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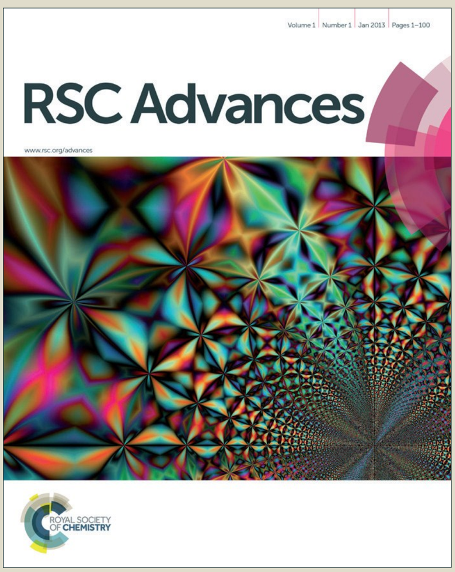

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Spray Conform 7075 Al

Chen YeGao; Zhong Yi; Yin JianCheng; Wang LiQiang; Yang Huan; Liu LiNa; Liu YingLi

Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming (+86 650000), Yunnan, China

Corresponding author: Zhong Yi

Email: zy5125990@163.com

Abstract

Spray Conform is a near-net-shape technology that combines elements of spray forming and Conform. 7075 aluminum alloy rods were fabricated by spray Conform followed by retrogression and reaging (RRA) heat treatment. The microstructure evolution and the mechanical properties of the spray Conform and the RRA spray Conform 7075 were researched. The spray Conform 7075 sample presents a microstructure with slight hardening precipitates within the matrix and at the grain boundaries, partial recrystallized regions, refined grains and low segregation of the main elements. The final microstructure at RRA aged condition is mainly composed by fine nanosized and homogeneous precipitates of AlCu and $MgZn_2$, more recrystallized regions and discontinuous precipitates separating out at grain boundaries. The microstructure, no matter of the spray Conform 7075 or of the RRA-7075, plays a critical role in achieving good mechanical properties combining with high stress-corrosion cracking resistance of the final products.

Keywords: spray Conform; microstructure; mechanical property; RRA; 7075 Al

1. Introduction

7075 Al, belonging to Al-Zn-Mg-Cu alloys, is used extensively for aerospace applications due to its high strength [1-4]. Several technologies have been made to manufacture the Al-Zn-Mg-Cu alloys of high performance [5-6]. Much of the progress achieved in the development of aluminum alloys can be attributed to new production methods, such as powder metallurgy (PM) and spray forming [7]. However, the PM process is hard to manufacture contamination free and fine powders due to the oxidation in the process of atomization and the difficulty in mechanical milling. The process of spray forming can only obtain the preform that is characterized by 1-10% pore [8-9]. Both technologies are not possible to process products directly. They are usually followed by pressure processing, such as hot extrusion [10-15]. Thus, the PM and spray forming technologies are energy and equipment intensive, and time-wasting.

Direct spray Conform technology [16-18], which combines elements of spray deposition [19-20] and Conform [21], is attractive because it may improve the economics of manufacturing aluminum products by eliminating the densification procedure of the deposited preform after spraying and blank preheating before forming until operations in conventional deposited preform processing while significantly reducing energy consumption. Spray Conform is a relatively new metal processing technology. In spray Conform, the process is finished by steps of the molten metal atomized using a high velocity inert gas, the resultant droplets cooled in flight, the spray deposited into the groove acting as a deposition substrate around extrusion wheel, the preform compacted in the container formed by extrusion wheel and extrusion shoe, the spray taken into extrusion cavity, and the dense material is extruded to form (Fig. 1). The alloy's latent heat is removed rapidly by the convection heat transfer from the atomized droplets teams in flight and the conductive cooling at the groove and extrusion cavity. The high solidification rates in spray Conform allow a wider range of alloys to be processed, and at higher production rates, than is currently possible in the conventional technological process of spray forming firstly and densification treatment afterwards [11-15, 22-23].

The success of spray Conform is related to faster cooling rates and near-net-shape processing, thus, preferred microstructures that produce superior mechanical properties and desired shaped products can be obtained. Rapid solidification process avoids common problems associated with conventional ingot metallurgy, such as alloy segregation and microstructural coarsening. Finer microstructures and reduced microsegregation can lead to reduced homogenization times during solution heat treatment and a variety of mesoscopic structure changes which lead to superior mechanical properties [7]. The successful exploitation of this technology will prompt the development of economic production of a diverse group of aluminum alloys with unparalleled combinations of strength and thermal stability.

