Influence of hydrogen-charging to copper-based materials for gas installation

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With the goal of net-zero emissions by 2045 there are dramatic changes upcoming to the energy sector. Fossil fuels must be replaced by climate-friendly alternatives, where hydrogen will play a major role. The tolerance of materials in contact with hydrogen is the key point, as different classes of materials (e.g. high-strength steels, Aluminum, Titanium) can take damage by hydrogen absorption, for example by showing embrittlement. It is therefore essential for design and development engineers to be aware of the materials' tolerance to (high pressure) hydrogen.

Copper-based alloys have a long tradition of usage in gas installations. The former so called "Stadtgas" or "Leuchtgas" was prior to natural gas used within the gas network. It was produced by coal gasification and contained an average of 51 Vol.-% while certain areas in Germany containing up to 70 Vol.-% Hydrogen. Besides Hydrogen the "Stadtgas" contained reasonable amounts of methane (≈ 20 Vol.-%) and Nitrogen (≈ 15 Vol.-%) and up to 10 Vol.-% of CO, which made it very toxic and promoted the switch to natural gas within the 1960s.

Unfortunately, most of this traditional knowledge from the past is related to lead containing alloys and has never been officially proven by scientific experiments.

Furthermore, related to the upcoming ban of leaded alloys, new machinable solutions have been developed and are now in the process of implementation for gas and water service.

Several new copper-based alloys have been tested by the Kupferverband and its member companies together with the Institute for Materials – Chair for Materials Testing of the Ruhr-University Bochum for their suitability to service under 100% hydrogen. The results of some lead-free successor materials to the lead containing standards are given in this paper.

New generations of machinable copper-based alloys are using e.g. Sulphur, silicon or manganese to enable chip breakage instead of lead. These new materials do not only show very good machining properties but also significantly increased advantageous mechanical properties such as higher yield and tensile strength. To evaluate their behavior for hydrogen service, a dedicated test program was carried out. After measurement of initial hydrogen content, tensile specimens were charged with pressurized hydrogen under 200°C and 275 bar for 23 days. The hydrogen content was measured after charging. To take annealing effects into account, another set of specimens were heat treated for the same time under 200°C without hydrogen. The

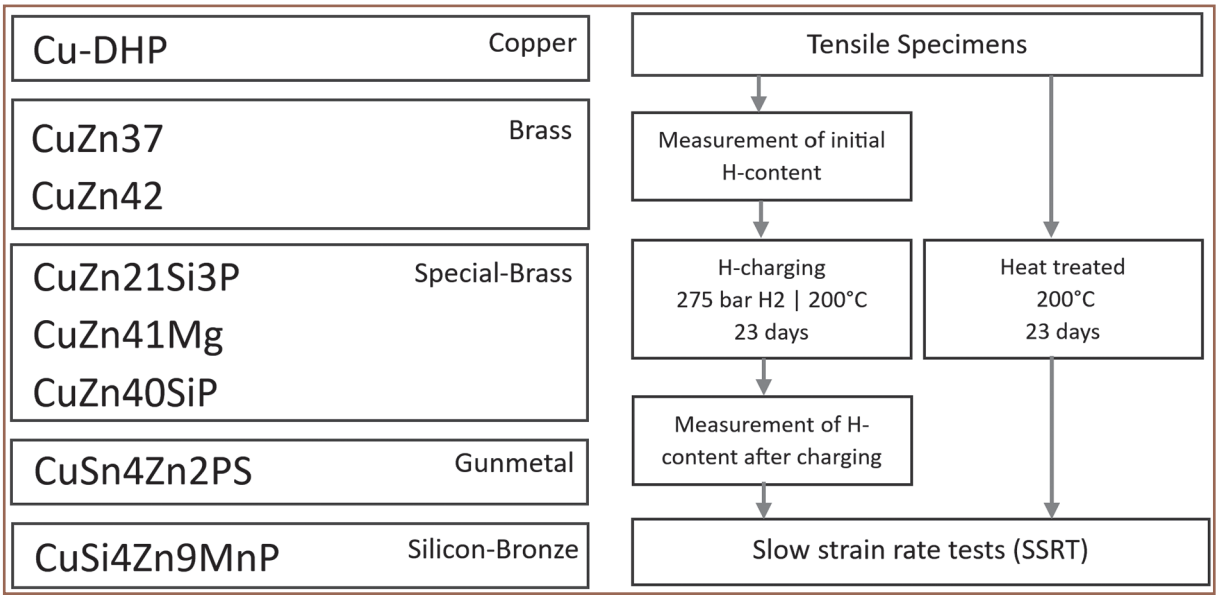


Figure 1: Selected materials and test program used.

