



HAL
open science

Hot Ductility and High Temperature Microstructure of High Purity Iron Alloys

K. Abiko

► **To cite this version:**

K. Abiko. Hot Ductility and High Temperature Microstructure of High Purity Iron Alloys. Journal de Physique IV Proceedings, 1995, 05 (C7), pp.C7-77-C7-84. 10.1051/jp4:1995706 . jpa-00253999

HAL Id: jpa-00253999

<https://hal.science/jpa-00253999>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Hot Ductility and High Temperature Microstructure of High Purity Iron Alloys

K. Abiko

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Abstract: The inherent properties of metals are affected by impurity elements, sometimes strongly. There are many brittle phenomena in iron and its alloys due to the harmful effect of trace impurities such as sulphur, phosphorus, hydrogen and so on. On the other hand, a large number of alloying elements also embrittle iron due to the transformation and precipitation of secondary phase. For example, the ductility of Fe-Cr alloy decreases with the increase in chromium content, although the strength and the corrosion resistance increase with chromium content. In Fe-Cr alloy containing high chromium, 475°C embrittlement and σ -phase embrittlement are well known. An Fe-50mass%Cr alloy of conventional purity is extremely brittle due to the formation of σ -phase. However, we found the highly purified alloy is essentially ductile. In the workshop of UHPM-94, the experimental results on the ductility of Fe-50mass%Cr alloy were presented and discussed. In this research, the effect of purification on the hot ductility of high purity Fe-18mass%Cr and Fe-50mass%Cr alloys was investigated by tensile testing at high temperature. It was found that the ductility of Fe-18mass%Cr alloy is remarkably improved by purification, especially by the reduction of interstitial impurities such as carbon and nitrogen. The highly-purified Fe-50mass%Cr alloy has astonishing ductility at the temperature range between room temperature and 1073K. Also in a high purity Fe-50mass%Cr alloy, the formation of the σ -phase was not observed during ageing for 1000h at 973K. These results are also very important for the development of high-performance Fe-Cr alloys and of the manufacturing process. Consequently, purification technology is very useful for progress in metal science.

Keywords: Fe-Cr alloy, σ -phase, Mechanical Properties, Hot ductility, Serration, Work hardening, High temperature strength, Dynamic recrystallization.

1. INTRODUCTION

It is very important for progress in metal science and the development of base metals that the inherent properties of metals, and the intrinsic effect of impurity elements and alloying elements on the properties, should be clarified [1].

There are many brittle phenomena in iron and its alloys due to the effect of harmful impurity elements such as sulphur, phosphorus, hydrogen and so on. For example, phosphorus and sulphur in iron and alloys reduce the cohesion of grain boundaries at near room temperature [2]. Temper embrittlement caused by the segregation of harmful impurities such as phosphorus, antimony and tin at grain boundaries is a serious problem in high strength, low alloyed steels [3].

The hot ductility of iron is also affected by impurity elements. Sulphur reduces the hot ductility of iron at temperatures between 873 and 1073K in tensile tests [4]. On the other hand, phosphorus increases the hot ductility of iron and steel above 773K [5,6].

Many alloying elements also affect the ductility of metals strongly. In the extreme case, the intermetallic compound is well known to be very strong, but brittle. These properties may be caused by strong bonding between compositional elements, and decohesion between impurities and compositional elements. In the case of a solid solution containing a large quantity of alloying elements such as Fe-Cr stainless steel, ductility decreases with the increase in chromium content. Interstitial impurities such as carbon and nitrogen enhance the work hardening of Fe-Cr alloys [7,8]. In other words, the ductility of Fe-Cr alloys is improved by purification, especially by the removal of interstitial impurities. 475°C embrittlement and σ -phase embrittlement in Fe-Cr alloy containing high chromium are well known.

In the workshop of UHPM-94, the experimental results on the ductility of Fe-50mass%Cr alloy were presented and discussed [9]. An Fe-50mass%Cr alloy of conventional purity is well known to be extremely brittle due to the formation of σ -phase. However, we found the highly-purified alloy is essentially ductile. Furthermore, in the highly-purified alloy, no σ -phase is observed after annealing at high temperature. Though this is an astonishing phenomenon resulting from the purification of the alloy, it is significant for progress in metal science and the development of high-performance metallic materials.