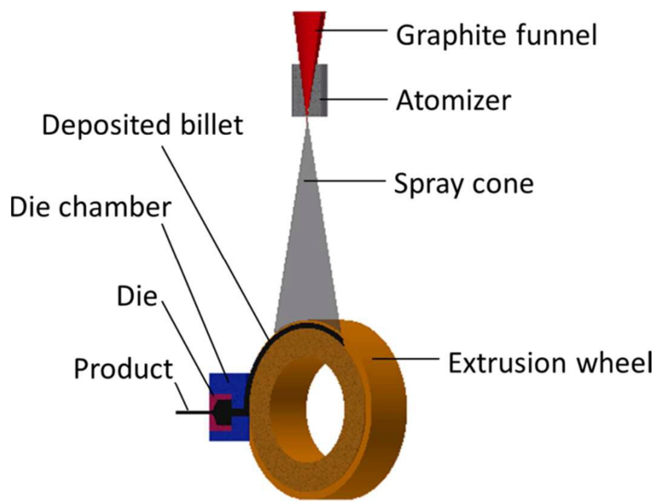


Fig. 1. Schematic of spray Conform.

2. Experimental procedure

The spray Conform equipment is modified by a LJ-350 Conform device and is mainly composed of Conform device, atomizer, controller and die. The atomizer is constructed above the extrusion wheel about 500mm, and the controller is designed between the atomizer and the extrusion wheel to control the spray to deposit into the groove of the extrusion wheel.

Raw 7075 alloy was heated in a box resistor-stove under no protective atmosphere, superheated to about 100℃ above the liquidus temperature, and transferred into an atomizer designed and constructed above the extrusion wheel. Atomized droplets atomized by nitrogen were sprayed vertically and deposited into the groove of the extrusion wheel, whose diameter is 340mm. The extrusion wheel has standard hot work tool-steel, H13, which was not water cooled in laboratory-scale. Pure aluminum was coated on the groove surface prior to a run for purpose of better connection between the substrate and the deposited preform. Both contain the same matrix material. Thus, better joints can increase frictional force, which is favourable for taking material to extrusion cavity and extruding to form. A nitrogen atmosphere within the spray apparatus minimized in-flight oxidation of the atomized droplets. Currently, the device is not equipped with a coiler, and an individual rod measuring about 1500mm long was produced by starting/stopping the spray (Fig. 2). For this study, the diameter of the melt delivery tube is 3mm, the atomizing pressure is 0.2MPa. The 7075 rods fabricated by spray Conform were heat treated to the RRA aging (120℃24h+200℃10min+120℃24h) after two-stage solution treated at 450℃ for 1 h and 475℃ for 2 h.

Fig. 2. Typical product of 7075 rod is fabricated by spray Conform.

Microstructure of the spray and rods was evaluated using a XJP-6A optical microscope (OM) and a Tecnai G2 TF30 transmission electron microscope (TEM) as well as a XL30-ESEM-TMP scanning electron microscope (SEM). Keller's etchant was used to show grain structure and highlight constituent phases. The TEM test was performed at 300 KV to see the distribution of the second phase and the structures of particles and crystal boundaries. The TEM specimens were 3mm in diameter and 100μm in thickness, and they were subsequently thinned by double-jet electropolishing with a 30% nitric acid solution at approximately -25℃. The tensile testing was performed with an AG-X100KN screw-driven test machine. The X-ray diffraction (XRD) experiments were performed on a Japanese Rigaku D/max 2200 diffractometer using Cu Kα radiation. For phase identification, XRD patterns were obtained in the diffraction angle (2θ) ranging of between 0 and 100°. The electric conductivity was measured by a LSR-3 Seebeck Linseis instrument. Fractographic features of the tensile sample were also studied by SEM.

