Ordering and Disordering Behaviors in δ -VMn Alloys*

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Taking advantage of a remarkable difference in length between the ordered and the disordered state, the ordering process in VMn alloys is investigated by means of measurements of lattice constant, thermal expansion and hardness. VMn alloys show a marked expansion during the disordering process on heating, as expected. The 730°C anomaly is also observed in the change of the thermal expansion coefficient. The average thermal expansion coefficient in the temperature range 300~600°C is larger in the disordered state than in the ordered state, and the coefficient in the disordered state above the transition temperature is remarkably large in the vicinity of the equiatomic composition. Pronounced softening at the equiatomic composition in the ordered state results in a V-shaped change in hardness with respect to composition.

Isothermal ordering of the VMn alloys proceeds with retardations. It is observed that the half-width of the (211) reflection increases, indicating the existence of lattice strain during the rapid change in the degree of order. The hardness increases during the retardation of ordering.

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I. Introduction

In a previous paper⁽¹⁾ the authors demonstrated the composition dependence of the CsCl-type order-disorder transition temperature in the V-Mn alloy system by means of thermal analyses. There was also a remarkable difference in length or volume between the ordered state obtained by slow cooling and the disordered state obtained by quenching, as compared with other superlattices. In an equiatomic VMn alloy a lattice contraction of 0.6% has been observed in the change from a disordered to an ordered state. Since the perfect order was not attained by the ordering treatment adopted, the difference would be more marked in an ideal case. As a marked change in physical properties during the phase transition is expected, the ordering and disordering processes may be easily examined in a VMn alloy. This superlattice alloy seems to be a suitable material to get a

general information about the ordering or disordering process and mechanism.

The changes in mechanical properties upon ordering have been widely studied⁽²⁾ in connection with intermetallic compounds, and several hardening mechanisms in the ordered structure have been proposed⁽³⁾⁽⁴⁾. When crystal structure symmetry is altered markedly upon ordering like in CuPt or CuAu superlattices, there is a strong influence of a large lattice strain on the mechanical properties. In view of the hardening mechanisms postulated, it can be expected in the VMn alloy that the mechanical properties are changed measurably upon ordering accompanying a less symmetry change but a large volume change.

In this study, the origin of the volume difference between the ordered and disordered states at room temperature was examined by a dilatometer beyond the transition temperature and the hardness changes at room and high temperatures were examined by microhardness testers. The characteristics of ordering and disordering processes in the VMn superlattice alloys are presented in this paper.

II. Experimental Procedures

The preparation of the specimens were

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carried out in the same manner as described previously⁽¹⁾. All of the specimens with equi-atomic composition employed in this experiment were prepared from the same ingot, which contains 49.82 at% of manganese. Dilatometric measurement was made using a Rigaku-Denki differential dilatometer and alumina was used as a neutral reference. The specimens had a cylindrical form of 5 mm in diameter and 5 mm in length. The rate of heating and cooling was 10°C/min in every case. Hardness was measured by a Vickers hardness tester, a Leitz micro-hardness tester and a Nihon-Kogaku high temperature micro-hardness tester. The measurement of lattice constant was performed in the same manner as in the previous paper. Isothermal ordering treatment was performed in a lead bath, the temperature of which was controlled within the accuracy of $\pm 2^\circ\text{C}$.

III. Results and Discussions

1. Thermal expansion behavior in the equi-atomic VMn alloy

Two heating curves and one cooling curve of dilatation in the equiatomic VMn alloy are shown in Fig. 1. The heating curve corresponds to the fully ordered state obtained by the ordering program⁽¹⁾ and the other to the disordered state obtained by quenching from 1050°C into ice brine. Although the

Fig. 1 Thermal expansion curves of ordered and disordered equiatomic VMn alloy.

results below 400°C are not shown in Fig. 1, a remarkable difference in length between the ordered and the disordered state at room temperature can be observed, as first indicated by the results of lattice constant measurement in the previous paper⁽¹⁾. According to Fig. 1, the ordered phase expands gradually and linearly on heating up to 700°C. As no structural changes occur at temperatures below 500°C, this is a reversible change corresponding to the usual thermal expansion in the ordered state. An unusual expansion indicates the occurrence of disordering at temperatures above 700°C and continues to the transition temperature of 845°C as previously revealed by thermal analyses. The disordered phase existing above this temperature expands again gradually and approximately linearly with usual thermal expansion. The expansion upon disordering, however, is not simple, that is, inflection points at about 730°C and 780°C are present on the dilatation curve. The features of the change may be better illustrated in Fig. 2, where they are reproduced as thermal expansion coefficients. Although the heating rate of 10°C/min in the dilatation experiment differs from that of 1~2°C/min in the specific heat measurement, the result of Fig. 2 is similar to the specific heat curve in the previous paper,

