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Evaluation of thermal embrittlement in 2507 super duplex stainless steel using thermoelectric power

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ABSTRACT

This research investigates the feasibility of using the thermoelectric power to monitor the thermal embrittlement in 2507 super duplex stainless steel (SDSS) exposed to a temperature between 280 °C and 500 °C. It is well known that the precipitation of Cr-rich α′ phase as a result of the spinodal decomposition is the major cause of the embrittlement and the loss of corrosion resistance in this material. The specimens are thermally aged at 475 °C for different holding times. A series of mechanical testing including the tensile test, Vickers microhardness measurement, and Charpy impact test are conducted to determine the property changes with holding time due to the embrittlement. The mechanical strengths and ferrite hardness exhibit very similar trends. Scanning electron microscopy images of impact-fractured surfaces reveal a ductile to brittle transition in the fracture mode as direct evidence of the embrittlement. It is shown that the thermoelectric power is highly sensitive to the thermal embrittlement and has an excellent linear correlation with the ferrite hardness. This paper, therefore, demonstrates that the thermoelectric power is an excellent nondestructive evaluation technique for detecting and evaluating the 475 °C embrittlement of field 2507 SDSS structures.

1. Introduction

Due to their excellent mechanical properties, good machinability, and high corrosion resistance, duplex and super duplex stainless steels (DSSs, SDSSs) are widely used in oil, chemical, nuclear and other power generation industries [1]. Their two-phase ferrite-austenite duplex microstructure enables combining the good properties of each phase into a single material microstructure. However, the properties of DSSs are deteriorated when exposed to a temperature between 280 °C and 500 °C [2–5]. This is due to the spinodal decomposition: α (ferrite) → α′ (Cr-rich) + α [6], which causes the embrittlement [2,3] and the loss of corrosion resistance [4,5]. The spinodal decomposition is referred to as the reaction that promotes the formation of two phases that have the coherent crystal structures but different chemical compositions and physical properties [6]. Since the embrittlement rate is highest at 475 °C [2,3], this phenomenon is also known as 475 °C embrittlement. It has been reported that other reactions in the ferrite such as the precipitation of the intermetallic G-phase also partially contributes to the embrittlement [7]. This embrittlement results in considerable changes in the mechanical properties [8], which is an important practical issue for applications of DSSs in the intermediate temperature range (280–500 °C). For this reason, it is important to be able to detect and/or evaluate the degree of the 475 °C embrittlement in DSSs.

The α′ precipitates are small (20–200 Å) and are highly resistant to coarsening even for long exposure times. Moreover, Fe and Cr, which are the two essential elements composing the α′ precipitates, have very similar atomic sizes, x-ray and electron scattering amplitudes, which along with their small size, makes their detection based on electron microscopy or x-ray diffraction, very difficult [9]. Some special techniques such as low-angle neutron scattering [10] and Mössbauer spectroscopy [2] are thus employed in detection studies. Traditionally, the electrochemical methods, potentiokinetic reactivation (EPR) and double loop EPR (DL-EPR), have been used to detect the thermal embrittlement in DSSs [11,12].

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The hardness measurement and impact testing can be used as an indicator of the embrittlement. All of the above-mentioned methods are, however, sample-based laboratory testing techniques. Especially for the evaluation of DSS components in service, it is highly desirable to have a nondestructive evaluation (NDE) method which is portable and simple enough to be deployed in a field environment.

The thermoelectric power (TEP) is a temperature dependent electronic property of conductors and semiconductors and is sensitive to changes in material microstructures [13] due to various causes such as the solute content, lattice strain, material processing, and time-dependent phase transformations. For this reason, the method has been effectively applied to metal sorting, flaw detection, thickness gauging, weld characterization, and microstructural analysis for various material systems [14,15]. As the material's chemical composition exerts the strongest effect on TEP, the TEP measurement can be an NDE technique in general to monitor change in properties of a material that undergo the precipitation of carbides and second phases. While the TEP measurements have been widely employed for material state evaluations (microstructure, phase transformation, strains, embrittlement, creep, corrosion), few works have been performed particularly for the embrittlement of DSSs. Kawaguchi and Yamanaka [16,17] investigated the mechanism of the changes in TEP due to thermal aging. They observed a decreasing TEP with Cr concentration in an Fe–Cr–Ni model alloy and then predicted the TEP using the Cr distribution in ferrite as well as the TEP-Cr concentration relationship. A similar trend has been qualitatively observed from TEP testing on an Inconel-718 weld in which TEP decreases with increasing local Cr content [18]. Lara et al. [19] employed the TEP measurement for assessing thermal aging due to the sigma phase precipitation at high temperatures in 2205 DSS. Ortiz et al. [20] used the TEP measurement to evaluate the intergranular corrosion susceptiblility of UNS S31803 DSS.

