Laser Shock-Induced High-Entropy Structure on Aerospace Aluminum Alloy Surface and Its Corrosion Resistance (Postprint)

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Date: 2023-03-19T00:00:00+00:00

Abstract

Laser shock surface modification experiments were conducted on 7075-T76 aviation aluminum alloy, utilizing SEM and TEM to analyze the microstructure of the shock-affected layer, the evolution process and formation mechanism of the amorphous/nanocrystalline composite high-entropy alloy layer obtained on the surface, as well as its mechanical properties and corrosion resistance. The results demonstrate that the adiabatic shear thermal effect induced by the ultra-high energy and ultra-rapid process of laser shock triggers an entropy increase effect and redistribution in the surface alloy system of the material. The increased mixing entropy of the alloy system promotes enhanced disorder among constituent elements, thereby mitigating the detrimental effects of impurity atoms. The external field energy supplied by laser shock facilitates the conversion of the entropy increment into a reduction of the Gibbs free energy ΔGconf required for amorphous structure formation in the alloy. During the process of multiple laser shocks under powerful external field energy, the multi-component aluminum alloy undergoes spontaneous reorganization among its constituent elements in accordance with Boltzmann' s law, while the dynamically precipitated nanocrystalline structures serve to coordinate the system' s degree of non-equilibrium, rendering the obtained high-entropy amorphous structure more thermodynamically consistent with the requirements of Boltzmann relationships. Through thermodynamic self-adjustment and microstructural reorganization, the laser shock layer ultimately comprises a composite of amorphous/nanocrystalline particles. Concurrently, the intense microscopic stress induced by the ultra-high strain rate of laser shock causes overall plastic deformation of the aging precipitated phases, generating parallelly distributed deformation twins that synergistically absorb the laser shock energy. Due to the elimination of grain boundary strengthening and reduction of dislocation density, laser shock primarily manifests as a structural reorganization effect. The hardness of the laser-shocked surface layer increases after a single laser shock, and gradually becomes comparable to the substrate hardness with increasing number of shock impacts. The intense deformation induced by laser shock can refine the nanocrystalline size within the aluminum alloy surface layer to 2–3 nm. The amorphous state eliminates galvanic corrosion around second phases, thereby significantly improving the corrosion resistance of the amorphous/nanocrystalline composite surface layer obtained through laser shock on 7075-T76 aviation aluminum alloy.

Full Text

Surface Layer High-Entropy Structure and Anti-Corrosion Performance of Aero-Aluminum Alloy Induced by Laser Shock Processing

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Supported by National Natural Science Foundation of China (Nos.51275220 and 51105179)

Manuscript received 2014-05-25, in revised form 2014-09-10

Abstract

Laser shock surface modification experiments were conducted on 7075-T76 aeronautical aluminum alloy. The microstructure of the shocked layer, the evolution process and formation mechanism of the amorphous/nanocrystalline composite high-entropy alloy layer obtained on the surface, and its mechanical properties and corrosion resistance were analyzed using SEM and TEM. The results show that the adiabatic shear thermal effect induced by the ultra-high energy and ultra-fast process of laser shock causes an entropy increase effect and redistribution in the surface alloy system. The increase in mixing entropy of the alloy system promotes higher randomness among components and weakens the adverse effects of impurity atoms. The external field energy provided by laser shock promotes the conversion of this entropy increase into a reduction of the Gibbs free energy ΔGconf required for amorphous structure formation in the alloy. During multiple laser shock processes with powerful external field energy, the components in the multi-element aluminum alloy spontaneously reorganize according to Boltzmann' s law, while the dynamically precipitated nanocrystalline structures coordinate the non-equilibrium degree of the system, making the obtained high-entropy amorphous structure more consistent with the thermodynamic requirements of the Boltzmann relationship. Through thermodynamic self-adjustment and microstructural reorganization, the laser shock layer is ultimately composed of amorphous/nanocrystalline composite structures. Meanwhile, the intense micro-stress induced by the ultra-high strain rate of laser shock causes overall plastic deformation of aging precipitates, generating parallel deformation twins that synergistically absorb laser shock energy. Due to the disappearance of grain boundary strengthening and reduction of dislocation density, laser shock mainly manifests as a structural reorganization effect. The surface hardness of the laser-shocked layer increases after a single shock, but gradually approaches the substrate hardness with increasing shock number. The intense deformation caused by laser shock can reduce the nanocrystalline size in the aluminum alloy surface layer to 2–3 nm. The amorphous structure eliminates galvanic corrosion around second phases, thereby significantly improving the corrosion resistance of the amorphous/nanocrystalline composite surface layer obtained on 7075-T76 aluminum alloy.

