

THE STABILIZATION OF 18R AND 2H MARTENSITES IN Cu-Zn-Al ALLOYS WITH AN ELECTRON CONCENTRATION $e/a = 1.534$

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Abstract

Stabilization has been studied in Cu-Zn-Al alloys with an electron concentration $e/a = 1.534$. In addition to the usual 18R and 6R martensites in which stabilization has been already investigated quite extensively, these alloys exhibit at low temperature a transformation to a 2H structure. Our results show that aging of the 18R phase leads to a stabilization of the 18R phase with respect to the parent $L2_1$ phase which is very reduced compared to the one observed in alloys with $e/a = 1.48$. In addition, stabilization of the 18R phase with respect to the 2H phase results in the suppression of the 18R \rightarrow 2H transformation which occurs normally upon unloading at low temperature. In contrast, no change is observed for the 18R \rightarrow 6R transformation. First results of the stabilization of the 2H phase with respect to the parent $L2_1$ phase are presented.

Introduction

When martensite is induced by cooling from the $L2_1$ phase in Cu-Zn-Al alloys and subsequently is aged for a sufficiently long time near room temperature to permit diffusion mechanisms to occur, an increase in the A_s temperature (or equivalently a decrease in the unloading stress) for retransformation to the $L2_1$ phase is observed. This effect is called stabilization /1/. Almost all previous studies of stabilization have been performed on alloys with an electron concentration near $e/a \cong 1.48$ and concern the 18R phase /2,3,4,5/. Only one recent study applies to the 6R phase /6/. However, at higher electron concentration, the hexagonal 2H phase, the face centered tetragonal 6R together with the 18R phase can be obtained and advantageously studied in the same specimen /7/.

In this paper, results of a study of the stabilization in Cu-Zn-Al alloys with an electron concentration of $e/a = 1.534$ are reported. In a first part, we focus our attention on the *aging of the 18R phase* and show how it influences the retransformation stress to the $L2_1$ phase (stabilization of the 18R with respect to the $L2_1$ phase) and the subsequent transformations to the 2H and 6R phases (stabilization of the 18R phase with respect to the 2H and 6R phase). This is reported in more details in ref /8/. In a second part, the effect of *aging of the 2H phase* on the retransformation temperature to the $L2_1$ phase (stabilization of the 2H phase with respect to the $L2_1$ phase) is analyzed (Fig 1).

Experimental

Cu-Zn-Al single crystals (see Table 1) were grown in sealed quartz tubes by the Bridgman method. Cylindrical samples of 3 mm diameter and 10 mm length with thicker shoulders to fit into the grips of the deformation machine were spark machined. Prior to each stabilization experiment the sample was

homogenized at 850 °C for 10 min, then slowly cooled to a temperature T_Q and quenched into a mixture of ice and water. The quenching temperature T_Q was chosen sufficiently high ($T_Q > 700$ °C) to avoid γ precipitation which is very rapid at such a high e/a /9/. The experiments were performed immediately after the quench with a minimum time delay for mounting the sample in the deformation machine (less than 180 s). The temperature of the sample was continuously monitored using a spot welded thermocouple.

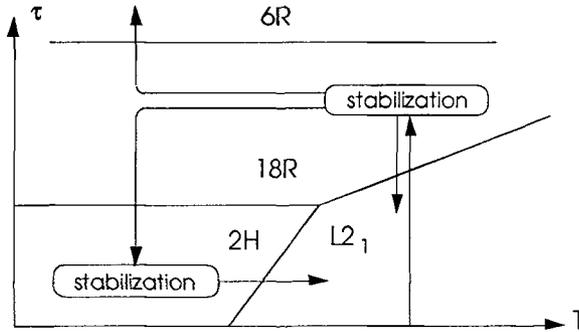


FIG. 1. Schematic drawing showing the way the different martensitic phases have been induced and stabilized in the present work (τ : resolved transformation stress, T : temperature). The 18R phase is first induced from the $L2_1$ phase. Then the influence of the stabilization of the 18R phase on the retransformation stress to the $L2_1$ phase or on the transformation to 6R and 2H phases is investigated. Finally, the 2H phase is induced from the 18R phase and the stabilization of this 2H phase with respect to the $L2_1$ phase is studied (diagram from ref./7/)

