Investigation of Quasicrystalline Phases Formation by mechanical Alloying of the Al – Cr and Al – Fe Alloys

أستقصاء تكوين الطور شبـه البللورى بطريقة السبك الميكانيكى لسبائك Al – Fe & Al – Cr

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ملخص البحث

للحصول على المركب $Al_{86}Cr_{14}$ بطريقة السبك الميكانيكى لعنصري Cr و Al تم بإستخدام الطاحونة ذات الكرة التقليدية. نتيجة للسبك الميكانيكى تم الحصول على Al مشبع بالكروم. بالتسخين عند درجة ٥٩٠ درجة مؤية، حصلنا على الطور شبه البللورى لهذا المركب بالأضافة الى طورين معدنيين آخرين و هما، $Al_{13}Cr_2$ و Al_4Cr. من جهة أخرى تم الحصول على المحلول الصلب فوق المشبع للمركب $\alpha - Fe (Al)$ و أيضآ الطور الشبه مستقر Al_6Fe بواسطة أيضآ الطاحونة ذات الكرة التقليدية لمخلوط من Al و Fe بالأضافة للمركب $Al_{84}Fe_{16}$. و لكن فى هذه بالرغم من المعاجة الحرارية لم نستطع الحصول على الطور شبه البللورى ولكن حصلنا على طور معدنى. بطريقة السبك الميكانيكى أمكن الحصول على حجم جزينات السبيكتين $Al_{86}Cr_{14}$ و $Al_{84}Fe_{16}$ فى حدود النانو 25 nm, 37 nm على الترتيب.

ABSTRACT

Mechanical alloying (MA) of elemental Al and Cr powders of nominal composition $Al_{86}Cr_{14}$ has been performed by using a conventional ball – mill. The MA process produced a supersaturation of Cr in Al. Isothermal annealing at 590 °C represented in the formation of quasicrystalline phase, in addition of two intermetallic phases $Al_{13}Cr_2$ and Al_4Cr.

A supersaturation solid solution of α – Fe (Al) and a metastable Al_6Fe phase were formed by MA of a mixture of Al and Fe elements containing of nominal composition $Al_{84}Fe_{16}$. However, thermal treatment fail to produce the quasi-phase, various intermetallic phase are obtained. For both alloy systems, milling structure have a nano size of ≈ 25 nm for $Al_{86}Cr_{14}$ and ≈ 37 nm for $Al_{84}Fe_{16}$, the thermal stability of the produced phases was also examined.

1. INTRODUCTION

Mechanical alloying (MA) has been successfully applied to the synthesis of various type materials. This technique has been used to obtain amorphous alloys from elemental crystalline powders mixtures [1], intermetallic phases [2], nanocrystlline alloys [3] and recently quasicrystals [4].

Al – Cr system is known to form icosahedral quasicrystal by rapid solidification [5–9] or by MA followed by heat treatment [3] over a wide composition range from about 5 to 16 at % Cr. However, the processing conditions are reported differently.

Considerable amounts of work has also been concentrated on the synthesis by MA of Al – Fe systems, where both quasi and amorphous phases formation are possible [1, 2]. The sequence of phases which appear following milling or milling followed by thermal treatment are in contradiction in there results [10, 11]. Therefore the aim of this work is to examine both systems (Al-Cr) and (Al-Fe) by MA in order to determine various factors which control the type of phase formation, mainly the quasicrystalline phase.

2. EXPERIMENTAL PROCEDURE

Pure aluminum (99.95 %), iron (97.7 %), and Chromium (98 %) are used as starting powders to make up the desired compositions. An organic surfactant (Stearic Acid) is added to the powders as 2 wt.% to act as a process control agent. Two nominal mixtures of Al, Fe and Cr are used, which based on the two compositions; Al – 14 at. % Cr and Al – 16 at. %Fe. Each of starting material mixture is charged into the attritor vial, and the ratio of ball to powders weight was 10 : 1 (100 gm of different diameter balls are used). To minimize contamination with oxygen and/or nitrogen, the mechanical alloying process is carried out under dry argon atmosphere.

