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INFLUENCE OF INTERMETALLIC COMPOUNDS ON GRAIN REFINEMENT IN 2XXX ALLOYS AFTER DIFFERENT THERMOMECHANICAL TREATMENT

WPŁYW ZWIĄZKÓW MIĘDZYMETALICZNYCH NA ROZDROBNIENIE ZIARNA W STOPACH TYPU 2XXX PO ZRÓŻNICOWANEJ OBRÓBCE TERMOMECHANICZNEJ

Fine equiaxial grain structure is a consequence of designing a material with a large contribution of intermetallic compounds of certain size and distribution. A 2XXX alloy with Fe, Ni, Mn and Zr additions was cast obtaining large amounts of Al-Fe-Ni and Al-Cu-Mg precipitates, in which the Al-Zr compounds appeared as dispersoids. After the application of a modified thermomechanical procedure, an alloy with average grain size of 12 μm with a large contribution of grains smaller than 10 μm has been obtained. Apart from that, elongated precipitates of 0.8–4.0 μm in size as well as globular ones about 0.3 μm large were produced in the alloy after recrystallization. The alloy revealed high resistance to grain growth at high temperatures, which was due to the appearance of intermetallic compounds (mostly Al-Fe-Ni) in grain boundaries.

Wytworzenie struktury o drobnym, równoosiowym ziarnie jest związane głównie z uzyskaniem stopu o znacznym udziale wydzieleń związków międzymetalicznych o określonej wielkości i rozłożeniu. W tym celu odlano stop typu 2XXX z dodatkami żelaza, niklu i manganu oraz cyrkonu, uzyskując znaczne ilości związków Al-Fe-Ni oraz Al-Cu-Mg. Dodatek cyrkonu tworzył dyspersoidy typu Al_3Zr. Po zastosowaniu odpowiednio zmodyfikowanej obróbki termomechanicznej uzyskano stop w stanie po rekrystalizacji o średniej wielkości ziarna ok. 12 μm z dużym udziałem ziarn poniżej 10 μm i wydzieleń o kształtach wydłużonych wielkości 0.8–4 μm oraz globularnych ok. 0.3 μm. Stop ten charakteryzował się wysoką odpornością na wzrost ziarna w wysokich temperaturach, co zawdzięczał obecności wydzieleń związków międzymetalicznych Al-Fe-Ni zlokalizowanych głównie na granicach ziarn.

1. Introduction

The generation of fine-grain structure of the solid solution as well as precipitates increases the strength of aluminium alloys at relatively high ductility and improve their

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ability to superplastic deformation [1, 2, 3]. The fine-grain structure can be achieved by introducing metallic additions which solve in the metastable solid solution and form intermetallic compounds after an appropriate thermal treatment.

The introduction of the additions like iron, nickel and manganese to the Al 2XXX alloy results in the appearance of binary and ternary compounds during solidification. The formation of these precipitates inhibits the grain growth during cooling and ensures the formation of the fine-grain structure. The cooling rate is a very important factor, which leads to a finer structure when high enough. Khaidar et al. [4] determined the phases formed in the Al-Fe-Ni-system. They were binary compounds of the Al-Fe and Al-Ni type (which were able to dissolve up to 11 at.% Ni and 4 at.% Fe, respectively) as well as ternary Al_9FeNi, in which Ni content was limited to 7–14 at.% and $Al_{10}Fe_3Ni$, whose existence domain lay from 5 to 10 at.% Ni and Al-content varied about 2 at.% [4], in dependence on the heat treatment applied. According to Matsuki et al. [5] and Gao et al. [6] in the 2XXX type alloys another group of precipitates can also appear. These are mostly Al_2CuMg and Al_2Cu compounds. In the presence of Fe the Al_7Cu_2Fe phase has been observed.

The fine structure of Al alloys is achieved and stabilised by dispersoids formed in the early stages of solidification. It is well known that in the Al alloys, Zr additions form the Al_3Zr intermetallic compound in the shape of globular dispersoids some hundreds nm big, whose presence have a great influence on the grain size refinement [7, 8, 9]. The presence of dispersoids and precipitates in the alloys is very important for the formation of fine-grain structure in the thermomechanical process. The dispersoids are stable during all the stages of the thermomechanical treatment and limit the grain growth by hindering the migration of grain boundaries and decrease the recrystallization rate by exerting dragging force on them [8, 10].

