論 文

Effect of Cr and N Additions in γ-TiAl Intermetallic Compounds

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γ-TiAl 금속간화합물에 Cr 및 N 첨가의 영향

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초 록

γ-TiAl 금속간화합물에 크롬과 질소첨가의 영향을 관찰하기 위하여 첨가량에 따른 열처리 전후의 미세조직과 기계적 성질을 비교 분석하였다. 그 결과 질소첨가량이 증가할수록 결정립이 미세화되고 항복강도가 증가되었으며 크롬과 질소의 동시첨가의 경우가 이들의 효과가 현저하였다. 또한 이들 원소의 첨가로 Ti_2AlN이 제3상으로 생성되어 열처리시 α_2/γ층상조직의 안정화를 보였으며 첨가량을 다량으로 하였을 때 결정립의 크기가 급격히 감소함에도 상온연성이 감소되는 것은 Ti_2AlN의 크기에 기인한 것으로 판단된다. 적정량의 크롬과 질소를 동시첨가하여 열처리시 상온연성 및 항복강도가 향상되었다.

1. Introduction

The intermetallic γ-TiAl alloy has attractive properties such as high melting temperature, low density, high resistance to oxidation and good elevated temperature strength[1]. This alloy has the potential for high temperature structural applications, particularly if its low temperature ductility can be improved[2]. Improving ductility is the primary subject of studies that lead to identification of potentially useful alloy compositions with improved ductility and reasonable strength. Addition of Cr, V and Mn to Ti-48Al nearly doubles the room temperature ductility[1,3] and the increase in ductility may be due to the difference in tetragonality ratio[4,5], variation of unit cell volume[4,5], site occupancy[6,7], enhanced micro-twinning [4] or changes in electronic structure[8]. However, additions of these elements decrease the oxidation resistance of gamma alloys[1]. Small additions of carbon and nitrogen improve creep resistance, while silicon, boron, nickel and iron decrease the melt viscosity and silicon may also yield some improvements in oxidation resistance and room temperature ductility[1,3]. Small additions of boron and silicon are known to refine the microstructure[1,3].

The mechanical properties of gamma based titanium aluminides have a strong effect on the microstructure [9 - 12]. Early microstructure studies have shown that grain refinement of the fully lamellar two-phase gamma alloys would be expected to exhibit more appropriately balanced mechanical properties [9-11]. The principle for alloy disign requires the grain refinement and stabilization of lamellar structure which is not stable at high temperature. But it is difficult exactly to explain the effect of alloying elements on ductility, since additions of elements coincide with the change of grain size and the third phase appearence besides TiAl and Ti_3Al phase. So far no systematic investigation has been reported regarding the effect of

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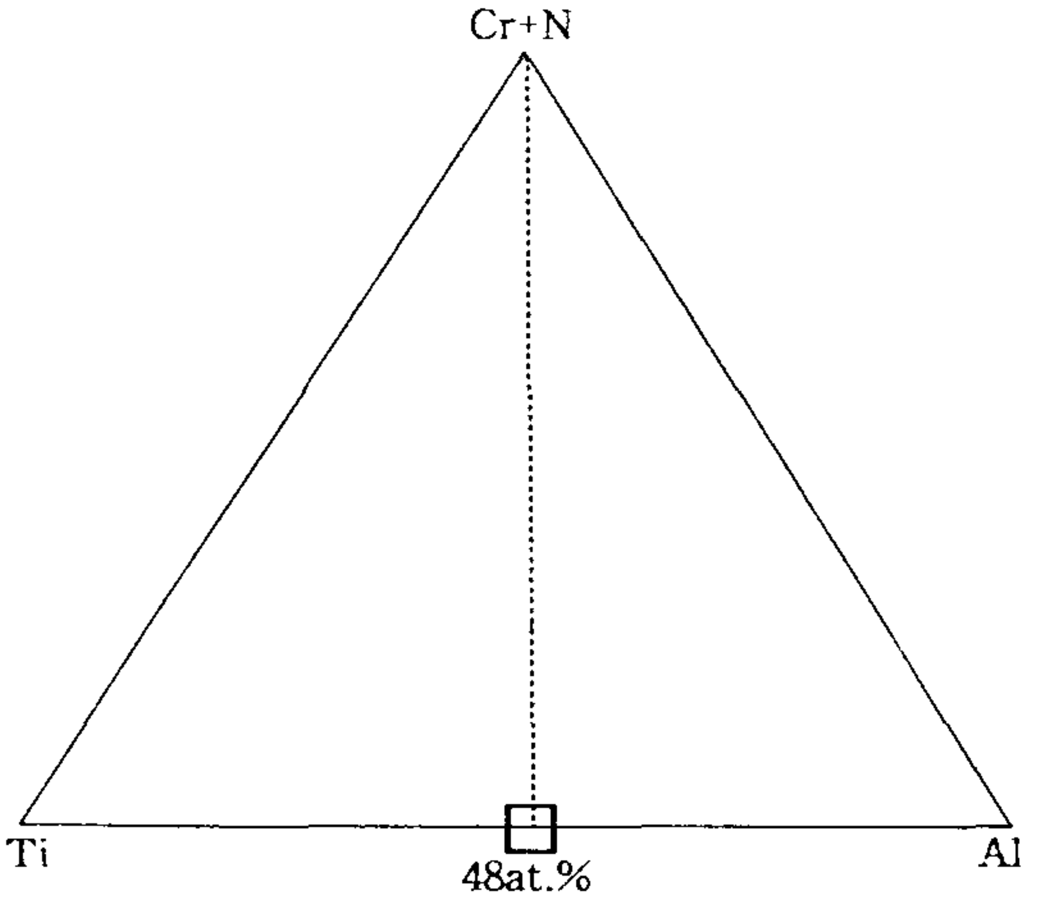
Cr and N addition.

