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2205 雙相不銹鋼之肥粒鐵離相與差排結構研究

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主持人： 楊哲人教授（國立台灣大學材料系）

The sinodal decomposition and dislocation structure in the ferrite phase of a 2205 duplex stainless steel

Abstraction

The effect of isothermal treatment (at temperatures ranging between 400 and 500℃) on the embrittlement of a 2205 duplex stainless steel (with 45 ferrite–55 austenite, vol%) has been investigated. The impact toughness and hardness of the aged specimens were measured, while the corresponding fractography was studied. The results show that the steel is susceptible to severe embrittlement when exposed at 475 ℃; this aging embrittlement is analogous with that of the ferritic stainless steels, which is ascribed to the degenerated ferrite phase. High-resolution transmission electron microscopy reveals that an isotropic spinodal decomposition occurred during aging at 475 ℃ in the steel studied; the original δ-ferrite decomposed into a nanometer-scaled modulated structure with a complex interconnected network, which contained an iron-rich BCC phase (α) and a chromium-enriched BCC phase (α′). It is suggested that the locking of dislocations in the modulated structure leads to the severe embrittlement.

Keywords: Duplex stainless steel; Embrittlement; Impact toughness; Hardness; Spinodal decomposition; Nanometer-scaled modulated structure.

1. Introduction

Duplex stainless steels have been widely used in oil, chemical and nuclear industries due to their high strength, good weldability, and high resistance to stress corrosion and pitting [1,2]. The superior properties of the duplex stainless steels come primarily from approximately equivalent amounts of austenite (γ) and δ-ferrite. However, these types of steels are intrinsically subject to embrittlement when exposed to temperatures above 300℃, because of solid-state reactions within the ferrite phase [3-5]. The 2205 duplex stainless steel is a progenitor of modern duplex stainless steels, and it is worth understanding the embrittlement phenomena. Previous work has been carried out on the microstructural stability and toughness properties of a 2205 duplex stainless steel aged in the temperature range of 650 - 975 ℃, where the formation of σ and χ phase is found to promote severe deterioration in toughness [6]. In the present work, an attempt is made to investigate the same steel aged in the temperature range of 400 - 500 ℃, where a miscibility gap for the decomposition of δ-ferrite presumably exists. The effects of low-temperature aging on the embrittlement and the corresponding phase transformation in a 2205 duplex stainless steel have been carried out. The atomic structure of decomposed δ-ferrite in this steel has been observed via a 300 kV field-emission-gun transmission electron microscope (FEG-TEM), Tecnai F30.

2. Experimental Procedure

The as-received material was a commercial wrought 2205 duplex stainless steel rod (with a diameter of 53 mm) produced by Gloria Material Technology Corporation through the fourfolded forging of a cast slab at 1160 - 1180℃ and annealing at 1050 ℃ for 30 min, followed by water quenching. The chemical composition of the alloy is listed in Table 1. In this work, aging treatments in the temperature range of 400 - 500 ℃ for various time intervals from 5 min to 64 h were carried out and the corresponding microstructural features, hardness and Charpy impact toughness were determined.

Specimens for optical metallography were prepared from the aged specimens and electrolytically etched in a 32 N KOH solution. Transmission electron microscopy specimens were also prepared from the aged specimens. The detailed microstructures and microanalyses on the aged specimens were investigated using a JOEL JEM 2000 EX Ⅱ equipped with an energy-dispersive X-ray spectrometer (EDS). Furthermore, the structural and compositional analyses of sub-nanometer scaled structures were examined using a FEG-TEM Tecnai F30 equipped with nanometer probe EDS.

