KINETICS AND MECHANISM OF HARDENING OF Mn – Pd ALLOYS

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In a study of Mn – Pd alloys [1] it was noted that they have a tendency to harden. The hardness reaches ~HRC 73 with even brief holding during tempering. Nonmagnetic and plastic materials in the original condition, with a high hardness, are of practical interest for instrument construction (cores, small bearings, etc.).

In accordance with the equilibrium diagram (Fig. 1), quenching from 1050°C fixes the ductile γ Mn phase, which during tempering decomposes with precipitation of β_1 phase and α Mn.

The unusual variation of the hardness of Mn – Pd alloys at 450-600°C was reported in [1] – an exceedingly sharp increase in hardness after a very short holding time (15 min) followed by a decrease in hardness and then an increase at longer holding times.

The reason for this variation of the hardness is not clear. It is known that the γ Mn phase and α Mn phase precipitated during decomposition are very hard and brittle: ~HRC 71. In previous studies of Mn – Cu alloys [2] the precipitation of the hard α Mn phase from the γ Mn solid solution during tempering led to a considerable increase in hardness. However, the maximum hardness of Mn – Cu alloys is less than half that of Mn – Pd alloys* and is reached only after prolonged holding at relatively high temperatures, i.e., with large quantities of α Mn phase precipitated; Mn – Pd alloys reach the maximum hardness after very brief holding (15 min).

In this connection it was assumed that the hardening of Mn – Pd alloys in the initial stage of decomposition (sharp peak on the curve) is due to precipitation of the β_1 phase (with a tetragonally distorted fcc lattice coherent with the original γ phase). The later drop of the hardness is evidently due to disruption of coherency. The following increase in hardness with holding for longer times is due to precipitation of the hard and brittle α Mn phase.

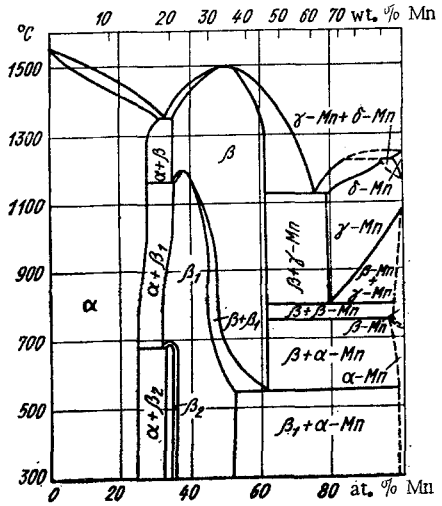

Fig. 1. Equilibrium diagram of Mn – Pd system.

This work concerns the kinetics of the hardening of Mn – Pd alloys in the initial stage of decomposition and the reason for the high hardness of these alloys.

It was necessary to determine the hardness of β_1 phase (alloys in the equiatomic region of concentrations in the Mn – Pd system) and the change in the hardness of the alloys with precipitation from γ Mn of only β_1 phase, which is possible in Mn – Pd – Ni alloys [3].

We investigated binary Mn – Pd alloys with different amounts of palladium (5, 10, 15, 20, 30, and 66 wt. %) and Mn – Pd – Ni alloys. Different phase conditions can be obtained after tempering, simulating the effect of separate phases.

*The alloying element is almost insoluble in α Mn in both systems.

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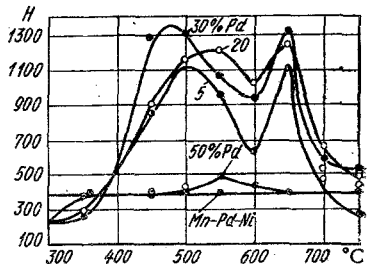

Fig. 2

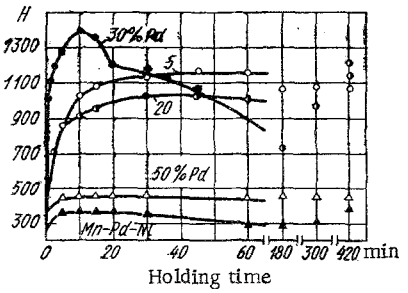

Fig. 3

Fig. 2. Variation of hardness with tempering temperature (holding 5 min) for Mn – Pd and Mn – Pd – Ni alloys quenched from the γ region.

