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Development of ultra high strength steels based on spinodal decomposition

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A new idea for the development of ultra high strength steels by utilizing the spinodal decomposition of the Fe–Mo binary system is proposed. The idea comprises the restraint of the brittleness of the Fe–Mo alloy by reducing the Mo-content necessary to spinodal decomposition and by microstructure refining such as grain refining, subgrain refining etc; the former is realized by the alloying with some elements which, in general, have a tendency towards ordering (i.e., negative interchange energy between the nearest neighbour atoms) when combined with iron, and the latter by thermomechanical treatment and/or cold rolling. On the basis of the idea, that hidden properties indispensable to high strength materials are successfully drawn from the Fe–Mo alloy; we have obtained a 4 GPa grade high tensile steel of Fe–Mo–Co–V. This idea is sure to contribute new suggestions to the development of high strength materials.

1. Introduction

Spinodal decomposition is well known as a phase decomposition mechanism of supersaturated solid solution. The development of a very fine and quite uniform microstructure is a marked feature of the spinodally decomposed alloy (sometimes called spinodal alloy). By making good use of this feature, some spinodal alloys have already been put to practical use for, e.g., magnetic materials [1]. Fig. 1 shows a typical example of the finely developed spinodal structure, i.e., the so-called $\langle 1\,0\,0 \rangle$ modulated structure, observed in Fe–20 at % Mo alloy; our group has for the first time discovered the occurrence of spinodal decomposition in Fe–Mo binary system [2]. This spinodal structure consists of a Mo-rich region (η-phase) and a Mo-poor region which are alternately and periodically distributed, and exhibits extremely high hardness: the maximum hardness exceeds 1000 in micro-Vickers hardness number (mHv) [2]. Hence we can easily expect from this fact that the spinodal structure has some potentially unforseen properties quite suitable to high strength materials.

In the Fe–Mo binary system, however, Mo-content of at least 17 at % is needed to cause spinodal decomposition and hence to make the alloy very hard [2]. Such large amount of molybdenum also makes the alloy extremely brittle [1] and seems to hide the useful mechanical properties. Therefore, if the brittleness of such Fe–Mo binary alloys can be eliminated by replacing a part of molybdenum with some alloying elements or by other means, we must be able to bring out the hidden properties necessary to attain a high strength material.

In the present paper, first we propose a new idea for the development of ultra high strength steels by utilizing the spinodal decomposition of the Fe–Mo alloy. Second we show an example of the development of an ultra high tensile steel based on the proposed idea. Lastly we discuss the applicability of the proposed idea to other high tensile steels.

2. Basic idea for the development of ultra high strength steels

When using the binary Fe–Mo spinodal alloy as a starting material, the important point to be overcome is to restrain the brittleness of the alloy. Our idea for realizing the restraint is as follows:

(a) some alloying elements are added to the Fe–Mo binary alloy in order to expand the spinodal region toward the lower Mo-content region,

(b) Fe–Mo base (ternary or quadruple) spinodal alloys with low Mo-content are subjected to thermomechanical treatment and/or cold-rolling in order to refine grain size.

2.1. Alloying elements for the expansion of the spinodal region of the Fe–Mo system

Our group has been studying the effect of alloying elements on the spinodal decomposition of an Fe–Mo alloy. Some of our results are shown in Fig. 2 [3]. In this figure, each circle denotes the composition at which the occurrence of spinodal decomposition at 773 K is recognized by transmission electron microscopy (TEM). Each thick curve in the figure indicates the coherent spinodal line at 773 K obtained by theoretical calculations; the spinodal region is to one side of the shadowed area. We can see that the spinodal region is expanded toward the lower Mo-content

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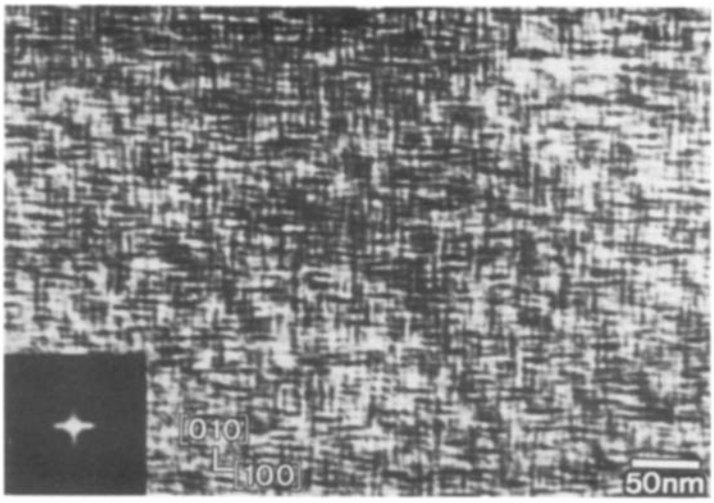