In general, the TMT processes are composed of a thermal treatment stage (supersaturation and ageing) and a plastic deformation stage followed by recrystallization [10–13]. During the first stage "large" precipitates (above 2 μm) of intermetallic compounds appear. During the second one, the deformation and shear bands are formed particularly in the vicinity of these "large" precipitates. The density of the bands depends on the amount of the precipitates and additions dissolved in the solid solution [12]. During the recrystallization, the nuclei of new grains appear at the rate depending on the amount of the bands. Since the dispersoids strongly hinder grain growth and due to the high rate of the nucleus formation a very fine-grain structure can be obtained. The recrystallization should be carried out at relatively high temperature and for a short time. The heating rate should be as high as possible [14]. Much higher refinement of the structure can be obtained in the modified TMT routes. In so called "double recrystallization treatment" D. H. Shin et al. [13] modified the Wert et al. process [10] by applying additionally overageing, plastic deformation and recrystallization of the samples after the first treatment. They reported a fine-grain structure with the grain size under 10 μm.

The presence of additions like Fe, Ni and Mn due to the formation of high temperature precipitates increases the heat-resistance of the alloys. Malcew [15] reported the high strength of 170 MPa at 573 K obtained in the alloy of the composition of Al-Cu2-Mg1.6-Ni1.5-Fe1.2-Ti0.02 due to the presence of Al_9FeNi intermetallic compound.

The aim of the work was to study how various parameters of thermomechanical treatment affect the final refinement of the structure and high plasticity of the investigated alloy.

2. Experimental procedure

2.1. Material and methods of investigations

The alloy for investigation was obtained in a two-stage process. In the first one, the basic alloy containing Al-Fe-Ni-Mn was prepared. The sequence of introducing the additions was important. At first, Fe and Ni (as Cu-Ni40 master alloy) were melted, then Mn was added followed by Al. They were melted under argon atmosphere in an induction furnace at 1900 K and cast into a copper mould. Next, the rest of Al, Cu, Mg and Zr (as Al-Zr10 master alloy) were melted into this basic alloy in a resistance furnace, under a salt cover, and cast at 1123 K, into the copper mould. The composition of the produced alloy was: Al-Cu4-Mg1.8-Mn0.7-Fe1.0-Ni1.5-Zr0.25 (in wt.%).

The structure studies were performed using the following methods:

- light microscopy, on the Neophot 32 on samples, which were polished and etched using Wilcox reagent
- transmission electron microscopy, on the PHILIPS EM-301 and CM-20 using thin foils produced by electropolishing in methyl alcohol/ nitric acid solution and ion beam thinning in the Gatan 660 ion mill. The EDS analyses were performed on EDAX equipment attached to CM-20
- scanning electron microscopy, on the PHILIPS XL-30 equipped with LINK energy dispersive spectrometer for quantitative analysis
- *X*-ray phase analysis on the PHILIPS PW 1710 diffractometer in the samples after subsequent stages of the TMT.

2.2. Thermomechanical treatment of the investigated alloy

The fine-grain structure of the investigated alloys was obtained in the thermomechanical treatment route generally composed of the following stages:

- heat treatment: solutionizing at 773 K during 8, 16 and 32 hours (in the resistance furnace under argon atmosphere) followed by water quenching and ageing at 673 K for 1 and 4 hours followed by water quench again,
- two-stage rolling: up to about 50% deformation heated to 623 K with reheating between passes (warm rolling) and to 85% at room temperature with single pass deformation from 6 up to17%,
- recrystallization at 753 K for 15, 30 and 60 minutes or at the second step, at 803 K during 15 and 30 minutes. Since the heating rate had a great influence on the grain