3. Results and Discussion

The optical micrographs shown in Figs 1(a) and (b) were obtained from the as-received 2205 duplex stainless steel bar studied in this experiment. The structure consists of white etched austenite (γ) islands embedded in a gray etched δ-ferrite matrix with no other secondary precipitates. As a consequence of being deformed in the two-phase region, a banded texture of elongated γ islands is observed on the longitudinal section (Fig. 1(a)), while the more isotropic structure of γ-grain is found on the transverse section (Fig. 1(b)). The volume fraction of γ phase measured by quantitative metallography is about 0.55. The concentrations of major alloying elements in the δ and γ phases have been analyzed by EPMA for the as-received specimen. The measured composition of δ-ferrite is 66.6 Fe - 23.8 Cr - 3.86 Ni - 3.92 Mo - 1.35 Mn - 0.44 Si (wt%).

Charpy impact toughness was determined at room temperature using three specimens for each combination of aging time and temperature. The results are presented in Fig. 2(a); it can be seen that the toughness decreases with increasing the aging time. In the cases of aging at 450, 475 and 500 ℃, a significant decrease in toughness occurs in the initial stage and subsequently an accelerated drop in toughness happens. However, the drop in toughness in the same early stages is negligible in the case of aging at 400℃. For the specimens aged at 475 ℃ for 8 h, the impact energy falls to less than half (150 J), when compared with the specimens without aging (i.e., the impact energy of the as-received material is 304 J). An impact energy of 10 ft-lb (13.5 J) is usually considered as a valid criterion for the complete embrittlement condition. For specimens aged at 475 ℃, it takes 32 h to reach this condition; the results are also consistent with those obtained from fractographic evaluations. It is evident that aging at 475 ℃ leads to severe deterioration in the toughness of the steel investigated. Fig. 2(b) shows the variation of Rockwell C hardness (HRc) as a function of aging time at different aging temperatures; it indicates that the hardness increases with increasing aging time at all temperatures except for the initial stage of the aging at 400 ℃. This result indicates that the embrittlement phenomenon is accompanied by an increase in hardness. Fig. 3 shows the indentations of Vickers micro-hardness on δ-ferrite and austenite phases in the specimens aged at 475 ℃ for different aging times; the size of indentations in δ-ferrite decreases with increasing of aging times, but in austenite hardness appears to be nearly the same. A plot of Vickers micro-hardness versus aging time for different aging temperatures is attached in Fig. 3; the data suggests that the embrittlement in the steel is mainly associated with the aging hardening of δ-ferrite.

During aging the hardness of the δ-ferrite increases significantly, but the hardness of austenite remains essentially constant. This result consistently suggests that the embrittlement phenomenon of the duplex stainless steel studied is presumably connected with the microstructural evolution of δ-ferrite. A series of microstructural features in the specimens aged at 475 ℃ for different aging times has been studied by TEM. TEM bright field images for the specimens aged at 475 ℃ for different aging times have been observed under a two-beam condition as illustrated in Fig. 4. In this study, the diffraction conditions of the two-beam render some dislocations invisible, however, the percentage of invisible dislocations can be calculated if it is assumed that all dislocations satisfying the invisibility criterion ($\vec{g} \cdot \vec{b} = 0$) are out of contrast. Evidently, aging produced a remarkable change in the dislocation structure of the δ-ferrite. The striking feature from the above TEM micrographs indicates that the evolution of dislocation structure occurs in a form of cross-stitch in δ-ferrite during aging. The decomposed δ-ferrite with the complex dislocation structure is assumed to be due to the differences in thermal expansion between δ and γ phases, and it is also related to the cross-slip of dislocations during aging. A similar observation has been reported by Miller et al. [7], who investigated a duplex stainless steel, CF8, aged at 400 ℃ for 7×10^4 h. In this work the dislocation structure with a cross-stitch pattern is significant, since it provides strong support to suggest that the immobilization of dislocations in δ-ferrite is detrimental to toughness. However, Further work is needed in this area to understand the formation mechanism of these pinned dislocations in the aged δ-ferrite.