Keywords: laser shock, aeronautical aluminum alloy, surface modification, high-entropy alloy, amorphous, nanocrystalline, anti-corrosion

Introduction

The study of intense laser-matter interaction has always been at the forefront of scientific research, with the most prominent phenomenon being the high-pressure shock wave effect. When the power density of a short-pulse laser is sufficiently high (>1 GW/cm^2), the energy conversion layer on the material surface rapidly vaporizes upon absorbing laser energy, simultaneously forming rapidly expanding high-temperature dense plasma that induces a high-temperature, high-pressure shock wave propagating into the material interior. This can be used to improve the surface mechanical properties and corrosion resistance of metallic materials [1–5].

7075 aluminum alloy belongs to the Al-Zn-Mg multi-component ultra-hard aluminum series and is a widely used ultra-high strength wrought aluminum alloy in the aviation industry. However, this 7××× series aluminum alloy rich in second phases has a tendency toward intergranular corrosion, especially in profiles where grains are deformed into elongated strips with parallel grain boundaries. When intergranular corrosion proceeds along the length direction under long-term environmental factors, the material becomes delaminated layer by layer, causing thickness-direction expansion of components. Consequently, exfoliation corrosion becomes a special form of corrosion for this alloy, accounting for numerous maintenance tasks for civil aircraft.

Yeh et al. [6] proposed the concept of high-entropy alloys. By selecting appropriate alloy systems, it is possible to obtain nanoscale particles with dispersion strengthening effects or even amorphous phase structures. High mixing entropy alloy systems have four main effects: high-entropy effect in thermodynamics, sluggish diffusion effect in kinetics, lattice distortion effect in crystal structure, and cocktail effect in properties. This new concept breaks traditional alloying design philosophy and opens a new field of alloy design. High-entropy alloys have attracted increasing research attention due to their enormous application potential [7-9]. Currently, high-entropy alloys are mainly obtained as bulk materials through vacuum arc furnace casting. Even for surface modification studies using high-entropy alloys, most researchers first obtain high-entropy alloy bulk materials through arc melting and then apply them to surface modification processes using other methods, such as obtaining high-entropy alloy coatings through subsonic flame spraying technology. This makes the application of high-entropy alloys in surface modification rather complex and hinders their application to some extent [10-14]. Additionally, as-cast high-entropy alloys have a tendency toward nanocrystallization and amorphization [15,16], and high-entropy alloy coatings can be obtained on alloy surfaces through laser remelting [17,18]. It is evident that high energy may cause microstructural reorganization on alloy surfaces. Laser shock possesses ultra-high energy and thermodynamic/kinetic loading characteristics far from equilibrium. When acting on alloy surfaces, it is worth exploring whether high-entropy alloy surface layers with specific properties can be obtained through reorganization of alloy components and microstructures in multi-component alloy materials. Therefore, this work applies laser shock surface modification technology to prepare an alloy layer on the surface of multi-element aluminum alloy materials with the same composition as the substrate but different properties, studies its microstructural evolution, and examines its corrosion resistance.

Experimental

Materials

The experimental material used was an age-hardening 7075-T76 aluminum alloy of the Al-Zn-Mg-Cu-Cr system. Its chemical composition (mass fraction, %) was: Zn 5.94, Mg 2.64, Cu 1.42, Cr 0.199, Zr 0.0151, Fe 0.172, Si 0.0925, Mn 0.0293, Ti 0.0244, Al balance. The T76 treatment consisted of heating at 480 °C for 2 h, water quenching, aging at 120 °C for 5 h, and then aging at 153 °C for 16 h [19]. Laser shock specimens measured 40 mm × 20 mm × 2.6 mm.