In this research, the inherent mechanical properties of Fe-18mass%Cr and Fe-50mass%Cr alloys, and the effect of purification on their hot ductility were investigated by tensile tests at high temperature. The recrystallization behaviour and the formation of σ -phase were also investigated by optical microscope observation .

2. EXPERIMENTAL PROCEDURES

Two kinds of high purity Fe-Cr alloys, Fe-18mass%Cr and Fe-50mass%Cr, were melted by different techniques for the present research. High purity electrolytic iron and high purity chromium were used as the starting materials for these alloys [10]. The mechanical properties of high purity Fe-Cr alloys at high temperature were investigated by tensile testing. The microstructure was observed by optical microscope in order to investigate the static and dynamic recrystallization behaviour .

2-1 High Purity Fe-18mass%Cr Alloy

An ingot of a high purity Fe-18mass%Cr alloy was melted in a crucible lined with high purity CaO. The chemical compositions of the starting materials and the melted Fe-18mass%Cr alloy(HP) were analyzed as shown in Table 1. The ingot was heated at 1273K in a high purity Ar atmosphere, then forged and rolled to rods of 6.5mm in diameter. The specimens for tensile testing were made from the rods by machining. The gauge length and diameter of specimens are 20.0mm and 3.00mm, respectively. The static recrystallization behaviour of a high purity Fe-18mass%Cr alloy after 85% reduction by cold rolling was investigated. Every tensile specimen was heat-treated for 10min at 1213K and quenched in oil at 273K. The grain size of heat-treated specimens was 30 μ m on average. The tensile tests on the high purity Fe-18mass%Cr alloy were mainly performed at a strain rate of 3.9×10^{-5} /sec, at temperatures between 293K and 873K, and in a vacuum better than 5×10^{-6} torr.

element	Cr	C	N	O	S	P	Al	Si	Ni	Mn
High purity electrolytic iron	0.0001	15	3	53	11	0.3	0.1	2	<0.1	<0.01
High purity chromium	99.8	70	40	130	3	10	10	50	10	20
High purity alloy(HP)	18.0	91	4	15	7	2	3	<1	2	2
	(mass%)	(massppm)								

Table 1 The chemical compositions of starting materials and the melted Fe-18mass%Cr alloy (HP).

2-2 Zone Refined Fe-18mass%Cr Alloy

The Fe-18mass%Cr rods of 10mm in diameter were specially purified by the zone refining method in high purity hydrogen flow, in order to obtain a tensile specimen with ultra-low interstitial impurities. The content in carbon, nitrogen and oxygen was analyzed for zone refined alloys(FZ1 and FZ2) as shown in Table 2. The purified rods with different carbon contents were cold-swaged to rods of 6.5mm in diameter, and then tensile specimens were machined from the rods. These specimens were heat-treated in a vacuum for 15min at 1023K and quenched in oil at 273K. The tensile specimen of a high purity Fe-18mass%Cr(HP) alloy was also heat-treated under the same conditions. The grain sizes of HP and FZ2 after the heat treatment were 75 μ m and 65 μ m on average, respectively. Tensile testing of these alloys was carried out under the same conditions as mentioned above.

alloy	C	N	O	S
FZ1	35	2	1	1
FZ2	3	1	1	3

(massppm)

Table 2 The contents of carbon, nitrogen and oxygen were analyzed for zone refined alloys(FZ1 and FZ2).

2-3 High Purity Fe-50mass%Cr Alloy

An ingot of Fe-50mass%Cr alloy was melted in a cold crucible made of copper. The chemical compositions of the starting materials and the melted Fe-50mass%Cr alloy were analyzed as shown in Table 3. The ingot was heated at 1323K in high a purity Ar atmosphere, forged and rolled to rods of 6.5mm in diameter. The specimens for tensile testing were made with the same process as for the high purity Fe-18mass%Cr alloy.

element	C	N	O	S	P	Si	Mn	Al	B
Iron	1.5	0.7	23	1.5	0.7	5	<0.01	0.3	0.1
Chromium	11	31	34	3	3	11	8	10	<0.05
Fe-50%Cr	8.2	13	71	4.4	6	9	3.9	1.9	0.28

(massppm)

Table 3 The chemical compositions of starting materials and the melted Fe-50mass%Cr alloy.

