Experimental assessment of the icosahedral phase of Al-Cu-Fe quasicrystalline alloy for enhanced solar absorption

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Abstract

This paper investigates the synthesis, microstructural characterization and thermal and optical properties of Al-Cu-Fe quasicrystalline system for selective solar absorption applications. A nominal composition of $Al_{64}Cu_{25}Fe_{11}$ was produced by mechanical alloying (MA) using high-energy ball milling. Subsequent annealing was performed on the quasicrystalline samples at temperature of 200 °C for 20 hours. This was done along with monitoring the samples crystallographic morphology via X-ray diffraction (XRD) through out the milling process and the subsequent annealing. The resulting alloys were examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to verify how efficient the inter-diffusion of the elements. Through the optical spectroscopy results, it is clear that the absorption performance of Al-Cu-Fe sample is better than TiO_2 in the whole range of spectrum of the optical test graph (300 nm to 1000 nm) regardless of the milling time and the annealing period. Also, Differential Scanning Calorimetry (DSC) was used to indicate the thermal stability of the formed solid solution as well as in the demonstration of the existing phases when correlated with the XRD graphs. High-energy ball milling has proven to be an effective method for producing homogeneous phases of quasicrystalline materials, with enhanced solar absorption properties.

Keywords: Quasicrystalline alloys; Al-Cu-Fe systems; selective solar absorbers; mechanical alloying

1. Introduction

In the past few years, the Al–Cu–Fe system with the developed icosahedral (I) quasicrystalline (QC) phase has been the focus of many studies. The components of the system are considered to be cheap, easily available and technologically promising compared to those of other systems [1]. The icosahedral quasicrystalline Al–Cu–Fe system has a 5-fold symmetry in its structure. It can be either produced to be stable or metastable depending on the methods used in the production process [2]. The formation of quasicrystalline phases can be accomplished through various process which include solidification of molten alloys, rapid quenching techniques by

either by melt spinning or gas atomization, electrodeposition, gas evaporation and mechanical alloying [3]. Mechanical alloying is used here to produce an alloy that possesses desirable mechanical and thermal, microstructural properties, and most importantly, optical properties for enhanced solar absorptivity [4, 5]. Mechanical alloying (MA) is commonly known for its ability to produce metastable alloys, but some studies shows that it is also capable of forming the i-phase in the Al-Cu-Fe ternary system [6]. Previous studies presented some optimal combination of ball milling and annealing was found to form the single-phase QC alloys [7, 8]. In this techniques pure constituents are ball milled together to form solid solutions with exact compositions under the forces of the collision, that causes continuous fracturing and cold welding [9]. There are many factors affecting this process, namely, milling time, milling temperature, post milling thermal processing, and alloy composition [10]. The formation of icosahedral phase (i-phase) by the method mechanical alloying can offer an insight into the development of the microstructure of the material and phase transformations that occurred during the milling.

This work investigates the feasibility of the synthesis of Al-Cu-Fe quasicrystalline alloy that would be suitable for enhancing solar absorption in the UV-Vis range. The synthesis of the alloys system is done through high-energy ball milling, which is a mechanical alloying technique, and the resulting microstructure and thermal and optical properties will be analyzed and measured as milling time is increased and attention is given to the phase transformations that occur during heating.

2. Experimental

2.1. Synthesis

An elemental blend of high purity aluminium (≥ 93 %, fine), copper (< 425 μm, 99.5 %) and iron (≥ 99 %, fine) powders corresponding to the nominal compositions of $Al_{64}Cu_{25}Fe_{11}$ has been mechanically alloyed. The grinding bowl initially held a sample of 10 g with six 10 mm zirconia as the milling media. A 450 rpm milling speed and (2:1) ball to powder weight ratio was maintained through the milling. Milling is paused after each hour to cool the equipment and a sample is taken every 4 hours for further heat treatment and characterization. Subsequent annealing was performed on the quasicrystalline samples at temperature of 200 °C for 20 hours to further develop the microstructure. The milling is terminated once the required microstructure is obtained.