In the present study, I chose Cr and N as alloying elements and investigated not only ternary but also quarternary alloying effects on the microstructure and mechanical properties of TiAl alloys before and after heat treatment.

2. Experimental procedure

Alloys were prepared in the form of 18g ingots by arc melting of high purity elements, Ti, Al, Cr and AlN, under an argon atmosphere. The alloy compositions are shown in Fig. 1. Melting was repeated more than five times to ensure homogeneity. Weight loss of sample was negligible so that nominal composition was assumed to be actual. After cutting all of ingots into half, one part of them were heat treated for 43.2ks at 1373K in vaccum and cooled down until 1073K in furnace. As cast and heat treated specimens for the tensile test were cut by spark erosion. The dimensions of specimen was 5mm in guage length, 2mm in width and 0.6mm in thickness. Experiments were conducted in air with an instron type universal testing machine at a strain rate of $2\times10^{-4}S^{-1}$. The microstructure of alloys before and after heat treatment were studied by optical microscopy, SEM and TEM. The third phases of alloys were carefully examined by applying quantitative energy dispersive X-ray spectroscopy and selected area diffraction.



$(Ti_{52}Al_{48})_{100-x}(Cr, N)_x$
where X = 0~3.75at.%

Fig. 1. Composition of TiAl alloys.

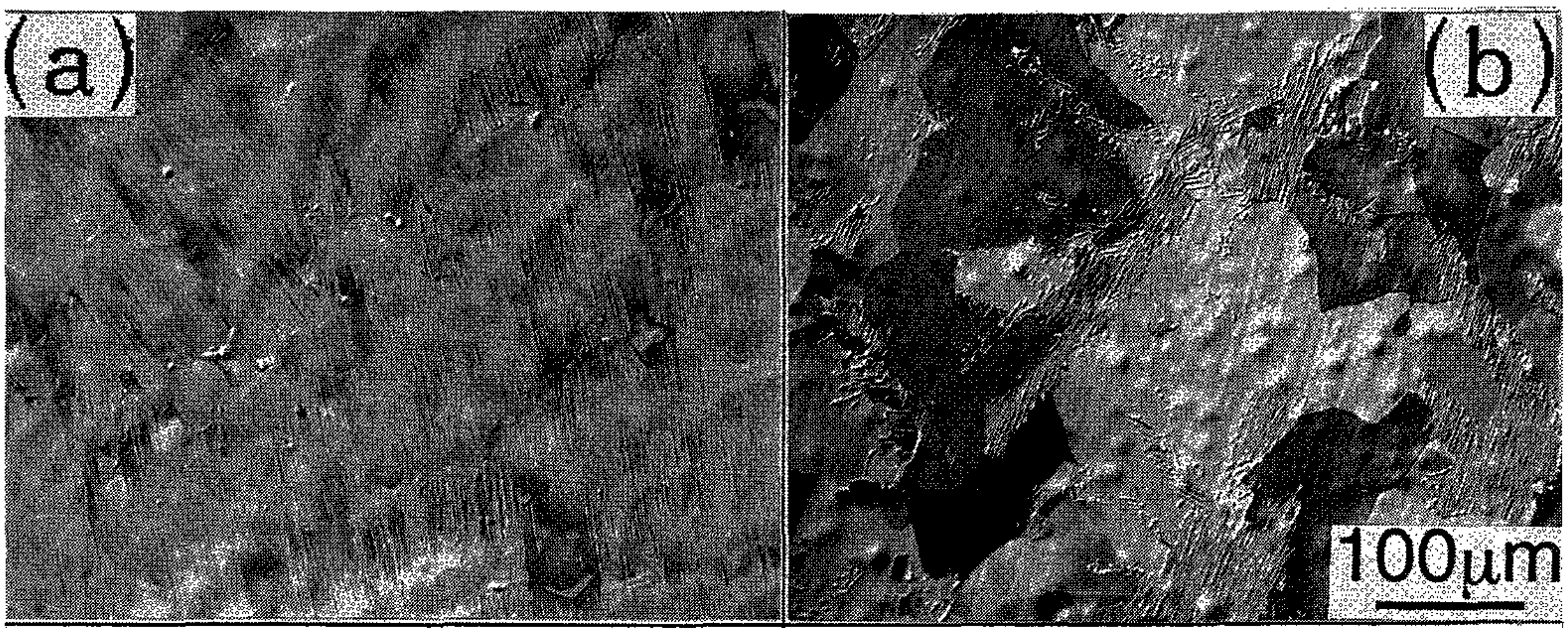
3. Results and discussion

3.1 microstructure

Fig. 2 shows optical photomicrographs and mechanical properties of Ti-48Al alloys before and after heat treating at 1373K for 43.2ks. Microstructure of as-cast Ti-48Al alloy exhibits α_2/γ lamellar structure and a small amount of primary γ structure and that of heat treating Ti-48Al alloy is composed of coarse γ structure, a small amount of lamellar structure and α_2 particles. With the heat treatment of Ti-48Al alloy under this conditions, the most of lamellar structure change to γ structure. And room temperature tensile elongation is increased to 0.9 but yield strength is a little smaller.

Optical photomicrographs of as-cast TiAl alloys with Cr and N additions are shown in Fig. 3. Microstructure of nitrogen additions exhibits a dendritic morphology with a nearly lamellar structure containing a small amount of γ grains seen in the interdendritic regions. Grain size depends on composition, becoming smaller with simultaneous additions of nitrogen and chromium. Drasti grain refinement was achieved by 2Cr0.75N and 3Cr0.75N additions. The 0.75N added alloys with or without Cr contain large precipitates within the lamellar grains.