X-ray diffraction study is carried out using a Siemens D5000 (computer controlled) powder diffractometer with a nickel filtered Cu-K$_\alpha$ radiation (wavelength $\lambda = 1.5406$ A$^\circ$).

The thermal stability of certain samples has been monitored with differential thermal analysis (DTA), Perkin-Elmer DTA7 (computer controlled). The sample is heated with a constant heating rate 15 K sec^{-1} in static air as a furnace atmosphere.

3. RESULTS AND DISCUSSION

3.1 Mechanical Alloying of Al$_{86}$Cr$_{14}$

X-ray diffraction patterns (XRD) of Al-14 at% Cr powder after milling for various intervals of time are shown in Fig. (1). It is generally observed that both peak intensities of aluminum and chromium elements decrease with increasing processes time, up to 60 h. This could indicate that there is no alloying occurs within the limit of milling time used. In that respect, amorphization is only expected at higher milling times which depend on the milling intensity.
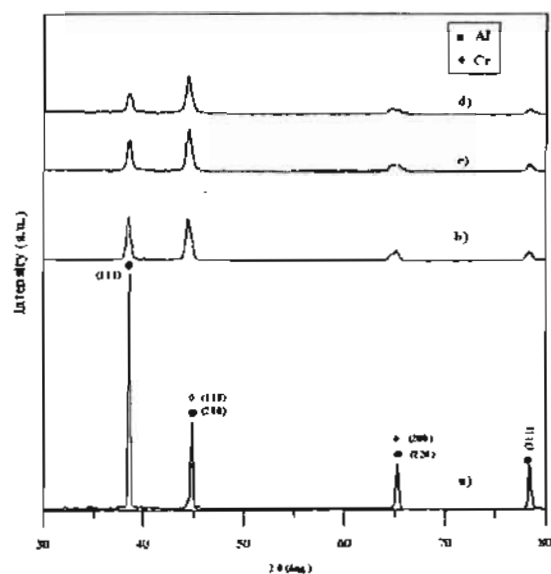
Fig. 1: XRD patterns of mechanically $Al_{86}Cr_{14}$ for: a) 0 h, b) 20 h, c) 40 h, d) 60 h

The observed small shift of peaks positions in XRD results with milling time as shown in Fig. (2) as an example, could be related to a possible formation of supersaturation solid solution phase of Cr in Al.
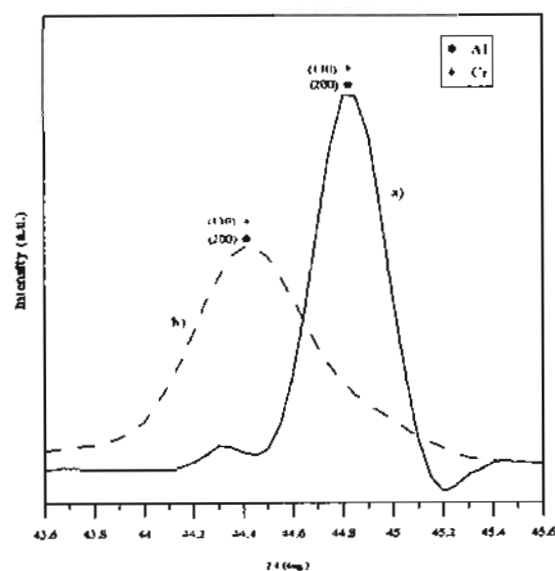

Fig. 2: The relationship between the peaks shift vesus the intensity for Al and Cr elements at different milling times