This research investigates the feasibility and sensitivity of using the TEP measurement to assess the embrittlement in a commercial 2507 SDSS and its correlation with hardness. 2507 SDSS specimens are thermally aged at 475 °C for different times. Besides the TEP measurements, Vickers microhardness to determine hardness changes in ferrite and austenite, tensile and Charpy impact tests to determine the degree of embrittlement, are carried out. Scanning electron microscope (SEM) images of the fracture surfaces of Charpy specimens are analyzed. A correlation between ferrite hardness and TEP is established, which demonstrates the feasibility of using the TEP measurement as a simple and reliable method for evaluating the 475 °C embrittlement in in-service 2507 SDSS structures.

2. Specimen preparation and mechanical tests

A 12.7 mm thick 2507 SDSS plate with the chemical composition given in Table 1 is used in this research. The SDSS has a Pitting Resistance Equivalent Number (PREN) of 42; a higher PREN designates a higher resistance to corrosion. Nine rectangular specimens are prepared from the plate, having dimensions $180 \times 50 \times 12.7$ mm^3. One specimen is left in as-received condition and eight samples are thermally aged at 475 °C for holding times, 10 min, 0.5 h, 1 h, 10 h, 50 h, 100 h, 300 h, and 500 h, being followed by water quenching. The Vickers hardness is measured using a computer controlled Mitutoyo microhardness tester that is equipped with a manually controlled *x-y* stage and digital micrometer heads with 1 μm spatial resolution. Five measurements of Vickers microhardness are made inside five different ferrite and austenite grains using a load of 10 g. Seven tension specimens are prepared for as-received and 1, 10, 50 100, 300 and 500 h holding times. The tensile specimens have a rectangular cross-section and a gauge length of 70 mm. All tests are conducted at room temperature on an MTS servo-hydraulic universal testing machine at a crosshead speed of 0.005 mm/min. Tensile properties, 0.4% offset yield strength (YS) and ultimate tensile strength (UTS), of the specimens are measured. Finally, Charpy impact test is also conducted on some specimens to investigate the microstructure on the fracture surfaces.

3. TEP measurement

The Seebeck effect states that when two dissimilar conductors make a closed circuit, a current will flow if the temperatures at the junctions of the two conductors are different as seen in Fig. 1. The electrons at the hot junction are excited to higher energies and lower their energies by diffusing to the cold junction; the hot and cold junctions consequently are positively and negatively charged. As a result, a voltage is produced which creates a current flow between them. The coefficient (S) that relates the voltage created (ΔV) to the temperature difference (ΔT) is known as the thermoelectric power (TEP), i.e. $\Delta V = S(\Delta T)$.

The measurement setup includes a material specimen with unknown TEP (S_S), two reference electrodes with known TEP (S_R), and a voltmeter. One electrode is heated to a preset temperature (T_h), while the other is left cold at room temperature (T_c), and then the induced voltage between the electrodes is measured. The measured thermoelectric voltage is written [21]:

$$\Delta V = S_{SR}(T_h - T_c) = S_{SR}\Delta T \quad (1)$$

where $S_{SR}(= S_S - S_R)$ is the TEP of the specimen relative to the reference electrodes so the absolute specimen TEP is calculated from the measured S_{SR} and the known electrode TEP, S_R. In the experimental realization, one of the electrodes is heated by electrical means to a preset temperature of 250 °C and the other, reference electrode is kept at room temperature. The temperatures

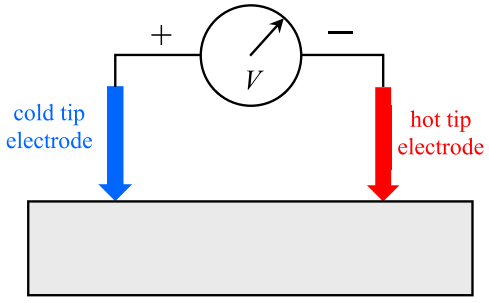

Fig. 1. Schematic diagram of the thermoelectric measurements using a two-tipped probe.

Table 1
The chemical composition of the 2507 super duplex stainless steel (wt.%).

