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Effect of hydrogen embrittlement on the characteristics of copper-based shape memory alloy

Because of the good shape memory effect and superelasticity, copper-based shape memory alloys (SMAs) with aluminum and beryllium as binary and ternary elements are widely used in many applications (Cu-Al-Be SMAs). However, they are prone to corrosion in atmospheric conditions. This alloy is susceptible to corrosion due to hydrogen. This affects the characterization of the SMAs by absorbing the hydrogen and results in hydrogen embrittlement, makes changes in SME and SE effect. The process of hydrogen absorption was carried out under electrolytic charging under constant current density and the charged specimens were aged in the air at room temperature. The results show the decrement in SME from 99.8 % to 62%, and the tensile test revealed an increment in the transformation stress level from 200MPa-290MPa in the case of the charged specimen.

Keywords: Shape memory alloy; Shape memory effect; Cu-Al-Be SMAs; hydrogen embrittlement; corrosion.

1.0 Introduction

The compatibility of SMAs for their biochemical and Biomechanical property made the SMAs to be considered for usage. The usage of NiTi in orthodontics for its superiority owes to recovery force once deformed due to shape memory behaviour. The combination of steel bracket with NiTi wires is commonly used in orthodontic treatment. The wires and brackets are prone to embrittlement due to the storage of hydrogen. The alloys in the presence of electrolytes get affected results in galvanic corrosion (Asaoka K et al. 2002, Schiff N et al.2006). It is noticed that the corrosion may be due to the fluorides mainly due to the usage of toothpaste and prophylactic agents (Schiff N et al. 2002, Schiff N et al. 2004) which makes the alloys absorb hydrogen and results in hydrogen embrittlement of the alloys. However, it is noticed that some wires break after a few months of setting by the dentist in the oral cavity and the deformability of the wire will be lost (E F Harriset al. 1998, J J Hudgins et al. 1990).

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The investigations on the hydrogen embrittlement mechanisms on NiTi alloys for thermal and mechanical behaviour were found that the presence of hydrogen suppresses the phase transformation and the enthalpies were decreased and there is an increment in the transformation stress level up to 90 MPa (CW Ng et al. 2020). The tensile behaviour of the alloys has reported the appearance of two parts of the plateau, the first part was non-charged zone and the second part was charged zone with a heightening in stress and there was a decrease in strain in the upper plateau (Wissem Elkhal Letaief et al. 2017). DSC measurements were reported for NiTi wires charged with hydrogen in the austenitic phase (Runciman A et al. 2006) and observed the transformation temperature reduces linearly. Few researchers tried hydrogen charging in the martensite phase and observed (Tomita M et al. 2008, Yokoyama K et al. 2007) that the martensitic phase absorbs more hydrogen. The fracture in case of tensile deformation test before and during stress-induced martensite also revealed the cause of fracture is due to hydrogen embrittlement (Yokoyama Ket al.2001, Gamaoun F et al.2014, Gamaoun F et al.2011).

2.0 Materials and method

Cu-Al-Be shape memory alloy wires prepared by ingot metallurgy route with Cu-88.03 Wt.%, 11.5 Wt.% Al and 0.45 Wt.% Be with wire diameter 0.5 mm was considered for the study. The prepared wires were subjected to homogenization for 30 minutes at 600^{o}C and cut to a length of 20 mm and the transformation temperatures were measured by DSC. The charging of hydrogen to the wires was done by electrolytic charging by DC. The wires were placed in sodium sulphate 1.0 Wt.% solution as cathode, austenitic stainless steel is made as an anode. The schematic view of the set up is shown in Fig.1.

The current density of 1000 A/m^2 was set up for the electrolytic charging process. Continuous monitoring of the electrical circuit was done by connecting a multimeter in series and the charging was done for 10 hours. The charged wires were subjected to aging studies for 10, 15 and 20 hours. The charged and aged SMA wires are tested for phase transformation behaviour. The samples were heated to 150^{o}C and cooled to 100^{o}C and again heated to 150^{o}C with a

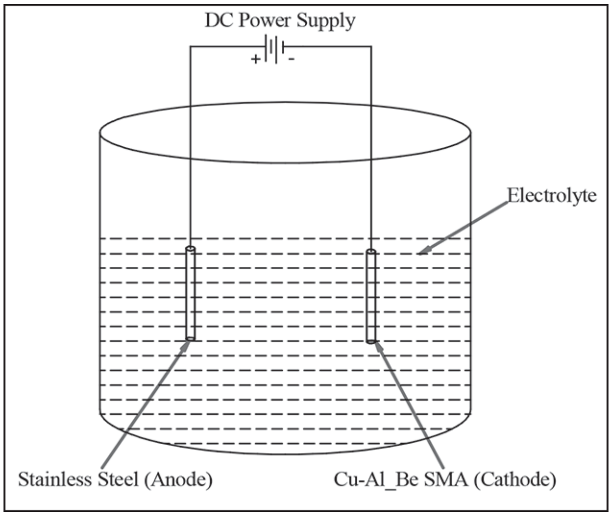

Fig.1: The schematic view of the experimental setup for hydrogen charging

constant heating and cooling rate of 10ºC/minute. A tensile deformation test was conducted at room temperature and the gauge length is 20mm. The wires were deformed up to 10% strain and unloaded with a loading and unloading rate of 1mm/minute.

