A nanocrystalline materials production technique for simultaneously improving several properties

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ABSTRACT
For engineering structural materials, it is necessary that their several properties should be synchronously considered because they usually suffer from several kinds of attacks during their service, such as corrosion, fatigue and wear. We introduced a production technique for bulk nanocrystalline metallic materials in this work. Nanocrystalline metallic materials produced by this technique can simultaneously improve their several properties, this technique can be also industrialized in steel factory.

Keywords: severe rolling technique, bulk nanocrystalline metallic materials, mechanics, corrosion, valence electron configuration

1 INTRODUCTION
The concept of nanocrystalline metallic materials was put forward in 1980s [1]. From then on, nanocrystalline metallic materials have been extensively studied [2]. The first and key problem that we should solve in their fundamental research and application is the production of nanocrystalline metallic materials because their production techniques can determine their production cost and the dimension of bulk nanocrystalline metallic materials, and their different properties, such as mechanics [3], corrosion [4] and thermodynamics [5] et al. Many production techniques for nanocrystalline metallic materials have been proposed by scientists, such as amorphous crystallization of alloys [6], severe plastic deformation [7], accumulative roll-bonding [8] et al. However, one kind of property of nanocrystalline metallic materials was usually improved at cost another property in published papers [9].

2 RESEARCH PROGRESS OF BULK NANOCRYSTALLINE MATERIALS
On the base of other preparation techniques for nanocrystalline metallic materials, we proposed another production technique for bulk nanocrystalline metallic materials, which was called as severe rolling technique [10]. After our investigation of bulk nanocrystalline metallic materials prepared by severe rolling technique for many years from 2002 to now, we could concluded that the features of this production technology are (1) this production technology can be industrialized because all the bulk nanocrystalline metallic materials, such as bulk nanocrystalline 304 stainless steel, ingot iron, industrial pure Al, 3003 Al alloy and 1Cr13 alloy studied in our group were prepared in steel factory rather than in laboratory; (2) the same property (such as corrosion resistance) of different bulk nanocrystalline metallic materials (such as ingot iron, industrial pure Al and 304 stainless steel), and the different properties of the same bulk nanocrystalline metallic material can be improved [11-13]. We introduced the research progress of the three kinds of nanocrystalline materials (ingot iron, 304 stainless steel, industrial pure Al).

The abbreviations of conventional polycrystalline ingot iron, 304 stainless steel and industrial pure Al are CPII, CP-SS304 and CP-Al, respectively; the abbreviations of bulk nanocrystalline ingot iron, 304 stainless steel and industrial pure Al are BNII, BN-SS304 and BN-Al, respectively.

2.1 Different Properties of BNII and CPII
For general knowledge in electrochemistry and materials science, the electrochemical corrosion of CPII in 0.05 mol/L H_2SO_4 + 0.25 mol/L Na_2SO_4 solution should be active dis-solution process. However, the potentiodynamic polarization curve of BNII appears passivation process with less corrosion current density and more positive corrosion potential, which means its enhanced corrosion resistance compared to CPII, and the polarization resistance of BNII is about nineteen times larger than that of CPII [11]. The pitting corrosion resistance of BNII is also improved, the density and diameter of corrosion pit on BNII are less than those on CPII after potentiodynamic polarization in HCl solutions with different concentrations at room temperature [12]. The wear resistance of BNII during lubricated friction is also enhanced in comparison with CPII, these results demonstrate that the wear rate and wear coefficient of BNII are less than those of CPII at both room temperature and 150 °C, the friction surface of BNII is also smoother than that of CPIII [13].