Fig. 2 Thermal expansion coefficient curves of ordered and disordered equiatomic VMn alloy.

and an anomalous specific heat behavior found there can obviously be observed here.

According to Figs. 1 and 2, the disordered state obtained by quenching expands linearly upon heating up to 600°C. The thermal expansion coefficient of the disordered state is larger than that of the ordered state. A remarkable contraction occurring in the temperature range between 650~750°C results in a negative thermal expansion coefficient, which corresponds to the formation of the superlattice. Above a temperature about 760°C the thermal expansion coefficient becomes positive due to the onset of disordering. Above 820°C the thermal expansion curve and its coefficient curve coincide with those obtained by heating from the ordered state. These features agree very closely with the results previously obtained by the thermal analyses. The cooling curve follows neither the heating trace of the ordered nor that of the disordered trace. This fact indicates that ordering does not occur sufficiently at a relatively rapid cooling rate of 10°C/min.

2. Thermal expansion coefficients in VMn alloys

Some examples of the thermal expansion behaviors of the ordered alloys with non-stoichiometric compositions are shown in Fig. 3. The dilatation curves of the 54.26 and 45.08 at%Mn alloys, which are located in nearly symmetrical positions around the stoichiometry, do not differ much from that of the equiatomic alloy. But, in the manganese-rich alloy the expansion by disordering initiates at lower temperature and the change corresponding to the 730°C anomaly is shifted to lower temperature than in the vanadium-rich alloy. This fact is well demonstrated in the results of the thermal analyses. The expansion upon disordering decreases gradually as the alloy composition is moved to the vanadium-rich side. This small expansion in low-manganese alloys corresponds to the endothermic change being regarded as an extension of the 730°C anomaly in the previous paper.

In Fig. 4, the thermal expansion coefficient is plotted against the composition. In the

Fig. 3 Some examples of thermal expansion curves of ordered VMn alloys.

Fig. 4 Changes in the thermal expansion coefficient of VMn alloys with the composition.

average thermal expansion coefficient in the temperature range of 300~600°C, where disordering or ordering scarcely occurs, an appreciable difference between the quenched state and the slowly-cooled state is revealed to indicate the existence of a superlattice in the alloys containing Mn more than 25 at%. The thermal expansion coefficients in the disordered state become larger with increasing

manganese content, and are larger than those in the ordered state. The difference between the two states is largest in the vicinity of the equiatomic composition. The average thermal expansion coefficient above the transition temperature up to 950°C increases steeply as the alloy composition approaches the equiatomic composition, leading to a maximum, as shown in Fig. 4. This result is closely related to the fact that the thermodynamical properties corresponding to the second derivatives of free energy, such as specific heat or thermal expansion coefficient, continue to decrease gradually after the steep drop at the transition temperature, shown in the previous paper⁽¹⁾ and in Fig. 2 in the present paper. The gradual decrease is due to the presence of short-range order, the degree of which is highest in the vicinity of the equiatomic composition.

3. Hardness of VMn alloys

The hardness at room temperature in the quenched and the slowly-cooled VMn alloys is shown in Fig. 5. The vanadium-rich alloys quenched were harder than the slowly-cooled one and the difference between them increased with decreasing manganese content. By tempering the quenched one at temperatures below 200°C, the hardness decreased to the value of the slowly-cooled one. Then, it can be assumed that hardening by quenching in the vanadium rich alloys is due to the solution

hardening of interstitial impurity such as carbon or nitrogen. Therefore, only the values of slowly-cooled vanadium rich alloys are shown in Fig. 5.

