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Preparation of Shape Memory NiTiNOL Filaments for Smart Textiles

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Abstract
A nickel-titanium alloy (NiTiNOL, nitinol) filament with a diameter of 200 µm was used for preparing a smart knitted textile fabric with a shape memory effect within the range of human body temperatures. The annealing of the filament at 500 °C for 30 minutes was followed by air cooling at 20 °C to achieve a suitable transition temperature from martensite to austenite phase within the range between room temperature and 75 °C. The tensile properties of filaments before annealing and after it were analysed on Instron 6022 dynamometer. The measurements of exact transition temperatures from soft martensite state at room temperature to hard austenite state at heating were made on a dynamic mechanical analysis instrument. From the annealed filament a left-right knitted fabric was hand made. The fabric was trained into a selected 3D form by cyclic heating in a strained form at 75 °C for 10 minutes and then cooled at room temperature. For a stable two-way memory effect, the nitinol fabric needed to make fifteen cycles of heating and cooling.
Keywords: smart textiles, shape memory materials, shape memory alloys, nitinol

1 Introduction

NiTiNOL (nitinol hereafter) is a shape memory nickel-titanium alloy, which can change its shape in a wide temperature range, from −50 °C to +166 °C [1]. It is one of rare shape memory alloys which with certain chemical composition show a shape memory also within the range of human body temperatures. In comparison to other shape memory materials, like shape memory polymers, nitinol distinguishes itself by better stability of shape memory [2] and super-elastic properties with up to 8% elastic deformation [3]. Nitinol alloys are the most often used shape memory alloys in the area of smart textile materials, especially in clothes.

The ability to memorize a desired shape is related to nitinol special crystalline structure, to its austenite and martensite crystal phases, which under the influence of temperature changes, heating or cooling, or stress changes can reversibly convert from one phase to another [4]. Temperatures at which the conversions happen depend on the chemical composition and the annealing process of nitinol. Transition temperatures are described: by a temperature at which the transformation from martensite to austenite phase starts (A_s), by a temperature at which this transformation is complete (A_f), by a temperature at which the transformation of austenite to martensite phase starts (M_s) and, finally, by a temperature at which this transformation is complete (M_f) (Figure 1a) [4].

Although numerous studies and patents of nitinol alloy for different uses were published in last decades, commercially successful products are today still relatively low, mainly due to the high price of nitinol and

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the complexity of nitinol alloys processing to achieve desired thermomechanical properties. The use of nitinol is meaningful primarily in the areas where traditional materials do not provide adequate solutions.

Textiles are flexible materials which can easily change shape and can also follow the forms of embedded shape memory fibrous materials. Beside the unique uses of nitinol for kinetic garments by designers [6, 7], some interesting functional prototype solutions have been developed, like NiTi micro-hook in Velcro fasteners [8], elastic compression knitting [9], smart curtains [10, 11], where nitinol filaments were integrated into woven or knitted fabric structures and trained into desired temporary forms.

Figure 1b showes an example of a shape changes diagram of a fabric with embedded trained nitinol fine filaments. At room temperature (point a2) the fabric is soft and deformable while the nitinol filaments are in a multiple variant of twinned martensite phase. Loading the fabric by stretching, shrinking, bending or folding etc. causes macroscopic wrinkling of the fabric which is accompanied with structural changes in the crystalline structure of nitinol filaments into a single variant of detwinned martensite state (point a3 and a4). After unloading, the fabric preserves the macroscopic form and soft touch. There is no conversion to multiplevariants and only a small elastic strain is recovered, leaving the material with a large residual strain [5]. The structure of nitinol filaments stays in detwinned martensite state (point a5). Heating the fabric up to a certain temperature causes that the fabric changes