2.2. Microstructural analysis via SEM and XRD

The powder X-ray diffraction (XRD) patterns, plotted for five powder samples collected at a two-hour interval for eight hours, provide an insight into extent and progress of crystallization and the composition and grain structure of the developing

solid solution. The X-ray patterns are recorded in the 2θ geometry between 40 and 90° at 0.02° 2θ s−1 with a Bruker D8 Advance DaVinci multipurpose X-ray diffractometer with Cu Kα radiation operating at λ = 1.5406 Å, 40 kV tube voltage and 40 mA current. Fused pieces of the material collected after 6 h milling time are examined under a scanning electron microscope (SEM) and the coupled energy dispersive X-ray spectrometer (EDX). The SEM is a VEGA3 XM by TESCAN, operating at 5 kV, while the EDX analysis is conducted with both map and point modes at the same operating voltage; the former was acquired during 3 min while the latter was from four different spots of the sample during 30 s live time.

2.3. Thermal analysis

Differential Scanning Calorimetry (DSC) is performed on the milled powders for the (2 h, 8 h, 16 h, 28 h, 36 h and 52 h) samples to provide insight on the energy of formation and mixing of the resulting alloy. The stability of these alloys is due to the balance between the effectiveness of the MA process and thermal decomposition at high temperatures. For an endothermic reaction, heat flow indicates the phase shift within the solid solution (a peritectoid reaction). The calorimeter used is a Q20 from TA Instruments, running on 120 V AC, 47 – 63 Hz, 500 W (4.5 A) and equipped with a liquid nitrogen cooling system (LNCS) that allows automatic and continuous temperature control within a full range of –180 °C to 550 °C. A few milligrams of as-is and 2, 4, 6 and 8 h powders is encapsulated in an aluminium pan, and an empty reference pan sit on a thermoelectric disk surrounded by a furnace. As the temperature of the furnace is changed, heat is transferred to the sample and reference through the thermoelectric disk. The differential heat flow to the sample and reference is measured by area thermocouples. The phase formation, total enthalpy and heat flow through 0 – 500 °C temperatures are examined for the current test.

2.4. Optical (spectroscopic) analysis

Spectral measurements of absorption in the ultraviolet, visible and near-infrared (UV-Vis-NIR) regions were carried out on the samples produced after different milling times as well as the 52 hours of milling along with 20 hours of annealing sample with an Ocean Optics HR2000 high-resolution spectrometer. The HR2000 has a 300 lines per mm diffraction grating, 10 μm entrance slit, a Sony ILX511 2048-Pixel element linear CCD array detector, and is operating in the effective wavelengths range 300 - 1100 nm. The spectrometer is connected to a fiber optic reflection probe R200-7-SR, 2-m long, and of a 200-μm-core diameter. The reflection probe consists of a tight bundle of 7 optical fibers in a stainless steel ferrule with 6 illuminating fibers around one axial read fiber, fixed at ~ 4 mm from the sample where losses due to scattering is assumed to be negligible, and all diffuse reflectance is collected at the probe. The source end of the reflection probe is connected to a tungsten halogen light source (Ocean Optics LS-1-LL). A reference

surface in the form of a reflection standard (B0071519) is used to store baseline absorptance (0 %) spectra to facilitate comparison between the various alloy compositions. The integration time was set to 30 ms to contain the intensity of the highest acquired peak. The recorded time-resolved spectra were averaged over 10 readings to increase the signal-to-noise ratio.

3. Results and discussion

3.1. SEM

Figure 1 below shows SEM scans for Al-Cu-Fe alloy with milling time of 2, 16, 24, 36, 44 and 52 hours at magnification of 1 kx. The average size of the grain can be roughly approximated by selecting random particles in the graph and average the readings. In general we can notice the progression of grain size as milling time increase. Where at 2 h, the grains were large (more than 50 μm), this indicate that the mixture has not reached the wanted outcome after 2 hours of milling. When the mechanical alloying proceeds, the size of the particle becomes significantly smaller, which can be clearly observed in the figures. The average grain size of 16, 24, 36, 44 and 56 h are 25.8, 11.6, 8.6, 8.2 and 7.7 μm, respectively. One can notice the exponential decrease of the average grain size with milling time. Because of the small particles the agglomeration of the particles is clear, such can be seen in 36 h, 44 h and 52 h.

