core-shell structure, high relative density, the good interfacial bonding, and grain refinement strengthening. A very strong interfacial bonding exists between the reinforcement and the matrix.
• The core-shell structure is coarsening resistant because the shell is connected to the core.
• The shell and the crystallite size being reduced significantly improves the compressive strength of the composites up to 694 ± 112 MPa at room temperature. Even at 400 °C, the compressive strength is 380 MPa, which is very significant at this temperature.
• The Brinell hardness of bulk pressed samples after 10 and 30 h milling are in the range of 275 and 329 HB, respectively.
• The PCA has a great effect on the milling process; however, the effect of the core-shell structure is more pronounced in the case of the sintered samples.

**Funding:** This work was carried out as part of the GINOP-2.3.2-15-2016-00027 project implemented in the framework of the Szechenyi 2020 program. The realization of this project is supported by the European Union.

**Acknowledgments:** The author would like to thank her present colleagues for help with different measurements.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Shobha, R.; Siddaraju, C.; Suresh, K.R.; Niranjan, H.B. Mechanical property evaluation of heat treated insitu Al-TiB₂ composite after severe plastic deformation. *Mater. Today Proc.* 2018, 5, 2534–2540. [CrossRef]
2. Ma, Z.Y.; Li, J.H.; Li, S.X.; Ning, X.G.; Lu, Y.X.; Bi, J. Property-microstructure correlation in in situ formed Al₂O₃, TiB₂ and Al₃Ti mixture-reinforced aluminium composites. *J. Mater. Sci.* 1996, 31, 741–747. [CrossRef]
3. Sadeghi, B.; Shamanian, M.; Cavaliere, P.; Ashrafizadeh, F. Effect of processing parameters on the microstructural and mechanical properties of aluminium–carbon nanotube composites produced by spark plasma sintering. *Int. J. Mater. Res.* 2018, 109, 900–909. [CrossRef]
4. Takata, N.; Ishihara, M.; Suzuki, A.; Kobashi, M. Microstructure and strength of a novel heat-resistant aluminum alloy strengthened by T-Al₆Mg₁₁Zn₁₁ phase at elevated temperatures. *Mater. Sci. Eng. A* 2019, 739, 62–70. [CrossRef]
5. Zhou, H.; Qian, Z.; Zhou, M.; Liu, X.; Li, Y.; Zhang, X. Synergistic balance of strength and corrosion resistance in Al–Mg–Er alloys. *Acta Metall. Sin. (Engl. Lett.)* 2020, 33, 659–670. [CrossRef]
6. Nakatsuka, S.; Ishihara, M.; Takata, N.; Suzuki, A.; Kobashi, M. Tensile Properties of a Heat-Resistant Aluminium Alloy Strengthened by T-Al₆Mg₁₁Zn₁₁ Intermetallic Phase. *MRS Adv.* 2019, 4, 1485–1490. [CrossRef]
7. Venkateswarlu, K.; Pathak, L.C.; Ray, A.K.; Das, G.; Verma, P.K.; Kumar, M.; Ghosh, R.N. Microstructure, tensile strength and wear behaviour of Al-Sc alloy. *Mater. Sci. Eng. A* 2004, 383, 374–380. [CrossRef]
8. Zhang, Y.Z.; Gao, H.Y.; Wang, Y.F.; Wang, J.; De Sun, B.; Gu, S.W.; You, W.R. Effects of y addition on microstructure and properties of Al-Zr alloys. *Trans. Nonferrous Met. Soc. China (Engl. Ed.)* 2014, 24, 2239–2243. [CrossRef]
9. Barlow, I.C.; Jones, H.; Rainforth, W.M. Evolution of microstructure and hardening, and the role of Al₃Ti coarsening, during extended thermal treatment in mechanically alloyed Al-Ti-O based materials. *Acta Mater.* 2001, 49, 1209–1224. [CrossRef]
10. Guoxian, L.; Zhichao, L.; Erde, W. Thermal stability and mechanical properties of mechanically alloyed Al-10Ti alloy. *J. Mater. Sci.* 1996, 31, 901–904. [CrossRef]
11. Prosviryakov, A.S.; Shcherbachev, K.D.; Tabachkova, N.Y. Investigation of nanostructured Al-10 wt.% Zr material prepared by ball milling for high temperature applications. *Mater. Charact.* 2017, 123, 173–177. [CrossRef]
12. Prosviryakov, A.S.; Shcherbachev, K.D.; Tabachkova, N.Y. Microstructural characterization of mechanically alloyed Al-Cu-Mn alloy with zirconium. *Mater. Sci. Eng. A* 2015, 623, 109–113. [CrossRef]
13. Knipling, K.E.; Dunand, D.C.; Seidman, D.N. Precipitation evolution in Al-Zr and Al-Zr-Ti alloys during aging at 450–600 °C. *Acta Mater.* 2008, 56, 1182–1195. [CrossRef]
14. Guo, Z.; Zhao, G.; Chen, X.G. Effects of two-step homogenization on precipitation behavior of Al$_2$Zr dispersoids and recrystallization resistance in 7150 aluminum alloy. *Mater. Charact.* 2015, 102, 122–130. [CrossRef]

