JOURNAL OF MATERIALS SCIENCE 19 (1984) 1343–1348

The effect of titanium additions on M_S of ß-CuZn

S. EUCKEN, E. HORNBOGEN
Institut für Werkstoffe, Ruhr-Universität Bochum, 4630 Bochum 1, West Germany

The effect of titanium additions to binary β-CuZn alloys was investigated: the concentration range of β at high temperatures (860° C), solid solution hardening of this phase, and the change in martensite temperature, M_S. Titanium in solution produces considerable solid solution hardening, both by replacing copper or zinc. Only replacement of zinc leads to a constant or increasing M_S, while replacing copper decreases it. Ageing of the β-phase causes strong hardening and a decrease in M_S. The results have been interpreted considering the role of thermodynamic and mechanical properties in determining M_S.

1. Introduction

Prerequisites for shape memory are:

1. a martensite transformation associated with minimum volume change but maximum shear;
2. a small hysteresis between the temperature of transformation (M_S) and reverse transformation (A_S);
3. transformation temperatures in the temperature range of intended use of the effect, usually at or slightly above ambient temperature.

A fourth requirement is strength of the alloy. In use it is exposed or expected to exert forces. These in turn are limited by the true yield stress, i.e. the stress at which considerable irreversible deformations occur [1]. Of equivalent importance is the fact that an elevated yield stress will reduce fatigue crack growth. This is important if the material is exposed to repeated thermal or mechanical cycles.

Out of the two important groups of shape memory alloys: β-NiTi and β-brass type [2] the application of the latter suffers from its lack of strength. Most alloy developments of copper-base alloys went into the direction of replacing zinc by aluminium and nickel [3–6]. The strength of these alloys is still inferior in respect to β-NiTi.

A very specific problem in the search of strong shape memory alloys is the coupling of martensite start temperature, M_S, and the yield stress, σ_y. Any hardening mechanism which increases the yield stress by $\Delta\sigma_y$ will lower M_S by ΔT, unless it is compensated by an increase of the thermodynamic equilibrium temperature T_0 [7].

$$M_S = T_0 - \Delta T = T_0 - \frac{V_m \gamma_{\alpha\beta} \tau_{\alpha\beta}}{\Delta S_{\alpha\beta}} \qquad (1)$$

V_m is the molar volume, $\gamma_{\alpha\beta}$ the amount of shear associated with the $\beta \rightarrow \alpha$ transformation, and $\Delta S_{\alpha\beta}$ is the transformational entropy. As the transformation has to take place inside of β, its resistance to shear has to be overcome by the newly forming α-crystal. This critical resolved shear stress is increased by hardening mechanisms such as solid solution-, radiation- or particle-hardening [8, 9]. Therefore, $\tau_{\alpha\beta}$ is proportional to the increase in yield stress, $\Delta\sigma_y$, if the mechanism of nucleation and growth of martensite crystals is not changed. (The constant C contains the factor of proportionality between τ and σ, as well as all the properties given in the second term of Equation 1.)

$$M_S = T_0(x) - C\Delta\sigma_y \qquad (2)$$

The equilibrium temperature T_0 is a function of the chemical composition of the alloy. The additional undercooling required to start the transformation increases with increasing yield stress. This investigation was conducted to explore the effect of titanium additions as solid solution strengthening agent to β-CuZn which can be expected from the atomic size ratios. In addition it is likely that replacement of zinc by titanium could increase T_0. This in turn would lead to an alloy which combines elevated strength without decreasing M_S. The purpose of this investigation was to test the limits of titanium contents which

0022–2461/84 $03.00 + .12

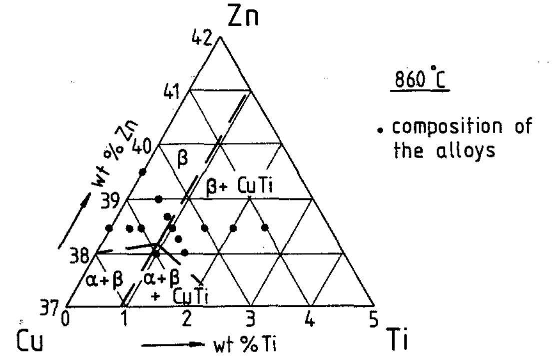

Figure 1 Section of the ternary phase diagram Cu–Zn–Ti indicating the extent of the β-field and the composition of the alloys used for this investigation.

can be dissolved in β-brass alloys with relatively high M_S (i.e. high copper content). Consequently the M_S temperatures and the shape changes associated with transformation in these alloys should be measured.

