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# 기계적 합금화한 ODS NiAl의 이차 재결정화 거동

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# Secondary Recrystallization Behavior in Mechanically Alloyed ODS NiAl

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초 록 Ni 및 Al 단원소 분말을 혼합하여 attrition mill을 사용하여 분위기 속에서 기계적 합금화 NiAl기 산화물 분산강화 금속간화합물을 제조하였다. 제조된 분말은 여러 가지 다른 미세조직을 얻기 위하여 각기 다른 공정으로 열간성형을 하였으며, 연이어 이차 재결정 조직을 얻기 위한 가공열처리(thermomechanical treatment)를 실시하였다. 이차 재결정이 일어날 수 있는 선수조건으로서의 초기 미세조직과 가공열처리와의 상관관계를 조사하였다. 정상 결정립 성장의 억제와 집합조직의 존재가 이차 재결정을 일으키기 위한 필요조건으로 판명되었다. 이 재료에 있어서, 잔류 변형에너지를 공급할 수 있고 결정립을 미세화 할 수 있는 특정 공정하에서 항온 열처리 후 이차 재결정이 생성됨을 알 수 있었다.

***Abstract*** NiAl based ODS(Oxide Dispersion Strengthened) intermetallic alloys have been produced by mechanical alloying of elemental powders in a controlled atmosphere using high energy attrition mill. The powders have been consolidated by several different techniques to obtain a variety of microstructures and followed by thermomechanical treatments to induce secondary recrystallization(SRx). The conditions for SRx to occur have been investigated, correlating the primary microstructure as a precursor and thermomechanical treatments. Inhibition of normal grain growth and the presence of texture were shown to be prerequisites for SRx to occur. SRx can be developed in these materials during isothermal annealing under certain processing conditions which provide residual strain energy and/or result in finer grain size.

## 1. Introduction

The $B_2$ structure nickel aluminide(NiAl) offers potential advantages over current superalloys for use in high temperature structural applications. These advantages include a higher melting temperature(1648℃), lower density(5.95 g/cc), excellent oxidation resistance and high thermal conductivity[1]. However, cast, polycrystalline NiAl suffers from poor ambient temperature ductility and poor creep resistance at intended service temperature, which indicates that the use of monolithic material is improbable.

In an effort to address these problems it is considered to synthesize oxide dispersion strengthened(ODS) NiAl by mechanical alloying (MA) of elemental Ni and Al powders[2]. The main role of the dispersoids in high temperature creep is to act as significant obstacles to the motion of dislocations and prevent grain boundary sliding[3]. Improvements in the creep resistance of dispersion strengthened Ni base superalloys are observed to results from increases in grain size[4]. The high temperature strength of ODS materials can be further improved by producing a highly elongated or fibrous grain microstructure aligned parallel to

Table 1. Chemical compositions of as-milled MA NiAl powder

| Element | Ni | Al | H | O | C | N | Fe | Ti |
|---|---|---|---|---|---|---|---|---|
| Atomic % | 47.46 | 49.60 | 218 ppm | 2.6 | 0.04 | 0.064 | 0.12 | 0.63 |

Table 2. Hot extrusion conditions

| Specimen | Powder size | Extrusion Temp. | Extrusion ratio |
|---|---|---|---|
| MAEX1 | Normal | 1127℃ | 16:1 |
| MAEX2 | Normal | 1077℃ | 16:1 |
| MAEX3 | Normal | 1127℃ | 32:1 |
| MAEX4 | Mix | 1127℃ | 16:1 |
| MAEX5 | Mix | 1077℃ | 16:1 |

the stress axis, which reduces grain boundary sliding and minimizes transverse rupture by control of cavitation on transverse boundaries[3~5].

There are two types of grain coarsening; normal grain growth(NGG) and secondary recrystallization(SRx). NGG is defined as being when the microstructure exhibits a uniform increase in grain size while SRx represents a special form of grain growth in which a small number of grains grow preferentially, consuming other grains which exhibit little or no growth[6,7]. Consequently, SRx can give a pronounced increase in grain size[6,7], and, because it develops very rapidly, can give coarse grain structures without concurrent dispersoid coarsening[5].