3. Results and discussion

3.1. Microstructure

In spray Conform, the extrusion wheel performs several functions. It acts as a substrate, absorbs the remaining latent heat, consolidates the deposited material, and offers an extrusion force to form fully-dense rods. The procedure of in-flight extracts most of the metal's latent heat by convection heat transfer to the relatively cold inert gas, nitrogen, which is entrained into the jet. The unsolidified liquid phase deposited out has the same component as the liquid metal feed. This highly restricts segregation because of the surrounding solid phase working as a heat extracter to quickly solidify the remaining liquid material [24]. Therefore, in spray Conform, solidification progress goes inwardly resulting in the enrichment in alloying additions to the final solidification material. It is significant to confine the fraction of liquid in the "slush" material to control foundry defects such as surface bleeds and sub-surface stringers of constituent phases, while processing materials with a broad freezing range, such as 7075 Al. Experience has indicated that this is much easier and more effectively solved during droplet formation and cooling rather than post-deposition thermo-mechanical processing.

In order to examine microstructure evolution during spray Conform, the extrusion wheel and spray were stopped simultaneously during operation of the device. A schematic diagram of the cross-section of spray Conform displays five distinct regions (Fig. 3):

(1) The depositional region where the spray is deposited into the groove.

(2) The preliminary densification region where the semi-solid material is initially compacted between extrusion wheel and die chamber.

(3) The blocking region where the material is changed its course by 90° and is further compressed.

(4) The extrusion cavity region where the billet is further consolidated.

(5) The forming area where the product rods form by the forming part of the die.

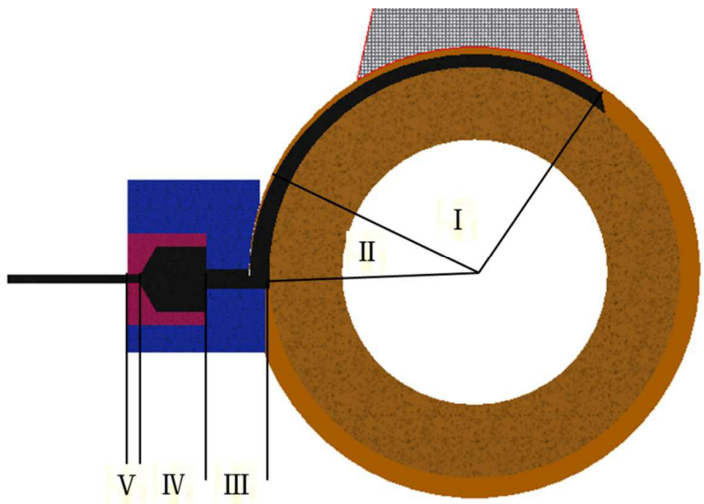


Fig. 3. Sketch of five regions of spray Conform: Ⅰ- The depositional region; Ⅱ- The preliminary densification region; Ⅲ- the Blocking region; Ⅳ- The extrusion cavity; Ⅴ- The forming area.

Typical microstructures of these regions are shown in Fig. 4. The depositional zone consisted of grains with an equiaxed and fine structure owed to rapid cooling and large numerous of heterogeneous nucleation, and contained random and isolated pores of various shapes, as shown in Fig. 4a. Finer grains were obtained at the groove surface than at the interior for better heat conduction conditions, but both remained equiaxed grains. This region resembled what is representatively observed when spraying onto a flat surface most [25-27]. It is proved that a very low value of segregation can be obtained when compared with conventional semi-continuous casting of the same alloy, which can reach a value of around 7% [28]. Thus, segregation occurred in the spray preform, but it was less severe than in the conventional casting of the alloy, resulting in a homogeneous microstructure. The preliminary compacted region is also characterized by an equiaxed and fine grain structure, but a decreasing concentration of pores as the material progresses toward the abutment, as shown in Fig. 4b. The preform is prevented from going along the rotational direction of the extrusion wheel when contacting the abutment. Thus, the deposited material stopped progressing is subject to compact force coming from the spray feed, and eliminated part of the pores. Fig. 4c shows the microstructure of the blocking zone where the compact spray changes its direction of motion by 90° perpendicular to the surface of extrusion wheel and is further compacted due to severe plastic deformation whose mechanism of deformation is similar to equal channel angular pressing [29]. In this area, most of the pores disappear under such high extrusion force, which brings the denser billet. Many coarse grains and precipitates, no matter within the grains or at the grain boundaries, are first cracked in this region. Fine grains and uniformly distributed small precipitates are the basis for getting superior performance. Nevertheless, there are still a few of pores as well as precipitates that are difficult to be eliminated in the matrix [30]. The extrusion cavity regions of spray Conform and Conform are clearly identical. Both are the places where blank gather and suffer huge extrusion force to occur intense plastic deformation. In this process, the porosity is virtually all eliminated at the extrusion cavity due to the further compacted, as shown in Fig. 4d. The consolidated material in the extrusion cavity is extruded to form products with homogeneous and fine microstructure as well as excellent mechanical properties. Fig. 4e shows the microstructure with typical anisotropic properties of the longitudinal section of the extrusion products with fine precipitates distribute along the extrusion direction. Most of the secondary phase generated during the spray process was broken by the shear stress [11]. However, it is inferred that unbroken coarse second phases induce stress concentration, which results in the formation of secondary cracks in the matrix and deteriorative effect on the ductility [31].

