Electro-healing cracks in nickel
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ABSTRACT

Healing cracks in metallic materials is challenging due to limited atomic mobility in solid state around ambient temperature. In this paper, we developed a novel crack-healing approach by means of an electrochemical process in which metallic ions in electrolyte are used as a healing agent. Pure Ni sheets with a through-thickness crack were taken as an example. Cracks with sizes in the micrometer range or larger are successfully healed by electro-healing. The electro-healing process starts with the vertical epitaxial growth of healing crystals from the original crack surfaces followed by lateral growth of healing crystals that bond with each other at atomistic level. Tensile tests exhibited that the healed samples have a comparable tensile strength as the virgin sample and some tensile ductility can be achieved for the sample of 100 μm thick. Post-fracture analysis indicated that part of the crack propagated along the substrate instead of healing crystals. The healing efficiency, ranging from 96% to 33% with an increasing sample thickness, is related to the fraction of fully-healed region and the strength difference between the substrate and the healing crystals.

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1. Introduction

Cracking is one of the most frequent ultimate failure modes for materials. Healing or repairing cracks in materials is highly desired not only from economic considerations but also for their sustainable and reliable applications. Generally speaking, conditions for healing cracks in solids include mobility of atoms of healing agent as well as bondability of these atoms to the crack surfaces [1]. A milestone work on crack healing in polymers was realized by using encapsulated polymer liquid with a substantial mobility at ambient temperature [2]. Since then significant achievements have been made in healing cracks in polymers and polymeric composites [3,4].

Crack healing in metals is challenging indeed and has been explored in recent years. Compared to polymers, metals that used as structure materials such as steels, Ti alloys and superalloys often possess high melting points. Atomic mobility or diffusivity is extremely low around ambient temperature. Attempts have been made to enhance mobility of metallic atoms by elevating temperatures to facilitate healing or repairing cracks or voids in metals. Gao et al. [5,6] reported that micro-cracks in alpha-Fe can be healed by heating the samples above 1000 K. Similar results were reported by Wei [7] and Li [8]. As the diffusion path in metals is very small, such a healing approach can only be applied for cracks with very small dimensions. In addition, elevating temperatures may alter the microstructure and properties of the base material, which may consequently result in a degradation of the material.

Recently it was realized that nano-scale open volume defects such as vacancies, vacancy clusters, and dislocations could be healed via precipitation in boron containing austenitic stainless steels [9–11]. Using positron lifetime and Doppler broadening spectroscopy, Hautakangas and co-workers [12,13] found that solute Cu atoms precipitated in the deformation-induced open-volume defects site and significantly reduced the concentration of open volumes in the Al–Cu–Mg alloys. In Fe–Cu alloys, He et al. [14] reported that Cu precipitation could be accelerated by the addition of B and N in the supersaturated alloy, facilitating defect-healing. Precipitation seems to be effective in repairing early stage damages including vacancies, vacancy clusters as well as nano-scale voids. Nevertheless, application of this approach is limited to those precipitation alloys [15].

Electropulsing was reported to be able to heal cracks partially in steels by generating a considerable temperature rise and a compressive stress state in the crack region [16,17]. Lucci et al. [18] documented the self-healing of aluminum alloy matrix reinforced with alumina (Al2O3) micro-tubes filled with a low melting point solder alloy. By heating above the melting point of the solder alloy, the molten solder moved into the crack and healed the crack completely or partially. Obviously, these healing approaches suffer from various limitations and do not have a general applicability for conventional metallic materials.

In fact, mobility of metal ions is rather high in electrolyte of aqueous solution or melted salt. Electrocrystallization,
commonly use procedure in surface modification and metallurgy refining industry, uses oxidation and reduction reaction on anode and cathode in aqueous solution or melted salt electrolyte [19]. More importantly, in electrocrystallization very strong chemical bonds can be formed between the substrate and the deposited layer. Hence, in principle it is possible to heal open spaces such as cracks in metals by using electrochemical processes with the component containing cracks as the cathode and metal ions in the electrolyte as healing agent. When an electrolyte potential is applied, metal ions near the crack surface can be reduced to metal atoms, bonding with atoms of the crack surfaces and eventually healing or repairing the crack. In the present paper, we verified this idea in pure nickel plates with through thickness cracks. The electrochemical process for healing cracks in metals is referred to as electro-healing. The electro-healing is a complex process including mass transportation, adsorption, diffusion, nucleation and growth of healing crystal, within a confined volume. The key to realize crack-healing depends upon efficient mass transportation and diffusion, which is controlled by proper electrolyte throwing power [20] and current density.

