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EFFECT OF IRON AND CERIUM ADDITIONS ON RAPIDLY SOLIDIFIED Al-TM-Ce ALLOYS

VPLIV DODATKOV ŽELEZA IN CERIJA NA HITRO STRJENE ZLITINE Al-TM-Ce

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The influence of the additions of the mass fractions 3 % of Fe and 1 % of Ce to an AlCr4Ti0.4 alloy is described in this paper. The iron addition modifies the phase composition of the material leading to the formation of the $Al_{13}Fe_4$ crystalline and $Al_{80}(Cr,Fe)_{20}$ quasicrystaline phases. It also causes a grain refinement that was proved with transmission electron microscopy and X-ray diffraction. The microhardness of the Fe-alloyed material is changed by about a factor of two in comparison to the material without Fe. On the other hand, the Fe addition has no influence on the thermal stability of the alloy. The effect of 1 % of Ce on the AlCr4Ti0.4 alloy hardly affects the microhardness but increases the thermal stability during long-term annealing at 400 °C.

Keywords: rapid solidification, aluminium, quasicrystals

V prispevku je opisan vpliv dodatka z masnim deležem 3 % železa in 1 % cerija zlitini AlCr4Ti0,4. Dodatek železa spremeni sestavo faz v materialu in povzroči nastanek $Al_{13}Fe_4$ kristalne in $Al_{80}(Cr,Fe)_{20}$ kvazikristalne faze. Povzroči tudi zmanjšanje zrn, kar je bilo dokazano s presevno elektronsko mikroskopijo in z rentgensko difrakcijo. Mikrotrdota z Fe legiranega materiala se spremeni za faktor dve glede na material brez Fe. Po drugi strani pa dodatek Fe ne vpliva na termično stabilnost zlitine. Učinek 1 % Ce v AlCr4Ti0,4 neznatno vpliva na mikrotrdoto, vendar pa poveča termično stabilnost med dolgotrajnim žarjenjem pri 400 °C.

Ključne besede: hitro strjevanje, aluminij, kvazikristali

1 INTRODUCTION

Rapidly solidified (RS) aluminium alloys are promising materials for structural applications. Their main advantage is the superior strain-to-weight ratio. The best mechanical properties and thermal stability are achieved in an aluminium rare-earth transition-metal (RE-TM) alloy system with aluminium contents higher than 80 %.[1,2] These alloys are usually prepared under the maximum available cooling rates that, together with the appropriate chemical compositions, lead to a formation of amorphous or partially amorphous alloys.[1] Such metastable materials are very interesting from the investigation point of view, but their potential for the applications at elevated temperatures is limited. The amorphous phase decomposes under the heat treatment, forming intermetallic phases in the fcc-Al matrix.[3] Depending on the heat-treatment regime, annealed materials can exhibit higher hardness and other mechanical properties such as the yield strength and the ultimate tensile strength.[1] The production of such materials is highly demanding with respect to processing and it would be considerably complicated to manufacture them in industrial conditions. This paper is focused on an investigation of the rapidly solidified alloys, prepared with the cooling rates achievable in industry.

The influences of single alloying elements on extremely rapidly solidified aluminium alloys are described in detail.[1,4] The authors usually focus on the effect of each element on the glass-forming ability (GFA), which qualifies the tendency of an alloy to form a glassy structure. Three empirical rules for a GFA determination were established:

1. The higher the number of elements in a system, the higher is GFA.
2. GFA is also high due to a negative mixing enthalpy of the components in a system.
3. A GFA increase is generally observed together with great differences in the atomic ratios of the elements.[1]

The definition of the GFA described for glassy alloys can be generalized as the ability to form a metastable phase (MPFA), indicating the tendency of a system to form not only the glassy state, but, generally, to form any metastable phase, e.g., amorphous and quasicrystaline phases and supersaturated solid-solution phases.