2. Materials and experimental procedures

The binary alloys had a composition of 60.5 wt % copper and 39.5 wt % zinc. Two sets of alloys were produced by induction melting in which either copper or zinc were replaced by titanium. Their chemical compositions are indicated in the ternary diagram (Fig. 1).

Cylindrical specimens were produced by turning ingots to a diameter of 10 mm or by drawing 1 mm wires. A homogenization treatment was followed by holding for 10 min at 860° C and brine quenching. Electrolytic polishing was required to follow mechanical polishing to obtain the surface quality required for the observation of the microstructure as well as the surface upheavals produced by the martensitic transformation.

The samples were cooled at a rate of about 20 to 40 K min^{-1} to liquid nitrogen temperature. Optical microscopy was used for determination of the transformation temperature, while the specimen temperature was measured with a thermocouple which was positioned 2 mm beneath the surface. The observations were made at least 2 mm away from the surface of the original specimens during heat treatment to avoid errors due to dezincification.

Ageing experiments were conducted up to 1000 h at 150° C and Vickers hardness used as an indication for property change in the β-phase.

The shape memory properties were explored by the application of bending stresses during cooling of the wire-shaped alloys.

3. Experimental results

The alloys were quenched from 860° C in order to obtain a homogeneous β-structure. Towards high copper contents this is limited by the formation of fcc α-phase by massive transformation [10], at higher titanium contents the two-phase field β + CuTi is approached [11]. Light microscopy reveals these two limits (Fig. 2b), and the findings are summarized in the phase diagram (Fig. 1).

Strengthening of the binary phase by titanium additions is considerable (Figs. 3a and b). The increase in hardness is somewhat more pronounced in the alloys with the higher copper content and the replacement of copper by titanium. Strengthening reaches about the same level at the highest titanium concentration which can be dissolved (~ 1 wt %) for both, replacement of copper or zinc by titanium.

Because of the stability of the transformation properties the ageing behaviour of the β-phase is of importance. An alloy with 0.8 wt % titanium was aged at 150° C and a considerable increase in hardness was found (Fig. 4a). No changes could be detected after several months at room temperature.

All metallographic measurements of the course of transformation show that the reaction was complete (M_f) at 20 to 30° C below M_S. The reverse transformation (A_S) started at or only a few degrees above M_S. An overheating of about 20° C was required for complete reversions. Therefore the total transformation cycle requires a temperature range of 40° C for all alloys which were investigated.

To show the effect of titanium additions only the measurements of M_S are shown in Figs. 5a and b. A replacement of copper leads to a lowering of the transformation temperatures, while replacement of zinc provides even a slight increase.

Finally, it could be shown that M_S is not only a function of chemical composition. It decreases with ageing of an 0.8 wt % titanium alloy (Fig. 4b). After about 10 h at 150° C M_S is lowered below − 200° C. Further ageing stabilizes the β-phase so far that transformations will not take place at any undercooling.

The results of all measurements of M_S are summarized in the β-field shown in the ternary phase diagram in Fig. 6.

