Journal of Alloys and Compounds, 182 (1992) 69–76
JALCOM 149

The influence of the microstructure of the ϵ phase of Mn–Al–C alloys on the stability and Curie point of the precipitated τ phase

Kh. Ya. Mulyukov and S. B. Khaphizov
Institute of Metals Superplasticity Problems, USSR Academy of Sciences, Khalturina 39, Ufa 450001 (Russia)

(Received July 18, 1991; in final form September 16, 1991)

Abstract

For the alloy Mn–Al–C the kinetics of the formation of the ferromagnetic τ phase from the coarse-grained and submicrocrystalline (submicrometre-grained) ϵ phase is investigated. It is shown that there exists a strong dependence of the formation rate and stability of the τ phase on the structural state of the initial phase. It is established that the Curie temperature T_C of the τ phase depends on the conditions of its formation.

1. Introduction

High hysteretic properties of Mn–Al–C alloys can be obtained due to the formation of the homogeneous fine-grained structure of ferromagnetic τ phase that has a large magnetocrystalline anisotropy [1]. Such a structure is usually obtained when the alloy has been subjected to plastic deformation at temperatures at which the ϵ phase exists (about 1050 K) and subsequent cooling with a controlled rate to room temperature [2, 3]. The τ phase, in different structural states, can also be obtained from the ϵ phase after quenching and subsequent tempering at lower temperatures [4, 5]. The second method allows the kinetics of the formation of the magnetic properties of the τ phase to be studied, when the τ phase is formed. The formation of the τ phase from the coarse-grained and microcrystalline ϵ phase is of special interest. In such cases the ferromagnetic phase will evidently be formed in different structural states and therefore its physical properties and stability can be different. For example, in ref. 6 it is shown that there is a strong influence of structure refining due to the effect of plastic deformation of Mn–Al–C (present as ϵ phase) on the rate of the ϵ–τ transformation and on the processes of the coercivity formation. Hence we studied the kinetics of the τ-phase formation, its stability and Curie temperature T_C in the cases when the τ phase was formed from the coarse-grained and microcrystalline ϵ phase.

2. Experimental procedure

In the present study the alloy with (wt.%) 70.6 Mn, 28.0 Al, 0.8 C and 0.6 Ni was obtained by melting in a vacuum induction furnace.

0925-8388/92/$5.00

The coarse-grained ϵ phase with a mean grain size of 50 μm was obtained by oil quenching the alloy from 1370 K. A microcrystalline state of the ϵ phase was reached by plastic deformation of the hardened alloy. For this purpose we used the torsion method and applied a quasi-hydrostatic pressure of 6 GPa reached in a Bridgman anvil-type pressure cell at room temperature, as described previously [7].

The amount of the ferromagnetic phase, formed in the course of the ϵ–τ transformation, was determined from the ratio [8]

$$V = M/M_{\max}$$

where M is the magnetic moment of the specimen after a given heat treatment, and $M_{\max}$ is the magnetic moment after cooling the specimen, which had been heated at 1100 K. In order to decrease the influence of the magnetocrystalline anisotropy the values M and $M_{\max}$ were measured at 475 K.

The temperature dependence of the magnetization $M = f(T)$ was measured on an autocompensatory magnetic balance in a field of 400 kA m^{-1}. The heat treatment and also the measurements of $M(T)$ of the specimens were made in a vacuum of 1.33×10^{-3} Pa. The temperature during the heat treatments was maintained with an accuracy of 0.5 K. The rate of temperature change during the $M(T)$ recording was 6 K min^{-1}. The Curie temperature was determined by means of extrapolation of the steepest part of the $M(T)$ curve with an accuracy of 1 K.

3. Results

3.1. *The kinetics of τ-phase formation from the coarse-grained ϵ phase*

Figure 1(a) shows the time dependence of the relative amount of the τ phase V of specimens annealed at different temperatures. It is seen that V increases with increasing tempering time and eventually reaches the limit $V = 1$. Formation of τ phase occurs very slowly at 773 K. With increasing tempering temperature the rate of τ-phase formation increases, and at 873 K the maximum amount of τ phase is reached after 8 min. At the tempering temperatures above 923 K the maximum amount of τ phase is formed even after 1 min (the technical conditions do not allow the tempering time to be fixed more accurately than 1 min) and then a gradual decrease is observed. The rate of τ-phase decomposition increases with increasing tempering temperature.