Field-emission gun transmission electron microscopy was used to investigate the detailed nano-scaled structure of the aged specimens. Fig. 5 is an image taken from the δ/γ interface of the specimen aged at 475 ℃ for 2 h. It is noticeable that there is a sudden change from the modulated contrast in δ-ferrite to an even contrast in γ. The mottled image of δ-ferrite can be seen much more clearly when the electron beam is aligned along the <001> zone axis. This result is consistent with that claimed by Nichol et al. [8]. The mottled image, which has the appearance of an orange peel, has been found in TEM bright field micrographs of aged ferritic and duplex stainless steels. The mottled aspect has been attributed to the nucleation and growth of Cr-rich α′ particles or to a spinodal decomposition reaction. The contrast mechanism is not clear, although it has been presumed to be due to differential oxidation of the two phases during the preparation of the TEM thin foils. Because of Fe and Cr partitioning at an extremely fine scale, the interpretation of the microstructural features should be made with care. However, earlier investigations using TEM failed to reveal the detailed nanometer-scaled structure and chemistry [9]. On the other hand, atom probe field ion microscopy has revealed the phase separation due to the spinodal decomposition into an ultrafine mixture of a Cr-enriched α′ and a Fe-rich α. Furthermore, the three-dimensional α′ phase has been reconstructed by Miller et al. [10] who suggest that the α′ phase forms a typical complex interconnected network structure.

In the present investigation, a periodically modulated contrast (Fig. 5) occurs in the ferrite without a denuded zone in the immediate vicinity of the δ/γ interfaces. The evidence strongly suggests that the phenomenon of spinodal decomposition occurs in δ-ferrite during aging at 475 ℃. The morphology of the modulated microstructure for the specimens aged at 475 ℃ is shown in Fig. 6. These micrographs reveal phase separation in the specimens aged for 2 - 64 h but it is difficult to resolve in specimens aged for less than 2 h. The scale of this two-phase modulated microstructure has been measured to be 1.7, 2.5, 3.3, 4.2, 4.3 and 5.0 nm for aging times of 2, 4, 8, 16, 32 and 64 h, respectively. The modulated microstructure is observed to coarsen with aging time, the morphology being similar. The sequences of FEG-TEM (Fig. 6) reveals that the two-phase mixture is irregularly shaped and fully interconnected as resembling a sponge, indicative of the typical nature of the isotropic spinodal structure [11]. Nanometer-scaled chemical analysis has been conducted using a FEG-TEM containing an EDS; the fine scale isotropic spinodal decomposition of δ-ferrite brings about Cr-rich bright image domains and Fe-rich dark image domains, i.e., α′ and α phases, separately. It also shows that Mo and Mn are partitioning to the α′ phase, while Ni is partitioning to the α phase. [100] electron diffraction patterns (Fig. 7(c)) taken from a selected area of the two-phase modulated structure shows only one set of BCC diffraction spots without flanking satellites. It is apparent that the lattice mismatch between α′ and α phases is extremely low (a_{Cr} = 2.885 Å, a_{Fe} = 2.866 Å for the pure elements) although the α′ phase has a high level of Cr. In the lattice image (Fig. 7(b)), it is difficult to identify the interfaces between the α′ and α phases. Indeed, this lattice image reflects the nature of the isotropic spinodal structure; the elastic coherent strain of the interfaces is negligible and consequently the two-phase mixture is interconnected without directionality in the three dimensions.

4. Conclusions

Aging embrittlement at temperatures ranging between 400 and 500 ℃ and a corresponding phase transformation in a 2205 duplex stainless steel have been investigated. A summary of the experimental outcome is given as follows :

1. The aging embrittlement at 475 ℃ corresponds to the development of a two-phase modulated microstructure in the aged δ-ferrite; the modulated structure coarsens with aging times, but the morphology is similar. FEG-TEM reveals that this two-phase mixture is irregularly shaped and fully interconnected as spongelike, indicative of a typical isotropic spinodal structure.
2. Dislocation structures with a cross-stitch pattern in the aged δ-ferrite provides strong evidence to suggest that the immobilization of dislocations in this modulated structure causes severe embrittlement.
3. The contrast mechanism for this modulated structure is not clear, and it needs further investigation to elucidate the factors which govern the mottled aspect in the present work.

