An Estimate of the Nucleation Time in the Martensitic Transformation

MARC A. MEYERS

A method for the determination of nucleation times for martensitic transformation is described. The method utilizes a shock wave that, upon being reflected at a free surface, generates a tensile wave with a pulse duration that increases as it moves away from the surface. Once the duration of the reflected pulse is large enough for nucleation to occur, transformation can take place. The width of the martensite free layer adjoining the surface is measured and compared with wave predictions. A nucleation time can be obtained. The method requires that the temperature, pulse amplitude, and alloy composition be such that only the reflected tensile wave induce martensite transformation. For the experimental conditions used by Snell, Syne, and Goldberg; the nucleation time is found to be less than 55 nanoseconds.

THE nucleation of martensite, for which there are two schools of thought—the lattice softening1,2 and the Olson–Cohen3,4 dislocation concepts—can be either rapid (athermal martensite) or slow (isothermal martensite). The purpose of this note is to describe a first attempt to obtain the time interval for athermal martensite nucleation. First, a technique is described that allows the determination of nucleation times for martensite formation; this technique uses the passage of a tensile plastic wave through the alloy as a trigger mechanism for martensite transformation. Second, the technique is applied to a real situation reported in the literature and an estimated nucleation time is calculated therefrom.

TECHNIQUE

A hypothetical experiment is described herein which will yield a time for martensite nucleation. A certain class of alloys is required; alloys wherein compressive shock waves do not induce martensite formation at a reasonable pressure, while tensile waves do. Meyers and Guimarães6 recently observed this behavior for an Fe–31 pct Ni–0.1 pct C alloy (Ms = 223 K). While the compressive shock wave induced only a cell-like dislocation substructure, tensile reflected waves caused transformation. These results are corroborated by other investigations for systems with Ms = 245 K2 and 240 K.8 These alloys, subjected to exclusively compressive shock waves of the same order of magnitude as Meyers and Guimarães’ systems, did not exhibit martensitic transformation. However, Meyers and Guimarães6 using an especially designed experimental set-up, were able to show that the tensile reflected wave generated martensite.

The state of stress induced by shock loading—uniaxial strain—can be decomposed into a hydrostatic and a deviatoric component. The deviatoric components are similar for the direct compressive and reflected pulse. The deviatoric (shear) components of the waves were ruled out as the cause of the martensitic transformation observed by Meyers and Guimarães because they are similar for both direct and reflected waves. The rationale for the response observed by Meyers and Guimarães is provided by Patel and Cohen.9 Compressive hydrostatic stresses generated by the direct shock wave lower Ms (223 K at atmospheric pressure); the tensile hydrostatic component of the reflected wave raises Ms. If the amplitude of the tensile wave is such that Ms is raised above the alloy temperature, conditions for martensitic transformation are propitiated. This will be discussed in greater detail in the section “Experiment.”

The hypothetical experiment is shown schematically in Fig. 1. An incident compressive shock wave traveling inside the alloy encounters a free surface at a time between t₀ and t₁. At times t₁, t₃, and t₄, the portions of the wave that would propagate beyond the free surface, if the medium were continuous, are represented by dashed lines. But the incident wave cannot propagate into the air, and it is reflected back as a tensile plastic wave. The reflected wave is nearly identical to the wave that would be transmitted into the air, but is of a tensile nature. It is represented by dashed lines in the lower parts of the diagrams at t₁, t₃, and t₄, in Fig. 1. In the interaction region between incident and reflected waves, cancellation of the waves takes place. In order to obtain the resultant wave, one subtracts the reflected from the incident wave. The resultant waves in Fig. 1 are cross-hatched. It can be seen that at t₂ the compressive wave has almost completely reversed itself. However, this procedure is not entirely correct, because the tensile reflected wave, as seen at t₂ and t₄, has a sharp front. Actually, tensile reflected waves are not “shock” waves, and the front gradually becomes sloped, as they advance. The phenomenon of spalling, that will eventually take place and fracture the material by the action of the tensile reflected wave, was ignored.

