Report on the Doctoral Thesis

EFFECT OF MICROSTRUCTURE ON FATIGUE OF SUPERELASTIC NiTi WIRES

Author: Ing. Ondřej Tyc

Hosting Institution: Czech Technical University in Prague
Faculty of Nuclear Sciences and Physical Engineering
Department of Materials

Topicality of the research

A degradation of performance and microstructure during service of NiTi-based shape memory components is a key issue which has been limiting their even wider applications in medical and engineering fields. One of the factors which contribute to this rather unsatisfactory state-of-the-art is irreversible plastic deformation which accumulates in superelastic or shape memory components during cycles through the austenite-martensite transformation range performed either under external load or in a stress free condition. Recent methods how to deal with these issues are mostly heuristic, based on the strengthening of the austenitic matrix prior to the component service. Further progress, which will help to overcome recent limitations, is critically dependent on the detailed understanding of the microstructural processes that govern the irreversible plasticity during functional cycles. Results presented in the thesis clearly document that the author set out on the right path and employed a number of experimental techniques, including the thermo-mechanical loadings using the unique MITTER testing stand, DSC, dilatometry and SANS. The combination of these characterization methods with a careful qualitative SEM and TEM/SAD microstructural investigations promotes the study up to an important contribution to the field of the shape memory research.

Format and elaboration

A thesis volume covers 118 pages, including 79 figures, 1 table and 140 references to literature. The overall volume is distributed between an introductory part (44 pages), a very brief part on materials and methods (3 pages only!), a part dedicated to the results (44 pages), which mostly presents outcomes of thermo-mechanical tests complemented with the detailed qualitative documentation of corresponding microstructural states and fracture surfaces. Fifteen pages are allocated for discussion and conclusions. More specific topical and technical comments are listed below, here I only provide their general summary. Unfortunately, the author often either completely overlooks or grossly misinterprets literature results which are of key importance with respect to the objectives of his study. In particular, this relates to the accumulation of dislocation density during stress-free thermal cycles through the transformation range (e.g. [T. Simon et al. ACTA MATERIALIA 58 (2010) 1850–1860] or [J. Zhang et al. ACTA MATERIALIA 60 (2012) 1999-2006]) or the role of R-phase transformation during superelastic cycles (e.g. [J. Olbricht et al. METALLURGICAL AND MATERIALS TRANSACTIONS A-PHYSICAL METALLURGY AND MATERIALS SCIENCE 42A (2011) 2556-2574] or [A. Condó et al. ESOMAT 2009, 02006 (2009) DOI:10.1051/esomat/200902006]). Statements in the thesis like ... *There are reports in the literature showing various kinds of dislocation defects created upon stress-free thermal cycling of NiTi across a range of transformation temperatures Mf-Af [115][116], which gives an impression that cyclic martensitic transformation proceeding even without external stress generates dislocation defects in the austenite lattice* ... sound almost like an insult to all the careful work which has so far been done on the subject. The well substantiated experimental facts showing that dislocations accompany the transformation front even during transitions without the assistance of external stress are not "*an impression*" but fully proven experimental results. It is not a business of the applicant to question these results but to put them in a proper perspective with respect to his findings. Other omissions or improper treatment of the literature are mentioned in my comments nos. 3, 5, 6, 7, 8, 10, 18 and 28 below.

Numbering of figures is independently done for the introductory part and for the rest of the thesis so that Fig. 1 in fact refers to two figures in the volume which causes confusion, see my comment no. 11. The part dedicated to the material and experimental methods is too brief. Here, in addition to a more complete presentation of the individual experimental techniques, a reader would truly benefit from a detailed description of the experimental protocols used later in experimental sections of the thesis, see the comment no. 12. The text of the thesis is written in very good English, reads smoothly except some typos and confusing statements which would need explanations. These issues are listed in comments nos. 1, 2, 4, 9, 14, 15, 16, 24 and 25. While I highly appreciate the careful and complete qualitative documentation of microstructures and fracture surfaces, I miss at least some quantitative data. I fully understand that an assessment of dislocation densities, volume fractions of deformation bands etc. might be challenging in microstructures with the grain size of the order of 100 nm, but, according to my experience, some quantitative results could have been achieved and presented. In a similar vein, it may be dangerous to interpret types of Burgers vectors based on results presented in the literature, not performing a proper g.b analysis, see comments nos. 19, 22 and 23. Finally, in the result and discussion sections, the author often refers to already published results in articles which are, beside him, co-authored by many other researches. This also matters the cases where the applicant is not even listed as an co-author (see e.g. comments no. 18 and 28). So, it is not clear what exactly has been here the contribution of the PhD applicant and it makes judgement on the applicant input difficult.