Figure 1 Electron micrograph of the ⟨1 0 0⟩ modulated structure and the 2 0 0 reflection spot surrounded by two sets of satellites, taken from the Fe–20 at % Mo alloy aged at 823 K for 1800 sec.

region; alloying the Fe–Mo binary system with cobalt or vanadium is quite effective in decreasing the Mo-content necessary for the occurrence of spinodal decomposition. The interchange energies between iron and any of the two elements are negative [4, 5]. Therefore, we can conclude that, in the Fe–Mo base alloys containing such an element as has negative interchange energy with Fe, the spinodal region, in general, expands toward the lower Mo-content region. Strictly speaking, in the Fe–Mo–X ternary alloys, we cannot neglect the effect of the interchange energy between molybdenum and X on the spinodal decomposition behaviour. When selecting some element for X, however, considering the interchange energy only between iron and X is enough for the first stage screening. This is our basic idea for selecting some alloy system as a candidate for ultra high strength steel.

2.2. Refinement of grain size

Developing a fine grain, fine subgrain, etc. is an essential factor in achieving the high strength metallic material [6]. In the present study, two types of mechanical workings are operated in order to refine microstructure, as follows (see Fig. 3):

1. before ageing, the sample is hot-rolled (about 80% reduction) during quenching from homogenizing (solution treatment) temperature to iced brine; the temperature at which the hot rolling is finished is just below the recrystallization temperature (hereinafter called the TM-treatment),
2. the sample subjected to the TM-treatment is rolled at room temperature (about 80% reduction) before ageing (hereinafter called TMC-treatment).

3. Experimental details

According to the idea (a) mentioned above, Fe–Mo–Co, Fe–Mo–Co–V and Fe–Mo–Co–Mn alloys were chosen to be candidates for high strength steel; their chemical compositions are listed in Table I. Each alloy was melted in a vacuum using a high frequency induction furnace and was cast into an ingot of 22 mm in diameter and of about 200 mm in length. The ingot was formed into a sheet of about 0.9 mm in thickness by forging and rolling (operated at 1573 K) or by TM-treatment.

Each alloy except the TM-treated one was solution-treated (homogenized) at the temperature listed in Table I for 3600 sec in an atmosphere of argon plus hydrogen gas, and was then quenched into iced brine. Ageing was performed in an atmosphere of argon plus hydrogen gas at 773 K for a suitable period of time to ensure the development of a spinodal structure. The metallurgical structure was characterized by means of TEM. Thin foil specimens for TEM observations were obtained by electropolishing the samples thus heat-treated.

Tensile tests were performed at room tremperature at the strain rate of $2.1 \times 10^{-3}\,\text{sec}^{-1}$ by using an Instron type testing machine. The gauge part of all the tensile test pieces except the TMC-treated ones was 2 mm in breadth, 0.5 mm in thickness and 8 mm in length; the gauge part of the TMC-treated test pieces was 2 mm in breadth, 0.1 mm in thickness and 8 mm in length.

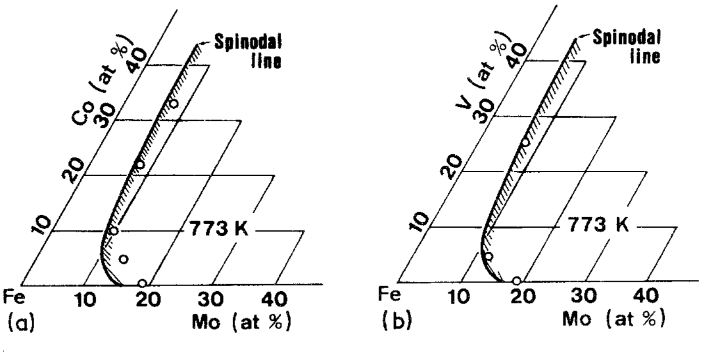

Figure 2 Coherent spinodal lines at 773 K calculated theoretically for the (a) Fe–Mo–Co and (b) Fe–Mo–V systems. Each open circle indicates the chemical composition at which the occurrence of spinodal decomposition is recognized.

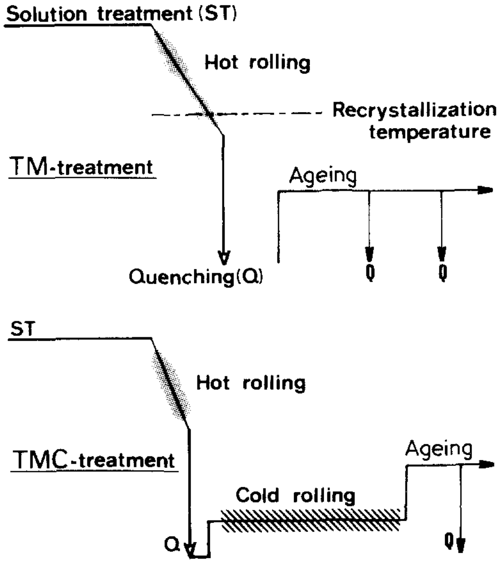

Figure 3 Schematic illustrations showing two types of mechanical workings operated in order to refine microstructure: thermomechanical treatment (TM-treatment); thermomechanical treatment followed by cold rolling (TMC-treatment).