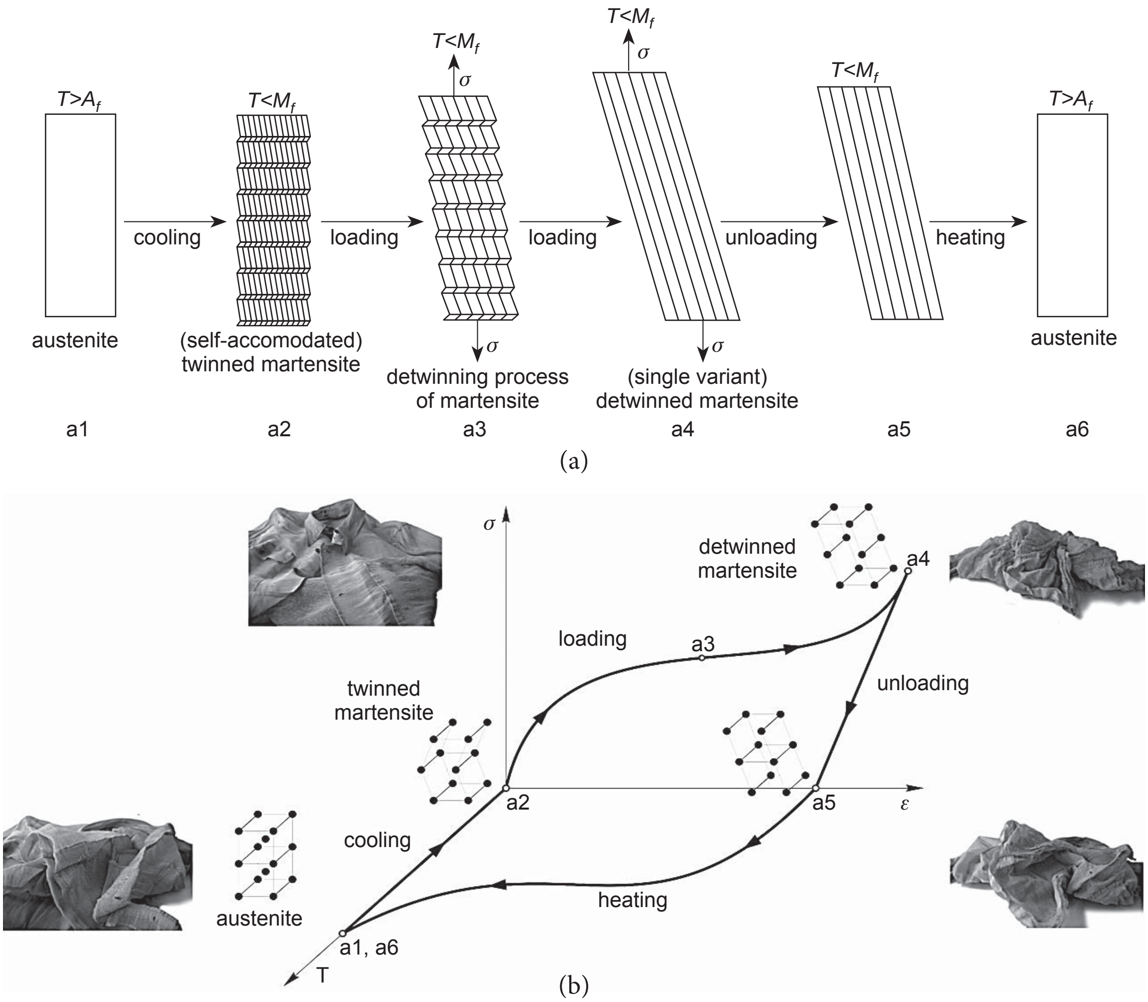


Figure 1: Shape memory effect: (a) diagram of crystal phases transformations of nitinol alloy by temperature and stress [5], (b) an example of shape changing of smart textile fabric with Nitinol filaments as function of stress (σ), temperature (T) and deformation (ε)

its shape into a preprogramed (unwrinkled) form (point a1/a6), which is followed by the changes into the austenite crystal microstructure. Cooling the fabric to room temperature leads to transition from hard and rigid austenite phase to soft twinned martensite state (point a2).

The area of using nitinol fibres in textiles is nowadays still largely restricted to unique uses. The main problems are the complexity of annealing nitinol filaments to set proper transition temperatures, the training process to set temporary desired shape and the problems connected with the integration of nitinol filaments into fabrics when using existing weaving or knitting machines.

The basic concept of the doctoral research, part of which is presented in this article, is the study of a weft knitted fabric made from 100% nitinol filaments, which would be inserted as interlining into a garment to create an air gap for increasing thermal insulation properties of such garment. In the article, properties of cold drawn and annealed nitinol filaments are compared beside the presentation of preparing a weft knitted fabric in its permanent and temporary shape memory forms.