Fig. 3. Variation of hardness with holding time at 450°C for Mn – Pd alloys.

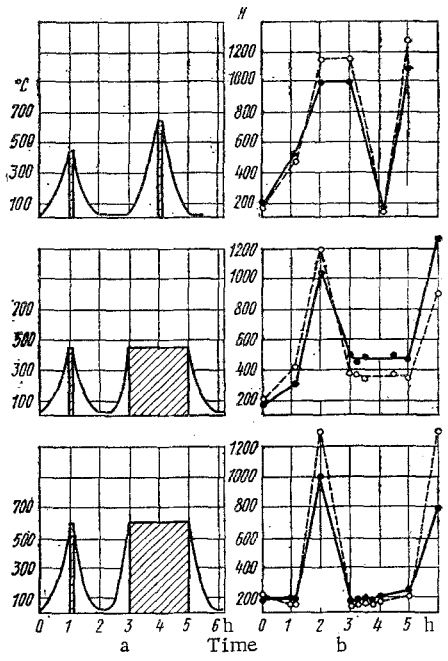

Fig. 4. Variation of hardness during heating of Mn – Pd alloy with 30% Pd. a) Heating conditions; b) variation of hardness during heating. ---) Deformed condition; ——) quenched condition.

The kinetics of hardening was investigated after tempering of samples quenched from different temperatures in a salt bath. Holding at each temperature was increased successively from 1 to 5 min (1 min intervals) and then at 5 min intervals up to 1 h, and then for 2 h up to a total of 10 h. After heating, the samples were quenched in water and the hardness was measured under loads of 100 and 200 g in the PMT-3 apparatus. Dilatometric studies were also made, and measurements of the hardness during heating, the density [4], erosion resistance, and random measurements of the modulus of elasticity.

The hardness during heating was determined with the VIM-1 apparatus.

Figure 2 shows the variation of the hardness of Mn – Pd and Mn – Pd – Ni alloys quenched from the γ region as a function of tempering temperature. After holding for 5 min, two peaks are observed on the curve for 5, 20, and 30% Pd – at 450-500 and 650°C. In the original quenched condition the hardness is H 220-230, while after tempering it reaches H 1100-1300, depending on the composition of the alloy. With increasing holding times the first peak occurs at the lower temperature (450°C), with retention of high hardness.

The hardness of β_1 phase (alloy with 50 at. % Pd) increases slightly with tempering; the decomposition of the γ Mn solid solution in the Mn – Pd – Ni alloy, with precipitation of β_1 phase alone, leads to a very slight increase of the hardness, the hardness being independent of the holding time or tempering temperature.

For Mn – Pd alloys with 15-30% Pd the hardness increases sharply in the first minute of holding; the increase is particularly sharp for the alloy with 30% Pd. The maximum hardness (H 1350) is reached with holding for ~10 min. Holding for a longer time leads to a gradual reduction of the hardness and then an increase of the hardness with holding for very long times (Fig. 3).

In connection with the relationships observed it was of interest to determine the hardness at the first (450°C) and second (600-650°C) peaks, corresponding to the regions of β Mn (bcc) + α Mn and β_1 (fct) + α Mn on the equilibrium diagram. For this purpose, the deformed and quenched samples of Mn – Pd alloys with 20-30% Pd were successively heated to 450 and 600°C under conditions shown in Fig. 4a. The hardness was measured at the heating temperature and after cooling to room temperature. The hardness of the quenched and deformed samples of the Mn – Pd alloy with 30% Pd was measured during holding at 450 and 600°C (Fig. 4).

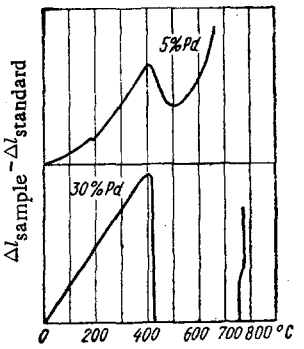

Fig. 5

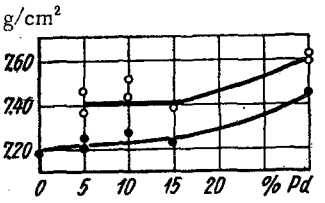

Fig. 6

Fig. 5. Dilatometric curves (heating) for quenched Mn – Pd alloys with 5 and 30% Pd.

