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Hydrogen-induced micro-void formation in copper used for spent nuclear fuel disposal canisters

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ABSTRACT

Spent nuclear fuel is planned to be deposited in the 50 mm thick copper canisters at about 500 m depth in the bedrock. Hydrogen uptake may occur in the disposal conditions in copper due to corrosion reactions and effects of irradiation. Therefore, it is important to know in which conditions the hydrogen uptake results in the formation of pressurized hydrogen bubbles near the copper surface. During the thermal desorption spectroscopy (TDS) measurements the existing hydrogen bubbles grow due to accumulation of dissolved hydrogen and build-up of hydrogen gas pressure inside the voids. The further growth of the voids occurs by plastic deformation and results opening of the voids near the copper surface due to increasing temperature. The friction-stir weld metal samples of phosphorous-doped oxygen-free copper were cathodically charged with hydrogen in a 1.0 N H_2SO_4 solution with added 10 mg/L thiourea at various electrochemical potentials, -0.95…-1.3 V_{SCE}. A threshold potential of -1.10 V_{SCE} was found for the marked increase of hydrogen uptake and hydrogen-induced void formation near the copper surface.

1. Introduction

In KBS-3 method of long-term geological disposal of spent nuclear fuel, the canister consists of a ductile cast iron insert and a copper shell (Fig. 1). The purpose of the copper shell is to act as a ductile corrosion barrier that prevents the release of the radioactive substances from the canister. The copper shell is made of electrolytically refined oxygen-free phosphorus-doped copper (Cu-OFP).

One of the key issues related to the safety of the canister is the effect of hydrogen on the canister materials [1]. The solubility of hydrogen in copper is low over a wide range of temperatures, but some hydrogen can become trapped in so-called hydrogen traps. One of the suggested traps in copper is the presence of oxide particles. The material used in the KBS-3 canisters is oxygen-free phosphorus-doped copper, but some oxygen may be introduced in the weld metal when the canister lid is friction-stir welded (FSW) to the copper shell without the use of sufficient gas shielding [2]. The hydrogen present in the material consists of the metallurgical hydrogen naturally present from the manufacturing with additional hydrogen coming from the environment. External intake of hydrogen may result from sulphide corrosion occurring on the surface of the copper canister in the final deposition environment [3–5]. There are also effects due to the irradiation from the spent nuclear fuel inside the canister that increase the hydrogen intake potential of the copper [6].

The mechanical properties of FCC materials such as copper are known to be affected by the presence of hydrogen, effect called hydrogen embrittlement (HE) [2,7–11]. The effects of hydrogen on copper are noticed under electrochemical hydrogen charging in constant load testing (CLT), where the creep rate of the material is enhanced in the presence of hydrogen, compared to the tests done in distilled water [8]. The mechanism of HE in this case is the formation of hydrogen-induced micro-voids along grain boundaries in the material [2,7–11].

Hydrogen can be charged into the copper samples under different non-equilibrium conditions. Typically, the copper sample is either exposed at an elevated temperature to a hydrogen-rich environment (thermal charging) [2,7], or the copper sample can be immersed at ambient temperature in a solution at an external negative overpotential (electrochemical charging) [8,9,11]. The chosen method determines the fugacity of hydrogen and the charging conditions determine how much hydrogen may enter into the copper material. In electrochemical hydrogen charging the difference between applied cathodic potential as compared to the equilibrium corrosion potential at the copper surface in the charging solution is the overpotential of the hydrogen evolution reaction. Hydrogen can damage the sample surface during charging and this damage

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Fig. 1. KBS-3 canister. Copper shell and lid on the left and cast iron insert and steel lid of the insert on the right. Posiva Oy.

Table 1
Specification and two composition measurements for the studied copper, Cu-OFP [12].

	Cu	Ag	As	Bi	Cd	Fe	H	Hg	Mn	Ni
Spec.	min. 99.99 wt.-%	<25	<5	<1	<1	<10	<0.6	<1	<0.5	<10
Measured	min. 99.992 wt.-%	13.9	0.92	0.13	<0.003	0.6	0.5	<0.5	<0.1	0.6
	min. 99.992 wt.-%	14.1	0.98	0.14	<0.003	0.7	0.3	<0.5	<0.1	0.8
	O	P	Pb	S	Sb	Se	Sn	Te	Zn	
Spec.	<5	30–70 ppm	<5	<8	<4	<3	<2	<2	<1	
Measured	1.8	51 ppm	0.26	5.0	0.06	0.1	0.06	0.08	<0.1	
	1.5	49 ppm	0.27	5.2	0.07	<0.1	0.06	0.07	<0.1	

is the evidence of the hydrogen influence on the mechanical properties of copper.