The current work is focused on an exploration of SRx and involves metallographic studies of the microstructural changes associated with extrusion parameter, isothermal annealing and thermomechanical treatment condition in MA NiAl to further improve its creep resistance.

## 2. Experimental Procedure

Elemental powder blends of -200 mesh Ni and -325 mesh Al were mechanically alloyed in high energy attrition mill under an argon atmosphere. The chemical composition of the as milled powder is shown in Table 1. The MA powders were consolidated by either hot extrusion or by hot pressing. For hot extrusion, the MA powders were placed in a mild steel can and sealed after degassing in vacuum at 800℃. Normally, hot extruded bar was produced at 1127℃ with an extrusion ratio of 16:1. In order to investigate the effect of extrusion parameters and the particle size distribution on the subsequent SRx responses, various conditions were also applied in the hot extrusion processes as specified in Table 2, where a normal powder size was for the powders sieved to -323 mesh, and mix size represented a blend of powders having 90 vol. % of -325 mesh and 10 vol. % of +170-140 mesh.

Hot pressed specimens(MAHP) were produced in a high strength graphite die with one inch inner diameter. Hot pressing was performed at 1050℃ and 58 MPa for 2 hours in a 50 ton hydraulic press, and Ar gas was supplied to the system to prevent excessive oxidation throughout the process.

In order to characterize grain growth and dispersoid coarsening in MA NiAl, hot pressed and hot extruded specimens(MAEX) were isothermally annealed in a vacuum furnace in the temperature range from 1000℃ to 1450℃ for an hour with a heating rate of 250℃/min and cooled to room temperature in air.

Thermomechanical treatments utilizing prestrain were carried out to induce SRx. First, in order to examine SRx response as well as secondary recrystallization temperature($T_{SRx}$), local

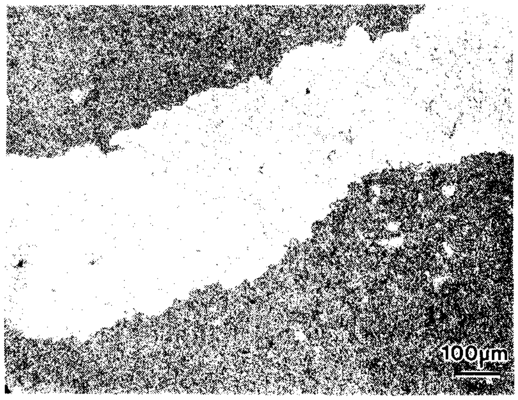


Fig. 1. Optical micrograph of MAEX1 showing occasional SRx during simple isothermal annealing at 1350 ℃ for 30 min.

prestraining by Rockwell hardness indenting was performed for both MAEX and MAHP specimens followed by isothermal annealing at 1100℃~1450℃ for an hour. Second, for a complete SRxed microstructure, cylindrical MAEX specimens (approximately 8mmΦ×15mm ℓ) were prestrained by uniaxial compression to the stress axis. This was performed in the temperature range of room temperature to 800℃. The amount of applied strain ranged from 0.5% to 5% below 450℃ and from 5% to 50% at 800℃.

## 3. Results and discussion

The primary microstructures after consolidation are typically fine grained with a grain size less than 1 μm, and contain a fine distribution of $Al_2O_3$ dispersoids in the range of 10~100nm[2,8,9].

During isothermal annealing treatment only NGG was observed in MAHP specimens while SRxed grains, as large as several mm in size, were observed occasionally in the MAEX1 specimens, Figure 1. As can be seen, SRx took place very rapidly beyond the Zener limit which was estimated as 20μm in this material[9]. SRx was found to occur only at the end of ex-truded bar which are presumably processed at a slightly lower temperature. This would result in a higher residual strain energy which is generally observed in lower extrusion temperature[10,11].

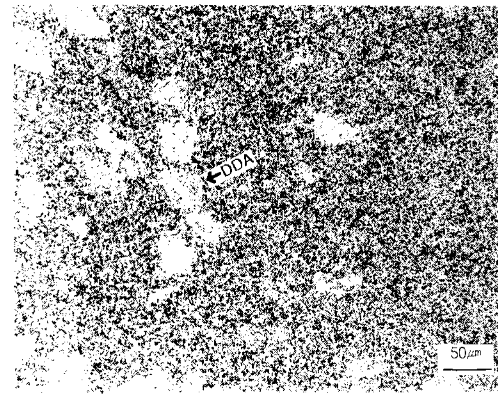


Fig. 2. Optical micrograph of transverse section of MAEX4.

