

Mechanical Behavior and Failure Mechanism of Nb-Clad Stainless Steel Sheets

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ABSTRACT

Because niobium-clad 304L stainless steel sheets are considered for use as bipolar plates in polymer electrolyte membrane (PEM) fuel cells, their mechanical behavior and failure mechanism are important to be examined. As-rolled and annealed specimens were tested in tension, bending and flattening. The effects of annealing temperature and time on the mechanical behavior and failure mechanism were investigated. Micrographic analyses of bent and flattened specimens showed that the as-rolled specimens have limited ductility and that the annealed specimens can develop an intermetallic layer of thickness of a few microns. The annealed specimens failed due to the breakage of intermetallic layer causing localized necking and the subsequent failure of Nb layer. The springback angles of the as-rolled and annealed specimens were also obtained from guided-bend tests. Nano-indentation tests indicated that the intermetallic layer exhibit much higher values of hardness and elastic modulus as compared to those of the stainless steel and Nb sheets.

INTRODUCTION

The growing interest in stainless steel for use as bipolar plates in PEM fuel cells [1,2] has been further accelerated by the recent advances in the micro-forming technology of metals, for example, see [3-5]. Efforts are also being made to model micro-scale forming processes and to investigate the effects of size scaling

[6-8]. Recently, hydro-forming has been used to develop micro-scale channels in thin stainless steel sheets for bipolar plate applications [9]. However, the use of stainless steel sheets for bipolar plates has two main problems. The first is the development of corrosive products in a low pH environment of the fuel cell and the second is the formation of surface passivation film [10]. The corrosive products are harmful to the membrane electrode assembly (MEA) and can interrupt the action of electrode catalyst. The passive film adversely affects the contact resistance of the bipolar plates. In order to overcome these issues, coated metal sheets are under investigation. Two types of coatings, carbon-based and metal-based, have been investigated for this purpose [11,12]. Metal-based coatings include noble metals, metal nitrides and metal carbides [13-15] but a viable and inexpensive commercial product is yet to be developed.

Weil et al. [10] evaluated the electrochemical properties of Nb-clad stainless steel sheets for application as bipolar plates in PEM fuel cells. Their test results demonstrated good corrosion stability under accelerated corrosion conditions. The use of Nb-clad sheets is intended to reduce the material costs of metallic bipolar plates as compared to the other coating schemes, by incorporating the conductive and corrosion resistant Nb as a thin layer roll clad to a more robust and inexpensive steel sheet. Hong and Weil [16] conducted an initial evaluation of the tensile and bend properties of Nb-clad stainless steel sheets. Their chemical analyses

indicated that an iron–niobium compound is present at both the interfaces. The exact chemical composition of the intermetallic compound is yet to be determined. In the present study, experimental investigation of Nb-clad stainless steel sheets is further pursued to study the effects of annealing conditions on the ductility and formability of these sheets.

EXPERIMENTAL PROCEDURE

A 304L stainless steel sheet with an initial thickness of about 12 mm was clad to a 1.3 mm thick Nb sheet by roll bonding with a 98% reduction in the total thickness. The final thicknesses were about 0.025 mm and 0.23 mm for Nb and stainless steel sheets, respectively. The rolled sheets were vacuum annealed to increase their ductility. In the present study, specimens with different annealing conditions were studied. These specimens were annealed at 850°C, 950°C and 1050°C for either 15 minutes or 60 minutes. The nomenclature for the specimens in this paper is such that the first identification number indicates the annealing temperature and the second number stands for the annealing time. Therefore, 850/15 represents a specimen that has been annealed at 850°C for 15 minutes.

The microstructure of the interfacial area was examined using the optical and scanning electron microscopy. Tensile tests were conducted to evaluate the mechanical properties of the clad assembly. Specimens were bent to 180° in a guided-bend test fixture using an MTS machine. Bent specimens were further flattened and the surface and cross-sections were microscopically examined. Nano-indentation tests were conducted to determine the mechanical properties of the individual layers in the clad assembly.

