EFFECTS OF ADDITIONS OF ALUMINUM AND TITANIUM ON RECRYSTALLIZATION OF 80Ni-20Cr ALLOYS

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Abstract

In order to evaluate the heat-resisting property of Nimonic type heat-resisting alloys, the effects of additions of aluminum and titanium up to 6% on the recrystallization behavior of 80Ni-20Cr alloy have been investigated. The proces of recrystallization is examined by Vichers hardness measurement, metallographic examination and lineal analysis. The X-ray diffraction patterns from the (331)-planes of γ matrix due to the $K\alpha$ doublet is also utilized for the examination of recrystallization process when it is complicated. When aluminum or titanium is added singly to this alloy, the recrystallization temperature increases with increasing content of aluminum or titanium excepting that it decreases for titanium addition above 3%. For the addition of aluminum and titanium together, the recrystallization temperature is higher than for the single of the same amount of aluminum or titanium. It is known that when the ratio of aluminum and titanium contents is about 1 to 1.5, the recrystallization temperature is the highest.

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Introduction

The high temperature strength of nickel-base superalloys is kept up because of the precipitation hardening effect of γ' phase particles by additions of aluminum or both aluminum and titanium. When the precipitate is stable up to high temperature and the softening temperature of γ phase matrix by recrystallization becomes higher, the heat-resisting property of the alloys is improved. There were few reports, however, which investingated the recrystallization temperatures of such alloys. The kind, amount, size, and rate of dispersion of the precipitate, and alloying content in the matrix are important factors that control the recrystallization temperature.

80Ni-20Cr alloy (Nichrome) is the original material for the development of Nimonic type heat-resisting alloys. And so this investigation was undertaken to know the effects of additions of aluminum and/or titanium on the recrystallization of this alloy.

Experimental Procedure

The materials used for this investigation were electrolytic nickel, electrolytic chromium, 99.99% aluminum and high-purity titanium. Aluminum and titanuim were used as a sheet. All alloys were melted into 100-gram button ingots in an arc-melting furnace with a nonconsumable tungsten electrode. The melting was done on a water-cooled copper hearth in a argon atmosphere. Aluminum and titanium were singly added from 1% to 6%, or together up to Al+Ti=2~6%, to Ni-20Cr alloy.

After melting, the ingots were hot-rolled to 2mm thick sheets, annealed for 2 hours at 1150°C, and then water-quenched to single-phase structure. Two sections were cut from each sheet; one section that was solution-treated to single-phase structure was used for study of precipitation process, and the other was reduced in thickness 70% by cold-rolling for examination of recrystallization.

Those specimens were isochronously annealed under 10^{-3} Torr at 400 to 1100°C for 2 hours and water-quenched after each 25°C increment. After this heat treatment, the processes of precipitation hardening and recrystallization softening of the specimens were examined by Vickers hardness measurement and metallographic examination. The X-ray diffraction patterns from the (331)-planes of γ matrix due to the $K\alpha$ doublet was utilized for the examination of recrystallization process when it was complicated. Recrystallized-fraction was measured with lineal analysis by Harbert counter. For metallographic examination the specimens were mechanically polished and etched anodically in aqueous solution of 20% phosphoric acid.

Alloys containing 1 to 6% Ti or 1 to 5% Al were easy to reduce in thickness 70% by cold-rolling, but alloy containing 6% Al was difficult to cold-work except for hot-working. The results of chemical analysis for chromium, aluminum, and titanium are given in Tables 1 and 2. Alloy compositions were proportioned in weight-percent.

Experimental Results

Hardness of Alloys in Solution-Treated Condition and in 70% Cold-Rolled Condition. The hardness values of cold-rolled alloys as shown in Fig. 1 decrease a little with the addition of small amounts of aluminum and /or titanium, but they become higher with more increasing amounts of those alloying elements. These alloys are markedly work-hardened by 70% reduction by cold-rolling, but in this case the hardness values are directly proportional to amounts of alloying elements, as shown in Fig. 2. The gradient of the contour lines of hardness distribution in Figs. 1 and 2 shows that alloying composition in which the hardness increases rapidly is at approximately a 0.7 to 1.5 weight ratio of aluminum to titanium.

Hardness/Annealing-Temperature Curves. Figs. 3 through 5 show the change of hardness with increasing annealing temperature for 80 Ni-20Cr alloy and alloys added singly aluminum or titanium. In the case of the alloys in the solution-treated condition, no change of hardness is noted for 80Ni-20Cr, 1Al, and 1 Ti alloys. But the hardness values of 4 Al and 4 Ti alloys change markedly and reach to the peak at about 800°C. In the case of the alloys in the cold-rolled condition, the temperature for the begining of softening by recrystallization of alloys containing aluminum is always higher than that of alloys containing titanium. Moreover, the temperature for the hardness-peak of cold-rolled alloys is lower than that of solution-treated alloys and goes down about 100°C for 4Al alloy or about 200°C for 4Ti alloy.

Figs. 6 and 7 show the change of hardness with increasing annealing temperature for alloys added aluminum and titanium together. The change of hardness is markedly noted for the solution-treated alloys containing small amounts of aluminum. The temperature for the begining of softening by recrystallization of cold-rolled alloys rises with increasing aluminum content, but, on the contrary, it decreases with the addition of a large amount of aluminum. The temperature for the hardness-peak of cold-rolled alloys goes more down about 100°C than that of solution-treated alloys with the exceptions of two or three. Generally, there is the peaks of the hardness values at about 800°C for solution-treated alloys and at about 700°C for cold-rolled alloys. Therefore, the contour lines of hardness distribution of solution-treated alloys at 800°C and cold-rolled alloys at 700°C are shown in Figs. 8 and 9. Alloying composition in which the hardness increases rapidly is at approximately a 0.25 to 1 weight ratio of aluminum to titanium.

The softening curves of all alloys containing aluminum and titanium together are compared in Fig. 10. 2Al-4Ti and 3Al-3Ti alloys have the highest softening temperature. The softening temperature decreases in order of 4Al-2Ti, 2Al-3Ti and 3Al-2Ti, and 1Al-5Ti and 5Al-1Ti alloys. And the alloys containing small amounts of both aluminum and titanium have lower softening temperature.

Microstructure. Photos. 1 and 2 show the recrystallization process of cold-rolled 1Al and 1Ti alloys respectively. The recrystallization always begins at slip band and grain boundary. The precipitate does not exist in 1 through 3Al alloys and 1 through 3Ti alloys in both the solution-treated and the cold-rolled conditions. Photos. 3 and 4 show changes in structure of cold-rolled 4Al and 4Ti alloys respectively.

γ'(Ni_3Al) phase particles in cold-rolled 4Al alloy precipitate preferentially along slip band and grain boundary zones prior to general precipitation of γ' fine particles in γ phase matrix, and then recrystallization starts along these zones. But η(hcp Ni_3Ti) phase flaky particles in cold-rolled 4Ti alloy precipitate discontinuously from slip band and grain boundary. This discontinuous precipitation zone extend to the whole γ phase matrix with increasing annealing temperature while γ' (fcc Ni_3Ti) fine particles precipitate generally in γ phase matrix. The recrystallization developes with increasing above grain boundary reaction. The general precipitation of γ' (Ni_3Al) phase particles in solution-treated 4Al and 5Al alloys begins at about 600°C by annealing. But η phase flaky particles in solution-treated 4Ti through 6Ti alloys appear at 600 to 650°C as the result of grain boundary reaction as seen in Photo. 5 and the reaction extend to the whole γ phase matrix with the intragranular precipitation with increasing annealing temperature.

Photo. 6 shows changes in structure of solution-treated 2Al-1Ti alloy. The discontinuous precipitation by grain boundaly reaction starts at 525°C and increases with increasing annealing temperature up to 650°C. But this precipitation decreases above 675°C and disappears at 775°C. General precipitation begins to take place in γ phase matrix at annealing temperature in which the discontinuous precipitation decreases. By dissolving the precipitate at 925°C, recrystallization begins to take place along grain boundary as shown in Photo. 6e.

Photo. 7 shows the changes in structure of cold-rolled 2Al-1Ti alloy. The discontinuous precipitation along slip band and grain boundary becomes more marked at lower annealing temperature becaus of working strain as compared with those of solution-treated alloy. The precipitation becomes the most marked at 600°C and decreases from 675°C. The precipitated phase grew as lamellare becomes globu-lar at 725°C while general precipitation appears in γ phase matrix. And the recrystallization begins at about 750°C, increases with increasing annealing temperature as shown in Photos. 7e through 7g, and finishes at 950°C as shown in Photo. 7i. The precipitate dissolves almost at about 925°C as seen in Photo. 8, and Photo. 8a shows that fine grain size is obtained in area existing residual precipitate in cold-rolled alloys.

η phase precipitates in 1Al-4Ti and 1Al-5Ti alloys only. Photo. 9 shows electron microscopic structure of cold-rolled 1Al-4 Ti alloy that η phase becomes near by recrystallized grain while γ' phase general-precipitates in γ phase matrix. In solution-treated 1Al-5Ti alloy, γ' phase general-precipitates with increasing annealing temperature, and η phase becomes along the grain boundary from about 925°C and grows at higher temperature, as seen in Photo. 10. In cold-rolled 1Al-5Ti alloy, η phase becomes from about 725°C with recrystallization, increases as shown in Photo. 11, and remains abundantly even at higher temperature as 1100° C. Photo. 12 shows that aluminum and titanium contents have influence on the sizes of precipitates in the matrix of alloys. The sizes become more coarse with increasing aluminum content and smaller with increasing titanium content.

The results shown in Fig. 11 are obtained by measureing fraction discontinuously precipitated at low temperature range in alloys containing both aluminum and titanium. In the case of solution-treated condition, there is little discontinuous precipitation in the alloys containing more than Al+Ti=4.46%. The fractions increase with lower alloying concentration in the alloys containing less than Al+Ti=3.5% and with alloys containing lower aluminum and higher titanium together, and all of them become maximum at about 650° C. As the solution-treated alloys were cold-rolled, the discontinuous precipitation becomes brisk and takes place up to the higher aluminum and titanium contents than the solution-treated alloys. Furthermore, the discontinuous precipitation becomes marked with the increase of the ratio of aluminum to titanium on the contrary of the case of the solution-treated alloys. But in the case of the cold-rolled alloys containing 2%Al-4%Ti and 3%Al-3%Ti the discontinuous precipitation rarely takes place and maximum occurrence of discontinuous precipitation in the cold-rolled alloys is at about 625° C.