Williamson-Hall plot method [12] is carried out for the various stages of XRD patterns in order to separate both particle size and strain, and an example of the results shown in Fig. (3).
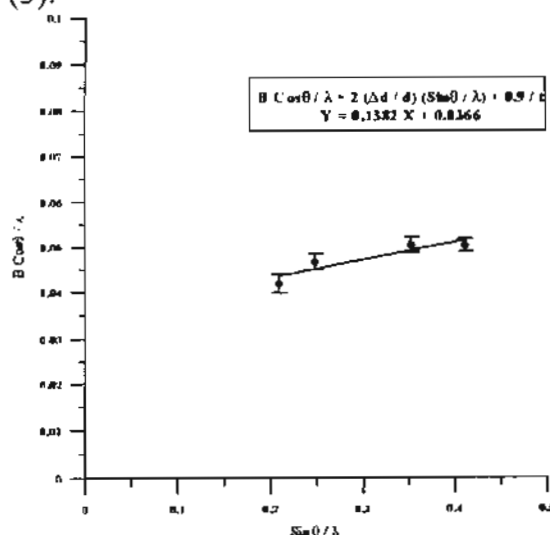

Fig. 3: Williamson-Hall plot for 40 h milled powder for $Al_{86}Cr_{14}$

Figures (4, 5) represent the obtained results of particle size and strain for the milled samples respectively. The particle size and strain are found to reach ≈ 25 nm and ≈ 0.067 after 40 h milling. The thermal treatment is carried after this stage of milling.
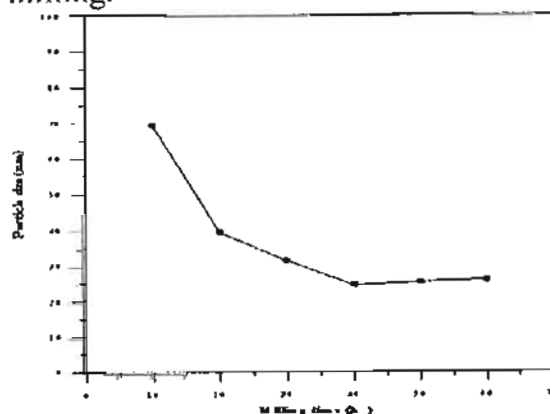

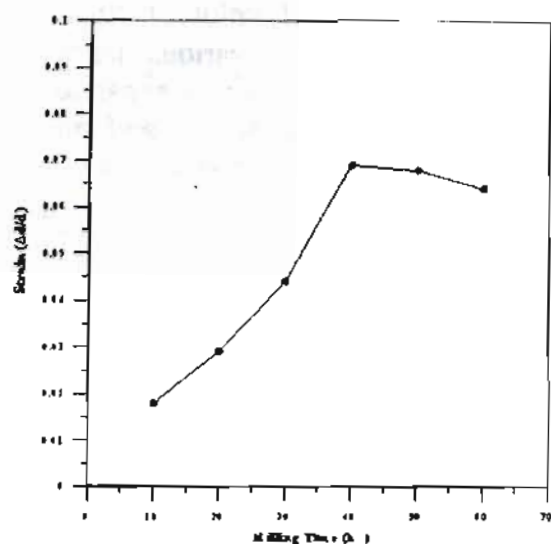**Fig. 4:** Particle size changes with milling time for $Al_{86}Cr_{14}$

Fig. 5: The relationship between the milling time versus strain for $Al_{86}Cr_{14}$

Figure (6), shows DTA result for 40 hs MA powder, heated at a rate 15 K sec^{-1}, where two exothermic peaks can be observed. The first one is very small and broad occurs at ≈ 372 °C, and a rather sharp peak is observed at 582 °C. It is most likely that the first one is related to annealing out the defects formed during milling process, i.e. stress-relieved process and the second one may be due to certain type of phase formation.
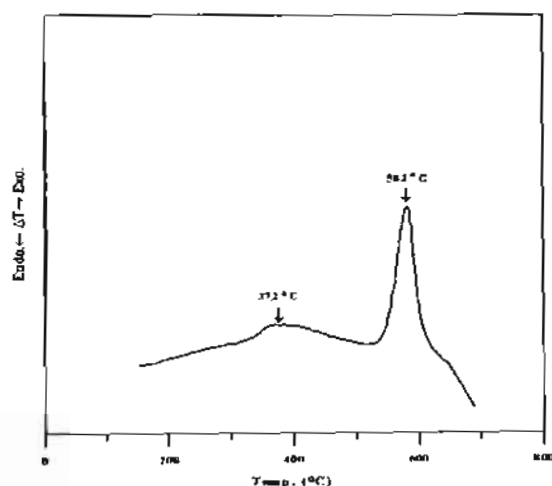

