Materials Science & Engineering A 587 (2013) 304–312

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Stress induced pop-in and pop-out nanoindentation events in CuAlBe shape memory alloys

C. Caër*, E. Patoor, S. Berbenni, J.-S. Lecomte

Laboratoire d'Étude des Microstructures et de Mécanique des Matériaux (LEM3), UMR CNRS 7239, Université de Lorraine, Arts et Métiers ParisTech, 57070 Metz, France

ARTICLE INFO

Article history:
Received 9 July 2013
Accepted 24 August 2013
Available online 6 September 2013

Keywords:
Nanoindentation
Martensitic phase transformation
SMA
Pop-in
Pop-out
Indentation Patel–Cohen factor

ABSTRACT

Constitutive models developed to predict Shape Memory Alloys (SMA) behavior are often based on a simplified phenomenological description of martensite variant activation under thermomechanical loading at the micro scale. This study aims at modeling and characterizing by nanoindentation the discrete variant activation events at the nanoscale. A new criterion is proposed to describe martensite variant activation beneath the indenter. Evidence of discrete martensitic transformation is observed during nanoindentation by the successive occurrences of pop-in and pop-out load events on the force versus displacement curve during respectively loading and unloading. Thus, the spatial-temporal discontinuity of phase transformation activation and propagation is highlighted at the nanoscale with the introduction of an indentation Patel–Cohen factor for both forward austenite–martensite and reverse phase transformations. Dislocation emission in pure nickel is first studied to validate both the nanoindentation testing procedure using a Berkovich indenter and the calculations of indentation Schmid factors to describe excursion bursts corresponding to dislocation activation and propagation. Good agreement is found between nanoindentation tests performed on a superelastic CuAlBe SMA and theoretical crystallographic dependence of pop-in and pop-out loads predicted by the new introduced indentation Patel and Cohen factor.

1. Introduction

Shape Memory Alloys (SMA) undergo a reversible thermoelastic martensitic phase transformation which is due to a displacive, diffusionless, first order phase transition. SMA can exhibit a specific behavior called superelasticity which is associated with stress induced transformation. When the material is loaded at some specific constant temperature the austenitic parent phase transforms from austenite to martensite and large amounts of inelastic strains are developed. Upon unloading back to the zero stress state the material undergoes a reverse phase transformation from martensite back to austenite where inelastic deformations are recovered [1]. Constitutive micromechanical models developed to predict Shape Memory Alloys (SMA) behaviors are often based on a simplified phenomenological description of martensite variant activation under thermomechanical loading at the microscale [2,3].

Instrumented indentation has been widely developed in recent years to study material's mechanical properties such as hardness, Young's modulus [4] or even local strain hardening [5] at small scales. This technique is very useful to characterize discrete mechanisms at the nanoscale such as oxide breaking [6,7], microcracking [8], homogeneous dislocation nucleation [9–13], and stress-induced phase transformation [14,15]. Incipient plasticity has been characterized on a wide range of materials by the occurrence of an excursion event, called pop-in, on the loading part of the nanoindentation curve. Woirgard et al. [16] observed a displacement burst during the unloa;ding of the nanoindentation curve on a silicon single crystal. This excursion event, denoted pop-out, was explained as phase transformation as neither slip lines associated with incipient plasticity nor microcracks were observed beneath the indenter.

Applied to superelastic SMA nanoindentation is an experimental way of investigating their thermomechanical properties and their evolution with heat treatments [17], but also to study the martensitic transformation at the nanoscale. Martensitic phase transformation has been mostly studied using nanoindentation in NiTi SMA [18–20] and a few studies have been led on superelastic CuAlNi [21,22]. This completely reversible phase transition is characterized on the nanoindentation curve (load versus displacement) by the occurrence of displacement bursts during both loading and unloading and by zero residual displacement after complete unloading. Frick et al. [23] have observed discrete phase transformation events on shape memory and superelastic NiTi

* Correspondence to: LEM3, Université de Lorraine, Arts et Métiers ParisTech, UMR CNRS 7230, 4, rue Augustin Fresnel, 57070 Metz, France. Tel.: +33 387 37 54 30.
E-mail address: celia.caer@ensam.eu (C. Caër).

0921-5093/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msea.2013.08.052

alloys using nanoindentation. These authors showed that the detection of such mechanisms by nanoindentation is very difficult due to the shortness of excursion events and the small loads at which these events occur. This is the reason why the relevance of the nanoindentation study is first validated on the pop-in detection in pure nickel (Ni). NiTi alloys are the most studied Shape Memory Alloys because of their industrial applications. However NiTi alloys are not the best candidates to study martensitic transformation at small scale because in these alloys phase transition is usually coupled with plasticity [24] and it is then difficult to set apart the effect of one inelastic mechanism from the other. The present study investigates a CuAlBe SMA. This copper-based alloy was chosen for its large grain size and for the presence of beryllium in the matrix. CuAlBe alloys present a large grain size compared to NiTi alloys which gives the opportunity to perform extensive nanoindentation tests on one single crystal. The addition of beryllium in interstitial solid solution hardens the matrix and increases the plastic yield stress of the parent phase, favouring phase transition activation and limiting plasticity nucleation [25]. One of the objectives of this paper is to show evidence of discrete phase transformation events at the nanoscale in a superelastic CuAlBe shape memory alloy identified as pop-in and pop-out events and to investigate the orientation dependence of martensitic variant activation at this scale.

