



Comments and Reply

Comment on: “Isothermal nature of the B2–B19’ martensitic transformation in a Ti–51.2 Ni (at.%) alloy”J.L. Pelegrina,^{a,b,*} A. Yawny^{a,b} and J. Olbricht^c^aCentro Atómico Bariloche, 8400 San Carlos de Bariloche, Argentina^bCONICET and Instituto Balseiro (Universidad Nacional de Cuyo), Argentina^cBAM Federal Institute for Materials Research and Testing, 12200 Berlin, Germany

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Fukuda et al. published a paper (Scripta Mater. 68 (2013) 984–987) in which they claimed to be able to determine the isothermal nature of the martensitic transformation in a Ti–Ni alloy. They analyzed the evolution of electrical resistance during isothermal holding stages and concluded that the variations were a consequence of the isothermal transition between austenite and martensite. In the following we will demonstrate that the discussed data do not allow the interpretation presented and that the isothermal nature is not proved.

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In a recent article, Fukuda et al. [1] investigated the time dependence of the electrical resistivity during the B2–B19’ martensitic transition in a Ni-rich Ni–Ti alloy (Ti–51.2Ni (at.%)). The authors concluded that the forward and reverse transformations are time dependent, and determined an incubation time for the forward transformation to proceed. As outlined by the authors, these results are contrary to previous findings reported by Otsuka et al. [2] and also to more recent studies performed by Kustov et al. [3]. Fukuda et al. [1] based their conclusions on electrical resistivity data obtained during thermal cycles through the entire transformation range, by varying the temperature in the (4–350) K interval. Their transformation cycle exhibits a maximum in the electrical resistivity vs. temperature curve on cooling at 154 K (Fig. 1 in Ref. [1]). When performing isothermal holding stages at temperatures around this maximum, a decrease in resistivity as a function of time was observed. At a temperature of 160 K, i.e. slightly above the maximum, and considered to be also above the martensitic transformation start temperature (M_S) by the authors, the presence of an incubation time of nearly 2500 s was detected (Fig. 2a in Ref. [1]). In contrast, only a negligible incubation time was observed when holding at 155 K (Fig. 2b in Ref. [1]). Fukuda et al. [1] attributed the observed decrements in resistivity to a

time-dependent “isothermal formation” of B19’ martensite from the B2 austenite.

The present authors consider that this conclusion is based on an erroneous interpretation of the electrical resistivity results. This assertion can be demonstrated by considering first the linear high- and low-temperature branches of the resistivity vs. temperature plot (Fig. 1 in Ref. [1]). The observed linear behavior with a positive slope as a function of temperature in these regions constitutes a typical property of metallic materials. In the case of shape memory alloys, it is usually attributed to the absence of transformation events, i.e. to temperature ranges with a thermodynamically stable phase condition like the fully martensitic/austenitic states at low/high temperatures. In this sense, as it is sketched in Fig. 1 (adapted from Fig. 1 in Ref. [1]), the high-temperature extreme is associated with the resistivity dependence of the B2 phase (the austenite). This is depicted by the lower straight line in Figure 1 (blue in the online version). The low-temperature linear regime is usually associated with B19’ martensite, although it could be a mixture of phases whose volume fraction and interfaces (type, amount, positions) remain unaltered. Similarly, its linear behavior is highlighted by the upper straight line in Figure 1 (red in the online version). These linear relationships can be extrapolated to lower (B2) and higher temperatures (B19’) as is suggested by the dashed lines in Figure 1. This analysis results in the conclusion that the electrical resistivity of the B19’ martensite should be higher than the electrical resistivity value of the B2 phase for the entire temperature interval considered. Then, a decrease in electrical resistivity in a cooling experiment could not be assigned to

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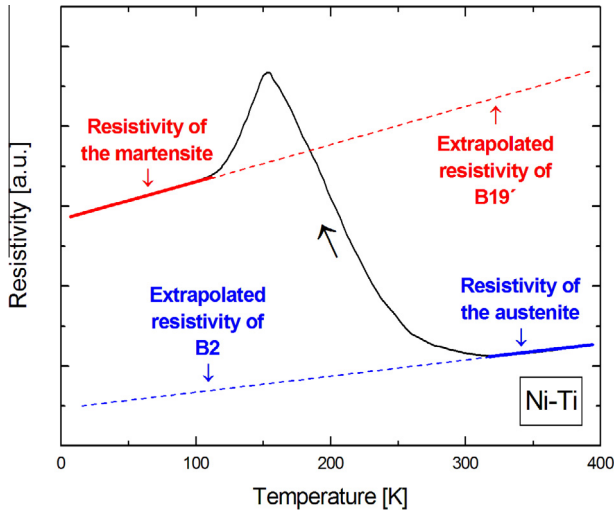