5. Acknowledgements
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6. References
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Table 1 Chemical composition of the 2205 duplex stainless steel studied (wt%)

C	Si	Mn	P	S	Cr	Ni	Mo	N	Fe
0.02	0.38	1.47	0.022	0.001	22.62	5.12	3.24	0.196	Bal

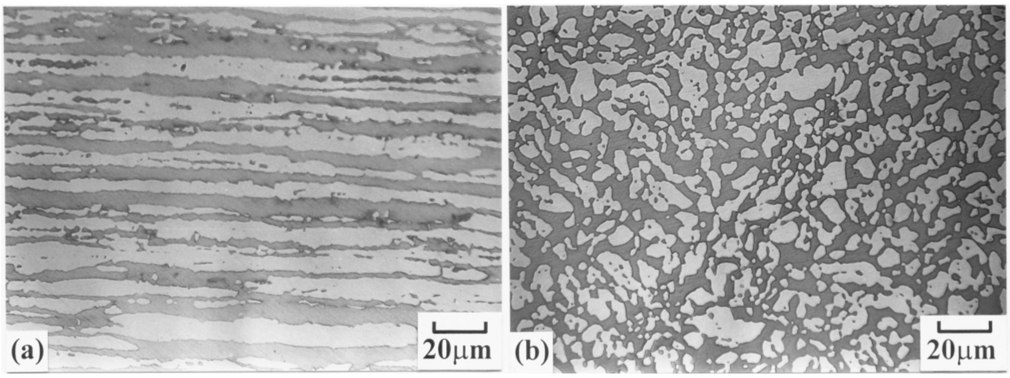

Fig.1 Optical micrographs of as-received steel bar (a) longitudinal section; (b) transverse section.

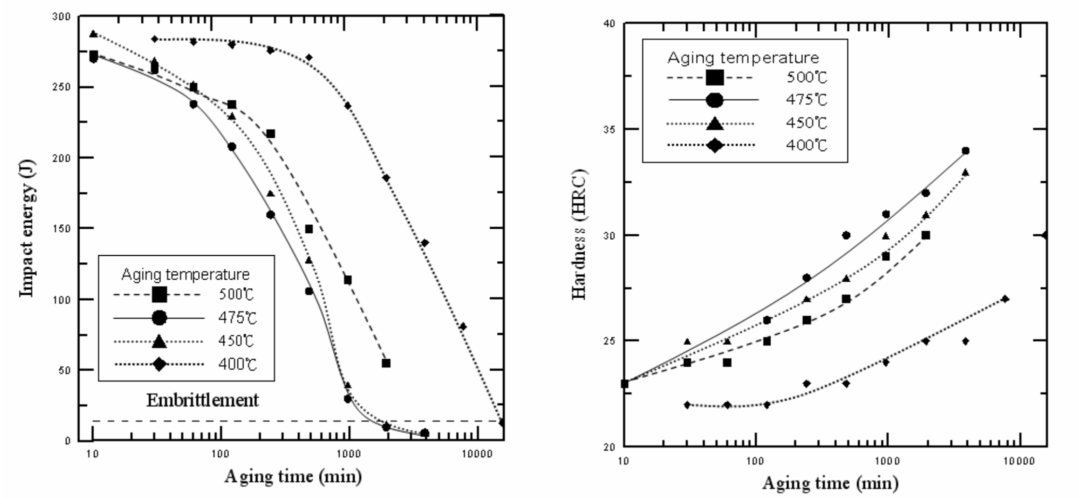

Fig. 2 Effects of aging treatments on Charpy V impact energy and HRc macro-hardness of 2205 duplex stainless steel at 400 – 500℃ (impact energy and hardness of as-received material being 304 J and

HRc 22, respectively).