The purpose of this study is to increase the general understanding of the HE phenomenon of copper and to establish a clear electrochemical threshold potential for the formation of hydrogen-induced micro-voids in the friction-stir weld metal of the canister copper, the most significant form of hydrogen embrittlement of copper.

2. Experimental methods

The formation of hydrogen-induced micro-voids was studied on friction-stir welded (in air) oxygen-free phosphorus-doped copper, Cu-OFP. The full-scale copper canister weld (50 mm thick) was chosen because of the small oxide particles entrapped to the copper weld metal microstructure which enhance the hydrogen uptake in the material and help study the hydrogen-induced micro-void formation. The microstructural analyses of the FSW copper canister welds have been performed in reference 12. The grain size in the FSW weld metal varies locally due to the varying heat inputs and strain rates in the different weld zones. Additionally, the welding process, operated in air without a shielding gas, leads to the introduction of oxide particles in the weld metal from the unshielded surfaces. EBSD imagining of the weld metal and the average grain size measured from the weighted average according to the area of each grain in the weld zone is presented in Fig. 2. The chemical composition of the material is shown in Table 1.

Specimens for hydrogen thermal desorption spectroscopy (TDS), Fig. 3, were cut from the retreating side (RS) of the friction-stir weld metal (Fig. 2a) of the canister copper material using electro-discharge machining (EDM). Specimens were mechanically ground using common wet grinding techniques to remove the affected layer from EDM machining. The specimens were finished with polishing down to 0.25 μm diamond paste.

The specimens were exposed to the electrochemical hydrogen charging in a three-electrode electrochemical cell with Hg/Hg_2SO_4 reference and Pt counter electrodes and a Gamry potentiostat for controlling the applied electrochemical potential. Electrochemical hydrogen charging was performed at 318 K (45°C) for 7.2 ks (2 h) at varying cathodic potentials (-0.95…-1.3 V_{SCE}) in a 1.0 N H_2SO_4 solution with added 10 mg/L thiourea. The equilibrium corrosion potential at the copper surface in the charging solution was between -0.41 and -0.45 V_{SCE}.

Hydrogen uptake and trapping were measured using a custom-made TDS apparatus designed and assembled at Aalto University. The device is based on the mass spectrometry measurement of hydrogen partial pressure in the ultra-high vacuum chamber under a constant controlled heating rate. The initial hydrogen partial pressure data were converted to the conventional hydrogen desorption rate (in at. ppm/s) vs. temperature using a calibration procedure based on the additional measurements of hydrogen concentration performed with the LECO technique. With a basic vacuum of 5×10^{-9} mbar, the hydrogen concentration measurements are accurate down to quantities of about 0.1 at.ppm. The equipment enables the heating rate to be varied between 1 and 10 K/min allowing the evaluation of the activation energy of the hydrogen trapping sites in the studied material. The operating temperature range is from room temperature (RT) to 1470 K (1,200°C). The heat-