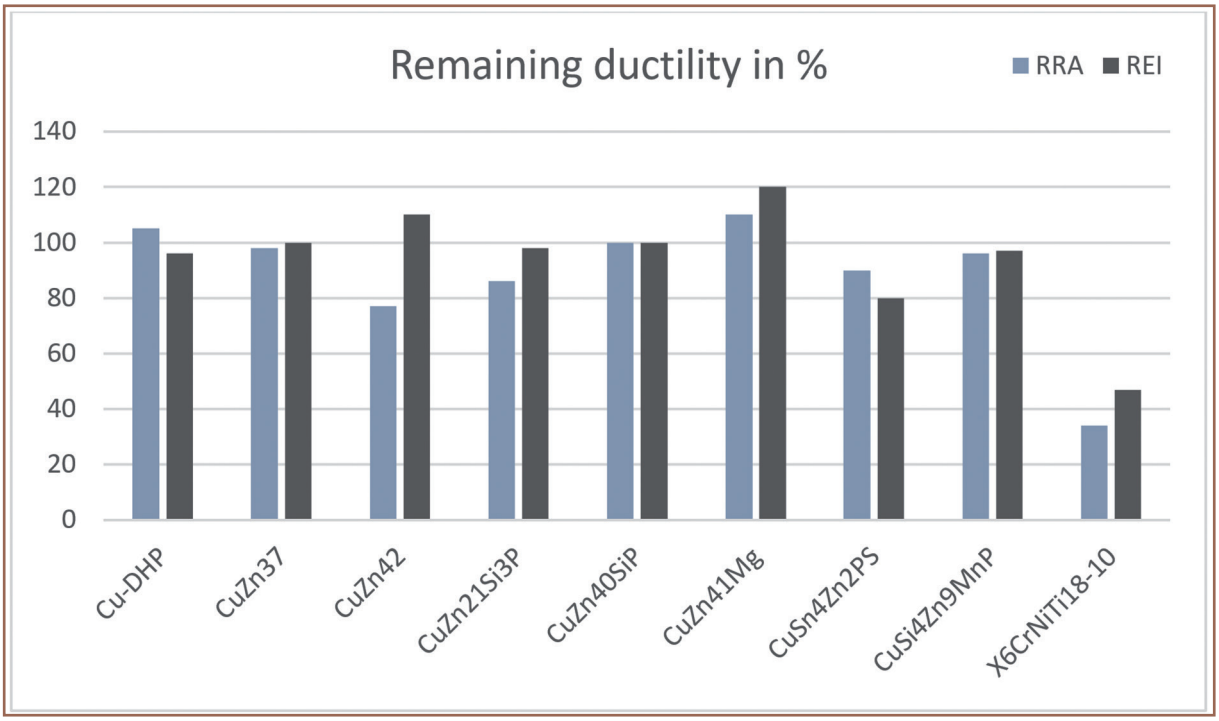


Figure 2: Remaining ductility of tested materials, using the area at fracture Z and the elongation at fracture A of H-charged and uncharged samples in comparison with X6CrNiTi18-10 [1].

specimens were afterwards tested using SSRTs (Slow-Strain-Rate-Tests). Initial, annealed and H-charged conditions were compared regarding their hydrogen content and their elastic and plastic behavior using embrittlement indexes RRA (Relative Reduction of Area) and REl (Relative Elongation) [1]. The remaining ductility of tested materials, gets calculated using the area at fracture Z and the elongation at fracture A of H-charged and uncharged samples in comparison. A fully ductile material will reach both RRA and Rel values of 100%. Materials with RRA and REl values significantly below 80% can be classified as sensitive to hydrogen in respect to the tested parameters.

$$RRA = \frac{Z_{H-charged}}{Z_{uncharged}} \qquad REI = \frac{A_{H-charged}}{A_{uncharged}}$$

The results are showing an excellent behavior of the tested alloys under hydrogen so that the initial deformability was almost fully preserved.

