

Metal and Ceramic Biomaterials

Volume II Strength and Surface

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Chapter 3

SHAPE MEMORY ALLOYS

R. Kousbroek

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I. INTRODUCTION

In the past few years the shape memory alloys have attracted the attention of metallurgists and design engineers because of a number of remarkable properties which open a revolutionary way of designing on the basis of entirely new principles compared with conventional alloys. The most striking features of this family of alloys are the shape memory effect, the pseudo-elasticity, and the very high damping capacity. A short definition of these effects will be given here for convenience, but a more extensive description of the shape memory effect and the pseudo-elasticity, which are important in the context of this chapter, will follow later.

Shape memory effect — This is the phenomenon by which, after an apparent plastic deformation, a metal alloy upon heating starts to remember its original shape at a certain temperature and returns to its deformed shape upon cooling.

Pseudo-elasticity — The effect by which a material recovers the induced "plastic" strain upon unloading is known as the pseudo-elasticity. The amount of this reversible strain is much greater than the classical, elastic strain. In contrast to the shape memory effect, the temperature remains constant.

High damping capacity — As a result of a change in internal structure, the damping capacity of these alloys can be varied considerably as a function of temperature, resulting in a very high damping capacity in certain temperature ranges.

These three features are associated with a martensitic transformation and this association limits the family of alloys exhibiting these special effects. In principle, all the alloys which exhibit a martensitic transformation are potential shape memory alloys, but experience shows that the effects only appear significantly in alloys having a reversible martensitic transformation, e.g., nickel- and copper-based alloys (e.g., Ti-Ni and Cu-Zn-Al).

Although the first basic information concerning the shape memory alloys was already observed about 40 years ago, it was in the 1960s that the usefulness was recognized. Since that time many potential applications of the shape memory alloys have been suggested.

In this review the potential uses of the shape memory alloys in medical applications will be highlighted (Section V). However, first, in order to understand fully the working principles of the biomedical devices, the basic metallurgical mechanisms of the shape memory alloys and the related effects will be discussed (Sections III and IV).

II. HISTORICAL BACKGROUND

The first observed shape memory phenomenon is the pseudo-elasticity. In 1932 Ölander observed this in a Au-Cd alloy and called it "rubber-like" behavior.¹ In the 1950s this phenomenon was also recognized in other alloys, e.g., In-Tl, Cu-Zn, and Cu-Al-Ni. Because of the great amount of reversible strain, this effect is also called "superelasticity". The maximum amount of reversible strain has been observed in a Cu-Al-Ni single crystal with a recoverable elastic strain of 24%.²

The first steps on the discovery of the shape memory effect were made in 1938 by Greninger and Mooradian,³ observing the formation and disappearance of martensite with falling and rising temperature in a Cu-Zn alloy. However, this basic phenomenon of the memory effects, the thermoelastic behavior of the martensite phase, was first extensively studied 10 years later by Kurdjumov and Khandros.⁴

Since the first observation of the shape memory effect in Au-Cd in 1951,⁵ the effect has also been reported in other alloys, e.g., Cu-Zn, In-Tl, Cu-Al-Ni, Ag-Cd, Ag-Zn, Cu-Al, Fe-Pt, Nb-Ti, and Ni-Al, but the great breakthrough came in the early 1960s, when Buehler et al.⁶ of the U.S. Naval Ordnance Laboratory (now called the U.S. Naval Surface Weapons Center) discovered the shape memory effect in an equiatomic alloy of nickel and titanium,

since then popularized under the name Nitinol (Nickel-Titanium Naval Ordnance Laboratory). With this alloy complete recovery of a maximum strain of 8% can be achieved by the shape memory effect, associated with a considerable force, which can perform work.^{7,8} As Nitinol is difficult and expensive to manufacture and fabricate, the attention of metallurgists reverted to one of the first shape memory alloys Cu-Zn (brass). With the discovery that addition of small amounts of aluminium to brass raised its transition temperature considerably,⁹ the shape memory effect of this new Cu-Zn-Al alloy could now be used in many practical applications at or near room temperature as was already possible with Nitinol. The great advantage of this Cu-Zn-Al alloy in comparison with Nitinol is that it is much cheaper and much easier to machine and fabricate. Since 1969, a major part of the fundamental research on Cu-Zn-Al shape memory alloys was done by Delaey et al.^{10,11}

Several applications of the Ti-Ni and Cu-Zn-Al shape memory alloys have been developed, e.g., tube fitting systems, self-erectable structures, clamps, greenhouse window openers, thermostatic devices, different thermomechanical applications for automobiles, heat-engines, and biomedical applications. Several international symposia have been devoted exclusively to these alloys. In 1968 a first symposium concerning the shape memory alloy Nitinol was held in the U.S.¹² followed in 1975 by the first international symposium on shape memory effects in alloys and applications at Toronto, Canada.¹³ Since 1976 shape memory alloys and the mechanisms are an ever recurring topic at such conferences as the International Conference on Martensitic Transformations (ICOMAT).

III. NATURE AND MECHANISM OF SHAPE MEMORY ALLOYS

The striking features of shape memory alloys are all closely related to the martensitic transformation. It is thus of value to describe the martensitic transformation and related phenomena first. It should also be noted that the exact nature and mechanism governing the behavior of shape memory alloys is not identical for all shape memory alloys.

A. Martensitic Transformation

Cohen et al.¹⁴ formulated the next definition of martensitic transformation: "A martensitic transformation is a lattice-distortive, virtually diffusionless structural change having a dominant deviatoric component and associated shape change such that strain energy dominates the kinetics and morphology during the transformation." If diffusion rules the transformation, atoms are changing places in the lattice in an uncoordinated way over long ranges. The resulting process can be fully described by the diffusion laws of Fick or by the method of Matano. However, if as is the case in the martensitic transformation, a diffusionless transformation occurs, a coordinated movement of large blocks of atoms is decisive for the resulting structure. The most well-known martensitic transformation is the phase transition responsible for the hardening of carbon steel caused by quenching after annealing at high temperature. In this case the austenitic, high-temperature fcc-structure changes into the martensitic, bct-structure on cooling.

From now on, regardless of the crystal structure, we will denote the high-temperature phase as the austenitic phase, while the product of the transformation will be called martensitic. In the present context, these terms are certainly not limited to ferrous materials.

Concomitant with the homogeneous lattice deformation, caused by the movement of the large blocks of atoms, dominant deviatoric shear displacements can cause an external measurable shape change. The associated strain energy will exert a dominant influence on the kinetics and morphology of the transformation. It is in this dominant influence of the strain energy on the growth characteristics that many nonferrous martensitic systems show the shape memory effect, whereas most ferrous martensites do not, because of differences in

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