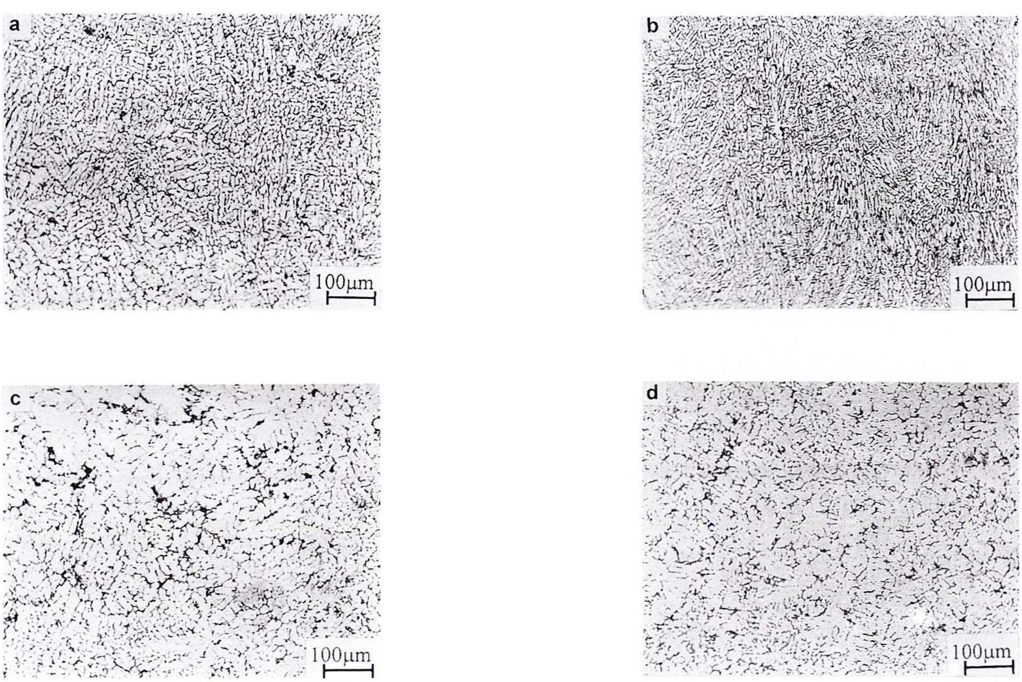
size of the alloy after the recrystallization, it was necessary to heat the samples as rapidly as possible (particularly between temperatures 593–673 K) [14].

Another so called "double thermomechanical treatment" was also performed. In that case, the whole TMT was applied once more. The ageing was performed at 673 K for 30 min. The rolling was carried out at room temperature only, at higher deformations in one pass (18–40%) [10, 16] up to 76 or 85%. The recrystallization was performed at 803 K for 15 min. According to the authors of paper [13] such "double thermomechanical" treatment should improve the grain refinement of the investigated alloys.

3. Results

3.1. Light microscopy studies

The alloy cast into a copper mould had a fine grain structure with a large amount of intermetallic compounds very different in size and distribution (they formed clusters of precipitates) and low porosity. The grain size of the solid solution and precipitates was different in dependence on the distance from the ingot bottom. In the middle part, the grain size was larger than at the bottom, which was caused by different cooling rate in various parts of the mould (Figs. 1a, 1b). In these figures it might be also seen that the intermetallic precipitates formed mostly at the grain boundaries (Fig. 1a).



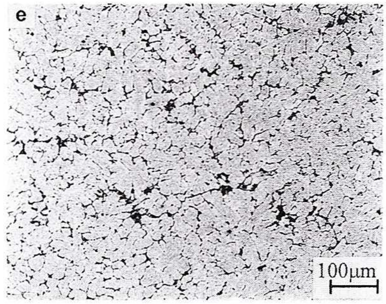


Fig. 1. Optical micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy: a) as cast from the middle part of the mould; b) as cast from the bottom part of the mould; c) after supersaturation at 773 K/8 hours; d) after overageing at 673 K/1 hour; e) after overageing at 673 K/4 hours

After the supersaturation, the grain size of the solid solution was observed to be 30–50 μm and it increased with the prolongation of the homogenisation time (Fig. 1c). The Al-Ni-Fe precipitates tended to form particularly large clusters.

The increased amount of precipitates was observed after the ageing stage (Fig. 1d). The change of the ageing time from 1 to 4 hours caused the growth of the grain size of the solid solution to about 60 μm and, at the same time, it increased the level of solute remaining in the solid solution [12] (Fig. 1e).

