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Enhancement of Mechanical and Dissolution Properties of a Cast Magnesium Alloy via Equal Angular Channel Processing

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***Abstract*—**Two decades of the Shale Revolution has transforming transformed the global energy market, in part by the adaption of multi-stage dissolvable frac plugs. Magnesium has been favored for the bulk of plugs, requiring development of materials to suit specific field requirements. Herein, the mechanical and dissolution results from equal channel angular pressing (ECAP) of two cast dissolvable magnesium alloy are described. ECAP was selected as a route to increase the mechanical properties of two formulations of dissolvable magnesium, as solutionizing failed. In this study, 1" square cross section samples cast Mg alloys formulations containing rare earth were processed at temperatures ranging from 200 to 350 °C, at a rate of 0.005"/s, with a backpressure from 0 to 70 MPa, in a brass, or brass + graphite sheet. Generally, the yield and ultimate tensile strength (UTS) doubled for all. For formulation DM-2, the yield increased from 100 MPa to 250 MPa; UTS from 175 MPa to 325 MPa, but the strain fell from 2 to 1%. Formulation DM-3 yield increased from 75 MPa to 200 MPa, UTS from 150 MPa to 275 MPa, with strain increasing from 1 to 3%. Meanwhile, ECAP has also been found to reduce the dissolution rate significantly. A microstructural analysis showed grain refinement of the alloy and the movement of secondary phases away from the grain boundary. It is believed that reconfiguration of the grain boundary phases increased the mechanical properties and decreased the dissolution rate. ECAP processing of dissolvable high rare earth content magnesium is possible despite the brittleness of the material. ECAP is a possible processing route to increase mechanical properties for dissolvable aluminum alloys that do not extrude.

***Keywords*—**Equal channel angular processing, dissolvable magnesium, frac plug, mechanical properties.

I. Introduction

After the apparent discovery of the majority of the globe's giant oilfields as evidenced by the overall decline of production from them, alternative resources were explored and developed [1]. Atypical geological formations, typically with lower permeability, were exploited by combining two techniques to economically extract oil and gas. Long horizontal wells are drilled within the target shale formation to allow the subsequent hydraulic fracturing of the formation [2]. Hydraulic fracturing is a stimulation technique wherein pressurized fluid is forced into the formation, enlarging existing fissures or creating new ones. High permeability sand within the fluid flows into these fractures, propping the fissures open and creating high permeability pathways in an otherwise low permeability formation [3]. Fracturing is performed after a perforating step along the length of the well in multiple stages to create many of these high permeability pathways [4]. Each stage requires a plug that will allow for pressure buildup behind in the area being fractured. The first zonal isolation devices were cast iron plugs that required coiled tubing to mill through to reestablish flow. Composite plugs were then developed to expedite the milling process and allow for conveyance in horizontal sections. The next advancement was the advent of dissolvable frac plugs, which minimized the need for coiled tubing and allowed for longer horizontal sections [5].

Dissolvable plugs are made from material that react aggressively when placed in wellbore fluids. Polymeric plugs are limited to a window of 80 to 130 °C. Metallic plugs are generally made from aluminum or magnesium, usually magnesium, and are used from 40 to 175 °C. These materials typically require a chloride, readily available in wellbore fluids, to accelerate the galvanic corrosion reaction to dissolve quick enough to bring the well production online [6]. The corrosion rate of these materials is controlled by the type and quantity of secondary phases in the α-phase magnesium matrix. These phases, which are modified by extrusion and/or heat treatment, also determine the strength. Secondary phases are more cathodic than the magnesium matrix, causing hydrogen gas and magnesium ions to form as a byproduct of the reaction [7].

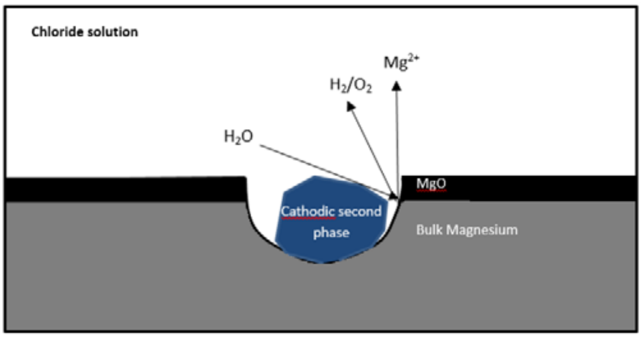

Fig. 1 Internal galvanic mechanism for dissolvable magnesium

Requirements for the plug material vary widely depending on the temperature, fluid, and individual component requirements. At a given temperature on a plug, one component may require high ductility where another requires high strength. The same plug design functioning at 95 °C may be inadequate at 175 °C due to temperature stability or accelerated corrosion

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of the base alloy. Materials with a wide array of properties must be available to match the varying wellbore conditions. The rate of development for new formulations can be outstripped by delivery dates for product.