TABLE I Chemical compositions and solution treatment temperatures of the alloys used in the present study.

	Chemical composition (at %)					Solution-treatment temperature (K)
	Fe	Mo	Co	V	Mn	
CO-1	bal.	13.8	5.4	–	–	1673
CO-2	bal.	9.7	10.0	–	–	1623
CO-3	bal.	8.2	22.2	–	–	1573
CO-4	bal.	6.1	31.4	–	–	1573
CO-5	bal.	7.2	42.1	–	–	1573
CV-1	bal.	8.89	35.71	3.67	–	1523
CV-2	bal.	9.87	31.81	7.65	–	(1373)
CV-3	bal.	9.41	27.68	11.43	–	*
CM-1	bal.	7.4	25.2	–	3.5	1523

*In the as-solution-treated state, we cannot obtain the one-phase structure.

4. Experimental results

4.1. Fe–Mo–Co ternary alloys

Among the five Fe–Mo–Co ternary alloys listed in Table I, only the CO-5 exhibits a considerable amount of elongation in the as-quenched (solution-treated) state; all the Fe–Mo–Co ternary alloys except the CO-5 are so brittle that sometimes the tensile test pieces were unobtainable. The CO-5 has a structure of lath martensite in the as-quenched state, as shown in Fig. 4a. When the CO-5 is aged at 773 K, the ⟨1 0 0⟩ modulated structure develops inside the lath because of spinodal decomposition (see Fig. 4b). During ageing at 773 K, the hardness of the CO-5 gradually increases and finally exceeds 1000 in mHv, as indicated by open circles in Fig. 5. However, the CO-5 becomes more and more brittle with ageing, as shown in Fig. 6.

4.2. Fe–Mo–Co–V quadruple alloys

The CV-1 quadruple alloy has the structure of lath martensite and exhibits the ⟨1 0 0⟩ modulated structure inside the lath by ageing at 773 K, as shown in Fig. 7. If the V-content is increased, a uniform one-phase structure of martensite cannot be obtained because of the precipitation of a large intermetallic compound containing molybdenum or an existence of the α-phase. In the case of CV-1, ageing at 773 K causes an increase in hardness as indicated by the full circles in Fig. 5 and improves the tensile strength especially in the early stage of ageing as shown in Fig. 6. However, the probability of intergranular fracture is tending upward with ageing and the maximum value of the strength obtained so far is limited to about 1.7 GPa (see Fig. 6).

4.3. Fe–Mo–Co–V quadruple alloys with refined grains

When the CV-1 is hot-rolled during quenching (hot rolling is continued from 1523 to 1073 K) and then is aged at 773 K (i.e., TM-treatment illustrated in Fig. 3), the ⟨1 0 0⟩ modulated structure is formed inside the lath, as shown in Fig. 8. The grain size is refined to about 4 μm and the maximum value of the tensile strength obtained so far is 2.98 GPa, as shown in Fig. 9. When the TM-treated CV-1 is subjected to cold rolling followed by ageing at 773 K (TMC-treatment illustrated in Fig. 3), the microstructure becomes more refined and the ⟨1 0 0⟩ modulated structure is also formed in the lath martensite (see Fig. 10). Consequently, the TMC-treated CV-1 exhibits extremely high tensile strength of 3.98 GPa although the plastic elongation is only a little, as shown in Fig. 9.