C	Cr	Ni	Mo	Fe	Cu	Si	Co	Mn	N	P	Nb	S
0.017	25.37	7.09	3.87	61.306	0.24	0.32	0.012	0.82	0.28	0.24	0.015	0.001

of the hot and cold electrodes are measured by temperature sensors in the equipment. Note that this temperature is high enough for consistent and sensitive measurement of TEP for a wide range of metallic alloys. The thermoelectric voltage is then read while both electrodes are pushed manually onto two separate locations on the specimen surface. The measurement needs to be done rapidly enough, like within a few seconds, before the hot electrode is cooled down by the thermal conduction into the specimen – otherwise, the thermoelectric voltage will drift which will cause inconsistency in measurements. This research uses Walker Scientific alloy thermo-sorter model ATS-6044T that has probes with cold and hot tips made of copper and gold, respectively. The effects of ambient temperature drift are automatically compensated since the TEP is determined by the relative temperature ($\Delta T = T_{hot} - T_{cold}$) and both temperatures are measured in each measurement. Moreover, the measurements are repeated about 40 times at each damage state. The reported TEP values have the averages and standard deviations which are substantially small compared with the change in TEP.

4. Results and discussion

Fig. 2 shows the yield strength (YS) and ultimate tensile strength (UTS) of 2507 SDSS as a function of holding time. Both YS and UTS increases rapidly until 100 h and then reach their asymptotic values, 900 MPa and 1121 MPa, respectively. So, the embrittlement affects these tensile properties immediately as the heat treatment starts and stops at 100 h.

Fig. 3 shows the Vickers hardness measured in five different grains of austenite and ferrite phases as a function of holding time. The hardness of austenite increases by 13% until 10 h and then remains almost unchanged for longer thermal exposure times. However, the hardness of ferrite increases continually while the increase slows down after 100 h as in the tensile properties. The hardness reaches a value of 631 HV at 500 h, which corresponds to an increase of 84% with respect to as received condition. The result indicates that the thermal aging has a much stronger impact on ferrite phase than on austenite phase; the hardness increase of ferrite is the major contributor to that of the 2507 SDSS. These hardness results and trends are in agreement with those presented by Weng et al. [22] for 2205 DSS. While the spinodal decomposition and G-phase precipitation occur in ferrite, other relatively weaker reactions such as precipitations of carbides and nitrides along grain boundaries and small amount of sigma-phase precipitation in austenite cause the hardening of the austenite phase. Unlike the tensile properties that exhibit no change after 100 h, the ferrite hardness keeps increasing after this critical time; the reactions (the α' and G-phase precipitations) are still in progress after 100 h.

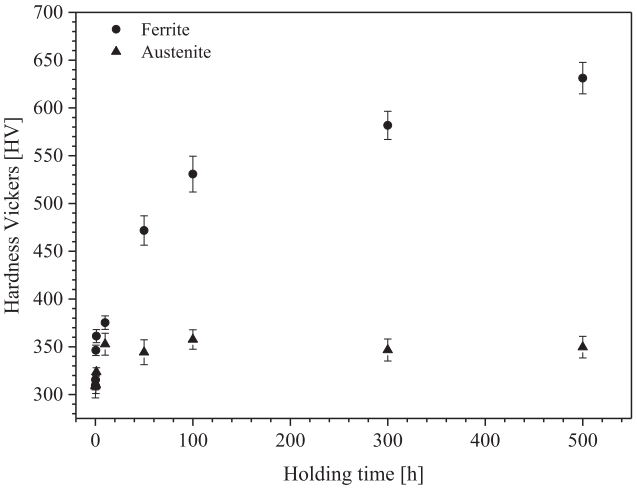

Fig. 3. Change on the Vickers microhardness of ferrite and austenite as function of holding time.

Fig. 4 shows the normalized TEP measured as a function of holding time. Unlike in some other DSSs (PM2000, SCS114A), the TEP values are always positive in this material (1.0–2.4 μV/K). The total change of the TEP from untreated to 500 h is about 132%. Note that this amount of change is much more significant than those from other sensitive NDE methods. For example, the nonlinear ultrasonic methods [23] show the changes in the nonlinearity parameter between 25 and 45% for the same set of specimens. Fig. 4 shows how the TEP and nonlinear ultrasonic results are compared. These demonstrate that the TEP measurement is an NDE technique which is reliable and sensitive to the microstructure changes in 2507 SDSS undergoing thermal aging. It is interesting to note that the TEP increases rapidly up to about 92% of the total change in the first 100 h and then tends to saturate. The trend of the TEP is markedly similar to that of the hardness of ferrite; the similarity is much better with the hardness than with the tensile properties. This indicates that the TEP is a physical quantity directly related to