X-ray Diffraction. Recrystallization process in cold-rolled alloys containing both aluminum and titanium is difficult to determine by hardness measurement and metallographic observation only because of the complicated structures. Therefore, X-ray reflection method was used together with above methods. $K\alpha$ line in X-ray by copper target begins separating to $K\alpha_1$ and $K\alpha_2$ when the incident angle exceeds 70°, and the degree of the separation increases with increasing the incident angle. But, in such a case as worked stress remains markedly in alloys, $K\alpha$ line has no more separation and the diffraction line is shown as a curve with smooth peak, because the spacing of lattice plane are continuously changed with the range of some width by the internal stress. However, $K\alpha_1$ and $K\alpha_2$ are distinctly separated when recrystallization is completed and lattice distortion is released. Thereupon, the X-ray diffraction patterns from the (331)-planes of γ matrix due to the $K\alpha$ doublet is utilized for the examination of recrystallization process. Figs. 12 through 15 show that recrystallization process was determined by using hardness measurement and metallographic observation coincides fully with that by the X-ray diffraction patterns.

Recrystallization Behavior. From above results the fractions recrystallized are shown in Figs. 16 and 17 for the alloys added aluminum or titanium singly, and in Fig. 18 for those added aluminum and titanium together. From these figures the temperature of 60% fraction is designated as recrystallization temperature, and the effect of the addition of aluminum or titanium singly is shown in Fig. 19, and that of aluminum and titanium together in Fig. 20. When aluminum or titanium is added singly to Ni-20Cr alloy, the recrystallization temperature increases with increasing content of aluminum or titanium excepting that it decreases for titanium addition above 3%. In the alloys added aluminum and titanium together, the alloying composition in which the recrystallization temperature becomes the highest is at approximately a 1 to 1.5 weight ratio of aluminum to titanium. The contour lines of solution temperature of precipitate in these alloys are shown in Fig. 21. The solution temperature is the highest in the alloys where weight ratio of aluminum to titanium is about 1. The recrystallization temperature and the solution temperature of precipitate on all the alloys used in this study are summarized in Tables 3 and 4.

Discussion of Results

The result in Fig. 19 shown the recrystallization temperature of the alloys added aluminum or titanium singly suggests that solubilities for aluminum and titanium in Ni-20Cr alloy and precipitate in the alloys containing these alloing elements are important factors that control the recrystallization temperature. Those solubility limits which have been determined by Taylor (1) are about 2.9 wt%Al and about 2.5wt%Ti at 750°C respectively. Moreover, from result that Nordheim et alii (2) has obtained, tentative saturation temperatures of Ni_3Al and Ni_3Ti in Ni-20Cr alloy are about 2.8wt%Al and about 3.6wt%Ti at 900°C respectively. Though 1 to 2%Al or Ti were added in Ni-20%Cr alloy, the hardness of the solution-treated alloys didn't been changed by annealing temperature (see Fig. 1).

As shown in Figs. 4 and 5, the effects of precipitation hardening of aluminum and titanium is seen in above 2.70%Al(3Al alloy) and 3.92%Ti(4Ti alloy) respectively. This phenomenon can understand from metallographic observation as given in Table 1. Therefore, the cause that the recrystallization temperature rises almost directly to about 2%Al or about 3%Ti contents may be considered due to increasing the concentration of alloying elements in γ single phase. Here, in the above content range, the recrystallization temperature of the alloy containing aluminum is a little higher than that containg titanium. This is due to that weight-percent was used. If it is shown in atomic-percent, both the temperatures become almost same.

However, the precipitation of γ'(Ni_3Al) phase raises markedly the recrystallization temperature of the alloy while that of η(Ni_3Ti) phase lowers it. Moreover, these phenomena are found from marked difference between the two softening curves for both the cold-rolled alloys shown in Fig.5. The precipitation of γ' phase particles in cold-rolled alloy begins discontinuously from slip band and distorted grain boundary while γ' phase fine particles general-precipitate in γ phase matrix. The sizes of γ' phase particles precipitated discontinuously are larger than those precipitated generally. From the discontinuours precipitation zone containing these larger γ' phase particles, recrystallization begins as shown in Photo. 3. But it doesn't develop unless the γ' phase fine particles in the γ phase matrix grow to some size with increasing annealing temperature.

Leslie et alii (3) showed that coarse oxide inclusion in an Fe-O alloy enhanced nucleation, and isolated inclusions, 10^{-4} cm or more in diameter, in the alloy deformed by 60%, were each associated with several new grain on annealing and caused an acceleration of the entire recrystallization process, but below this diameter, precipitates were apt to slow down recrystallization. The resistance of sintered aluminum powder ($Al-Al_2O_3$ alloys) to recrystallization after a 98.8% rolling reduction increases steeply with alumina content, and is maintained to the neighborhood of melting point of the alloy (4). It is said that the critical radius of a viable nucleus in recrystallization will lie between 1.5×10^{-6} cm and 10^{-4} cm (5) (6). Even if the size of dispersed particle is less than 1μ, when the particle separation is more than 1to2μ, the large numbers of second-stiring nucleation points depress the recrystallization temperature and fine grain size is showed (7). For the retardation of recrystallization, it needs to have particle size that is less than 1μ and particle spacing that is critical nucleus or cell size for growth of recrystallization or less than the size. With increasing aluminum content, many Υ' phase particles precipitate finely in Υ phase matrix, the precipitates remain to high annealing temperature. And when the precipitates become coarse to more than 1μ size, recrystallization is accelerated regardless of the existence of the particles.

The recrystallization temperature which rises rapidly in the alloys containing above about 2%Al, because of the appearance of Υ' phase particles, increases gradually with increasing more aluminum content, but the degree of the increase goes down little by little. This fact shows that the coagulation of Υ' phase particles is accelerated at high temperature, even if the amount of the precipitate becomes larger and the solution temperature (the maximum solubility temperature) of that becomes higher with increasing aluminum content. Table 3 shows that 100% recrystallization temperature and solution temperature of precipitate are almost same in 3Al alloy in which the recrystallization temperature increases rapidly, and the difference between the above both temperatures become more marked with higher aluminum content. Gorelik (8) showed that the activation energy of recrystallization has the lower values at low temperatures which are entirely in the two-phase region, becomes extremely high when the temperature range embraces those temperatures which cover part of the two-phase and part of the single-phase regions (namely, near by line of maximum solubility), and again becomes lower values at high temperatures which are entirely in the single-phase region. The large amount of Υ' phase particles precipitate in 4Al and 5Al alloys, and the recrystallization of those alloys are completely performed becouse of the coagulation of the particles at high annealing temperature. But as the solution temperature of the precipitate doesn't reach to the line of maximum solubility yet, the coarse particles remain in the recrystallized grains.

However, the recrystallization temperature decreases markedly with precipitation of η phase flaky particles in the alloy added titanium only while that increases markedly with Υ' phase particles. η phase particles in 4Ti(3.92%Ti) alloy precipitate along the slip band and the grain boundary from 525°C, and then extend to the whole grains as shown in Photo. 4. As shown in Photo. 5, this discontinuous precipitation is distinctly grain boundary reaction that the nucleation and growth process is controlled by grain boundary diffusion. The grain boundary moves into the supersaturated matrix and the whole γ phase grains are covered with this reaction at 700°C. The grain boundary reaction zone is the two-phase region consisting of the precipitated η phase flaky particles and the γ phase matrix recrystallized by the precipitation. The recrystallization extends with the growth process of the above zone. Moreover, the sizes of η phase flaky particles are markedly larger than that those of γ′ phase particles. This grain boundary reaction takes place at lower annealing temperature with increasing titanium content, therefore the recrystallization temperature decreases. Because the solution temperature of η phase precipitate rises with increasing titanium content. The difference between 100% recrystallization temperature and solution temperature of precipitate becomes more marked with increasing titanium content.

The solubility for aluminum and titanium together in Ni-20Cr alloy decreases more than that for the single of the same amount of aluminum or titanium. Ni-20Cr alloy containing 0.6wt%Al and 1.1wt% Ti shows γ single phase structure at 750°C, but that containing 1.0wt%Al and 1.4wt%Ti is in γ+γ′ region at same temperature (1). Moreover, the solubility for both aluminum and titanium in 80Ni-20Cr alloy is 0.8wt%Al+1.6wt%Ti at 750°C, and 1.2wt%Al+2.4wt%Ti at 900°C (9). It is found that γ′ phase particles precipitate in 1Al-1Ti alloy containing 1.28%Al and 0.85%Ti, by marked hardening curve for the solution-treated alloy shown in Fig. 6. Moreover, Figs. 6and 7 show that hardness in the as solution-treated condition increases and the degree of precipitation hardening decreases, with increasing aluminum content in the alloy containing fixed titanium. The grain boundary reaction as shown in Photo. 6 in solution-treated alloy containing both aluminum and titanium takes place in alloys containing to Al+Ti ≑ 3.6wt%. As shown in Fig. 11, the fraction becomes maximum at about 650°C, and generally increases to about 10% with increasing titanium content.

In cold-rolled alloy, however, discontinuous precipitation is found to Al+Ti ≑ 5.8wt.%, the fraction becomes more marked, and the maximum is obtained at about 625°C. In the case of this, the fraction increases in the alloy containing larger amount of aluminum than titanium. But the discontinuous precipitation takes place hardly in 3Al-3Ti and 2Al-4Ti alloys.

Above result in solution-treated alloy shows that discontinous precipitation takes place easily at about 650°C. But the temperature decreases to about 625°C in cold-rolled alloys. This fact shows that because activation energy which is required for nucleation and growth of precipitate becomes smaller with increasing crystal lattice strain by cold working, the precipitation process in alloys which show marked precipitation hardening takes place at lower annealing temperature. Therefore, the precipitation hardening in cold-rolled alloys becomes maximum at about 700°C while that in solution-treated alloys becomes maximum at about 800°C. The result on that discontinuous precipitation along slip band and grain boundary decreases at above 625 to 650°C, shows that general precipitation becomes more marked at above these annealing temperature.

Under this experimental condition that isochronous annealing of 2 hours was performed at each temperature, alloy is annealed to higher temperature by passing the temperature region in wich the discontinuous precipitation takes place on the way of the annealing. The passing time becomes shorter with increasing annealing temperature, therefore the fraction of discontinuous precipitation becomes maximum at 625°C. Since precipitation decreases with decreasing both both aluminum and titanium contents, the fraction of discontinuous precipitation decreases. In the case of solution -treated alloys, since the grain bounbary reaction becomes more marked for the addition of titanium only, the fraction becomes more marked with increasing titanium content for the addition both aluminum and titanium. In the case of cold-rolled alloys, however, on the contrary, the fact that the fraction of discontinuous precipitation increases with increasing aluminum content is thought because the growth of γ' phase particles is accelerated.