An important parameter for designing components is the yield strength of the material, defined as the maximum stress that can be applied before it irreversibly deforms. The elongation is another key parameter that is the percentage of stretch from the original length to the point of failure [8]. The mechanical properties for a given chemistry may be modified by a variety of processes such as heat treatment [9], extrusion [10], or severe plastic deformation [11]. At a microscopic level in a polycrystalline metal, these properties are partially determined by the number and movement of dislocations in the lattice under applied external stress. A high density of dislocations formed by strain hardening will cause overlapping strain fields, impeding additional movement. Intersections of dislocations as well substitutional atoms, interstitial atoms, grain boundaries, and differing phases structures will impede grain boundaries [12].

Grain size reduction will impede dislocation motion due to the abrupt random changes in grain orientation as there a potential energy demand for a dislocation to pass from one grain through the boundary to the next on a common or similar slip plane. Smaller grains will cause more dislocation pileups proportionate to larger grains, thus decreasing the dislocation travel distance. An increase in yield strength will result, as expanded on by the Hall-Petch relationship [13]:

$$\sigma_y = \sigma_0 + kd^{-1/2} \quad (1)$$

where σ_y is the yield strength, σ_0 is lattice resistance, k is the material correlation coefficient that measures the relative hardening contribution of the grain boundaries, and d is the average grain size. The relationship is not valid for extremes in grain sizes. When the average grain size is below 100 nm, the yield strength and ductility of the material is significantly improved [14]. Processing of bulk ultrafine-grain materials with grains less than 1 µm is economically feasible through severe plastic deformation (SPD) processing techniques [15]. A popular method of SPD is ECAP, which can process many alloys to obtain ultrafine grains, thus enhancing mechanical and physical properties. In ECAP, a billet with the dimensions of the channel is pressed through an angled section, emerging with the same cross-sectional dimensions and a high imposed strain [16]. The billet may be rotated and passed through repeatedly to create different microstructures that will generate differing mechanical and physical properties [17].

A major limitation of magnesium alloys is the hexagonal close pack (HCP) structure and its limited slip systems [18]. As a result, magnesium alloys generally have poor mechanical properties and limited processing routes. The accelerated corrosion rate of magnesium far surpasses that of other available metals, making it indispensable for fracturing operations. The widespread use of magnesium in fracturing has pushed investigation into potential process routes that will enhance strength and ductility. Stronger alloys would allow a reduction in the overall metal used in a plug, which would result in quicker dissolution times for the plug. Magnesium alloys that are more ductile would allow for more design freedom and increase reliability by eliminate cracking in components due to the inherent anisotropy of magnesium. Economically available high-elongation magnesium alloys are limited and are a major design restraint.

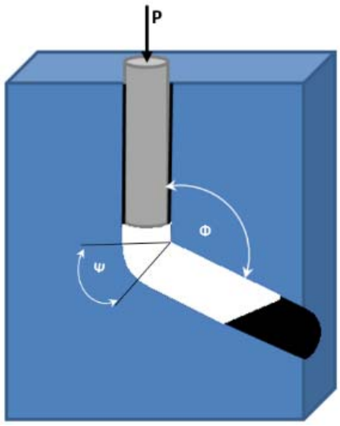

Fig. 2 Schematic of ECAP processing. A billet is pushed through the channel with a plunger creating pressure P. Φ represents the die channel angle and Ψ the corner angle [16]

ECAP would allow for end users to optimize purchased dissolvable magnesium rather than depend on vendors to create a new formulation or attempt to create their own. For example, a purchased alloy could be processed to have more ductility if a component is required to have a high degree of deformation.