3.2. *The kinetics of τ-phase formation from the microcrystalline ϵ phase*

Mn–Al–C alloys when present in the form of the coarse-grained ϵ phase acquire a microcrystalline structure (the electron microscopic image of which is presented in Fig. 2) after strong plastic deformation. The sizes of crystallites can be estimated not only from the microstructure, but from the electron diffraction pattern as well. The dark field image of the microstructure shows a high density of defects in the crystallites.

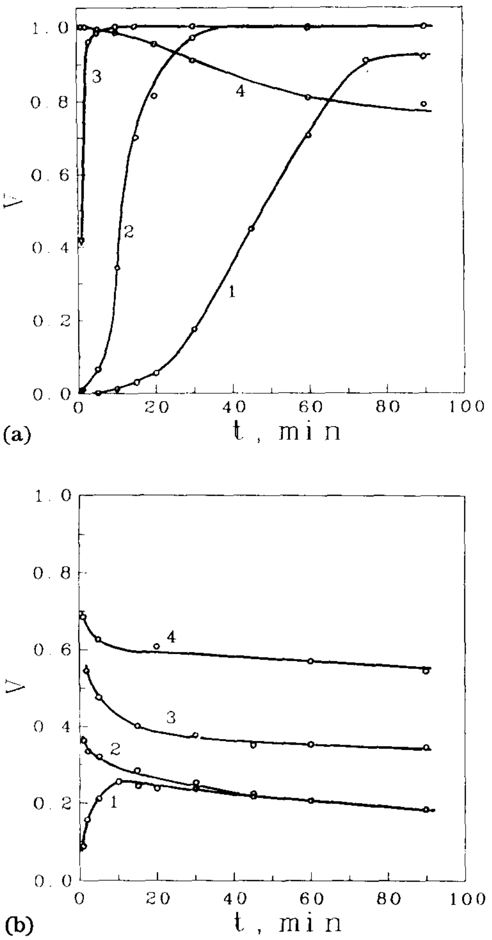


Fig. 1. The dependence of the amount of τ phase formed during annealing at temperatures of 773 K (curves 1), 823 K (curves 2), 873 K (curves 3) and 973 K (curves 4): (a) coarse-grained state of ϵ phase; (b) microcrystalline state of ϵ phase.

The aging time dependence of V for the microcrystalline ϵ phase annealed at different temperatures is rather different from that of coarse-grained material (Fig. 1(b)). During tempering at 773 K the V value increases for the first 10 min but later it begins to decrease slowly. Tempering at higher temperatures leads to approximately identical changes of V. The maximum amount of the ferromagnetic phase at a given temperature has already been reached during the 1 min tempering treatment. The amount of the ferromagnetic phase begins to decrease immediately upon tempering. The following peculiarities should be pointed out. First, the decrease of V diminishes with the increasing tempering time. Secondly, the lower the tempering temperature, the smaller the amount of the τ phase formed in the specimen. Thirdly, the amount of the τ phase formed at all tempering temperatures does not reach its maximum