15. Souza, P.H.L.; Do Vale Quresma, J.M.; De Oliveira, C.A.S. Precipitation evolution and modeling of growth kinetics of L1$_2$-structured Al$_2$Zr particles in Al-0.22Zr and Al-0.32Zr (wt.%) alloys isothermally aged. *Mater. Res.* 2017, 20, 1600–1613. [CrossRef]

16. Janghorban, A.; Antoni-Zdziobek, A.; Antion, C.; Mazingue, T.; Pisch, A. Phase equilibria in the aluminium-rich side of the Al-Zr system. *J. Therm. Anal. Calorim.* 2013, 114, 1015–1020. [CrossRef]

17. Ostwald, W. Über die vermeintliche Isomerie des roten und gelben Quecksilberoxyds und die Oberflächenspannung fester Körper. *Z. Phys. Chem.* 2017, 34, 495–503. [CrossRef]

18. Mursalat, M.; Schoenitz, M.; Dreizin, E.L. Composite Al-Ti powders prepared by high-energy milling with different process controls agents. *Adv. Powder Technol.* 2019, 30, 1319–1328. [CrossRef]

19. Zhang, L.; Guo, X. Effects of Process Control Agents on the Mechanical Alloying Behavior of Nb-Ti-Si Based Alloy. *Mater. Trans.* 2018, 59, 528–537. [CrossRef]

20. Cipolloni, G.; Pellizzari, M.; Molinari, A.; Hebda, M.; Zadra, M. Contamination during the high-energy milling of atomized copper powder and its effects on spark plasma sintering. *Powder Technol.* 2015, 275, 51–59. [CrossRef]

21. Srinivasarao, B.; Suryanarayana, C.; Oh-Ishi, K.; Hono, K. Microstructure and mechanical properties of Al-Zr nanocomposite materials. *Mater. Sci. Eng. A* 2009, 518, 100–107. [CrossRef]

22. Louzguine-Luzgin, D.V.; Zadorozhnyy, V.Y.; Ketov, S.V.; Wang, Z.; Tsarkov, A.A.; Greer, A.L. On room-temperature quasi-elastic mechanical behaviour of bulk metallic glasses. *Acta Mater.* 2017, 129, 343–351. [CrossRef]

23. Shi, H.; Zhao, W.; Wei, X.; Ding, Y.; Shen, X.; Liu, W. Effect of Ti addition on mechanical properties and corrosion resistance of Ni-free Zr-based bulk metallic glasses for potential biomedical applications. *J. Alloys Compd.* 2020, 815, 152636. [CrossRef]

24. Zhang, L.; Li, Z.; Hu, H.; Wang, W.; Zhai, S.; Xu, J.; Niu, Z.; Wang, Y. Microstructure and property characterization of Al-based composites reinforced with CuZrAl particles fabricated by mechanical alloying and spark plasma sintering. *Adv. Powder Technol.* 2018, 29, 1695–1702. [CrossRef]

25. Shi, H.; Li, Z.; Hu, Z.; Ding, Y.; Tang, T.; Shen, X. Enhancing strength and plasticity of Zr-based bulk metallic glasses by Zr partially substituted Fe and isothermal annealing. *J. Non-Cryst. Solids* 2020, 543. [CrossRef]

26. Dutkiewicz, J.; Rogal, L.; Wajda, W.; Kukula-Kurzy Niec, A.; Coddet, C.; Dembinski, L. Aluminum Matrix Composites Strengthened with CuZrAgAl Amorphous Atomized Powder Particles. *J. Mater. Eng. Perform.* 2015, 24, 2266–2273. [CrossRef]

27. Dudina, D.V.; Geor garakis, K.; Aljerf, M.; Li, Y.; Braccini, M.; Yavari, A.R.; Inoue, A. Cu-based metallic glass particle additions to significantly improve overall compressive properties of an Al alloy. *Compos. Part A Appl. Sci. Manuf.* 2010, 41, 1531–1557. [CrossRef]

28. Scudino, S.; Liu, G.; Prashanth, K.G.; Bartusch, B.; Surreddi, K.B.; Murty, B.S.; Eckert, J. Mechanical properties of Al-based metal matrix composites reinforced with Zr-based glassy particles produced by powder metallurgy. *Acta Mater.* 2009, 57, 2029–2039. [CrossRef]