2 Experimental

In the research, a cold worked nitinol filament with a diameter of 0.2 mm (Fort Wayne Metals, Ireland) with the characteristics listed in Table 1 was used.

Table 1: Properties of nitinol filament used in the research [12]

Properties	Nitinol #6 alloy
Thickness [mm]	0.200
Content of nickel/titanium [%]	55.47/44.53
Breaking force [N]	56.01
Tensile stress* [MPa]	1772
Breaking elongation* [%]	8.2
Yield load [kg]	4.23
Modulus of elasticity [GPa]	54.7309
Cold work [%]	44.5
A_f [°C]	+40 to +80

* Testing conditions: gage length 254 mm, testing speed 25.4 mm/min.

The cold worked filament with A_f temperature in between +40 °C and +80 °C was annealed at 400 °C, 450 °C and 500 °C for 30 minutes in a furnace.

The transition temperatures of nitinol filaments were measured by differential scanning calorimetry (DSC) on Mettler DSC 1 apparatus (Mettler Toledo, Swizerland) at speed 5 °C/min in a temperature range from −50 °C to 100 °C. A dynamic mechanical analysis (DMA) of only transition temperatures of nitinol filaments at heating was made on Q-800 apparatus (TA Instruments, USA) at a frequency of 10 Hz in the temperature range from 0 °C to 120 °C with a heating speed 2 °C/min.

The tensile properties of nitinol filaments were measured on Instron 5567 dynamometer (Instron, GB) at gage length 250 mm and testing speed 5 mm/min.

3 Results and discussion

The purchased cold worked nitinol filament was characterised by its mechanical properties and a range of austenite temperatures (Table 1). For being used in smart textiles as shape memory material, the worked cold nitinol filaments were firstly annealed to set proper transition temperatures. For NiTi alloy application the transition temperature should be within the range slightly above the temperature of a human body. DSC thermograms showed the transition temperatures (M_s, M_f, A_s *and* A_f) of annealed nitinol filaments. The most proper annealing temperature for the intended use of nitinol filaments was at 500 °C, where nitinol filaments existed in a soft pure martensite phase at room temperature and in a stiff pure austenite state at 75 °C (Figure 3).

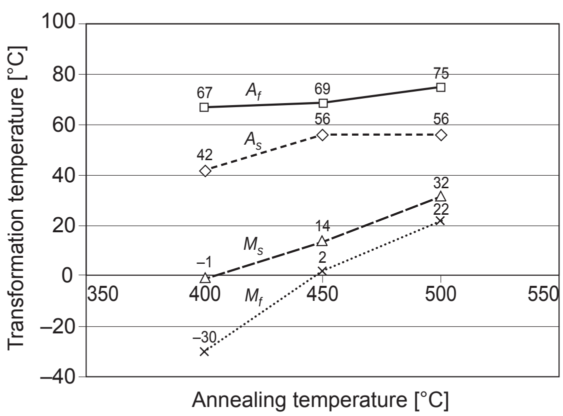


Figure 3: Transition temperatures of nitinol filaments versus annealing temperatures

The tensile properties of the cold worked and annealed nitinol filaments at 500 °C were determined at room temperature (20 °C) and at 100 °C (Figure 4):

- the average measured breaking force of the cold worked nitinol filaments at 20 °C was 55.2 N at average breaking elongation 5.1% (Figure 4a), which is consistent with the declared data given in Table 1;
- the average measured breaking force of the annealed nitinol filaments at 20 °C was (Figure 4b) 34.0 N at average breaking elongation 7.6%;
- the breaking force of the cold worked nitinol measured at 100 °C (Figure 4c) showed a little lower average breaking force of 50.9 N at average breaking elongation of 4.5% than at room temperature;
- the average average breaking force of the annealed nitinol filaments at 100 °C (Figure 4d) was 33.3 N at average breaking elongation of 12.2%.