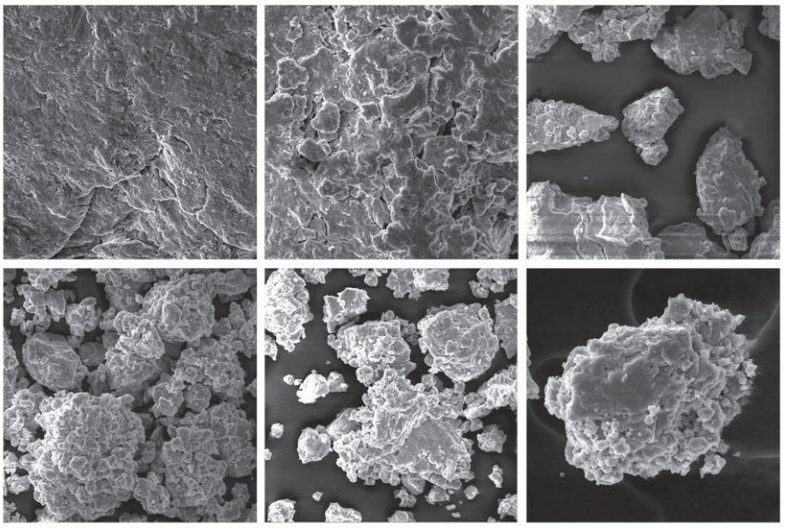

Figure 1. SEM graphs for (clockwise from upper left) 2, 16, 24, 52, 44 and 36 h milling time at 1kx magnification.

3.2. XRD

The microstructural evolution of a mixture of elemental powders with a composition of $Al_{64}Cu_{25}Fe_{11}$ is shown in Figure 2. The figure shows a number of selected diffraction patterns as a function of milling time obtained for the samples milled at 400 rpm up until 56 hours. The XRD patterns shown here are for (2, 16, 24, 36 and 56 h), where the other cases of milling samples undergo no significant changes in the phases included in the XRD patterns, except for the broadening of the peaks due to mechanical disordering along with particle refinement (smaller grain sizes), which is expected during the milling. The X-ray diffraction peaks, corresponding to the elemental Al, Cu and Fe-phases, were observed to be dominant for the early milling times. After 16 hours of milling the elemental peaks decreased significantly and new peaks appeared. One of the phases that evolved during the milling is θ-Al_2Cu, which was observed in both after 24 h and 36 h. The small amount of θ-Al_2Cu suggests the occurrence of a partial reaction between Al and Cu, which is also why the intensity of the Cu peaks is becoming lower as the milling continues. The final sample was obtained after 56 hours, and it shows multiple peaks that correspond to the intermetallic compound β-Al(Fe,Cu), along with a few elemental peaks for aluminum. This is in good agreement with the work of X. Yong et al [11]. Yet, there was no icosahedral QC phase observed in the powder samples during the milling, which indicates the need of heat treatment.

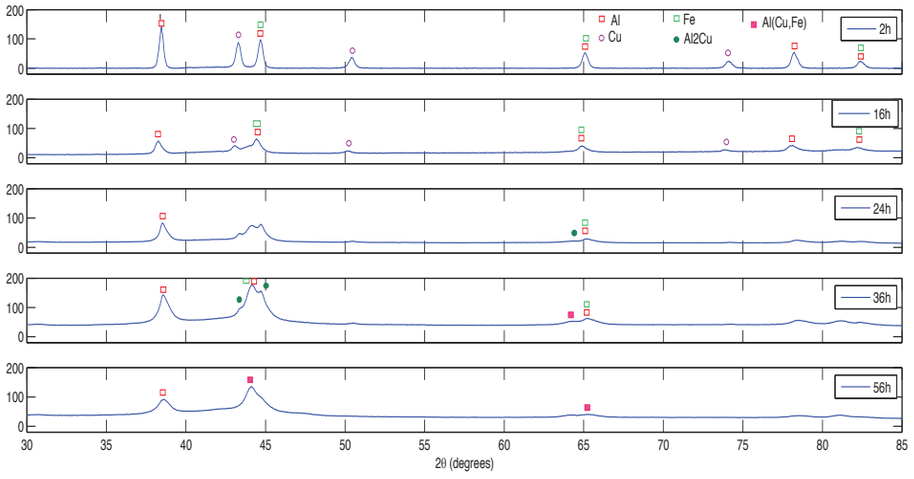

Figure 2. - XRD patterns at different milling time for $Al_{64}Cu_{25}Fe_{11}$ before annealing.

