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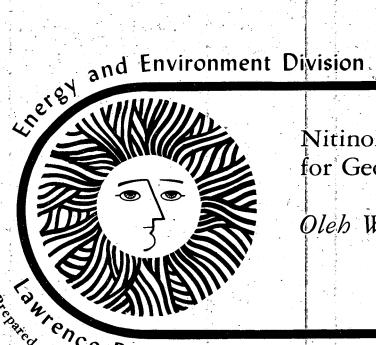
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NITINOL SELF-DESCALING SURFACE FOR GEOTHERMAL SCALE CONTROL

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I. The Shape Memory Effect

The shape memory effect is a thermomechanical phenomenon exhibited by some alloys when they undergo a diffusionless phase transformation.

The higher temperature phase of these alloys (the <u>Austenite</u> phase) is hard and rigid. The low temperature phase (the <u>Martensite</u> phase) is soft and easily deformed. At moderate stress levels and strain amplitudes this deformation occurs by the migration of twinning planes. (The twinning planes are, in most cases, produced as part of the phase transformation which occurs on cooling.) The crystallography of the phase transformation is such that these twin planes in the Martensite are mirror planes in the Austenite, i.e., they are merely lattice planes and not lattice defects in the Austenite phase. This means that the Martensite reverts to the same initial Austenite structure regardless of the amount of deformation via twin plane migration it may have undergone. \(\begin{align*} \text{1} \text{ and migration it may have undergone.} \end{align*} \)

Macroscopically, this manifests itself as a reversion of the shape of the specimen to whatever it was when the specimen was initially in the Austenite phase. This reversion is accompanied by considerable mechanical force. The force and spontaneous deformation attainable in this way are far greater than is the case with superficially similar thermal expansion related ("bimetallic") phenomena. Prototype heat engines which make use of this shape memory effect (SME) have been built at LBL. In order to distinguish it from ordinary irreversible plastic deformation, the reversible deformation of the Martensite is called quasi-plastic deformation.

The most promising <u>shape memory alloy</u> (SMA) appears to be equiatomic NiTi, also called <u>Nitinol</u>. Its advantages are a very high attainable

specific mechanical energy output (1 kj/kg/cycle or greater¹) and good corrosion resistance.³ The zero-stress phase transformation temperature may easily be adjusted over a wide range by making min or variations in the chemical composition of the alloy.

The shape mamory effect is demonstrated in Figures 1 a, b, and c. The specimen employed is an air annealled 6" x 0.05" piece of commercial NiTi wire with a transformation temperature of about 120°F. Figure 1 a shows its "remembered shape." Figure 1 b shows it after it has been deformed under cold water by coiling it with the fingers. In Figure 1 c it has regained its shape by having been immersed in near boiling water.

II. The Second Memory Phenomenon

It has been observed that Nitinol wires which have been working in a heat engine for some time develop a second remembered shape which they spontaneously deform to when cooled to below the transformation temperature. Thus, a piece of Nitinol which has a second memory will reversibly change from one shape to another when repeatedly heated and cooled without the need for an externally applied force. The Nitinol specimen in Figure 1 has only a weak second memory. It is responsible for the slight difference in shape between 1 a and 1 c. The wire was dipped into cold water before 1 a was taken, and this put it into its "second memory form" which is slightly more tightly bent than is the primary shape shown in 1 c and 1 e. The origin of the second memory phenomenon is not yet clearly understood. It differs from the shape memory effect proper in that it is induced by a definite "course of training" rather than being an intrinsic property of the wire. Also, the force associated with it is much smaller than that

associated with the SME proper.

III. Application of the SME for Scale Control: Basic Principles

There are two ways in which the SME may be applied to scale control.

1) The metal is in the Martensite phase under routine operating conditions, and scale deposits on it as it would on any other metal. The system is periodically descaled by temporarily increasing the temperature enough to induce the phase transformation. This causes the metal to change shape and, thereby, throw off the scale.

A simple laboratory demonstration of this method is shown in Figures 1 d and e. In Figure 1 d the piece of Nitinol wire has been deformed into a tight coil (as in Figure 1 b) and completely covered with several millimeters of plaster of Paris. Figure 1 e shows it after it has once again been immersed in hot water. The broken pieces of plaster are faintly visible around it. This complete reversion and simulated "descaling" took less than 3 seconds. The rate seems to be controlled mostly by the rate of heat conduction through the plaster.

2) The metal is in the Austenite phase under routine operating conditions. It is periodically descaled by cooling it down to below the transformation temperature and applying external force to quasi-plastically deform it enough to flake off the scale. The original shape of the Nitinol is restored after descaling by simply returning it to normal operating temperature.

The latter concept has been demonstrated with actual geothermal brine by Dr. H. Papazian and J. Angevine at the ERDA Geothermal Component Test Facility at East Mesa, California. The specimen was an air annealled 6" x 1" x 0.012" piece of sheet Nitinol which was screwed onto a heavy piece of stainless steel and exposed to flashing geothermal brine for nine days. It came out with an adherent coat of a few tenths of a millimeter thickness of what appeared to be carbonate scale on it.

Bending the scaled up specimen with an axis parallel to its short dimension cracked the scale but did not remove it because of the limited surface curvature attainable in this way. After this initial bending it was restored to its original shape by immersion in boiling water.

