

## The stabilization of martensite in Cu-Zn-Al-Ti-B shape memory alloys

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**Abstract.** Recent studies on aging effects in the martensite phase have shown that the addition of Ti-B to Cu-Zn-Al shape memory alloy has a notable influence on stabilization characteristics of this alloy. The overall process is delayed and the stabilization magnitude is significantly diminished. In an attempt to understand this effect the experimental results are analyzed within a cluster rearrangement model. The characteristic energy values are determined and compared with those obtained in single crystal experiments. The obtained results suggest the formation of vacancy-Ti complexes that increase the average vacancy migration energy for about 25%.

### 1. INTRODUCTION

It is well known that both the parent and the martensitic phase in Cu-based shape memory alloys are susceptible to low temperature aging. The martensite in Cu-Zn-Al alloys is particularly prone to aging effects even at room temperature. The transformation temperature of martensite to parent  $\beta$  phase rises after aging. This diffusional vacancy-aided behavior is known as stabilization of martensite and when the reverse transformation is induced recovery takes place quickly with kinetics controlled by the migration of vacancies in the  $\beta$  phase. Notwithstanding that in special cases stabilization can be used to raise temporally the critical temperature of the reverse transformation, this effect remains as an unwanted effect in shape memory applications, which require reliable and reproducible transformation temperatures without appreciable shift.

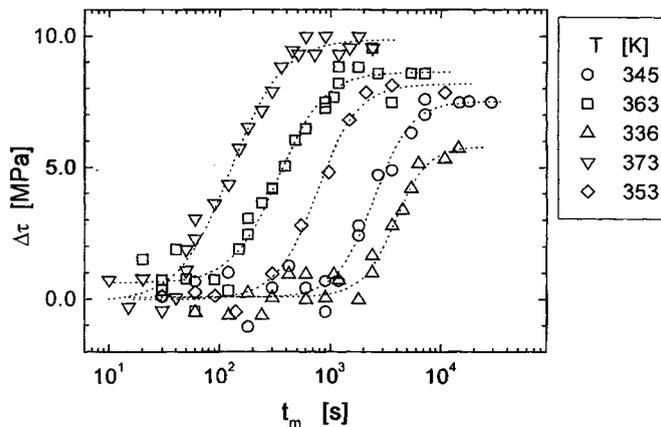
In previous papers [1, 2], the present authors have pointed out that the addition of Ti-B to the Cu-Zn-Al has a strong influence on the martensitic stabilization. The long time aging martensitic stress induced experiments show that the magnitude of stress shift due to stabilization in TiB added alloy is lower than the corresponding to the TiB free alloy. Besides, the overall stabilization process is delayed. In this work the above mentioned results are analyzed in the context of a martensitic stabilization model of rearrangement of atomic cluster configuration which takes into account a variable vacancy concentration. The associated energy changes are calculated. Furthermore, the role of the Ti atoms in solid solution on the observed effects is discussed.

### 2. Stabilization in Cu-Zn-Al-Ti-B

The results analyzed in this work are taken from reference [1], consequently experimental details are given there. Only a brief description and additional information are included here. From ingots, whose nominal composition was Cu- 13.65%Zn-16.99%Al-0.35%Ti-0.40B, slices were cut and hot rolled at 1123 K to 60% thickness reduction. After rolling, the slices remained at 1073 K for about 10000 s, under this thermomechanical treatment recrystallization takes place almost completely and during subsequent thermal treatment the grain size remains nearly constant (0.8mm). Ti and B are mainly found in the form