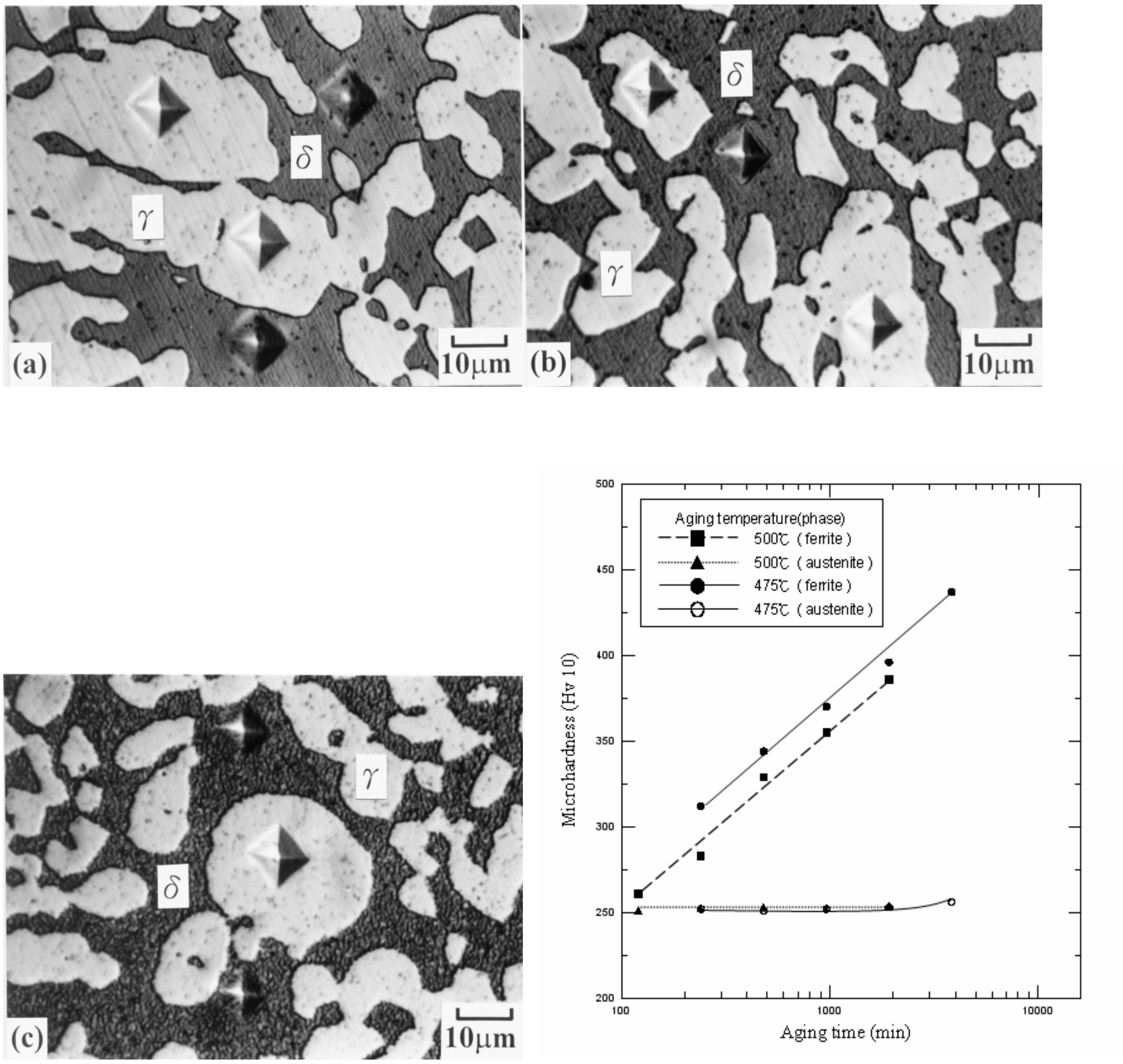

Fig.3 Vickers-hardness indentations of δ and γ phases in the samples ages at 475℃ for (a) 4 h; (b) 8 h; (c) 64 h. A plot of Vickers micro-hardness versus aging time for different aging temperatures is attached..