2.2 Properties of BN-SS304 and CP-SS304
It is a well-known fact that 304 stainless steel is inevitably to suffer from pitting corrosion in solutions containing Cl\(^-\), which is its fatal shortcoming during its service in corrosive environment. However, BN-SS304 scarcely suffered from pitting corrosion, and the corrosion rate of BN-SS304 is less than that of CP-SS304 after thirty-day immersion in 0.5 mol/L hydrochloric acid solution at room temperature [13]. Figures 1a-1d represent the corrosion morphologies of CP-SS304 (a and c) and BN-SS304 (b and d) after thirty-day immersion test in 0.5 mol/L hydrochloric acid solution at room temperature. The density of corrosion pit on BN-SS304 is obviously less than
that on CP-SS304, and corrosion pit was scarcely found in Figure 1b and 1d. Figure 1d also demonstrates compact oxide film can form on BN-SS304. The result of weight loss test indicates that the corrosion rate of BN-SS304 is less than that of CP-SS304 [13]. It should be noted that the corrosion rates of Fe, Cr and Ni atoms in BN-SS304 are less than those of their corresponding atoms in CP-SS304. The yield and tensile strengths of BN-SS304 are 331 MPa and 129 MPa larger than those of CP-SS304 respectively, the elongation of BN-SS304 is larger than 25%, the elastic strain of BN-SS304 is about one time larger than that of CP-SS304 as shown in Fig. 2. However, the elongations of a lot of other nanocrystalline metallic materials are about 10%. The larger elongation and elastic strain of BN-SS304 mean the improved mechanical properties of BN-SS304.

The resistance of high-temperature oxidation of BN-SS304 is enhanced in comparison with CP-SS304, the high-temperature oxidation rates of BN-SS304 are less than those of CP-SS304 during the whole oxidation processes (initial oxidation from room temperature to 900 °C for about thirty seconds and isothermal oxidation at 900 °C for 24 hours), the oxide film on BN-SS304 is more compact and thinner than those on CP-SS304 [16]. Our present experimental results also demonstrate the improved resistances of stress corrosion of BN-SS304 (larger yield and tensile strengths, and lower susceptibility of stress corrosion cracking) in 1 mol/L hydrochloric acid solution at room temperature and the enhanced hot corrosion resistance of BN-SS304 (less oxidation rate) in molten NaCl+ KCl+ Na2SO4 at 600 °C for 41 hours.

2.3 Properties of BN-Al and CP-Al

It is known that industrial pure Al is also unavoidable to suffer from localized corrosion in solutions containing Cl-. CP-Al suffered from severe localized corrosion, while the localized corrosion resistance of BN-Al is obviously improved in comparison with CP-Al in 0.25 mol/L hydrochloric acid after nine-day immersion at room temperature [17]. Figure 3 shows the corrosion images of BN-Al (b and d for seven and nine-day respectively) and CP-Al (a and c for seven and nine day respectively) after immersion tests in 0.25 mol/L HCl solution at room temperature. The density of localized corrosion pit on BN-Al is less than that on CP-Al. According to Figure 3 and the results of loss weight measurement, the corrosion rate of BN-Al is also less than that of CP-Al. These results indicate that both the uniform and localized corrosion resistances of BN-Al are simultaneously improved in comparison with those of CP-Al in 0.25 mol/L HCl solution for nine-day immersion test at room temperature.

Figure 1: The corrosion surface morphologies of CP-SS304 (a and c) and BN-SS304 (b and d) after thirty-day immersion test at room temperature.

Figure 2: The stress-strain curves of BN-SS304 and CP-SS304 at room temperature.

Figure 3: Corrosion images of BN-Al (b and d) and CP-Al (a and c) in 0.25 mol/L HCl solution at room temperature. a and b: seven-day immersion; c and d: nine-day immersion.
In 0.01 and 0.05 mol/L HCl + 0.25 mol/L Na2SO4 solutions at room temperature, the oxide films on BN-Al were not thicker than those on CP-Al; the oxide films on CP-Al were not compact than those on BN-Al. However, the uniform and pitting corrosion resistances of BN-Al were simultaneously improved in comparison with those of CP-Al in 0.01 and 0.05 mol/L HCl + 0.25 mol/L Na2SO4 solutions at room temperature [12]. Figure 4 and 5 represent the XPS (X-ray photoelectron spectroscopy) results about the electronic structures of oxide films on BN-Al and CP-Al. The details of XPS experiment and result analysis is described In Ref. [12]. Figure 4 means that the atomic percentages of Al3+ in the oxide films on CP-Al are the same as those on BN-Al in 0.01 and 0.05 mol/L HCl + 0.25 mol/L Na2SO4 solutions.

Figure 4: The atomic percentages of Al3+ in the oxide films on CP-Al and BN-Al in 0.01 (a) and 0.05 (b) mol/L HCl + 0.25 mol/L Na2SO4 solutions at room temperature.