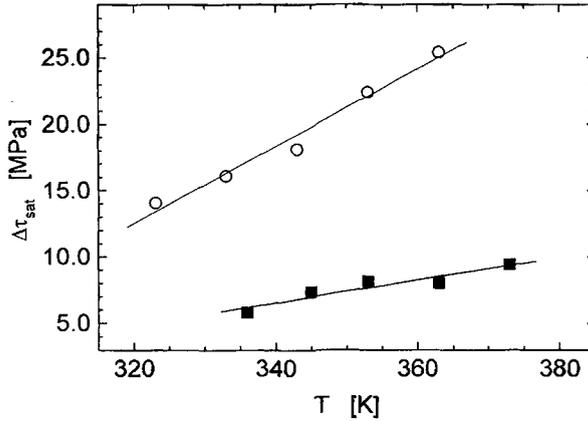
of particles of  $\text{TiB}_2$  primary precipitation. The volume fraction in the as cast samples was  $(2.3 \pm 0.3) \%$  while in the thermomechanical treated samples decreased to  $(1.5 \pm 0.3) \%$ . Square section compression samples with a dimension of  $4.0 \text{ mm} \times 4.0 \text{ mm} \times 11.5 \text{ mm}$  were used. The average transformation temperature  $M_s$  was  $313\text{K}$ . The samples were homogenized for  $900 \text{ s}$  at  $1073 \text{ K}$ , and then quenched at  $373 \text{ K}$ , remaining at  $373 \text{ K}$  for  $900 \text{ s}$ . This time is sufficiently large to anneal out the quenched in  $\beta$ -phase disorder, but short enough to retain an appreciable vacancy concentration. Subsequently, the martensite was induced by applying compressive stress in a Shimadzu DSS-10T-S deformation universal machine at a strain rate of  $4 \cdot 10^{-4} \text{ s}^{-1}$ . Between the quench and the deformation a time of  $900 \text{ s}$  had elapsed. The transformation and stabilization tests were performed in a temperature range between  $323\text{K}$  and  $373\text{K}$ , and the stabilization time was  $0 \leq t_s \leq 30000\text{s}$ .

In stress induced martensite test the stabilization information is obtained from the pseudoelastic cycles. When stabilization takes place a hysteresis increase effect is observed. From the applied stress drop the change in resolved shear stress was determined by means  $\Delta\tau(T, t_m) = \Delta\tau_m(T, t_m) - \Delta\tau_0$ , where  $\Delta\tau_m(T, t_m)$  is the measured resolved shear stress after stabilization time  $t_m$ , at temperature  $T$  and  $\Delta\tau_0$  is the initial stress hysteresis width. The  $\Delta\tau$  behavior is shown in Figure 1, as can be seen for all temperatures, after some time where no changes are detected, an increase in  $\Delta\tau$  is observed. For sufficiently long stabilization time a saturation value  $\Delta\tau_{\text{sat}}$  is reached. This saturation value is reached faster as the temperature increases.



**Figure 1:** Stress drop ( $\Delta\tau$ ) behavior as a function of stabilization time  $t_m$  for the studied samples, for different temperatures  $T$  indicated in the figure. Dot line is only for eye – guiding.

In figure 2 the stress saturation values  $\Delta\tau_{\text{sat}}$  as a function of the aging temperature are presented, for comparison single crystals data under similar thermal treatment are included [3]. For all the studied temperatures the stabilization effect is higher in Cu-Zn-Al single crystals than in Cu-Zn-Al-Ti-B polycrystalline samples. Furthermore, the magnitude of the  $\Delta\tau_{\text{sat}}$  increase with stabilization temperature is higher in Cu-Zn-Al than in Ti-B doped samples.



**Figure 2:** The stress drop for saturation  $\Delta\tau_{\text{sat}}$  as a function of stabilization temperature for Cu-Zn-Al-Ti-B (■) and Cu-Zn-Al single crystal (○).

### 3. Discussion

The experimental results shown in Figure 1 are analyzed within a modified Abu Arab - Ahlers model [4] in which a variable vacancy concentration is considered [2]. The stabilization is described as a vacancy-aided process of rearrangement of atom clusters, each cluster containing a few atoms. The cluster concentration  $\varphi_0$  can be written as  $\varphi_0 = \varphi_1(t_m) + \varphi_2(t_m)$ , where  $\varphi_2(t_m)$  is the cluster fraction which changes its configuration with the stabilization time  $t_m$ , ( $\varphi_2(0)=0$ ). The time evolution is written as:

$$d\varphi_2(t_m)/dt_m = \nu C_v(T_Q, t_m) \cdot \left[ \varphi_1 \exp\left(-\frac{\Delta U + \Delta\varepsilon_m/2}{kT}\right) - \varphi_2 \exp\left(-\frac{\Delta U - \Delta\varepsilon_m/2}{kT}\right) \right] \quad (1)$$

with the aging time and quenching temperature,  $T_Q$ , dependent vacancy concentration given by:

$$C_v(T_Q, t_m) = C_i(T_Q) \exp\left[-\rho_m \nu \exp\left(-\frac{E_{Mm}}{KT}\right) t_m\right] \quad (2)$$

here  $\nu$  is a frequency of the order of Debye frequency  $\nu_D \approx 10^{13} \text{ s}^{-1}$ ,  $\Delta\varepsilon_m$  is the change in martensite phase energy due to stabilization,  $\Delta U$  is the activation energy term independent of configuration,  $C_i(T_Q)$  is the initial vacancy concentration which depends on the thermal treatment previous martensitic transformation,  $\rho_m$  is the martensite vacancy sink density and  $E_{Mm}$  is the martensite vacancy migration energy. In order to relate  $\varphi_2$  to the measured changes in transformation stress the following relationship is used [4]:

$$\Delta\tau = (\Delta\varepsilon_\beta - \Delta\varepsilon_m)\varphi_2/V\gamma \quad (3)$$

where  $\Delta\varepsilon_\beta$  is the change in  $\beta$  phase energy produced by the cluster rearrangement in martensite,  $V$  is the molar volume, and  $\gamma$  is the transformation strain. Assuming that  $\Delta U = E_{Mm}$ , the integration of equation 1 leads to:

$$\Delta\tau(t_m) = \left(\frac{\varphi_0}{V\gamma}\right) \left(\frac{\Delta\varepsilon_\beta - \Delta\varepsilon_m}{1 + \exp\left(\frac{\Delta\varepsilon_m}{kT}\right)}\right) \cdot \left\{1 - \exp\left(\frac{2C_i}{\rho_m} \cdot \cosh\left(\frac{\Delta\varepsilon_m}{2kT}\right) \cdot \left\{\exp\left[-\rho_m v t_m \exp\left(-\frac{E_{Mm}}{kT}\right)\right] - 1\right\}\right)\right\} \quad (4)$$

On the other hand, using Equation 3 and for short aging time Equation 1 can be rewritten as:

$$\Delta\tau(t_m) = \nu C_v \exp\left(-\frac{\Delta U}{kT}\right) \cdot \left[(\Delta\varepsilon_\beta - \Delta\varepsilon_m) \left(\frac{\varphi_0}{V\gamma}\right) \exp\left(-\frac{\Delta\varepsilon_m}{2kT}\right) - \Delta\tau(t_m) 2 \cosh\left(\frac{\Delta\varepsilon_m}{2kT}\right)\right] \quad (5)$$

Calling:

$$A = \nu C_v \exp\left(-\frac{\Delta U}{kT}\right) \cdot (\Delta\varepsilon_\beta - \Delta\varepsilon_m) \left(\frac{\varphi_0}{V\gamma}\right) \exp\left(-\frac{\Delta\varepsilon_m}{2kT}\right) \text{ and } B = \nu C_v \exp\left(-\frac{\Delta U}{kT}\right) \cdot 2 \cosh\left(\frac{\Delta\varepsilon_m}{2kT}\right) \text{ equation}$$

(4) results:  $\Delta\dot{\tau}(t) = A - B\Delta\tau(t_m)$ . In Figure 3 a plot of  $\Delta\dot{\tau}(t_m)$  vs.  $\Delta\tau(t_m)$  for  $T = 373\text{K}$  is presented.

From  $\ln A$  against  $T^{-1}$  and  $\ln(B/A)$  against  $T^{-1}$  plots the  $\Delta U$  and  $\Delta\varepsilon_m$  values can be estimated, see Figures 4 a, b. The best least square linear fit produces  $\Delta U = (1.1 \pm 0.1) \text{ eV}$  and  $\Delta\varepsilon_m = (0.17 \pm 0.03) \text{ eV}$ . While the corresponding values for Cu-Zn-Al single crystal are [3]  $\Delta U = (0.88 \pm 0.03) \text{ eV}$  and  $\Delta\varepsilon_m = (0.15 \pm 0.03) \text{ eV}$ . It must be emphasized that, within the experimental scatter,  $\Delta\varepsilon_m$  remains approximately constant while  $\Delta U$  for Ti-B doped alloy increases for about 25%. It is worth mentioning that the vacancy migration energy in the martensitic phase measured by mean a positron annihilation technique is  $E_{Mm} = (0.80 \pm 0.03) \text{ eV}$  [5], which is close to the  $\Delta U$  obtained for single crystals. These results justify the earlier assumption.

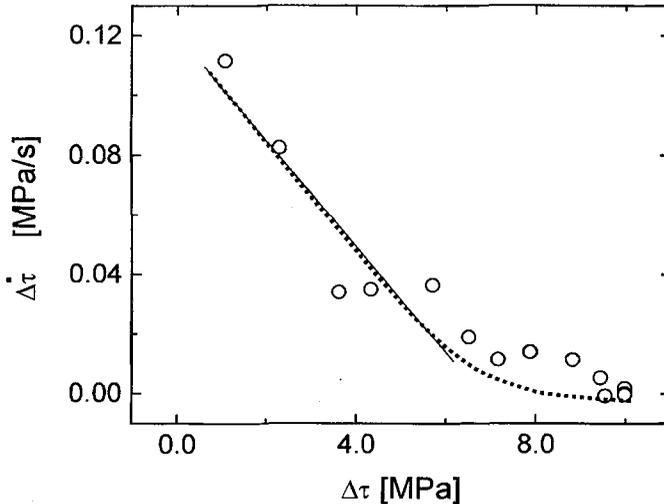


Figure 3:  $\Delta\dot{\tau}$  vs  $\Delta\tau$  behavior for Cu-Zn-Al-Ti-B at  $T = 373 \text{ K}$ . Dot line is only for eye – guiding. The linear fit for short aging time  $t_m$  is shown (full line).