Characteristic deformation structure was obtained after rolling. The considerably elongated grains and bands of strongly refined intermetallic precipitates arranged in the rolling direction are shown in Fig. 2.

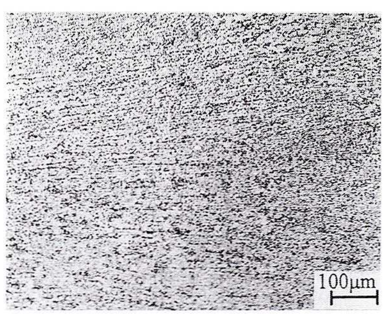


Fig. 2. Optical micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after rolling

The result of the recrystallization at 753 K for 60 min is shown in Fig. 3a. The recrystallized grains were 10–20 μm large, but only a small part of the sample was recrystallized. Thus, the recrystallization temperature was increased to 803 K, while the time was shortened to 15 or 30 min. The microstructure of the sample recrystallized at 803 K for 15 min is shown in Fig. 3b. Although the shape of some grains was equiaxial, a large fraction of them was still elongated. The change of time to 30 min decreased strongly the contribution of the elongated grains (Fig. 3c).

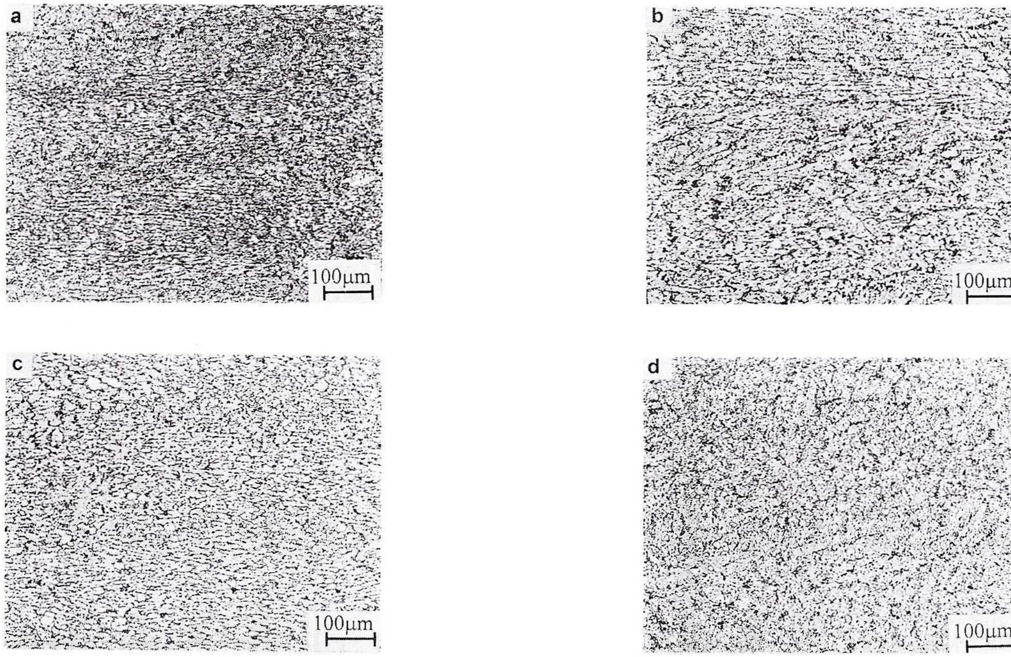


Fig. 3. Optical micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy: a) after recrystallization at 753 K/60 min; b) after recrystallization at 803 K/15 min; c) after recrystallization at 803 K/30 min; d) alloy after "double thermomechanical treatment"

The structure of the investigated alloy after the "double treatment" was more refined. The samples after the first thermomechanical treatment were aged at 673 K for 30 min, cold rolled to 76 or 85% (at room temperature) and recrystallized at 803 K for 15 min. The morphology of the sample was considerably inhomogeneous with grain size 5–20 μm. The contribution of the grains below 10 μm was very high, while the grains of 20 μm were hardly ever observed (Fig. 3d).