It was also found that the SRxed grains were mostly associated with surface flaws or cracks[8]. It was considered that the SRx response in this case was associated with an additional driving force present in the form of residual strain energy adjacent to the crack. Grain boundary energy which is the principal driving force for SRx is not always sufficient for coarsening[7,12], and it has been suggested that residual strain energy can enhance the degree to which SRx occurs[11,12]. It appears likely that the strain energy increases the driving force acting on the boundaries of the secondary grains or the driving force for the grain rotation into favorable low energy configuration coincident site lattice boundaries[13,14], thus increasing the rate of grain boundary migration and permitting the SRx process to continue in some instances when it might cease if some degree of NGG occurs.

It is also worth noting that further increasing annealing time as an attempt to induce the growth of the secondary grains has not shown any further increase in grain size, but results in NGG in the matrix. This implies that the amount of residual strain energy in the extruded bar is not homogeneously distributed resulting in only partial SRx, and that subsequent normal grain growth in the matrix leads to a decrease in the driving force for SRx.

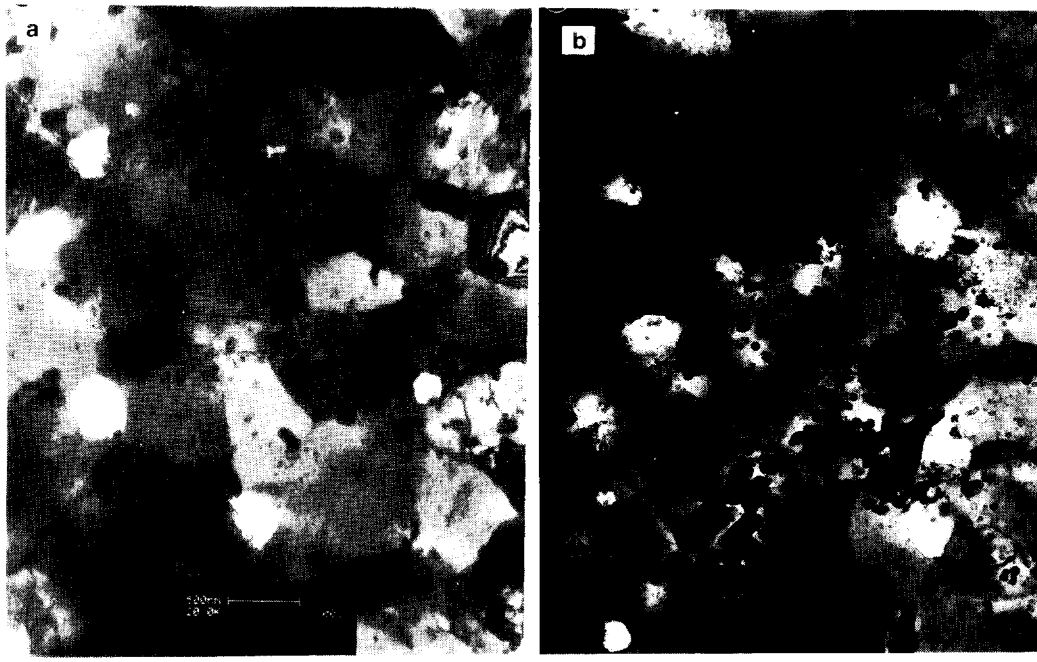


Fig. 3. TEM micrographs of (a) as-extruded MAEX1 and (b) as-extruded MAEX2.