S.A. Yunganov et alii (10) have shown that the size of γ' phase particles increases with the Al/Ti ratio and the number of those diminishes as the Al/Ti ratio rises. The variation in the growth rate of γ' phase particles as a function of the Al/Ti ratio is attributed to the degree of crystal lattice distortion on the interface between the γ' phase and the matrix. In the case of solution -treated alloys, since genaral precipitation takes place more preferentally with increasing both aluminum and titanium contents, grain boundary reaction is prevented. In the case of cold-rolled alloys containing large amount of both aluminum and titanium, discontinuous precioitation takes place by the above caus as the Al/Ti rato is higher and by the acceleration in grain boundary reaction due to titanium as the Al/Ti ratio is lower. But in the case of the Al/Ti ratio is about 1 to 0.5, discontinuous precipitation is prevented because γ' phase particles is finer, those growth is slower, and general precipitation is apt to take place.

450 to 550°C that is the beginning temperature of discontinuous precipitation shown in Fig. 11 are almost the same with the starting temperature of hardening in hardness/annealing-temperature curves shown in Fig. 6 and 7. Moreover, the curves show to increase discontinuously in hardness at 625 to 700°C that discontinuous precipitation decreases and general precipitation becomes more marked. In the case of both solution-treated and cold-rolled condition, the hardness increases with increasing general precipitation, becomes maximum at about 800°C in the former and at about 700°C in the latter, and then becomes softer with increasing the coagulation of precipitate, the solubility of precipitate in the matrix, and the recrystallization. The begining temperatures of softening in cold-rolled alloys are almost the same with those of recrystallization.

As shown in Table 4, η phase precipitates in 1Al-4Ti and 1Al-5 Ti alloys only. η phase acicular particles in these alloys are found along the grain boundary from about 900°C in the solution-treated condition, and from about 850°C in the cold-rolled condition (see Photos. 9 and 10). And the fine general precipitates that exist at lower then these temperatures are γ' (fcc Ni_3Ti) while η phase (hcp Ni_3Ti) precipitates exist in discontinuous precipitation zone. N.E. Rogen et alii (11) have shown that during the initial growth period the titanium content of γ' ($Ni_3(Al,Ti)$) phase precipitate decreases, and then increases. Moreover they have shown that the Ti/Al(at%) ratio can go as high as 1.5 [Al/Ti (wt%) natio is 1.5 alsa] before the solubility for titanium in γ' phase is exceeded, but when this solubility is exceed, the hexagonal Ni_3Ti phase (η) is precipitated. However, η phase didn't appear in Ni-Cr-Al-Ti alloy containing 20.71wt%Cr, 2.98wt%Ti and 1.43wt%Al that they used, and the Ti/Al (at%) ratio in γ' phase was 0.82 after 216hr. annealing at 760°C and 0.81 even after 60hr. annealing at 816°C. In order that this ratio becomes easily to 1.5, it is known from the compositions of 1Al-4Ti and 1Al-5Ti alloys that it needs about 0.3 as Al/Ti (wt%) ratio.

The recrystallization of alloy containing higher titanium than aluminum content developes with the precipitation of η phase, therefore the recrystallization temperature becomes as lower as in the case of the alloy containing titanium only. J.R. Mihalisin et alii (12) have shown that residual cold work accelerates the decomposition of nonequilibrium γ' to η both at grain boundaries and intragranularly. Replacing titanium by aluminum retards both the cellular and intragranular conversion of nonequilibrium γ' to η, and the magnitude of the retardation increases with the degree of substitution, therefore the recrystallization temperature increases. Fig.20 shows that the maximum response of recrystallization temperature is at approximately a 1 to 1.5 weight ratio of aluminum to titanium. The recrystallization temperature always decreases because γ' phase particles become unstable in higher titanium content than in the above ratio and grow easily in higher aluminum content than that as shown in Photo. 12. Moreover, the disregistry between γ matrix and γ' phase precipitate is the greatest when Ti/Al (at%) ratio is approximately 1.7 to 1 [Al/Ti (wt.%)= 1.2~2] (12). Since the lattices of γ and γ' phases are both fcc and closely enough matched to allow coherency, the coherency straining provided by the greatest mismatch between γ and γ' raises the hardness, stabilizes γ' phase fine particles to higher temperature, embarrasses the diffusion of atoms, and raises the recrystallization temperature.

Figs. 8 and 9 show that the hardness near by the peak of precipitation hardening in both solution-treated and cold-rolled alloys is at approximately a 1 weight ratio of aluminum to titanium. Similarly, Fig. 21 shows that the highest solution temperature of precipitate is at approximately a 1 weight ratio of aluminum to titanium. Table 4 shows that in the case of increasing both aluminum and titanium contents excepting higher titanium content, the increase of solution temperature of precipitate is almost same with that of 100% recrystallization temperature. If the large amount of precipitate remains to higher annealing temperature, since both aluminum and titanium contents in γ phase matrix increase with increasing the solubility for the precipitate, it is a matter of course that the recrystallization temperature increases. By the above some factors, the highest recrystallization temperature is obtained at approximately a 1 weight ratio of aluminum to titanium.

Figs. 1 and 2 show that the maximum hardness values of both solution-treated and cold-rolled alloys which have γ single phase are at approximately a 1 weight ratio (a 2 atomic ratio) of aluminum to titanium too. This fact suggests that the maximum degree of crystal lattice strain in γ phase matrix after precipitate dissolved completely in that is at approximately a 1 weight ratio of aluminum to titanium, and it corresponds to the result of the recrystallization temperature of the matrix. In the case of Al/Ti (wt.%)=1, if it is 2wt.%Al+2wt.%Ti=4wt.% (Al+Ti)≑6at.% (Al+Ti), the hardness value for this addition of aluminum and titanium together becomes larger than that for single addition of 4wt.%Al≑8at.%Al. It is probable that the atomic diameter of titanium (2.93 Å) is larger than that of aluminum (2.80 to 2.85 Å), and titanium compared with aluminum lowers more the stacking-fault energy of nickel alloy, accelerates forming the partial dislocation, and has more effect to strengthening the matrix (13). But the hardness value for single addition of 4wt.%Ti≑4at.%Ti becomes lower than that of 4wt.%Al≑8at.%Al because of the smaller atomic percent. This fact shows that the addition of both aluminum and titanium as Al/Ti (wt%)=1 gives the crystal lattice strain to the γ phase matrix by the optimum combination of the aluminum content and the titanium content that titanium has larger atomic size and stronger pile up effect to the stacking-fault than aluminum.

Summary

In order to evaluate the heat-resisting property of Nimonic type heat-resistant alloys, the effects of additions of aluminum and/or titanium on the recrystallization behavior of 80Ni-20Cr alloy have been investigated.

The followings are some highlights of this investigation:

1. The recrystallization temperature of Ni-20Cr alloy can be raised to the similar extent by including up to about 2%Al or about 3%Ti. And the recrystallization temperature can be raised steeply as the aluminum content in the alloy increased more but lowered titanium content adversely. These phenomena made clear in terms of the solid-solubility of aluminum and titanium in the alloy, the morphology of the precipitates and the mechanism of the precipitation.

2. The hardness for both solution-treated and cold-rolled alloys is the highest at approximately a 1 weight ratio of aluminum to titanium.

3. 2Al-4Ti and 3Al-3Ti alloys have the highest resistivity for softening at elevated temperature, and are followed by 4Al-2Ti, 2Al-3Ti and 3Al-2Ti, and 1Al-5Ti and 5Al-1 Ti alloys.

4. Discontinuous precipitation takes place in the solution-treated alloys up to around 3.6 weight percent of aluminum plus titanium and in every cold-rolled alloys with the exception of 2Al-4Ti and 3Al-3Ti alloys. The cold working of the alloys raises the possibility of the discontinuous precipitation, and the starting temperature and the brisk temperature of the discontinuous precipitation in the solution-treated alloys decrease from 525°C to (450~500°C) and from 650°C to 625°C respectively.

5. The hardness of the alloys rises as the discontinuous precipitation takes place and rises more rapidly at annealing temperature that the general precipitation becomes brisk with the dulness of the discontinuous precipitation. This annealing temperatures are 675 to 700°C for solution-treated alloys and 650 to 675°C for cold-rolled alloys.

6. The temperature that shows the peak of hardening owing to the general precipitation in the solution-treated alloys at about 800°C is lowered to about 700°C by cold working. But the peak in the cold-rolled alloys containing large amount of titanium is lowered with the range of 550 to 600°C. Moreover, the hardness of solution-treated alloys at 800°C and cold-rolled alloys at 700°C become maximum at approximately a 1 to 0.25 weight ratio of aluminum to titanium.

7. In the alloys included titanium more than about 3% individually, the discontinuous precipitation of η phase takes place at above 550°C, and the recrystallization temperature of the alloys is lowered with the development of the grain boundary reaction. In the alloys included both aluminum and titanium, η phase precipitates in less than a 0.3 weight ratio of aluminum to titanium, and the annealing temperature that the nonequilibrium titanium rich η phase changes to the equilibrium η phase is at above 850°C. This change starts from the grain houndary in the solution-treated alloys and from the recrystallized region in the cold-rolled alloys.

8. The recrystallization temperature of the alloys becomes the highest at approximately a 1 to 1.5 weight ratio of aluminum to titanium. This phenomenon was made clear in terms of the solid-solubilities for aluminum and titanium in the alloys, the morphology and the stability of the precipitates, and the disregistry between precipitate and matrix.

9. The solid-solution temperature of precipitate is the highest at approximately a 1 weight ratio of aluminum to titanium, and is almost the same with the completion temperature of recrystallization with the exception of the alloys containing large amount of titanium.

10. γ' phase particles in the alloys which have approximately a 1 to 1.5 weight ratio of aluminum to titanium keep stable and fine up to the higher annealing temperature, and as the result the recrystallization temperature of the alloys can be raised. But γ' phase particles in the alloys containing more aluminum and η phase flaky particles in the alloys containing more titanium than the above ratio respectively both coagulate and grow rapidly at high annealing temperature, and as the result the recrystallization temperature of the alloys can not be raised.

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Table 1. Chemical Composition of Ni-20Cr-Al and Ni-20Cr-Ti Alloys (wt.%).

Alloys	Cr	Al	Ti	Ni
80Ni-20Cr	19.59	—	—	Bal
1Al	19.70	0.84	—	Bal
2Al	19.41	1.71	—	"
3Al	19.56	2.70	—	"
4Al	20.56	3.51	—	"
5Al	19.93	4.51	—	"
1Ti	19.39	—	0.81	Bal
2Ti	20.05	—	2.06	"
3Ti	19.90	—	2.77	"
4Ti	19.70	—	3.92	"
5Ti	19.46	—	4.92	"
6Ti	19.57	—	5.88	"

Table 2. Chemical Composition of Ni-20Cr-Al-Ti Alloys (wt.%).

