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Chemical and mechanical treatments to improve the surface properties of shape memory NiTi wires

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Abstract

In this paper the results of an experimental study concerning the effect of different surface treatments on NiTi shape memory alloy wires are presented. These treatments were conducted in order to improve the adhesion properties between the NiTi wires and an epoxy resin, acting as the matrix of a composite material.

Mechanical and chemical surface treatments (immersion in acid and alkaline solutions), and different combinations of the above surface preparation procedures were studied.

For the characterisation of the resulting alloy surface conditions electrochemical impedance spectroscopy, polarisation curves and potential versus time measurements were carried out.

The alloy wire/epoxy matrix adhesion was characterised through pull out tests. The results proved that all adopted treatments can remarkably influence the electrochemical properties of the wires. The acid treatments favour the formation of a surface passivation layer, while the alkaline treatments are effective in producing a rougher surface morphology. Moreover, these basic treatments significantly reduce corrosion resistance of the alloys, another material property that has been incidentally investigated in the present context. The main effect of the mechanical surface treatment, consisting in abrading the alloy wires using an emery paper, was to increase the homogeneity of surface roughness.

From the experimental results clear indications on the most promising surface treatments can be inferred.

Keywords: Shape memory materials; Surface treatments; NiTi alloys; Composite materials; Pull-out test

1. Introduction

Shape memory alloys (SMAs), in view of their peculiar functional properties, are becoming increasingly interesting over recent years for several applications [1].

In view of their peculiar features and functional properties, SMAs are used for actuators, fittings, biomedical applications, clamping systems, etc. Another field, which is disclosing interesting perspectives, is the use of SMA wires as reinforcing and functionalising fibres in polymer matrix composites [2,3]. SMAs are definitely attractive candidates to be added to composites, as they exhibit properties and behaviours, like actuation capability, superelastic response and self-recovery, damping capacity [4], that can extend the application fields of these materials. Several papers report on the use of SMAs in composites, for the control of the component shape and residual internal stress [2].

One of the most widely investigated alloy system, i.e., NiTi, displays in addition to the typical shape memory phenomenology an excellent corrosion resistance in different electrolytes [5,6]. The high concentration of titanium in these alloys renders all processing and manufacturing steps, namely those carried out at high temperatures, particularly critical as concerns the risk of oxidation and, in general, oxygen contamination. Indeed, the formation of a surface oxide layer, e.g., TiO_2, may change the temperature range for the phase transition, on which the relevant aspects of the shape memory effect are based and that is very sensitive to the actual alloy composition [1]. The temperature shift observed in these cases can be ascribed to nickel surface enrichment, as this element is contributing to a lower

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extent than titanium to the formation of the outer oxide layer [1]. Similar modifications in the transition temperatures may be also induced by thermomechanical treatments, possibly involved with the processing of the SMA components, that can be subsequently recovered by suitable anneals [7,8]. All these aspects are to be considered as concerns both composite processing and application.

Moreover, in view of the final applications, the adhesion properties of the alloy-matrix interface have been evaluated [3,4,9,10], with particular reference to the influence of surface topography and surface finishing [11]. An optimised alloy-matrix interface is particularly important to fully exploit the potentials and the properties of shape memory materials [6]. Too a weak adhesion between fibre and polymeric matrix prevents or hinders an effective stress transmission. Moreover, partial or complete detachment of the alloy from the matrix may result in the loss of composite functionality.

The interface stability against corrosion is another important issue, as the formation of corrosion products at the fibre-matrix interface can unpredictably reduce the adhesion strength.

For these reasons several research efforts have been devoted to developing methods for modifying the surface of SMA fibres, in order to improve their corrosion behaviour and, thereby, adhesion to a polymer matrix [12]. As concerns native oxides, it should be mentioned that, although they usually enhance the adhesion strength between fibre and matrix because of their higher roughness [13], on the other hand, they may also show two drawbacks: reduction of the alloy volume that displays shape memory effect and debonding from the matrix, when a de-cohesive failure of the oxide occurs.

Other studies have considered the influence on interface adhesion of surfactants, silanes, titanates or of complex surface finishing processes [14,15]. Laser [16,17], excimer laser [18] and laser gas nitriding [19–22] treatments, strain-hardening and chemical passivation treatments [23] are alternative routes that have been explored over the years. The improvements descending from laser treatments are explained in terms of homogenisation of surface morphology and composition induced by melting. A positive effect has been also ascribed to surface hardening due to nitrogen incorporation in the native oxide layer, that for this reason results comparatively thicker [18].

Other treatments, that have been investigated to improve surface properties of NiTi materials are plasma immersion and ion implantation [24–30]. Mechanical abrasion was also considered and an improvement in the adhesion properties was generally observed [31,32].

Particularly attractive are chemical passivation treatments, that can be easily carried out by just dipping the SMA materials into a nitric acid solution, which induces the formation of a well protective titanium oxide layer, that remarkably improves corrosion resistance [33,34].

With electrolytic procedures it is possible to remove the heat-affected zones, modified by thermal treatments, even in small, finely structured components [34].

Chen et al. [33] have developed a two step treatment (nitric acid followed by a basic solution), which renders the oxide layer more porous.

We present herewith the results of a systematic investigation on several surface treatments conducted on two NiTi alloy wires with the intention of achieving an general improvement of their adhesion to a polymer matrix. The two alloys have been selected so that at room temperature in each of them one of the two polymorphs of the NiTi intermetallic is stable.

Surface treatments having effects on both chemical composition of the surface reaction products and on the topography of the alloy surface itself have been selected. The interplay between surface morphology and corrosion resistance has been also characterised using electrochemical and microscopy techniques.

The surface treated wires were subsequently embedded in a polymeric resin in order to check their adhesion using pull out test. In this respect the proposed approach represents a novel methodology to improve the performances of SMA functionalised composite materials.

2. Experimental

In the present study, NiTi wires with a diameter of 0.8 mm, made of two commercial NiTi alloys purchased from Memory Metalle Gmbh (D), have been investigated.

The first one (H_{sa}), has composition: Ni–45.23Ti wt.%; the second one, (M_{cw}): Ni–44.62Ti wt.%.

In the factory, before being delivered to our laboratory, the Hsa was straight annealed (sa) at 450 °C for 1 h and has a martensite to austenite transition peak temperature (Ap), equal to 91 °C (see below).

As discussed in the paper, the different surface conditions induced by the thermomechanical treatments, including composition changes of the outer layers of the two materials, are playing a major role in determining the observed results. Nevertheless, the different compositions of the selected alloys have been observed to induce detectable differences in the reported results.

The cold-worked (cw) M_{cw} alloy was not recovered after drawing and, therefore, it was still strain hardened when used in our experiments. The hardened condition stabilises the austenite phase down to −50 °C. All thermal data, provided with the product technical data sheet, have been actually confirmed by differential scanning calorimetry (DSC) tests we carried out on our own to measure all relevant transition temperatures. In particular, the M_{cw} material remained austenitic down to cryogenic temperatures. As concerns the H_{sa} alloy, the following transition temperatures were measured, to confirm the product specifications:

Martensite start (M_s)=45 °C
Martensite finish (M_f)=29 °C
Austenite start (A_s)=87 °C
Austenite finish (A_f)=99 °C

Therefore, from DSC results we can conclude that, as expected, at room temperature the H_{as} and the M_{cw} alloys are martensitic and austenitic, respectively.

Two kinds of surface treatments have been selected, after cleaning the surface of the wire specimens with acetone in an