Another major limitation of magnesium is that many magnesium alloys have a steep decline in properties at elevated temperatures. Testing has shown that a measurable decline begins at 95 °C, with a significant loss in strength at 150 °C.

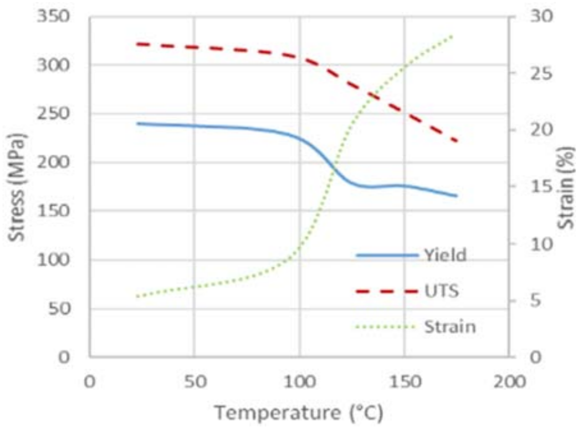

Fig. 3 Decline in measured mechanical properties of a magnesium alloy tested from 23 °C to 175 °C. Note the precipitous decline in the yield and UTS starting at 125 °C

Temperature stable magnesium alloys have been developed for high temperature applications up to 200 °C by the additions of rare earth elements (REEs). However, the phases developed after processing inhibit corrosion [19]. The market for high temperature dissolvable magnesium plugs is small, with dissimilar conditions from one well to another. The chloride concentration in one well may prematurely dissolve a plug functioning in a well at the same temperature with less chloride. Altering the grain size may influence the corrosion rate of the magnesium alloy. While literature is not clear on if a decreasing grain size will increase or decrease the corrosion rate, it is probable that it will decrease due to decrease in locally activated galvanic cells [20]. A direct cast and ECAP of dissolvable magnesium alloys, specifically those containing rare earth, would be advantageous for bypassing extrusion and potentially resulting in enhanced metallurgical properties alloying for more improved plug performance.

II. Materials and Experiment

All magnesium alloys were processed in a die with a die channel angle of X. After processing, microtensile specimens were extracted from the extruded direction (ED) and flow direction (FD-perpendicular to ED) and tested from 23 °C to 150 °C [21]. Microhardness was used to survey the resultant material to determine the hardness of alloy. An optical microscope was employed to survey the resultant microstructure to inspect the changes made by processing and connect those changes to the resultant mechanical properties.

Fig. 4 Representative tensile specimens extracted from the ECAP magnesium billet

Dissolution testing of a 1.5x2x2.5 cm sample was conducted in 1 liter of 95 °C 1% KCl. Every 2 hours, the sample was removed from solution, dried, weighed with the lengths, widths, and heights recorded, and replaced in solution. The resultant dissolution rate between two-time intervals was determined by (2):

$$D = \frac{\frac{\Delta m}{\Delta SA}}{\Delta t} \quad (2)$$

where Δm is the change in mass, ΔSA is the change in surface area, and Δt is the time interval length. A comparison of the pre and post ECAP values will indicate whether the transformation to a bulk ultrafine microstructure will increase or decrease the corrosion rate.