Laser Shock Processing

Experiments were conducted on a GAIA-R series Nd:YAG solid-state pulsed laser system. The laser employed a multi-mode stable resonator structure with Pockels cell Q-switching. Its main technical parameters were: output of energy-flat-top beam, laser pulse output energy 12.5 J, energy stability root-mean-square value 5.1, output spot diameter approximately 3 mm, central wavelength 1064 nm, laser pulse width (FWHM) approximately 10 ns, divergence angle 9.52 mm · mrad, and maximum repetition frequency 5 Hz. The laser shock experimental setup is shown in [Figure 1: see original paper]. The shock scanning route employed radius overlap in both longitudinal and transverse directions, with specimens subjected to 1–3 laser shocks. Before laser shock, the specimen surface was covered with a 0.1 mm thick specialized Al foil as an energy conversion layer, with flowing water as the confinement layer. The pulsed intense laser caused the covering layer to ionize, and the induced shock wave bombarded the sample surface.

Characterization Methods

Corrosion tests were conducted according to the GB/T 7998-2005 method for determination of intergranular corrosion of aluminum alloys. A HVS-1000 digital microhardness tester was used to measure the hardness distribution from the surface along the depth direction at strengthened locations. An S-3400N scanning electron microscope (SEM) was used to observe microstructural evolution in the laser shock cross-section, and a JEM-2100 high-resolution transmission electron microscope (TEM) was used for microstructural analysis. Thin-film specimens of the laser shock modified layer were first cut along the depth direction using wire electrical discharge machining to obtain predetermined thin layers, then pre-thinned from the substrate side toward the surface, followed by dimpling, and finally twin-jet thinning. The twin-jet solution consisted of 94% ethanol and 6% $HClO_4$ by volume fraction, with temperature and voltage of -30 °C and 30 V, respectively. Final thinning was performed on both sides using a GL-6960 ion miller until the thin area of the crystal specimen met observation requirements.

Results and Discussion

2.1 Original Microstructure Before Laser Shock

The 7075-T76 Al-Zn-Mg-Cu-Cr aluminum alloy substrate consisted of an alloy solid solution with reduced saturation, with relatively high dispersion aging precipitates distributed throughout. These fine particles precipitated from the supersaturated solid solution at aging temperatures, with early stages being GP zones and h phase. GP zones have a coherent relationship with the matrix, while h phase has a semi-coherent relationship with the matrix. The final precipitates in the alloy are larger h and h phases [20]. [Figure 2: see original paper] shows TEM images of the original microstructure of 7075-T76 aluminum alloy plate. Figure 2a shows the matrix microstructural state, where original grain boundaries, rod-shaped and larger granular precipitates, and some dislocation networks and tangles are visible. Among the precipitates, the keyhole-shaped ones are Mn-phase $(FeMn)Al_6$, hundreds of nanometers long; the irregular disc-shaped ones are Cr-phase $Al_{18}Cr_2Mg_3$, approximately 200 nm in diameter. Figure 2b shows the dispersed distribution state of aging precipitates in the matrix.

2.2 Surface Layer Morphology After Laser Shock

[Figure 3: see original paper] shows SEM images of the surface layer of 7075-T76 aluminum alloy after different numbers of laser shocks. As shown, the surface layer morphology changed significantly after different numbers of laser shocks. After etching with corrosive agent, the laser shock strain layer and substrate both have clear boundaries, with total strain layer depth of approximately 100 m, but grain morphology cannot be distinguished within the strain layer. Notably, the shock strain layer consists of two parts. After a single laser shock, a thin layer approximately 20 m deep appears along the surface within the strain layer, as shown in [Figure 3: see original paper]a. After three laser shocks, this layer thickness increases to over 40 m, but the total laser shock strain layer thickness remains essentially unchanged ([Figure 3: see original paper]b), indicating that during laser shock, the original grain structure within the surface layer undergoes component and microstructural reorganization after shock plastic strain, and the number of laser shocks has a significant effect on the formation of the surface thin layer. The total depth of the laser shock strain layer is mainly related to laser shock energy and also to the flat-top energy distribution of the laser beam output from the new GAIA laser, which enables uniform distribution of laser energy within the shock layer and results in more uniform strain layer thickness than that obtained under Gaussian energy distribution.