In the case of amorphous alloys, the functions of all the REs are approximately the same with respect to the increasing GFA.[5] The influences of single TMs on Al-based alloys cannot be simplified only in terms of GFA, because they vary significantly[5] on the basis of the interatomic interactions. The Al-based alloys containing Fe are very exceptional. It was reported that there is a strong

interaction between the Al and Fe atoms in the amorphous Al-RE-Fe alloys[6] and even in the alloy melts.[7] It was found, in the amorphous Al-Ce-Fe alloys, that the Ce atoms are basically randomly distributed and that the Fe atoms are surrounded by many Al atoms.[6] This is in agreement with the idea that the icosahedral Al-Fe clusters are present already in the melts.[2,7] It is generally supposed that the melt clusters are formed by the elements with the lowest negative mixing enthalpies. Interestingly, the behavior of the Al-Ce-Fe alloys is in disagreement with this rule because the mixing enthalpy of Al-Fe is –11 kJ/mol [8] and the mixing enthalpy of Al-Ce is -38 kJ/mol.[9] It was also shown that an Fe addition changes the crystallization mechanism of an Al86Mm4Ni10 alloy (Mm means mischmetal – an alloy of Ce, La, Nd and Pr), increasing its thermal stability.[6]

Ce precipitates from the Al-TM based amorphous alloys in the form of an Al_4Ce phase.[7,10] This phase is formed due to a decomposition of the $Al_{92}Ce_8$ metastable phase[11] and is one of the main strengthening phases. It was also reported[12] that REs can be present in four different phases in the Al-RE alloys or Al-TM-RE alloys rich in REs. This possibility of nucleating various phases can represent a "confusion principle" for an alloy. On the other hand, when Fe is added to an alloy, a formation of intermetallic phases is preferred.[12] The question is in which form Ce will be present in the crystalline RS alloys and whether it will significantly influence the alloys.

In this paper, the influence of a mass fraction 3 % Fe addition on the structure, hardness and thermal stability of the nanocrystalline AlCr4Ti0.4Ce1 alloy will be shown. This influence will also be compared to the influence of a 1 % Ce addition to the AlCr4 Fe3Ti0.4 alloy.

2 EXPERIMENT

The alloys with the compositions given in **Table 1** were studied in this paper. Ingots of the alloys were prepared by melting the appropriate amounts of master alloys and pure metals (AlCr11, AlTi4, Al, Fe and Ce) in a vacuum induction furnace. Consequently, RS ribbons were prepared by melt spinning. The cooling wheel diameter of the melt-spinning equipment was 14 cm. The cooling wheel velocity was 1800 r/min, corresponding to the circumferential speeds of 28 m/s. Melt-spinning procedures were performed in air. The rapidly solidified alloys were produced in the form of thin foils with a thickness of approximately 50 μm and a width of 4–5 mm. The chemical composition was determined with X-ray fluorescence spectroscopy (XRF) using a spectrometer ARL 9400 XP for Ce, and with atomic absorption spectroscopy (AAS) using GBC 932plus for the other elements.

Table 1: Chemical compositions of the studied alloys in mass fractions (*w*/%) determined with an XRF analysis
Tabela 1: Kemijska sestava preiskovanih zlitin v masnih deležih (*w*/%), določenih z XRF-analizo

Alloy	Al	Cr	Ti	Fe	Ce
AlCr2	97.24	2.13	0.38	0.25	0
AlCr4Ce1	93.96	3.84	0.40	0.96	0.84
AlCr4Fe3	91.70	4.16	0.63	3.51	0
AlCr5Fe3Ce1	90.33	4.93	0.29	3.43	1.02

The microstructure of the cross-sectioned ribbons was examined using a scanning electron microscope (SEM) Hitachi S 4700 (30 kV) and a light microscope Neophot 2 in the immersion mode. The samples were etched in a solution of 0.5 % HF for 20 s. The phase composition of the materials was determined with X-ray diffraction (XRD) (PAN analytical X'Pert PRO + High Score Plus, Cu anode). All diffraction measurements were performed on the wheel side of the RS ribbons. The grain size was estimated from XRD diffraction patterns as the size of the coherently diffracting domain using the Scherrer formula (1),[13] attributing the peak width expansion only to the influence of the average grain size:

$$\textit{Crystallite size} \text{ (average)} = \frac{K\lambda}{B\cos\theta} \qquad (1)$$

In equation (1) λ describes the wavelength of the incident X-rays, K is the constant that varies with the method of taking the line width ($0.89 < K < 1$) and B describes the structural broadening, given by the difference in the integral profile width between the standard and the unknown samples:[13]

$$B = B_{\text{obs.}} - B_{\text{std.}} \qquad (2)$$

The peak at the 2Θ position of about 78° corresponding to the diffraction on the Al (311) plane was used for the estimation. The Rietveld structure refinement was performed with the program Topas 4. The samples were examined using a transmission electron microscope (TEM) Jeol 3010 (an accelerating voltage of 300 kV, LaB_6). Thin foils for TEM were prepared by grinding the free sides of the RS ribbons until the final thickness reached approximately 50 μm, and by subsequently electropolishing the mixture of C_2H_5OH:HNO_3 with the ratio of 3:1 at 10 V and –20 °C. The structural investigation was completed with the EDS (Oxford Instruments) measurements. The Vickers hardness HV 0.02 was also measured on the cross-sectioned ribbons. The load of 20 g was chosen to be the optimum one for measuring the average hardness of the ribbons. The indentor always pointed to the middle of the ribbons.