Every tensile specimen was pre-heated for 60min at 1373K and quenched in oil at 273K, and then heated for 60min at 1123K and quenched in oil at 273K. The grain size of heat-treated specimen was about 100 μ m on average. Tensile testing for the high purity Fe-50mass%Cr alloy was performed under the following conditions : at a strain rate of 4.15×10^{-5} /sec, at a temperature between 293K and 1073K, and in a vacuum better than 5×10^{-6} torr

Furthermore, the effect of tungsten on solid solution hardening at high temperature and the hot ductility of a high purity Fe-50mass%Cr alloy were investigated by tensile test.

3. RESULTS AND DISCUSSION

3-1 Hot Ductility of High Purity Fe-18mass%Cr Alloy

The stress-strain curves of a high purity Fe-18mass%Cr alloy(HP) with 91massppm carbon at various temperatures are shown in Fig.1. The strain rate is 3.9×10^{-5} /sec. A sharp yield drop is observed in the stress-strain curves at the temperature between 293K and 773K. The stress-strain curve at 873K shows the shape of dynamic recrystallization during tensile test. Serration is observed in the stress-strain curves at the temperature range between 473K and 773K. According to the degree of serration, the work hardening rate and the ultimate tensile strength increase, but the elongation decreases. The elongation of a high purity Fe-18mass%Cr alloy shows a minimum value at the temperature of 823K. Elongation at temperatures above 873K is more than 50%. On the other hand, the reduction in area of every specimen after tensile testing is more than 80% at temperatures between 293K and 873K.

It is well-known in Fe-C and Fe-N alloys that serration is caused by the interaction between interstitial impurities and movable dislocations [11-13]. Cottrell reported in the investigation on strain-ageing of Fe-N alloy that the activation energy for serration is equal to the activation energy of diffusion of interstitial impurities [14]. Keh et al. reported the same relation in the study on strain-ageing of plain carbon steel [15].

In order to confirm the mechanism of serration in a high purity Fe-18mass%Cr alloy, tensile tests were carried out with different strain rates. When the strain rate increases, the degree of the serration decreases. Then no serration is observed above some strain rates at different temperatures. By the relation between the temperature of the tensile test and the strain rate at which serration occurs as shown in Fig.2, the activation energy for serration is found to be 27.8Kcal/mol. This value should be the activation energy for the diffusion of carbon in Fe-18mass%Cr alloy after the Cottrell model.

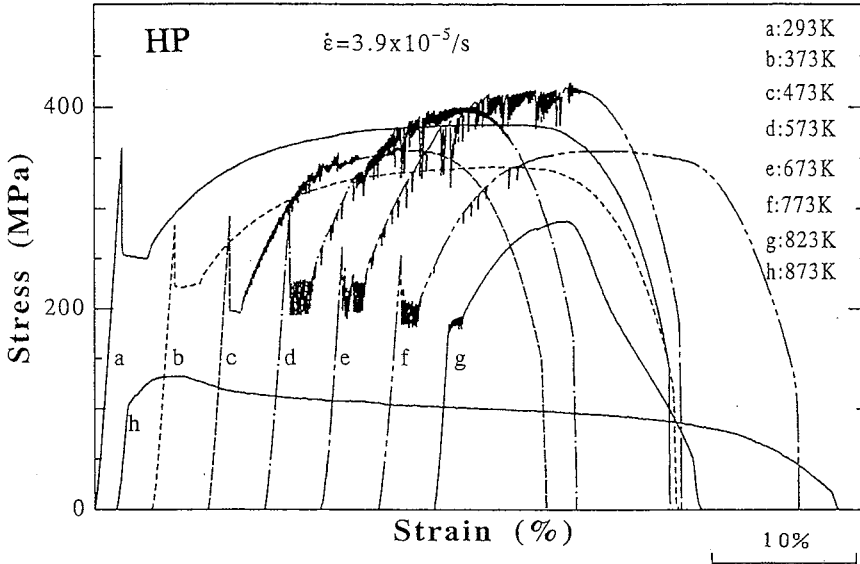


Figure 1 Stress-strain curves of a high purity Fe-18mass%Cr alloy(HP) at various temperatures.