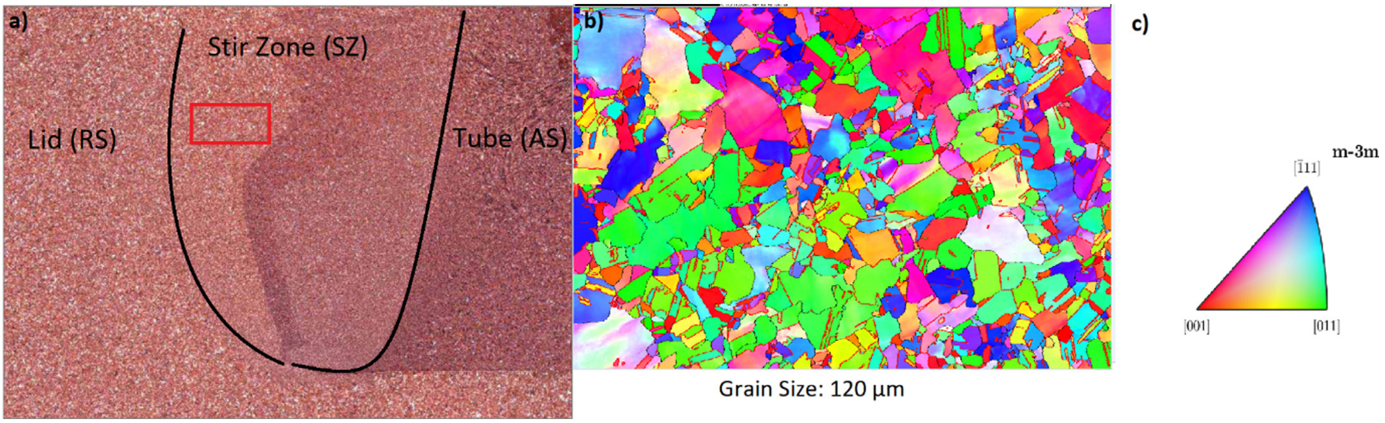


Fig. 2. (a) The location of studied specimens on the retreating side (RS) of the friction-stir weld. (b) EBSD image of microstructure and grain size of the studied stir zone. (c) The inverse pole figure color coding for the EBSD. [2]

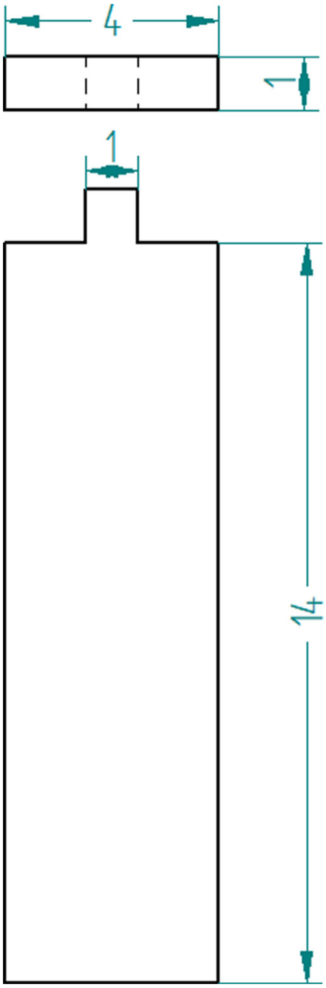


Fig. 3. The shape and size of the studied TDS specimens.

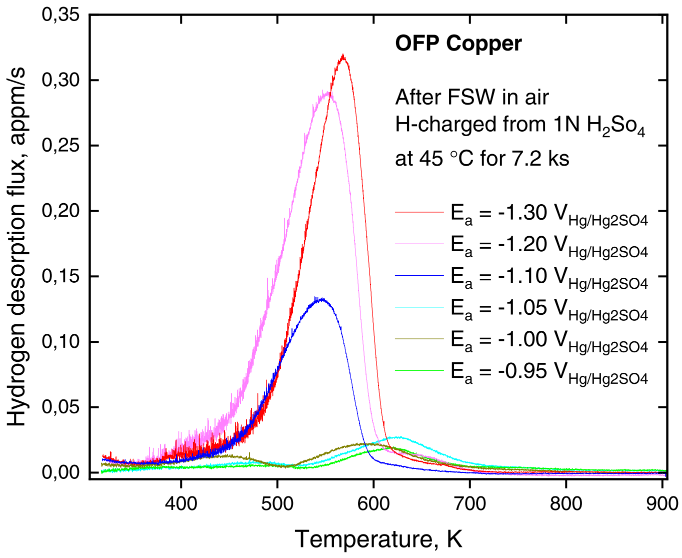


Fig. 4. The TDS measurements of hydrogen-charged OFP copper specimens after charging at various cathodic potentials (-0.95…-1.3 VSCE) for 7.2 ks/2 h in 1.0 N H2SO4 solution with added 10 mg/L thiourea.

ing rate of 10 K/min was used from RT to 920 K (650°C) to study the release of hydrogen and the behavior of various trapping sites in a full-scale copper canister weld.