The combination of long milling times (36 h, 40 h, 44 h, 48 h and 52 h) and subsequent annealing (20 h at 200 °C) was studied through XRD patterns for the

$Al_{64}Cu_{25}Fe_{11}$ system, which can be seen in Figure 3. The annealing was performed to induce the formation of QC-phase. After the annealing of the samples it was noticed that many peaks appeared that were not in XRD patterns of the samples prier to the heat treatment. The annealed samples show similar XRD patterns, so the powder sample of the Al-Cu-Fe system with 52 hours of milling was studied in more detail to identify the exact phases that exist in the material as can be seen in Figure 4. The sample was found to consist of θ-Al_2Cu, β-Al(Cu,Fe), ω-Al_7Cu_2Fe and few iQC-phase as can be seen in figure 4. The dominant phase in the annealed sample was the Al_7Cu_2Fe. In contrast the existence of θ-Al2Cu and β-Al(Cu,Fe) was minor after the annealing although β phase was the main existing phase in the 52h sample before annealing. The existence of the iQC-phases indicates that the $Al_{64}Cu_{25}Fe_{11}$ is a valid composition that can produce icosahedral microstructure but only after a sufficient time of annealing and milling. The appearance of iQC-phases is both very interesting and exciting for two reasons. The first is that this exact composition was not tested previously literature for the formation of quasicrystalline phases and other reason is that quasicrystalline Al–Cu–Fe alloys are known have a huge potential in light absorption applications because of its enhanced optical properties [12].

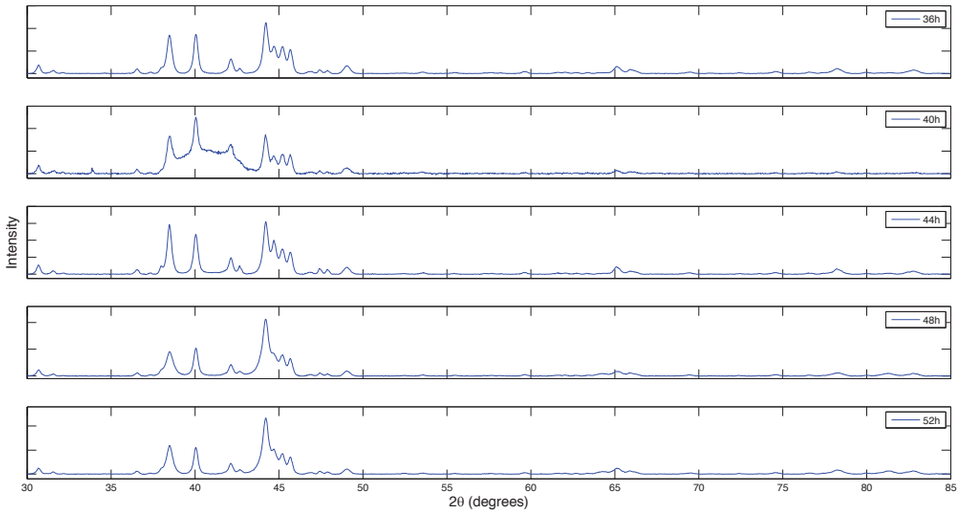

Figure 3. XRD pattern for annealed Al-Cu-Fe system after different milling hours.