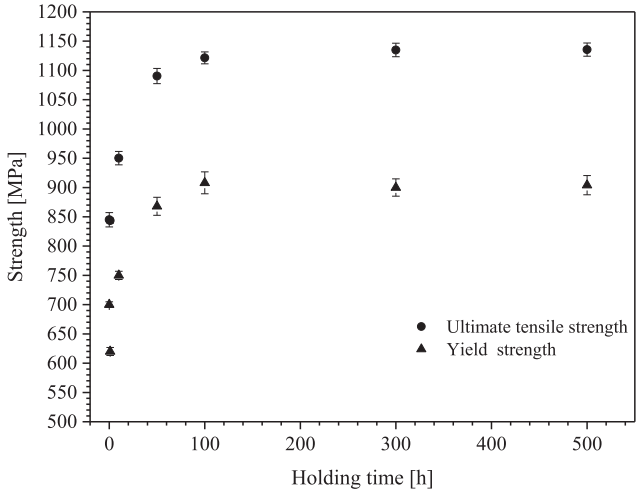

Fig. 2. UTS and yield strength as function of holding time for aged 2507 SDSS.

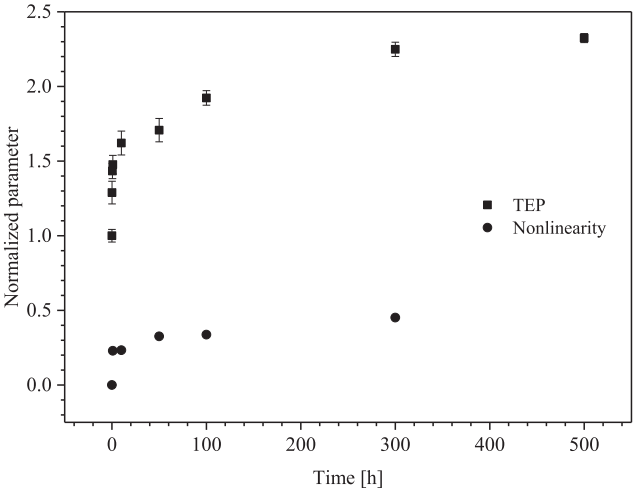

Fig. 4. Change on the TEP and nonlinear parameter from Ref. [23] as function of holding time.

the microstructure changes in ferrite which is the main cause of the embrittlement phenomenon in this material. The reason for the increasing trend of the TEP with aging time can be explained as follows. First of all, the fundamental physics that the TEP measurement exploits to evaluate the thermal embrittlement is that the TEP decreases with increasing local Cr content. The α′-phase and G-phase are both Cr-rich, with Cr contents of 36% and 29%, respectively [24], which are higher than the Cr content in unaged ferrite (25%). The initially uniform Cr concentration distribution with a peak concentration at 25% (i.e., the nominal Cr content) becomes very nonuniform with the formation of the α′- and G-phase precipitates as these absorb Cr atoms. The peak Cr distribution shifts down to a lower concentration [16,17] with holding time. For this reason, an aged specimen with the Cr distribution peak lower than 25% has effectively a higher TEP than its unaged state because the TEP is higher when Cr is lower. Therefore, it can be deduced that the cause of embrittlement, i.e. the formation of α′- and G-phases is directly related to the TEP, which consequently makes the TEP useful for the evaluation of the embrittlement in this material.

Fig. 5 shows the SEM images of specimens thermally aged at 475 °C for (a) 50 h and (b) 500 h of SDSS 2507 respectively. No significant change is observed in the austenite (light gray) and ferrite (dark gray) phases of the specimen aged for 50 h. On the other hand, visible changes due to intensive corrosion in the interior and boundaries of the ferrite grains are observed after 500 h. It has been reported that the highly localized corrosion attack in the ferrite phase is caused by local impoverishment of Cr resulting from α-α′ separation [25–27].

The correlation between ferrite hardness and TEP is shown in Fig. 6 where there are two distinctive characteristics with different slopes. The hardness values for the TEP in 1.0–1.65 μV/K exhibit below 380 HV. At these hardness values the alloy can absorb impact energy up to 220 J according to impact tests performed on untreated and 10 h exposed specimens. On the contrary, the absorbed impact energy reduces below 70 J for the TEP above 1.72 μV/K. This two-regime behavior of the hardness-TEP relationship is similar to the result of Massoud et al. [28] who made TEP measurements on a cast DSS used for the primary loop in PWR nuclear power plants.