From the stress/elongation diagrams of cold worked and annealed nitinol filaments (Figure 5) the comparison of their tensile properties in the whole deformation range can be made:

- a cold worked filament shows a similar tensile behavior at 20 °C and 100 °C up to 2% elongation and a little higher tensile stress and elongation within the range between 2% and breaking elongation at 20 °C in comparison with 100 °C. Both curves are very steep with distinct elastic behavior. The curves demonstrate a similar microstructure of the cold worked nitinol filament at 20 °C and at 100 °C;
- the shape of the stress/elongation curves of annealed nitinol filament differs substantially from the shape of the curves of cold worked filaments and is typical for shape memory nitinol alloys. At 20 °C, the annealed material is in martensite state. The curve has a short elastic deformation, and shows no pseudoelasticity. The annealed nitinol filament at 100 °C is in austenite phase. On the stress/elongation curve it shows a more pronounced elastic area, and extremely higher modulus of elasticity

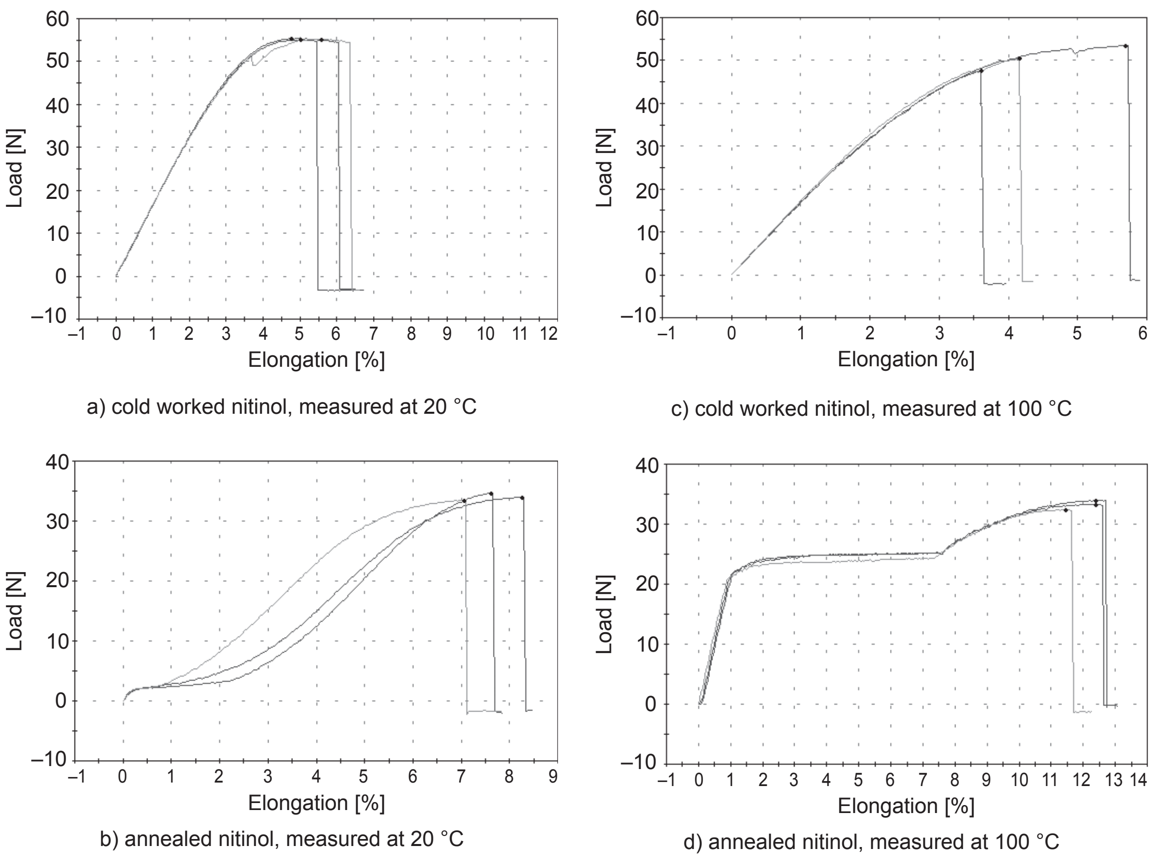


Figure 4: Tensile load/elongation diagrams of cold-worked (a, c) and annealed (b, d) nitinol filaments, measured at 20 °C and 100 °C

of 60.4 GPa as the annealed filament at 20 °C that is only 8.95 GPa. The breaking stress of the annealed nitinol filament at 100 °C is 1.06 GPa which is for about 38% higher than for annealed filament at 20 °C, with the breaking stress of 0.656 GPa. The annealed nitinol filament is at 100 °C in a pseudoplastic state in the elongation range of 1–8%, where the stress-induced austenite to martensite transformation occurs. It is followed by a plastic deformation that leads to the breaking of the filament.