Alloys	Cr	Al	Ti	Al+ Ti	Ni
1Al-1Ti	19.78	1.28	0.85	2.13	Bal
1Al-2Ti	19.80	0.82	1.94	2.76	Bal
2Al-1Ti	19.91	1.64	1.13	2.77	"
1Al-3Ti	19.72	1.02	2.63	3.65	Bal
2Al-2Ti	19.84	1.78	1.72	3.50	"
3Al-1Ti	19.61	2.65	0.95	3.60	"
1Al-4Ti	19.40	1.06	3.40	4.46	Bal
2Al-3Ti	19.78	1.88	2.58	4.46	"
3Al-2Ti	19.45	2.81	1.71	4.52	"
4Al-1Ti	19.60	3.92	0.73	4.65	"
1Al-5Ti	19.48	1.20	4.14	5.34	Bal
2Al-4Ti	19.53	2.29	3.54	5.83	"
3Al-3Ti	19.63	2.45	2.56	5.01	"
4Al-2Ti	19.54	4.07	1.67	5.74	"
5Al-1Ti	19.45	5.07	0.73	5.80	"

Table 3. Recrystallization Temperature, Solution Temperature of Precip
and Microstructure of 70 % Cold-Rolled Ni-20Cr-Al and Ni-20Cr

Alloys	Recrystallization Temperature (° C) 1 ~ 2% Recrystalli.	60% Recrystalli.	100% Recrystalli.	Solution Temperature of Precipitate (° C)	Mi St
80Ni-20Cr	~ 575	635	~ 660	N	
1Al	~ 575	670	~ 710	N	
2Al	~ 600	685	~ 720	N	
3Al	~ 725	825	~ 845	N	
4Al	~ 775	890	~ 900	925	
5Al	~ 775	915	~ 950	1000	
1Ti	~ 575	645	~ 680	N	
2Ti	~ 575	675	~ 700	N	
3Ti	~ 625	695	~ 730	N	
4Ti	~ 575	640	~ 700	975	
5Ti	~ 550	600	~ 690	1050	
6Ti	~ 550	590	~ 675	1075	

N = No Precipitation Evident

Table 4. Recrystallization Temperature, Solution Temperature of Precipit
and Microsturucture of 70 % Cold-Rolled Ni-20Cr-Al-Ti Alloys.

Alloys	Recrystallization Temperature (°C) 1 ~ 2% Recrystalli.	60% Recrystalli.	100% Recrystalli.	Solution Temperature of Precipitate (°C)	Micr Stru
1Al-1Ti	~725	830	~855	875	[illegible]
1Al-2Ti	~750	885	~920	925	[illegible]
2Al-1Ti	~750	905	~930	925	[illegible]
1Al-3Ti	~800	965	~1000	1000	[illegible]
2Al-2Ti	~800	970	~1000	1000	[illegible]
3Al-1Ti	~825	965	~980	1000	[illegible]
1Al-4Ti	~775	940	~1010	1100	γ+
2Al-3Ti	~800	1025	~1060	1100	[illegible]
3Al-2Ti	~850	1030	~1060	1075	[illegible]
4Al-1Ti	~850	975	~1010	1025	[illegible]
1Al-5Ti	~700	880	~960	1100	γ+
2Al-4Ti	~775	1015	~1110	1125	[illegible]
3Al-3Ti	~725	1030	~1120	1125	[illegible]
4Al-2Ti	~725	1020	~1105	1125	[illegible]
5Al-1Ti	~725	955	~1060	1075	[illegible]

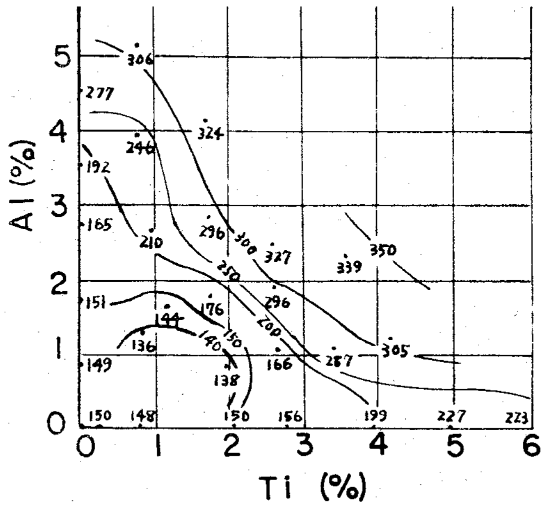


Fig.1. Contour lines of Vickers hardness (5Kg) distribution of solution-treated alloys.

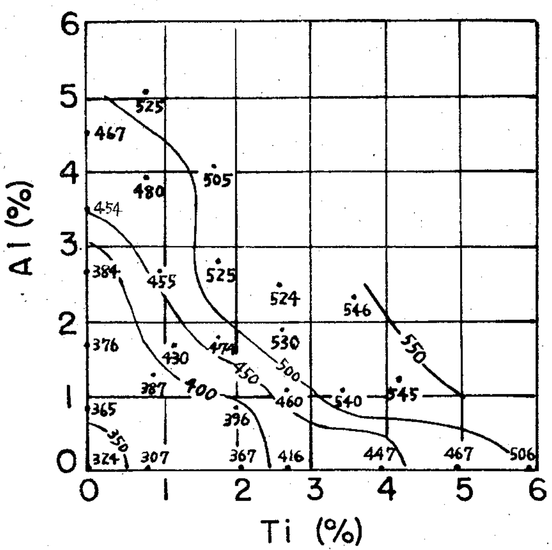


Fig.2. Contour lines of Vickers hardness (5Kg) distribution of 70% cold-rolled alloys.

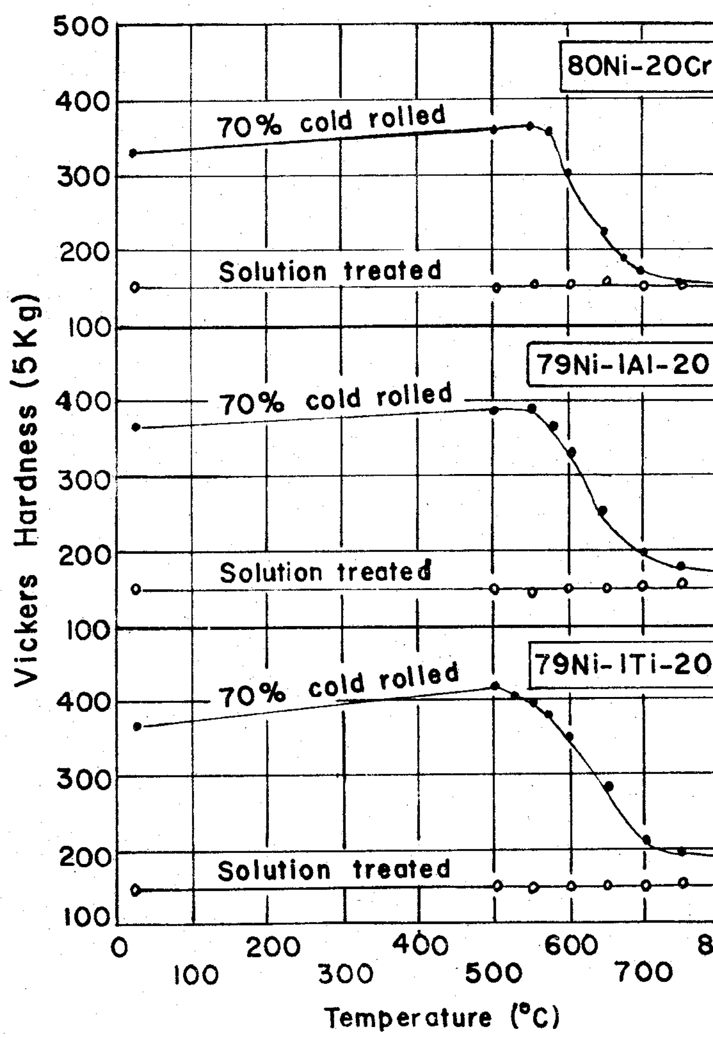


Fig.3. Hardness/annealing-temperature
80Ni-20Cr, 79Ni-1Al-20Cr and 79Ni-
alloys.

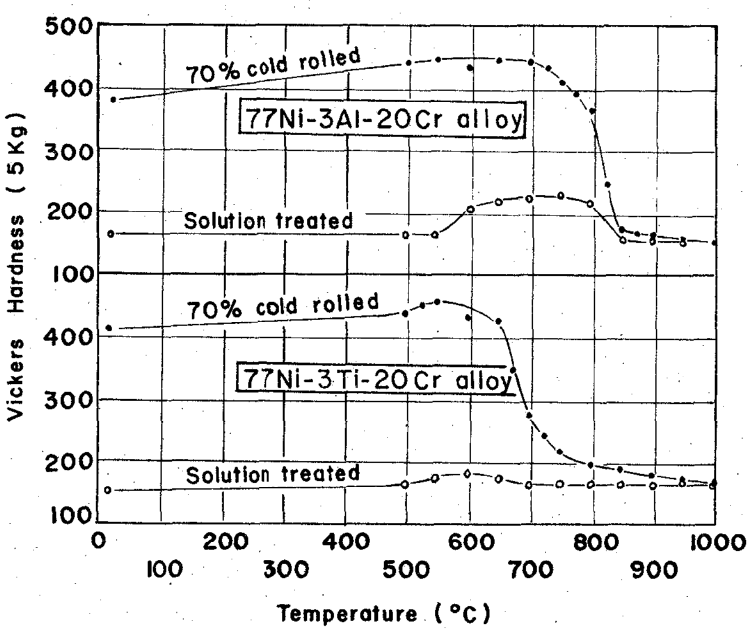


Fig.4. Hardness/annealing-temperature curves for 77Ni-3Al-20Cr and 77Ni-3Ti-20Cr alloys.