Fig. 4 shows optical photomicrographs of TiAl alloys with Cr and N additions after heat treatment. With increasing the nitrogen content, volume fraction of lamellar structure increased and grain size became small-



Yield strength : 319 MPa Elongation : 0.6(%)	Yield strength : 308 MPa Elongation : 0.9(%)

Fig. 2. Optical photomicrographs and mechanical properties of Ti-48Al alloys.
(a) as-cast, (b) after heat treating at 1373K for 43.2ks.

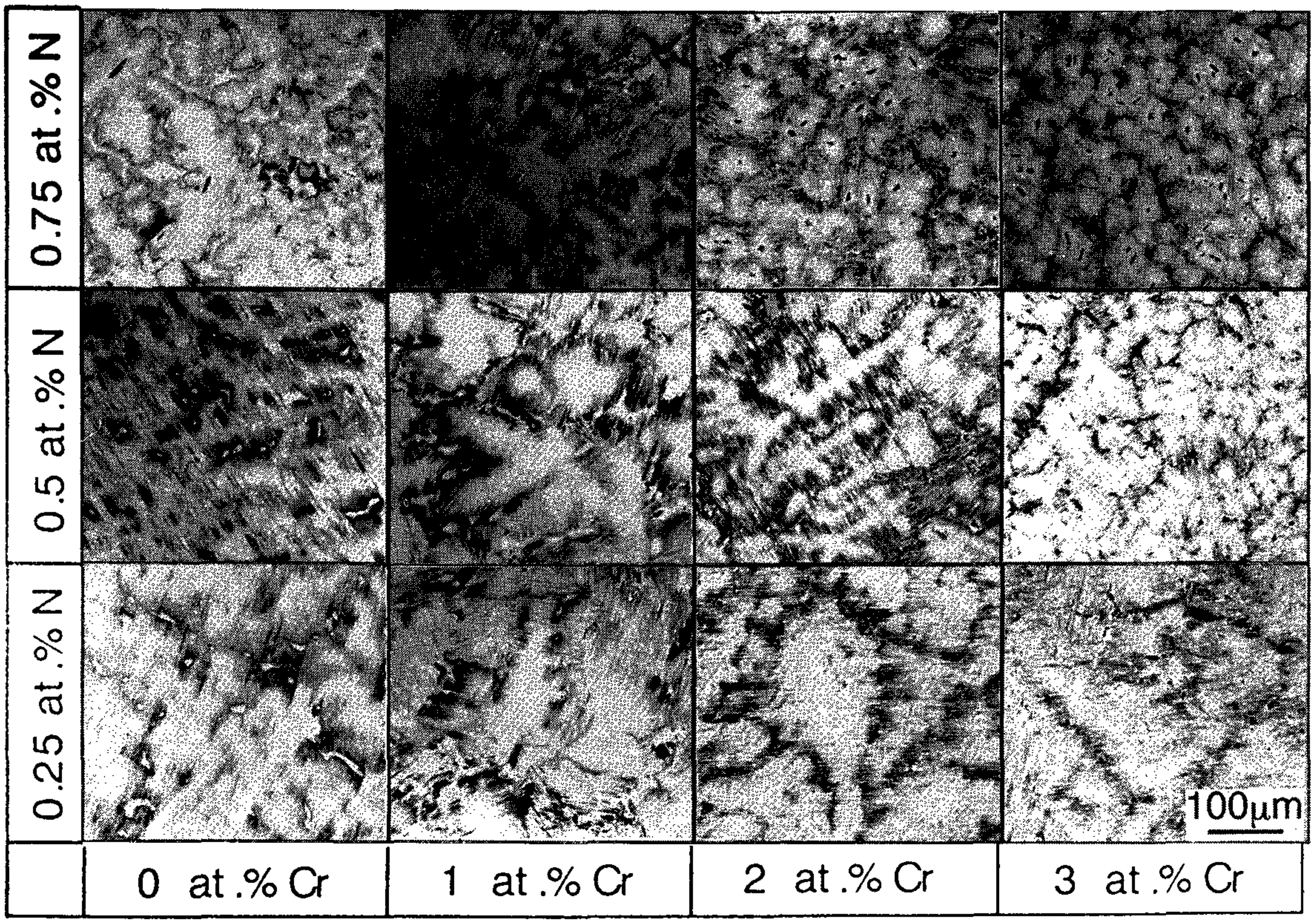


Fig. 3. Optical photomicrographs of as-cast TiAl alloys with Cr and N additions.