A long-term annealing of the alloys was carried out in an electric resistance furnace. Selected samples were annealed at 400 °C to determine the thermal stability of the materials. After the long-term annealing (25, 50, 75 and 100) h, the room-temperature hardness HV 0.02 was measured.

3 RESULTS AND DISCUSSION

All the RS ribbons showed structural gradients in the cross-sections, as illustrated in **Figures 1** and **2**. The cooling wheel sides of the ribbons, shown at the bottom

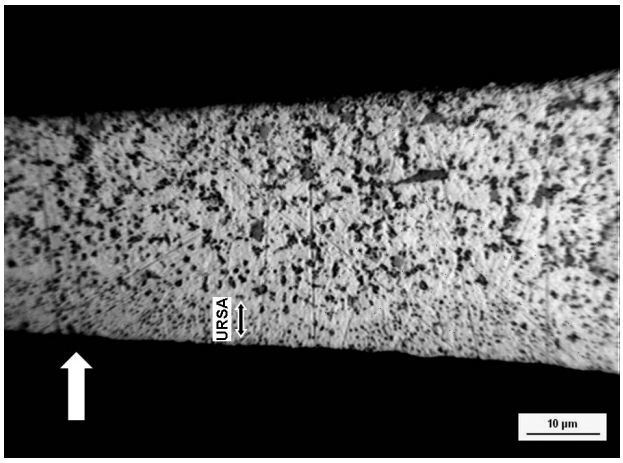

Figure 1: LM micrograph of a cross-section of a rapidly solidified ribbon of the AlCr4Ce1 alloy
Slika 1: Posnetek prereza hitro strjenega traku zlitine AlCr4Ce1

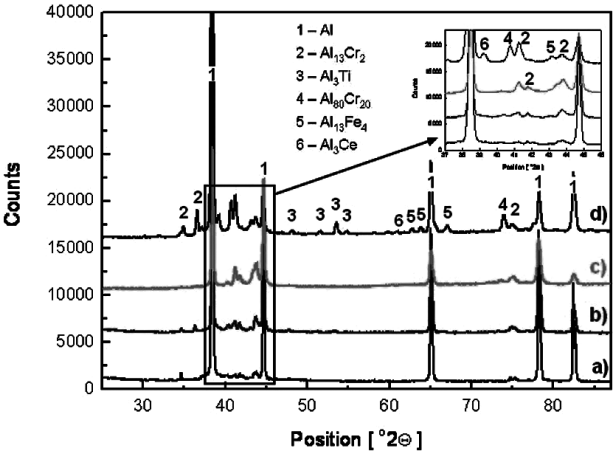

Figure 3: XRD patterns of: a) AlCr2, b) AlCr4Ce1, c) AlCr4Fe3 and d) AlCr5Fe3Ce1 alloys
Slika 3: Rentgenski posnetki zlitin: a) AlCr2, b) AlCr4Ce1, c) AlCr4Fe3 in d) AlCr5Fe3Ce1

of **Figures 1** and **2** and marked with arrows, exhibit a very fine microstructure, called an ultra-rapidly-solidified area (URSA). The thickness of URSA depends on two main factors: 1) experimental parameters and 2) alloy properties. Experimental parameters include the cooling wheel speed, the atmosphere of the experiment and the geometry of the experimental device. These characteristics were identical during the preparation of all the rapidly solidified alloys. Therefore, all the differences among the rapidly solidified ribbons can be assumed to result from the chemical compositions of the alloys.