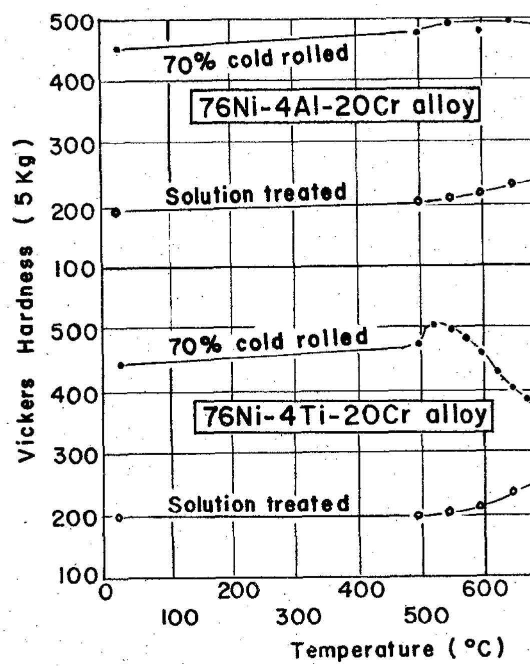


Fig. 5. Hardness/annealing-temp

for 76Ni-4Al-20Cr and 76Ni-4

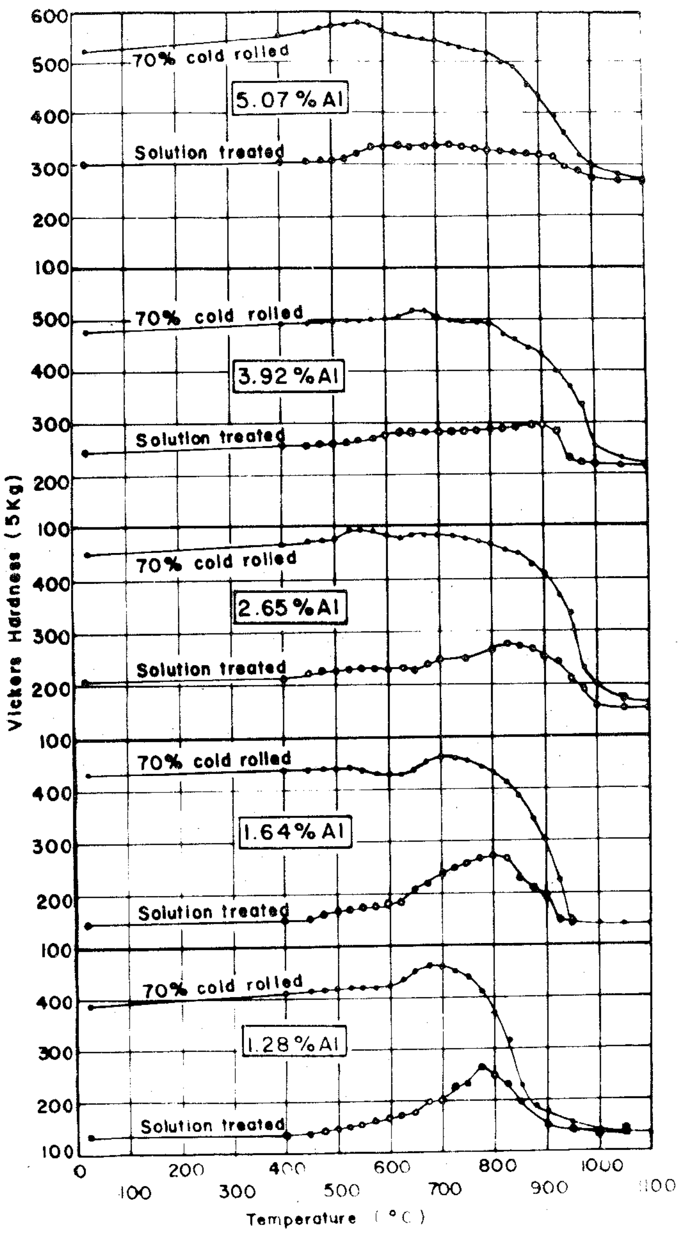


Fig 6. Hardness/annealing-temperature curves for alloys containing 0.73~1.13% Ti

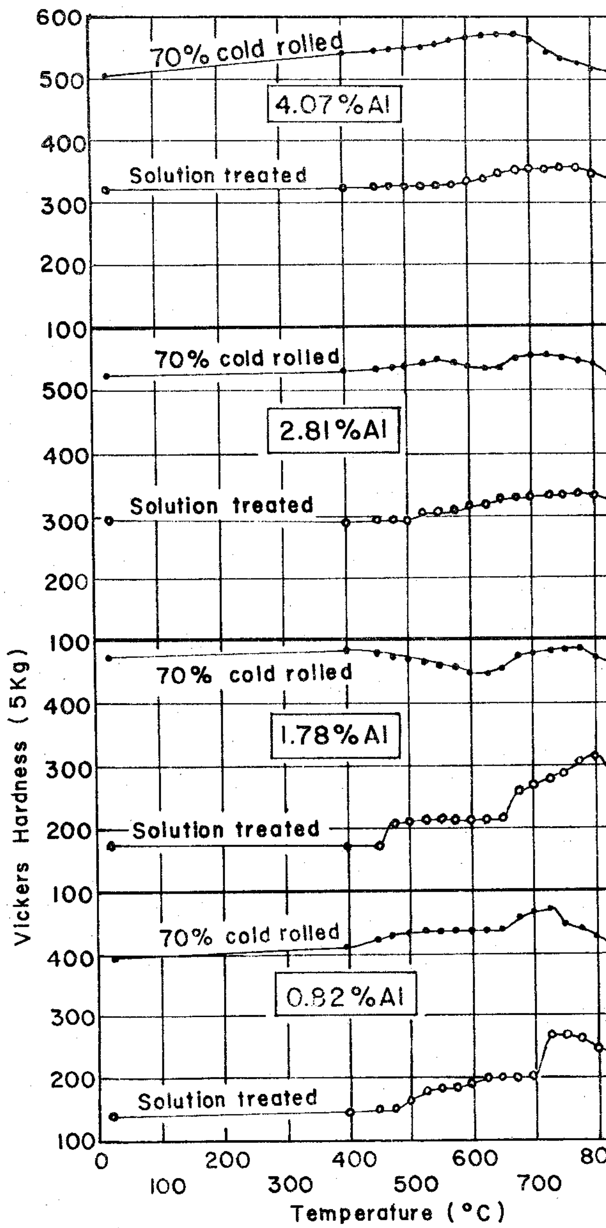


Fig. 7. Hardness/annealing-temperatur

alloys containing 1.67~1.94 % Ti.

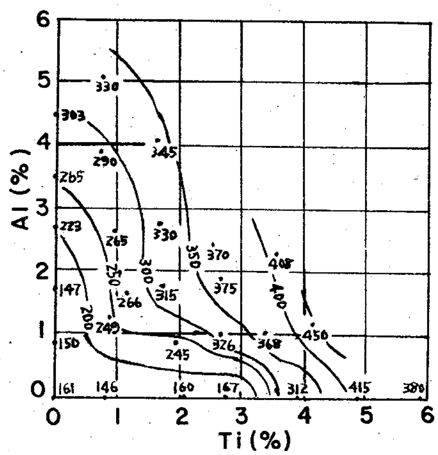


Fig.8. Contour lines of Vickers hardness (5Kg) distribution of solution-treated alloys by annealing at 800°C for 2 hr.

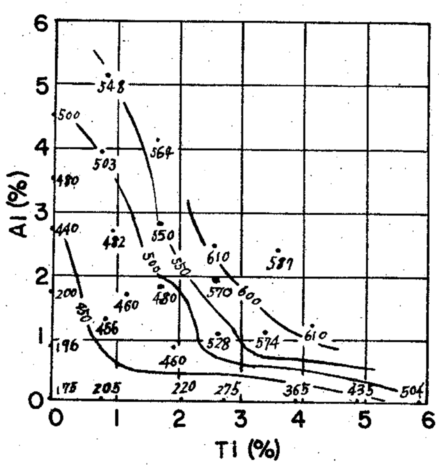


Fig.9. Contour lines of Vickers hardness (5Kg) distribution of 70% cold-rolled alloys by annealing at 700°C for 2 hr.

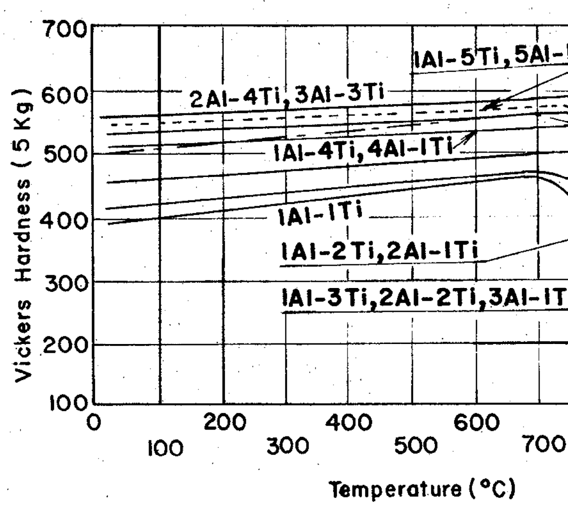


Fig.10. Softening curves of 70% co

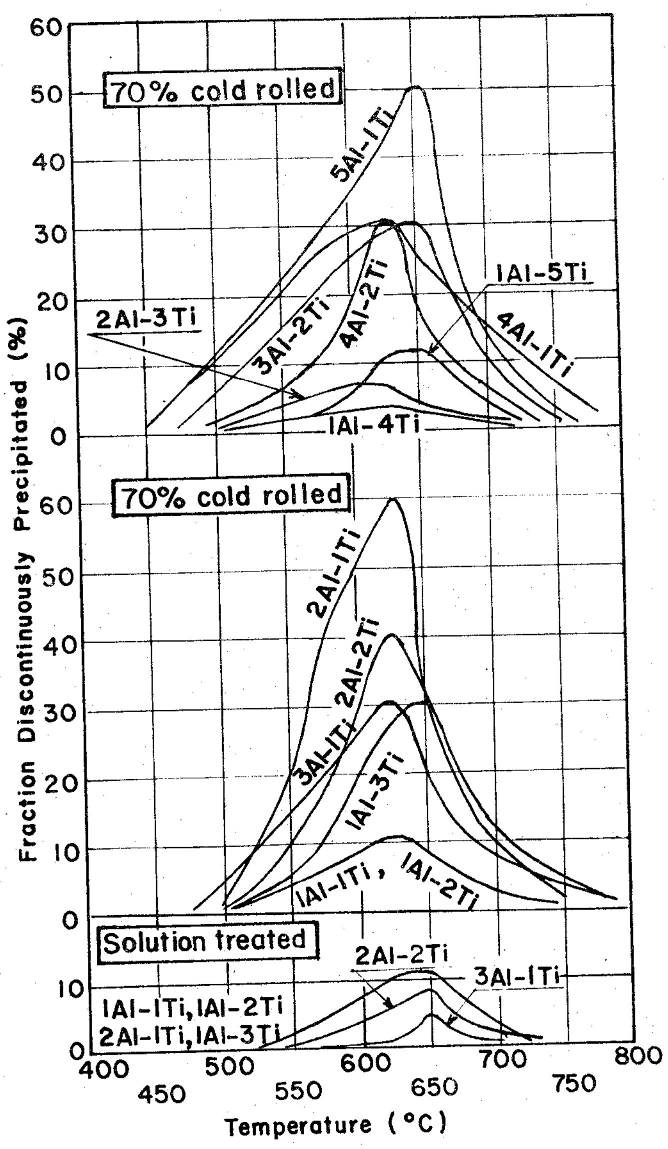


Fig.11. Discontinuously precipitated-fraction/annealing-temperature curves of alloys.