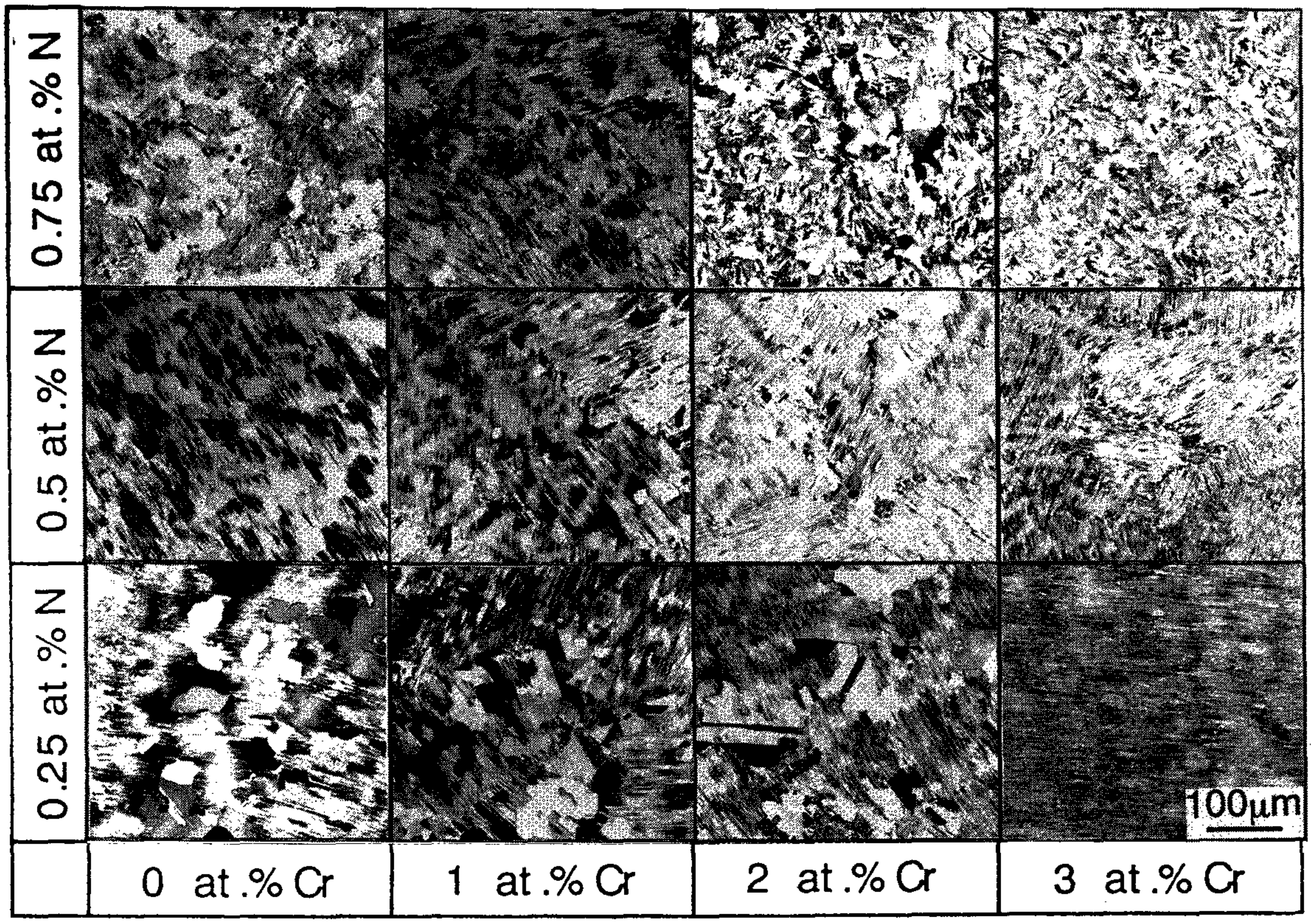


Fig. 4. Optical photomicrographs of TiAl alloys with Cr and N additions after heat treating at 1373K for 43.2ks.

er. The 2Cr0.75N and 3Cr0.75N additions reduced the grain size significantly. Simultaneous additions of Cr and N were more effective in stabilizing the lamellar microstructure and refining grain size although fully lamellar structure was not observed within given compositions. Fig. 5 shows SEM microstructure of precipitates in heat treated alloys with (a) 0.75N and (b) 3Cr0.75N additions. Large precipitates remained in the 0.75N added alloy without or with Cr. When the precipitates of TiAl3Cr0.75N and TiAl0.75N are compared, those of TiAl3Cr0.75N are larger than TiAl0.75N. While the number of precipitate less than 5μm is very fewer in TiAl3Cr0.75N, TiAl0.75N has many small precipitates.

In the previous studies of Ti-Al-N ternary system[13], the aluminonitride Ti_2AlN was known to coexist with Ti_3AlN at temperature below 1300℃. The solubility of nitrogen in the α_2 phase appears to be much greater than in γ phase[14]. Most nitrogen in two-phase gamma alloys is soluble in α_2 phase. During solidification, the metastable α_2 phase with nitrogen decomposes to TiAl and Ti_2AlN[15], while supersaturated nitrogen in γ phase precipitates as Ti_3AlN with decreasing temperature[16].

The atomic ratio of Ti and Al in both large precipitates of TiAl0.75N and TiAl 3Cr0.75N was estimated to be 2:1 and Cr was not detected in precipitate by EDAX. It appears that the precipitates are Ti_2AlN, as