Figure 1 shows the structure of a cross-sectioned ribbon of the AlCr4Ce1 alloy. In comparison with the AlCr5Fe3Ce1 alloy, documented in **Figure 2**, its URSA is thinner and the microstructure is not so fine, because intermetallic particles (the dark areas) are observed on the free (top) side of the ribbon. In the URSA, a high-entropy alloy is formed. The ability to form such an alloy is increased with the number of elements in the system, especially with the number of transition metals. For this reason, the URSA of the AlCr5Fe3Ce1 (quaternary) alloy is much larger than that of the AlCr4Ce1 (ternary) alloy.

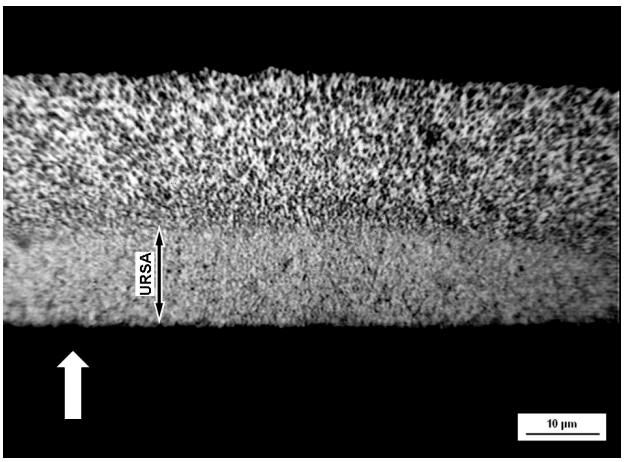

Figure 2: LM micrograph of a cross-section of a rapidly solidified ribbon of the AlCr5Fe3Ce1 alloy
Slika 2: Posnetek prereza hitro strjenega traku zlitine AlCr5Fe3Ce1

According to XRD (**Figure 3**), the AlCr5Fe3Ce1 alloy is composed of the fcc-Al, $Al_{13}Cr_2$, $Al_{13}Fe_4$, Al_3Ti and Al_3Ce crystalline intermetallic phases and the $Al_{80}(Cr,Fe)_{20}$ decagonal quasicrystalline phase. The AlCr4Ce1 alloy, on the other hand, contains neither $Al_{13}Fe_4$ nor the quasicrystalline phase. This suggests that the Fe addition leads to a formation of two very different intermetallic phases – $Al_{13}Fe_4$ and quasicrystalline $Al_{80}(Cr,Fe)_{20}$ – therefore, strongly increasing the MPFA due to the so called "confusion principle".[14,15]

The fcc-Al matrix grain size determined with the Scherrer formula and Rietveld analysis is given in **Table 2**. The values are different because of the used methods and their limitations, but the grain-size trend is in sufficient agreement. The total amount of the alloying elements (Cr, Ti, Fe, Ce) in the AlCr2 alloy is significantly lower than in the other alloys. This results in a lower number of crystallization nuclei of the intermetallic phases during the solidification and in a huge grain size of the AlCr2 alloy.

Table 2: Grain size of the fcc-Al matrix in nm determined with the Scherrer formula and Rietveld analysis
Tabela 2: Velikost zrn fcc-Al osnove v nm, določena po Scherrerjevi enačbi in z Rietveldovo analizo

Alloy	Scherrer formula	Rietveld analysis
AlCr2	232	118
AlCr4Ce1	123	76
AlCr4Fe3	49	50
AlCr5Fe3Ce1	46	32

The addition of the mass fraction 1 % Ce causes a mild grain refinement. The reason for this is not only a higher amount of the alloying elements. The possibility

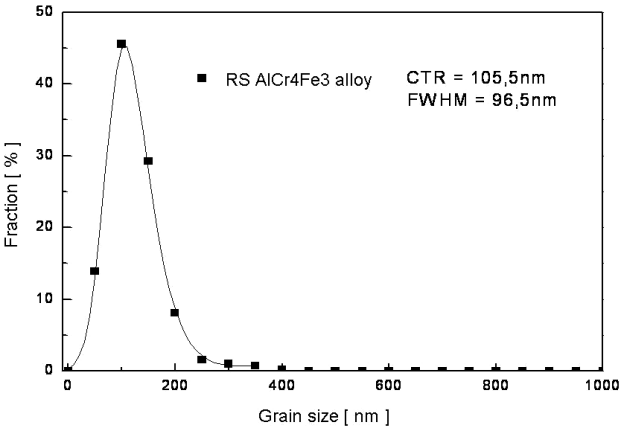

Figure 4: Grain-size distribution of the RS AlCr4Fe3 alloy
Slika 4: Razporeditev velikosti zrn hitro strjene zlitine AlCr4Fe3