The microstructural analysis was performed with a Zeiss Ultra 55 field emission gun scanning electron microscope. In addition to examining the exposed surfaces, the samples were also prepared for cross-sectional analysis. In order to examine the edges of the cross-sections, where the hydrogen-induced micro-voids are expected to be found, the specimens were coated using electroless nickel plating (ENP). The utilized ENP protocol was from Table A-1 from Ref. [13] with a palladium-based activation solution from European Patent 2 233 608 B1 [14]. After the coating, the specimens were mounted using Struers PolyFast resin and were prepared using conventional wet grinding and polishing techniques down to 0.25 µm diamond paste. Before EBSD imaging, the sample surfaces were finished with vibratory polishing in colloidal silica with a Bruker VibroMet II vibratory polisher for 5 h.

3. Results

3.1. Thermal desorption spectroscopy

The copper samples were cathodically hydrogen charged at varying electrochemical overpotentials and the results of the TDS measurements are shown in Fig. 4. Electrochemical hydrogen charging at cathodic potentials higher than -1.10 V_{SCE} manifests only a small hillock in the hydrogen desorption spectrum around 625 K corresponding to the metallurgical hydrogen. The samples that were charged below this threshold electrochemical potential show a large peak of hydrogen desorption around 550 K. The hy-

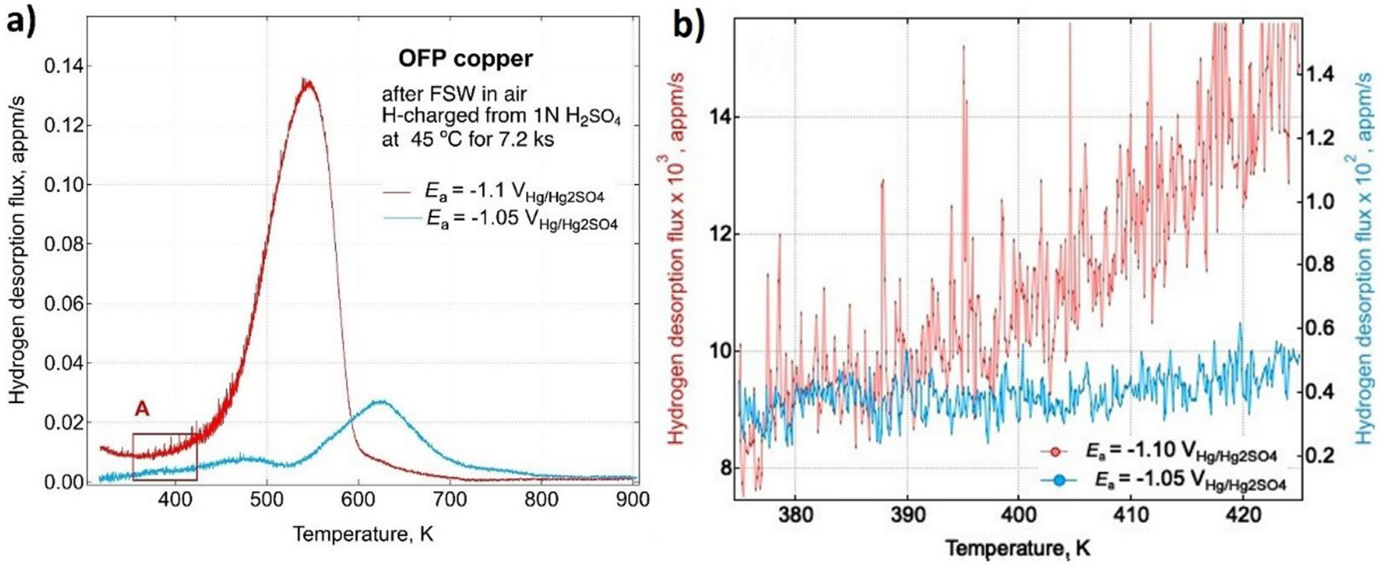
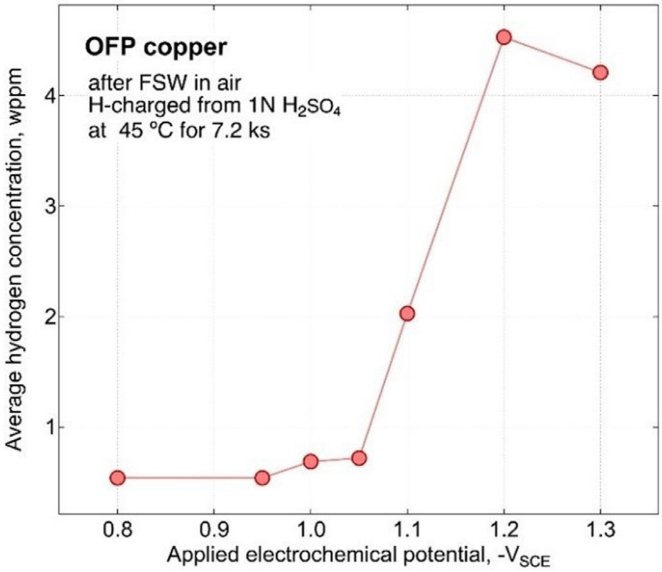