1) Primary microstructure effect on SRx

SRx is expected to occur even if normal grain growth occurs, provided the initial grain size distribution is sufficiently broad[9]. An attempt to produce a broad distribution of initial grain size was made by introducing coarse particles before consolidation, MAEX4 and MAEX5. As reported previously[15], some dispersoids deficient areas(DDA), which were resulted from partially processed coarse particles, were occasionally observed in MA processed materials. The dispersoid deficient areas were shown to have much larger grains, typically 3-5㎛, which were attributed to rapid grain growth during hot consolidation due to the lack of grain boundary pinning point. As expected, dispersoid deficient areas were more frequently observed in MAEX4 and MAEX5 in which 10% of coarse particles(−170#−140#) were intentionally added in order to produce broad grain size distribution, Figure 2. However, the microstructure after isothermal annealing did not provide any evidence of the occurrence of SRx in MAEX4 and MAEX5. The initially large grains with an absence of pinning mechanism in the dispersoid deficient areas were not shown to act as SRx nuclei presumably due to the lack of driving force. The results suggest that SRx is not driven by the boundary curvature as a consequence of broad grain size distribution but rather related with constant driving force resulting from strong inhibition of grain boundary movement. Similar results have been shown in MA superalloys[16,17], as well as in computer simulations[7].

Some inhibition of NGG is necessary otherwise it preempts the development of secondary grains. Furthermore, stability of the matrix grain structure affords a constant driving force for SRx leading to a characteristically rapid development of the structure[7,18]. The inhibition typically results from dispersoids[7,18], though other factors such as the existence of low mobility boundaries in structures possessing a strong texture have been proposed[7,17,18].

2) Extrusion parameter effect on SRx

In order to examine the effect of extrusion temperature and ratio on the SRx response

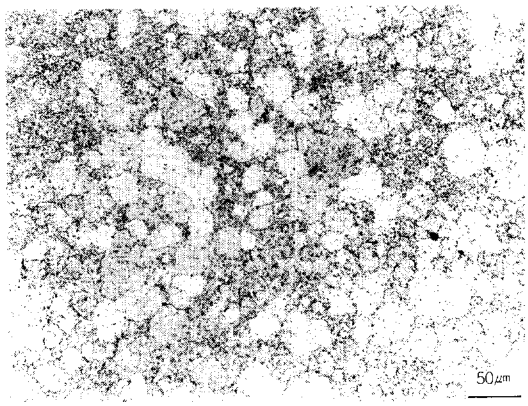


Fig. 4. Optical micrograph of MAEX2, annealed at 1300℃ for 1 hour.

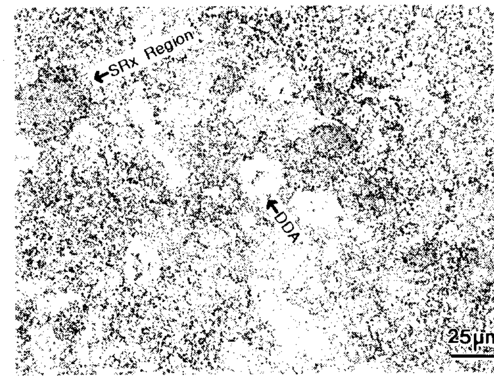


Fig. 5. Optical micrograph of MAEX5, annealed at 1300℃ for 1 hour.

which is usually enhanced by lowering the extrusion temperature and increasing the extrusion ratio in MA superalloys[10,11], the microstructures after isothermal annealing from MAEX1 ~MAEX5 were investigated. As can be seen in Figure 3(a) and (b), the grain size of MAEX2 is slightly smaller than that of MAEX1, as a result of the lower extrusion temperature. It has been reported that decreasing extrusion temperature or increasing extrusion ratio results in higher residual strain energy[10,11]. It was shown that lowering extrusion temperature by 50℃ enhanced the SRx response, Figure 4. This is presumably due to a smaller initial grain size and/or higher residual strain energy providing a higher driving force. In annealed specimens with a broad distribution of dispersoid deficient areas such as in MAEX5, secondary grains are distinguishable from the dispersoid deficient areas which typically consist of many grains, indicating again that SRx is not associated with initially large grains especially those without pinning mechanisms, Figure 5. On the other hand, increasing the extrusion ratio(MAEX3) did not lead to any SRx after isothermal annealing. It can be postulated that increasing the extrusion ratio results in a higher dislocation density which might induce primary recrystallization or provide short circuit diffusion path, consequently leading to grain coarsening which reduces the driving force for SRx. Even though SRx was shown to occur under certain extrusion conditions, no complete SRx development was observed throughout the simple isothermal annealing treatments on the given materials. This suggests that primary grain size must be fine and residual dislocation density should be homogeneously distributed in a given material for complete SRx.