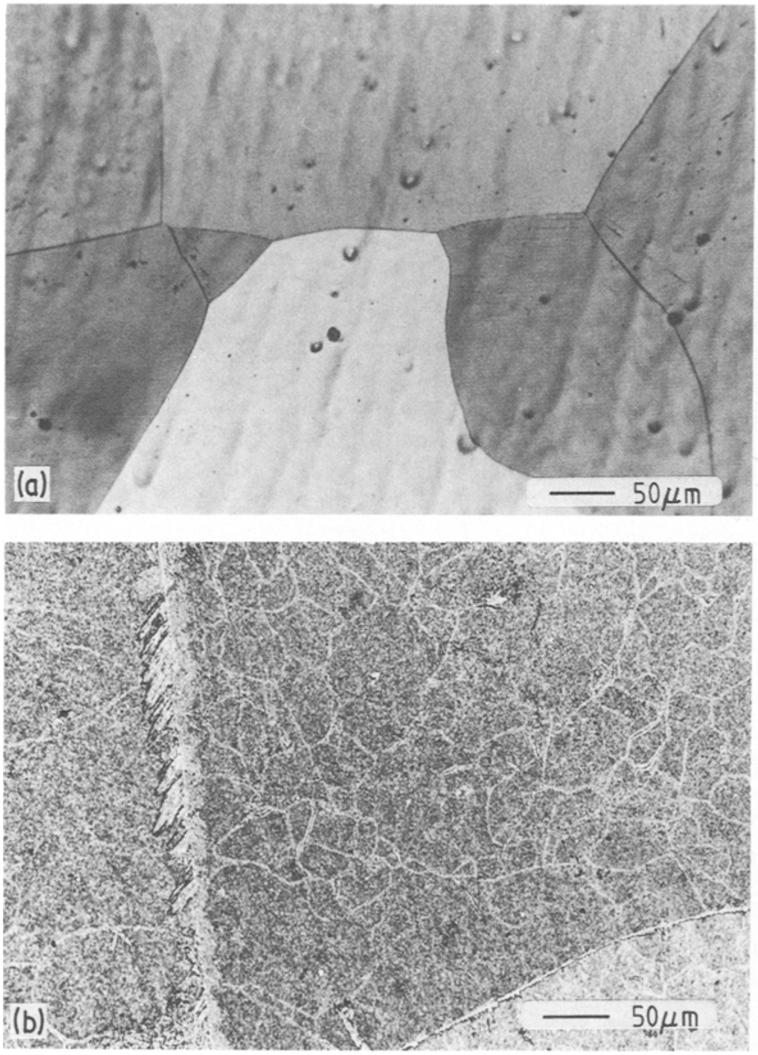

Figure 2 Light microscopy of the as-quenched alloys (T_Q = 860° C). (a) 61 wt % copper, 38.5 wt % zinc, 0.5 wt % titanium, homogeneous β-phase. (b) 60.5 wt % copper, 38.3 wt % zinc, 1.2 wt % titanium, massive α and fine scale precipitation of intermetallic compound.

4. Summary and conclusions

Additions of titanium to β-brass lead to considerable solid solution hardening by both, replacement of copper or zinc atoms. The differences in atom radii make it likely that this is due to solid solution hardening of the ordered β-CuZn phase, and not to an increase of ordering energy. The compositional range in which a homogeneous β-phase can be

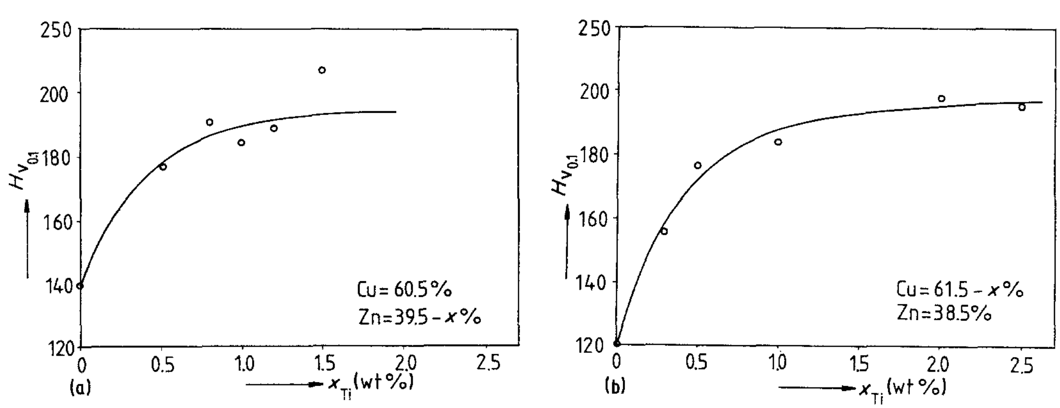

Figure 3 Solid solution hardening by titanium additions.

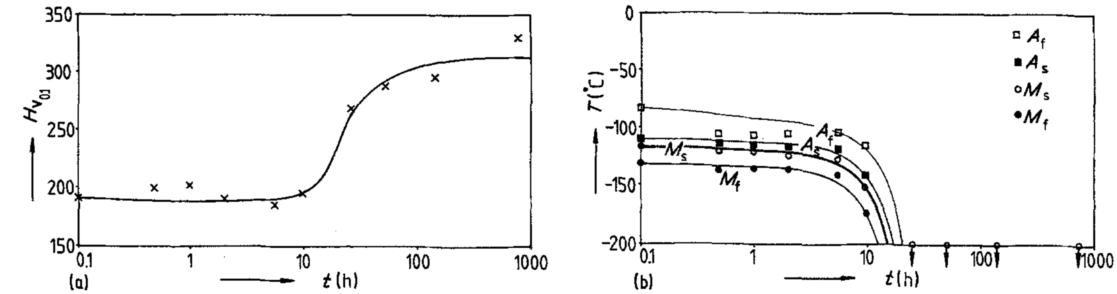

Figure 4 Effects of ageing at 150° C (60.5 wt % copper, 38.7 wt % zinc, 0.8 wt % titanium). (a) age-hardening, and (b) lowering of the martensite start temperature, M_S.