Figure 5 shows the atomic percentages of Al3+ (a) and O2- (b) in oxide films on BN-Al and CP-Al in 0.1 mol/L HCl + 0.25 mol/L Na2SO4 solutions at room temperature, and means that the oxide film on CP-Al is more compact than that on BN-Al due to the larger atomic percentages of Al3+ and O2- in oxide films on CP-Al. The larger atomic percentages of O2- in oxide films on CP-Al demonstrates the less density of defects in the oxide film on CP-Al because O0 is adsorbed in its oxide film through those defects. However, the more compact oxide film on CP-Al cannot result in its larger corrosion resistance [12].

The mechanical properties and corrosion resistances of nanocrystalline 3003 Al alloy are also simultaneously enhanced in comparison with conventional polycrystalline 3003 Al alloy, while there no space to introduce the results about them in this paper.

3 DISCUSSION

According to above results of these bulk nanocrystalline metallic materials produced by severe rolling technique, the different properties of the same nanocrystalline metallic material and the same property of different nanocrystalline metallic materials can be synchronously improved in comparison with their conventional polycrystalline metallic materials, which is the feature of severe rolling technique different from other preparation technologies for nanocrystalline metallic materials. It is an interesting question that which factors can cause these results. In fact, the nature of corrosion (electrochemical and chemical corrosion) are the exchange process of valence electrons between metallic atom in metallic material and ions in solution, and the transportation process of corrosion.
products between the metallic material/oxide film interface, in oxide film and between oxide film/solution interface. Therefore, the valence electron configurations of metallic material and the electronic structures of oxide film should be responsible for the corrosion properties of metallic materials. In term of this point of view, the valence electron configurations of metallic materials and the electronic structures of oxide films were characterized by ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy respectively. The valence electron configurations of BN-Al and CP-Al are shown in Ref. [17], the valence electron configurations of BN-SS304 and CP-SS304 are shown in Ref. [13], the physical meanings of valence electron states in ultraviolet photoelectron spectroscopy of BN-Al, CP-Al, CP-SS304 and BN-SS304 are explained in Ref. [13,17]. The enhanced corrosion resistances of these bulk nanocrystalline metallic materials are attributed to the larger binding energies of their valence electrons, the less weights of valence electrons with low energy level, the weaker adsorption and smaller binding energy of Cl2p3/2 on their oxide films [12-14, 16-18].

For the improved mechanical properties of bulk nanocrystalline metallic materials produced by severe rolling technique, they also should be related to their valence electron configurations because the mechanical properties of metallic materials derive from the interaction between their valence electrons and the movement of the atoms (valence electron also move) in metallic materials. During tensile, fatigue, wear and other damage processes, the spatial position of valence electrons and atoms were changed, the interaction between them were changed at the same time. It is very complicated to understand the mechanical properties with the valence electron configurations of metallic materials. However, the valence electron configurations of metallic materials should be considered as one of the intrinsic microstructure parameters for corrosion and mechanical properties. However, the conventional microstructure parameters, such as grain size, dislocation, and strain et al cannot be considered as the intrinsic microstructure parameters for corrosion and mechanical properties because corrosion and mechanical properties cannot consistently change with the variation of these the conventional microstructure parameters according to many published results. For example, the Hall-Petch relation means that the strength of metallic materials increase with the decreasing the grain size. However, the fact for the strength of nanocrystalline material with grain size about more than a dozen nano-meters, its strength decreases with the decrement of its grain size, which means inverse Hall-Petch relation [19].

4 CONCLUSIONS
Many bulk nanocrystalline metallic materials can be produced by severe rolling technique. This technique can synchronously enhanced the different properties of the same material and the same property of different materials, and is potential to be industrialized in steel factory. In fact, the conventional microstructure parameters for materials science, such as grain size, dislocation and strain et al are not the intrinsic parameters for many properties of metallic materials. However, the valence electron configurations of metallic materials should be considered one of the intrinsic parameters for corrosion and mechanical properties of metallic materials because their valence electron configurations can intrinsically decide their some properties. In addition, the corrosion resistance of metallic material depends on the combination of its self and its oxide film.

REFERENCES