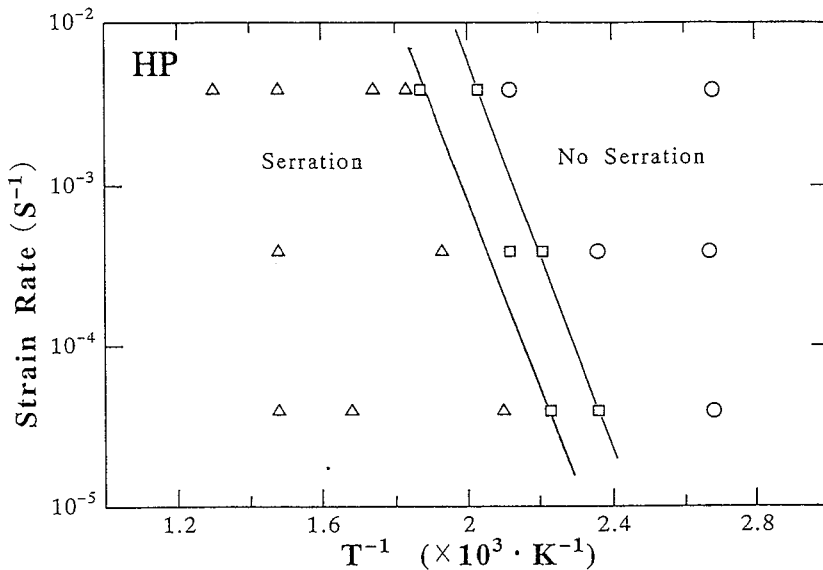


Figure 2 Relation between the temperature of tensile test and the strain rate at which serration occurs.

3-2 Hot Ductility of Zone Refined Fe-18mass%Cr Alloy

The zone refining treatment for Fe-18mass%Cr alloy was performed in high purity hydrogen, in order to clarify the mechanism on the serration of Fe-Cr alloy and the intrinsic effect of carbon on the mechanical

properties. Table 2 shows the contents of interstitial impurities in a high purity Fe-18mass%Cr alloy and zone refined Fe-18mass%Cr alloys. Figures 3 and 4 show the stress-strain curves of HP, FZ1 and FZ2 at 293K and 673K, respectively. The proof stress, the tensile strength and the work hardening rate decrease strongly with the decrease in interstitial impurities. Ductility increases remarkably after the removal of carbon and nitrogen. For example, the elongation of FZ1 and FZ2 at 293K and 673K increases more than 10% from that of HP.

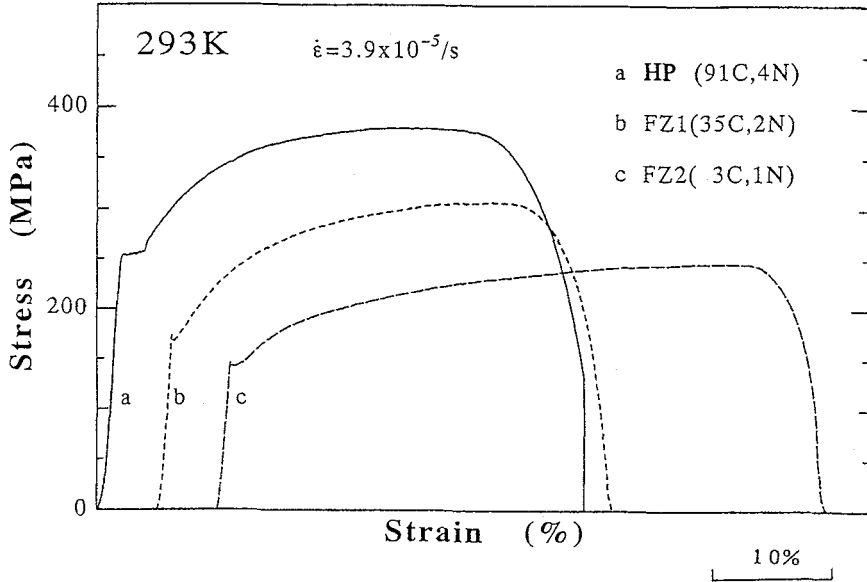


Figure 3 Stress-strain curves of 91(HP), 35(FZ1) and 3(FZ2) massppm at 293K.