2.3 Surface Hardness After Laser Shock

[Figure 4: see original paper] shows the hardness distribution curves of 7075-T76 aluminum alloy after different numbers of laser shocks. As seen, laser shock has an obvious effect on the surface hardness of 7075-T76 aluminum alloy, but differs from general laser shock hardness variation patterns. In the case of a single laser shock, hardness near the surface first decreases, then increases with depth, reaching a maximum approximately 11% higher than the substrate hardness of the actual specimen state, with an affected layer depth exceeding 80 m, then gradually decreasing to the substrate hardness. After three laser shocks, the surface hardness of the shock layer becomes relatively stable, essentially matching the substrate hardness of the specimen material.

2.4 Microstructural Evolution Mechanism

2.4.1 Energy Conditions for High-Entropy Evolution Laser shock energy has a high-temperature effect on the material surface. Due to the extremely short laser shock duration and shallow penetration depth, the relationship between material surface temperature T and shock time t is [21]:

The time tm required for laser shock to reach the melting point Tm on the metal surface is:

For typical laser power densities used in metal laser shock processing, which generally reach 10^9 W/cm^2, and without considering changes in metal physical properties, the time tm required to reach the melting point of aluminum alloy (660 °C) during laser shock strengthening is 2.61×10^{-3} ns.

2.4.2 Microstructure of Single Shock Surface Layer TEM images of the microstructure in the surface layer of 7075-T76 aluminum alloy after a single laser shock are shown in [Figure 5: see original paper]. Laser shock induces numerous dislocations and dislocation tangles in the matrix. Compared with the original material, in addition to aging precipitates, the originally clear matrix exhibits a large number of dense, fine dark dot-like structures, indicating obvious laser shock deformation strengthening effects. [Figure 5: see original paper]b shows an HRTEM image of the dot-like structures in [Figure 5: see original paper]a, where nanocrystalline structures have diameters of 6–8 nm, with the remainder being amorphous structure. The boundary state between the two structures cannot be distinguished, indicating that under the ultra-high energy of laser shock, re-partitioning and recrystallization of alloy components occur within material surface grains. Since laser shock is a transient thermal process with extremely large undercooling, the recrystallization process in the shock layer causes the system to undergo an entropy increase process, meaning laser shock significantly increases the disorder degree of alloy atoms within the shock layer.

[Figure 6: see original paper] shows TEM images and electron diffraction patterns of typical micro-areas in the single laser shock surface layer. The microstructure and contrast of the laser shock layer are relatively uniform. Combined with [Figure 5: see original paper]b, it can be seen that this region is a mixed microstructure area of amorphous and crystallized phases, i.e., nanocrystalline grains are uniformly embedded in the amorphous phase. This indicates that after formation of the laser shock strain layer, both amorphous and crystallized phases exist, and the original components have undergone re-partitioning behavior [22].

Since the power density of laser shock strengthening is extremely high ($>10^9$ W/cm^2), the time required for the metal surface to reach the vaporization point under high laser power density irradiation is less than 1 ns. Due to the extremely short maintenance time of laser shock strengthening, real-time measurement of the laser shock temperature field is currently not feasible. Therefore, during laser shock, due to the shallow action depth, good thermal conductivity of the specimen, and large temperature difference between surface and substrate, the instantaneous solidification rate of the molten gaseous plasma is also on the nanosecond scale, which can completely suppress the heat-affected zone (HAZ), providing extremely favorable external conditions for amorphous phase formation. Meanwhile, 7075 aluminum alloy material basically satisfies the three empirical principles proposed by Inoue and Takauchi [23] for high amorphous alloy forming ability: (1) more than three main component elements; (2) atomic radius difference of main components greater than 12%; (3) negative mixing enthalpy between components. Therefore, the different atomic sizes in 7075 aluminum alloy composition play an important role in amorphous formation. Different atomic size elements cause crystal cell size expansion and crystal distortion energy, which reduces crystal stability and improves alloy glass-forming ability. Additionally, large-size atoms can form network-like or skeleton-like structures with neighboring atoms that constrain each other. Such structures can hinder atomic diffusion or atomic cluster migration, reducing the ordering degree within the system while enhancing the stability of the supercooled melt, inhibiting nucleation and growth of crystalline phases, and increasing the possibility of amorphous phase formation [24]. More importantly, almost all binary alloys in 7075 aluminum alloy have negative formation enthalpy across the entire composition range. For example, the mixing enthalpies of Al-Si, Al-Mn, and Al-Fe compositions reach -39395.31, -46331.42, and -76730.52 J/mol, respectively [25,26]. The large differences in negative mixing enthalpy values among components indicate that large negative mixing enthalpy can strengthen inter-component reactions, promote structural disordering, and thus favor amorphous formation.