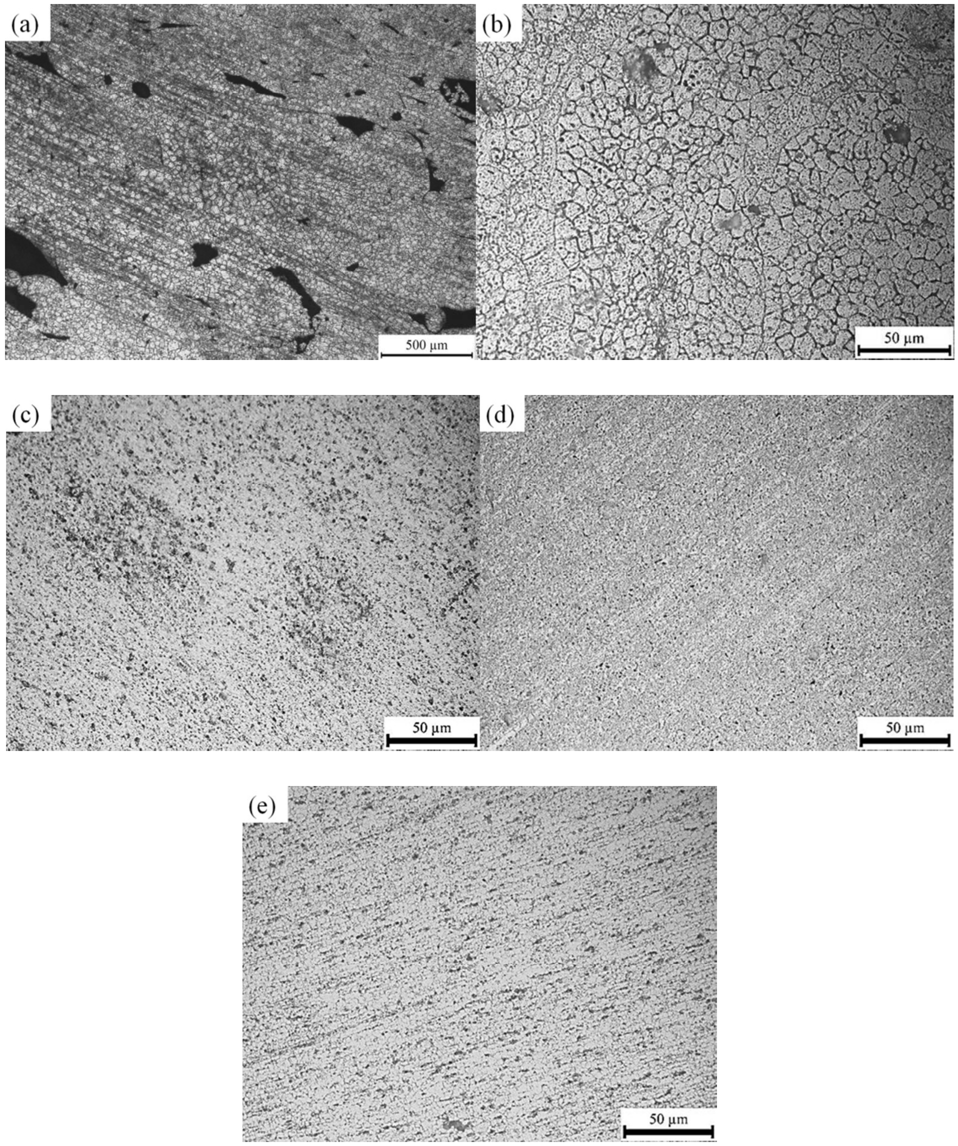


Fig. 4. OM Photomicrographs illustrating microstructure evolution of 7075 Al during spray Conform. (a) The depositional region. (b) The preliminary densification region. (c) The blocking region. (d) The extrusion cavity region. (e) The fully-consolidated rod.