3.2. X-ray phase analysis

The types and comparative quantity of the phases and intermetallic compounds formed in the investigated alloy after different stages of the thermomechanical treatment were studied using the X-ray phase analysis method and the results are presented in Fig. 4, where:

- A refers to the as cast samples, in which Al_9FeNi, Al_2CuMg, Al_3Ni_2 and Al_2Cu phases were found
- B contains the results in the supersaturated state: small quantities of the Al_9FeNi, Al_2CuMg, Al_3Ni_2, AlFe, and $Al_5Mg_2Cu_6$ were recorded
- C comprises the effect of ageing: the amounts of the Al_9FeNi, Al_2CuMg, Al_3Ni_2, AlFe and $Al_5Mg_2Cu_6$ precipitates increased strongly

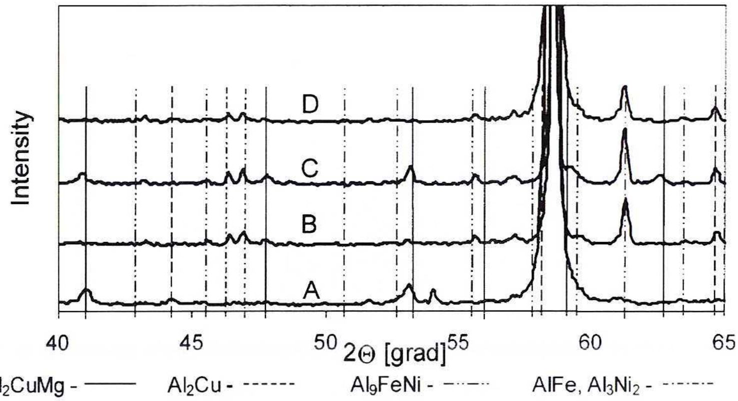


Fig. 4. X-ray diffraction patterns of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after the stages of TMT: A. as cast; B. supersaturation; C. overageing; D. recrystallization

– D shows the diffraction pattern obtained from the recrystallized samples. The amounts of the Al_9FeNi, Al_2CuMg, Al_3Ni_2, AlFe precipitates were found to decrease slightly; and a new $Al_7Mg_6Cu_3$ phase was formed in a relatively small quantity.

In all the stages, the matrix was formed as the solution of Al with different additions, which is shown by the shift of diffraction lines from the ones of pure Al. The largest displacement of the lines, which described the highest degree of supersaturation, was found in the investigated alloy after ageing for 4 hours at 673 K. This high degree of supersaturation of the solid solution was very advantageous for the formation of shear bands during plastic deformation stage of the TMT [10] and the grain refinement of the solid solution.

3.3. Transmission electron microscopy

The investigations were carried out using a PHILIPS EM-301 and CM-20 with EDAX. Thin foils were prepared from samples after different stages of the thermomechanical treatment.

The globular dispersoids of the Al_3Zr type in the samples after supersaturation were observed at high magnification (88 000 X; Fig. 5). An increase of the amount of Zr above 7 wt.% according to EDS measurements performed in the field shown in Fig. 5 was stated (Fig. 6).

The precipitates of the plate-like shape appeared in the alloy after supersaturation and ageing. According to the EDS analysis, these were intermetallic Al_2CuMg and Al_3Ni_2 compounds. Fe was found in a small amount (about 0.4%), probably substituting part of Ni in the Al_3Ni_2 compound (Fig. 7). Irregular in shape precipitates of the Al_xCu_yNi composition with about 1% Fe content were recorded in the grain boundaries (Fig. 8). According to the X-ray analysis they are the Al-Cu and Al-Ni type compounds. In all the compounds containing Ni, the presence of Fe between 0.3 to 1.0 wt.% was recorded.