RESULT AND DISCUSSION

MICROSTRUCTURAL ANALYSIS - The cross-sectional micrograph of a 1050/60 specimen in Figure 1 shows that there is no interfacial porosity or voids even after annealing the specimens at 1050°C for 60 minutes. It also shows that an intermetallic layer of a few microns in thickness was formed in the annealed specimen between the Nb sheet and stainless steel core. The thickness of the intermetallic layer is dependent on the annealing temperature and time. The sizes of the intermetallic layer in the 850/15 and 950/15 specimens are very small and high magnification SEM micrographs were used to identify the layers in these specimens as shown in Figure 2. It is observable in these figures that the intermetallic in the 850/15 specimen is present as irregular and intermittent inclusions along the entire bond line instead of a nearly continuous layer as shown in the 950/15 specimen. The thicknesses of the intermetallic layer for different annealed conditions were measured from the SEM images. The approximate values of these thicknesses are listed in Table 1. An estimated value for the inclusion dimension is reported for 850/15 specimen.

A chemical analysis [16] of similar specimens suggested the presence of a transition metal reaction phase. An EDX analysis [16] indicated that the intermetallic compound observed in the Nb-clad stainless steel after annealing is likely to be the elusive η -phase compound. This compound was reported by Kripyakevitch et al. [17] in ferroniobium alloys annealed at 900°C in an inert argon environment. The transition metal η -phase is metastable which can be stabilized by very small amounts of phosphorus and sulfur [18]. The brittleness of the intermetallic compounds and their low fracture strength is a known issue. Moreover, these compounds also suffer from environmental embrittlement problems [19]. Their brittle nature has limited their utility and applications.

TENSILE TESTS - Tensile specimens with a gauge length of one inch were tested at a constant crosshead speed of 1 mm/min according to the ASTM standard E 8-04 [20]. The nominal stress-strain curves are shown in Figure 3. It is clear that the annealed specimens exhibited a significant drop in the yield strength along with an increased elongation before failure caused by the recrystallization of the stainless steel core. Some of the mechanical properties which were obtained from these tests are listed in Table 2 [21].

Annealed specimens started to warp along the longitudinal axis after a tensile extension of about 10%, producing a shape like the bottom of a canoe [22]. The Nb layer was in the outside of the canoe while the stainless steel sheet was in the inside. Figure 4 shows this effect in the 850/60 and 1050/60 specimens. It is noted from Figure 4 that the “canoeing” phenomenon was more pronounced in the specimens that were annealed at higher temperatures. The radius of curvature decreased with the amount of uniaxial strain. This phenomenon may be explained by the mismatch of the transverse strains of different layers under tensile loading conditions. A similar warping behavior was reported by Choi et al. [23] where the tensile deformation of stainless steel clad aluminum sheets was investigated.

Another observation noticed from the tensile tests was de-bonding of the Nb layer from the stainless steel core at strains above 25%. Figure 5 illustrates this type of delamination observed in a 1050/60 specimen. It is likely that the less ductile intermetallic layer between Nb and stainless steel sheet developed cracks perpendicular to the direction of tensile extension. These cracks are likely to promote the interfacial crack growth causing the peeling-off of the Nb layer from the stainless steel core. A detailed micrographical analysis is planned for the cross sections of the specimens that have been deformed to different strain values to investigate this phenomenon in detail. The Nb layer did not delaminate in other annealed specimens.

BEND AND FLATTENING TESTS - Specimens were bent to 180° and flattened as described in the ASTM

standard E 290-97a [24] with the Nb layer on the outside of the bend. The bend was produced by a guided-bend test fixture using a plunger of radius of 5.5 mm. Surface examination of the bent tip revealed no scratches or defects in any of the samples, which meant that they can survive this type of bend with the plunger of the given radius. The final bend angle was measured after the 180° test to determine the springback after elastic recovery. A comparison of the springback angles for different annealing conditions is shown in Figure 6. Annealing reduced the springback by about 50%, 58% and 65% in the 850/15, 950/15 and 1050/15 sheets, respectively, as compared to the as-rolled specimen.