3) Local prestrain effect on SRx

In order to stimulate SRx behavior by introducing plastic strain energy, specimens were prestrained locally by Rockwell hardness($R_B$) indenting followed by isothermal annealing. While no SRx was observed at any indents at any annealing temperatures in HP specimens, SRx was observed to take place at all of the indents on annealing the extruded materials (MAEX1) above 1120℃[5], as shown in Figure 6. This indicates that the presence of texture[2,8,9], as in the extruded specimens, is necessary to induce SRx. In the indented MAEX1, only partial SRx occurred at 1115℃, Figure 7, and SRx was not observed at 1100℃. One of the characteristics of SRx is that there is well defined critical temperature($T_{SRx}$) below which SRx does not take place[11,18]. Since $T_{SRx}$ is shown to depend on heating rate[19] and amount of prestrain[20], $T_{SRx}$ for the locally prestrained MA NiAl with a heating rate of 250 ℃/min can be estimated to be about 1120℃. The results shows that prestraining before annealing

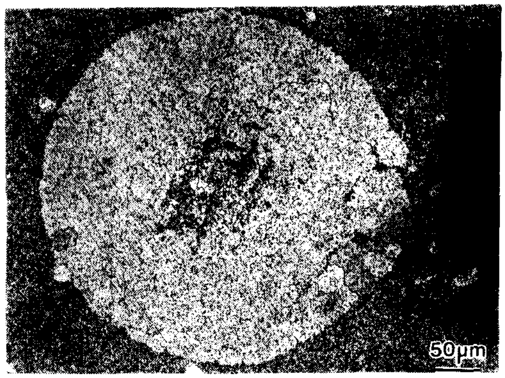


Fig. 6. Optical micrograph of MAEX1, showing SRx at $R_B$ indent after isothermal annealing at 1120℃ for 1 hour.

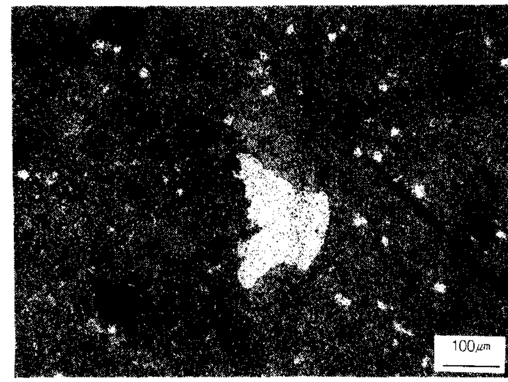


Fig. 7. Optical micrograph of MAEX1, showing partial SRx at $R_B$ indent after isothermal annealing at 1115℃ for 1 hour.

can stimulate SRx behavior in MA NiAl, in contrast to ODS Ni base superalloys in which prestraining deteriorates SRx response, resulting in a smaller SRx grain size or primary recrystallization (PRx) due to an excess amount of strain energy[11-13]. The SRx was shown to take place very rapidly, but the secondary grains did not seem to grow further and stopped at the end of the prestrained region since the sizes of all the SRxed regions at the $R_B$ indentations were apparently the same. This indiates again that strain energy is necessary as an additional driving force for SRx and should be homogeneously distributed for complete SRx. It was also shown primary recrystallization took place at the center area of the $R_B$ indent close to the surface, indicating an upper limit of strain for SRx[5]. When too much prestrain is imposed, PRx can be expected to occur rather than SRx[13], presumably because the PRx mechanism is more favorable to reduce the excess strain energy.

4) $T_{SRx}$ Measurements

In order to produce a completely SRxed structure in the extruded specimens, overall restraining was performed by uniaxial compression parallel to the extrusion axis. Before annealing, it is necessary to determine $T_{SRx}$ for the overall straining which could be different from the critical temperature estimated from $R_B$ indenting experiments since $T_{SRx}$ was shown to depend on the amount of prestrain[20], and heating rate[19]. In order to produce a coarse grain structure, in combination with fine dispersoid size, annealing in the vicinity of $T_{SRx}$ is necessary since annealing well above the $T_{SRx}$ frequently results in a smaller secondary grain size corresponding to a higher nucleation rate[11,12]. It can also be expected that annealing well above the $T_{SRx}$ can lead to NGG or undesirable dispersoid coarsening.