Fig. 6: DTA curve of 40 h milled powder for $Al_{86}Cr_{14}$

Based on the thermal analysis results, various intervals of annealing times ranging from 30 mins to 6 h are carried at 590 °C for the 40 hs milled powder. Figure (7) shows XRD of the 40 h milled sample after 30 mins to 6 h annealing at 590 °C. Phase formation readily observed and appears to be rather time dependent. The quasicrystalline phase was identified in the XRD after 30 mins isothermal annealing and continue to increase in quantity up to 4 h annealing after which it decreases. The annealed structure contain two other phases, the first one can be indexed as Al_4Cr hexagonal type, using the recently [13] reported d-values of this phase which is known to be isomorphous with $\mu-Al_4Mn$, therefore it is called $\mu-Al_4Cr$ type.
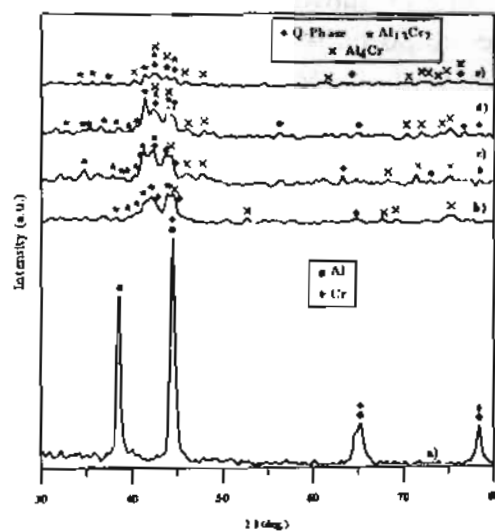

Fig. 7: XRD patterns for 40 h mechanically alloyed $Al_{86}Cr_{14}$ annealed at 590° C for a) as milled, b) 30 min., c) 2 h, d) 4 h, e) 6 h

Moreover, present XRD patterns indicated the existence of a third phase of $Al_{13}Cr_2$ in the annealed material, this phase is also reported [8] to coexist

with icosahedral rapidly quenched Al-Cr, and both phases (quasi and intermetallic $Al_{13}Cr_2$) seemed to be more or less stable by regard to Al_4Cr.

It is expected that the quasiphase will occur on α-Al (Cr) supersaturated phase enriched in chromium which is formed during milling, while the phases Al_4Cr and $Al_{13}Cr_2$ are expected to form due to the interaction between the remaining Al and Cr elements during milling.

3.2 Mechanical Alloying of $Al_{84}Fe_{16}$

XRD patterns of Al with 16 at% Fe after various processing times are shown in Fig. (8). It is possible to observe that, increasing milling time caused the peaks to broaden and decrease in intensity. The beak broadening is a result of refinement of particle size and the introduction of strain. Williamson-Hall plot method as indicated before [12] was applied for the XRD patterns of the milled powder up to 60 h. The analysis indicated that, the particle size and strain are ≈37 nm and ≈0.072 after 40 h milling respectively. Further, Al-lines shift slightly toward higher angles suggested alloying of Fe with Al leading to a solid solution formation, similar to that in Al-Cr system. However, a few new low intensities peaks mainly in the low angle region of $2\theta = 38-44°$ appeared in XRD pattern after 40 h milling and continue up to 60 h milling. For 40 h milling pattern, those lines could be indexed as a metastable Al_6Fe phase. On the other hand, it is not likely that the metastable Al_6Fe will transform to the rather stable Al_3Fe phase with increasing milling time at this stage.