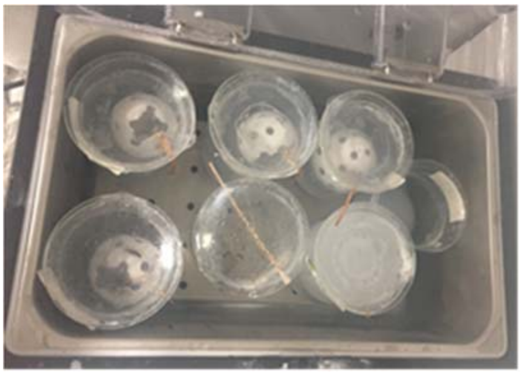

Fig. 5 Water bath setup for dissolution testing of samples

A commercially available cast and extruded dissolvable magnesium alloy, DM-1, was cut into a 2.5x2.5 cm cross section billet for processing by ECAP. The processing temperature was 200 °C via 4A route with 20 MPa backpressure at an extrusion rate of 0.125 mm/sec. Route A was selected as it will reduce twinning in magnesium alloys. If twinning is activated, it will cause issues with formability. The resultant materials were characterized with the methods above. After positive results from processing, billets of two as-cast magnesium-rare earth alloys for use in high temperature applications were processed by ECAP. Alloy DM-2 had the nominal composition of Mg-3Gd-2Y. Alloy DM-3 had the nominal composition of Mg-11Al-8Gd-5Zn. The ECAP parameters for DM-2 and DM-3 were initially selected to be identical to DM-1. Large cracks appeared in the billet after initial ECAP trials, necessitating an increased back-pressure to minimize cracks [22]. Temperature was increased to 350 °C and backpressure to 55 MPa. Cracking from ECAP in ensuing billets was largely eliminated. Samples were extracted for mechanical and physical property evaluation.

III. Result and Discussion

A. Back-Pressure

TABLE I
Summary of the ECAP Processing Parameters and Results for Extruded DM-1 and As-Cast DM-2 & DM-3

Billet ID	Temp. (°C)	Backpressure (MPa)	Route	Result
DM-1	200	20	4A	Success
DM-2.1	200	20	4A	Fractured
DM-2.2	350	20	4A	Shallow crack
DM-2.3	350	55	4A	Success
DM-2.4	350	55	4A+180°+2A	Success
DM-3.1	200	20	4A	Shallow crack
DM-3.2	250	20	4A	Shallow crack
DM-3.3	200	70	4A	Mushrooming
DM-3.4	350	0	4A	Success
DM-3.5	350	7	4A+180°+1A	Success

Processing with back-pressure is significant and necessary as the cracking in initial trials was reduced or eliminated in subsequent ones. Further, the use of back-pressure likely allowed for processing rare earth alloys at a lower temperature. Use of multiple passes helped develop a fine untwinned microstructure from an otherwise large grained initial structure that could develop a bimodal grain structure [23].

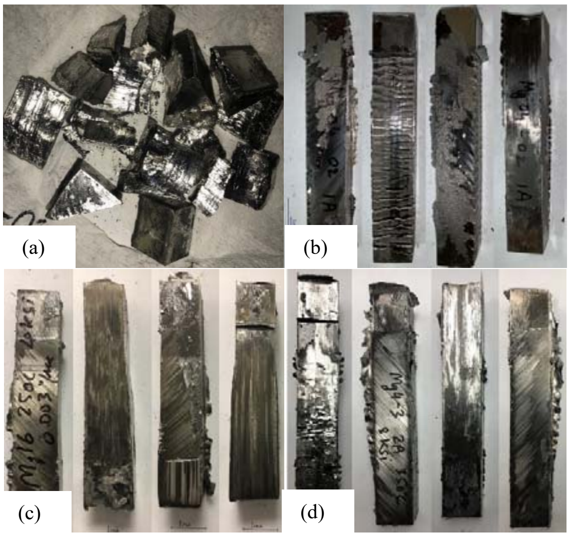

Fig. 6 (a) An example of a billet that fractured during processing (b) A billet that experienced shallow surface cracks (c) a billet that mushroomed due to high back-pressure (d) a successful billet

B. Tensile Testing

Tensile testing indicates that the ductility of all material has been improved via ECAP. The strengthening mechanisms in the ECAP processed alloys include solid solution strengthening, precipitate strengthening and grain boundary strengthening [24].

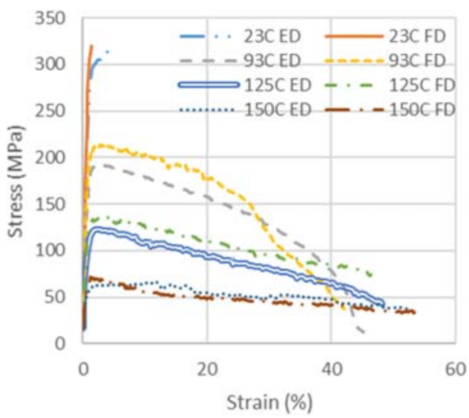

Fig. 7 Plotted values of ECAP DM-1 mechanical testing

DM-1 demonstrated equal to or greater mechanical properties at room temperature, with a similar yield but greatly improved ductility at 95 °C where DM-1 is generally used. DM-1's ductility showed an improvement on the as-extruded alloy, but experienced a steeper high temperature property decline. The 125 °C ECAP yield was roughly half of the extruded material. Regardless, the improvement in ductility is attractive considering magnesium's anisotropic properties which usually reduce the properties in the flow direction. Route A was expected to yield unidirectional properties. Material should be softer along the long length of the grain axis, as dislocations have longer to travel. Instead, properties were similar.