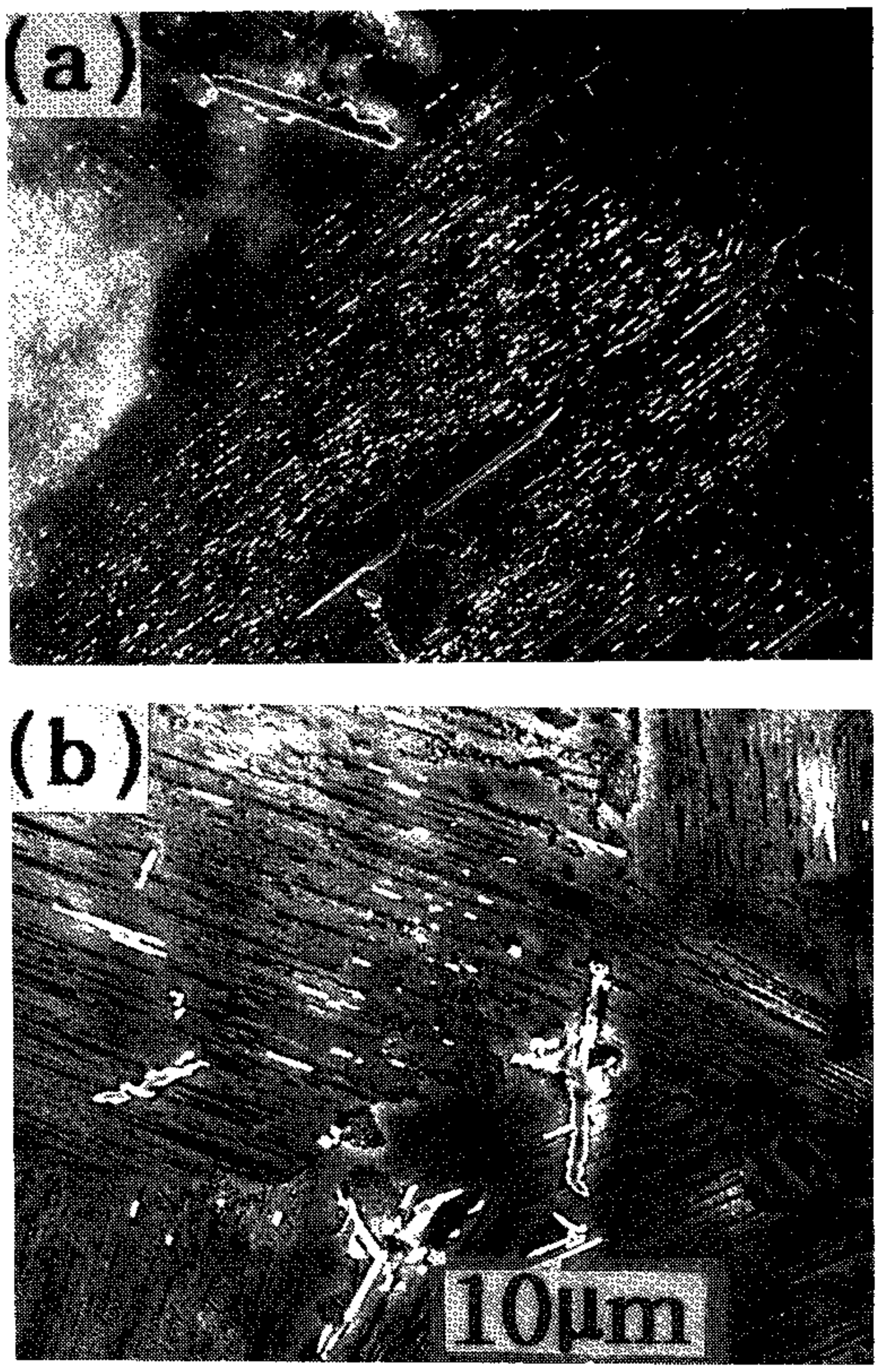


Fig. 5. SEM microstructure of precipitates in heat treated TiAl alloys with (a) 0.75N and (b) 3Cr0.75N.

supported by Fig. 6. Relatively small nitrides show the orientation relationship with γ lamellae.

The interface between Ti_2AlN nitride and TiAl matrix, parallel to both (001) of matrix and the basal plane of nitride, was observed and the interface was found to atomatically smooth by HREM[17]. It is considered that Ti_2AlN nitrides stabilize the lamellar structure after heat treatment and large precipitate is more effective to stabilize the lamellar structure.

Fig. 7 shows transmission electron micrographs of γ phase in heat treated alloys with 0.75N and 3Cr0.75N additions. Very fine precipitates in γ phase were observed in TiAl0.75N but not in TiAl3Cr0.75. Precipitation occures homogeneousely in matrix of TiAl phase and heterogeneously on the line defects and precipitate-free-zones of fine precipitates are also present. The fine precipitates are assumed to be Ti_3AlN having a crystal structure of perovskite type and have an orientation relationship with TiAl phase, <001] direction of TiAl parallel to ⟨001⟩ direction of precipitate and {100} plane of TiAl parallel to {100} plane of precipitate, in agreement with Ref[18].