3.0 Result and discussion

3.1 Composition and transformation temperatures of the SMAs

The prepared samples were subjected to compositional analysis and DSC measurements to know the composition and transformation temperatures. The composition and transformation temperature of the prepared alloy are listed in Table 1.

The DSC plot (Fig.2) for the alloy shows the transformation temperatures.

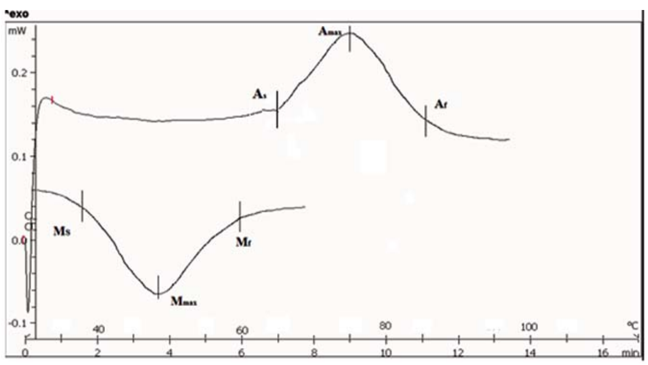

Fig.2: DSC plot of the SMA sample. CAB 1

The specimens were subjected to DSC analysis (Figs.3 and 4) which reveals that there is no much change in reverse transformation temperature for the charged and 10 hours aged alloy. The charged and aged specimens of more than 15 hours and 20 hours shown a shift in A_f temperature from 86.6ºC to 94.5ºC and 95.2ºC. By observing the trend of the peaks, they may disappear in both exothermic and endothermic reactions foraging more than 25 hours. There is more effect on transformation from A to M, which may be due to the absorption of H_2 and diffusion of H_2 into the core of the specimens. The presence of H_2 in the CuAlBe matrix adds to the resistance to the transformation during M to A.

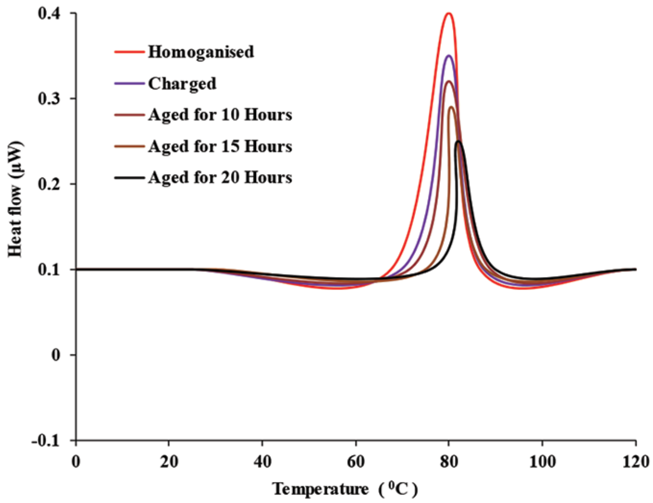

Fig.3: DSC plot of the SMA sample s after charging and ageing.

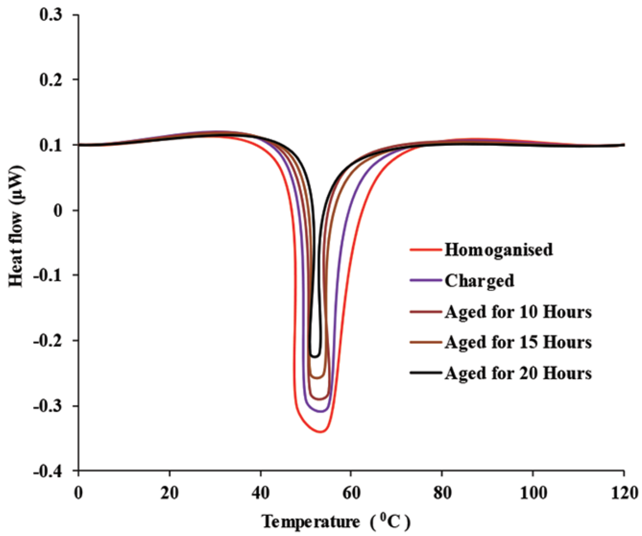

Fig.4: DSC plot of the SMA samples after charging and aging. (Martensitic transformation)