Questions, topical and technical comments

Scientifically, there are some interesting issues that are also relevant for the results of the thesis and need to be explained by the applicant:

1) There are discrepancies between DSC data and dilatometry in a sense of the topical comment no. 13, WHY?

2) Why there is a huge difference in the As temperature during the stress-free back transformation of the 15 ms wire in a sense of the topical comments nos. 20 and 30? Please provide a thermodynamic analysis and related explanation.

3) Please explain phase composition and its changes during the full stress-strain-temperature path of the experiment documented in Fig. 11 in the result section. In particular, why the stress increases between 100 and 500 MPa upon heating from -40 to +80°C (Fig. 11b).

4) In a sense of comments nos. 10, 17, 19, 27 and 29, explain why dislocation slip, which accompanies the transformation front in the coarse grain material (and very likely also in the nanograin wire), is almost fully reversible in nanograins contrary to the coarse grain microstructure. In other words, why the transformation cycle B2<->(R)<->B19' leaves behind much less remnant dislocation defects in the nanograin structure.

5) Give some reasons for the drop of the upper plateau stress during superelastic cycles in a sense of comment no. 26 and discuss a potential role of the R-phase in the process.

6) Please explain the meaning of the term single domain martensite used in the thesis (e.g. page 97) in light of the classical terminology *lattice correspondence variant*, *lattice invariant shear* and *habit plane variant*, see [K. OTSUKA, C.M. WAYMAN, Shape Memory Materials, Cambridge University Press, 1998, ISBN 0-521-663849]. Do the words "domain" and "*habit plane variant*" have the same meaning, see also comment no. 31? Similarly, please explain whether the meaning of deformation band introduced in the thesis in relation to the twinning in the martensite phase corresponds to the classical term *deformation band* as used in the plasticity research, as it was coined by C.S. Barrett and L.H. Levenson [Trans. AIME, 135 (1939), pp. 327-352].

Topical and technical comments:

1) page 17, 1st line: "*Precipitation often takes place in several superelastic stages*, ?"
Please explain.

2) page 17, lines 7-9: "*Maximal attainable supersaturation in the Ni-rich NiTi is around 57 at.% Ni. On the other hand, only about 51 at.% Ti supersaturation is attainable in the Ti-rich NiTi matrix. The alloy exhibits weak dependence of transformation temperatures on composition in this region and Ms (martensite start) temperature is around 60-70 °C.*"
Strong dependence on the Ni content above 51% Ni, see e.g. Frenzel [98]!

3) page 17, Fig.4: Dependence presented by Frenzel [98] is much better substantiated and accurate as compared to Tang diagram [50].

4) page 20, 2nd§: external stress and orientation of habit planes? Please explain.

5) page 24, 2nd§: R-phase transformation in superelastic alloy during tensile loading – full account was given by J. Olbricht et al. METALLURGICAL AND MATERIALS TRANSACTIONS A-PHYSICAL METALLURGY AND MATERIALS SCIENCE 42A (2011) 2556-2574.

6) page 25, Fig. 13 and related main text: Full account of multi-step transformations in aged Ni-rich NiTi was given by Allafi [64] and Dlouhy [PHILOSOPHICAL MAGAZINE, 2003, VOL. 83, NO. 3, 339–363] well before [57].

7) page 28, Fig. 16: Residual martensite in wires after cycles? See [A. Condó et al. ESOMAT 2009, 02006 (2009) DOI:10.1051/esomat/200902006.]

8) page 33, line 5: see comment 7), evidence provided by Polatidis is weak.

9) page 40, 1st line: *martensite bend front* -> martensite band front.

10) page 45, objectives: dislocation density grows even during stress-free thermal cycles (under zero external load), see J. Zhang et al. ACTA MATERIALIA 60 (2012) 1999-2006.

11) page 46 and on: figure numbers go back to 1, why? It may create a confusion.

12) page 47, 1st §: *Since the used higher strain rate affects a stress-strain response [114] owing to the exothermic/endothermic character of the forward/reverse martensitic transformation, tensile cycles at lower strain rate (0.1 %/s) were included during the fatigue tests to monitor the evolution of stress-strain response upon cycling.*
A confusing description of testing procedures, more attention should have been given to the presentation of the methods.

13) page 49, 2nd §: 10 ms wire – DSC on cooling shows B2-R transition (comparable to 13 ms wire) but this transition is missing in the dilatometry record (in contrast to 13 ms wire), WHY?
Wire 13 ms + 400°C/1h – … *cooling under stress that produces oriented martensite shows much higher Ms = -51 °C, which better represents the change in the stress-strain response* … WHY there is a substantial difference between dilatometry and DSC data and WHY NOT in the case of 13 ms wire?