Fig. 5. (a) Appearance of hydrogen spikes in the TDS spectra of hydrogen-charged OFP copper specimens charged at -1.05 and -1.1 VSCE in 1.0 N H2SO4 solution with added 10 mg/L thiourea. (b) Close-up of the low temperature range of the TDS curve (A) showing the spiking behavior in the spectra.



File	E, V	t, ks	C_H, wppm
FSW_CuP_H8	-0.8	7.7	0.54
FSW_CuP_H11	-0.95	7.2	0.54
FSW_CuP_H7	-1.0	7.2	0.69
FSW_CuP_H12	-1.05	7.2	0.72
FSW_CuP_H3	-1.1	7.25	2.03
FSW_CuP_H9	-1.2	8.5	4.53
FSW_CuP_H4	-1.3	7.2	4.21

Fig. 6. The relationship between the applied electrochemical potential and the hydrogen content in the copper weld metal showing a significant increase in hydrogen uptake below -1.1 VSCE.

drogen peak has a complex shape and a number of spikes appear in the temperature range from 400 to 500 K (Fig. 5b), similar to the results reported in [11]. The spikes are caused by the growth and opening of the hydrogen-induced voids/bubbles, which are filled with hydrogen gas of elevated pressure and located just beneath the specimen surface. The hydrogen spiking events correspond to sudden increases of the pressure in the UHV chamber of the TDS apparatus, when the ligaments of the material between the voids and the specimen surface break under the build-up of hydrogen gas pressure inside the voids with increasing temperature.

The temperature position of the hydrogen desorption peak depends on the effective trapping sites of hydrogen, as well as on the heating rate of the specimen. The magnitude and shape of the hydrogen desorption peak are related to the hydrogen release in each of the trapping sites. Thus, the area under the desorption peaks corresponds to the amount of hydrogen trapped at these sites (Fig. 6). Previously it was found that the studied as-supplied copper that was friction-stir welded in air had a metallurgical hydrogen content of 0.79 wppm [15].

4. Electron microscopy

The specimen surfaces were studied before and after TDS measurements to observe the origin of the hydrogen spiking in the TDS spectra. All samples showed some effects of the hydrogen charging by formation of voids in the specimen surfaces. There, however, was a large difference in the character of the voids between the samples charged above and below the threshold potential of -1.1 V_{SCE} observed in the TDS measurements.

The specimens that were charged at higher cathodic potentials, above -1.1 V_{SCE}, show voids with maximum diameter of 200 nm. The specimen surfaces otherwise remained relatively smooth (as seen in Fig. 7a) with some imperfections that are part of the mi-