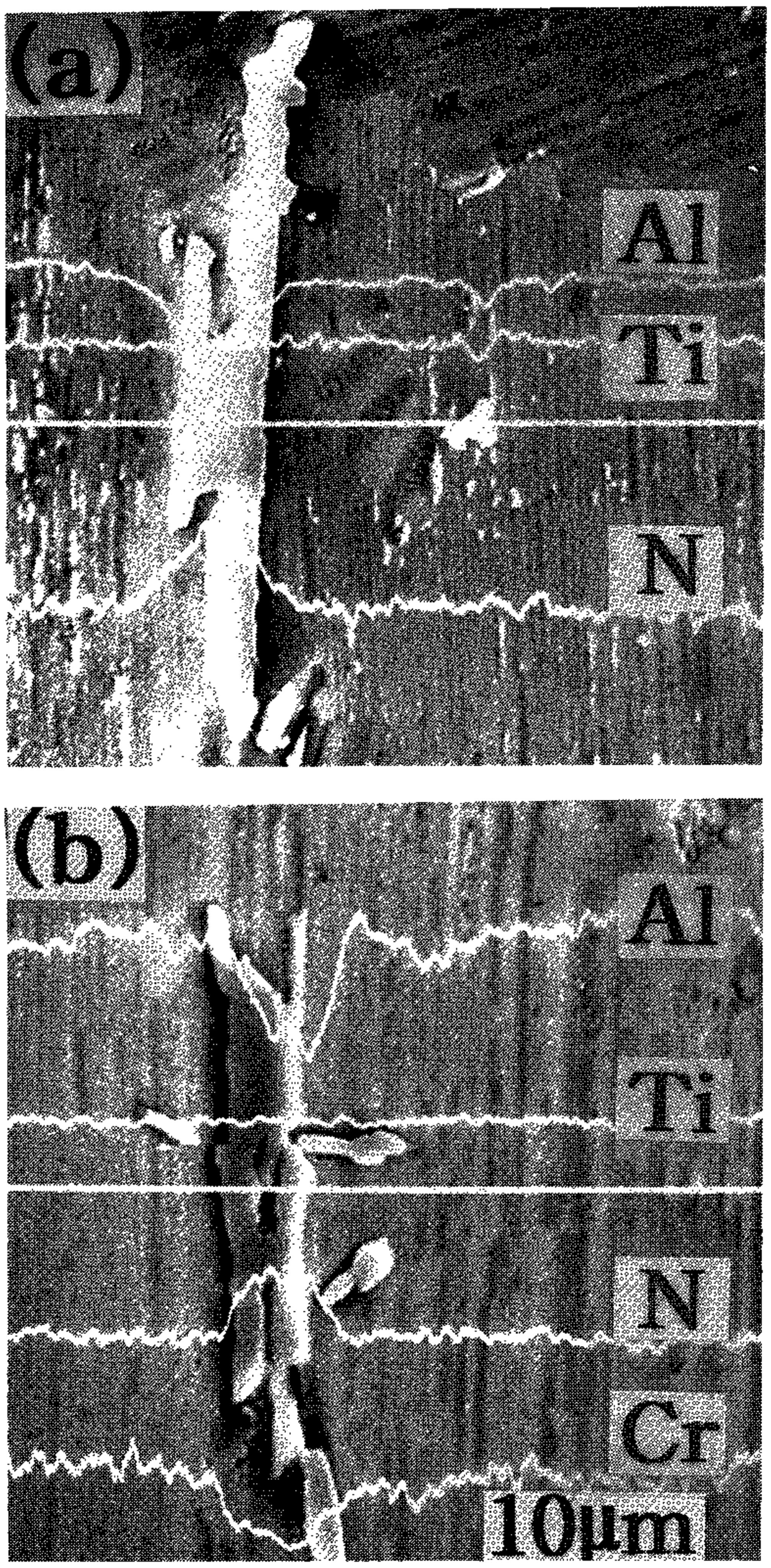


Fig. 6. EPMA line analyses of precipitates in (a) TiAl0.75N and (b) TiAl3Cr0.75N.

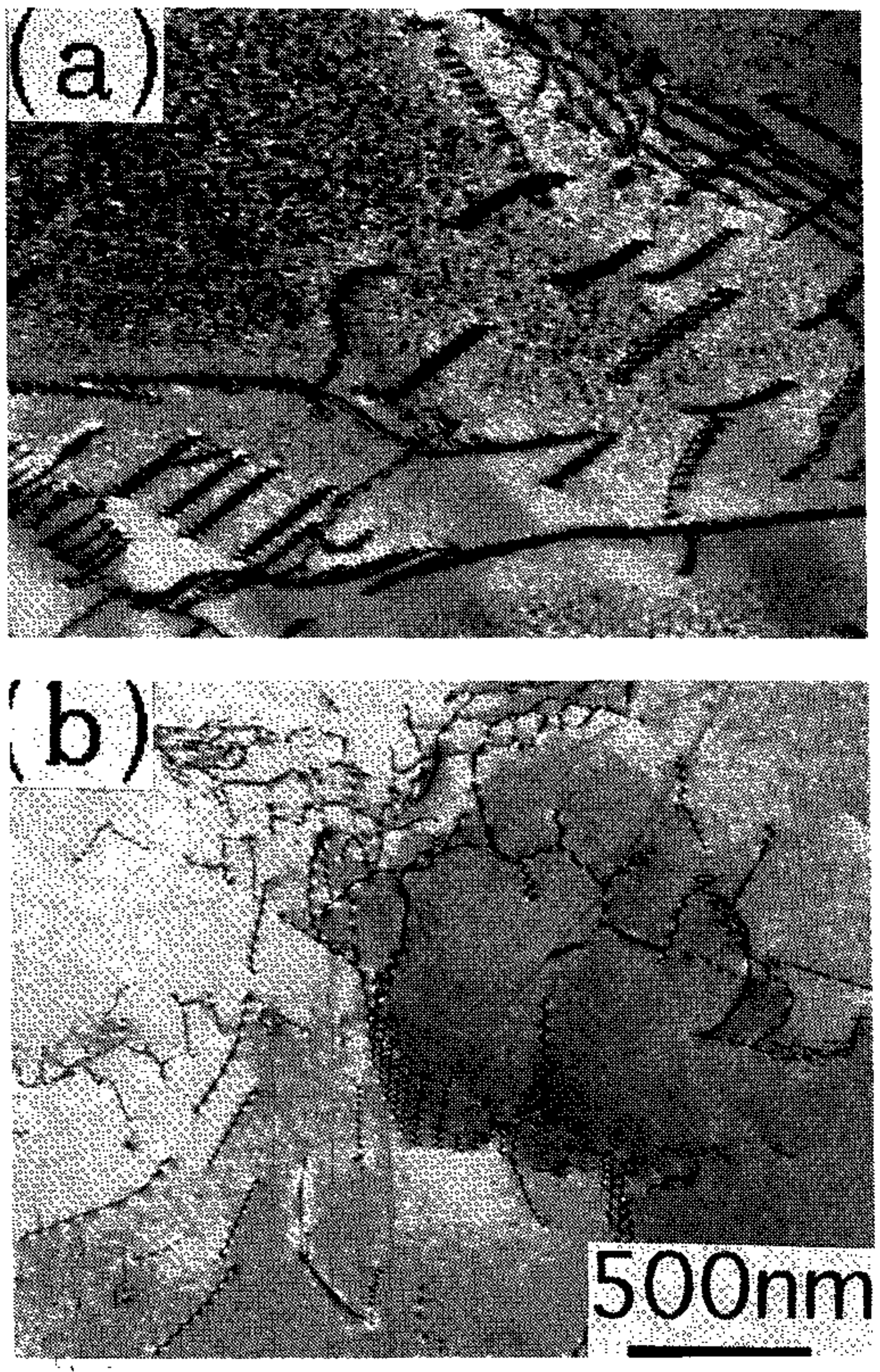


Fig. 7. BF image of precipitates and γ phase in heat treated TiAl alloys with (a) 0.75N and (b) 3Cr0.75N additions.