The effect of the compressive and tensile stress pulses can be better assessed by examining the stress history at various points within the material. This is shown in the sequence displayed in Fig. 2. These stress–time plots were obtained from Fig. 1; stress-distance at a certain time is transformed into stress–time at a certain position by using the velocity of the
shock wave at the specified pressure. The velocities of the compressive shock and reflected plastic waves were assumed to be the same: $4.87 \times 10^5$ m/s. Time zero was taken as the moment that the front reaches the back surface of the plate. All plots shown in Fig. 2 have a common origin at time zero. These stress histories were computed at the back surface of the plate and at distances of 0.5 to 6 mm inside the plate. Beyond this distance the stress history is the same, assuming that there is no spalling. Spalling would absorb energy. Figure 2(a) shows the stress-time plot at the surface. When the front of the compressive shock pulse reaches the back surface, it begins being reflected. Thus, a pressure spike with infinitely short duration is produced. A plate at 0.5 mm from the free surface (Fig. 2(b)) experiences first a compressive pulse and then a tensile pulse. And, following the sequence depicted in Fig. 2(a) to (h) one sees that the duration of both the compressive and reflected tensile pulses increases as the distance from the free surface increases. Beyond the plane situated at 6 mm from the surface, the direct compressive and reflected tensile pulses should remain essentially unchanged; this maximum distance is determined by the initial pulse duration. The method herein described assumes, sensibly, that the growth of martensite takes place, once an embryo becomes critical. The time required for growth is very small and can be computed. Assuming that, in a polycrystalline metal, martensite plates will grow to a size of 5 $\mu$m, and that they can grow at a velocity of 1000 m/s, full growth would have been achieved in five nanoseconds. Even if one assumed that growth would be stopped once the pulse had passed (and this is rather unlikely) one would still be able to observe microscopically fragmented debris.

By applying the Patel-Cohen analysis one can determine the threshold tensile hydrostatic stress, $P$, at which martensite can form at, say, ambient temperature. If one assumes that the incident stress pulse is square (infinitely large rarefaction rate), and if $P$ is the hydrostatic tensile stress required for triggering the martensitic transformation, then one has the situa-
tion depicted in Fig. 3(a). The time at the stress $P$ increases linearly with distance from the free surface, until the wave has completely reversed itself; this happens at a distance $\lambda$ equal to the pulse width. The nucleation time is equal to the pulse width divided by the velocity of the wave $U_s$. The slope of the line is $\frac{x}{U_s}$. If one obtains a martensite-free layer of thickness $x$, then the time required for the nucleation of martensite is:

$$t_p = \frac{x}{U_s} \tag{1}$$

Figure 3(b) shows the same plot for a stress pulse having a finite attenuation rate. This plot has units along the coordinate axes; it is obtained from the diagrams in Fig. 2. Figure 2(c) shows the stress $P$ and the time $t_p$ required for nucleation. Since the reflected pulse is not square, there is a region (between the surface and 0.5 mm) in which the reflected stress will not be high enough for nucleation. This is shown in Fig. 3(b); the sloped line does not pass through the origin. The point corresponding to a time interval $t_p$ at the stress $P$ (Fig. 2(c)) is shown in the plot. On the sample plot, the dashed line represents the situation if the pulse were square. If one had a martensite-free region with a thickness of 1 mm, a nucleation time of $t_p$ would be predicted for a square pulse and of $t_p$ for a sloped pulse. Consequently, the assumption of a square pulse leads to an overestimation of the nucleation time.