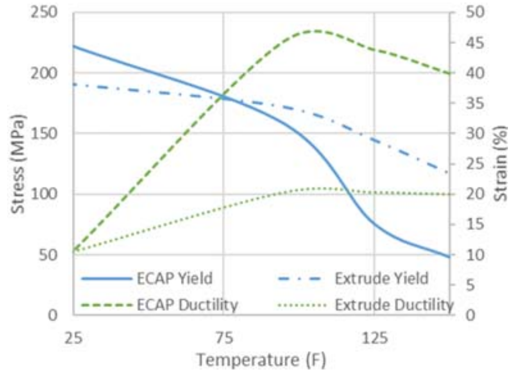

Fig. 8 Plot comparing the extruded and ECAP values from DM-1

DM-2 as-cast properties displayed high temperature stability, but low mechanical properties. Direct ECAP increased the yield and UTS while resulting in a lowered ductility. DM-3 as-cast properties also displayed high temperature stability, but low mechanical properties. Direct ECAP at least double mechanical properties.

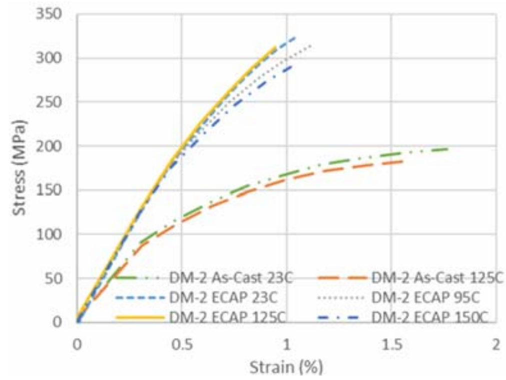

Fig. 9 The plotted mechanical properties of DM-2 as-cast and after ECAP

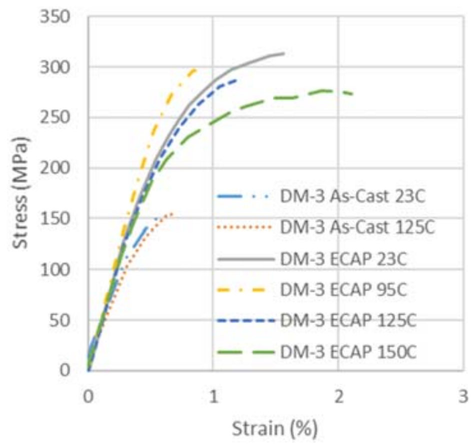

Fig. 10 The plotted mechanical properties of DM-3 as-cast and after ECAP

C. Dissolution Testing

Dissolution testing of an extruded and extruded-ECAP DM-

1 sample shows nearly identical dissolution rates. The results are extremely surprising consider the reduction in grains size and anticipated kinetics change in the galvanic reaction.

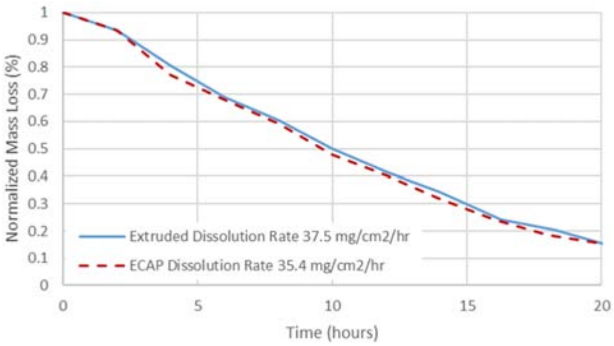

Fig. 11 Normalized mass loss of extruded and ECAP DM-1

Dissolution testing of DM-2 and DM-3 was in line with expectations, with the dissolution rate for each dropped below 1 mg/cm^2/hr. It is likely due to the extreme grain reshaping that the dissolution rate dropped, as the galvanic effect was less effective in detaching grains from the bulk material.