Table 1: Chemical composition and transformation temperature of SMA

Alloy ID	Chemical compositions (in Wt.%)			Transformation temperatures in ºC			
	Cu	Al	Be	M_f	M_s	A_s	A_f
CAB 1	88.03	11.5	0.47	42.3	57.2	67.6	86.6

3.2 The Shape Memory Effect (SME)

The shape memory effect (SME) of the alloy was calculated by bend test using the relation (θ_m /180º– θ_e), the angle recovered on heating (θ_m) is 90º, the angle recovered on unloading (θ_e) is 90º and SME obtained for a sample is 100% for the specimen without embrittlement.

The SME for the charged and aged specimen shows the decrement in the SME may be due to the formation of precipitates with aging which changes the composition of the alloy thereby alters the SME. Table 2 shows the % of the change in SME.

Table 2: Variation of SME in % by bend test

Alloy	Before ageing	After 10 hr.	After 15hr	After 20hr
CAB	99.8	96	84	62

3.3 Tensile deformation behaviour of SMAs

The micrographs (Fig.5) of the specimens before ageing reveals the ductile nature of fractography and for the aged samples, it is observed the fractured surface appears to be brittle due to the corrosion effect in the specimens.

Fig.6 shows the insight into the tensile behaviour of the charged and aged specimens. The stress-strain curves of the non-charged specimen manifest superelasticity. The non-charged specimen has a stress level of around 200MPa which is less compared to the charged specimen. There is an increment in the transformation stress levels up to 290 MPa for the charged specimen. The ageing at room temperature for 10, 15 and 20 hours increases the stress up to 300MPa, 320MPa and 350MPa. The increment in the stress levels in the charged and aged specimens indicate the diffusion and presence of hydrogen restrict the orientation of martensitic transformation which needs more energy to activate the process.

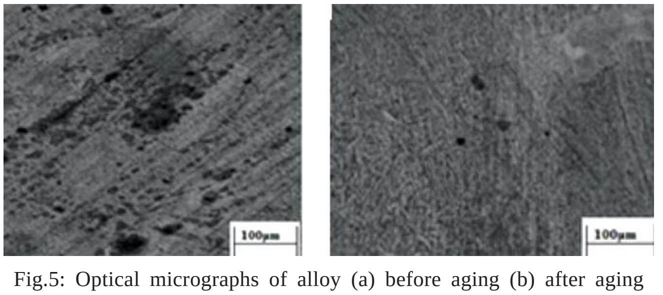

Fig.5: Optical micrographs of alloy (a) before aging (b) after aging 15 hrs.

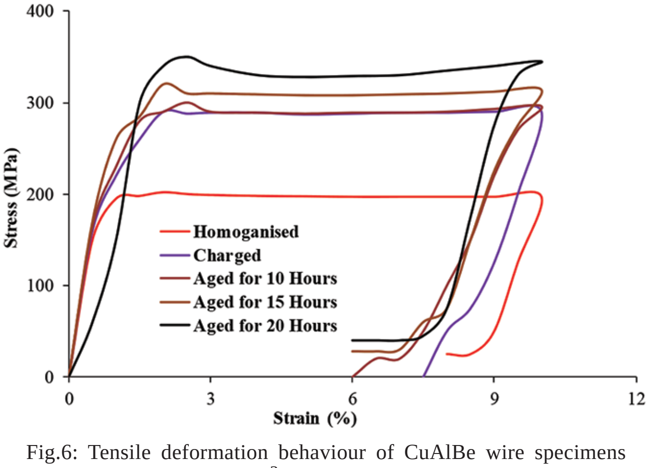

Fig.6: Tensile deformation behaviour of CuAlBe wire specimens charged at 1000A/m^2 and aged at room temperature

The residual strain in the charged and aged specimen after unloading is less than the normal specimen may be due to the propagation of stress plateaus in a non-flat manner.

Conclusions

The SME of the specimen decreased from 100% to 62% for the charged and aged (20 hours) alloy.The absorption of hydrogen in the specimen suppresses the phase transformation and the transformation peaks may disappear on more ageing. The enthalpies of austenite and martensite phase transformation were decreased. The fractured surface in aged samples appears to be brittle due to the corrosion effect in the specimens. The increment in the transformation stress level from 200MPa-290MPa in the case of charged specimen indicates the charging causes the martensite reorientation to occur at higher transformation levels.

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