**EXPERIMENT**

The results recently obtained by Snell, Shyne, and Goldberg\(^{10}\) (SSG) give an excellent indication of the distance $x$. SSG report profuse martensite formation in a sample shock-loaded to a pressure between 3 and 10 GPa. Their Fig. 6 is reproduced here as Fig. 4. Upon shock-loading a Fe-20.8 pct Ni-0.605 pct C alloy ($M_s = 237$ K) at room temperature at pressures ranging from 3 to 10 GPa they found profuse martensite transformation, as evidenced by the dark etched regions of Fig. 4. They were not able to explain the "strangely nonuniform distribution of stress-assisted martensite", that was "typical of the 15 different shock-loaded samples that were examined". The martensite distribution found by SSG agrees precisely with the contention of martensite generated by tensile waves. If it were generated by compressive waves, then the uppermost portion of the disc-shaped sample shown in Fig. 4 would exhibit the largest amount of martensite. Clearly, such is not the case; the region adjacent to the bottom of the sample, where spalling occurred (due to the absence of a protective spall plate) is the richest in martensite. The amount of martensite decreases as the tensile wave attenuates itself in its upward trajectory, after being reflected at the bottom surface of the disc. However, the experimental feature of Fig. 4 that incontrovertibly proves the proposed mechanism is the remarkable martensite-free region at the bottom of the disc. It corresponds to the region where the compressive wave and the reflected tensile wave interact.

The fact that there is a 0.22 mm martensite free layer indicates that in this region either the pressure or the pulse duration were not sufficient for the nucleation. It will be assumed that the growth of martensite plates proceeds automatically, once the nucleation took place. The paucity of information given by SSG precludes a detailed analysis of the pulse. Nevertheless, an estimate of the nucleation time $t_p$ can be obtained. The velocity of the shock wave for this alloy can be ob-

![Shock impact direction](image)

**Fig. 4**—Cross-section of cylindrical, disc-shaped sample impacted at room temperature. The dark etching constituents are martensite that formed preferentially near the back surface of the disc, leaving however a 0.2 mm region free of martensite, indicated by mark inside the circle. From Snell et al.\(^{10}\) (by permission of Elsevier-North Holland).
tained by applying the method of mixtures in the
determination of the parameters C and S in Eq. [2],
relating the shock and particle velocities \( u_s \) and \( u_p \),
respectively. The coefficients C and S were inter-
polated for a 79 pct Fe-21 pct Ni alloy from the coef-
cient for pure Fe and Ni given in Ref. 11. One has:

\[
\begin{align*}
\quad u_s &= C_{\text{Fe-Ni}} + S_{\text{Fe-Ni}} u_p \\
C_{\text{Fe-Ni}} &= 3.785 \times 10^3 \text{ m/s} \\
S_{\text{Fe-Ni}} &= 1.824 \\
\rho_{\text{Fe-Ni}} &= 7.8 \text{ g/cm}^3 \text{ (density)}
\end{align*}
\]

The Hugoniot equation for the conservation of mo-
momentum (Eq. [3.2] in Ref. 12) is then used, and one can
obtain the shock velocity at a specified pressure:

\[
P - P_0 = \rho_0 u_s u_p
\]

For a pressure of 3 GPa (the lowest pressure re-
ported by SSG) one has a shock velocity of \( 4 \times 10^3 \) m/s.
The thickness of the martensite-free layer shown in
Fig. 4 is approximately 0.22 \times 10^{-3} m. Assuming a
square pulse as a first approximation and applying
Eq. [1], one obtains

\[
t_p = \frac{0.22 \times 10^{-3}}{4 \times 10^3} = 0.055 \times 10^{-6} \text{ s}
\]

One can conclude that, for the system investigated by
SSG, the nucleation of martensite takes 55 nanoseconds.
One has to realize that this is only a first estimate
based on a calculation where several simplifying as-
sumptions were made. Nevertheless, one can say that
the nucleation time is 55 nanoseconds or less. There
are several sources of errors in the analysis. The
most important is the assumption that the pulse is
square. This leads to an overestimation of the nuclea-
tion time, as shown in Fig. 3(b). The shock wave
velocity might also not have been very accurately
estimated. This error should however not amount to
over 10 pct. The velocity of the reflected wave differs
slightly from the direct compressive wave because one
has to subtract the velocity of the particles in the for-
mer from the velocity of elastic waves.

Elastic waves and their interactions were completely
ignored in the analysis of SSG's observations. The fol-
lowing argument shows that this approach is correct.
The alloy has an \( M_s \) of 237 K; tensile tests conducted
by Maxwell, Goldberg, and Shyne on the same alloy
and reported in another paper show that stress-assisted
martensite only forms, at room temperature, after
considerable plastic deformation. Martensitic trans-
f ormation in the elastic range was only observed at
temperatures slightly above (a few degrees K) the \( M_s 
\) temperature. It can be concluded therefore that
elastic precursor waves do not have a sufficient am-
splitude to trigger the martensite transformation; the
temperature at which they are propagating is around
60 K above \( M_s \). Therefore, the elastic precursor waves
and their interactions can be neglected.