Fig. 6. Change in density of Mn – Pd alloys with composition and treatment.

TABLE 1

Heat treatment	E, kg/mm²	x · 10⁻⁶	H	σ_b, kg/mm²	δ, %	Density, g/cm³
Quench, 1050°C	11500	–	200	70	30	7,45
Quench + temper 450°C, water	20500	13–14	1100	Brittle fracture		7,60

It can be seen from Fig. 4b that the hardness of the quenched and deformed samples measured at 450°C after holding for 5 min is considerably higher than the original and reaches H 500-600. After cooling to room temperature the hardness is more than double the hardness at the tempering temperature. With subsequent heating to 600°C the hardness decreases sharply, and after holding for 5 min it is below the original hardness. However, cooling to room temperature leads again to a sharp increase of the hardness to a value of the same order as after tempering at 450°C.

Increasing the holding time at 450°C to 2 h (Fig. 4) does not lead to any change in the hardness measured at this temperature. Increasing the holding time to 2 h at 600°C leads to slight gradual increase of the hardness.

Thus, the measurements of the "hot" hardness indicate that the high hardness is due mainly to formation of β phase. In the region of $\beta_1 + \alpha$ Mn at 450°C the hardness is already high after holding for 5 min and does not change with prolonged holding at this temperature. At 600°C, in the $\beta + \alpha$ Mn region, the hardness is low. Increasing the holding time to 2 h at this temperature leads to a gradual increase of the hardness, since the quantity of α Mn increases with the holding time. Cooling from 600°C to room temperature leads to a sharp increase of the hardness, since the $\beta \rightarrow \beta_1$ transformation occurs during cooling. As is known, β phase is not fixed at room temperature even with sharp cooling [5].

The decomposition of the γ Mn solid solution in Mn – Pd alloys is accompanied by substantial reduction in volume (Fig. 5). For the alloys with a low palladium content (5%) the contraction is considerably smaller than for the alloy with 30% Pd, with the highest hardness. For the alloy with 30% Pd this effect is very large, and with heating above 400°C at any heating rate it is instantaneous. Thus, after tempering leading to hardening the density of the alloy increases considerably (Fig. 6).

The decomposition of the γ phase with precipitation of β_1 phase alone (in the Mn – Pd – Ni alloy) is not accompanied by any change in volume and does not lead to any noticeable hardening. It is possible that this is due to the small quantity of β_1 phase precipitated. It can be assumed that the maximum hardness of Mn – Pd alloys held for several minutes depends not so much on the properties of β_1 phase as on the internal stresses that occur during decomposition of the γ phase, accompanied by a very large volume effect.

Besides the increase in hardness after tempering at 450°C there are changes in several other properties of the Mn – Pd alloy with 30% Pd that are of interest for practical use (see Table 1).

CONCLUSIONS

1. We investigated the kinetics of hardening in manganese alloys quenched from the γ Mn region – the distinguishing characteristic is the exceedingly sharp increase of the hardness during the first minute of holding (1-10 min) at 450-500°C. The hardness peak after very short holding times is due to the

formation of β_1 phase. With holding for longer times secondary hardening occurs due to precipitation of the hard and brittle α Mn phase.

2. The maximum hardness with holding for a short time is higher for the alloy with a large palladium content (30%), which is accompanied by the volume effect of the $\gamma \rightarrow \beta_1 + \alpha$ Mn transformation.

3. The hardness of β_1 phase is relatively low and varies little with the tempering time.

4. The high hardness of Mn – Pd alloys after holding for a short time is evidently due to the particular condition of the β_1 phase at the time of precipitation from the γ Mn solid solution and the internal stresses that occur.

5. In the hardened condition the Mn – Pd alloy with 30% Pd is nonmagnetic, has a high modulus of elasticity, and has satisfactory corrosion resistance.

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