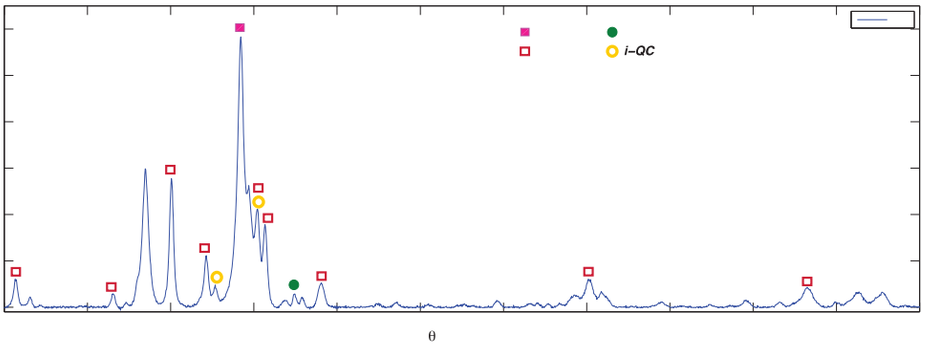

Figure 4. XRD patterns for Al64Cu25Fe11 after 52h milling and 20h annealing at 200° C.

3.3 Thermal analysis results

DSC is the most frequently used technique in thermal analysis; it is used to study the behaviour of materials as a function of temperature or time: Melting point, crystallization behaviour and chemical reactions, are some of the properties that we can get out of DSC data. In this project, the thermal stability of the composite is assessed using DSC results, which are presented with respect to the milling at increments from 2 h up to 52 h in the below figure. The observed peaks indicate the exothermic reaction due to dissociation of the phases present. First, one can notice a major exothermic peak between 470 °C and 490 °C. The peak location is seen to retreat to smaller temperatures with increased milling time, indicating less stable phases. This is expected and reported in literature [13] as multiple phases form when milling time increases. However, this peak reduced for higher milling time. It is interesting to note that at 16h the DSC graph had 3 peaks, a new one occurred at 432 °C, a phase formation at 2θ of 43° that can be observed in the XRD for the 16h. Also, a small exothermic peak at 320 °C can be linked with the formation of ω-Al_7Cu_2Fe phase as seen in previous work of Proveti et al. [14] When the ω phase is recognized as an indicator of the simultaneous formation of the ψ and β phases [15, 16], the high energy exothermic peaks witnessed in all milling times in the range of 432 to 458 ° C, could be correlated to a huge formation of both phases.

As milling time increase, the hot peak kept declining and shifting to lower temperature, in addition to a new colder peak and that indicate a different phase transition. In 28 h and 36 h of milling both peaks appear, at almost 440 °C and 300 °C. It was reported that θ phase formation could be seen at this range of temperatures [15], relating to the XRD there's a θ-Al_2Cu formed at 2θ = 81°. With milling, the hotter peak started to decrease, in contrast to the colder one that kept rising until the 44 h. The segregation of phase in the DSC can be correlated with the

XRD graphs, since there's a peak at 2θ = 65° that disappeared with milling. At 56 h, the high-energy exothermic reaction peak is gone and we have a small peak at 305 °C, and this is due to the development of β phase at 2θ = 44.1°.

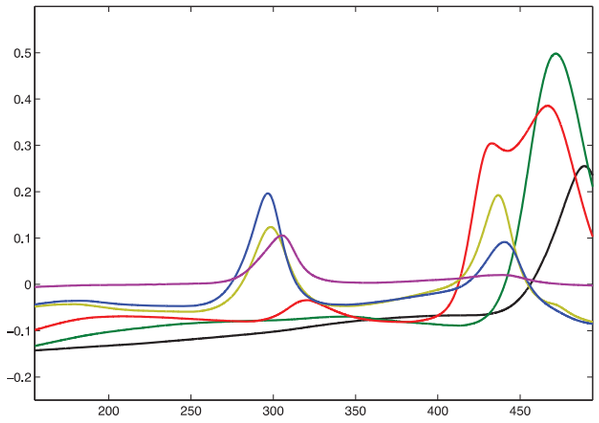

Figure 5. DSC plots for progression of milling times for Al-Fe-Cu alloy.