Fig. 5 shows SEM micrographs of the cross section of the spray Conform 7075 rods. The precipitation has occurred as a consequence of the extrusion temperature employed in the experiments, which gives the supersaturated structure the necessary energy to achieve the equilibrium by the precipitation of the phases [30]. The size of uniformly distributed precipitates is less than 5μm, as shown in Fig. 5a. In addition, Fig. 5b shows some regions exhibiting fine and equiaxed microstructure within the samples. In theory, it is impossible to generate so many and large continuous precipitates due to high cooling rates during spray deposition. Rapid solidification of molten alloy allows no enough time and temperature for alloy elements to segregate and form compounds. Considering from the morphology viewpoint，it exhibits the equiaxed microstructure, which is corresponding with the recrystallization grains. Additional, E.M. Mazzer et al. found the recrystallization microstructure in the extruded 7050 alloy that was processed by spray forming firstly and then was hot extruded [11]. Thus, we conclude that the fine and equiaxed microstructure was recrystallized grains.

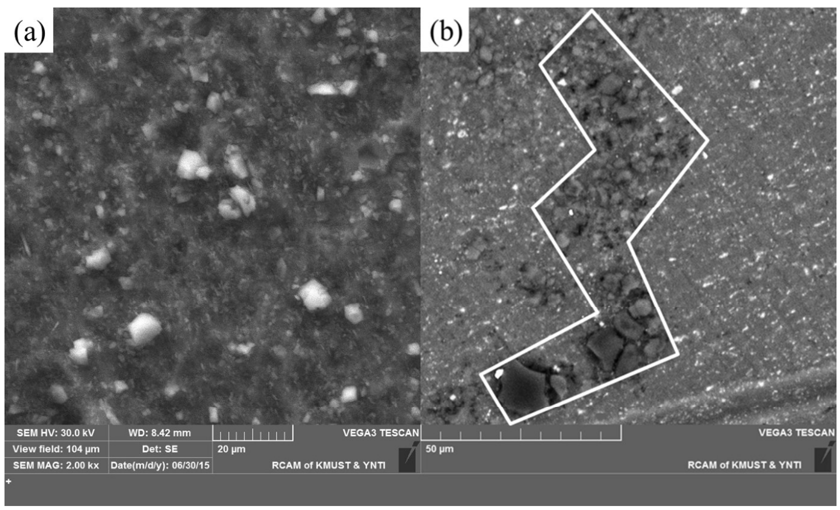


Fig. 5. SEM micrographs of the extruded bar in the cross direction showing (a) precipitation in matrix and (b) partial recrystallization in irregular polygon.

However, the XRD diffraction pattern of the spray Conform 7075 is presented in Fig. 6 showing no intermetallic phases originating from the spray process and from precipitation. The results are at odds with the conclusion mentioned above. This is due to the rapid cooling rates of the melt in the spray process. Despite the segregation of the alloying elements in this step, the precipitation phenomenon is weaker [11]. Thus, the quantity of precipitates generating in spray Conform is too lack to be examined by XRD method.

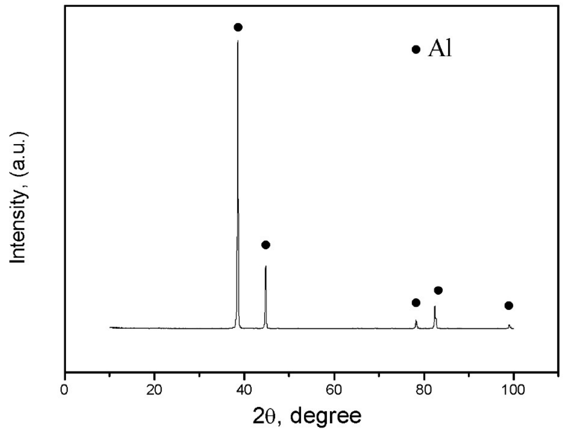
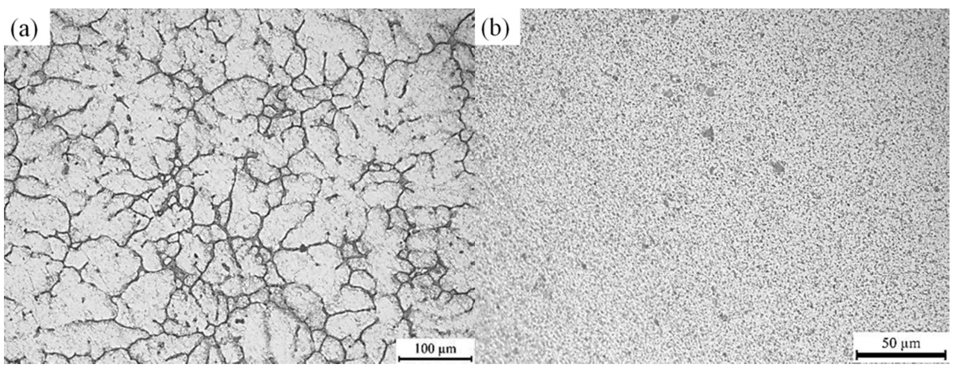