It is confirmed that the degree of serration and work hardening are strongly affected by the amount of interstitial impurities, especially the amount of carbon in this case. These results are very important for the development of high-performance Fe-Cr alloys and of the manufacturing process.

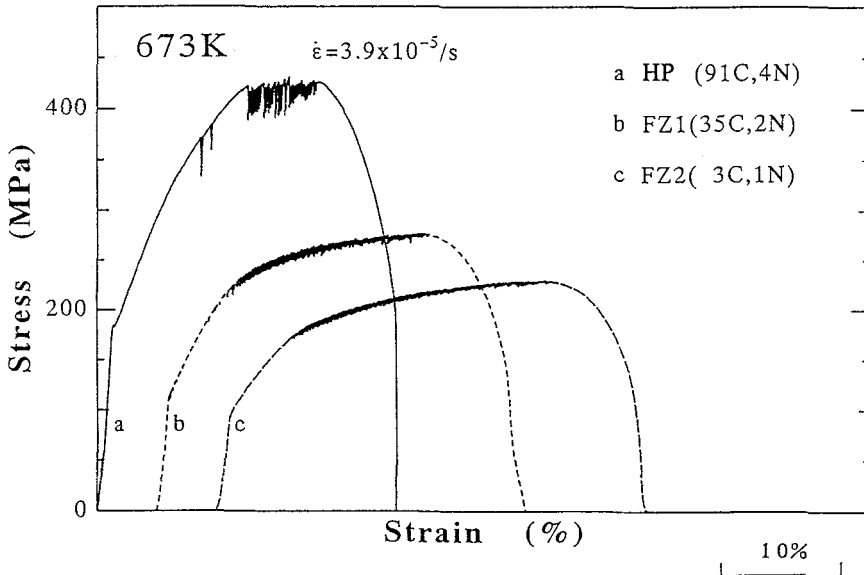


Figure 4 Stress-strain curves of 91(HP), 35(FZ1) and 3(FZ2) massppm at 673K.

3-3 Hot Ductility of High Purity Fe-50mass%Cr Alloy

The ductility of Fe-Cr alloys is remarkably improved by purification, especially by the removal of interstitial impurities as mentioned above. In Fe-Cr alloy containing more than 35mass% chromium, 475°C embrittlement and σ -phase embrittlement appear.

In the workshop of UHPM-94, we briefly presented the ductility of a high purity Fe-50mass%Cr alloy [9]. An Fe-50mass%Cr alloy of conventional purity is extremely brittle due to the formation of the σ -phase. However, we found that the highly-purified Fe-50mass%Cr alloy is ductile enough for forging and rolling at elevated temperatures, and also for cold rolling at room temperature. Figure 5 shows, for example, the seamless tubing of the alloy which was deformed from the bar at 1573K.

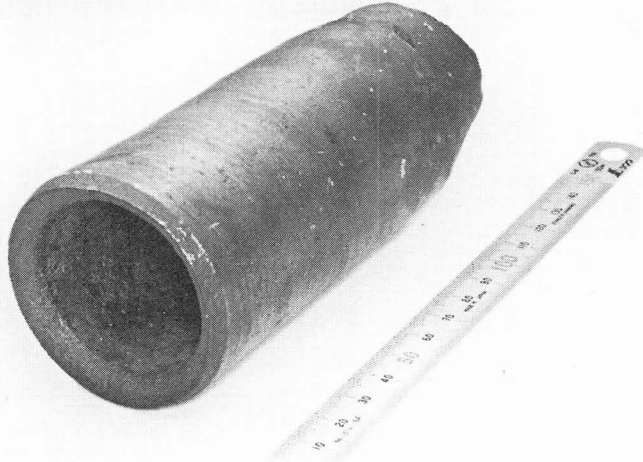


Figure 5 Seamless tubing of a high purity Fe-50mass%Cr alloy deformed from the bar at 1573K.