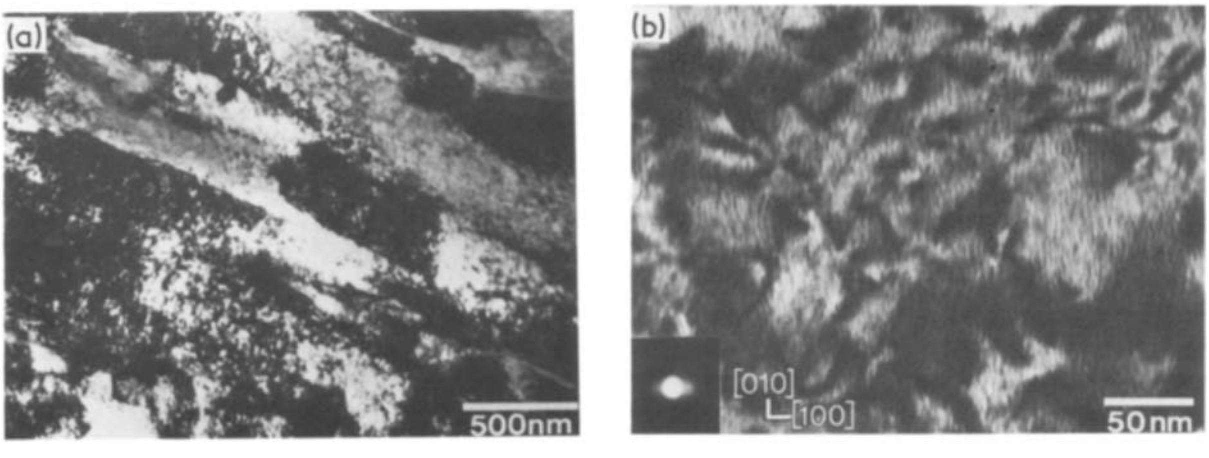

Figure 4 TEM images of CO-5 alloy (Fe–7Mo–42Co): (a) as-solution-treated; (b) aged at 773 K for 1200 sec. The as-solution-treated structure consists of lath martensite and the ⟨1 0 0⟩ modulated structure is developed inside the lath by ageing.

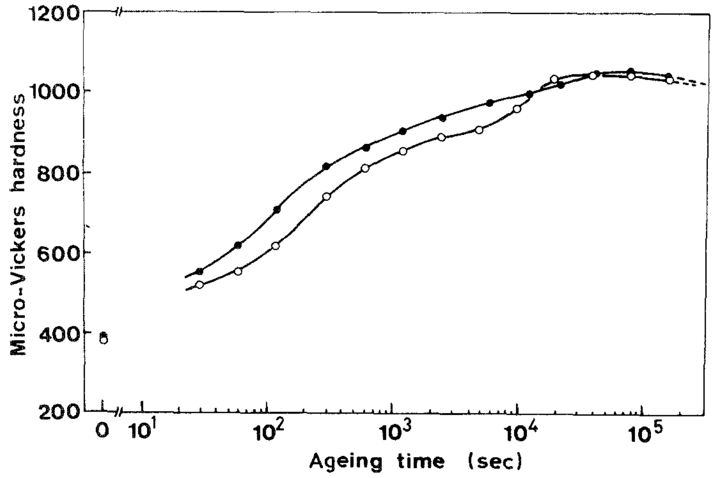

Figure 5 Age-hardening curves of (○) CO-5 (Fe–7Mo–42CO) and (●) CV-1 (Fe–9Mo–36Co–4V) alloys aged at 773 K.

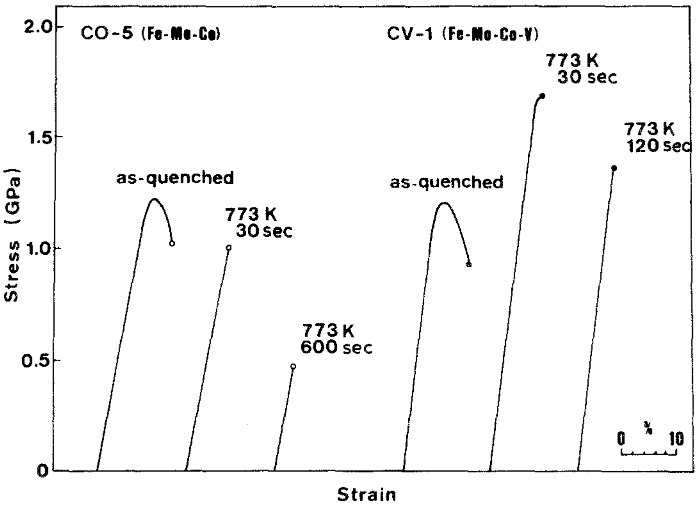

Figure 6 Stress–strain curves obtained at room temperature for CO-5 (Fe–7Mo–42Co) and CV-1 (Fe–9Mo–36Co–4V) alloys aged at 773 K.

5. Discussion

5.1. Course of winning a 4 GPa grade high tensile Fe–Mo–Co–V alloy

The CO-5 is an Fe–Mo–Co ternary alloy obtained by adding a considerable amount of cobalt to the Fe–Mo binary system which is considered to have some potentially desirable properties for high strength steel. The effect of alloying with cobalt is an expansion of the spinodal region of Fe–Mo binary system toward the lower Mo-content region; furthermore, the addition of a large amount of cobalt gives a one-phase structure of lath martensite. The CO-5 is improved in ductility to some extent in the as-quenched state. Far from strengthening, however, the ageing, which aims at strengthening the CO-5 by spinodal decomposition, brings an unstable fracture at the stress level lower than that of the as-quenched state.