TABLE II
SUMMARY OF THE ECAP PROCESSING PARAMETERS AND RESULTS FOR EXTRUDED DM-1 AND AS-CAST DM-2 & DM-3

Dissolution Rate (mg/cm2/hr)			
Material	As-Cast	Extruded	ECAP
DM-1	-	37.5	35.4
DM-2	12	-	0.7
DM-3	1	-	0.5

D. Metallographic Analysis

Metallographic analysis shows a remarkable refinement of grains in DM-1. The new grains grew within existing grains during processing, implying dynamic recrystallization occurred [25]. The refined grains did not substantially increase the strength, but did increase ductility. It is possible that grain size is not the only factor influencing the mechanical properties.

Elongated grains were observed in ECAP DM-2, along with shear bands. As-cast grains were not refined, but were elongated. The elongation of the grains and the secondary phases would arrest the movement of dislocations, explaining the increase in strength. The elongated grains of the rare earth secondary phases increased the corrosion resistance of the bulk material.

The as-cast DM-3 had two distinct phases, with the second phase segregated at the grain boundary. Grain refinement with no twinning is observed after ECAP, demonstrating grain recrystallization due to the high temperature. The large interconnected secondary phase in the as-cast material was broken down in SPD. In the as-cast material, the interconnected grains arrest the dissolution rate. ECAP further reduced the dissolution rate as corrosion resistant phases are interspersed throughout the matrix.

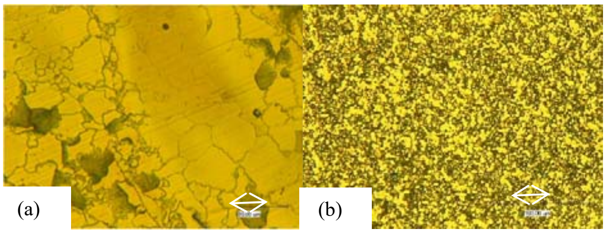

Fig. 12 1000x metallographic results with scale bar at 100 µm for DM-1 from (a) as-cast condition and (b) ECAP, from the flow plane.

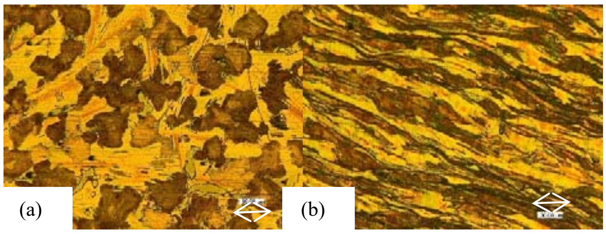

Fig. 13 1000x metallographic results with scale bar at 100 µm for DM-2 from (a) as-cast condition and (b) ECAP, from the flow plane

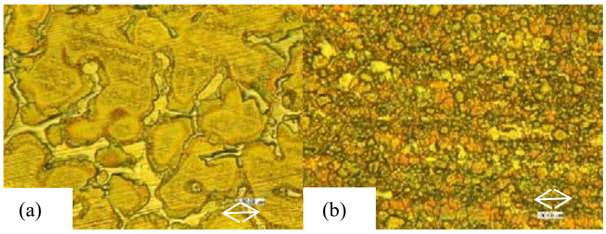

Fig. 14 1000x metallographic results with scale bar at 100 µm for DM-3 from (a) as-cast condition and (b) ECAP, from the flow plane.

IV. CONCLUSION

A study of dissolvable magnesium in two conditions, cast and extruded, was completed to understand their response to ECAP. An assessment of the mechanical and dissolution properties showed variable results:

(1) An extruded alloy DM-1 had similar dissolution rates, higher ductility, but lower yield at elevated temperatures. Dynamic recrystallization was responsible for the high ductility.
(2) An as-cast alloy DM-2 saw an increase in yield but decrease in ductility and dissolution rate, with grains elongating rather than reducing.
(3) Mechanical properties of another as-cast magnesium alloy DM-3 all at least doubled and demonstrated high temperature stability with grain refinement occurring. The initially low dissolution rate was also reduced.

Bimodal microstructures were avoided through ECAP. The study demonstrated that it is feasible to ECAP commercial dissolvable magnesium to modify mechanical properties for specific applications without changing dissolution rate. It is also viable to ECAP as-cast alloys directly, but homogenization beforehand may be an improvement over directly ECAP. The enhanced mechanical properties are useful for advanced performance dissolvable components and frac plugs.

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