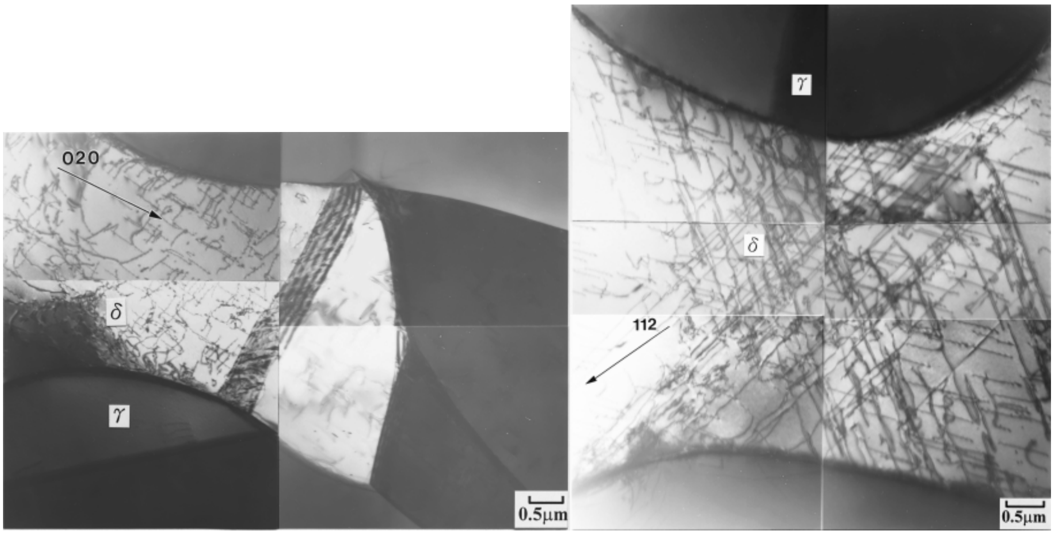

Fig. 4. Dislocation structure in δ-ferrite of the specimens aged at 475℃ for 16 h (left) and 64 h (right). Observation under two-beam conditions g = [0 2 0] and [1 1 2], respectively.

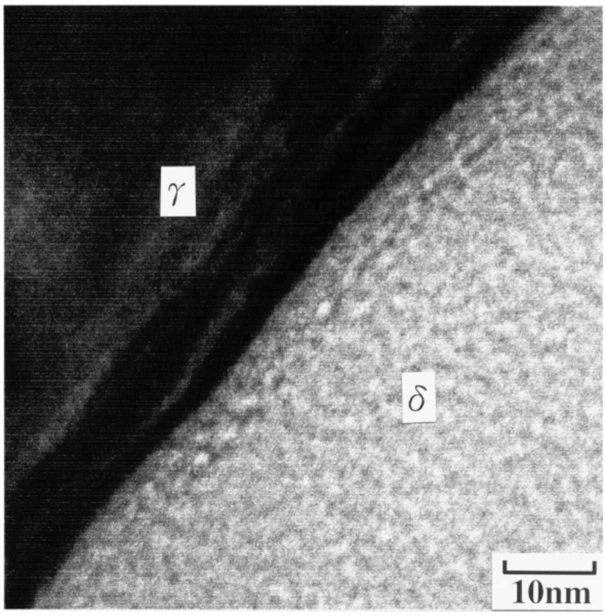

Fig. 5 FEG-TEM showing δ and adjacent γ in the specimen aged at 475℃ for 2h.