In order to assess the effect of the embrittlement on the fracture characteristics of 2507 SDSS, Fig. 6 shows SEM fractographs of the untreated and specimens aged for different periods of time. Fig. 7(a and b) which are for unaged and 10 h aged specimens illustrate dimpled fracture surfaces that are typical of microvoid coalescence in the ductile fracture. The fracture behavior changes completely

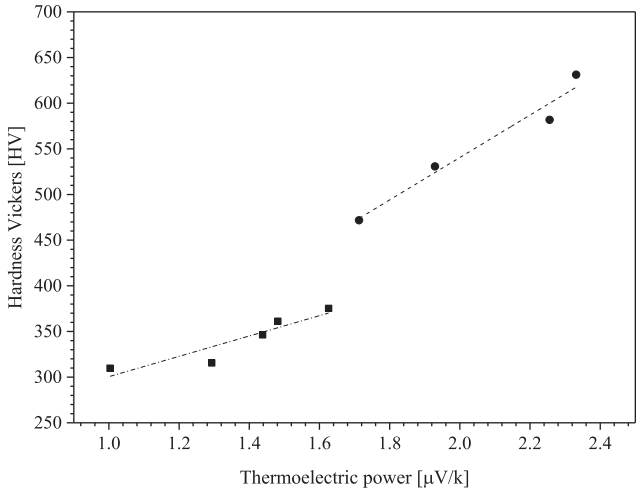

Fig. 6. Correlation between Vickers microhardness and TEP coefficient.

for holding times of 100 h and 300 h as seen in Fig. 6(c and d), respectively. The presence of the cleavage type fracture is observed throughout the fracture surfaces indicating a brittle fracture. These results are supported by findings of Chandra et al. [29] who concluded that the presence of α' precipitates is a strong influence causing shearing of the austenite at the cleavage planes. Similar results were reported by Silva et al. [27] who found that the presence of cleavage fracture is related to the presence of α' precipitates. According to these results, it is clear that the formation of α' phase has a considerable effect on the embrittlement of thermally aged 2507 SDSS.

5. Conclusion

This work investigates the feasibility and sensitivity of the thermoelectric power measurement for monitoring 475 °C embrittlement of 2507 SDSS. It is shown that the TEP is sensitive to the α' precipitation in ferrite and it is well correlated with the ferrite hardness, clearly distinguishing the ductile and brittle fracture modes. The tensile properties and the combined analysis of the result from Charpy impact test and the fractographic images confirm that the α' precipitation has a considerable effect on the thermal embrittlement of the 2507 SDSS. The TEP measurement

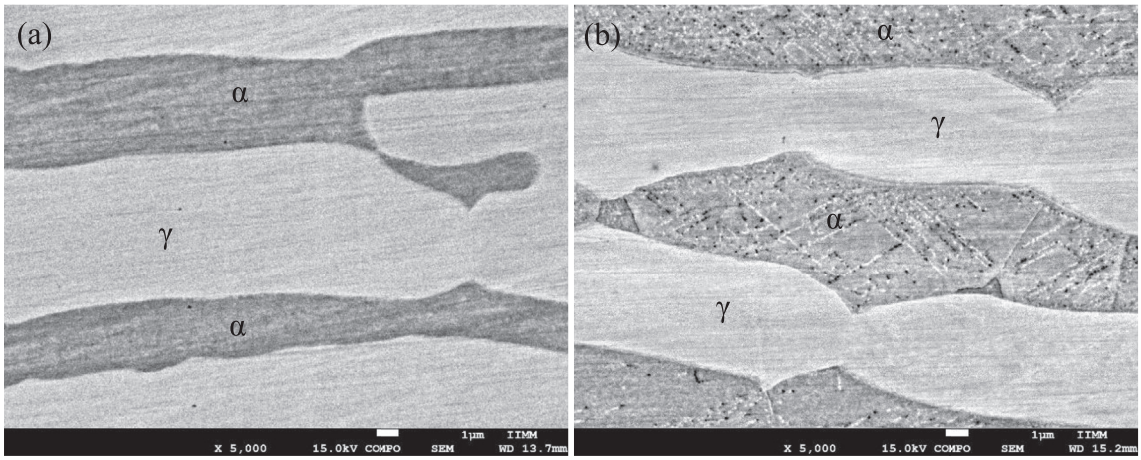

Fig. 5. High magnification SEM micrograph of austenite (γ) and ferrite (α) phases in a 2507 SDSS aged for (a) 50 h and (b) 300 h after DL-EPR test.

