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Introduction

The crystallization processes of the as-deposited, amorphous NiTi thin films have been studied in detail using techniques such as differential scanning calorimetry and, in-situ TEM [1-6]. The kinetic data have been analyzed in terms of Johnson-Mehl-Avrami-Kolomogrov (JMAK) semi-empirical formula [7-8]. The kinetic parameters determined from this analysis have been useful in defining process control parameters for tailoring microstructural features and shape memory properties. Due to the commercial push to shrink thin film-based devices, unique processing techniques have been developed using laser-based annealing to spatially control the microstructure evolution down to sub-micron levels. Nanosecond, pulse laser annealing is particularly attractive since it limits the amount of peripheral heating and unwanted microstructural changes to underlying or surrounding material. However, crystallization under pulsed laser irradiation can differ significantly from conventional thermal annealing, e.g., slow heating in a furnace. This is especially true for amorphous NiTi materials and relevant for shape memory thin film based microelectromechanical systems (MEMS) applications.

There is little to no data on the crystallization kinetics of NiTi under pulsed laser irradiation, primarily due to the high crystallization rates intrinsic to high temperature annealing and the spatial and temporal resolution limits of standard techniques. However, with the high time and spatial resolution capabilities of the dynamic transmission electron microscope (DTEM) constructed at Lawrence Livermore National Laboratory, the rapid nucleation events occurring from pulsed laser irradiation can be directly observed and nucleation rates can be quantified [1,9]. This paper briefly explains the DTEM approach and how it used to investigate the pulsed laser induced crystallization processes in NiTi and to determine kinetic parameters.

The DTEM Technique

The DTEM can capture irreversible, transient material dynamics with 15 nanosecond exposure times. The high time resolution of the *in situ* observations are enabled by replacing the thermionic electron source with a pulsed UV laser driven photoelectron source. To observe the crystallization process in NiTi, the TEM specimen is first irradiated with a 12 ns, 1064 nm laser pulse to heat the sample and induce crystallization (fluences of ~200 mJ cm^{-2}). Then, after a predefined time delay, the UV laser is triggered and irradiates a photocathode, generating an intense, 15ns pulse of photoelectrons with sufficient intensity to capture a snap-shot image of the crystallization process (see ref[1,9]). In a typical DTEM experiment, a pulsed electron image is acquired before laser heating, at some time delay after the "pump" laser strikes the sample, and after the specimen has cooled to room temperature (several minutes after the pump laser pulse).

Results and Discussion

Figure 1 shows an example of a series of nanosecond time resolved, DTEM images of pulsed laser induced crystallization process in the NiTi. The 15ns delay image is taken 1.5μs after the pump laser irradiates the sample; the center of the pulsed laser spot (120 μm $1/e^2$ diameter) is located in the upper left-hand corner of the image. Note the semi-circular pattern of the newly formed crystallites (light contrast) in the amorphous matrix (dark background) that radiates outward from the center of laser irradiated zone. The pulsed laser crystallization exhibits a radially propagating crystallization front that propagates inward as well as outwards with varying nucleation rates and crystallization times proportional to the temperature gradient across the gaussian laser heated zone. Figure 2 shows the variation in number density of nuclei and size. At radial distances close to the center of the gaussian heated zone where temperatures approach an estimated 1500K, the density of nuclei and nucleation rates are quite low (>$5x10^4$ nuclei μm^{-3}

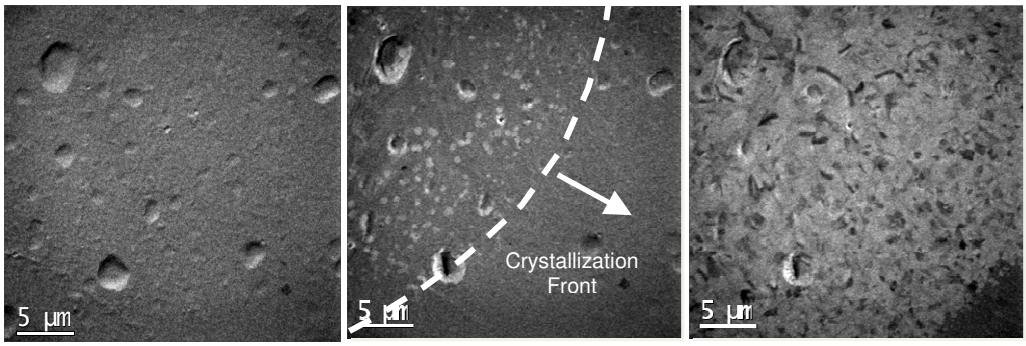

Figure 1. Series of 15ns exposure pulsed electron images, left image taken before laser heating, middle image taken 1.5μs after laser strikes foil, right image taken after foil cools to 300K

s^{-1}). However, the grain sizes are large (>1μm) due to high growth rates. At distances of 25μm from the center where temperature are estimated to be around 1200K, the nucleation rates are quite high (10^6 nuclei μm^{-3} s^{-1}). At temperatures below 900K, no nucleation is observed. This crystallization behavior can be described under classical phase transformation theory as the competition between thermodynamic driving force and kinetics, which can be further illustrated in Figure 3.