From the perspective of free energy for high-entropy alloy formation, the external field energy of laser shock inevitably changes the free energy of the alloy system. Its Gibbs free energy ΔGconf follows the relationship:

$$\Delta \mathrm{Gconf} = \Delta \mathrm{Hconf} - T_1 \Delta \mathrm{Sconf}$$

where ΔHconf is the mixing enthalpy, T_1 is the thermodynamic temperature, and ΔSconf is the mixing entropy. The large negative mixing enthalpy in the system, combined with the instantaneous high temperature, ultra-high energy, and entropy increase caused by increased atomic disorder from laser shock, not only does not cause a counterbalance between ΔHconf and ΔSconf, but actually favors enhanced mutual dissolution of elements and prevents formation of long-range ordered phase structures and intermetallic compounds. The external field energy of laser shock promotes the conversion of this entropy increase into a reduction of ΔGconf required for amorphous structure formation in the alloy. At this point, TΔSconf related to the dynamic process of laser shock plays a more dominant role than the inherent thermodynamic parameter ΔHconf of the alloy system. Therefore, during laser shock, entropy increase leads to reduced Gibbs free energy, providing sufficient energy conditions for amorphous alloy formation.

During laser shock, once the shock wave formed by plasma is completed, temperature drops sharply. Within the sustained time period, this is sufficient to cause rapid cooling of the shock layer and form amorphous phases. After the first shock wave bombards the material surface to form an amorphous structure, and given that the frequency in this experiment is 5 Hz, approximately 0.2 s elapses before the second shock wave bombards the adjacent surface area. By this time, the surface temperature has already decreased. Although the second shock may dissipate heat to the surroundings, according to the loading characteristic that laser shock has no HAZ, even if temperature rises occur, they cannot cause complete crystallization of the amorphous phase due to thermal lag, meaning they cannot exert a comprehensive annealing effect on the already-formed amorphous layer to form fully crystallized structures.

However, the amorphous state is a metastable state thermodynamically with high free energy that will spontaneously transform toward lower energy states under certain conditions. During laser shock, plasma temperature exceeds 3000 K, making the temperature within the shock spot much higher than the amorphous transition temperature of the alloy. Therefore, during the cooling process of repeated shocks, the laser shock layer may cause a deglassing process of the amorphous structure formed by previous shock passes, dynamically precipitating nanocrystals [27,28]. Due to the ultra-fast process and super-strong undercooling of laser shock, this far-from-equilibrium state can provide extremely high nucleation rates for the deformation layer structure, yet cannot provide the coarsening time and growth rate of slow solidification processes, making it impossible for them to grow and leaving them in an embryonic state. This becomes one of the important reasons for obtaining dispersed nanocrystals in the laser shock layer. Consequently, a composite surface layer coexisting with amorphous and nanocrystalline structures forms after laser shock completion.

2.4.3 Microstructure of Multiple Shock Entropy-Increase Layer

[Figure 7: see original paper]a shows TEM images of the matrix structure after two laser shocks on 7075-T76 aluminum alloy. Numerous extremely dispersed black dot-like structures are visible. These black dots are not aging precipitates, as the precipitates in this alloy have been measured to be at least 50–100 nm in scale, as shown in [Figure 7: see original paper]b.

7075 aluminum alloy has complex composition. The high energy and ultra-fast speed of laser shock provide energy conditions for composition reorganization, which can induce adiabatic shear thermal softening effects (adiabatic shear effect, ASE) in the deformation region. Within the laser shock confinement zone, surrounded by a large amount of relatively cold substrate structure, the adiabatic shear zone belongs to a thermodynamically isolated system. Most plastic work manifests as "thermal function," promoting material softening and accelerated plastic flow, while another portion directly converts into energy required for micro-defect development [29,30].

