INFLUENCE OF RRA TREATMENT ON MICROSTRUCTURE AND STRESS CORROSION CRACKING BEHAVIOR OF SPRAY FORMED 7075 ALLOY

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The effects of retrogression via under pre-aging on microstructure, mechanical properties and stress corrosion cracking behavior of spray formed 7075 aluminum alloy were investigated by transmission electron microscope, tensile test and slow strain rate test. The results show that with under aging at 120°C for 16 h as pre-aging, the strength of the alloy can maintain at a high level and grain boundary precipitates are discrete after retrogression and re-aging treatment. However, retrogression treatment is uncontrollable by shortened retrogression period. After retrogression at 200°C for 8 min and re-aging, the ultimate tensile strength, elongation and SCC index of the alloy is 791 MPa, 8.5% and 0.155 respectively.

Keywords: *spray forming, 7075 alloy, under aging, retrogression, stress corrosion cracking, strength.*

The 7075 (Al–Zn–Mg–Cu) alloys have been widely used in the aerospace industry, due to their desirable specific mechanical properties [1–4]. Until spray forming has been used on 7075 alloy in 1990s, the strengths are elevated to over 730 MPa [5, 6]. Many papers have reported the effects of heat treatments on 7075 alloy which belongs to aging strengthening aluminum alloy. Silva et al. [7] and Ricker et al. [8] report that both high strength and corrosion sensibility are obtained in 7075 aluminum alloys after T6 treatment. The authors [9–11] find loss of strength of about 10…15% after T73, T74 or T76 treatment in their studies of over-aging on corrosion resistance of 7075 alloys.

For the contradiction between strength and corrosion resistance, Cina [12] (Israel Aircraft Industries Ltd., 1974) present a three-stage treatment (retrogression and re-aging, RRA). In next researches [13, 14] find that the strength is maintained at T6 level by RRA treatment and the stress corrosion cracking (SCC) resistance is close to T7 at the same time. Su et al. [15, 16] report that the RRA treatment also can improve the intergranular corrosion and exfoliation corrosion sensibility of a spray formed 7075 alloy.

The RRA treatment is divided into pre-aging, retrogression and re-aging. Ohnishi [17, 18] consider the peak aging to be the best pre-aging in RRA treatment process. This type of pre-aging has been used until now. In recent years, scholars report some different opinions. Lin [19] mentions that the peak aging is not a perfect pre-aging in a U.S. patent and then Han et al. [20] also discover the similar conclusion. With regard to pre-aging in RRA treatment, some arguments in the academia and studies on the type and reason of pre-aging have not been reported.

The common retrogression is always treated at high temperature for a short time, which is only dozens of seconds and even several seconds. Wu et al. [21] and Reda et al. [13] find that the sufficient retrogressed effects can be received by long-time retrogressions at a temperature below 200°C but the mechanical properties are lost at the same time.

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So to offer a data to optimize aging treatments on spray formed 7075 alloy and references for the next step research, this paper studies the retrogression on microstructure mechanical properties and SCC behavior of spray formed 7075 alloy via under aging by transmission electron microscope (TEM), tensile test and slow strain rate test (SSRT).

Experimental. The experimental material was 7075 alloy, with composition (wt.%): 5.48 Zn; 2.21 Mg; 1.48 Cu; 0.189 Cr; 0.371 Fe and 0.121 Si.

The technological parameters of spray forming were as follows: atomization gas was nitrogen (N_2), spray distance – 370…380 mm, substrate eccentricity – 60…65 mm, conduit bore – 3.6 mm, angle of incidence – 37°…39°, spray temperature – 770…780°C, crucible temperature – 735…745°C, horizontal velocity – 0.15 mm/s, and vertical velocity – 0.18 mm/s.

The bars after hot extrusion (temperature – 400°C; ratio – 30:1; rate – 1.5 mm/s) were made into test samples of the diameter 12.8 mm for two-stage solid solution (450°C for 1 h and 475°C for 2 h, water quenched to room temperature). Specimens were pre-aged at 120°C for 16 h, retrogressed at 160; 200 and 240°C for ~4 h, and re-aged at 120°C for 24 h.

SCC behaviors were tested by SCC-1 stress corrosion experimental system corresponding to international standard ISO 7539-7: 2005 (Corrosion of metals and alloys – Stress corrosion testing, Part 7: Method for slow strain rate testing), strain rate was 10^{-6} s^{-1} in dry air or 3.5 wt.% NaCl solution at 35±1°C until cracking.