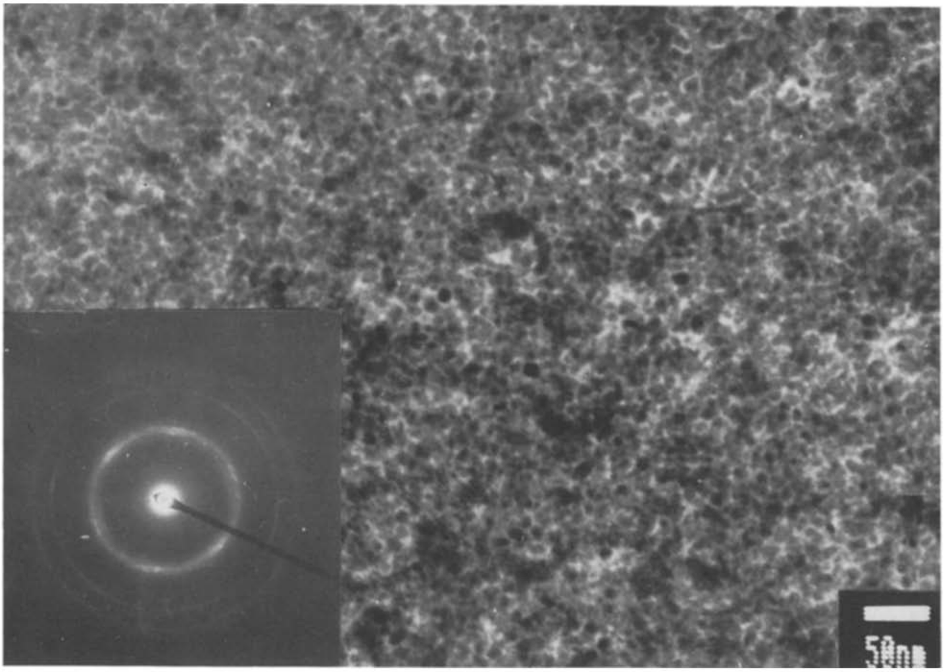


Fig. 2. The microstructure and electron diffraction pattern of ϵ phase, after strong plastic deformation.

value. The latter is achieved when the specimen is cooled after heating up to 1100 K.

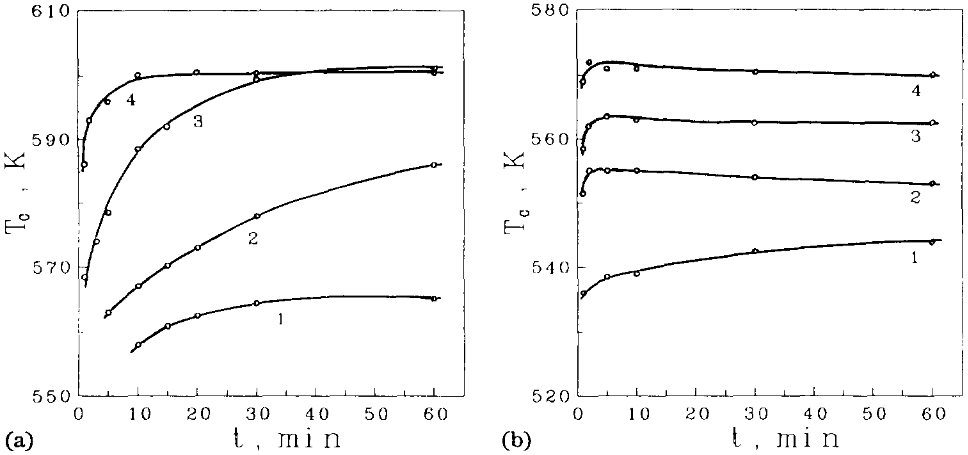
3.3. *The Curie temperature of the coarse-grained τ phase*

The dependence of T_C of the ferromagnetic τ phase on the conditions of its formation, which we have established in the present work, is of substantial interest. For example, in Fig. 3(a) we show the dependence of T_C on tempering time at different temperatures. At all temperatures an increase of T_C is observed with increasing tempering time. The higher the tempering temperature, the faster it grows and reaches its maximum value, which is equal to 601 K after tempering at 873 K. However, after tempering at 973 K the T_C value, having reached the value of 598 K, stops changing.

The values of T_C given in Fig. 3(a) correspond to the formation of the τ phase as a result of the tempering of the hardened ϵ phase. When the τ phase is formed during slow cooling of the specimen, heating up to the τ–ϵ transformation temperature (higher than 1100 K) does not raise T_C above 590 K.