Thermodynamically isolated systems obey the entropy increase law. According to multi-principal-element high-entropy alloy design theory, the molar entropy change ΔS_1 when n equivalent elements form a solid solution or amorphous phase is:

$$\Delta S_1 = R\ln(n)$$

where R is the universal gas constant. From Boltzmann' s law, mixing entropy increases with the number of element types n. The components in 7075 aluminum alloy reorganize according to Boltzmann' s law, placing nanocrystalline structures in a coordinating position and providing good buffering for the system. After multiple laser shocks, nanocrystalline structures further refine and become more dispersed, indicating that during repeated adiabatic processes of multiple laser shocks, spontaneous adjustment continues among atoms within the material surface layer, making the high-entropy amorphous structure more consistent with thermodynamic requirements of the Boltzmann relationship while making the self-adjusted nanocrystals more dispersed. This occurs because originally larger nanocrystalline structures can continue to contribute atoms required for high-entropy amorphous structure formation through partitioning during subsequent shocks, aiming to achieve structural and energy compatibility. Nanocrystals essentially become the residual phase of the amorphous phase caused by entropy increase. [Figure 8: see original paper] shows HRTEM images of the matrix after three laser shocks. The morphology in [Figure 8: see original paper]a is basically amorphous structure, where black patches may be metastable transition phases; [Figure 8: see original paper]b shows a mixed structure of amorphous and nanocrystalline grains. At this point, nanocrystal size has decreased to 2–4 nm.

2.4.4 Strain of Precipitates in Laser Shock Layer Deformation twinning is another common mode of plastic deformation in metal crystals besides slip, but its occurrence probability is much lower than slip due to factors such as stacking fault energy. However, in 7075-T76 aluminum alloy with laser shock-induced surface high-entropy evolution, twinning phenomena were observed in aging precipitates for the first time, indicating that large internal stresses were generated within the surface layer rich in aging precipitates during the high-entropy evolution process, causing these precipitates to undergo twinning strain. This phenomenon has not been found in other laser-shocked alloy materials [31]. [Figure 9: see original paper] shows TEM and HRTEM images of aging precipitates and their interface with the matrix after three laser shocks.

As is well known, aging precipitates in aluminum alloys belong to intermetallic compounds whose strength is generally significantly higher than the matrix phase. In microstructural evolution studies of laser shock in other materials, no evidence of plastic deformation of aging precipitates has been found, mostly showing that the matrix undergoes semi-coherent or pseudo-coherent plastic deformation through dislocation movement at the interface with precipitates to accommodate laser shock external field energy [32]. The deformation twins found in aging precipitates in the laser shock layer all show parallel grid-like distributions, which is very similar to twin microstructures induced by laser shock in pure Fe, stainless steel, and titanium alloys. Although twin widths in these three crystalline materials are also at the nanoscale, they mostly originate from grain boundaries and terminate within grains [33], indicating that when the ultra-high strain rate of laser shock acts on the material surface, the precipitates as a whole are subjected to powerful internal stresses from the surrounding entropy-increased matrix. Under conditions where the coherent relationship is destroyed, a “suspended shear” forms. That is, during laser shock, when high-entropy evolution occurs within original grains, microscopic internal stresses favorable for inducing overall shear of precipitates are generated, and only shear mode can better match the ultra-high strain rate of laser shock, thus forming deformation micro-twins that penetrate through precipitates. Since fcc-type aluminum alloys belong to crystals with relatively high stacking fault energy, twins are generally not observed during conventional deformation [34], while disc-shaped aging precipitates in 7××× series aluminum alloys are generally hcp-type h phase or its precursors [35]. The reason for this twinning phenomenon in precipitates after laser shock can be attributed to the ultra-high energy, ultra-high strain rate, and high-entropy evolution process-induced microscopic internal stresses during laser shock.