Because there is a volume increase of about 5 pct
associated with the formation of martensite, there is
necessarily an effect of hydrostatic pressure. Assum-
ing that the free energy for the formation of martensite
is constant for this alloy, the calculations conducted
by Patel and Cohen can be adapted to the present
situation. Patel and Cohen calculated and experi-
mentally determined the effect of a compressive hydro-
static pressure for an Fe-30 pct Ni alloy and obtained
values of \( -55 \) and \( -83 \) K/GPa, respectively. Since the
calculated results can equally well be applied to tensile
hydrostatic stresses with the appropriate change in
sign, it was decided to verify the effect of a pressure of
3 GPa (the lowest pressure used in SSG’s experi-
ments) on the \( M_s \) temperature. Using the experi-
mental results, a temperature increase of 165 K is
obtained; this corresponds to a corrected \( M_s \) of 402 K.
Conversely, one can calculate the hydrostatic tensile
stress required to raise \( M_s \) to ambient temperature.
The stress should be equal to 61/83, or roughly 0.75
GPa. Some simplifying assumptions were made in the
discussion above. First, it was assumed that the \( M_s 
\) temperature varied linearly with pressure; it is
known that the compressibility of metals deviates from
a linear dependence of pressure at high values of the
pressure. Secondly, Patel and Cohen's rationalization
applies to purely hydrostatic stress states, that do not
generate plastic deformation. As mentioned in the
previous section, shock loading produces shear
stresses, in addition to hydrostatic stresses. It is well
known that a defect substructure has a sensible effect
on \( M_s \). This effect was neglected. Additional factors
that have to be considered in a rigorous analysis are
the transient and residual temperature changes, the
changes in free energy due to the effect of pressure on
the free energy change of transformation. However,
it is not expected that these effects would significantly
affect the result that the reflected tensile wave raises
the \( M_s \) temperature of the alloy (~400 K for 3 GPa
pressure) much above the temperature of the sample
during the shock wave experiment (~300 K), propitiat-
ing conditions for martensitic transformation.

Further evidence that the martensite plates were
induced by the reflected tensile waves is provided by
their morphology. SSG’s Fig. 9 shows that the
martensite plates and their midribs have a curiously
wavy appearance. The martensite is actually being
formed in a structure that had been highly distorted by
the compressive shock wave that preceded transforma-
tion. Therefore, it inherits the distortions of the parent
phase.

The incipient spall fracture that can be seen in Fig. 4
at about 2 mm from the lower surface of the sample
is generated by the tensile reflected wave when its
pulse duration becomes large enough to allow the initi-
ation and propagation of the fracture. It should contrib-
ute to the attenuation of the reflected wave. Spalling
does not have any bearing on the method described
herein, because the martensitic transformation pre-
cedes it.

**CONCLUSIONS**

a. A method is presented that allows the determina-
tion of the nucleation time for martensite transfor-
mation.

b. This method involves the use of shock waves
reflecting themselves at a free surface and generating
tensile waves. The reflected wave starts at the surface
with a pulse duration equal to zero. Its duration increases as it moves into the material. The width of the martensite-free region can be used to calculate a nucleation time.

The method is applied to experimental results obtained by SSG and an estimated nucleation time of 55 nanoseconds is found from preliminary calculations for the conditions imposed by their experimental setup. It should be noticed that the martensite is being formed in a material highly predeformed by the compressive shock wave that precedes the tensile wave.

ACKNOWLEDGMENTS

Funds for this research were provided by National Science Foundation under Grant No. DMR-7728278. Appreciation is extended to Drs. R. N. Orava and G. A. Stone for critically reviewing the manuscript. The comments of the reviewers and, in particular, the suggestion to introduce Fig. 3 are gratefully acknowledged.

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