3.2 mechanical properties

Mechanical properties of as-cast TiAl alloys with Cr and N additions are plotted in Fig. 8. In general, additions of nitrogen increase the yield strength and reduce the elongation. TiAl3Cr0.75N shows the highest yield strength of 622MPa, indicating the refinement of grain size is effective in increasing the yield strength of alloy, but the elongation remains very low at about 0.2%.

Mechanical properties of TiAl alloys with Cr and N additions after heat treatment are plotted in Fig. 9. The N additions without Cr or with 1Cr show nearly same yield strength value in range from 390 to 415MPa, while the N additions with 2Cr or 3Cr increase the yield strength significantly. TiAl3Cr0.75N shows the highest yield strength of 614MPa, approximately twice higher than that of binary alloy. Effect of the amount of N addition on the mechanical properties is estimated with microstructure and the relation of interface between TiAl matrix and nitride. According as 0.75N additions decrease grain size and the remained nitrides stabilize lamellar structure, yield strength is increased but elongation is rather decreased than as-cast binary alloy shown lamellar structure with large grain size. With decreasing the amount of N addition, the size of nitrides also decreases. The large nitride which is obtained by increasing nitrogen content decreases the degree of coherency between the matrix and the surface of nitride. When the coherency is good, disloca-

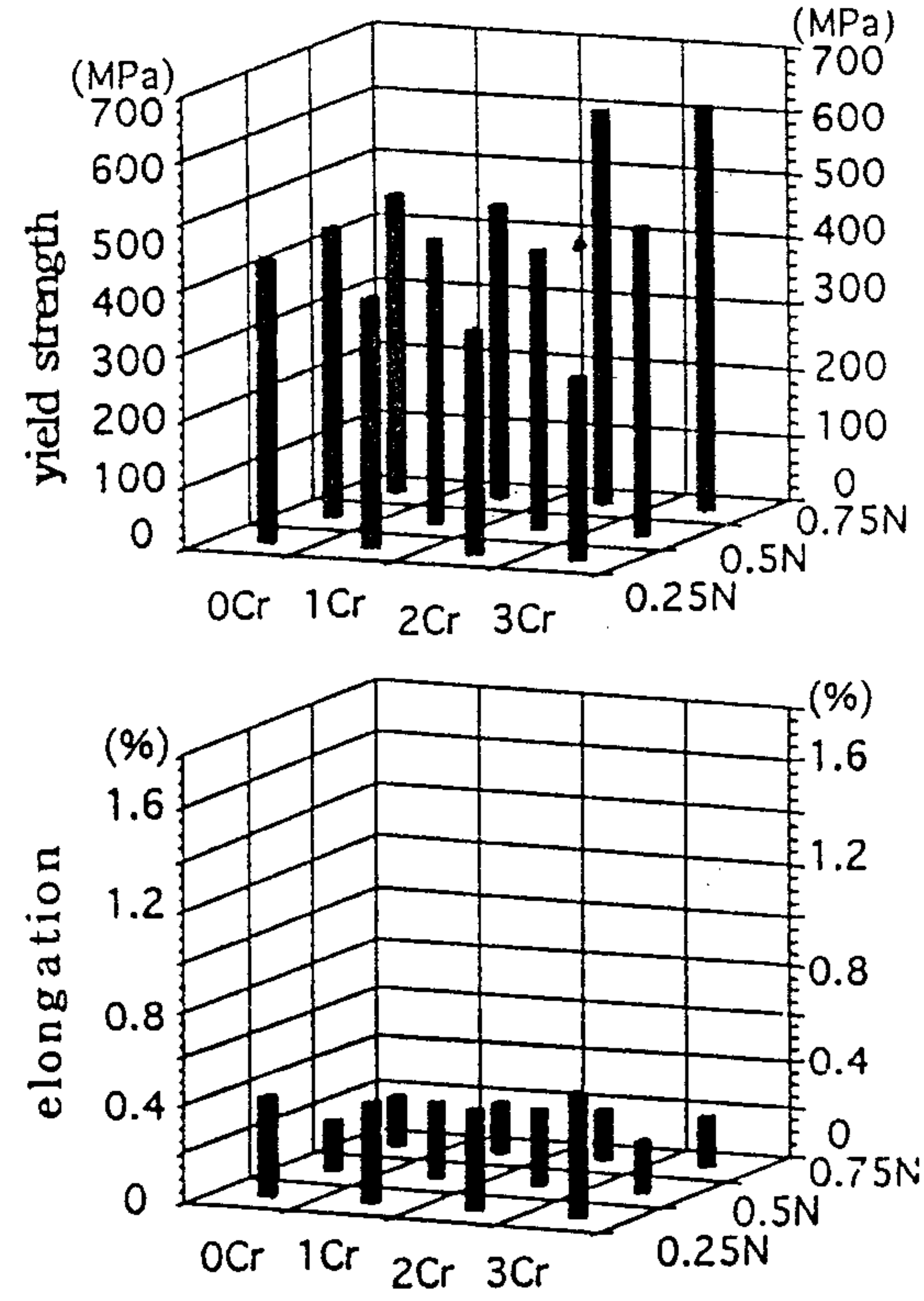


Fig. 8. Mechanical properties of as-cast TiAl alloy with Cr and N additions.