2. Experimental methods

2.1. Sample preparation

Polycrystalline nickel plates with a purity of 99.84 wt% and grain sizes ranging from 100 to 150 μm were used in this study. Pre-cracked samples were prepared by using the method reported by Zhou et al. [17]. As schematically illustrated in Fig. 1, samples were machined into a cylinder of 15 mm in diameter and 35 mm in height. A hole with a diameter of 1 mm was drilled through the cylinder along the radial direction in the axial center by using electric discharge machining (EDM). The samples were compressed gently into a drum shape with a final height of 25 mm on a UH-F 1000 KNC universal testing machine with a compressing rate of 2 mm/min. The hole was then closed as a line, which would be used as a crack. Slices with various thicknesses (100, 150, 200 and 300 μm) were cut from the drum sample parallel to the axial direction. Dogbone-shaped specimens for tensile tests were finally cut by using EDM from the slices with a through-thickness crack in the center. The gauge length and the width of the sample were 7 mm and 5 mm, respectively.

2.2. Electro-healing

Before electro-healing, the cracked samples were pre-treated by alkaline degreasing and then electro-polished in a solution with a mixture of concentrated phosphoric acid (H₃PO₄), concentrated sulfuric acid (H₂SO₄), and distilled water (H₂O) with the mass fraction of 63%, 15%, and 22%, respectively. Afterwards the samples were partially insulated by adhesive tape with an exposed area of 4 mm × 4 mm with the crack in the center. After being electro-polished for a short time to activate the sample, the specimens were rinsed in distilled water and dipped into the electro-healing solution.

A high throwing power (HTP) healing solution contains a mixture of 100 g/L NiSO₄·6H₂O, 200 g/L NiCl₂·6H₂O and 40 g/L H₃BO₃. With this solution, a relatively uniform distribution of current density could be derived for the specific geometry of the crack compared with that in the conventional Watts bath. The samples were electro-healed for 2 h at 40 °C with a current density of 4 A/dm². For thicker samples (with a thickness greater than 150 μm), a low current density (LCD) solution consisting of 262.7 g/L NiSO₄·6H₂O, and 31 g/L H₃BO₃ is used at a relatively low current density and a higher temperature to minimize the unfavorable mass transportation effect to electro-healing. With the LCD solution, samples were healed for 20 h at 55 °C with a current density of 0.4 A/dm². Each as-healed sample was annealed at 673 K for 2 h to eliminate internal stress. After annealing the redundant plated layer on the sample surface was removed by grinding.

2.3. Morphology observation and mechanical property tests

Morphologies of cracks (before and after electro-healing) were observed on a FEI Nova scanning electron microscope (Nano-SEM) operated at 10–15 kV. The electron backscatter diffraction (EBSD)
measurements were executed at a voltage of 20 kV and a current of 6.0 nA with a step size of 30 nm. Post-fracture morphology observations after tensile tests were carried out on the Nano-SEM as well. A Tecnai G² F20 transmission electron microscope (TEM) operated at 200 kV was used for TEM and high-resolution TEM (HRTEM) observations. Samples for TEM and HRTEM observations were prepared by using FEI Nova 200 Nanolab FIB-SEM system operated at a voltage of 30 kV.

Tensile tests were performed on Instron 5848 Micro Tester at ambient temperature at a strain rate $3 \times 10^{-3}$ s$^{-1}$. A contactless MTS LX300 Laser extensometer was used to calibrate and measure strains of the tested sample during loading. At least 3 samples were tested for each condition. Micro-hardness tests were performed on Mitutoyo MVK-H300 Micro-Hardness Tester with a load of 50 g and a loading time of 10 s. Hardness values were obtained by averaging at least 15 indents.

3. Results and analysis

3.1. Morphology of the healed crack

Fig. 2(b) is a typical pre-crack artificially made by the method described in the experimental section. After electro-healing, from both sides of the sample one can see that the original crack is fully filled with the healing crystals without visible voids (Fig. 2c). The healed region and the substrate are distinguishable from the contrast difference. Observations of various through-thickness sections of the 100 μm-thick samples revealed some voids or unhealed regions inside the crack. The unhealed volume increases with an increasing depth from the surface, reaching several percent at ~50 μm deep (thickness center) where majority of the original crack is filled with healing crystals. Micrometer-sized pores are frequently observed in the near parts of the crack close to the tips (with an opening below 10 μm). In the two crack tips with extremely small opening (< 1 μm), healing crystals are not formed owing to the dimension effect on surface tension which affects cleaning and activating processes.

Close observations of the healed crack in the through-thickness center of the sample (Fig. 3a) indicated that Ni crystals grow from both sides of the crack surfaces towards the crack center, in form of roughly equi-axed ultrafine grains in the initial stage (attached to the original crack surface) followed by subsequent columnar growth. Composition measurements showed that the Ni healing crystals are of high purity, about 99.96 wt%. Growth twins are frequently observed in some columnar micro-sized grains. Growing crystals from both sides meet in the crack center, forming a meeting-line (plane). It implies the crystal growth rates are roughly identical from both sides.