The promising idea which first occurred to us is the addition of some alloying element to the CO-5 ternary alloy. A series of the CV alloys listed in Table I are those obtained by replacing a part of the cobalt in the CO-5 with vanadium; with respect to the expansion of spinodal region toward the lower Mo-content region, the addition of vanadium has a similar effect to that of

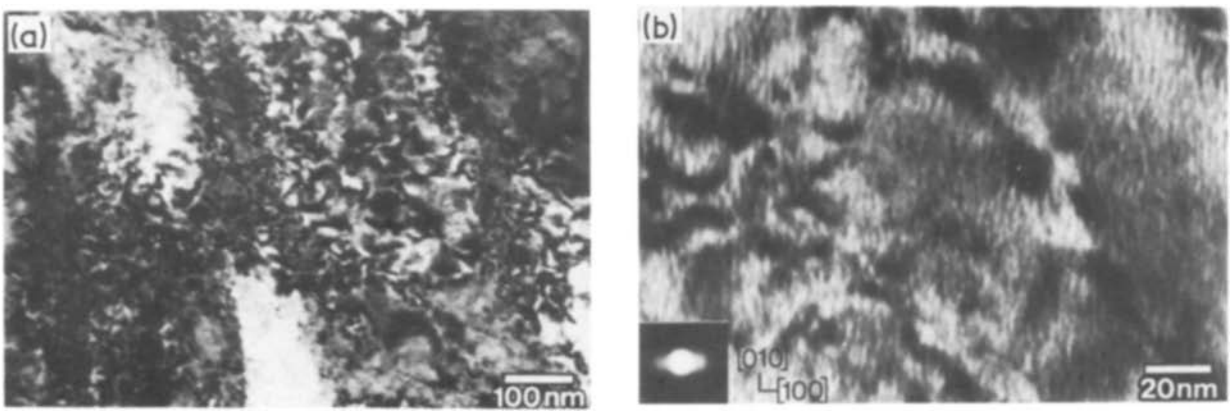

Figure 7 TEM images of CV-1 alloy (Fe–9Mo–36Co–4V) aged at 773 K for 120 sec: the $\langle 100 \rangle$ modulated structure develops inside the lath, which is quite similar to that of CO-5 alloy.

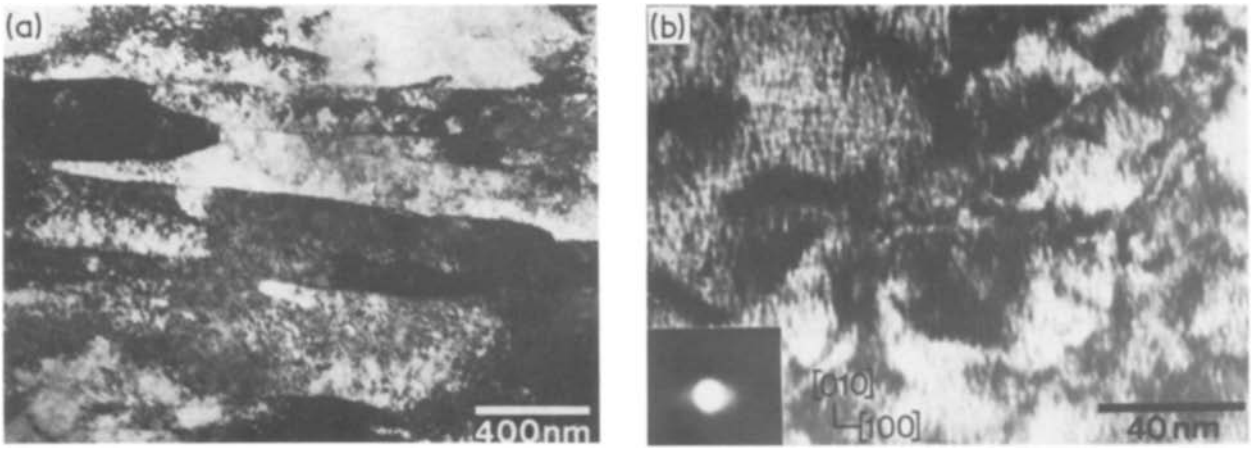

Figure 8 TEM images of TM-treated Fe–9Mo–36Co–4V (TM-CV-1) alloy aged at 773 K for 180 sec: the ⟨1 0 0⟩ modulated structure develops inside the lath.

cobalt, as illustrated in Fig. 2. In these Fe–Mo–Co–V alloys, we must note that the one-phase uniform structure (of martensite) is difficult to obtain when the V-content is unneccessarily high: the CV-1 is the most desirable one among them. Although strengthened by ageing for a short period of time, the tensile strength of CV-1 is also decreased with further ageing because the unstable fracture occurs at low stress level.

Judging from the interior structure of grains, i.e., the ⟨1 0 0⟩ modulated structure obtained by spinodal decomposition, the CV-1 seems to be the strongest by far. However, the truth is that the CV-1 fails at the stress level much lower than that expected. Scanning electron microscopy (SEM) indicates the occurrence of intergranular fracture. Taking the fracture mode into consideration, drawing the ability for high strength material from the CV-1 requires clearing the harmful influence of grain boundaries.