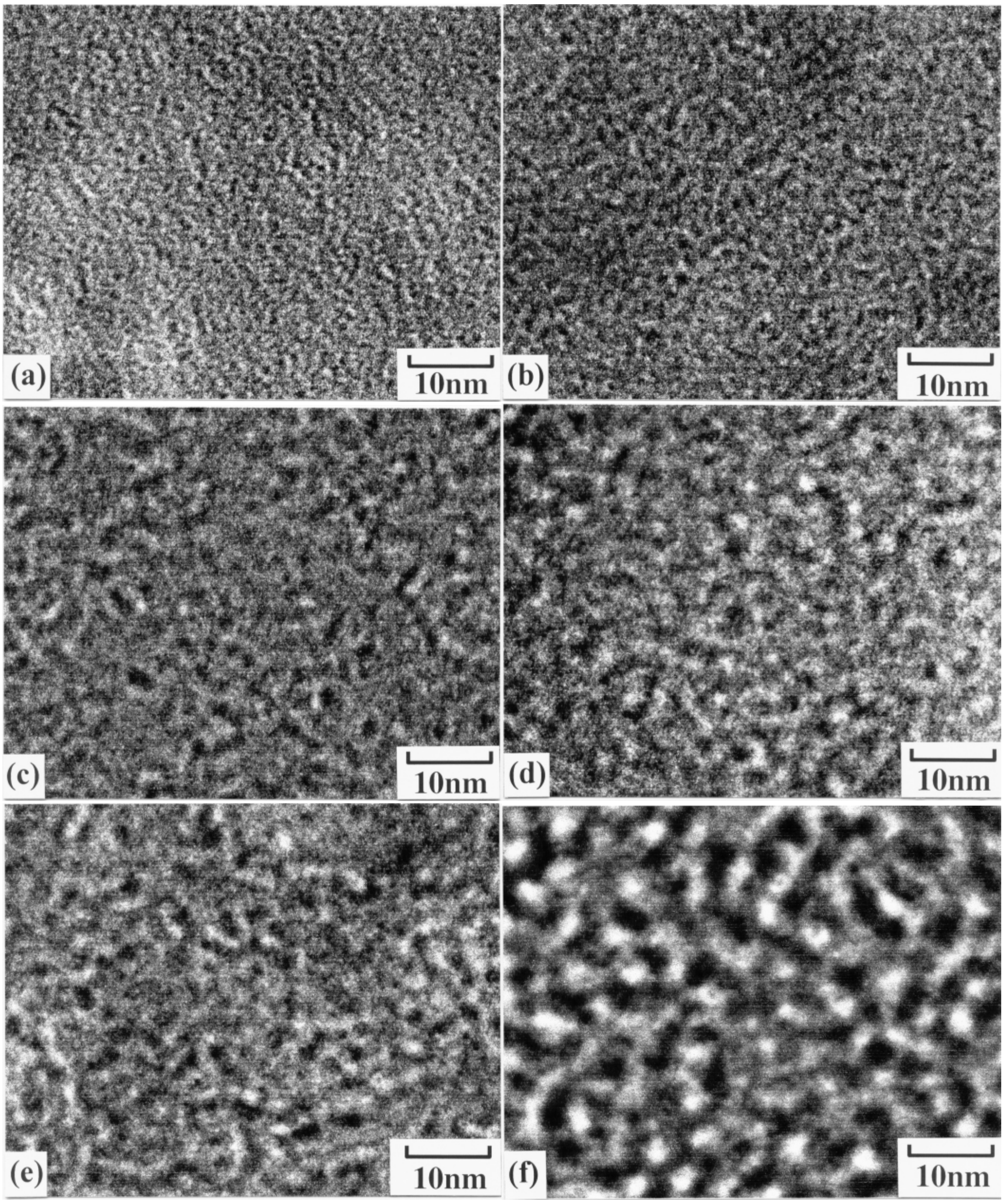

Fig. 6 FEG-TEM showing the morphology of modulated microstructures for specimens aged at 475℃ for different time intervals: (a) 2 h; (b) 4 h; (c) 8 h; (d) 16 h; (e) 32 h and (f) 64 h.