29. Tan, W.; Huang, L.; Li, S.; He, J. Microstructure and Mechanical Properties of Zr–Al–Ni–Cu Metallic Glassy Particles Reinforced 7056 Al Alloy Matrix Composites Obtained by Spark Plasma Sintering. *Adv. Eng. Mater.* 2019, 21, 1801267. [CrossRef]

30. Janovszky, D. Influence of the Oxide and Ethanol Surface Layer on Phase Transformation of Al-based Nanocomposite Powders under High-Energy Milling. *Materials* 2019, 12, 1305. [CrossRef]

31. Trivikantoro; Toma, D.; Meuris, M.; Köster, U. Oxidation of Zr-based metallic glasses in air. *J. Non-Cryst. Solids* 1999, 250, 719–723. [CrossRef]

32. Köster, U.; Jastrow, L. Oxidation of Zr-based metallic glasses and nanocrystalline alloys. *Mater. Sci. Eng. A* 2007, 449, 57–62. [CrossRef]

33. Kematick, R.J.; Franzen, H.F. Journal of Solid State Chemistry. *J. Solid State Chem.* 1984, 54, 226–234. [CrossRef]

34. Kaptay, G. A new equation for the temperature dependence of the excess Gibbs energy of solution phases. *Calphad* 2004, 28, 115–124. [CrossRef]

35. Tamim, R.; Mahdouk, K. Thermodynamic reassessment of the Al–Zr binary system. *J. Therm. Anal. Calorim.* 2018, 131, 1187–1200. [CrossRef]
36. Laik, A.; Bhanumurthy, K.; Kale, G.B. Intermetallics in the Zr-Al diffusion zone. Intermetallics 2004, 12, 69–74. [CrossRef]
37. Alexander, W.B.; Slifkin, L.M. Diffusion of solutes in aluminum and dilute aluminum alloys. Phys. Rev. B 1970, 1, 3274–3282. [CrossRef]
38. Marumo, T.; Fujikawa, S.; Hirano, K. Diffusion of zirconium in aluminum. J. Jpn. Inst. Light Met. 1973, 23, 17–25. [CrossRef]
39. Beke, D.L. Diffusion in Nonequilibrium Materials. Key Eng. Mater. 1995, 103, 51–78. [CrossRef]
40. Mantina, M.; Wang, Y.; Chen, L.Q.; Liu, Z.K.; Wolverton, C. First principles impurity diffusion coefficients. Acta Mater. 2009, 57, 4102–4108. [CrossRef]
41. Kidson, G.V.; Miller, G.D. A study of the interdiffusion of aluminum and zirconium. J. Nucl. Mater. 1964, 12, 61–69. [CrossRef]
42. Wagner, C. The evaluation of data obtained with diffusion couples of binary single-phase and multiphase systems. Acta Metall. 1969, 17, 99–107. [CrossRef]
43. Mehta, A.; Dickson, J.; Newell, R.; Keiser, D.D.; Sohn, Y. Interdiffusion and Reaction Between Al and Zr in the Temperature Range of 425 to 475 °C. J. Phase Equilibria Diffus. 2019, 40, 482–494. [CrossRef]
44. Hu, H.; Zhao, M.; Wu, X.; Jia, Z.; Wang, R.; Li, W.; Liu, Q. The structural stability, mechanical properties and stacking fault energy of Al3Zr precipitates in Al-Cu-Zr alloys: HRTEM observations and first-principles calculations. J. Alloy. Compd. 2016, 681, 96–108. [CrossRef]
45. Jin, N.; Zhang, H.; Han, Y.; Wu, W.; Chen, J. Hot deformation behavior of 7150 aluminum alloy during compression at elevated temperature. Mater. Charact. 2009, 60, 530–536. [CrossRef]
46. Huang, X.; Zhang, H.; Han, Y.; Wu, W.; Chen, J. Hot deformation behavior of 2026 aluminum alloy during compression at elevated temperature. Mater. Sci. Eng. A 2010, 527, 485–490. [CrossRef]
47. Choi, S.-H.; Sung, S.-Y.; Choi, H.-J.; Sohn, Y.-H.; Han, B.-S.; Lee, K.-A. High Temperature Tensile Deformation Behavior of New Heat Resistant Aluminum Alloy. Procedia Eng. 2011, 10, 159–164. [CrossRef]
48. Yamasaki, S.; Okuhira, T.; Mitsuura, M.; Nakashima, H.; Kusui, J.; Adachi, M. Effect of Fe Addition on Heat-Resistant Aluminum Alloys Produced by Selective Laser Melting. Metals 2019, 9, 468. [CrossRef]