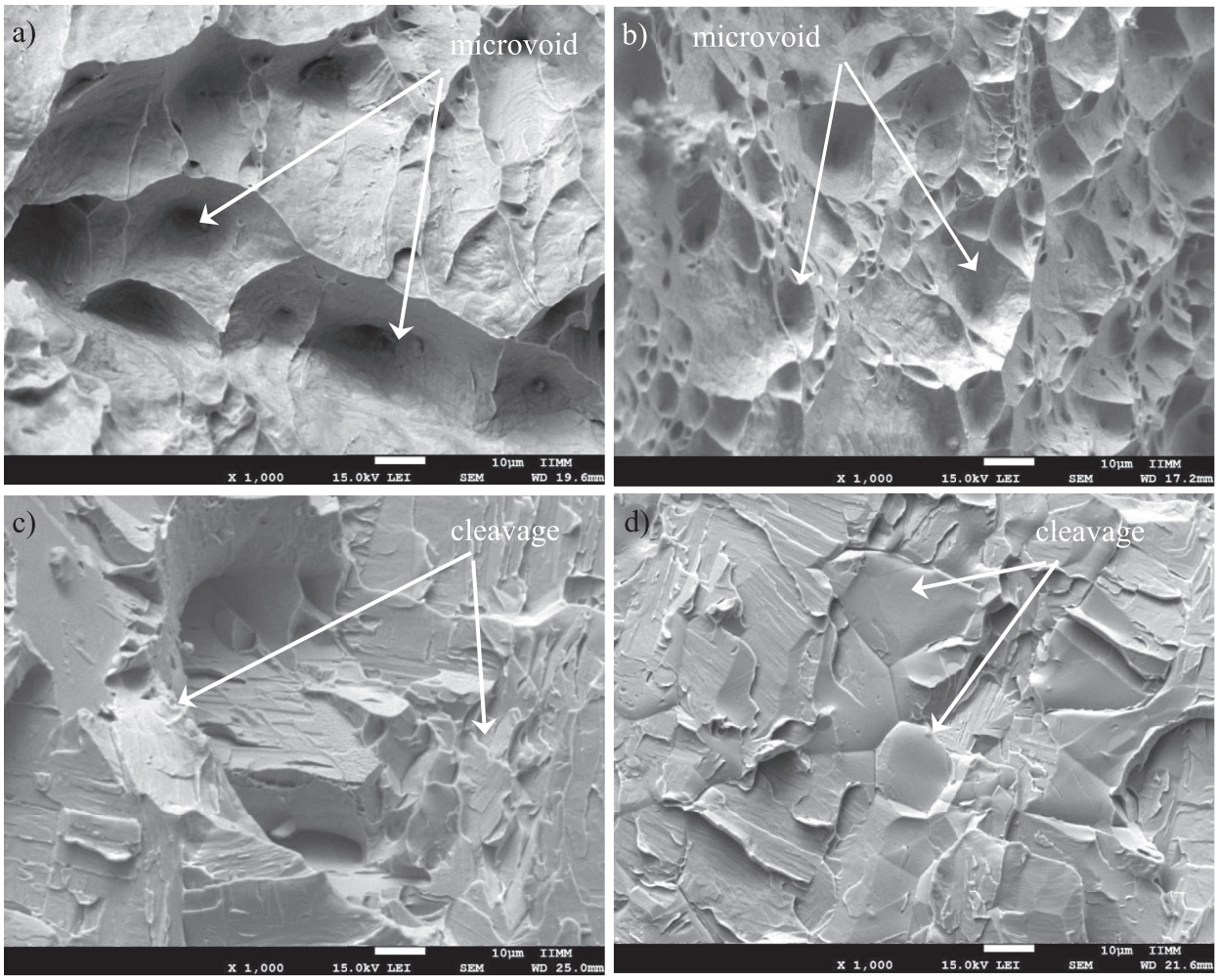

Fig. 7. Fracture surfaces of impact specimens for (a) untreated; and aged for (b) 10 h, (c) 50 h and (d) 300 h.

technique can therefore be used for an in-situ detection and quantitative evaluation of the 475 °C embrittlement damage in this material.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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