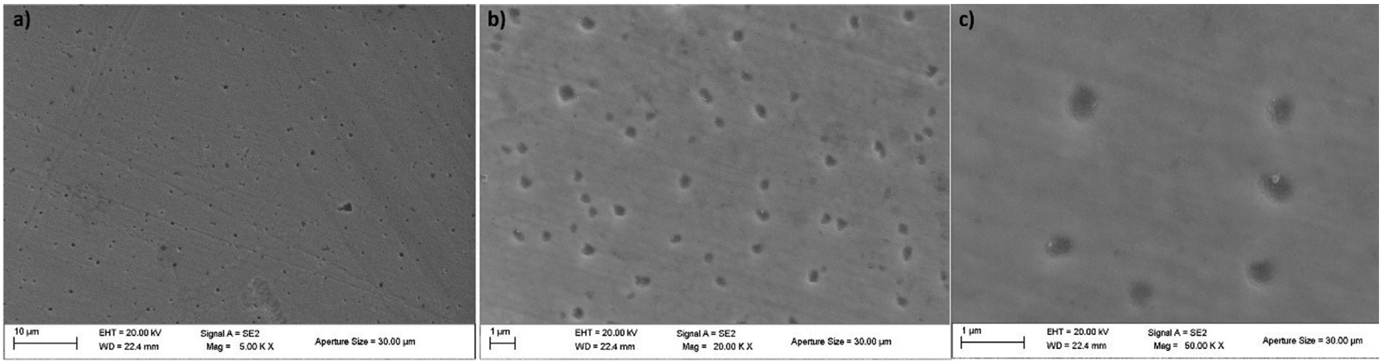


Fig. 7. Surface of copper specimen charged at -1.05 VSCE in 1 N H2SO4 solution with added 10 mg/L thiourea. (a) The surface shows no significant damage after hydrogen charging. (b) Small and shallow depressions in the material surface are present locally. (c) Close-up of depressions that have not developed to clear voids, yet.

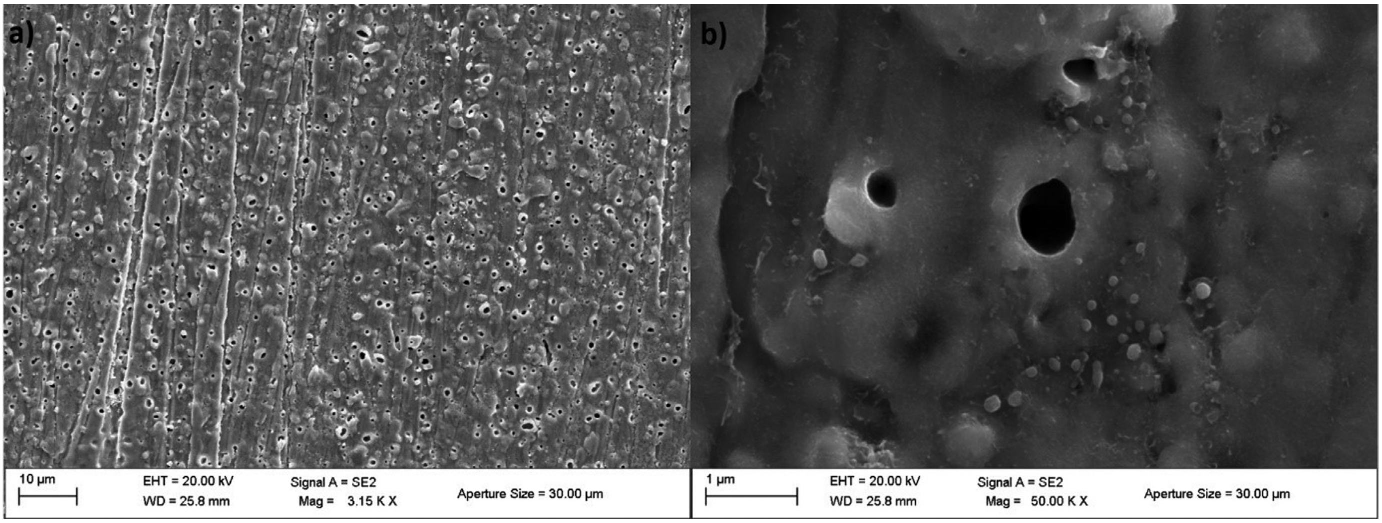


Fig. 8. Specimen charged at -1.10 VSCE in 1 N H2SO4 solution with added 10 mg/L thiourea. (a) Specimen surface damage shows small opening voids with diameters up to 1 µm. (b) Close-up of the voids.

crostructure. Small depressions were observed locally which can be correlated to the minor hydrogen spikes in the TDS spectra (Fig. 5).

A significant damage was observed in the specimen surfaces hydrogen charged below the threshold potential of -1,1 V_{SCE} (Fig. 8). The whole specimen surface was covered with small opening voids with diameters up to 1 µm indicating that a marked hydrogen-induced void formation occurred close to the specimen surface during hydrogen charging.