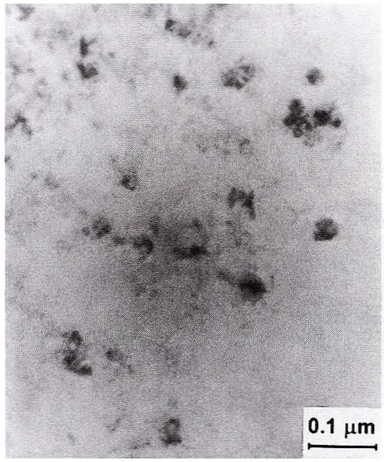
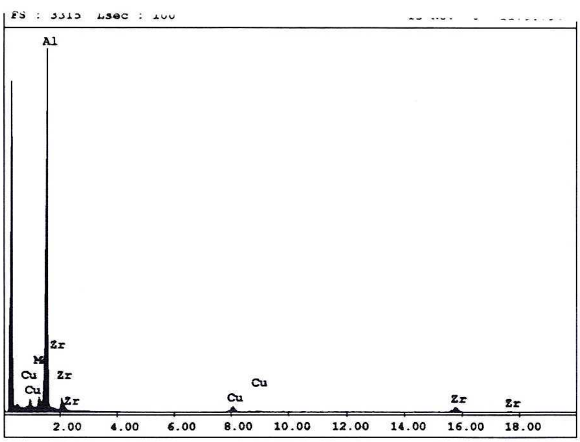


Fig. 5. TEM micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after supersaturation showing dispersoids



Thin Apx
KAB Set : User, Elements

Element	Weight %	Atomic %
MgK	3.9	4.6
AlK	86.2	91.9
CuK	2.8	1.3
ZrK	7.2	2.3
Total	100.0	100.0

Fig. 6. X-ray chemical analysis (EDAX) from the area showed in Fig. 5

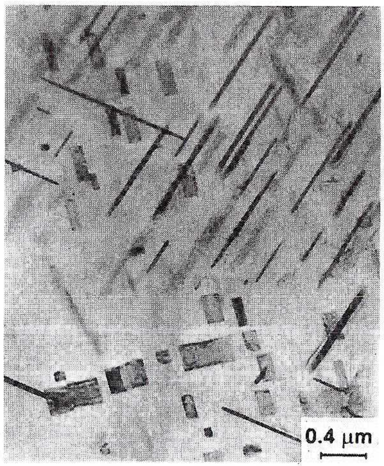


Fig. 7. TEM micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after overageing at 673 K/4 hours. Precipitates of the intermetallic compounds visible in the matrix

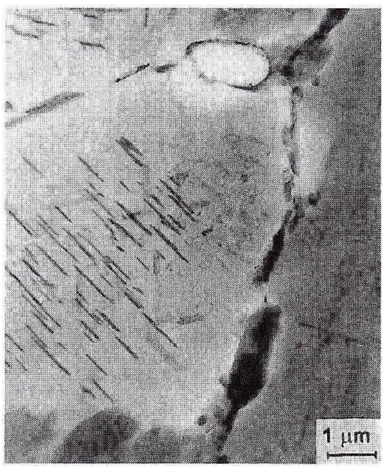


Fig. 8. TEM micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after recrystallization showing precipitates of intermetallic compounds lying in the grain boundaries

The needle-like precipitates with high Fe-content (up to 9%) were found in this alloy after recrystallization at 803 K (Fig. 9). They might be Al_9FeNi and/or AlFe intermetallic compounds, which is in good agreement with the *X*-ray results. The precipitate of irregular shape, situated between two elongated particles, was probably the $Al_3Ni_2(Fe)$ compound with a small amount of Fe, according to EDS measurements. The isolated, irregular precipitates of the Al_3Ni_2 type but with much higher amount of Fe were found in the alloy after the recrystallization (Fig. 10). The EDS measurements of the composition of the solid solution showed that after ageing stage it contained about 3% Mg, above 2% Cu and 0.4 to 0.6% Ni and Fe, which was confirmed by the *X*-ray measurements.

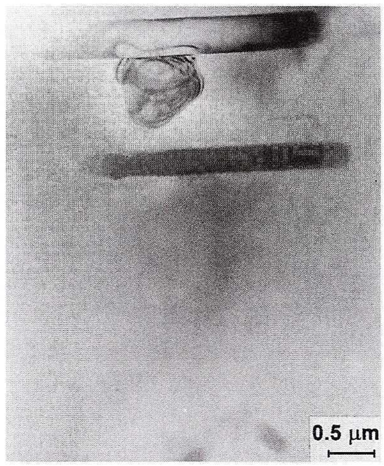


Fig. 9. TEM micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after recrystallization at 803 K/30 min. showing precipitates of intermetallic compounds of different shapes inside the grain