of an intermetallic-phase formation increases with the Ce addition and so this addition supports the alloy metastability on the basis of the confusion principle. The Ce addition also enables the existence of an alloy melt at lower temperatures, because the Al-Ce system exhibits a eutectic. The Fe addition has a strong effect on the grain-size refinement, as it can be seen from the difference between the grain sizes of the AlCr4Ce1 and AlCr5Fe3Ce1 alloys. A very small grain size of the RS materials is caused by a suppression of the diffusion rate due to a very high quenching rate. Surprisingly, the AlCr4Fe3 and AlCr5Fe3Ce1 alloys exhibited almost the same grain sizes. This was the reason for determining the grain sizes of these alloys also with an image analysis and the results of the grain-size distribution are given in **Figures 4** and **5**. The values of the grain size determined from the XRD pattern are about half of the values determined from the TEM image. This is usual because what is seen, in a TEM micrograph, as single grains, can be more coherent diffracting domains for the X-ray methods. However, all the methods showed that the grain sizes of the AlCr4Fe3 and AlCr5Fe3Ce1 alloys are

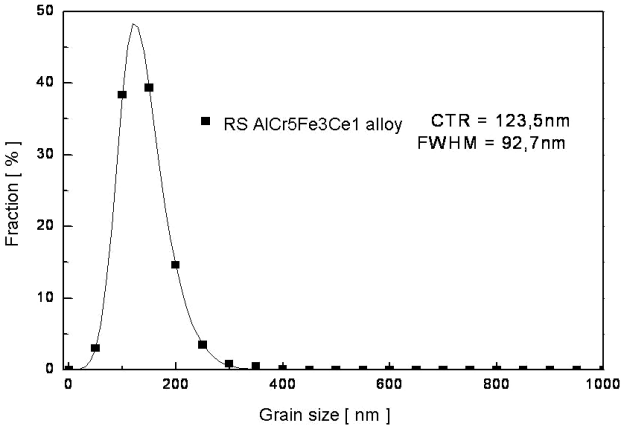

Figure 5: Grain-size distribution of the RS AlCr5Fe3Ce1 alloy
Slika 5: Razporeditev velikosti zrn hitro strjene zlitine AlCr5Fe3Ce1

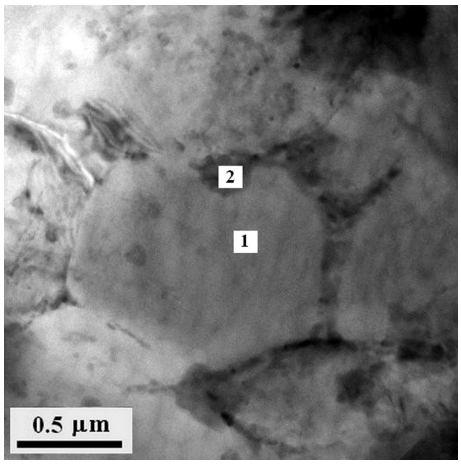

Figure 6: TEM micrograph of a cross-section of a rapidly solidified ribbon of the AlCr4Ce1 alloy (1 – Al grains, 2 – $Al_{13}Cr_2$)
Slika 6: TEM-posnetek prereza hitro strjenega traku zlitine AlCr4Ce1 (1 – Al zrna, 2 – $Al_{13}Cr_2$)

approximately the same. In the Fe-containing alloys the grain refinement is predominantly caused by the Fe addition and the influence of Ce on the grain size is almost negligible. The interaction of Al and Fe in a melt and during the solidification is so strong that it probably leads to a primary formation of very fine intermetallic phases. These phases can act as solidification nuclei for the fcc-Al matrix. These phases are then located at the grain boundaries or at the triple points of the matrix grains, protecting the alloys from a consequent grain coarsening.[16]

Figure 6 presents the structure of the AlCr4Ce1 alloy composed of the Al grains and intermetallic particles containing mainly Al and Cr. These intermetallics are most likely $Al_{13}Cr_{12}$, see the XRD patterns in **Figure 3**. The microstructure of the AlCr5Fe3Ce1 alloy is shown