Thus, the phenomenon of hardness in multiple laser shock layers being basically equal to the substrate is closely related to laser shock-induced surface microstructural reorganization and the strengthened state of the material before shock. Since 7075-T76 aluminum alloy is already in a high solid solution strengthening state, material strength changes during the entropy increase process caused by laser shock due to composition reorganization and changes in microstructural composition relationships. The structure obtained by laser shock is neither completely nanocrystalline nor completely amorphous, but rather an amorphous/nanocrystalline composite structure that isolates nanocrystals from each other, eliminating grain boundary support for strength. Meanwhile, the coherent relationship between precipitates and matrix is destroyed, greatly weakening dislocation strengthening effects. Although the precipitates themselves have some degree of strain strengthening, their "suspended" state makes it difficult to properly evaluate their contribution to surface strengthening. However, their participation in overall strain within the laser shock layer absorbs some energy, which is beneficial for coordinating the overall entropy increase process.

2.5 Anti-Corrosion Performance

A NaCl solution with pH 7.5 was prepared in the laboratory according to the GB/T 7998-2005 method for determination of intergranular corrosion of aluminum alloys for corrosion testing of laser-shocked 7075-T76 aluminum alloy. The surface and cross-section morphologies after corrosion are shown in [Figure 10: see original paper] and [Figure 11: see original paper].

The original galvanic corrosion situation constituted by the matrix and h-phase precipitates on the alloy surface has undergone essential changes. The amorphous and nanocrystalline composite structure can no longer constitute positive and negative electrodes of a galvanic cell, and the corrosion characteristics of the amorphous/nanocrystalline composite material surface layer itself are completely different from those of the alloy before laser shock. Compared with the corrosion morphology of the unshocked specimen ([Figure 10: see original paper]a), the amorphous/nanocrystalline composite high-entropy alloy surface layer obtained by laser shock shows significantly improved corrosion resistance, with no cracks caused by corrosion and noticeably reduced white flocculent corrosion products. In addition to Al, 7××× series aluminum alloys contain Zn, Cu, Mg, Mn, Fe, and other metals with certain chemical activity, leading to severe surface corrosion in Cl^--containing solutions. Etch pits commonly appear on the raw material surface. From an electrochemical perspective, areas near etch pits formed during initial corrosion stages become positive due to metal cation appearance, while the sample surface surrounded by Cl^- becomes negative, forming micro-electrodes near the sample surface. The anode in corrosion pits attracts more Cl^-, causing further corrosion near the pits and increasing surface roughness. Due to the characteristics and structural uniformity of the amorphous/nanocrystalline high-entropy structure alloy layer on the 7075-T76 aluminum alloy surface, although Cl^- corrosion is selective for elements, the sample surface shows basically uniform corrosion morphology.

As seen from [Figure 11: see original paper], the laser shock high-entropy alloy surface layer exhibits excellent corrosion resistance. Etch pits on the original structure surface are continuously distributed and obviously develop deeper, while the high-entropy alloy surface layer remains intact.

Conclusions

1. The total depth of the strain layer obtained by laser shock on 7075-T76 aluminum alloy surface reaches approximately 100 m. The surface layer microstructural characteristic is a large number of nanocrystalline structures dispersed in an amorphous matrix. The high-entropy layer consists of two parts: after one shock, the depth is about 20 m with nanocrystal diameters of 6–8 nm; after three laser shocks, this layer thickness increases to over 40 m with nanocrystal diameters of 2–3 nm.
2. The amorphous and nanocrystalline composite structure obtained on the 7075-T76 aluminum alloy surface originates from the increased mixing entropy of the alloy system induced by the instantaneous high-energy, high-pressure effect of laser shock plasma. The high-disorder effect of multiple components causes re-partitioning of the material surface alloy system.
3. Due to the disappearance of grain boundary support for strength and weakened dislocation strengthening effects in nanocrystals, along with the disappearance of coherent strengthening between aging precipitates and matrix, the hardness of the amorphous/nanocrystalline structure layer gradually approaches the substrate hardness after multiple laser shocks.
4. The ultra-high strain rate of laser shock causes intense strain in the surface layer, where microscopic stress makes aging precipitates undergo overall plastic deformation, producing parallel deformation twins that synergistically absorb laser shock energy.
5. The special corrosion resistance of the amorphous structure and chemical stability of nanocrystalline grains in the laser shock high-entropy structure layer effectively improve the intergranular corrosion phenomenon of 7075-T76 aluminum alloy. The amorphous structure also prevents pit-

ting corrosion around aging precipitates by destroying the galvanic effect, further preventing corrosion occurrence.

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