After electroless nickel plating of the surface, the cross-sections of the specimens were examined. The nickel plating protects the edge of the specimen cross-section during the polishing process and allows the examination of the immediate edge (Fig. 9). The surface and subsurface of the material exhibited spherical voids up to diameters of 2 µm and up to a depth of 25 µm.

The specimen surface was finished with vibratory polishing in colloidal silica and examined using EBSD. It was observed (Fig. 10) that the voids are located also in the copper matrix of the material.

5. Discussion

The TDS curves show that the electrochemical overpotential of the hydrogen charging affects the intake of hydrogen into the copper material significantly. The lower potentials result in a higher intake of hydrogen, and below the threshold potential of -1.10 V_{SCE} the material surface damage occurs during charging and the hydrogen intake increases markedly, see table in Fig. 6.

The hydrogen spiking in TDS measurements is correlated to the opening of hydrogen-filled voids near the specimen surface. The magnitude of the hydrogen spikes is related to a large number of opening voids on the material surface, with some voids forming in the subsurface layer. These hydrogen-induced voids have been observed also in earlier studies [7,9] with much more severe hydrogen charging conditions. This study shows that they occur at and below the threshold electrochemical potential of -1.10 V_{SCE} in the studied mild environmental conditions of 1 N H_2SO_4.

Previously, the penetration depth of hydrogen in Cu-OFP was calculated to be 280 µm, but the hydrogen-induced micro-voids were only observed up to a depth of 50 µm [9]. In this study, with mild electrochemical hydrogen charging conditions, micro-voids were observed up to a depth of 25 µm. The difference is due to the different hydrogen charging conditions and to the significant difference in the duration of the experiments.

The voids were observed to form in the copper matrix (Fig. 10). The material is the FSW weld metal and known to have small oxide particles that may act as initiation sites for the accumulation of hydrogen in copper.

The formation of the hydrogen-induced micro-voids, the most significant form of hydrogen embrittlement of copper, may not occur in the environments relevant to the final disposal conditions where the sulphide concentrations are in the range 10^{-7} to 10^{-4} mol/L [4] and corrosion potential of copper (close to the equilibrium potential of Cu/Cu_2S reaction) is always markedly above -0.8 V_{SCE} [3]. Thus, the corrosion potential of the copper canister

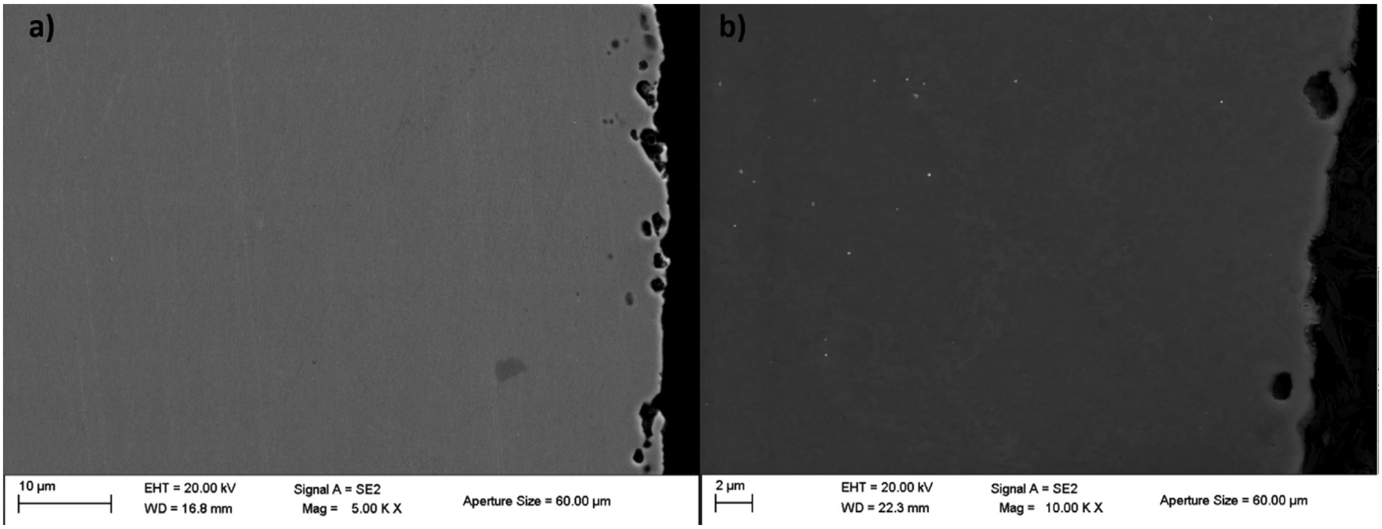


Fig. 9. The cross-sections of specimen hydrogen charged at -1.3 VSCE in 1 N H2SO4 solution with added 10 mg/L thiourea. Specimen was coated using ENP to protect the surface during sample preparation. (a) and (b) show the microvoids on and under the surface of the material.