While the majority of the meeting-line is solid, some micrometer-sized pores are detected along the meeting-line where the growing crystals have not met each other, frequently observed in the narrow parts of the crack. It is interesting to see that in the very narrow part of the crack with an opening as small as 1–2 μm, crystals are also able to grow from both sides forming a solid meeting line (Fig. 3b). The crystal sizes are of submicrons, larger than that of the equiaxed grains attached to the crack surfaces at large crack openings.

Electron backscattering diffraction (EBSD) images of the healed crystals indicated that the healing crystals have random crystallographic orientations without an obvious preferred texture (Fig. 4). An interesting phenomenon is that the orientations of those ultrafine grains attached to the crack surfaces have almost identical orientations to the substrate.

3.2. Characterization of interfaces

Interfaces between the healing crystals and the crack surfaces (substrates) were characterized by using TEM and HRTEM. Frequently observed are the identical crystallographic orientations between the healing crystals and the attached substrate, i.e., the interfaces between them are coherent. The healing crystals grow epitaxially from the substrate in the initial stage of growth. As shown in Fig. 5, owing to the epitaxial growth of the healing crystals, the interface between the healing crystals and the substrate can be hardly distinguished in the HRTEM images. Some dislocations are found along the epitaxial interfaces.

Epitaxial growth of crystals from the substrate during electrocrystallization has been documented in the literature [21,22]. In Ni electroseeding on oriented Cu and Ni substrates from Watts baths, Amblard et al. [23] found that the deposition can be an epitaxial growth or a non-epitaxial growth, depending upon the orientations of the substrate and the preceding treatment prior to deposition. Epitaxy is generated when the substrate has been properly prepared. Considering that the growth of healing crystal is on a native substrate in the present case with zero or negligible lattice misfit, formation of epitaxial layer may follow the layer-by-layer crystal growth mode [24,25], where adatoms (here Ni adatoms from the healing solution) attach preferentially onto the crystal surface of the substrate, resulting in an atomically smooth and fully coherent layer. Other epitaxial growth mode such as spiral-island and step flow growth mode cannot be excluded because the substrate is polycrystalline. The epitaxial crystal growth transits to a stage to form finer crystallites as more
interfaces are needed to relax the strain energy accumulated due to inclusion of various defects and impurities. The thickness of the epitaxial layer in the present work is about a few hundred nanometers, which is much larger than that in the electrodeposited Ni layers on a polycrystalline Cu (about 100 nm) where the lattice misfit of the substrate/deposit is much more pronounced [26].

Bonding of healing crystals grown from the opposite sides of the crack along the meeting-line is equally important for crack healing. HRTEM observations along the meeting line (Fig. 6a) showed that the two grown crystals from the opposite directions (G#1 and G#2) are bonded at the atomistic level. The interface structure is actually not different from that of a normal grain boundary, as seen in Fig. 6b where a normal grain boundary is formed between two neighboring grains (G#1 and G#3) grown in the same direction from the substrate. Formation of conventional grain boundaries along the meeting-line is not difficult to understand. The healing crystals are formed at the crystals-solution interfaces during the electrocrystallization process. Although macroscopically the healing crystals grow vertically from the crack surfaces, microscopically the 3D crystal growth consists of the formation of mono-atomic or multi-atomic steps in the

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**Fig. 3.** (a) An SEM image of the central part of a healed crack at ~50 μm deep from the surface. (b) An SEM image showing the healed crystal grown in the region with a crack opening below 2 μm. The dot-short segment lines designate the boundary of the healing crystals grown from the opposite crack surfaces. (c) An SEM image showing the lateral crystal growth after the growing crystal tips from both sides encounter.

**Fig. 4.** An electron backscatter diffraction (EBSD) image of the central part of the healed crack at ~30 μm deep from the surface, showing random orientations of the healing crystals (X₀ indicates the overall growth direction of the healing crystals).
vertical direction and propagation of these steps in the lateral directions. When the growing crystals from both sides of crack surfaces meet each other, vertical growth is restricted and lateral crystal growth becomes dominant, see Fig. 3c. Hence, the meeting-line of the growing crystals is basically composed of grain boundaries from the lateral growth, which is identical to the boundaries formed in the vertical growth process.

3.3. Tensile tests

Uni-axial tensile tests were performed to assess the bonding condition of the healing crystals and the healing crystal/substrate interfaces. Fig. 7 presents typical quasi-static engineering stress–strain curves of the original 100 µm-thick sample (“without crack”), the cracked and the healed specimens, respectively. The ultimate tensile stress (UTS) of the cracked sample (249 MPa) is much lower than that of the original sample (418 MPa), so is the tensile plasticity (elongation-to-failure of the cracked specimen is only a fraction of the virgin sample). The strength drop is reasonable by considering the crack length. No uniform elongation is observed from the cracked sample, a signature of an obvious strain concentration at the crack tips in tension.