3.4. *The Curie temperature of the τ phase formed from the microcrystalline ϵ phase*

The behaviour of T_C in the microcrystalline samples is different from that of samples consisting of the coarse-grained ϵ phase. First, it should be



(a) (b)

Fig. 3. The dependence of the Curie temperature of the τ phase on the tempering time at temperatures of 773 K (curves 1), 823 K (curves 2), 873 K (curves 3) and 973 K (curves 4): (a) coarse-grained ϵ phase; (b) microcrystalline ϵ phase.

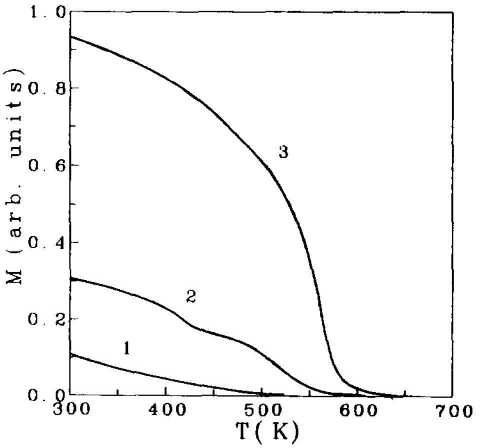


Fig. 4. The temperature dependence of the magnetization of microcrystalline specimens: curve 1, after the tempering at 673 K for 10 min; curve 2, after the tempering at 823 K for 90 min; curve 3, on slow cooling from 1100 K.

noted that after tempering at 673 K for 10 min the $M(T)$ curve has the shape of a hyperbola (Fig. 4, curve 1). Consequently, determination of T_C was impossible. Secondly, tempering at temperatures higher than 773 K results in the formation of two ferromagnetic phases with $T_{C1} = 433$ K and T_{C2} ranging from 555 to 571 K depending on the heat treatment conditions (Fig. 4, curve 2).

Figure 3(b) shows the T_{C2} dependence on tempering time at different temperatures. Here T_C changes only after tempering at 773 K, similarly to the case of the coarse-grained ϵ phase. After tempering at higher temperatures

T_C is practically independent of the tempering time. In this case the higher the tempering temperature, the larger the T_C value. Unlike the coarse-grained ϵ phase, the T_C of the τ phase was equal to 583 K, when formed at low cooling rates from the strained specimen at the high temperature (1100 K) (Fig. 4, curve 3). This T_C value is higher than the values obtained at tempering of the microcrystalline ϵ phase.

4. Discussion

4.1. *Coarse-grained structure*

The difficulty with which the τ phase nucleates from the coarse-grained ϵ phase at low tempering temperatures, as mentioned above (Fig. 1(a), curve 1), is probably due to a small amount of nuclei, because the coarse-grained ϵ phase contains only few defects and the grains have perfect boundaries. The initial decrease in the amount of the τ phase during the tempering at higher temperatures (curve 4 in Fig. 3(a)) can probably be explained by the onset of the transformation of the τ phase into the equilibrium phases.

The strong dependence of T_C on the tempering temperature and time reflects the change in properties of the τ-phase crystallites during their growth. This may be caused both by a decrease of the carbon concentration, and by the attainment of a more perfect crystallite structure as their sizes increase. At the initial stage of τ-phase nucleation the carbon concentration in crystallites is probably higher than the equilibrium concentration. In the course of reaching crystallite perfection the carbon concentration tends to reach the equilibrium value. The decrease of carbon in τ phase, as shown in ref. 9, results in an increase of T_C.

The beginning of the decrease of T_C in the τ phase, formed in the course of tempering at 973 K, may have two reasons. First, at this temperature the decay of τ phase begins (Fig. 1(a)), resulting in the corresponding changes of the crystal lattice. Secondly, with increasing temperature the equilibrium carbon concentration in the τ phase probably increases by diffusion from other phases. Of these two reasons the first seems the more probable.

4.2. *Fine-grained structure*

It is known that a microstructure, consisting of extremely fine defect-rich crystallites, is formed under the conditions of high plastic deformation at room temperature [7]. Such a microstructure, as shown also in Fig. 2, provides favourable conditions for τ-phase nucleation. Indeed, even at 673 K a notable quantity of τ phase is formed during the first 10 min. Here it exists apparently in a superparamagnetic state, as the $M(T)$ curve has the shape of a hyperbola (Fig. 4, curve 1). All this indicates the formation of a large number of extremely fine nuclei of the τ phase under these conditions.