The 3 mm diameter disks for TEM observation were punched out directly from samples which were mechanically ground down to 60 μm thickness after aging. These disks were electropolished using a DJ-2000 twin-jet electropolisher with a 30% nitric acid solution in methanol at −30°C. TEM examinations were performed using a JEM-2100 transmission electron microscope.

Results. Figure 1 shows the ultimate tensile strength (UTS) and conductivity of the alloy during retrogression at 160; 200 and 240°C and corresponding re-aging. From Fig. 1, it can be seen that all tensile strength curves of retrogression decline abruptly at first, subsequently rise since falling to a certain degree, and finally declined again. Three tensile strength curves during retrogression have the similar characteristics, but the times of reaching the minimum and peak of strength are different, which depend on retrogression temperatures. Because the diffusion rate of solute and vacancy is positive correlation with retrogression temperature, it implies that the time is shortened by high retrogression temperature.

The tensile strength curves during RRA are also similar. With the retrogression time extension, the tensile strength increased firstly and then reduced after a peak value. The timing of peak strength is between the minimum and the peak of tensile strength of the retrogression curve. With the retrogression temperature increase the time of reaching peak strength is obviously shortened after RRA. The strengths are also influenced by retrogression temperature. When the samples are retrogressed at 160°C, the peak tensile strength of the alloy after RRA is 772 MPa (see Table). With the retrogression temperature increase, tensile strength of the alloy increases gradually. When the samples are retrogressed at 200°C, the peak tensile strength of the alloy after RRA is 791 MPa. Then, when the retrogression temperature is increased to 240°C, the peak tensile strength of the alloy after RRA is only 773 MPa, which is less than that via retrogression at 200°C.

It also can be seen that the conductivities rise sharply incipiently and then gently with the retrogression time extension. The regularity of conductivities is also influenced by retrogression temperature. When the samples are retrogressed at 160°C, the rangeability of conductivity is small. In case of the retrogression above 200°C, the amplifi-

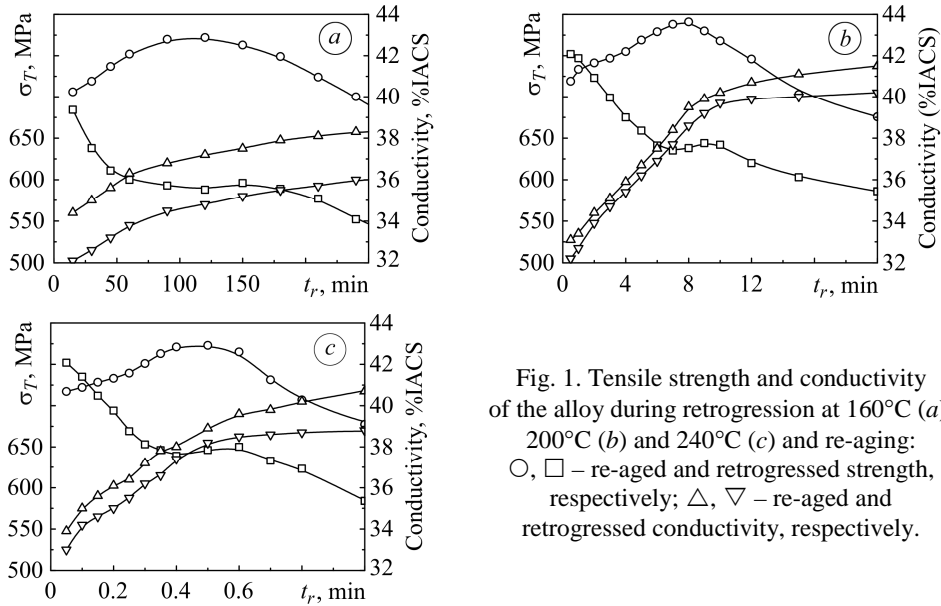cation of the conductivity is obvious. The conductivities can be improved to 40% IACS and more.

Fig. 1. Tensile strength and conductivity of the alloy during retrogression at 160°C (*a*), 200°C (*b*) and 240°C (*c*) and re-aging: ○, □ – re-aged and retrogressed strength, respectively; △, ▽ – re-aged and retrogressed conductivity, respectively.