It is striking to see that yield strength (0.2% offset) and UTS of the crack-healed sample (about 394 MPa and 412 MPa, respectively) are comparable to that of the virgin sample. These data indicate that the bonding strength between the healing crystals and the crack surfaces, as well as that among healing crystals, is at least as high as the substrate strength. Considering the fact that there exist some pores and unhealed volumes in the healed crack, the bonding strength might be even higher than that of the
3.4. Fracture morphology of crack-healed specimens after tensile tests

A notable uniform elongation in the healed sample (> 1%), in contrast to that in the cracked sample, revealed that uniform plastic deformation occurs in the substrate as well as in healing crystals in the initial stage of plastic deformation under tension.

UTS of the healed samples with thicknesses of 100, 150, 200, and 300 μm (Fig. 8) indicated that UTS decreases with sample thickness, the UTS of these samples are 410, 400, and 375 MPa respectively when the thickness are 150, 200, and 300 μm, the thicker the sample is, the lower the UTS of these samples are 410, 400, and 375 MPa respectively when the thickness are 150, 200, and 300 μm.

3.5. Healing efficiency

Statistic measurements in the 100 μm-thick samples showed that type-I surface constitutes about 60% of the total crack area (S₁), type-III is a few percent (SIII, averagely 3%), and type-II is less than 40% (SII). Assuming that healed regions of type-II surfaces do not contribute to the strength of the healed sample (σH), one may have

$$\sigma_s = C(S_1 + S_{III})\sigma_{hc} + (1 - C)\sigma_0$$  (1)

where C is the cross-sectional area fraction of the original crack,  σhc and  σ0 are strengths of the healing crystals and the virgin sample, respectively. In terms of the hardness measurements, we take approximately  σhc = 1.5 σ0. The calculated tensile strength of the healed sample is about 406 MPa for the 100 μm-thick sample, which is coincident with the measured UTS of 412 MPa. In terms of the tensile strength, the healing efficiency η can be defined as

$$\eta = (\sigma_s - \sigma_c)/\sigma_0 \times 100\%$$

where  σc is tensile strength of the cracked sample. With the measured data, we get a healing efficiency of about 96% for the 100 μm-thick Ni plate samples.

For the thicker samples, area fractions of the unhealed regions become larger and so is SII for the type-II crack surfaces.
measurements of the post-fracture surfaces indicated that the sum of \( (S_I + S_{III}) \) drops linearly with the sample thickness, as in Fig. 10a. For a sample thickness of 300 \( \mu \)m, it is about 28%. The calculated tensile strength of the 300 \( \mu \)m-thick sample is about 397 MPa, which is reasonably consistent with the measured strength (343 MPa). A good agreement can be seen between the measured and the calculated strength from the post-fracture surface analysis for the samples with various sample thicknesses (Fig. 10b).

A decreasing healing efficiency is observed with an increasing sample thickness (Fig. 10b). When sample thickness is 300 \( \mu \)m, the healing efficiency drops to an average of 33%. The decreasing healing efficiency originates from a larger area fraction of poorly-healed regions due to non-uniform current density distribution associated with the geometry of the crack and the early close-up of the crack opening by growing healing crystals. Further investigations by adjusting chemical constitutions of the electrolyte are in progress to deal with this issue.

4. Conclusions

The present results demonstrated that through-thickness cracks in Ni sheets with sizes in the micrometer range or larger can be successfully healed by electro-healing. The electro-healing process starts with the vertical epitaxial growth of healing crystals from the substrates (the original crack surfaces) followed by lateral growth of healing crystals with the depletion of healing agent. The healing crystals bond with each other at atomistic level. These crystals have finer grains and higher strength compared with the substrate. Tensile tests exhibited that the healed samples have a comparable tensile strength as the virgin sample and some tensile ductility can be achieved for the sample of 100 \( \mu \)m thick. Post-fracture analysis indicated that part of the crack propagated along the substrate instead of healing crystals. The healing efficiency, ranging from 96% to 33% with an increasing sample thickness, is related to the fraction of fully-healed region and the strength difference between the substrate and the healing crystals.
Electrochemical processes are routinely used in deposition of other metals and alloys, such as Fe, Cu, Ag and their alloys. It is realistic to anticipate that the electro-healing process can be applied to heal or repair cracks in other metallic materials. Other types of cracks, e.g., single sided cracks, might also be healed using appropriate healing solutions and electrochemical parameters.

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