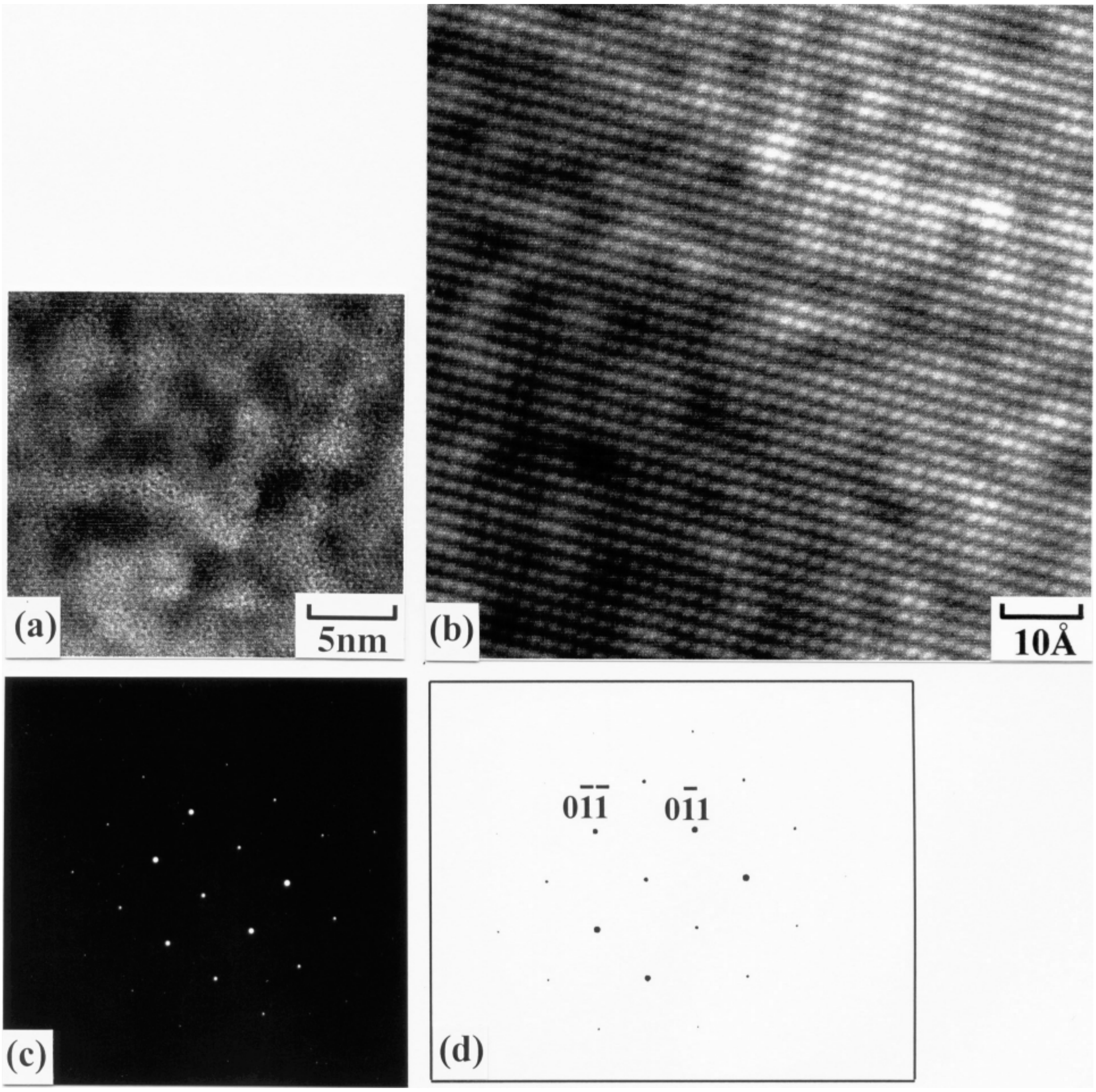

Fig. 7 High resolution images of a typical isotropic spinodal structure obtained from the specimen aged at 475℃ for 64 h: 9a0 modulated microstructure; (b) lattice image; (c) SAD diffraction pattern with [1 0 0] zone axis; (d) schematic interpretation of (c).