As shown in Fig. 5, the solution hardening of vanadium by manganese is prominent, but the hardening rate decreases with increase of the manganese content. The solution hardening of manganese by vanadium may also be observed on the manganese side. In the vicinity of the equiatomic composition in the disordered state, hardness depends little on the composition, showing a constant value, Hv 400. The softening which suggests the formation of a superlattice becomes appreciable in the range between 35 and 60 at% manganese and is most remarkable at the equiatomic composition. Consequently the change in hardness with the composition takes the shape of the letter V in the ordered state.

This tendency has also been recognized in other superlattice alloys and intermetallic compounds having a solubility region. For example, it has been observed that the hardness of the disordered solid solution of the Mg–Cd alloy, which is obtained by quenching, becomes largest nearly at the equiatomic composition and that slow cooling reveals troughs of hardness at the compositions A_3B , AB and AB_3 corresponding to the formation of the superlattices⁽⁵⁾. Namely, the ordered lattice with a stoichiometric composition, in which the number of unfavorable, like pairs of atoms is smaller and the degree of order is fully developed, is softest in general. In intermetallic compounds having a solubility range, similar features have been observed. For example, it has been reported that the hardness of AgMg having a CsCl-type structure shows a minimum at the stoichiometry, similar to Fig. 5⁽⁶⁾.

4. Disordering and ordering by heating

Figure 6 shows changes in hardness with temperature in the equiatomic VMn alloy measured by a high-temperature micro-hardness tester. The results on an equiatomic FeCo alloy are also shown for comparison. The average heating rate employed here was approximately 2°C/min. On heating the ordered and the disordered states, hardness first

Fig. 5 Changes in the hardness of ordered and disordered VMn alloys with the composition.

Fig. 6 Changes in the hardness at elevated temperatures of equiatomic VMn and FeCo alloys.

decreases with increasing temperature and then increases slightly to make a maximum at a temperature of about 800°C, i.e., a temperature just below the transition temperature. Above this temperature, a rapid softening takes place in the process changing into disorder state. In the FeCo alloy, a peak in hardness is also observed at 680°C just below the transition point. This result is in good agreement with that obtained by Stoloff and Davis⁽⁷⁾ with the measurement of flow stress at the temperature in a FeCo alloy containing 2%V. Such a phenomenon as an increase in hardness or flow stress in the stage of a considerably low degree of order at temperature or at room temperature has been observed in many other superlattice alloys, and several mechanisms for it have been proposed. Stoloff and Davis⁽³⁾ have interpreted the strengthening at low degree of order, noting that the distance of a dislocation pair in superlattice matrix is inversely proportional to the square of the order parameter, s .

The variation in hardness at room temperature by isochronal aging of the equiatomic VMn alloy is shown in Fig. 7. The step by step aging was performed for 15 min at each temperature. Changes in the lattice constant as well as changes in the half-width of the (211) reflection are also shown in this figure. The process toward disordering is in general accompanied by an endothermic reaction,

Fig. 7 Changes in the lattice constants, half-width of the (211) reflection and hardness of an equiatomic VMn alloy. Sample is kept at each temperature for 15 min and tested at room temperature. Open circle refers as ordered and closed circle as disordered at initial state.

expansion and increase of hardness. A scheme for the change in lattice constant is in good agreement with that of the dilatation curve obtained on heating the ordered state. It has been known that hardness, one of the structure sensitive properties, does not always change with the variation in degree of order, but depends on the substructure. This is shown by the fact that the hardness at room temperature changes in a fairly complicated manner in Fig. 7, as compared with the thermal behavior.

In Fig. 7, on heating the disordered state, a remarkable peak in hardness at 700°C does not correspond to any change in the results obtained by the thermal analyses. On heating the ordered state, an obvious hardening peak is present at 640°C and then another hardening follows above 700°C. After the curves of the ordered and the disordered state fall on the same curve above 800°C, a slight increase in hardness is also observed in accordance with the results of the high-temperature hardness measurement.

5. Ordering process by isothermal aging

The hardening upon heating the disordered state, which has a peak at 700°C, and the hardening upon heating the ordered state, which has a peak at 640°C, may not be regarded

Fig. 8 Changes in the lattice constants, half-width and hardness during isothermal ordering of an equiatomic VMn alloy.

as concomitant phenomena such as the effect of impurities, but the phenomena directly related to the development of order. The ordering process of the equiatomic VMn alloy is examined isothermally. The change in hardness, lattice constant and half-width upon ordering are shown in Fig. 8. At an early stage of the ordering at any aging temperature the hardness change has a tendency towards softening. Then, hardening shows a peak, followed by re-softening. At lower aging temperatures, such as 645 or 615°C, however, a second hardening takes place.