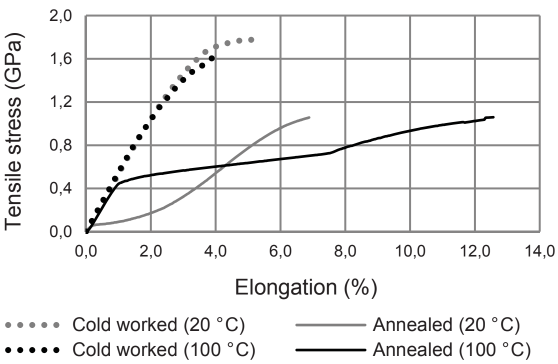


Figure 5: Stress/elongation curves of cold worked and annealed nitinol filaments at 20 °C and 100 °C

From the results of the DMA measurements the transition temperatures, storage modulus (E'), loss modulus (E") and tangent delta (tgδ) depending on the heating temperature and the frequency (ν) have been detected (Figure 6):

– storage modulus (E') of the cold worked nitinol filament (Figure 6a) decreases with heating. The value of 28.44 GPa at temperature of 11 °C monotonously decreases to a value of 26.29 GPa at 98 °C. There is no heat loss in the absence of relaxation passages, that is why the storage modulus (E') remains within the range of 0.2 GPa (0.213–0.205 GPa). Even the tangent delta (tgδ) curve, which illustrates the internal movements and damping, shows an extremely small value, about 0.007 (0.007–0.009), as there is no relaxation oscillations and displacements. On the curve of length changes in dependence of temperature spontaneous flat shrinking of the sample is seen: –0.029 mm, or 0.38% to a temperature of 101 °C;

– according to the data of the manufacturer (Table 1), the annealed nitinol filament has transformation temperatures from martensite to austenite phase between 40 °C and 80 °C. This transition is seen on Figure 6b between 60 °C and 80 °C. The value of storage modulus (E') of 30.38 GPa is reducing by applying heat up to the 50 °C and then continuously increasing due to the transformation of a less regulated monoclinic cell crystal structure of martensite phase in a highly regulated cubic crystal structure of austenite phase. Due to increasing regulation of the crystal structure of austenite, the stress and the storage modulus (E') for the same deformation are higher: up to 100 °C the storage modulus (E') rises up to 59.87 GPa. The maximum transition temperature is at 66.95 °C. Within the temperature range between 60 °C and 80 °C the storage modulus increases from 30 GPa to 56 GPa;

– loss modulus (E") also detects the transformation of martensite to austenite phase at temperature of 58.96 °C: this is the largest heat energy dissipation at the crystal lattice transformation;

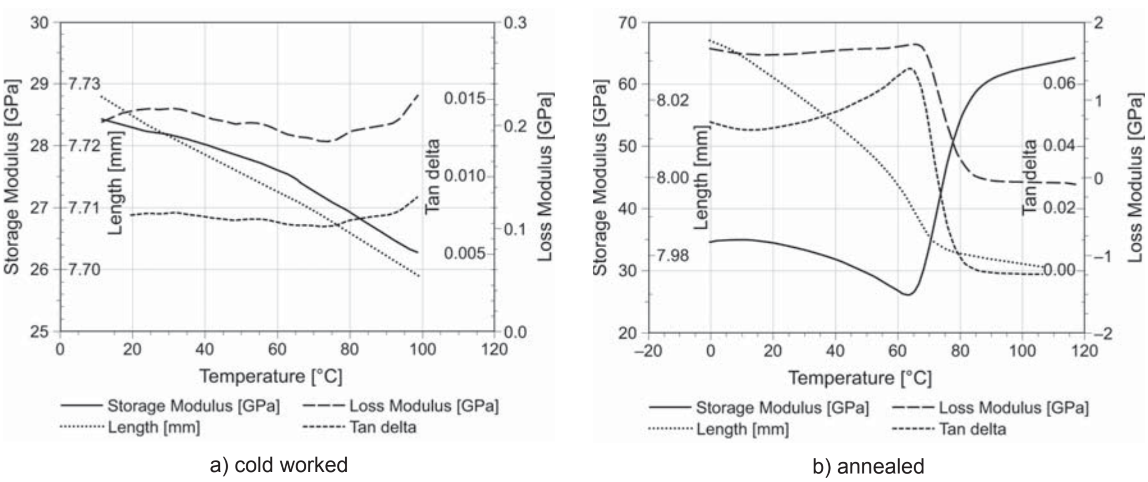


Figure 6: Dynamic mechanical behaviour of cold worked (a) and annealed (b) nitinol filaments