Since, Al_3Fe phase has a complex monoclinic structure with a large unit cell, where a higher atomic mobility is needed and is not likely to be provided by milling process under the present conditions.
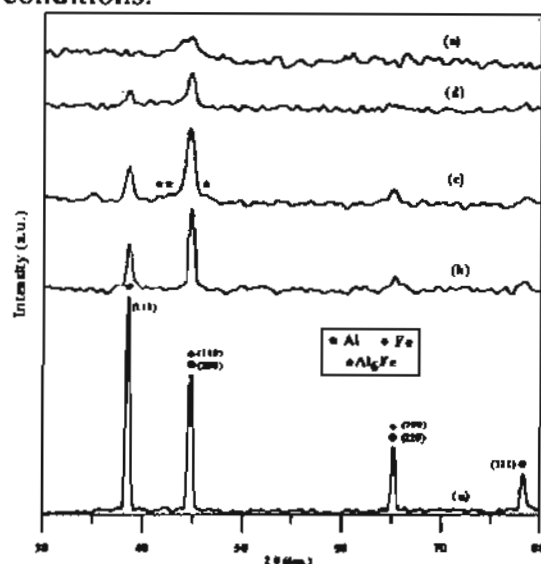

Fig. 8: XRD patterns of mechanically alloyed $Al_{84}Fe_{16}$ for a) 0 h, b) 20 h, c) 40 h, d) 60 h, e) 190 h

A Differential thermal analysis study was carried out for the 40 h MA powder because the appearance of new phases at this stage of milling Fig. (8). The sample was heated at a rate of $15°$ C sec^{-1}, and the DTA curve is shown in Fig. (9), where two exothermic peaks can be observed. The first one is very small occurs at ≈352 °C, and the second is a rather sharp peak at 410 °C. Isothermal heating for various time interval are carried at 500 °C on the 40 h milled specimens in order to examine the possible phase evolution during annealing.
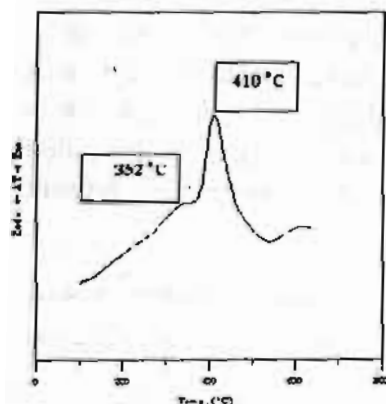
Fig. 9: DTA curve for 40 h milled powder for "$Al_{84}Fe16$"

XRD after different annealing times Fig. (10) indicated a changes mainly in the metastable Al_6Fe phase lines leading to the formation of both $Al_{13}Fe_4$ and Al_3Fe, through the interaction with the elemental lines of α-Al and α-Fe. It is to be noted that Al_6Fe lines are still observed even after 4 h annealing, i.e. the dissolution or rather the transformation process has a slow-rate.
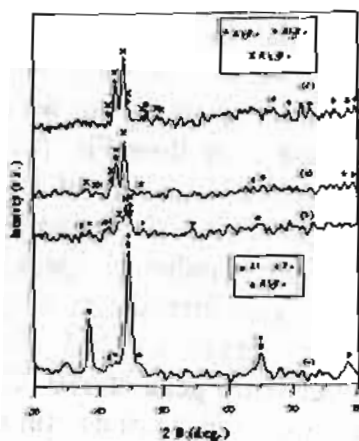

Fig. 10: XRD patterns for 40 h mechanically alloyed $Al_{84}Cr_{16}$ annealed at 500° C for a) as milled, b) 30 min, c) 2 h, d) 4 h

Different sequence of phase transformation have been given by several authors [1, 14], from which it is possible to show that the initial processing conditions and annealing temperature control to large extent the final structure produced by milling and subsequent annealing treatment.

4. CONCLUSION

MA and subsequent heat treatment of $Al_{86}Cr_{14}$, led to the formation of quasicrystalline phase, $Al_{13}Cr_2$ and Al_4Cr. Also MA and subsequent heat treatment of $Al_{84}Fe_{16}$, led to the formation of stable Al_3Fe and $Al_{13}Fe_4$ phases, beside the metastable Al_6Fe phase. In both compositions nanocrystalline powders particle size ≈ 25 nm and ≈ 37 nm have been obtained for $Al_{86}Cr_{14}$ and $Al_{84}Fe_{16}$ respectively.

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