KINETICS OF ORDERING IN Ni₃Mn ALLOY WITH ADDITIONS OF COPPER

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Neutron-diffraction analysis and measurements of electrical resistance were used to investigate the kinetics of ordering in Ni₃(Mn, Cu) alloys preliminarily tempered at 900°C, containing 0.45–9.29 at.% copper. It was established that introducing copper atoms in place of manganese atoms in the alloy Ni₃Mn leads to slowing of the ordering process. The degree of long-range order inside antiphase domains in Ni₃(Mn, Cu) alloys is less than in the binary alloy.

1. It is known [1-4] that when a third component is added to a binary alloy the ordering processes are significantly changed; in some cases, ordering is more rapid, in others less rapid. In [3, 4] it was established that for alloys Ni₃(Mn, Me), where Me = Co, Fe, Cr, Al, the effect of the third element on the rate of ordering depends on which element is added and in what concentration. With the exception of cobalt, all of the third elements listed above in Ni₃Mn take the place of Mn atoms, increase (or leave unchanged) the critical temperature of the order–disorder transformation (Tc), and in amounts of ~4 at.% increase the rate of ordering, at least in the early stages [3-5].

In this paper, the effect of copper on the kinetics of ordering in the alloy Ni₃Mn is investigated by neutron-diffraction analysis and electrical-resistance measurements. The reasons for choosing copper were as follows. Although Cu atoms, as well as the other atoms mentioned above, are introduced in the Ni₃Mn alloy in the place of Mn atoms, they take up positions usually occupied by Ni atoms in the ternary alloy [5]. This distribution of Cu atoms in Ni₃(Mn, Cu) alloys leads to disruption of the Ni₃Mn superstructure and decrease in Tc. Therefore, it may be expected that adding copper to Ni₃Mn should significantly alter the kinetics of ordering in the alloy.

2. The compositions of the alloys investigated are shown in Table 1. The structural state in the alloys was measured using neutron-diffraction analysis and electrical-resistance measurements. For the neutron-diffraction studies, cylindrical samples of length 55 mm and diameter 7.5 mm were used. The neutron patterns were recorded at room temperature on a TKSN-400 diffractometer (λ = 1.19 Å). The λ/2 contribution to the (100) reflection was ± 0.5%. The initial state of the samples was produced by annealing at 900°C for 2 h and then quenching in water. The kinetics of the ordering process was investigated at two tempering temperatures: at T = 400°C (by neutron-diffraction and electrical-resistance measurements) and at T = 450°C (by electrical-resistance measurements). The degree of long-range order S was calculated from the (100) superstructural reflection and the (200) main reflection. The value of S and the size of the antiphase ordering domains (APD) were determined by the methods of [3, 5]. The electrical resistance R was measured at room temperature using a double Thomson bridge with accuracy ±10⁻⁵ Ω on wire samples of diameter 1 mm and length 80 mm.

<table>
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<th>TABLE 1. Composition of Alloys Investigated, at.%</th>
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Fig. 1. Change in size of antiphase domains $\xi$, Å, in alloys 1-4 as a function of time of isothermal tempering at 400°C.

Fig. 2. Change in long-range-order parameter $S$ in alloys 1-4 as a function of time of isothermal tempering at 400°C.

3. The main results of the investigation are shown in Figs. 1-3.

The changes in the neutron-diffraction patterns of the alloys with the time of isothermal tempering resemble those given in [6] for Ni$_3$(Mn, Al) alloys, and hence are not given here. Note only in Ni$_3$(Mn, Cu) alloys after quenching from 900°C in water the resulting state is more disordered than in Ni$_3$(Mn, Al) alloys. On the neutron-diffraction diagrams of the quenched Ni$_3$(Mn, Cu) alloys, unlike those for Ni$_3$(Mn, Al) alloys, only diffusional increase in the background is observed at points of superstructural reflection.

Samples for measurement of $R$ were tempered for a minimum of 30 sec; samples for neutron-diffraction study, for a minimum of 30 min.

After tempering for 30 min at $T_{tem}$ = 400°C, the superstructural reflection was very weakly resolved only in alloy 3. On the neutron-diffraction diagrams of alloys 2 and 4 at points of superstructural reflection, no significant variation was observed. Additional tempering of alloys 2 and 4 at 400°C for 16 h led to the appearance of broad, poorly resolved superstructural reflections. These data indicate that on replacing atoms of manganese by copper atoms, the kinetics of ordering in Ni$_3$Mn becomes slower.

In Figs. 1 and 2 the changes with increase in the tempering time in $S$ and the size of the APD are shown for alloys 1-4. (The alloy numbers are shown on the curves.) It is evident that adding Cu to Ni$_3$Mn slows the development of APD and $S$. It is interesting that the size of the APD in alloy 3 is close to that in the binary alloy, and practically identical to it after 187 h of tempering (Fig. 1), whereas the value of $S$ in alloy 3 is considerably less than in the binary alloy (Fig. 2). These results indicate that long-range order inside the domains in alloy 3 is considerably less than in the binary alloy and, evidently, this is entirely true also of alloys 2 and 4.

It appears from Fig. 1 that adding 0.45 at. % Cu to Ni$_3$Mn sharply reduces the rate of development of APD. In the alloys with 0.98 at. % Cu the APD are comparable in size with those found in the binary alloy, and in the alloys with 1.7 at. % Cu the domains are smaller than those in the binary alloy and in alloy 3.

In accordance with the nonmonotonic changes in the development of domain structure in Ni$_3$Mn with addition of Cu atoms, the electrical resistance also changes with tempering time. In Fig. 3, the value of $\eta = (R - R_q)(R_q - R_{ord})$, %, in alloys 1-6 is shown as a function of tempering time at 400°C. It is evident that in alloy 2, $\eta$ remains higher than zero for 64 h; in the Ni$_3$Mn alloy at this point the change in $\eta$ is 66%. In alloy 3 the change in $\eta$ is qualitatively the same as in the binary alloy, but the rate and general effect of the change in $\eta$ is smaller. In alloy 4, as in alloy 2, there is a comparatively long stage when $\eta > 0$, and then after 5 h of tempering $\eta$ decreases, but the general effect of the change is less than in alloy 3. When Cu is added to Ni$_3$Mn in larger amounts, $\eta$ rises throughout tempering periods of up to 136 h at 400°C; $\eta$ increases more sharply as the Cu concentration is increased.

These data, together with the neutron-diffraction results, indicate that addition of Cu to the alloy Ni$_3$Mn reduces the rate of ordering.

In [5] it was shown that adding Cu to Ni$_3$Mn leads to a reduction in the critical ordering temperature $T_c$. In alloy 5, $T_c$ was not determined. On the other hand, adding 5 at. % Cu to Ni$_3$Fe reduces $T_c$ by 450°C [7].

*The quantity $R_{ord}$, which appears in the formula for $\eta$, corresponds to the equilibrium value of $R$ in the given alloy at the given $T_{tem}$. 