14) page 50, caption to Fig. 3: parts e and f show TEM results, not stress-strain curves.

15) page 51, 2nd §: Fig. 3f does not present microstructure of 13 ms + 400°C/1h wire.

16) page 51, 2nd §: … *The ~ 30°C difference in Ms temperature of samples with and without the additional aging (Fig. 3b)* corresponds … .
In Fig. 3b, Ms temperatures -81°C (wire 13 ms) and -77°C (wire 13 ms + 400°C/1h) are approximately the same!

17) page 55, 2nd §: see the comment 10).

18) page 56, 2nd §: … *The reader is referred to OUR related paper [35], in which these slip dislocations were analyzed …*
First, the author of the thesis is not a co-author of [35]. Second, in this case, the full analysis should have been presented in the thesis. I do not think that a practice, when (already published) results of other authors are presented in the RESULT section of the thesis, is acceptable. It raises a question regarding whether the applicant at least contributed to all the results presented in the thesis.

19) pages 57-58: … *There are reports in the literature showing various kinds of dislocation defects created upon stress-free thermal cycling of NiTi across a range of transformation temperatures Mf-Af [115][116], which gives an impression that cyclic martensitic transformation proceeding even without external stress generates dislocation defects in the austenite lattice. Although this might be true as concerns point defects or faults [116] (difficult to resolve by conventional TEM), our results clearly prove that no slip dislocations, twins, or other lattice defects easily observable by TEM were created during the first 10 thermal cycles at low stress 6.5 MPa. The most likely explanation of this contradiction is that the literature studies were typically performed on solution-treated NiTi alloys, while our experiments were performed on superelastic NiTi wire possessing nanograin microstructure.…*
First, the strain amplitude is very small (of the order of 0.5 %). As a consequence, R-B19' transformation likely only proceeds in a limited part of the wire. There is no guarantee (and even low likelihood) that the tiny FIB lamella hits the volume which underwent the transformation. Second, even if the TEM observation has been performed on a proper niche, reliable quantification of dislocation density would be needed to compare with the virgin wire in its as-heated state. The structure shown in Fig. 9a2 can easily host a dislocation density of the order of 10^{13} m^{-2}.

20) page 60, Fig.10b: According to PTTs recorded for the 15 ms wire during its stress-free back transformation, the reverse transformation B19'->B2 should start at about -40°C, see Figs. 3a and c in the result section. However, Fig. 10b suggests that during the stress-free heating the As is about +5°C, this is more than 40°C difference, WHY?

21) page 61, Fig. 11: Please explain phase composition and its changes during the full stress-strain-temperature path of the experiment and in particular, why the stress increases from 100 to 500 MPa upon heating from -40 to +80°C.

22) page 62, last lines: … *there are fewer slip dislocations and fewer deformation bands in both microstructures* … What about some quantification? Similar comment applies to micrographs in Fig. 13 and related text on page 65.

23) page 69, line 3: g.b analysis performed?

24) page 81, lines 7-8: … *effect of irreversible R-phase is excluded in Fig. 32a* …
Does it mean subtracted, neglected or denied?

25) pages 85-86, Figs. 34-37: Magnification markers are unreadable!

26) page 93, section 5.1: … *Moreover, the decrease in* σ_p^{up} *by approx. 200 MPa always occurs regardless of the virgin microstructure or low accumulation of* ε_{us} *(Figs. 28-31).* …
See A. Condó et al. ESOMAT 2009, 02006 (2009) DOI:10.1051/esomat/200902006!

27) page 93, section 5.2, text before the sentence: … *This is the key result of this work.* …
May be in the material with nanograins, otherwise it is not true, see comment 10). But also in the nanograin wire it may be questionable, see comment 20).

28) page 95, 2nd §: see comment 18), the author of the thesis is not a co-author of [35].

29) page 95, 4th §: Now isolated dislocation loops and segments are reported in relation to Fig. 9a while text on page 57 says differently … *no lattice defects were found in the wire microstructure after 10 cycles* … . So what is true?

30) page 96, 2nd §: Does it make any sense from the thermodynamics point of view? The reorientation of martensite variants required external work on the system which either increased the martensite internal energy or got dissipated in a form of heat or both in a proportion. In the case of the increment of internal energy, the martensite with higher internal energy should be less stable, see also comment 20).

31) page 97, 4th §: What is a difference between … *single domain of the B19' phase* … and … *martensite variant* … ?

Conclusion
In spite of the issues mentioned in this report, I do recommend to the commission the thesis being accepted for a further promotion and the defence.

Brno, 10.11.2021

Prof. RNDr. Antonín Dlouhý, CSc.