obtained by quenching encounters two limits. At high copper-contents ($x_{Cu} > 61$ wt%) massive transformation into α becomes rapid. The experiments showed that this limit is not shifted towards higher copper contents by titanium, as is known for additions of aluminium. The second limit originates from the tendency to form and precipite a titanium-rich phases (CuTi via coherent metastable stages*). For titanium additions of more than 1 wt % the tendency for precipitations becomes so pronounced that its formation cannot be suppressed by quenching, even if at 860° C a homogeneous β-phase has existed. This in turn leads to a higher sensibility to ageing effects in the high titanium alloys. Age-hardening becomes considerable even at temperatures not too high above ambient.

The major concern was the effect of titanium on the course of the martensitic transformation, especially on M_S (Figs. 4b, 5 and 6). Equations 1 and 2 can be used for an interpretation of these results. Any alloy addition, x, which causes solid solution hardening, $\Delta\sigma_y$, will lead to an increasing difference ΔT between M_S and T_0:

$$\frac{d\Delta\sigma_y}{dx_{Ti}} \sim \frac{d\Delta T}{dx_{Ti}} < 0 \qquad (3)$$

The same alloy addition may also affect the temperature T_0. Depending on whether it favours the thermodynamic stabilization of the β- or α-phase T_0 may be increased or decreased:

$$\frac{dT_0}{dx_{Ti}} \gtrless 0 \qquad (4)$$

It is not known which effect titanium additions have on T_0 of β-CuZn. Pure titanium is stable in a close packed phase α up to a rather high temperature (882° C). Therefore a favourization of the α-structure, i.e. an increase in T_0 could be possibly expected, but it cannot be measured directly.

The measurement of M_S contains terms from Equations 3 and 4:

$$\pm\frac{dM_S}{dx_{Ti}} = \pm\frac{dT_0}{dx_{Ti}} - \frac{d\Delta T}{dx_{Ti}} \qquad (5)$$

Consequently M_S will decrease unless the effect of solid solution hardening on ΔT is overcompensated by an increase in T_0.

$$\left|+\frac{dT_0}{dx_{Ti}}\right| > \left|-\frac{d\Delta T}{dx_{Ti}}\right| \qquad (6)$$

The experimental results have been interpreted along the lines shown in the schematic diagram of

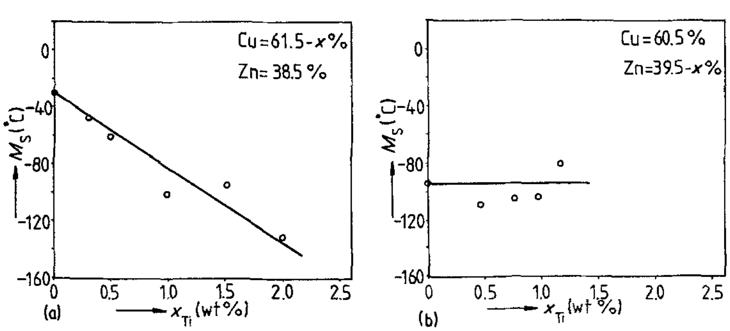

Figure 5 Effects of titanium-additions on M_S. (a) Replacement of copper by titanium, and (b) replacement of zinc by titanium.

*Formation of a ternary CuZnTi compound also cannot be excluded.

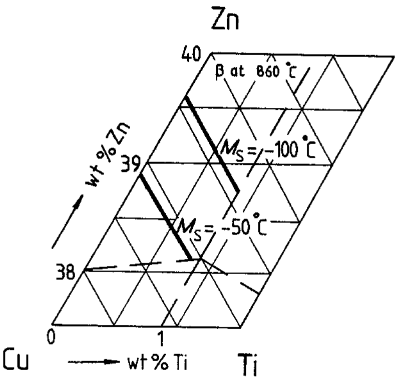

Figure 6 M_S temperatures of the β-phase in the Cu–Zn–Ti phase diagram.