Properties of the alloy after different retrogressions and re-aging treatment

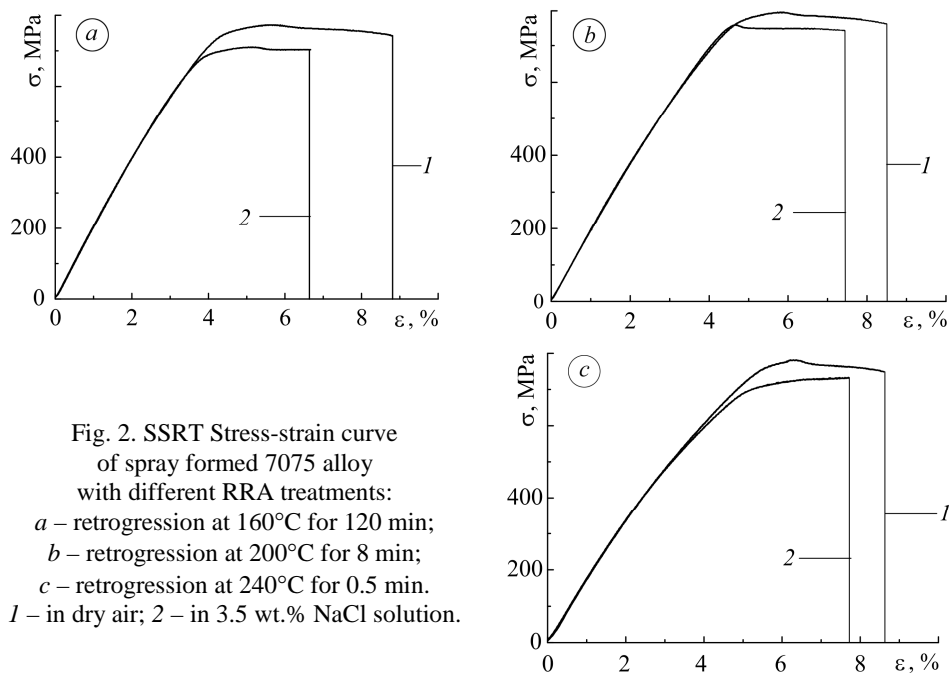| Pre-aging, °C×h	Retrogression, °C×min	Re-aging, °C×h	Conductivity, % IACS	UTS, MPa		Elongation, %		I_{SSRT}
				air	NaCl	air	NaCl	
120×16	160×120	120×24	37.2	772	710	8.8	6.6	0.287
120×16	200×8	120×24	39.5	791	756	8.5	7.4	0.155
120×16	240×0.5	120×24	38.8	773	737	8.6	7.7	0.136

Figure 2 shows the stress-strain curves of SSRT in dry air and 3.5 wt.% NaCl solution after three kinds of RRA treatments. From Fig. 2, it can be found that the decrements of UTSs in NaCl solution are similar. However, the decrements of elongations in NaCl solution among three kinds of RRA treatments are very different. With the retrogression at 160°C for 120 min, the elongation falls down from 8.8% (in dry air) to 6.6% (in 3.5 wt.% NaCl solution). This decrement of elongation is 25%, which is far more than those for other RRA treatments with retrogression at 200°C and 240°C.

To judge the SCC resistance, SCC index I_{SSRT} was defined by processing various mechanical properties of SSRT.

$$I_{SSRT} = 1 - \frac{\sigma_{NaCl} \times (1 + \delta_{NaCl})}{\sigma_{air} \times (1 + \delta_{air})},$$

where σ_{NaCl}, σ_{air} – the UTS in 3.5 wt.% NaCl solution and in dry air (MPa), respectively; δ_{NaCl}, δ_{air} – elongation in 3.5 wt.% NaCl solution and in dry air (%), respectively. With the I_{SSRT} close to 0, the SCC resistance increases. SSRT properties of spray formed 7075 alloy after various RRA treatments are also listed in the Table.

Fig. 2. SSRT Stress-strain curve
of spray formed 7075 alloy
with different RRA treatments:
a – retrogression at 160°C for 120 min;
b – retrogression at 200°C for 8 min;
c – retrogression at 240°C for 0.5 min.
1 – in dry air; *2* – in 3.5 wt.% NaCl solution.