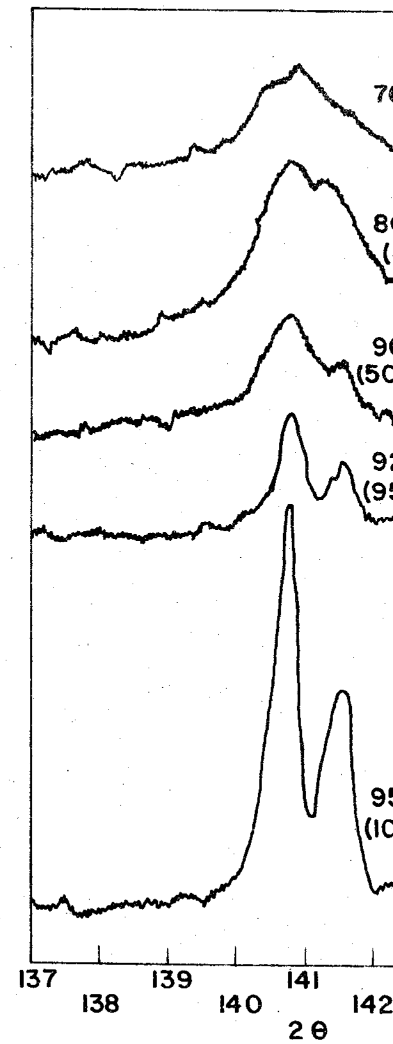


Fig.12. Recrystallization b
2Al-1Ti alloy by X-ray
patterns.

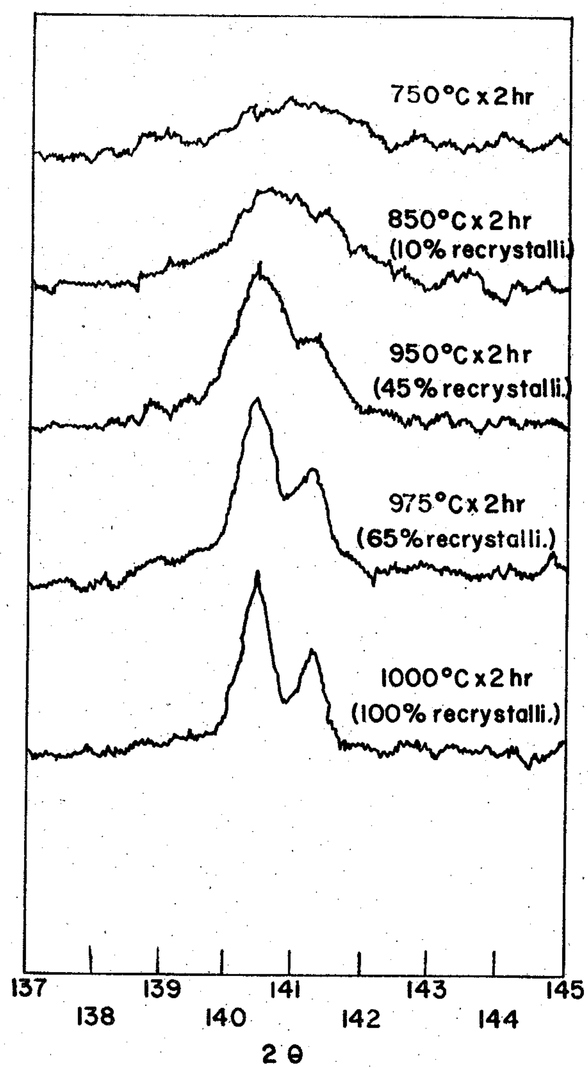


Fig. 13. Recrystallization behavior of 2Al-2Ti alloy by X-ray diffraction patterns.

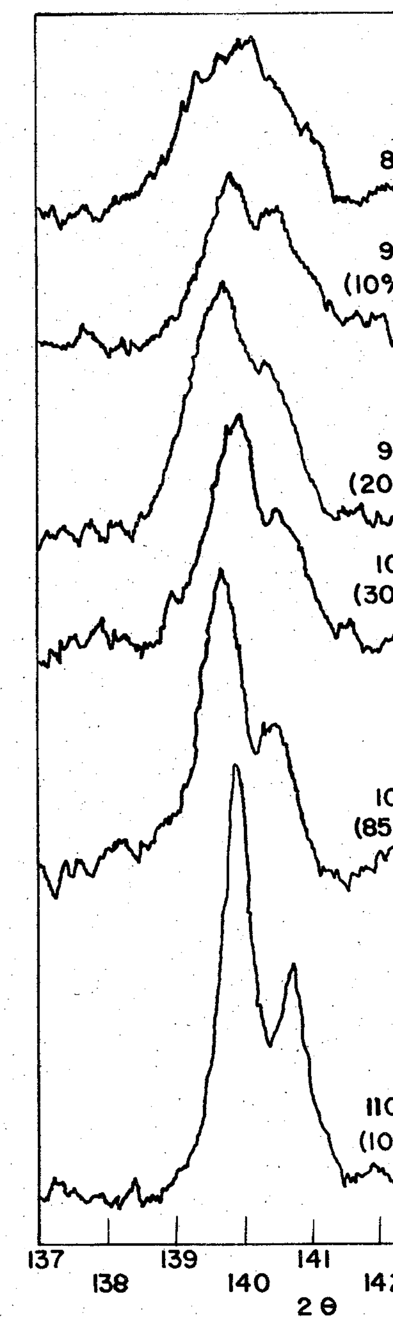


Fig. 14. Recrystallization
3Al-2Ti alloy by X-ray
patterns.

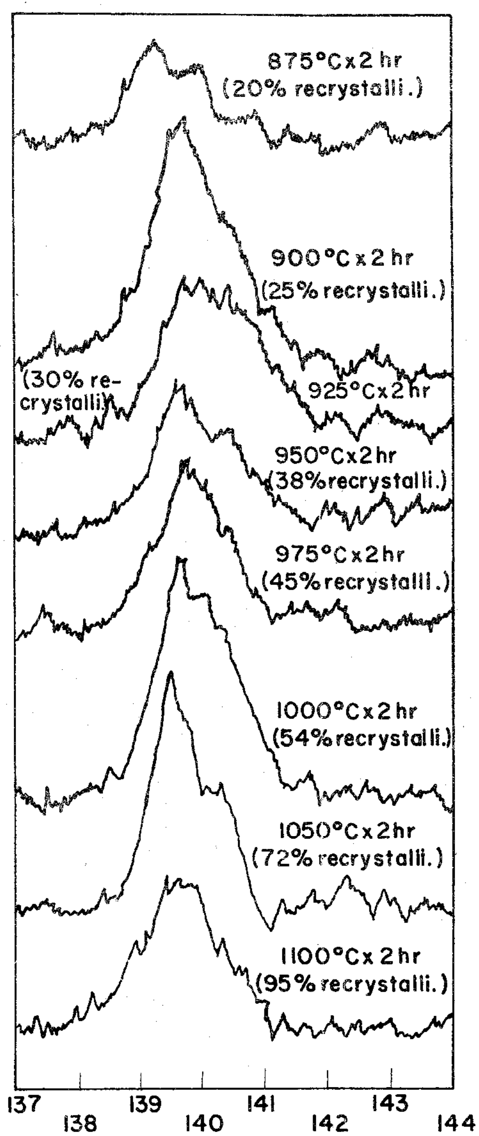


Fig. 15. Recrystallization behavior of 4Al-2Ti alloy by X-ray diffraction patterns.

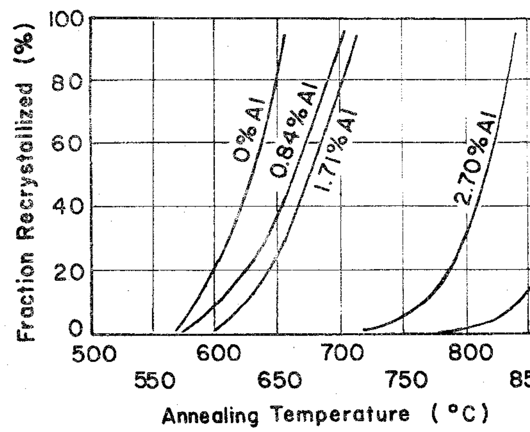


Fig. 16. Recrystallized-fraction/ann
temperature curves of Ni-20Cr-

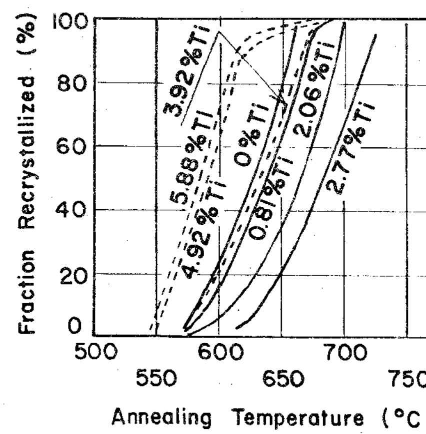


Fig. 17. Recrystallized-fract
annealing-temperature cur
of Ni-20Cr-Ti alloys.