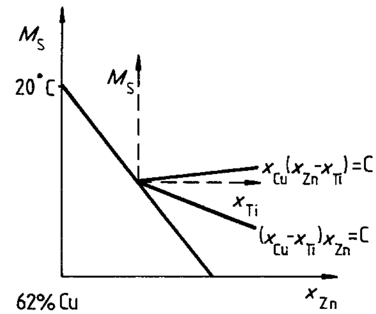

Figure 7 Effects of alloying elements on M_S, semi-schematic. M_S of binary β-Cu–Zn alloys, and of replacement of copper or zinc by titanium.

Fig. 7. Replacement of zinc by titanium in the original binary alloy should lead to an increase in T_0, which compensates or overcompensates the solid solution hardening effect (Fig. 5a). Lowering the copper content by titanium additions should decrease T_0, but to a lesser extent, as additions of zinc would do. Thus the sequence copper → titanium → zinc indicates an increasing tendency to stabilize the α-phase and therefore to increase T_0. The effects of ageing of the β-phase can be explained along the same lines. Corresponding phenomena are known from substitutional alloys of iron [12]. Precipitation hardening by coherent particles makes it necessary that these are sheared together with the matrix. An addition driving force and therefore undercooling ΔT is required for the transformation (Equation 3). Only if a non-coherent phase precipitates, which in turn causes an increase in T_0 in the transforming matrix, may M_S increase again. This has not been observed for the present ageing conditions (Fig. 8).

The compositional range which exists for conventionally solidified and quenched alloys does not permit production of β-Cu(ZnTi) alloys, which transform around ambient temperature. The experiments have indicated that they show good shape memory properties at lower temperatures. Attempts are underway to produce a homogeneous β-structure with an elevated copper content of about 62 wt %. This alloy should transform around ambient temperature (Fig. 7).

Acknowledgement

Our thanks are due to Dr Dürrschnabel, Wieland-Werke AG, Ulm, for provision of the CuZn alloy used for this investigation.

References

1. E. HORNBOGEN and G. WASSERMANN, *Z. f. Metallkde.* **47** (1956) 427.
2. J. PERKINS, "Shape Memory Effect in Alloys" (Plenum Press, New York, 1975).
3. L. DELEAY and H. WARLIMONT, *Prog. Mater. Sci.* **18** (1974).
4. L. DELEAY, E. AERNOUDT and J. ROOS, *Metall.* **31** (1977) 1325.
5. K. OISHI and L. C. BROWN, *Met. Trans.* **2** (1971) 1971.
6. K. OTSUKA and K. SHIMIZU, *Scripta Metall.* **4** (1970) 469.
7. M. COHEN, E. S. MACHLIN and V. G. PARANJPE, in "Thermodynamics in Physical Metallurg." (ASM, Metals Park, Ohio, 1950) s. 242.
8. E. HORNBOGEN, *Arch. Eisenhüttenw.* **43** (1972) 307.
9. K. MUKHERJEE, Thermodynamics and Kinetics of Martensitic Transformation, ICOMAT-82, Summer Course, Katholieke Universiteit Leuven, Belgium.
10. T. B. MASSALSKI, in "Phase Transformations"

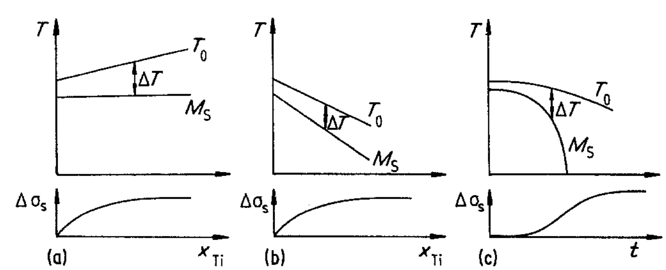

Figure 8 Components of the martensite temperature, schematic. (a) Alloy addition increases T_0 and hardens β. (b) Alloy addition lowers T_0 and hardens β. (c) Precipitation leads to lowering of T_0 and precipitation hardening.

(ASM, Metals Park, Ohio, 1970) pp. 433–95.
11. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill Book Company, New York, 1958).
12. E. HORNBOGEN and W. A. MEYER, *Arch. Eisenhüttenwes.* **39** (1968) 73.

Received 22 July and accepted 29 July 1983