A valid explanation for these findings can be based on the hydrogen analyses. Fig. 3 summarizes all results for both the diffusive hydrogen (measured at 300 °C

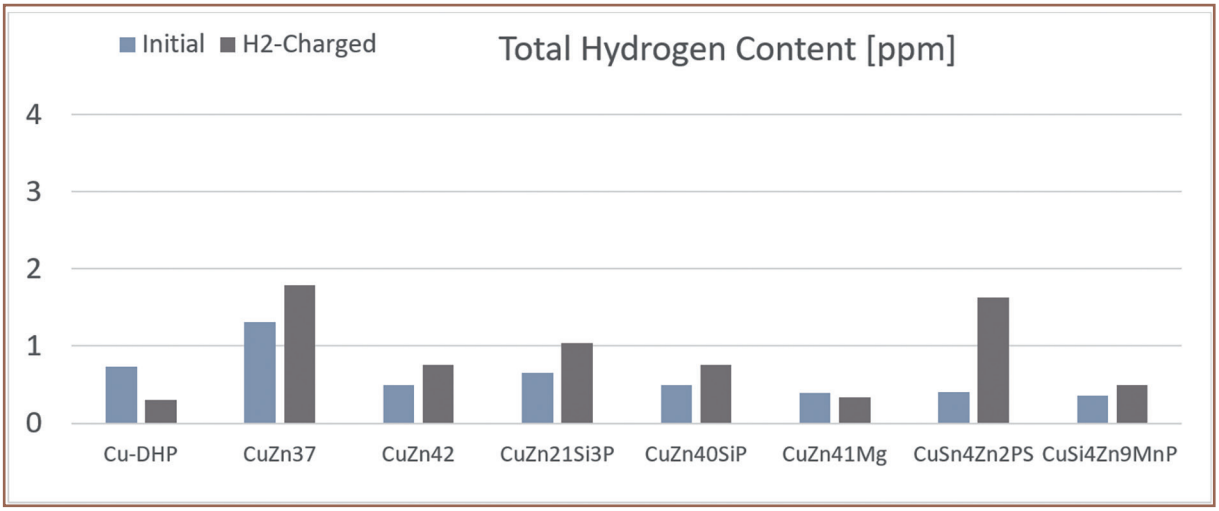


Figure 3: Hydrogen contents in initial state and after hydrogen charging. The before mentioned steel X6CrNiTi18-10 shows 26,8 ppm.

by means of TDMS) and trapped hydrogen (measured by MS-ME). The total hydrogen concentration is derived from the sum of these individual measurements. Prior to charging, most of the investigated materials exhibited a total hydrogen content well below 1.0 ppm. The amount of diffusible hydrogen after the hydrogen charging was for all given materials even below 1.0 ppm.

Based on the hydrogen content, the most obvious assumption seems to be that hydrogen embrittlement cannot take place due to the lack of diffusive hydrogen within the materials. Therefore, it is concluded that even high temperature and high hydrogen pressure do not yield a relevant hydrogen absorption in the alloys tested. With respect to potential applications, this conclusion is most relevant as Cu-based alloys have proven to be hydrogen safe. This proves, that even in former times copper and copper alloys have been used for good reasons in pure hydrogen or hydrogen containing services and that new lead free copper alloys do show both excellent machinability but at the same time excellent properties for safe hydrogen usage. However, Cu-based alloys have the potential to be used in more demanding hydrogen applications, such as high-pressure storage compartments or tanks.

References

[1] Jürgensen, J.; Frehn, A.; Ohla, K.; Stolz, S.; Pohl, M. Effect of Hydrogen Charging on the Mechanical Properties of High-Strength Copper-Base Alloys, Austenitic Stainless Steel AISI 321, Inconel 625 and Ferritic Steel 1.4511. Metals 2024, 14, 588. https://www.mdpi.com/2075-4701/14/5/588

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