Fig. 6. XRD diffraction pattern of the spray Conform 7075 rods.

Fig. 7 shows the microstructure of the cross section of the spray Conform 7075 Al as well as the ingot cast 7075.



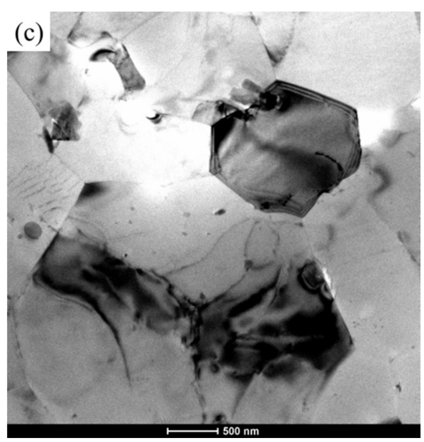


Fig. 7. (a) and (b) OM Photomicrographs of ingot cast 7075 and transverse section of spray Conform 7075, respectively, (c) TEM of transverse section of spray Conform 7075.

The ingot-cast sample is characterized by a coarse dendritic structure and severe interdendritic segregation of the solute-rich phases in Fig. 7a. However, spray Conform specimens show much finer grains than as-cast ingot and almost equiaxed structure with very small, angular precipitates of Al-Zn-Mg-Cu phase uniformly distributed in aluminum matrix, as shown in Fig. 7b. Fig. 7c presents the more detailed grain structures including recrystallized grains and subgrains and an accumulation of dislocation at the grain boundaries owing to the extrusion process. It shows that the grain size is about 1-2μm, and less precipitates can be observed both in the matrix and at the grain boundaries due to the rapid cooling rates. Fine recrystallized grains and subgrains are formed after hot deformation. The decrease in growth of recrystallized grain is also an important factor to increase yield strength and elongation [29].

Fig. 8 shows the microstructure of spray Conform 7075 Al with RRA ageing heat treatment. Partial recrystallization was observed in the spray Conform condition. Further RRA treatment was not enough to complete recrystallization, as shown in Fig. 8a and b. The grain morphology of a recrystallized alloy lies on many elements, such as the extrusion ratio, aging mode, and solidification rate during processing. The fine and uniformly distributed second phase particles play a significant role in recrystallization behavior. The recrystallized grains grew up along the extrusion direction, and precipitates distributed internal the grains and of grain boundaries. Fig. 8c shows the TEM micrographs of the RRA heat treated 7075. Nanoscale precipitates can be seen within the grains and at the grain boundaries. It is evident that the precipitates separating out at grain boundaries are discontinuous, which is a normal phenomenon in 7xxx aluminum alloy after RRA ageing [32-34]. The discontinuous morphology plays a significant role in increasing stress-corrosion cracking resistance without decreasing of the strength [32, 35]. Electric conductivity of the alloy is 24.9 MS/s, which is 9.7% higher than that in Ref. 36 [36]. Thus, it can be considered that the 7075 material fabricated by spray Conform subsequently with RRA ageing has a superior stress-corrosion cracking resistance. Secondary particles uniformly precipitate in the Al matrix with size of less than 150 nm and the shape is close to sphere. From Orowan mechanism, it is obvious that the strengthening depends on not only the particle size distribution, but also the uniformity of the dispersion [37]. The precipitates are of similar size and distribute homogeneously, which results in superior mechanical properties.