TABLE 1: Data of the alloys used in this study

Sample	Composition (at%)	Measured M_s [°C] ($L2_1$ -2H)
A ₁	Cu-7.18Zn-23.12Al	-10
A ₂	"	-23
B	"	-23
C	"	-15
D	Cu-18.52Zn-14.74Al	-90 ($L2_1$ -18R)
E	Cu- 7.18Zn-23.12Al	-22
F	"	-23
G	Cu-6.10Zn-23.65Al	+8

Sample A₁ and A₂ have been cut from the same crystal A

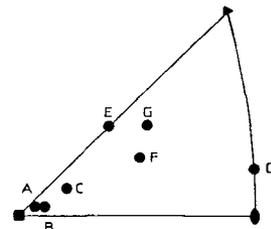


FIG 2: Single crystal orientations of the samples in Table 1 plotted in the unit stereographic triangle

Results

Stabilization of the 18R phase with respect to the $L2_1$ phase

The difference in resolved transformation stress $\Delta\tau$ between loading and unloading after stabilization in the 18R phase is shown in Fig. 3a as a function of stabilization time. It is worth noting that the normal hysteresis (~10 MPa) has already been subtracted. The curves have an S-shape. After a certain time, the stabilization reaches a saturation value which is observed (Fig. 3b) to increase with temperature. The delay to reach saturation (Fig. 3a) is temperature dependent and indicates a thermally activated process. Following the same procedure as in ref. /5/, we have extrapolated the linear part of the curves to zero stabilization to deduce a characteristic time t_0 for each temperature. The slightly different slope associated with each curve most likely originates from the temperature dependence of the saturation stabilization. The characteristic times t_0 given by the intercepts are presented in the Arrhenius plot of Fig. 4. From its slope an activation energy of 0.83 eV/at is deduced which is in reasonable agreement with the values of Scarsbrook et al: .90 eV/at /3/, Mantel: .88 eV/at /4/, Abu Arab: 1 eV /5/, and is consistent with a stabilization kinetics controlled by the migration energy of vacancies in CuZnAl martensite (~0.8 eV/at /10/).

In contrast, the stabilization amplitude shows a big difference with respect to the published results for alloys of lower e/a . Whereas in ref. /5/ the stabilization amounts to more than 100 MPa at saturation at the

temperature of 42 °C, we hardly find more than 55 MPa at the same temperature (see Fig. 3b). In order to see whether this discrepancy would be due simply to the different quenching temperatures used, 200 °C - 500 °C in ref. /5/ and 750 °C in the present experiments, we have applied the same quenching treatment to a sample with $e/a = 1.534$ and another with $e/a = 1.48$ but similar M_S . The result is shown in Table 2.

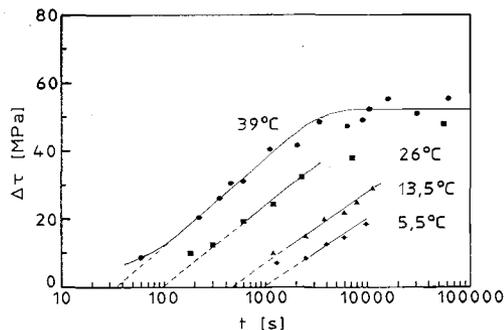


FIG. 3a. Difference $\Delta\tau$ between the resolved transformation stress on loading ($L2_1 \rightarrow 18R$) and unloading ($18R \rightarrow L2_1$) as a function of stabilization time in the 18R phase for various stabilization temperatures. Normal transformation hysteresis has previously been subtracted. $T_Q = 750^\circ\text{C}$

We observe that for the same quenching temperature $T_Q = 750^\circ\text{C}$, the stabilization is almost the double for the sample with $e/a = 1.48$ compared to the sample with $e/a = 1.534$ whereas it does not vary significantly when changing the quenching temperature. Actually, it does not mean that the change in the electron concentration is the reason for the observed difference because the composition also varies at the same time. In particular the samples with $e/a = 1.534$ have a much higher Al content. This can be put in relation with the CuAlNi alloys which also exhibit little stabilization /11/. However, the origin of this effect is still not known.