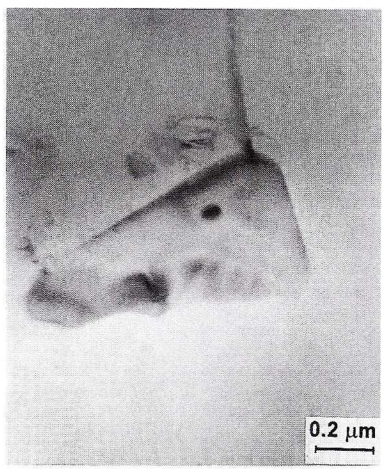


Fig. 10. TEM micrograph of the Al-Cu 4-Mg 1.8-Mn 0.7-Fe 1-Ni 1.5-Zr 0.25 alloy after recrystallization at 803 K/30 min. showing precipitates of intermetallic compounds of irregular shape inside the grain

4. Discussion

The relatively fine morphology of the aluminium alloys, according to Humphreys et al. [17] in the as cast state was achieved in a cold, flat copper mould, which ensured high cooling rates. The higher the Cu content, the smaller grains form in the alloy according to Watanabe [18]. The great influence on the formation of the fine-grain alloy had the presence of the high temperature resistant intermetallic compounds of the Al-Fe-Ni-Mn-type, the appearance of the precipitates of different shapes and sizes (2–4 μm) and particularly the Zr dispersoids [1, 5]. The Al-Fe-Ni-Mn-Cu precipitates in the form of binary, ternary or even quaternary compounds deviated from the stoichiometric composition due to the partial substitution [4] as it was found in the Al-Cu-Ni precipitates, where a part of Ni was substituted by Fe. At higher Fe content (about 4%) Gao et al. [6] found the ternary $Al_{23}CuFe_4$ compound. In our case, at 1% Fe addition, the Al_9FeNi was observed. Al built the precipitates with Fe, Ni or Mn of irregular shape, which often formed clusters [6].

The shape affected the ductility of the alloy. The ability to the superplastic deformation increased if the shapes of the grains and precipitates were near equiaxial. Since the Al-Cu-Mg and some of Al-Cu-Ni precipitates had plate-like forms, their ability to the deformation was smaller than in the case of the globular ones. The precipitates with Fe and in some cases with Ni had higher ability to formation of irregular shapes of precipitates.

The alloys treated in the modified thermomechanical route, according to D.H. Shin et al. [13], by applying double thermomechanical treatment achieved higher refinement of the solid solution grains and precipitates of the investigated alloy. According to the TEM and optical microscopy investigations, grains of size 5–20 μm with the high fraction of grains below 10 μm were obtained, while grains of 20 μm were hardly ever observed. The thin sample could be rolled at much higher deformation (above 30% per pass) resulting in a higher refinement of the precipitates. During rolling with a high deformation per pass, high amount of shear bands was formed, which in the recrystallization stage gave high nucleation rate and, in the end, very fine-grain structure.

As it has already been stated by G. J. Mahon et al. [12], the high amount of solute left in the solid solution after overageing was required to obtain the high-rate formation of the shear bands during plastic deformation. So, the overageing prolonged to 4 hours enriched the solid solution in Mg and Cu and to a smaller extent in Fe and Ni. The fine grain structure (about 10 μm), formed in the investigated alloy was the result of this high level of solute remaining in the solid solution.

The high-temperature-resistant additions like Fe, Ni and Mn formed the fine intermetallic compounds, refined the structure and increased the ductility of the investigated alloy, during the stages of the thermomechanical treatment.

5. Conclusions

1. The additions of the Fe, Ni and Mn, refined the grain size of the investigated alloy after thermomechanical treatment applied.
2. Fine intermetallic compounds particularly of the Al-Fe and Al-Ni type, which formed in the alloy during ageing were responsible for the grain refinement and its stability.
3. The relatively high level of solute of Mg, Fe and Ni remaining in the solid solution contributed to the generation of shear bands during deformation and the grain refinement of the solid solution at recrystallization.
4. The more refined but inhomogeneous morphology (as long as grain size is considered) was achieved after the "double thermomechanical treatment" as compared to the single one.

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