Discussion. The usual precipitation sequence of 7xxx series aluminum alloys can be summarized as [2]: SSS (super-saturated solid solution) → GP zones → metastable $\eta' \to$ stable η. GP zones are metastable, coherent solute clusters of Zn, Mg and Cu. The metastable η' phases, Al, Cu and Mg components based on a solid solution of $MgZn_2$, $Mg(ZnCuAl)_2$ or $Mg(Zn_2, AlMg)$ appear as discrete platelet particles that are semi-coherent with the matrix, which are known to populate within the grains, and η is pseudostable, non-coherent of the same phase appearing as rods or plates, which are known to populate the grain boundary.

There is the intimate relationship between the microstructure and properties of 7xxx series aluminum alloys. The properties of the 7xxx series aluminum alloys depend on matrix precipitates (MP), grain boundary precipitates (GBP) and precipitate free zones (PFZ). According to the selected optimized heat treatment process, combination property can be obtained by cooperation of these above-mentioned three microstructures.

In microstructures the strength of the alloy mainly relies on MP. In the whole aging process, the strength of the alloy changes with the GP zone characteristic, η' and η. The best strength depends on thin homogeneous dispersive MP. Plasticity, toughness and SCC resistance of the alloy are remarkably influenced by structure and chemical property of GBP. There is a popular belief that continuous GBP are harmful to the alloy properties. Because relative movement of crystalline grains in deformation process has been impeded by continuous GBP, plasticity and toughness of the alloy are completely injured. On the other hand, the continuous GBP are preferentially dissolved as anodes in anodic dissolution theory. Because the potential of GBP, PFZ and matrix is −1.05 V; −0.85 V and −0.75 V, respectively, the potential difference (PD) between GBP and PFZ is less than the PD between GBP and matrix [22]. With regard to SCC resistance of the alloy, widening of PFZ can remit SCC sensibility and improve SCC resistance of the alloy.

Figure 3 shows the TEM images of the alloy pre-aged at 120°C for 16 h and 24 h. From Fig. 3*a*, it can be found that the MPs are small and rare after early aging at 120°C for 16 h. Because precipitation is deficient, the GBPs are small, continuous and semi-continuous. After T6 treatment (120°C for 24 h), the MPs are dispersively distributed,

most sizes are 1…2 nm, but some big size precipitates are more than 10 nm, which are formed by precipitates growing during aging (Fig. 3b) GBPs are discrete, but close, like a chain. There are few PFZ at grain boundaries after pre-aging treatments. Continuous or chain-shaped GBPs are harmful to SCC resistance of the alloy, so the SCC sensibility is high in 7075 alloy for T6 treatment.
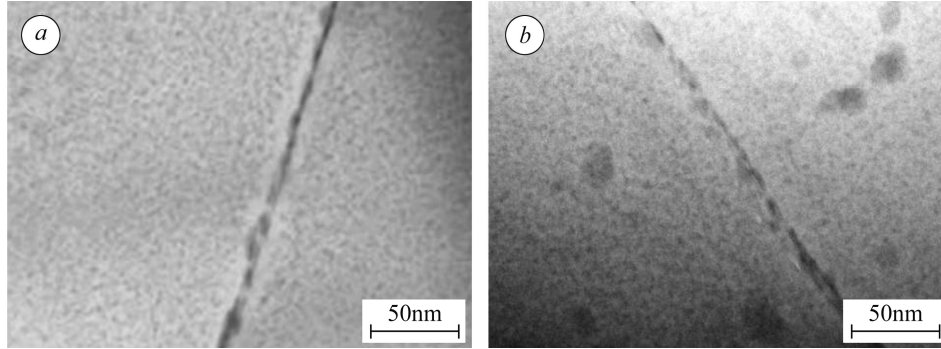

Fig. 3. TEM images of alloy pre-aged at 120°C for 16 h (a) and 24 h (b).

Figure 4 shows TEM images of the alloy after different retrogression and re-aging treatments. The MP are only partly redissoloved in the matrix after retrogression at a low temperature (160°C) via pre-aging at 120°C for 16 h, GBPs are discrete and the obvious PFZ are left at the grain boundaries (Fig. 4a). After RRA with under pre-aging and low temperature retrogression, thin homogeneous dispersive MP are separated out again in the matrix, which average sizes are less than 5 nm. PFZ width is 15…20 nm.