The annealing temperature for a sharp decrease in microhardness frequently indicates the transition temperature since the microhardness decrease is generally due to a dramatic increase in grain size by SRx or to a $\gamma'$ dissolution associated with SRx in ODS nickel base superalloys[11]. However, the abrupt microhardness drop in MA NiAl at around 1375℃ was shown to be associated with NGG and dispersoid coarsening[9].

DSC or DTA is frequently used to determine the $T_{SRx}$ since the sudden release of boundary energy by SRx is manifested as an exothermic peak at $T_{SRx}$[19]. Thus extruded specimens having 5% prestrain were placed in a DSC, and heated to 1300℃ with a heating rate of 2, 5, 20 ℃/min in order to determine $T_{SRx}$ in MA NiAl. However, no exothermic peaks for SRx were observed throughout the experiment even


Fig. 8. Optical micrograph of SRx occurred during DSC run in MAEX1, heating to 1350℃ with a rate of 5℃/min.

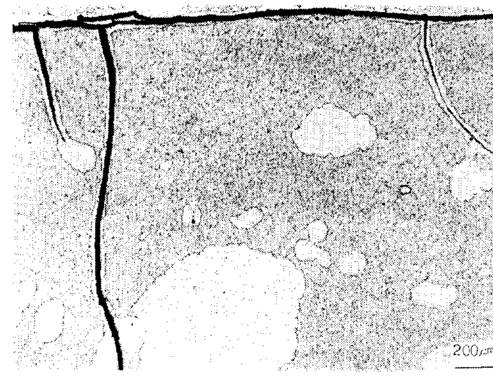


Fig. 9. Optical micrograph showing SRx developed along the crack lines in MAEX1 : 5% prestrain plus annealing at 1350℃ for 1 hour.

though SRx occurred during the course of the DSC run. SRx in MA NiAl is expected to be rather sluggish due to the predominance of low mobility boundaries[21]. Almost complete SRx was developed during the DSC experiments, as shown in Figure 8. However, The grain size dependence of SRx on heating rate[19] was not observed in MA NiAl in this DSC study.

Determination of $T_{SRx}$ was made by microstructural observations performed as a function of strain and temperature. The results show that partial SRx took place above 1250℃ in both MAEX1 specimens with 3 % and 5 % strains, and almost full SRx took place above 1265℃ in the specimen with 5% strain. It was also observed that SRx occurred at 1200℃ in the MAEX2 specimen with 7% strain but not with 3% or 5% strain. These results are consistent with a $T_{SRx}$ that decrease with increasing amount of prestrain as found by Antonione *et al* in Fe[20]. It can also be deduced that $T_{SRx}$ decreases with lower extrusion temperature presumably due to additional driving force provided by a smaller grain size and a higher residual dislocation density.

The $T_{SRx}$ for the extruded specimens having 3 to 5% strain was approximately 1265℃, however it was decided to use an annealing temperature of 1300℃ or above for subsequent work in order to ensure complete SRx.

5) Overall prestrain effect on SRx

Overall prestraining was performed over a range of temperatures from room temperature to 800℃ followed by isothermal annealing above $T_{SRx}$. All the extruded specimens given 2~6% prestrain at temperatures below 450℃ followed by isothermal annealing yielded SRx, whereas no SRx was observed in the specimens given 6%~50% prestrain at 800℃ followed by annealing. However, second attempt of prestraining by $R_B$ at room temperature plus annealing above $T_{SRx}$ in the specimen, in which no SRx was shown after 10% prestraining at 800℃ plus annealing above $T_{SRx}$, yielded SRx around the $R_B$ indentations. These results show that only dislocation density and/or structure produced on prestraining at low temperature is effective in promoting SRx. These results indicate that there is a prestrain window for SRx, with SRx absent for strains less than 2% and excessive strains leading to primary recrystallization.