Attempting to bend one of the ends of the specimen where one of the mounting holes had been drilled caused it to break through the hole. We believe this to have been due mostly to mechanical damage near the hole and, perhaps, in part to crevice corrosion. Away from the mounting holes the metal did not seem to have been embrittled.

After it had cooled down, the specimen was again bent but about an axis parallel with its long dimension. This caused almost all of the scale to flake off. Immersion in boiling water once again restored it to approximately its initial form.

The specimen was sectioned and microscopically examined by V. Nagurajan of LBL (MMRD). No internal corrosion at all was observed. In most areas the surface was also free of corrosion. In some areas, however, there were observed shallow pits. In some pitted areas there remained a thin, tenaciously adherent scale which electron microprobe analysis revealed to consist of corrosion products and brine derived scale materials. The pitted areas appeared to be those which had previously corroded to some degree during the air annealling. Such corrodible areas should prove easy to eliminate by annealling in an inert atmosphere and suitable surface

finishing.

Figure 2 a shows the edge of one of the pitted areas. Figure 2 b shows a section through an area with shallow pitting and adherent scale. (Note that the featureless area at the top is the interior of the metal.)

All in all, this experiment suggests that no serious NiTi corrosion problems should be encountered at least in the relatively benign brines of the East Mesa field.

IV. SME Scale Control: A Specific Proposed Application

The major scaling problem which has been encountered at the hot brine geothermal plant at Cerro Prieto, Mexico is the deposition of hard silica and carbonate scales in the wellbores and steam/water separator units. The deposition of these scales is due to loss of heat and gases from the brine as part of it flashes to steam in the wellbore and separator. The wellbore scaling is severe enough to require annual "drilling out" at a cost of \$10,000 or more per well.

This sort of scaling could be controlled by putting a NiTi (or other suitable SMA) liner inside the well casing or separator. The alloy composition would be such that its transformation temperature is above the normal flowing brine temperature but lower than the static temperature (i.e., approximately the downhole temperature). Thus, during normal operation the metal would be in the soft Martensite phase, and would be firmly pressed against the casing or separator wall by the pressure of the brine. Descaling would be accomplished by throttling brine flow beyond the point to be descaled. This would cause the brine pressure and temperature to rise and cause the metal to transform. The NiTi liner

would contract, pull away from the wall, and crack off the scale deposited on it. This would, of course, require some means of pressure compensation behind the liner. This would be easiest to supply by letting brine into the annulus between liner and wall.

Brine flow would then be restarted. The ensuing temperature drop would cause the metal to transform to the Martensite phase again, and a suitable release of the brine between liner and wall would force the liner back up against the wall. The shed scale would be removed from the system by diverting the first of the resumed brine flow to a suitable separation facility.

The above is presented merely as an example. Numerous variations on the principle are clearly possible. The concept should also prove easy to extend to deal with non-geothermal scale problems such as are encountered in oil field practice and boiler operation.

The second memory phenomenon may also prove to be of use despite the much smaller forces associated with it. For example, it may prove sufficiently powerful to eliminate the need for external force in the quasiplastic deformation step of the descaling cycle.

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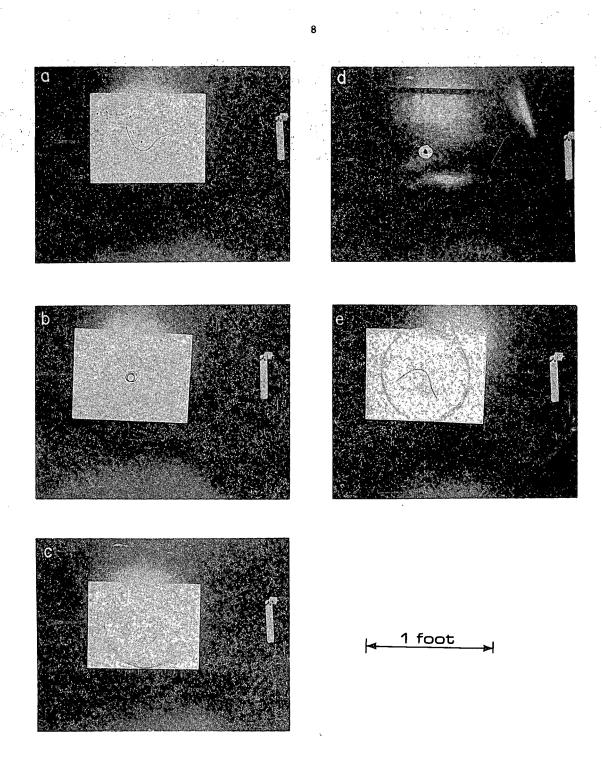
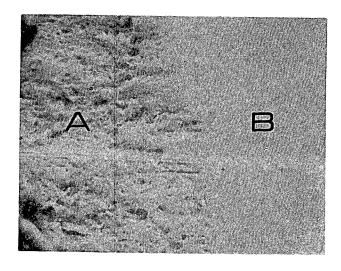
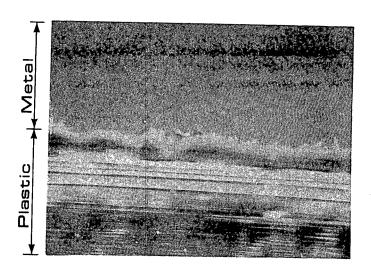


FIG. 1

9



2a



2ь

FIG. 2

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