TABLE 2 Comparison of the saturation stabilization $\Delta\tau$ for different electron concentrations e/a and quenching temperature T_Q .

Sample	e/a	T_S [°C]	t_S [s]	T_Q [°C]	$\Delta\tau$ [MPa]
A	1.534	39	8×10^4	750	52
D	1.48	39	7×10^4	750	100
D	1.48	39	8×10^4	500	110

T_S : stabilization temperature, t_S : stabilization time

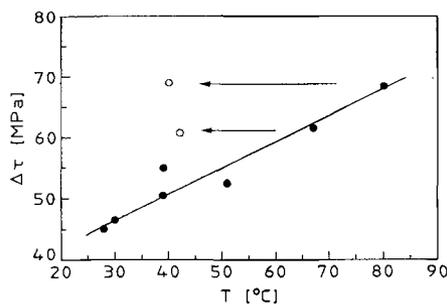


FIG. 3b. $\Delta\tau$ for saturation as a function of the stabilization temperature (full circles). Arrows indicate that if the sample is stabilized to saturation at a given temperature and is stabilized again to saturation at a lower temperature (stabilization time $> 6 \times 10^4$ s) the stabilization $\Delta\tau$ is not modified (open circles)

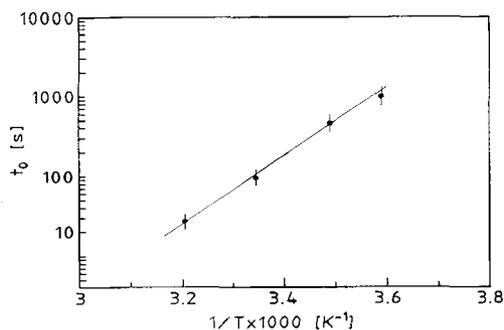


FIG. 4. Time t_0 for linear extrapolation of the curves of Fig. 3a to $\Delta\tau = 0$ as a function of $1/T$ where T is the stabilization temperature.

In Fig. 3b it is shown that the saturation stabilization increases with the stabilization temperature (full circles Fig. 3b). However, if a sample is first stabilized to saturation at a high temperature, then the temperature is lowered and the sample is again stabilized to saturation at this lower temperature, the corresponding

lowering of stabilization is not observed. The stabilization remains the same (open circles Fig. 3b). This fact, already observed by Abu Arab, suggests that caution has to be taken before considering the temperature dependence of stabilization as related to a true equilibrium state.

Experiments have been carried out to know to what extent the sample was ordered immediately after the quench. It turned out that L2₁ ordering was actually not perfect and that further ordering during aging in martensite was probably responsible for an unwanted contribution to the stabilization of the order of 10 - 20 MPa. More details on this subject as well as on the influence of previous aging in L2₁ phase can be found elsewhere (see ref /8/).

Stabilization of the 18R phase with respect to 2H and 6R phases

The effect of stabilization in the 18R phase on the subsequent transformations to other compact phases has also been investigated. In this case the specimen is first stabilized (or not) to saturation in the 18R phase at 39° C, then cooled at constant stress to a test temperature which is lower than the M_s temperature for spontaneous transformation to 2H and finally loaded again to induce the 6R phase or unloaded if the transformation to 2H is desired (see Fig. 1). The tensile stresses for these transformations are given in Table 3. Data of Pelegrina /7/ is also presented for comparison.

TABLE 3 Influence of previous stabilization of 18R phase (time t_{18R}) on the resolved transformation stresses τ for subsequent transformations to 6R and 2H phases.