Though prestrains larger than 5% at room temperature yield SRx after annealing, microcracks were occasionally observed due to the higher strain. It was observed that SRx was preferentially developed along the microcrack lines which were formed during prestraining, Figure 9. This indicates that the residual strain energy adjacent to the crack provides addi-


Fig. 10. Optical micrograph of fully SRxed in the longitudinal section of MAEX1, annealed at 1300℃ after 5 % prestraining.

tional driving force for SRx to initiate. It was also observed that SRx was developed at the crack tip, clearly indicating the crack tip plastic zone.

A substantially SRxed microstructure was produced in the material homogeneously prestrained about 5% followed by isothermal annealing above 1300℃, Figure 10. It is commonly observed that no SRx take place at the ends of specimens. It is believed that this corresponds to the undeformed regions(dead zone) due to the friction on compression. The microstructure of sections parallel to the extrusion axis typically consists of well developed elongated, SRxed grains having grain aspect ratio of 5. This type of elongated grain structure is commonly observed after isothermal annealing or zone annealing of ODS superalloys[10~12]. It has been suggested that this reflects either the alignment of the dispersoid along the extrusion axis restricting lateral growth or a texture effect which leads to lateral grain boundaries being mobile than others[10,11]. As can be seen, stringers of dispersoids along the extrusion axis are clearly observed in the SRx condition, indicating that SRx occurs by break-away process with the second particles left.

6) Texture effect on SRx

Hot pressed specimens were also prestrained and annealed but no SRx was observed. As reported previously[21], extruded MA NiAl had a strong fiber texture whereas hot pressed specimens had a random texture. These results indicate that the texture present in the extruded materials is prerequisite for SRx. Comparison of the relative intensity of diffraction peaks before and after SRx indicates that the ⟨110⟩ texture in extruded material is enhanced after SRx, Figure 11. Secondary structures often have a texture which is different from that of the initial structure, but are related to it by an orientation relationship[15], but it is also reported that primary texture can be retained during SRx depending on pinning mechanisms ($\gamma'$ dissolution or dispersoid coarsening)[22]. It has been reported that SRx triggered by $\gamma'$ dissolution, which is quite common in ODS Ni base superalloys, results in texture change from ⟨111⟩ to ⟨110⟩ while that by dispersoid coarsening results in strengthening in ⟨111⟩ texture in ODS superalloys[22].

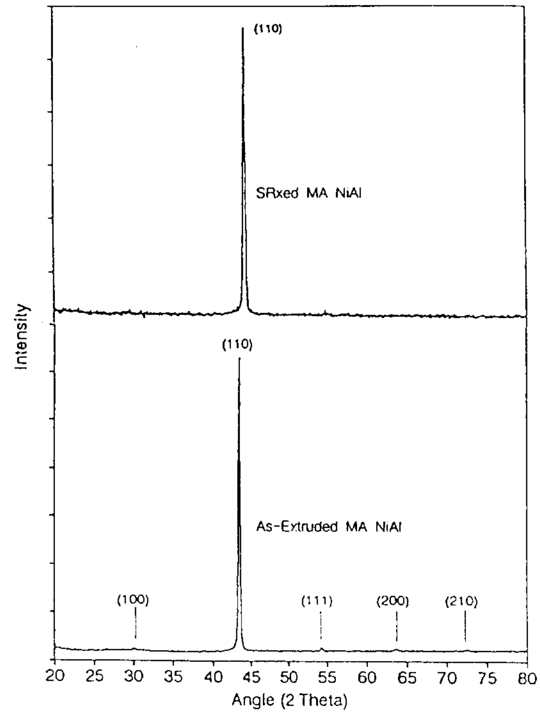


Fig. 11. XRD pattern of as-extruded MA NiAl and SRxed MA NiAl.

## 4. Conclusions

Inhibition of normal grain growth and the presence of texture were shown to be prerequisites for secondary recrystallization to occur. SRx can be developed in these materials during isothermal annealing under certain processing conditions which provide residual strain energy and/or finer grain size. The occurrence of SRx was shown to be enhanced by providing additional driving force in the form of strain energy of cold work.

Large elongated grains having a grain aspect ratio of 5 were produced by SRx after the thermomechanical treatments. The secondary recrystallization temperature($T_{SRx}$) depends on extrusion parameters and amount of prestrain. The ⟨110⟩ texture in the as-extruded MA NiAl is strengthened after SRx.

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