At any temperature the lattice constant is decreased with aging time, but exhibits a retardation at the time when hardness shows a peak. The retardation of the decrease in the lattice constant may indicate that the ordering does not proceed at this stage. The half-width has a maximum at the initiation of hardening and decreases at the peak of the hardness curve. The increase of the half-width corresponds to the steep change in lattice constant, that is, the rapid development of ordering. Similar observation has been done in the case of the isochronal step aging in Fig. 7. The relation between the logarithm of time when the first hardening peak is observed and the reciprocal of the aging temperature is represented by a straight line, as shown in Fig. 9. From the slope in Fig. 9, the apparent activation energy of ordering in the VMn alloy can be estimated

Fig. 9 The relation between the reciprocal of temperatures and the time required to reach the first peak in hardness during isothermal ordering.

to be 54.8 kcal/mol. This value is nearly the same as those obtained in the ordering of FeCo alloys, 53.5⁽⁸⁾, 51⁽⁹⁾ and 52⁽¹⁰⁾ kcal/mol.

The second hardening occurs, as described above, in the aging at temperatures of 645°C and 615°C. At these temperatures, after the first retardation the ordering begins to proceed again with an increase of the half-width, and then the second retardation occurs, accompanied by hardening. Although the second hardening is vague or not appreciable at aging temperatures higher than 675°C, retardation of the decrease in lattice constant is observed, as indicated in the result of the aging at 705°C. These results lead to the conclusion that the first and second hardenings originate from the same mechanism and that the ordering in the VMn alloy proceeds with the retardations. Furthermore, the 700°C hardening observed in the step by step aging of the disordered state may correspond to the first hardening in the isothermal aging. The 640°C hardening observed in the aging of the ordered state seems to correspond to the second hardening in the isothermal aging, considering the temperature range and the degree of order at which the hardening takes place.

The ordering process and the accompanying changes in physical and mechanical properties

have been examined in a variety of superlattice alloys and many theoretical considerations for ordering have been proposed^{(3)(4)(11)~(22)}. Because the increase of the half-width which indicates the generation of lattice strain is observed at the stage of the rapid development of order and the ordering is accompanied by a large volume contraction, it may be suggested that the atomic ordering in the δ -VMn alloy develops by the nucleation and growth mechanism⁽¹⁹⁾ or the fluctuation mechanism⁽²³⁾⁽²⁴⁾ rather than the homogeneous one. Since, isothermal treatment was done on the same specimen and then interrupted at each time during the measurement at room temperature, it would be interesting to know if the retardation of ordering found in this experiment is valid in continuous isothermal ordering. At present, more quantitative X-ray analysis on powder specimens, measurement of the change in physical properties during continuous isothermal ordering and the structure observation by a transmission electron microscope are in progress.

IV. Conclusion

Noting a remarkable difference in length between the ordered state and the disordered state, the ordering process in the VMn alloys is investigated by means of measurements of lattice constant, thermal expansion and hardness. The results obtained are summarized as follows:

(1) In the VMn alloys, a marked expansion is observed in the disordering process on heating, as expected from the results of the lattice constant measurements. The 730°C anomaly is observed in the change of thermal expansion coefficient, which is quite analogous to that in specific heat.

(2) The average thermal expansion coefficients in the temperature range 300~600°C are larger in the disordered state than in the ordered state. The average thermal expansion coefficient in the disordered state between the transition temperature and 950°C is remarkably large in the vicinity of the equiatomic composition. These facts are presumably due to the presence of the short range order in this

range of composition and temperature.

(3) In the *bcc* disordered solid solution of the V-Mn system, the solution hardening of vanadium by manganese is prominent. Pronounced softening at the equiatomic composition in the ordered state results in a V-shaped change in hardness when plotted against composition.

(4) As has already been known in many superlattice alloys, increase in hardness in the state of appreciably lower degree of order is also observed in the VMn alloy at the temperature just below the transition point.

(5) Ordering of the VMn alloy by isothermal aging proceeds with retardations. Half-width of the (211) reflection increases to show the existence of the lattice strain during the rapid change in the degree of order. Also hardness increases during the retardation of ordering.

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