After RRA treatment (Fig. 4b) it is because of high strength that the MP are separated out by alloy elements where lots of the MPs smaller than critical dimension are dissolved under retrogression treatment. GBPs are thick and discrete. Those GBPs can constitute an obstacle to forming the galvanic corrosions and improve corrosion resistance of the alloy. The data shows that the conductivity increases and the SCC index I_{SSRT} decreases [23].

It can be seen (Fig. 4c) that most of MP have been redissolved in the matrix after retrogression at 200°C. Parts of GBP have been redissolved, and others grow up along the grain boundaries. So the GBPs are long and discrete. After re-aging, the MPs are thin, homogeneous and dispersive and GBPs are rounded and discrete obviously. The MP size is about 2 nm. The average size and spacing of the GBP is 5…7 nm and more than 10 nm respectively (Fig. 4d). The SCC resistance of the alloy is improved by those discrete GBPs.

With the retrogression at 240°C (Fig 4e) the situation of MP mostly redissolved in matrix is similar to that after retrogression at 200°C. But the morphology at grain boundary is different. The GBPs are semi-continuous, the sizes and spacing of the GBPs are small and some GBP are arranged side by side. After re-aging, the MPs are coarsened and grown, whose sizes increased from 1…2 nm to 3…5 nm. The GBPs are still semi-continuous and the phenomenon of GBP arranged side by side disappeared. The PFZ are widened to 5 nm, but they are still less narrow than at others effects of retrogression treatments, as shown in Fig. 4f. The SCC resistance of the alloy can be improved to a certain extent by aforementioned grain boundary structures.

The short time of retrogression at 240°C is the main factor of the alloy after RRA treatment effect on the properties. Because the retrogression time is only dozens of seconds, there occur the phenomena of nonuniform heat treatment of the samples, even though thin sheets. When the optimum effect has been found on the surface of the sample, the inside of the sample is uncompleted. When the inside of the sample is suited by

retrogression, the surface of the sample has already been an overtreatment. So the strength, conductivity and SCC index I_{SSRT} of the alloy via retrogression at 240°C all are not better than that via other retrogression treatments.
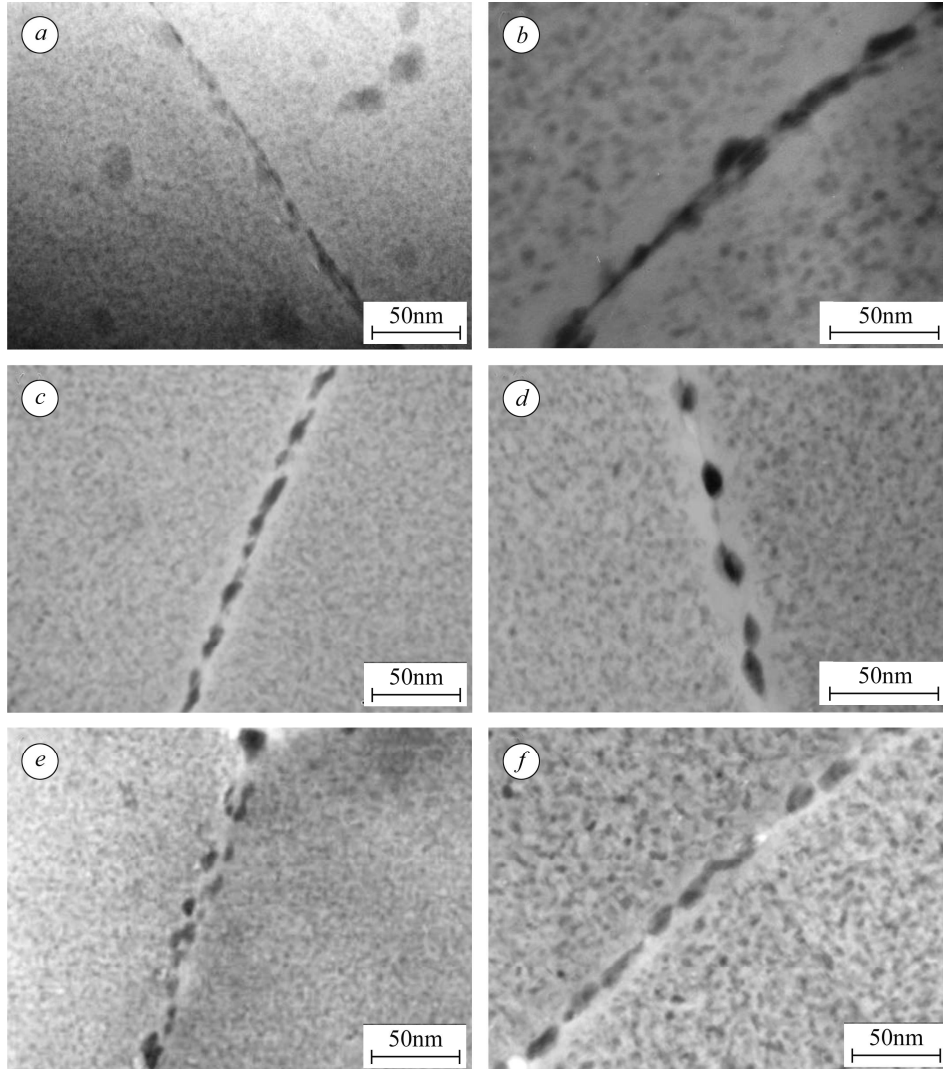