Whereas martensitic transformation has been experimentally investigated using nanoindentation, few efforts have been made to develop activation criteria in order to understand phase transformation under such mechanical tests. Pfetzing-Micklich et al. [26] studied the influence of crystal orientation on martensitic transformation beneath the indenter in NiTi SMA using molecular dynamics simulations. They found that the hardness curves can be correlated with the martensite volume occupied beneath the indenter which is dependent on crystal orientation, however they did not study pop-in and pop-out events at small loads. The present study investigates a new criterion called indentation Patel–Cohen factor, based on a continuum thermo-micromechanics approach and Hertzian elastic contact theory to predict the activation of the first martensite variant beneath the indenter as a function of crystal orientation. This Patel–Cohen factor relies on the computation of the driving forces associated to variants activation during the first pop-in load. Conversely, it is also shown that the indentation Patel–Cohen factor can also be applied to the last pop-out load corresponding to the reverse phase transformation from martensite back to (elastic) austenite. The validation of the stress tensor calculation is first performed on the indentation Schmid factors in comparison with the recent work of Li et al. [27]. Then, the indentation Patel–Cohen factors are discussed in the light of the present experimental nanoindentation curves and results performed on CuAlBe SMA. To the knowledge of the present authors such a criterion has not been described in the literature.

This paper is organized as follows. In Section 2, Ni and CuAlBe specimens used in this study are presented. Both surface preparation and nanoindentation experimental procedure are detailed for each material. In Section 3, the main equations using the elastic contact with axisymmetric indenter are used to calculate the indentation Schmid factor for crystal plasticity and the new indentation Patel–Cohen factor for direct and reverse phase transformations. In Section 4, the nanoindentation results are presented for several crystallographic orientations in Ni and CuAlBe specimen. The calculations of indentation Schmid factor are applied to three orientations in the case of Ni, in order to validate both stress field analysis and experimental procedure. Finally, nanoindentation results for three different crystallographic orientations of the CuAlBe SMA specimen are presented, discussed, and compared to the calculated indentation Patel–Cohen factors. Section 5 concludes and sketches some perspectives to this work.

2. Experimental procedure

2.1. Materials

A polycrystalline plate of CuAlBe shape memory alloy (Cu–12 wt% Al–0.5 wt%Be) was used in the present investigation. The specimen exhibits the following transformation temperatures: Ms = 269 K, Mf = 279 K, As = 243 K and Af = 265 K (respectively martensite start and finish and austenite start and finish temperature). The sample specimen is initially in the austenitic state (f.c.c. crystallographic structure) at room temperature and shows a superelastic behavior. The average grain size of the specimen is about one millimeter which is large enough according to the indenter size to consider the indented grain as a single crystal. In addition a polycrystalline specimen of commercially pure Ni (> 99.99%) (FCC crystallographic structure) was also used in this study to validate the experimental procedure. The grain size of the Ni specimen is around 140 μm which is also large enough to consider nanoindentation on a crystal.

2.2. Surface preparation

Both specimens were first mechanically polished with decreasing SiC paper and particulate diamond paste. The final mechanical polish was performed with a 1 μm diamond paste. Finally they were electro-polished in a solution of (C_2H_5OH (25 mL) + H_3PO_4 (25 mL) + H_2O) with a DC voltage of 20 V for CuAlBe and in a solution of (H_2SO_4 (20 mL) + CH_3OH (80 mL)) with a DC voltage of 35 V for the Ni specimen. Prior to nanoindentation tests EBSD mappings were performed in order to determine the crystallographic orientation of the grains.

2.3. Nanoindentation

Nanoindentation measurements were conducted using a commercial CSM Instruments "NHT2" nanoindentation head. This device is fitted with a reference ring taking the depth reference directly on the specimen surface, to avoid long waiting for thermal drift stabilization. Tests were performed using two Berkovich tips. The radius of curvature of the indenter tips were estimated on the basis of AFM measurements to be approximately 300 ± 33 nm for the tip used on Ni and 1 ± 0.3 μm for the indenter used on the CuAlBe specimen.

Nanoindentation measurements were performed on Ni on three grains A_1, A_2, A_3 with a crystal orientation respectively close to [001], [101], [111], and on three grains B_1, B_2 and B_3 of CuAlBe with respective orientation close to [001], [001], [111]. The indented grain orientations are close enough to ideal orientations to approximate their properties with ideal orientations properties.

Distinct nanoindentation procedures were set up for CuAlBe and Ni. For both materials nanoindentation tests were performed under applied load P with a constant rate of $\dot{P}/P = 0.125\ s^{-1}$ for Ni and $\dot{P}/P = 0.01\ s^{-1}$ for CuAlBe. In the case of the superelastic SMA, it is possible to perform several indentations at the same location considering each test independently from others due to the superelastic behavior of the material and the absence of residual strain (no plastic deformation) after a nanoindentation measurement. Thus, for the SMA the loading test sequence was made up of four loading–unloading cycles up to 100 μN for grains B_1 and B_2 and 500 μN for grain B_3. The minimum load P between two consecutive cycles was set to 2 μN to keep contact between the Berkovich indenter tip and the specimen surface. The objective of the first cycle is to break the oxide layer, and the data from the three following cycles were used for the study. These cycles of loading–unloading at the same position are not relevant for tests on Ni, were irreversible plasticity is produced. Nanoindentation tests on this material were set up of a unique cycle of loading–unloading up to a maximum load of 800 μN.