In the TM-treated CV-1 the harmful influence of grain boundaries is designed to be reduced by grain refining. This idea has achieved a fair success: we have actually obtained a high strength of about 3 GPa. Here, we must avoid the unnecessarily high temperature TM-treatment, e.g., near 1523 K, lest the intermetallic compound containing molybdenum should precipitate. The reduction in thickness by TM-treatment should also be about 80%. We cannot see any essential difference between the ⟨1 0 0⟩ modulated structure in the TM-treated CV-1 and that in the non-TM-treated CV-1 (see Figs 4 and 8). In other words, the spinodal decomposition takes place regardless of the lattice defects (e.g. grain boundaries, dislocations, etc.) introduced by previous working. This is a good example of the availability of spinodal decomposition to the development of new types of alloys.

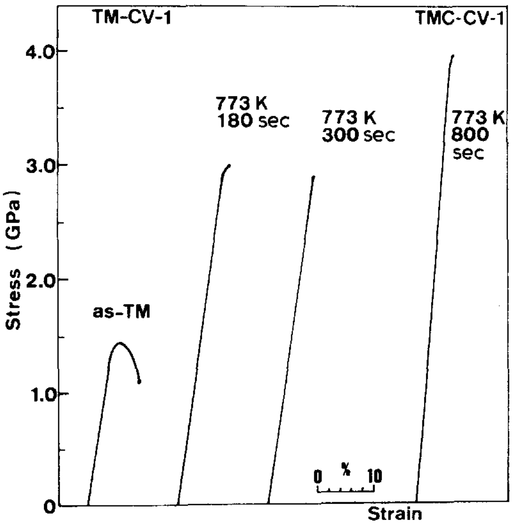

Figure 9 Stress–strain curves of TM-treated and TMC-treated Fe–9Mo–36Co–4V alloys, i.e., TM-CV-1 and TMC-CV-1, respectively, aged at 773 K.

Now, it is expected from the extremely high hardness that the Fe–Mo–Co–V alloy should still have a latent ability to exhibit a strength higher than that of the TM-treated CV-1. In the TMC-treatment, the cold rolling aims at refining further the microstructure of the TM-treated CV-1. In this case also, the feature that the spinodal decomposition is not virtually influenced by any previous mechanical working contributes to the gaining of a 4 GPa grade high tensile Fe–Mo–Co–V alloy: in the TMC-treated CV-1, the ⟨1 0 0⟩ modulated structure is well-developed inside the very fine subgrains of lath martensite (see Fig. 10).

The tensile strength data for Fe–Mo–Co and Fe–Mo–Co–V alloys obtained in the present study are summarized in Fig. 11; the open symbols represent the occurrence of local constriction, the shadowed ones the occurrence of yielding prior to fracture, the full ones the occurrence of unstable fracture at low stress levels without yielding. This figure clearly illustrates the course of winning a 4 GPa grade high tensile steel explained before. The TMC-treated CV-1 is fractured at about 4 GPa after a yielding actually occurs, and furthermore the SEM observation indicates the fractured surface exhibits a kind of ductile fracture; these experimental facts prove the availability of the Fe–Mo–Co–V quadruple alloy to be a high strength material.

However, it should be noted that a prolonged ageing brings the precipitation of stable λ-phase (Fe_2Mo) and hence the occurrence of unstable fracture; the precipitation of the λ-phase takes place in a little over 2000 sec, as shown in Fig. 11. Further strengthening is probably realized by the addition of some alloying elements which retard the precipitation of λ-phase together with the microstructure refining.

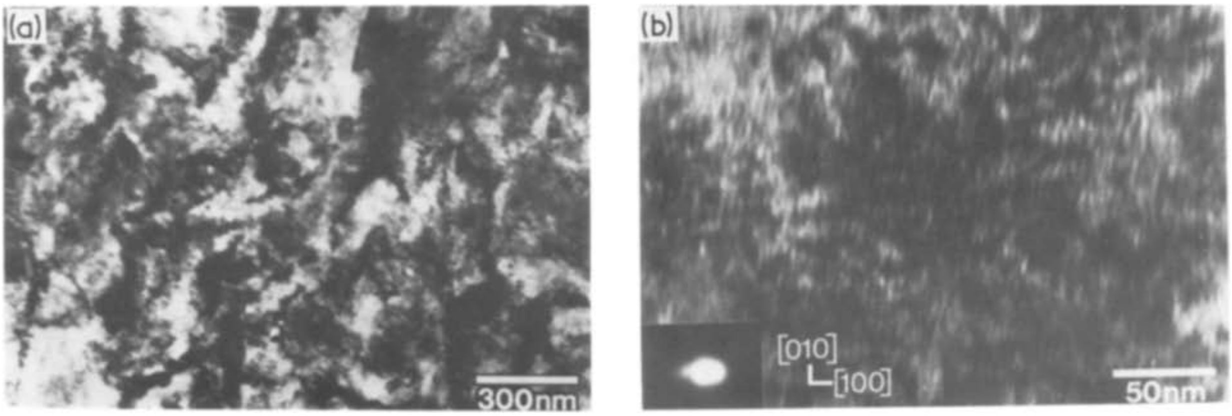

Figure 10 TEM images of TMC-treated Fe–9Mo–36Co–4V (TMC-CV-1) alloy aged at 773 K for 800 sec: (a) the lath martensite structure becomes refined, and (b) the ⟨1 0 0⟩ modulated structure develops inside the lath.