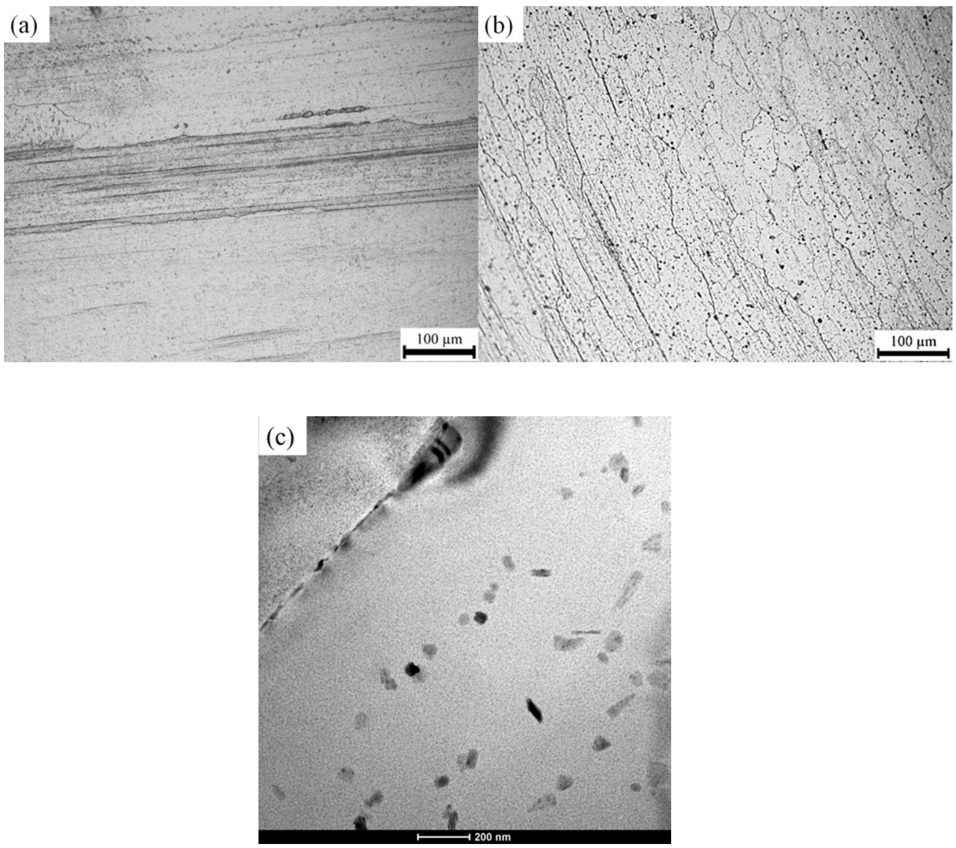


Fig. 8. (a) and (b) OM micrographs of longitudinal section and cross section of the RRA aged sample, respectively, (c) TEM micrograph of cross section of the RRA aged sample.

The XRD pattern of the RRA-7075 is presented in Fig. 9. If both XRD patterns concerning the spray Conform rods and the RRA-rods are compared, it is observed that the intensity of the phase peaks is stronger in the RRA heat treated bar. This is because the process of RRA aging after spray Conform forces the precipitation of the secondary phases both in the matrix and at grain boundaries. The clearly resolved peaks of 7075 aluminum rods subjected to RRA heat treatment corresponding to

AlCu and $MgZn_2$ constituent phases and Al matrix.

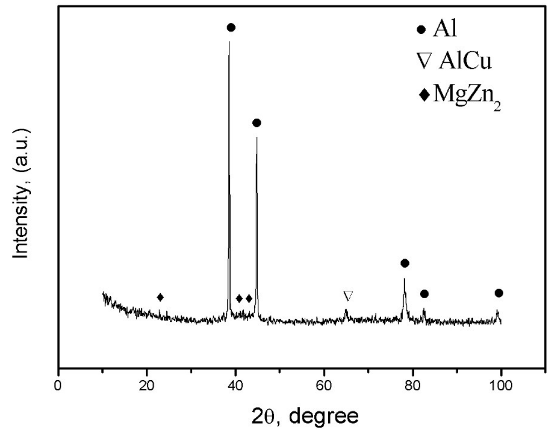


Fig. 9. X-ray diffraction pattern of the RRA heat treated 7075 Al.