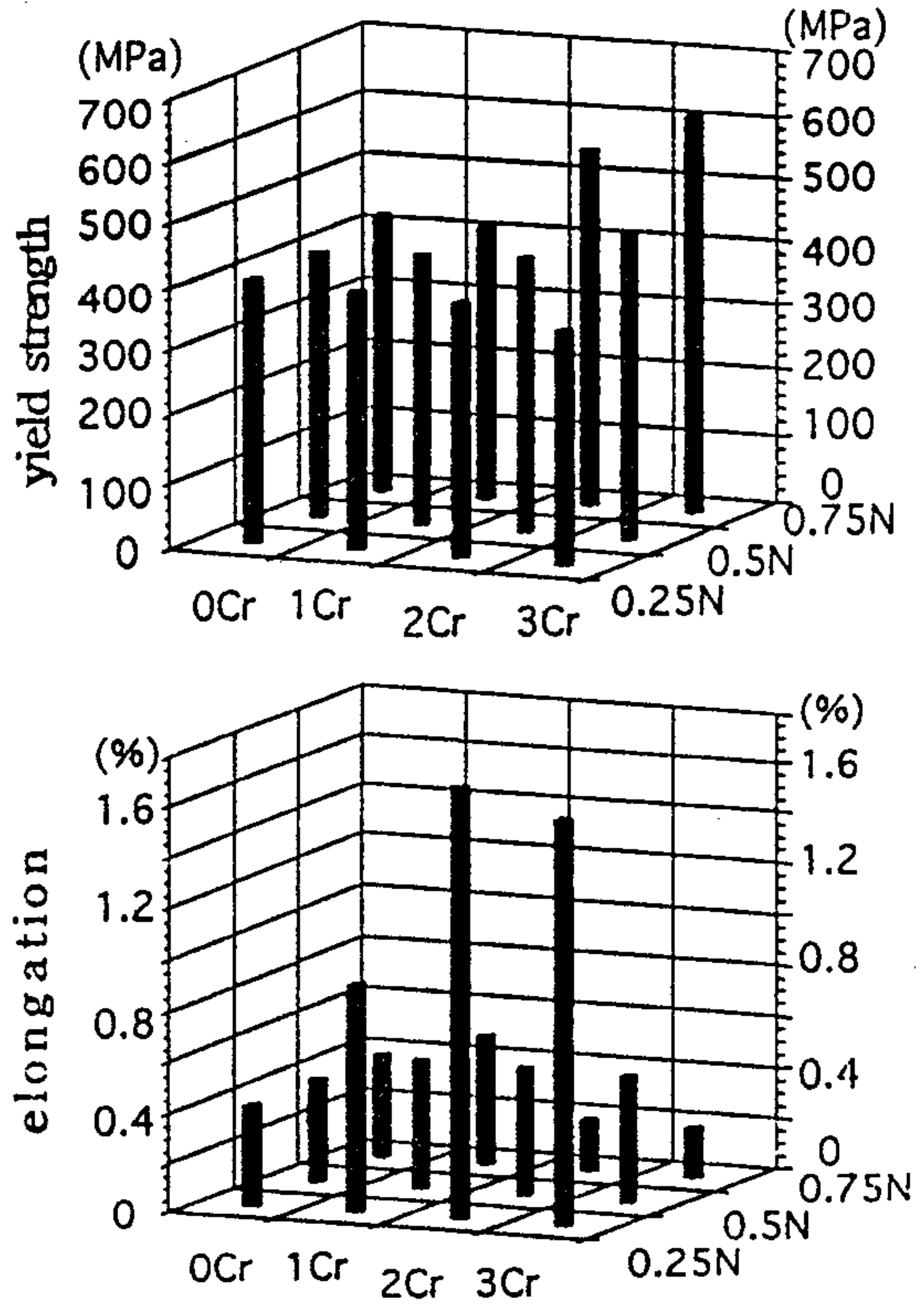


Fig. 9. Mechanical properties of TiAl alloys with Cr and N additions after heat treating at 1373K for 43.2ks.

tions are observed in the nitride though the hardness value is about 5 times larger than that of matrix[17]. Since the interfaces between matrix and the side surface of nitride are flat and smooth and the nitride has the ability of deform, a crack initation at the interface is very few[17]. Since the size of nitrides has influence on deformation, large nitride formed by increasing nitrogen content reduces the elongation values though grain size is decreased. In this experiment, 0.25N addition with 2Cr or 3Cr show good elongation.

4. Conclusions

In order to investigate the effect of Cr and N addition in γ-TiAl alloy, the microstructure and mechanical properties before and after heat treatment were studued. The obtained results were as follows;

1) With increasing N content, grain size of TiAl alloys became smaller. Drastic grain refinement was achieved by simultaneous additions of Cr and N.

2) Simultaneous additions of Cr and N were effective in stabilizing the lamellar microstructure of TiAl alloys after heat treatment.

3) The addition of N with or without Cr formed a third phase which was indentified to be Ti$_2$AlN. It was found that Ti$_2$AlN was capable of stabilizing lamellar microstructure after heat treatment. Very fine Ti$_3$AlN in γ phase were observed in TiAl0.75N but not in TiAl3Cr0.75N.

4) Room temperature tensile elongation of as-cast alloys with N additions was decreased but yield strength was increased. While good ductility with high strengh of heat treating alloys could be achieved by simultaneous additions of Cr and N.

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