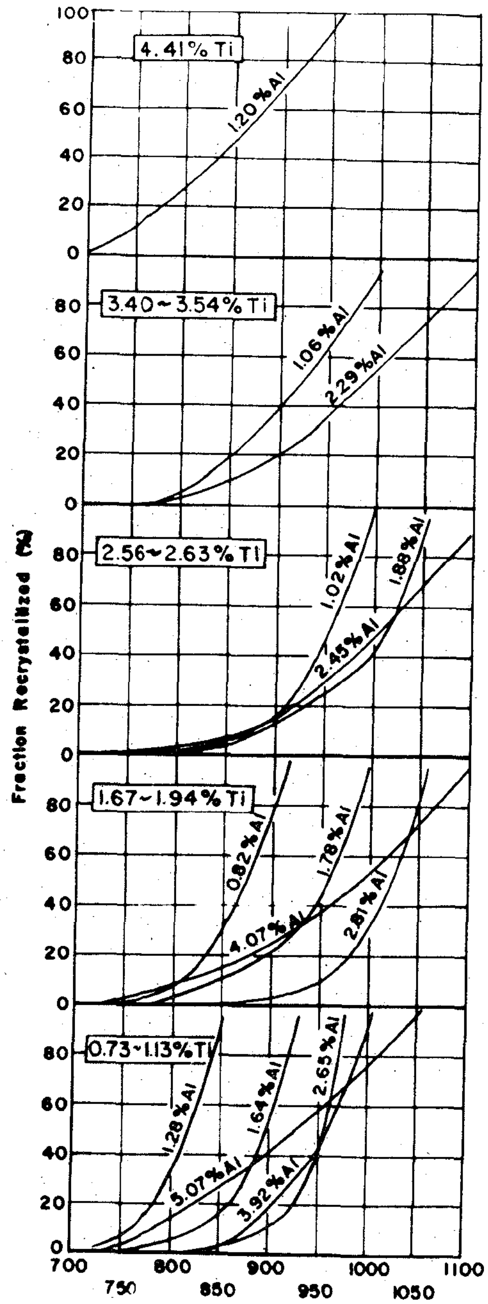


Fig 18 Recrystallized-fraction/annealing
-temperature curves for 70% cold-rolled

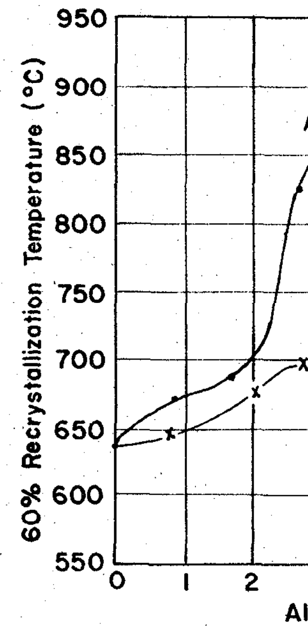


Fig. 19. Effect
and titanium o
zation tempera
alloy cold rolle
solution treate

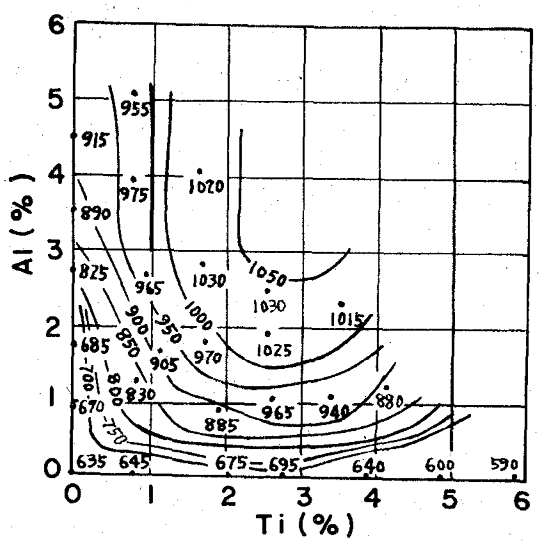


Fig. 20. Contour lines of 60% recrystallized-temperature (°C) distribution of 70% coled-rolled alloys.

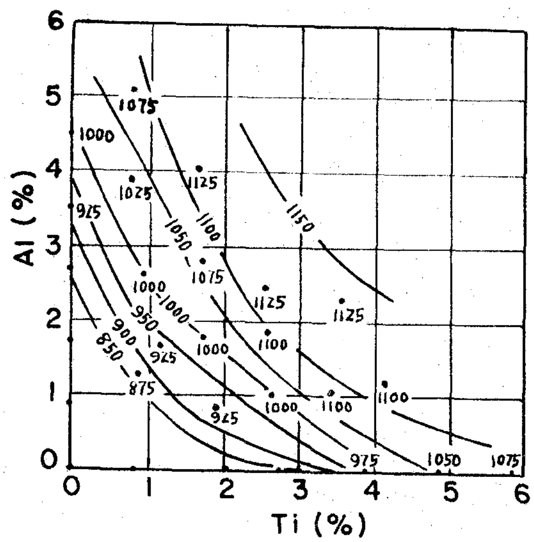
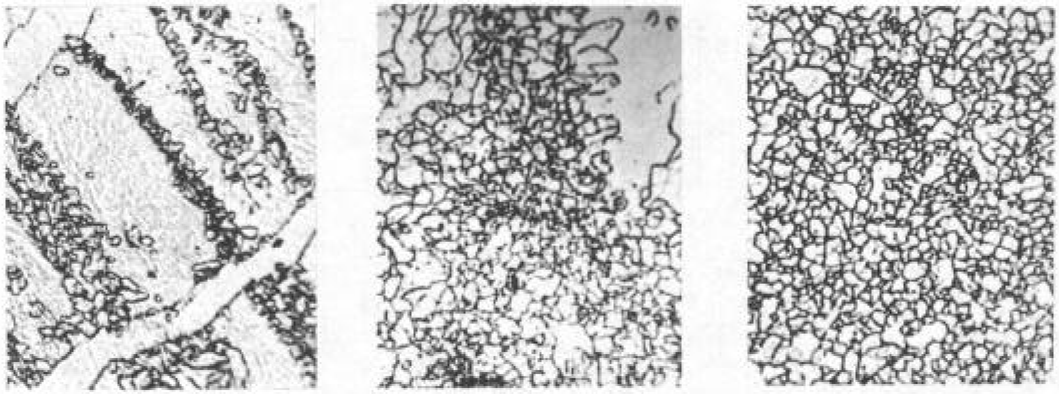
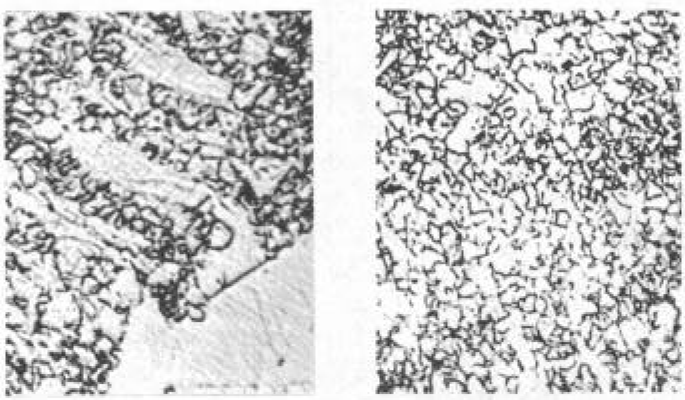


Fig. 21. Contour lines of solution temperature (°C) of precipitate in 70% cold-rolled alloys annealed for 2 hr.



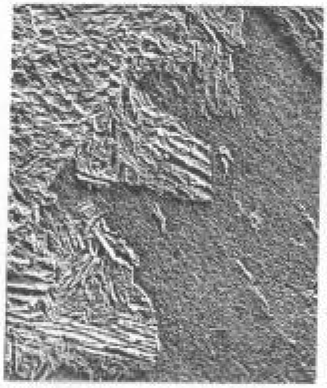
a. 650° C × 2hr. b. 700° C × 2hr. c. 750° C × 2hr.

Photo. 1 . 70 % cold-rolled 1Al alloy (× 200).



a. 650° C × 2hr. b. 675° C × 2hr.

Photo. 2 . 70 % cold-rolled 1Ti alloy (× 200).

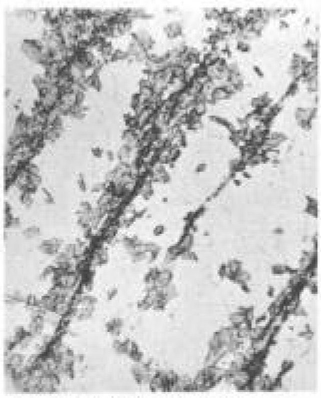


Electron microscopic structure
(×5000)

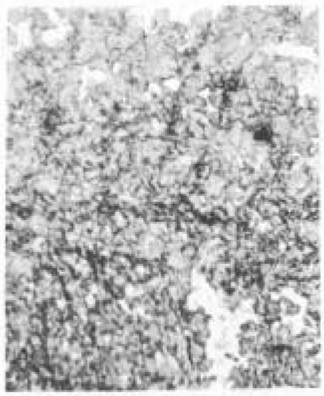
875°C × 2hr.
(×1000)

Electron microscopic structure
(×5000)

Photo. 3. 70 % cold-rolled 4Al alloy.



a. 600°C × 2hr.
(×400)



b. 650°C × 2hr.
(×400)

c. 775°C × 2hr.
(×5000)
Electron microscopic structure

Photo. 4. 70 % cold-rolled 4Ti alloy.

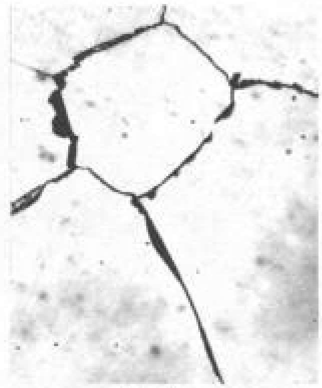
a. 650°C × 2hr.

b. 750°C × 2hr.

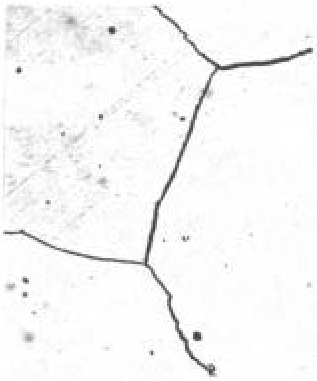
Photo. 5. Electron microscopic stuructures of solution-treated 6Ti alloy (×5000).

a. 525°C X 2hr. (X 400)

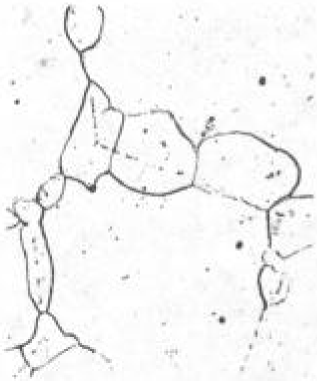
b. 650°C X 2hr. (X 400)



c. 675°C X 2hr. (X 400)

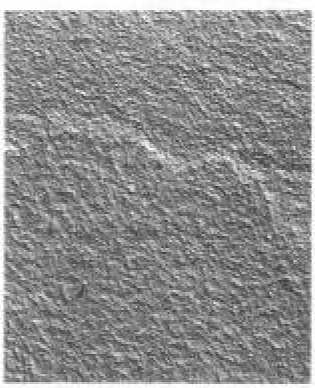


d. 775°C X 2hr. (X 400)



e. 925°C X 2hr. (X 400)

Electron microscopic structure (X 5000)



Electron microscopic structure (X 5000)

f. 900°C 2hr. (X 5000) Electron microscopic structure

Photo. 6. Solution-treated 2Al-1Ti alloy.

a. 525° C × 2hr.
(× 400)

b. 600° C × 2hr.
(× 400)

c. 650° C × 2hr.
(× 400)

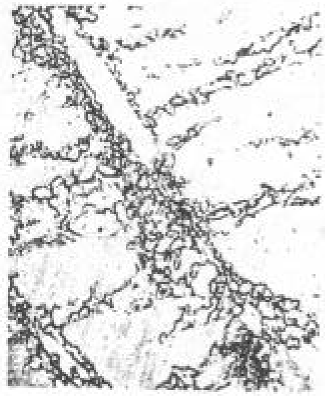
Electron micro-
scopic structure
(× 5000)

Electron micro-
scopic structure
(× 5000)