The formation of the σ -phase is the key to the improvement of hot ductility in an Fe-50mass%Cr alloy. The microstructure of a high purity Fe-50mass%Cr alloy was therefore observed after ageing for various periods at elevated temperatures. Also, the static recrystallization behaviour of the cold rolled alloy was investigated, because the strain may enhance nucleation of the σ -phase. Figure 6 shows one example of the microstructure after ageing for 1000h at 973K in a vacuum. Many points in Fig. 6 are etching pits. Consequently, no σ -phase was observed under these ageing conditions.

Figure 7 shows the stress-strain curves of a high purity Fe-50mass%Cr alloy at various temperatures. A small yield drop is observed in the stress-strain curves at temperatures between 293K and 573K. Slight serration in the stress-strain curves is observed at the temperature range between 573K and 673K. On the other hand, a large serration, which seems to be twin deformation, appears between 723K and 823K. According to the degree of the large serration, the work hardening rate and the ultimate tensile strength increase, but the elongation decreases. The elongation of a high purity Fe-50mass%Cr alloy reaches a minimum value at the temperature of 773K. However, the elongation at the temperature of 1073K is more than 120%. At tensile test temperatures above 873K, dynamic recrystallization may occur suddenly after the elastic region.

Furthermore, we investigated the effect of tungsten on the solid solution hardening at high temperatures and the hot ductility of a high purity Fe-50mass%Cr alloy. Tungsten suppresses dynamic recrystallization. The increment of the tensile strength by the addition of 8mass%W is 80MPa at 1073K due to the solid solution hardening of the tungsten. Surprisingly, elongation and reduction in area at 1073K are improved by the addition of tungsten.

Why does the σ -phase nucleate easily in an Fe-50mass%Cr alloy of conventional purity? What is the difference in compositional effects in the conventional alloy and the high purity alloy? This is of great interest in the mechanism of nucleation of the σ -phase, and the intrinsic effect of impurities and alloying elements such as tungsten on the high temperature strength and hot ductility of an Fe-50mass%Cr alloy.

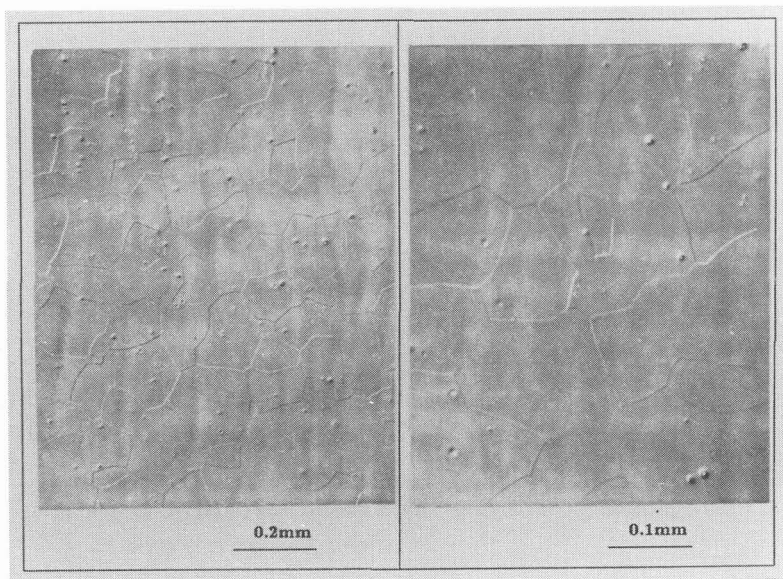


Figure 6 Microstructure of a high purity Fe-50mass%Cr alloy after ageing for 1000h at 973K in the vacuum.