– tangent delta (tgδ) curve detects the mobility of atoms from one crystal lattice to another at the temperature of 56.19 °C. The change in length influenced by the temperature, indicates that the sample is rapidly shrinking up to 70 °C faster than after the transformation of the austenite structure. Full shrinkage of the sample is –0.03 mm, or 0.29%.

From the cold worked nitinol filament, a hand weft knitted fabric was prepared (Figure 7). For the purpose of annealing and training of the knitted fabric, a special metal prefabricated mould was prepared from a stainless steel and aluminium. Before annealing, the fabric was clamped in a mould framework in a flat state without a pre-stress (Figure 8a). The annealing in a furnace at 500 °C for 30 minutes was followed by cooling in the air at temperature below 22 °C for 20 minutes. The annealed fabric was trained to achieve a two-way shape memory. The training process covered heating of annealed fabric at 75 °C in an oven for 10 minutes with a subsequent cooling in the air below 22 °C for 20 minutes. After repeating this procedure several times (more than 10-times), the material got a two-way shape memory: it took a temporary form at heating and returned to a permanent form at cooling. The knitted fabric was trained to a temporary three-dimensional half-sphere form (Figure 8b) and into a flat permanent form (8c).

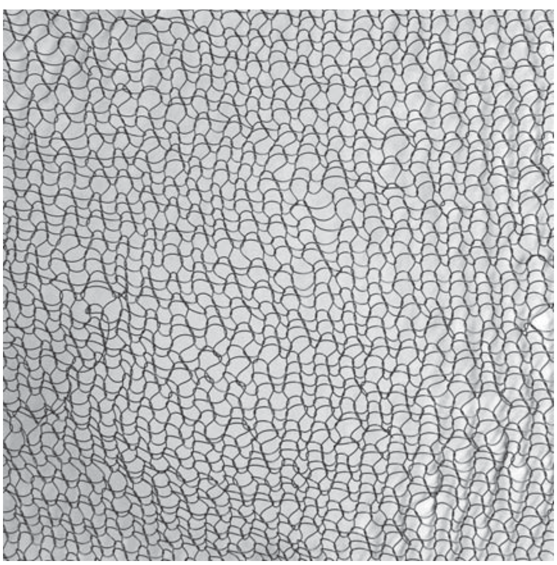
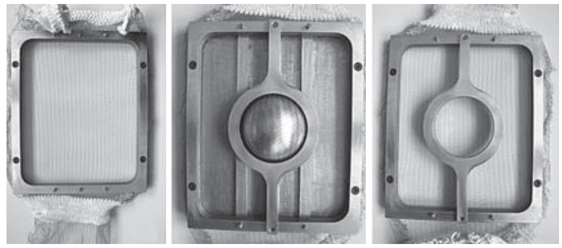


Figure 7: A knitted fabric hand-made from a nitinol filament of a diameter 0.2 mm



a) b) c)

Figure 8: A clamped knitted nitinol fabric: (a) in a mould, prepared for annealing, (b) clamped in a three-dimensional half-sphere form prepared for training with heating, and (c) clamped in mould in a flat form prepared for cooling

4 Conclusion

The most important properties of nitinol alloy for integration in textiles and suits are high enough fineness and related flexibility, abrasion and fatigue resistance and rate of shape changing. Due to the high price of shape memory alloys, only unique products and prototypes have been developed until now.

In the study, we successfully trained the nitinol filaments and prepared a functional knitted fabric to be potentially useful as interlining in a personal protecting suit that could dynamically regulate a thickness of air layer to protect a body from high environment heating and feel comfortable in a suit at normal environmental temperatures.

Acknowledgements

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