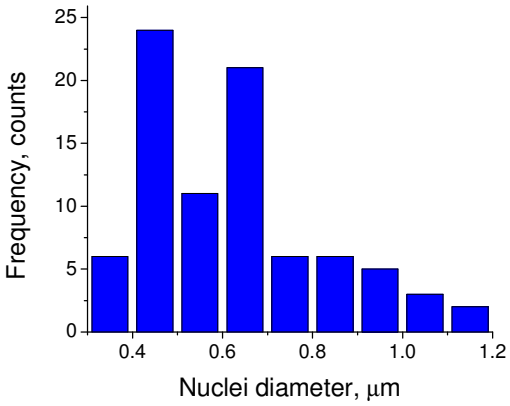

Figure 2. Plot of the number density of nuclei as a function of nuclei size

The plot in Figure 3a shows the curve for 90% crystallization as a function of time for pulsed laser annealing. Note that the high rates of crystallization occur at temperatures around 1200K (the nose of the C-curve). At temperatures above 1200K, the thermodynamic driving force for nucleation decreases, but growth rates are kinetically enhanced at the higher temperature, leading to large grains. At temperatures below 1200K, the nucleation rates are high due to higher driving forces but the crystallite growth is kinetically limited, leading to fine-grained microstructures. The time-resolved DTEM image in Figure 3 b) taken at a delay of 6μs displays a direct measurement of this C-curve behavior, where the crystallization fronts are propagating inwards and outwards and the radial variation in grain size. The direct measurement of nucleation and growth rates as function of temperatures allows prediction and control of grain size, which is necessary for fabrication of devices.

Conclusions

Using the DTEM, rapid nucleation and growth phenomena can be directly observed and quantified with ns time resolution. With this high time resolution, we can gain insight into the subtle details of materials processes in previously unexplored regimes such as crystallization processes at high temperature.

Acknowledgements

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References

[1] LaGrange T., Grummon, D.S., Reed, B.W., Browning, N.D., King, W.E., Campbell, G.H., *Applied Physics Letters,* Vol. 94, (2009) p. 184101

[2] Vestel, M. J. Grummon, D. S.,. Gronsky, R., Pisano, A. P. *Acta Materialia* Vol. 51**,** (2003) pp. 5309-5318.

[3] Liu, K. T., Duh, J. G., *Journal Of Non-Crystalline Solids,* Vol. 353**,** (2007) pp. 1060-1064.

[4] Kim, J. J., Moine, P., Stevenson, D. A. *Scripta Metallurgica*, Vol. 20, (1986) pp. 243-248

[5] X. Wang, M. Rein, and J. J. Vlassak, *Journal of Applied Physics* Vol. 103, (2008) p. 023501

[6] Lee, H. J. Ni, H. Wu, D. T., Ramirez, A. G., *Applied Physics Letters,* Vo. 87**,** (2005) p.124102.

[7] Avrami, M., *Journal of Chemical Physics,* vol. 7**,** (1939) pp. 1103-1111.

[8] Johnson A., Mehl, R. F., *Transactions of the American Institute of Mining and Metallurgical Engineers,* Vol. 135**,** (1939), pp. 416-442.

[9] LaGrange, T., Campbell, G.H., Reed, B.W.,Taheri, M. Pesavento, J.B Kim, J. S., Browning, N.D., *Ultramicroscopy* Vol. 108**,** (2008) pp. 1441-1449.

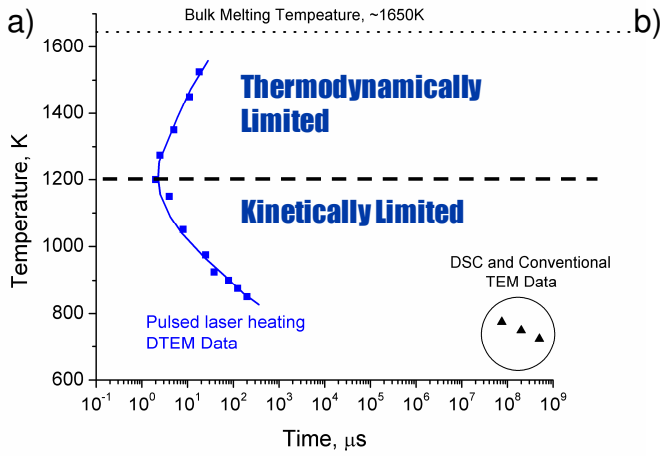

Figure 3. a) plot of the 90% crystallized volume as function of temperature and time. Note the classical C-curve behavior for diffusional phase transformation. b) 15ns exposure of the crystallization taken 6μs after the laser pulse hits the foil, The center of the gaussian laser spot is located in upper left-hand corner.