3.2. Mechanical properties

Tensile properties of spray Conform 7075 rods and RRA heat treatment 7075 rods are summarized in Table1. It is possible to observe a considerable increase on the properties after RRA aging heat treatment due to the fine precipitation of the AlCu and η phase, which are responsible for the hardening of the matrix. It is obvious that the spray Conform technique plays an important role in the strength and the ductility of the rods, reflecting the high elongation of both states. As mentioned before, it is well known that many fine dispersoids can be obtained with spray Conform due to its rapid solidification, although it is hard to be observed by XRD. Another important feature of the process is the improvement of the solid solubility of alloying elements. The contribution in the strength by the phenomena is due to the difference of the atom sizes [31].

Analysis of the fracture surface of the tensile samples indicates ductile mode of fracture. The dimples from samples of both states can be observed from Fig. 10. Dimples from the spray Conform sample seem to be smaller but more than the RRA heat treated sample. However, dimples from the RRA heat treated sample seem to be deeper. It evidences that the deeper and much dimples indicates the better plastic deformation ability.

Table 1
Tensile properties of the spray Conform 7075 Al and the RRA-7075.

Condition	UTS (MPa)	YS (MPa)	Elongation (%)
Spray Conform	363	255	11
RRA	547	493	12.6

The mechanical properties obtained present higher YS and elongation than specified in the aeronautical standard AMS 4050 H for this material. According to this standard the acceptable limits of YS and elongation for rods up to 51mm are 450 MPa and 10%, respectively. After RRA aging heat treatment YS and elongation values achieved 493 MPa and 12.6%. The results show that the precipitates of AlCu and $MgZn_2$ promoted an increase in the strength, but it is still keeping a good ductility. This is explained by the reduced size of the precipitates and low segregation after the RRA ageing.

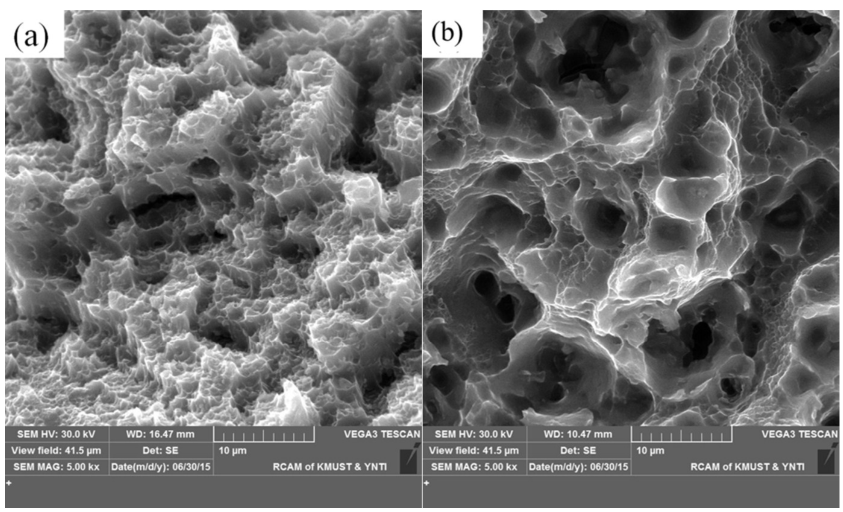


Fig. 10. Fracture surface of the tensile tested samples: (a) spray Conform condition, (b) RRA ageing state

4. Conclusions

The microstructure and mechanical properties achieved showed that the spray Conform process was successful in producing products with fine and uniform microstructure as well as good mechanical properties. After spray Conform, partial recrystallized regions as well as fine and low level of segregation microstructure were found. The second phases precipitated in the process of spray Conform were hard to be identified by X-ray diffraction method due to the rapid solidification, accomplished through convection cooling of atomized droplets in flight and conduction cooling at the groove. After the RRA heat treatment the fine nanosized and homogeneous precipitates of AlCu and $MgZn_2$ distributed within the matrix and at the grain boundaries, which resulted in the good combination of the strength and ductility and the stress-corrosion cracking resistance. Thus, the spray Conform process followed by heat treatments showed to be a promising alternative processing route for recycling 7075 aluminum alloy.

Acknowledgments

The authors gratefully acknowledge support by National Natural Science Foundation (508740655) and Yunnan Province Natural Science Foundation (2007E0013Z).

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