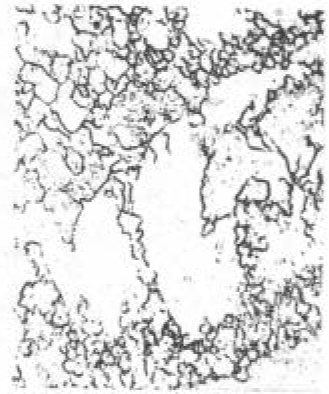
d. 725° C × 2hr.
(× 400)

Photo. 7. 70 % cold-rolled 2Al-1Ti alloy.

e. 800°C × 2hr. (×400)

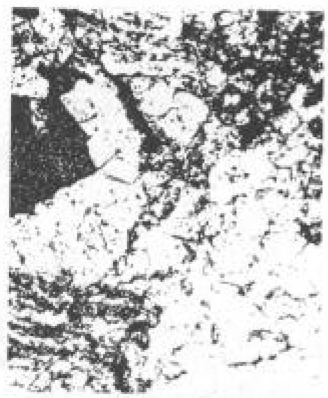


f. 875°C × 2hr. (×400)

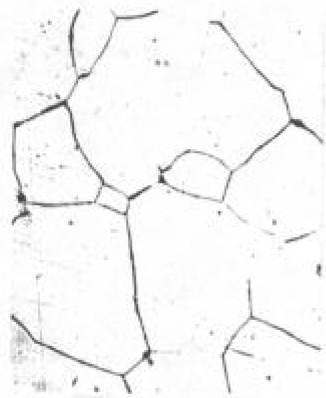


g. 900°C × 2hr. (×400)

Electron microscopic structure (× 5000)

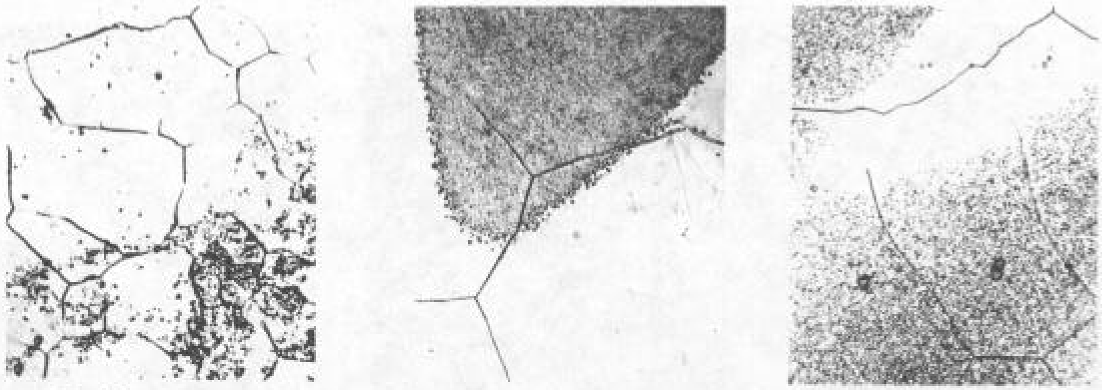


h. 925°C × 2hr. (×400)



i. 950°C × 2hr. (×400)

Photo. 7. 70 % cold-rolled 2Al-1Ti alloy. continued

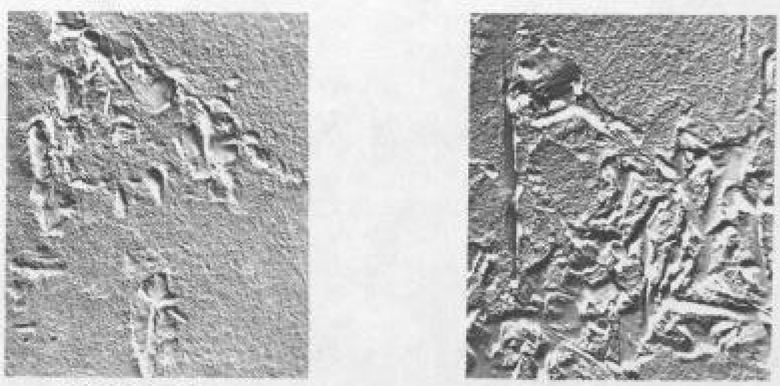


a. 70 % cold-rolled 2Al-2Ti alloy, 1000° C × 2hr.

b. Solution-treated 3Al-1Ti alloy, 1000° C × 2hr.

c. Solution-treated 3Al-3Ti alloy, 1000° C × 2hr.

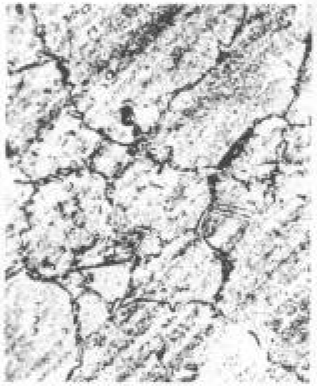
Photo. 8. Status of precipitate in the neighborhood of solution temperature (× 400).



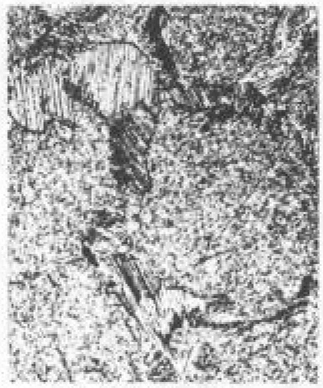
a. 800° C×2hr.

b. 850° C × 2hr.

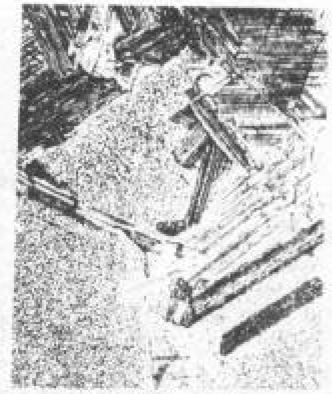
Photo. 9. Electron microscopic structure of 70 % cold-rolled 1al-4Ti alloy (× 5000).



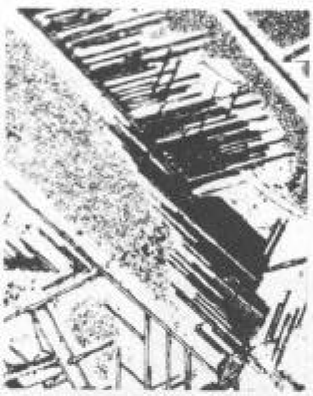
a. 925°C x 2hr.



b. 1000°C x 2hr.



c. 1050°C x 2hr.

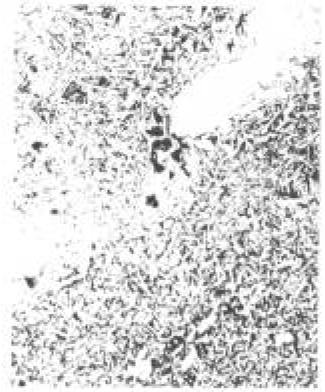


d. 1100°C x 2hr.

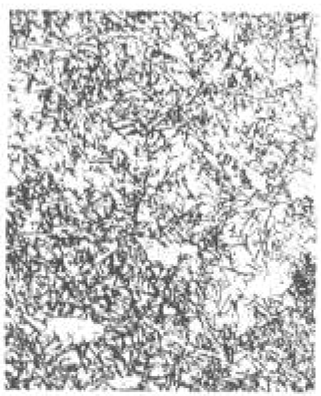
Photo. 10. Solution- treated 1Al-5Ti alloy (x 400).

a. 750° C × 2hr.

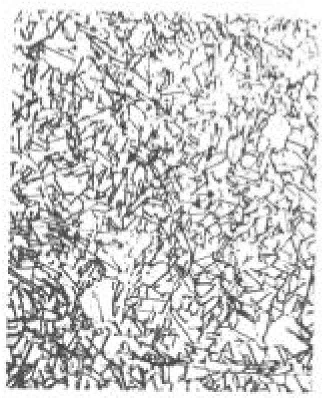
b. 850° C × 2hr.



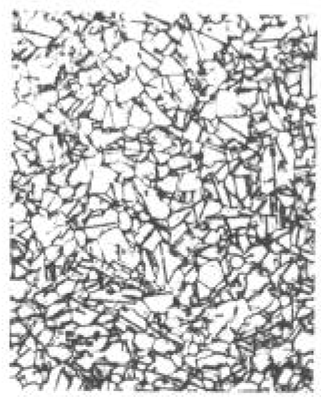
c. 925° C × 2hr.



d. 975° C × 2hr.

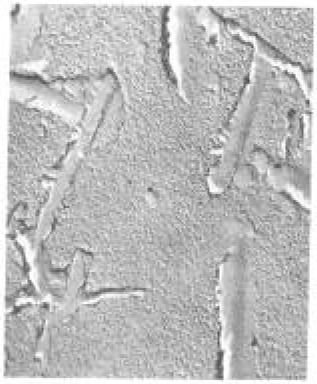


e. 1050° C × 2hr.

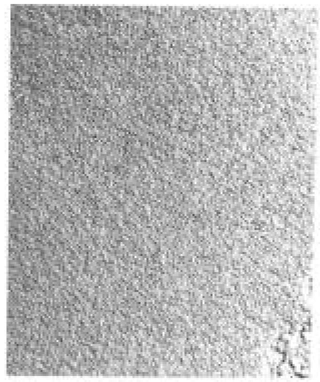


f. 1100° C × 2hr.

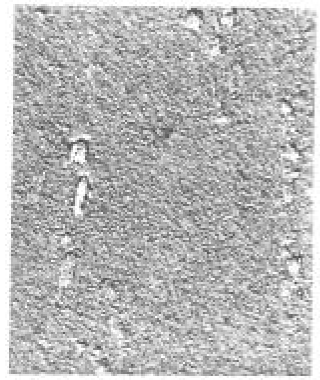
Photo. 11. 70 % cold-rolled 1Al-5Ti alloy (× 400).



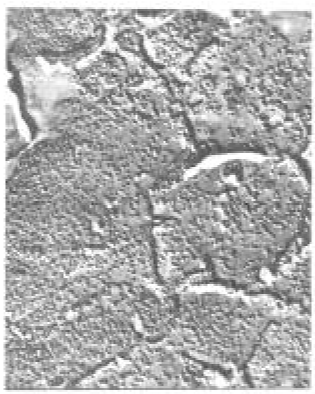
a. 1.20%Al-4.14%Ti



b. 2.81%Al-1.71%Ti



c. 3.92%Al-0.73%Ti



d. 5.07%Al-0.73%Ti

Photo. 12. Electron microscopic structure compared sizes of precipitates in matrix of 70 % cold-rolled allos annealed for 2 hours at 900°C (× 5000).