Figure 1. Cooling branch of the electrical resistivity vs. temperature plot presented in Figure 1 of Ref. [1]. Lines representing the linear dependencies observed at both ends of the temperature range corresponding to the behavior of the non-transforming phases were included. These lines were extrapolated to the whole temperature interval by dashed lines.

an increase in the volume fraction of the B19' phase by martensitic transformation from the B2 austenite phase, as claimed in Ref. [1].

An additional important aspect deserving further attention is the particular evolution of the resistivity vs. temperature behavior of Ni–Ti shape memory alloys (in general, and in particular for the material studied in Ref. [1]). This is related to the peak observed in the interval from nearly 100 K to 200 K upon cooling, with resistivity values clearly overshooting the extrapolated line of the martensite (Fig. 1). The special character of its resistivity evolution can be identified by contrasting it with the corresponding behavior of a Cu–Zn–Al shape memory alloy exhibiting a single step transformation (see Fig. 2). In this case, the normal linear temperature dependence of each phase (at the

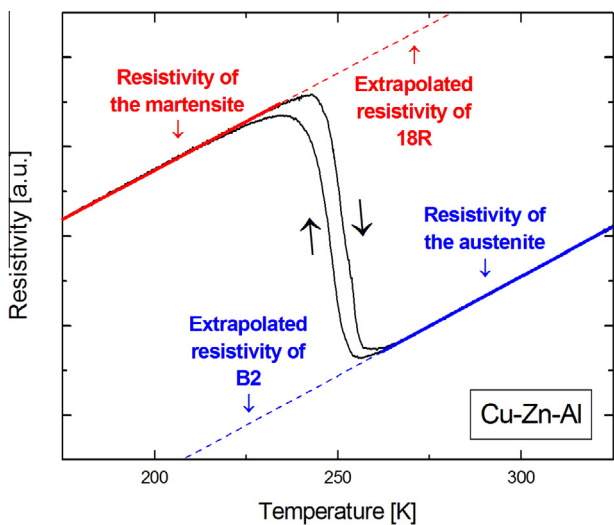


Figure 2. Representative cooling and heating branches of the electrical resistivity vs. temperature behavior for a Cu–Zn–Al shape memory alloy. Lines were added following the same reasoning used for Figure 1.

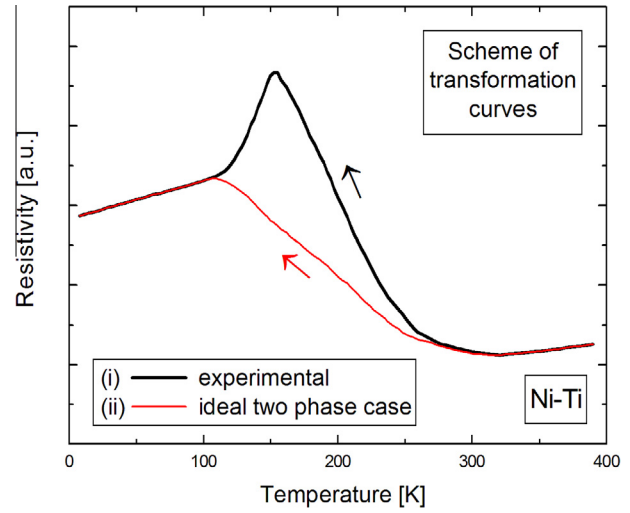


Figure 3. Experimental transformation behavior of Ni–Ti between the high-temperature austenite and the low-temperature martensite (black curve corresponding to the transformation branch taken from Ref. [1]) and hypothetical normal behavior in the absence of the R-phase, similar to the one exhibited by Cu–Zn–Al as exemplified in Figure 2.

high/low temperature extremes) is interrupted in the temperature range in which the transformation takes place and the electrical resistivity gradually varies between the values of the two phases as the forward or reverse transformations proceed. In Figure 3, a schematic comparison is provided of (i) the behavior on cooling observed for the Ni–Ti alloy considered in Ref. [1], and (ii) the behavior that would be expected if it would follow the type of behavior just discussed for Cu–Zn–Al. Obviously, a single step transition as expected for the formation of B19' martensite from B2 is not sufficient to rationalize the presence of a resistivity peak and additional mechanisms need to be considered.