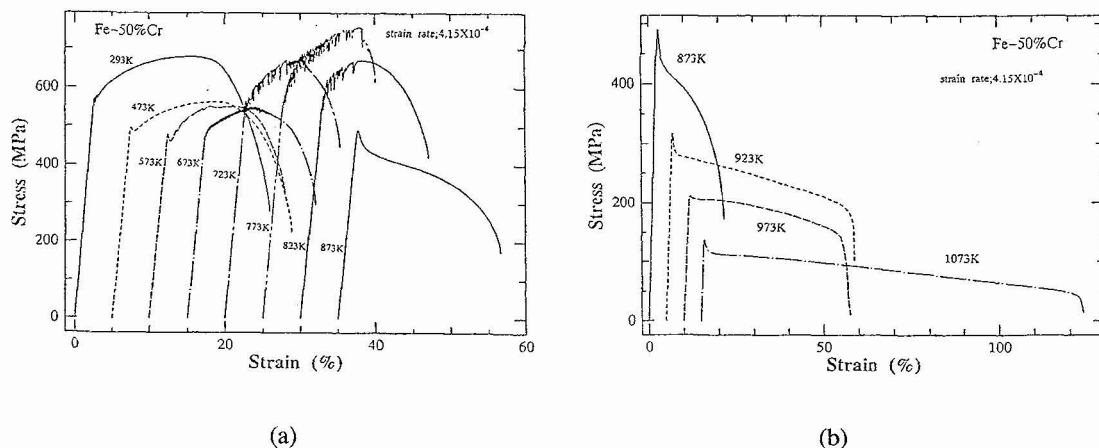


Figure 7 Stress-strain curves of a high purity Fe-50mass%Cr alloy at various temperatures.

4. CONCLUSION

Ductile Fe-Cr alloy containing high chromium will be used as a heat resistant material in many fields of industry in the near future. However, without further fundamental investigation of high purity Fe-Cr alloy, we cannot expect great advances in metallic materials for high temperature service in modern heavy industry.

It is absolutely necessary to establish a new metal science for the discovery of high-performance base metals with desirable properties corresponding to the demands of the age. We conclude that the following investigations into ultra-high purity base metals will offer a new direction for progress in metal science.

- (1) preparation of ultra-high purity base metals,
- (2) analysis of very small amounts of impurity elements in purified base metals,
- (3) clarification of the inherent physical and chemical properties of purified base metals, leading to the creation of a database,
- (4) creation of new equipment for research on purified base metals.

I hope for further advances in materials science by ultra-high purification technology at UHPM-96.

REFERENCE

- [1] Ultra High Purity Base Metals, Proceedings of The First International Conference on Ultra High Purity Base Metals (UHPM-94), May 24-27th, 1994, at Kitakyushu-City, Japan, Edited by K. Abiko, K. Hirokawa and S. Takaki, Published by The Japan Institute of Metals.
- [2] K. Abiko: *ibid.*, p. 1.
- [3] C. J. McMahon: *ibid.*, p. 352.
- [4] C. M. Liu, T. Iyama, H. Suenaga, K. Abiko and M. Tanino: *ibid.*, p. 500.
- [5] K. Abiko, R. L. Bodnar and D. P. Pope: Ductility and Toughness Considerations in Elevated Temperature Service, Edited by G. V. Smith, ASME, New York, 1979, pp. 1.
- [6] K. Abiko, C. M. Liu, M. Ichikawa and M. Tanino: to be published in Proceedings of The Second International Conference on Ultra High Purity Base Metals (UHPM-95), June 10-16th, 1995, at Saint-Etienne, France.
- [7] K. Akiyama: Master Thesis of Tohoku University, (1992).
- [8] K. Abiko, S. Takaki, C. M. Liu and M. Tanino: Inherent Properties of High Purity Fe-Cr Alloys, published by ISIJ, (1994), p. 138.
- [9] K. Abiko: Ultra High Purity Base Metals, (1994), p. 522.
- [10] T. Daicho, N. Arisawa and K. Abiko: *ibid.*, p. 397.
- [11] F. R. N. Nabarro: Report on Strength of Solids, Physical Society, London, (1948), p. 38.
- [12] J. Friedel: Dislocation, Pergamon, (1964), p. 411.
- [13] B. A. Wilcox, G. C. Smith: Acta Met., 12 (1964), p. 371.
- [14] A. H. Cottrell: Phil. Mag. 74 (1953), p. 829.
- [15] A. S. Keh, Y. Nakada, and W. C. Leslie: Dislocation Dynamics, McGraw-Hill, (1968), p. 381.