Sample	t _{18R} [s] (T = 39 °C)	$\tau_{18R - 6R}$ [MPa] (T = 28 °C)	$\tau_{18R - 2H}$ [MPa] (T = 28 °C)	$\tau_{2H - 18R}$ [MPa] (T = 28 °C)
A	0	223 ± 5	46 ± 10	140 ± 10
A	7.5 x 10 ⁴ s	213 ± 5	no transformation	-
E	0	188	47 ± 10	146 ± 10

Data of sample E is taken from ref. /7/. In calculating the Schmid factor for the transf. 18R - 2H it has been taken into account that the so called variant 2 is induced /12,13/.

Previous stabilization of 18R phase does not produce significant variation in the tensile stress for transformation to 6R. This is in agreement with the results of Saule for samples with a lower electron concentration /6/. It suggests that aging of the 18R phase stabilizes the 6R phase with respect to the L2₁ phase by the same way and by the same quantity as it stabilizes the 18R phase regardless of the change of electron concentration or composition. In the case of the transformation to 2H and in the absence of any stabilization in 18R, transformation stresses have been obtained upon unloading which are in reasonable agreement with the data of ref. /7/. In contrast, if stabilization is allowed to proceed in the 18R phase, further transformation to 2H is suppressed (Table 3). In fact, the transformation to 2H is probably possible but only in compression. Of course, it does not imply that the stabilized 18R phase is the most stable phase at zero stress. More likely, the 18R phase is stabilized by the large transformation hysteresis of the 2H phase. Anyway, the drop in transformation stress indicates that a modification of the atomic configuration occurs during stabilization in 18R phase which is not energetically favorable for the 2H phase. This cannot be explained if only first and second neighbors pair interactions are considered. These pairs are not modified by only changing the stacking of the close-packed planes. This suggests that either these effects are due to higher order pair interactions or as pointed out by Saule et al /6/ are related to atomic distance relaxation.

Stabilization of the 2H phase with respect to the L2₁ phase

Attempts have been made to stabilize the 2H phase produced by unloading the 18R phase at temperatures below M_s (see Fig 1). This has been made first in samples with a low M_s (\cong -23°C). In these samples, because of the low temperature, it was not possible to obtain any stabilization even for long aging times. However, according to Fig. 5, under suitable applied stress ($\tau \cong$ 250MPa) the stability range of the 2H

phase can be extended up to room temperature. For this reason the stabilization of the 2H phase was carried out in applied stress. Some stabilization experiments were done at 20°C for long aging times, others for 1 hour at 20°C and then for longer times at 39°C or more in order to compare with the stabilization in the 18R in the same conditions. After stabilization, the stress was removed and the stabilization was measured by recording the modified 2H-L2₁ retransformation temperature A'_s. The degree of stabilization is given by $\Delta A_s = A'_s - A_s$ where A_s is the normal retransformation temperature. As shown in Table 4, samples A₁ and A₂, which have their tensile axis near (001)_{L2₁}, show a stabilization of roughly 60°C. Apparently, the degree of stabilization increases with temperature (if we consider the aging times sufficient to reach the saturation). The stabilization at 39°C is comparable to what was observed for the 18R phase at the same temperature ($\Delta\tau = 52\text{MPa}$ (Table 2) + $\Delta A_s \cong 50^\circ\text{C}$).

Experiments were performed in samples with other tensile axis. Surprisingly, for samples F and G no retransformation to the L2₁ phase was observed unless they were heated up to above 380°C. Near this temperature, the samples were observed to recover their original shape suggesting a change of phase. But, it is not sure that the new phase is really the L2₁ phase because at this temperature precipitation is expected to occur.

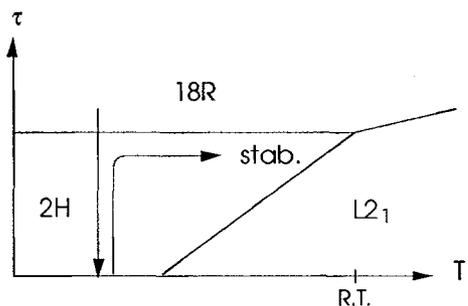


FIG 5. In applied stress the stability range of the 2H phase is extended up to near room temperature (R.T.)