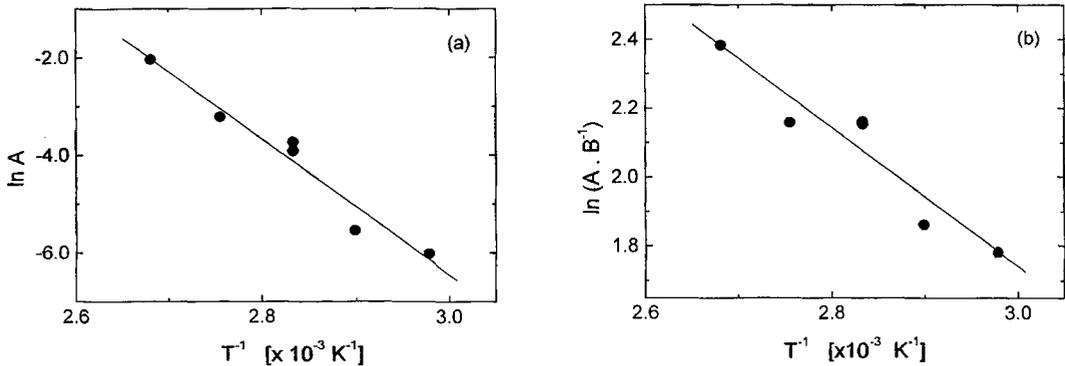


Figure 4: a)  $\ln(A)$  as a function of  $T^{-1}$ . b)  $\ln(A/B)$  as a function of  $T^{-1}$ . For explanation see the text.

### 3.1 The role of Ti atoms

The presented results show that the addition of Ti-B has a considerable influence on the martensitic stabilization in the Cu-Zn-Al alloy. The effects of Ti addition to binary Cu-Zn system have been studied by Eucken and Hornbogen [6]. Ti strengthens the binary phase, this effect is attributed to the difference in atom radii. The addition of Ti decreases the transformation temperatures for about 45K each atomic % [6]. Moreover, the tendency to form and precipitate titanium-rich phases limits the solid solution range to 1 wt % [6]. In  $\beta$ Cu-Zn-Al the solubility of Ti at 1123K is about 0.45 at.% [7]. Then, it is possible that, in the present case, after thermomechanical treatment small quantities of Ti remain in solution without an appreciable change of the critical transformation temperatures. On the other hand, in Cu-based alloys boron tends to form metallic borides or boron precipitates, as has been observed in Cu-Al-Ni alloys [8], not remaining consequently in solid solution.

Recently it has been found that the addition of Ti reduces the vacancy mobility and consequently retards the martensitic stabilization in Cu-Zn-Al alloys [9, 10]. Moreover, the effect of Ti addition on lattice parameter of  $\alpha$ -Cu has been recently determined, it was found that the increase in lattice parameter for Ti is significantly higher than for the solutes such as Zn, Ni, Al, etc. in solid solution with copper [11]. Therefore it is possible that in Cu-Zn-Al martensite the vacancies tend to remain near Ti atoms forming vacancy-Ti atoms pairs or complexes contributing thus to the lattice relaxation. This vacancy-Ti agglomerates should be more stable than free vacancies. The  $\Delta U$  and  $\Delta \epsilon_m$  values obtained in this work are in agreement with the above argument since  $\Delta U$  is linked to the average vacancy migration energy in martensite, while  $\Delta \epsilon_m$  is associated with the energy change in the martensitic phase due to the stabilization process and consequently is not affected by vacancy mobility.

Finally, as has been mentioned above, under the same thermal treatment, in Ti-B doped samples the stabilization magnitude is smaller than the Cu-Zn-Al single crystals (see Figure 4). According to equation 4, for sufficiently long aging time, and provided that the  $\Delta \epsilon_m$  is the same, the magnitude of stabilization depends only on the  $C_i/\rho_m$  value. Therefore, it is possible that Ti atoms also contribute to modify the vacancy sink density.

### Acknowledgments

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