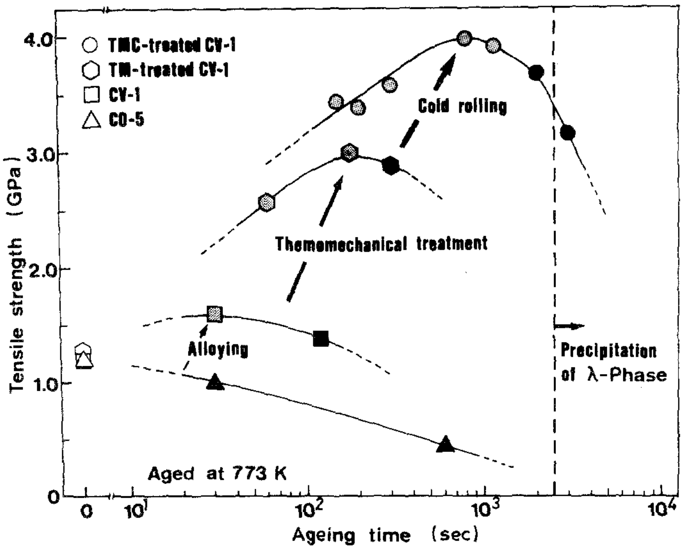

Figure 11 Schematic illustration showing our course of winning a 4GPa grade high tensile steel of Fe–Mo–Co–V: open symbols indicate the occurrence of local constriction; shadowed ones the occurrence of yielding; full ones the occurrence of unstable fracture without yielding.

5.2. Fe–Mo–Co–Mn quadruple alloys

With respect to the effect on the spinodal decomposition in the Fe–Mo system, it is expected that manganese should behave in a quite similar way to vanadium because the interchange energy between iron and manganese is near zero [7]. Therefore, the Fe–Mo–Co–Mn alloy, which is obtained by the addition of manganese (instead of vanadium) into the Fe–Mo–Co ternary alloy, is also considered to be a promising candidate. To obtain the one-phase structure of lath martensite by quenching, and furthermore to develop a spinodal structure inside the lath by ageing, the chemical composition must be kept around that of the CM-1. The CM-1 aged at 773 K exhibits the maximum hardness of about 1000 mHv and the ⟨1 0 0⟩ modulated structure inside the lath (see Figs 12a and 13, respectively). The ageing of the TM-treated CM-1 at 773 K results in the high tensile strength of 2.78 GPa (see Fig. 12b). These results are as we have expected beforehand and prove the availability of our idea proposed in the present paper. (The details of the results obtained for the Fe–Mo–Co–Mn alloys will be presented elsewhere.)

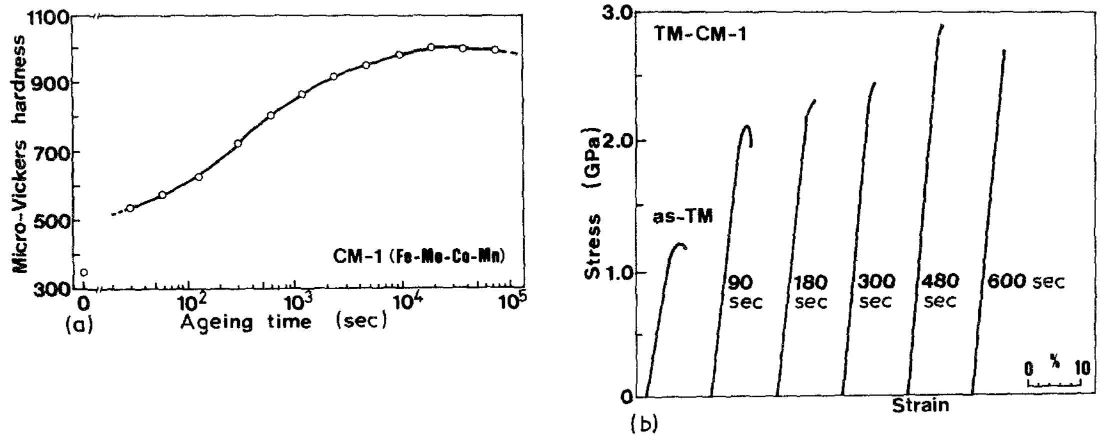

Figure 12 (a) Age-hardening curve of CM-1 alloy (Fe–7Mo–25Co–4Mn) aged at 773 K, and (b) stress–strain curves of TM-treated CM-1 alloy (TM-CM-1) aged at 773 K.