TABLE 4: Stabilization of 2H martensite with respect to the L2₁ phase.

Sample	A _s [°C]	τ[MPa]	T _s [°C]	t _s [S]	A' _s [°C]	ΔA _s [°C]
A ₁	7	-	-	≅ 0	≅ 7	≅ 0
"	"	170	20	70 × 10 ⁴	57	50
"	"	170	55	40 × 10 ⁴	78	71
"	"	170	55	40 × 10 ⁴	78	71
A ₂	-10	170	39	7 × 10 ⁴	53	63
"	"	170	39	7 × 10 ⁴	52	62
F	-12	170	39	6 × 10 ⁴	>380	>392
"	"	170	39	7 × 10 ⁴	>380	>392
G	20	170	39	6 × 10 ⁴	>380	>360
"	"	0	39	6 × 10 ⁴	95	75

τ: applied stress, T_s: stabilization temperature, t_s: stabilization time, A_s: normal retransformation temperature, A'_s: retransformation temperature after stabilization in 2H phase.

In order to check whether the stress has an influence on the stabilization, a sample with A_s=20°C was used (sample G). With such a high A_s, it was possible to compare the stabilization with or without applied stress. We observed that, if stress was applied during stabilization, the sample did not retransform below 380°C. In contrast, when the stabilization was performed at zero stress, a normal stabilization (ΔA_s=75°C) resulted. This suggests that stress and crystallographic orientation have an influence on the stabilization of the 2H phase.

In order to see whether this difference in retransformation temperature would be due to an important modification at the microscopic level as for instance disordering, lattice parameter change or precipitation, transmission electron microscopy observations were done. From a sample which had not retransformed at normal temperatures, a small disc was cut and observed in the microscope. No obvious difference was detected with respect to the normal 2H phase observed by Pelegrina /9/ and Tolley et al /12/. The sample had a 2H structure and L2₁ type ordering. No precipitates were observed. In addition, the disc was

apparently a single variant crystal. This is in agreement with previous observations /13/ which have shown that applied stress produces a detwinning of an originally twinned 2H crystal. In addition, the applied stress favors the variant which has a common basal plane with the original 18R crystal (the so-called variant 1). This variant is stabilized at zero stress by further aging in applied stress.

We have to mention that according to Fig. 5 there is another way of inducing the 2H phase: directly from the L2₁ phase. Some experiences have been done in this sense. A sample stabilized in the 2H phase was observed to retransform near 70°C but some others did not retransform below 380°C. However, it was difficult to find any systematic in these results. It is worth to mention that, according to Pelegrina /9/, this mode of transformation induces much more lattice defects than the indirect one. Therefore, it is in principle better to study the stabilization in a 2H phase produced from the 18R phase.

Hence, the aging behavior of the 2H phase seems more complicated than the one of the 18R phase. Although it appears clearly that the 2H phase can be stabilized with respect to the L2₁ phase, more experiments are needed in order to understand why some of the samples stabilize so differently than others. It is not yet clear whether the stabilization is due to a change of thermodynamic equilibrium, as is clearly the case in the 18R phase near room temperature /5/, or if nucleation problems also play a role.

Summary

The stabilization of the 18R phase has been studied in Cu-Zn-Al alloys with an electron concentration of $e/a = 1.534$. The main results are the followings:

- 1) The general features and kinetics of the stabilization of the 18R phase with respect to the L2₁ phase are the same as those found in alloys with e/a near 1.48. However, the saturation stabilization is only about one half of that observed for these alloys.
- 2) The stabilization of the 18R phase has no influence on the tensile stress for subsequent transformation to the 6R phase but leads to the suppression of the 18R - 2H transformation.
- 3) A stabilization of the 2H structure with respect to the L2₁ phase is observed. However this stabilization seems to depend on stress and crystallographic orientation.

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