The 180° bent specimens were further flattened between two platens under a predefined maximum load per specimen width (15 kN/m or 60 kN/m) or until a preselected separation between the bent legs was reached. A surface examination of the flattened tip showed signs of cracking in the as-rolled and 1050/60 specimens as shown in Figures 7(a) and 7(d), respectively. Rough surfaces were observed in the 950/60 and 1050/15 specimens as shown in Figures 7(b) and 7(c), respectively. Other specimens produced no visible surface defects. The cross-sections of the flattened specimens were further examined to investigate the failure mechanism in the clad sheets. Figure 8 shows micrographs of an as-rolled specimen and a 1050/60 specimen after flattening by a load per width of 60 kN/m. The failure mechanism of the as-rolled flattened specimen is different from that of the annealed specimen. Lack of ductility causes the failure of the protective Nb layer in the as-rolled specimen. However, for the annealed specimen the failure initiates at the brittle intermetallic layer when the layer breaks at almost evenly spaced intervals. The fracture of the intermetallic layer produces strain concentration sites which causes localized necking and subsequent failure of the Nb layer.

De-bonding of the Nb sheet is also noticeable from Figure 8(b) as the cracks propagate in the intermetallic layer. This type of failure mechanism was also observed by Matsumoto et al. [25] in Al-clad Mg-Li plates. Note that the thickness of the intermetallic layer depends on the annealing temperature and time. The damage due to flattening was more pronounced in 1050/60 specimens than in 1050/15 specimens. Other specimens showed relatively moderate defects while 850/15 and 950/15 specimens developed very small voids along the bond line between the outer Nb sheet and the stainless steel core.

NANO-INDENTATION - These tests were carried out using a Berkovich diamond tip which has a three-sided pyramid geometry. The total downward displacement was limited to 0.5 µm. Indentations were made in the outer Nb sheet, intermetallic layer and the stainless steel core. Figure 9 shows the nano-indentation images in different layers of a 1050/60 specimen. As it was difficult to position the nano-indenter tip on the intermetallic layer

in specimens with very thin layers and because the effect of the surrounding material was dominant in the case of a thinner intermetallic layer, only the data obtained from the 1050/60 specimen could be used to determine the mechanical properties such as the hardness and the elastic modulus of the intermetallic compound. The values of the hardness and elastic modulus for the Nb layer, the interface region and the stainless steel core are plotted and illustrated in Figures 10(a) and 10(b), respectively, for an as-rolled specimen and a 1050/60 specimen. For the interface region of the as-rolled specimen, there is no intermetallic layer of a significant thickness. Therefore, the values of the hardness and elastic modulus of this region just relates to the average mechanical properties of the material near the interface. On the contrary, the values of the hardness and elastic modulus of the interface region for the annealed 1050/60 specimen represents the mechanical properties of the intermetallic layer.

The values of the elastic modulus obtained from these tests are very close to the typical values available in the literature. The average measured value of the elastic modulus for the stainless steel core was 208 GPa which is in good agreement with a value of 200 GPa, that can be found in [26]. Similarly, for the Nb layer the average measured value of the elastic modulus was 130 GPa as compared to a value of 105 GPa which is quoted in [26]. It was also observed that the hardness of the Nb layer remained nearly the same in the as-rolled and annealed specimens. It is likely that the Nb layer did not recrystallize after annealing at 1050°C. However, the hardness decreased in the stainless steel core after annealing due to the recrystallization of grains. The effect of the intermetallic layer is visible from the values of the hardness and elastic modulus which are much higher than those of the interface region of the two constitutive layers as shown in Figures 10(a) and 10(b). A higher elastic modulus is in accord with the observation that the modulus of the intermetallic materials lie between those of the metals and the ceramics [19]. It is also worth mentioning that no cracks are found at the indentation sites which indicate that the adhesion is strong between the two sheets although a brittle intermetallic compound is formed at the interface after annealing.

CONCLUSION

The mechanical behavior and failure mechanism of Nb-clad stainless steel sheets were investigated. A microstructural analysis of roll-bonded specimens suggested a good metallurgical bond free of interfacial defects. The as-rolled specimens were annealed to increase their ductility. The annealing also reduced the amount of springback as compared to that of the as-rolled specimen. Annealing caused the development of a brittle intermetallic layer at the Nb and stainless steel interface. Tensile tests showed increased ductility in terms of lower yield strength and larger elongation before failure. A “canoeing” effect during tensile tests