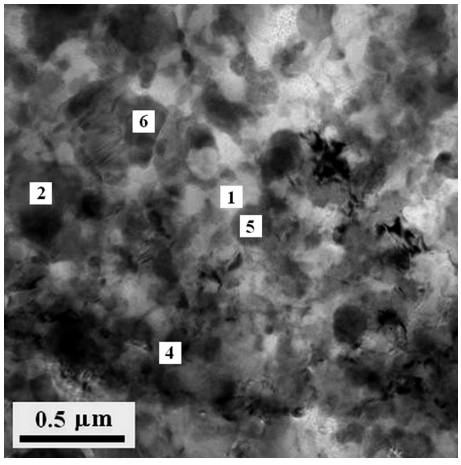

Figure 7: TEM micrograph of a cross-section of a rapidly solidified ribbon of the AlCr5Fe3Ce1 alloy (1 – Al grains, 2 – $Al_{13}Cr_2$, 4 – $Al_{80}(Cr,Fe)_{20}$, 5 – $Al_{13}Fe_4$, 6 – Al_3Ce)
Slika 7: TEM-posnetek prereza hitro strjenega traku zlitine AlCr5Fe3Ce1 (1 – Al zrna, 2 – $Al_{13}Cr_2$, 4 – $Al_{80}(Cr,Fe)_{20}$, 5 – $Al_{13}Fe_4$, 6 – Al_3Ce)

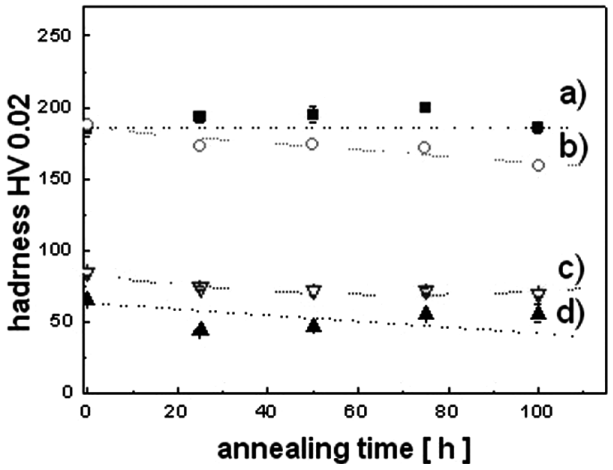

Figure 8: Room-temperature hardness dependence on the annealing time at 400 °C for: a) AlCr5Fe3Ce1, b) AlCr4Fe3, c) AlCr4Ce1 and d) AlCr2 alloys

Slika 8: Odvisnost trdote pri sobni temperaturi od časa žarjenja pri 400 °C za zlitine: a) AlCr5Fe3Ce1, b) AlCr4Fe3, c) AlCr4Ce1 in d) AlCr2

in **Figure 7**. Beside the Al grains and $Al_{13}Cr_2$ intermetallics in **Figure 7**, there are also spherical particles of the $Al_{80}(Cr,Fe)_{20}$ quasicrystalline phase as well as the $Al_{13}Fe_4$ and Al_3Ce phase particles.

Figure 8 shows the dependence of the room-temperature hardness on the annealing time after annealing at 400 °C. The microstructure of the AlCr5Fe3Ce1 alloy is supposed to be very stable because its hardness value did not change even after 100 h of annealing. The hardness of the other alloys slightly decreased. The Fe addition also caused a significant increase in the initial hardness of the rapidly solidified ribbons. In comparison with the AlCr5Fe3Ce1 alloy the hardness of the AlCr4Fe3 alloy slightly decreased with time. This suggests that the Ce addition stabilizes the alloy. The Al_3Ce particles, present in the AlCr5Fe3Ce1 alloy, are placed mainly at the grain boundaries suppressing the grain coarsening during the thermal exposure.

4 CONCLUSION

An addition of a few mass fractions of Fe significantly modifies the microstructure and the hardness of the rapidly solidified Al-Cr-Ti alloys. This results in an increase in the thickness of the ultra-rapidly-solidified areas of ribbons. It also causes a decrease in the fcc-Al matrix grain size and a significant increase in the hardness of the RS ribbons. An influence of the Fe addition on the thermal stability of the alloy during the heat treatment was not observed.

An addition of a very small amount (1 %) of Ce leads to the thermal stabilization of the alloy at the elevated temperatures of about 400 °C. The influence of Ce on the matrix grain size was not observed in the Al-Cr-Fe-Ti alloy. In the Al-Cr-Ti alloy, the Ce addition causes a mild decrease in the grain size.

Acknowledgement

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