Resistivity evolutions similar to those reported in Ref. [1] have frequently been reported for Ni-rich Ti–Ni alloys (e.g. [4,5]). They are typically attributed to the presence of an intermediate martensitic structure, referred to as the R-phase [6,7]. In the contribution by Fukuda et al. [1], the presence of the R-phase was unfortunately not considered, although previous works strongly indicate it might be playing a role. As discussed in more detail in Refs. [4,5], the appearance of the R-phase is associated with higher electrical resistance values than the ones corresponding to the B2 austenite and B19' martensite phase. At present, however, it is not known whether the high resistivity constitutes an intrinsic property of the R-phase structure or if it is, at least partially, related to the amount and type of interfaces that are formed during the additional transformation step.

With regard to the ageing process and related resistivity changes in Ti–Ni, the experimental evidence given in Ref. [1] is restricted to electrical measurements. In the opinion of the present authors, the lack of complementary observations (e.g. dilatometry, diffraction experiments) does not allow conclusions to be drawn on the mechanisms responsible for the change in resistivity during isothermal hold periods. Most importantly, no evidence is available that would prove the anticipated variation in the volume fractions of the phases with time. As pointed out in Ref. [8], a great variety of factors such as temperature, lattice defects, atomic arrangements, internal stresses and sample

geometry may contribute to the measured resistance. Therefore, the change in the volume fraction of the phases anticipated in Ref. [1] can only be considered as one possible explanation for the reported observations, and alternative mechanisms, e.g. the relief of internal stresses, should not be excluded. This could happen through:

- the reorientation of the austenitic grains;
- the growth of a martensitic variant at the expense of other variants of the same structure;
- the accommodation of the volume fraction of two coexisting martensitic phases (R and B19'), without altering the fraction of austenite.

In conclusion, the electrical resistivity can depend on the elastic stresses and the amount and orientation of the interfaces in such a complicated way that it would be possible to anticipate either resistivity increases or decreases.

It is acknowledged that, in recent years, several articles have reported the existence of so-called “isothermal martensitic transformations” in different shape memory alloys [2,3,9,10]. This term was applied when the volume fraction of the martensite was found to depend on both temperature and time. In the special case of the volume fraction depending solely on temperature, the transition has been referred to as an “athermal martensitic transformation”. Unfortunately these terms are confusing, since the martensitic transformation is of a diffusionless character with the interphase moving at high speeds, as measured for example in Cu-based alloys [11]. Therefore, special care should be taken before considering a martensitic transition as time dependent.

A martensitic transformation occurs once the necessary driving force is reached and stops when constraints, such as internal stresses or composition gradients, begin to play a role. For this reason, in the presence of time-dependent behavior, one should look for the cause in changes of the concomitant phases. For example, it is well known that in Cu–Zn–Al alloys M_S can be decreased up to 40 °C by a quench from 300 °C into water at room temperature [12]. This shift disappears as a function of time when the specimen is annealed at temperatures even as low as 0 °C. Therefore, it would be possible to observe an isothermal martensitic transformation, on ageing the sample in the appropriate temperature interval after a quench, due to the evolution of the austenite. It has also been reported that the transformation can be reversibly shifted by ageing the austenite under load [13]. In this case the transition would isothermally appear when, afterwards, the material rests in an unstressed condition. Therefore, martensitic transformations should, at least initially, always be considered as

athermal and the “transition shifting” phenomenon carefully elucidated in each particular case.

Time-dependent effects have also been reported to occur in Cu-based (e.g. [14,15]) and Ni–Ti [16] shape memory alloys under various conditions. It is also well known that self-heating and self-cooling effects associated with the enthalpy of transformation give rise to a rich variety of time-dependent phenomena that might be erroneously interpreted as indicators of isothermal martensitic phase transformations. The latter are especially noticeable in Ni–Ti alloys [17].

For the reasons discussed above, it is believed that the evidence provided in Ref. [1] does not provide proof that the martensitic transformation exhibits an isothermal character or nature. In addition, the incubation time invoked when speaking about the results in Figure 2 of Ref. [1] cannot be directly associated with the martensitic transformation from B2 to B19'. A careful analysis of the real causes is essential.

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