Fig. 4. TEM images of the alloy after different retrogression and re-aging treatments via under pre-aging: *a*, *b* – retrogressed at 160°C for 120 min and re-aged, respectively; *c*, *d* – retrogressed at 200°C for 8 min and re-aged, respectively; *e*, *f* – retrogressed at 240°C for 0.5 min and re-aged, respectively.

CONCLUSION

With the under aging at 120°C for 16 h as pre-aging in RRA treatment, the following conclusions have been drawn on three retrogression treatments of spray formed 7075 alloy:

– most of the matrix precipitates (MP) are redissolved in matrix and the grain boundary precipitates (GBP) are discrete obviously after retrogression at 200°C for 8 min. After re-aging, the UTS, elongation and SCC index of the alloy is 791 MPa, 8.5% and 0.155, respectively.

– MPs are only partly redissoloved in the matrix after retrogression at a low temperature (160°C), the GBPs are discrete and the obvious PFZ are left at the grain

boundaries. After RRA with low temperature retrogression, thin homogeneous dispersive MP are separated out again in the matrix, which average sizes are less than 5 nm.

– MPs separated out of the matrix during pre-aging are effectively redissolved and GBPs are interrupted by retrogression at 240°C, but the retrogression of the time of dozens of seconds is hardly controlled. There are some differences in the degree of treatment between the surface and inside of the sample, so the properties of the alloy after RRA are not perfect.

– the SCC index I_{SSRT} is influenced by a combined action of GBP and PFZ. Continuous GBP and narrow PFZ increase the SCC susceptibility and SCC index I_{SSRT} of the alloy. However, the discrete GBP and wide PFZ can improve SCC resistance and reduce SCC index I_{SSRT} of the alloy.

РЕЗЮМЕ. Вивчено вплив RRA-обробки, яка полягає у витримці сплавів після штучного старіння у соляній ванні при 200°C і повторному штучному старінні, на мікроструктуру і механічні властивості алюмінієвого сплаву 7075. Для досліджень використано трансмісійний електронний мікроскоп. Зразки випробовували на розтяг за малої швидкості деформації. Встановлено, що після RRA-обробки вторинні частинки уздовж меж зерен виділяються дискретно. Під час такої обробки при 200°C упродовж 8 min границя міцності за розтягу, відносне видовження та коефіцієнт чутливості до корозійного розтріскування сплаву становлять 791 MPa, 8,5% та 0,155 відповідно.

РЕЗЮМЕ. Изучено влияние RRA-обработки, заключающейся в выдержке сплавов после искусственного старения в соляной ванне при 200°C и повторном искусственном старении, на микроструктуру и механические свойства алюминиевого сплава 7075. Для исследований использован трасмиссионный електронный микроскоп. Образцы испытывали на растяжение и при малой скорости деформации. Выявлено, что после RRA-обработке вторичные частицы вдоль границ зерен выделяются дискретно. При такой бработке при 200°C в течение 8 min предел прочности при растяжении, относительное удлинение и коэффициент чувствительности к коррозионному растрескиванию сплава составляют 791 MPa, 8,5% и 0,155 соответственно.

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