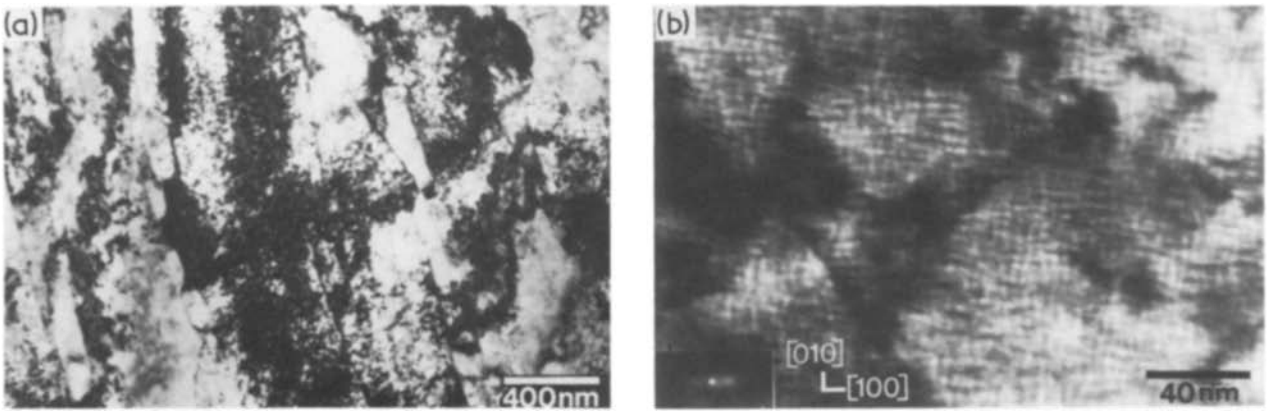

Figure 13 TEM images of CM-1 alloy (Fe–7Mo–25Co–4Mn): (a) solution-treated; (b) aged at 773 K for 300 sec. The ⟨1 0 0⟩ modulated structure develops inside the lath.

5.3. Fe–Mo–Co–Ni quadruple alloys

Another alloying element which seems to act as a substitute for vanadium is nickel because the interchange energy between iron and nickel is near zero [8]. The TEM observation and the theoretical calculation actually indicate that the alloying with nickel expands the spinodal region of the Fe–Mo binary system toward the lower Mo-content region, as shown in Fig. 14. When being chosen so as to cause spinodal decomposition in lath martensite, the chemical composition finally obtained becomes close to that of 3.5 GPa grade Fe–Ni maraging steels, e.g., Fe–14 mass% Mo–18 mass% Co–8 mass% Ni (i.e., Fe–9 at% Mo–18 at% Co–8 at% Ni) reported by Mihalisin and Bieber [9]. In this type of maraging steels, the ⟨1 0 0⟩ modulated structure due to spinodal decomposition has been observed (e.g., Fe–14 mass% Mo–21 mass% Co–8 mass% Ni) [10] and the tensile strength as high as 4 GPa has been reported (e.g., Fe–12 mass% Mo–18 mass% Co–10 mass% Ni–2 mass% Ti) [11]. According to such facts, it is certain that the high strength of the Fe–Ni maraging steels is attributed to the occurrence of spinodal decomposition. These types of Fe–Ni maraging steels fall under the same category proposed in the present study: it is obtained by alloying the Fe–Mo–Co ternary system with nickel which coincides with such an element as expands the spinodal region of the Fe–Mo binary system toward the lower Mo-content region.

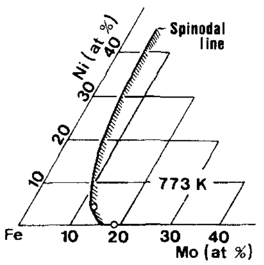

Figure 14 Coherent spinodal line at 773 K calculated theoretically for the Fe–Mo–Ni ternary system. Each open circle indicates the chemical composition at which the occurrence of spinodal decomposition is recognized by TEM.

6. Conclusion

The behaviour of spinodal decomposition is easily controlled by alloying with some appropriate elements which, in general, have a tendency toward ordering when combined with iron. Furthermore, the spinodal decomposition is hardly influenced by lattice defects such as grain boundaries, dislocations, etc. Actually, we have successfully developed an ultra high strength spinodal alloy by using thermomechanical treatment and cold rolling with the modification of alloy composition. There are many spinodal alloys having latent availability for high strength material because of the existence of a very fine and quite uniform microstructure. The method which we have proposed in the present study is sure to be a success in improving the mechanical properties of such alloys: there is good hope for success in obtaining various kinds of high strength materials by utilizing spinodal decomposition.

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