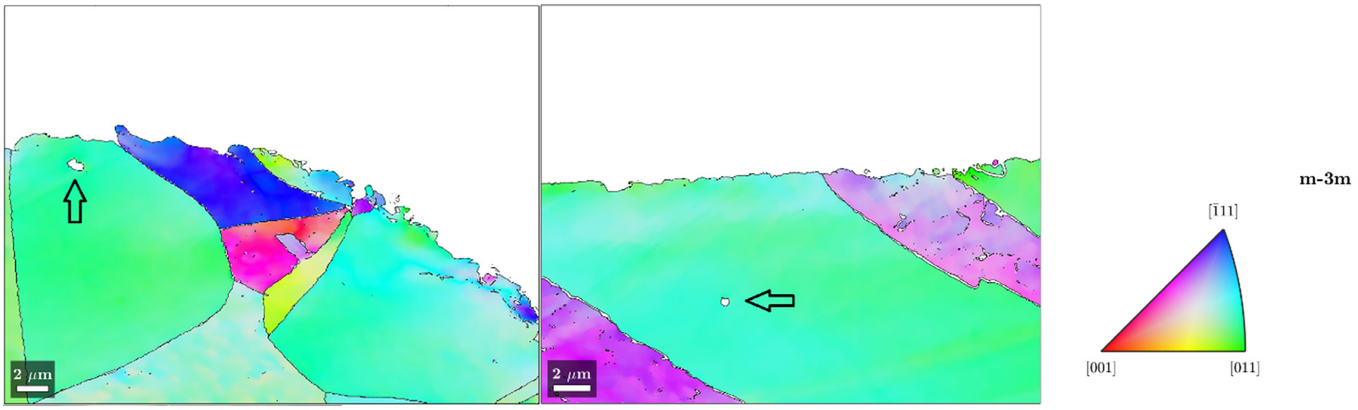


Fig. 10. EBSD images of specimen hydrogen charged at -1.3 VSCE in 1 N H2SO4 solution with added 10 mg/L thiourea. In (a) and (b) the arrows point to voids in the copper matrix.

surface is much higher than the observed cathodic threshold potential for hydrogen-induced void formation and both the cathodic current density (depends on the rate of sulfide ion transport to the copper canister surface) and the hydrogen gas pressure are low.

6. Conclusions

It was demonstrated for oxygen-free phosphorus-doped copper (Cu-OFP) FSW weld metal that under specific conditions electrolytic hydrogen charging will damage the specimen surface. The friction-stir weld metal specimens of Cu-OFP were cathodically charged with hydrogen in a 1.0 N H_2SO_4 solution with added 10 mg/L thiourea at various electrochemical potentials, -0.95…-1.3 V_{SCE}. A threshold potential, -1.10 V_{SCE}, was found for the marked increase of hydrogen uptake and hydrogen-induced bubble/void formation near the copper surface. During the thermal desorption spectroscopy (TDS) measurements the existing hydrogen bubbles grow due to accumulation of dissolved hydrogen and build-up of hydrogen gas pressure inside the voids. The further growth of the voids occurs by plastic deformation and results in blistering and opening of the voids near the copper surface due to increasing temperature. Hydrogen influence on the mechanical properties of copper is related to the hydrogen-induced bubble/void formation near the copper surface which is the most significant form of hydrogen embrittlement of copper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Patrik Sahiluoma: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Yuriy Yagodzinskyy:** Conceptualization, Methodology, Software, Formal analysis, Data curation. **Sven Bossyut:** Conceptualization, Resources, Supervision, Project administration. **Hannu Hänninen:** Conceptualization, Methodology, Resources, Writing – review & editing.

Data Availability

Data will be made available on request.

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