The monotonous growth of V (Fig. 1(b), curve 1) observed after tempering at 773 K for 10 min indicates the growth of the crystallites of the τ phase. However, with increasing tempering time the process of crystallite coarsening stops and decay of the τ phase begins. At temperatures of 823 K and higher the maximum possible volume of τ phase is apparently formed for a very short period of time (due to the high density of nucleation sources). During tempering of the microcrystalline material consisting of the initial ϵ phase the ultrafine-grained τ phase [6] is formed, which, as the present results confirm (Fig. 1(b)), proves to be unstable. The reason of such instability lies not only in the small size of the crystallites of the new phase, but also in the high density of defects in them inherited from the initial phase. The decrease of the precipitation rate of the τ phase with increasing tempering time is to be connected with the higher perfection of crystalline structure of the new phase due to the constantly ongoing process of fault redistribution.

The proportionality between the amount of τ phase and the tempering temperature allows us to state that at higher temperatures more coarse and perfect crystallites of the new phase are formed. The data on T_C corroborate this view. Really, every tempering temperature corresponds to T_C which practically does not depend on the tempering time. The higher tempering temperatures correspond to higher T_C. Consequently, crystallites of the τ phase, formed at higher temperatures, are more perfect and contain less carbon.

It seems impossible to explain the appearance of the second low temperature magnetic phase with T_{C1} on the basis of magnetic measurements only.

5. Conclusions

The obtained data and their analysis allow us to come to the following conclusions.

(1) The rate of ferromagnetic phase formation during the ϵ–τ transformation of Mn–Al–C alloys depends on the microstructure of the initial ϵ phase. In specimens with a microcrystalline structure the τ phase begins to form at lower temperatures.

(2) The τ phase, when formed from the microcrystalline ϵ phase, reveals a very low stability.

(3) The Curie temperature of τ phase depends on the conditions of its formation. When the τ phase is formed from a coarse-grained ϵ phase, its T_C increases with tempering time and reaches its maximum value of 601 K after tempering at 873 K (20 min).

When the τ phase precipitates from a microcrystalline ϵ phase its T_C has a considerably lower value than when it is formed from a coarse-grained specimen. Also in the former case T_C increases with increasing tempering temperature.

Acknowledgment

We would like to thank G. F. Korznikova for performing the structural investigations.

References

1 T. Ohtani, N. Kato and S. Kojima, *IEEE Trans. Magn.*, *13* (1987) 1328.

2 Y. Sakamoto, A. Ibata, S. Kojima and T. Ohtani, *IEEE Trans. Magn.*, *16* (5) (1980) 1056.

3 A. V. Shangurov, E. I. Teytel, A. E. Ermakov and M. A. Uimin, *Fiz. Met. Metalloved.*, *60* (1985) 1171 (in Russian).

4 Z. A. Ellenkamp and H. Zijlstra, *Z. Angew. Phys.*, *16* (1964) 400.

5 N. I. Sokolovskaya, N. N. Shchegoleva and L. M. Magat, *Fiz. Met. Metalloved.*, *33* (1972) 893 (in Russian).

6 E. I. Teytel, M. A. Uimin, A. E. Ermakov and A. V. Shangurov, *Fiz. Met. Metalloved.*, *8* (1990) 83 (in Russian).

7 E. I. Teytel, M. A. Uimin and A. E. Ermakov, *Fiz. Met. Metalloved.*, *7* (1990) 95 (in Russian).

8 Kh. Ya. Mulyukov, R. Z. Valiev, G. F. Korznikova and V. V. Stolyarov, *Phys. Status Solidi A*, *112* (1989) 137.

9 L. Paretti, F. Bolzoni, F. Leccabue and A. E. Ermakov, *J. Appl. Phys.*, *59* (11) (1986) 3824.