3.4 Spectroscopy

The milling process has a strong effect on the microstructure of the material which is strongly related to the optical property of the material can be seen here as in the Al-Cu-Fe system shown in Figure 6. There is an overall trend for the absorptivity of all the milled powders going from 2 hours of milling up to 36 hours of milling. Where the absorption starts with a very high value at 380 nm and then it decreases steadily until it reaches 480 nm at which it assumes a parabolic shape with an apex at 650 nm and plateaus from 850 nm to the rest of the spectrum. The absorption curves don't have a clear relation with the milling time, as it can be seen from the graphs, the absorption of the 4h and 6 h sample is lower than the 2 h sample. In contrast, the absorption of the 8h and 16 h samples are higher than the 4 h and 6 h milled sample. However, it is worth mentioning that the absorption of the 28 h, 32 h and 36 h is the highest among the others with very close values for the absorption. This behaviour of the absorption can be explained by considering the microstructural changes of the material with the milling time and the continuous appearance and disappearance of phases in the materials which can be observed by looking at the development of the XRD patterns. Figure 6 also shows the absorption graph of the TiO_2 compared to the milled sample of the Al-Cu-Fe system. Its clear that the absorption performance of the milled powders is better than the TiO_2 in the whole range of wavelength displayed in the graph (300 nm to 1000 nm). This indicated that the Al-Cu-Fe with the composition of 64 %wt Al, 25 %wt Cu and 11 %wt Fe has the potential of being used in solar applications.

Figure 7 compares the absorption of the 52 hours of milling and 20 hours of annealing at 200 ^{o}C with that of TiO_2 powder, and exhibits an increased of 94.9 % if the values are integrated over the 350-1000 nm range. As it was seen from the XRD patterns the 52-h sample has some quasicrystalline phases after the annealing of 20 hours. This increases support the fact that Al-Cu-Fe icosahedral quasicrystalline has the potential of being a great absorber of solar radiation.

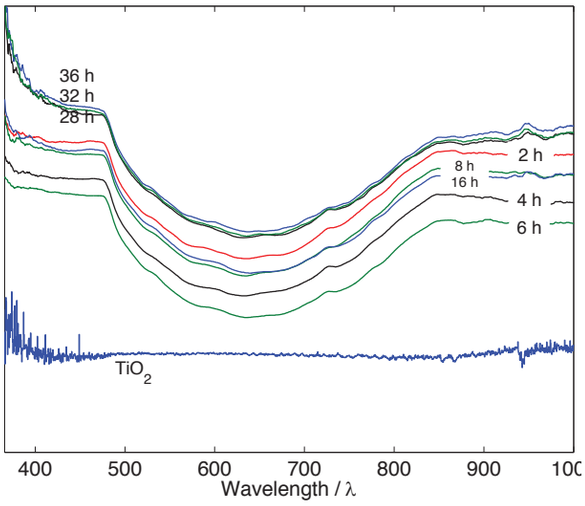

Figure 6. Absorptivity results at different milling times for Al-Cu-Fe system compared to TiO_2.

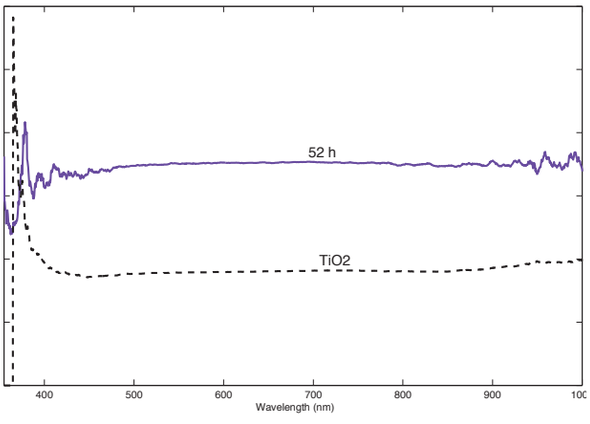

Figure 7. Absorptivity results of 52 hours of milling and 20 hours of annealing compared to TiO_2.

4. Conclusion

In this paper mechanical alloying (MA) was proposed as simple method of synthesis with significant technical advantages; economical, environmental friendly and uses minimum amount of energy comparing to other materials synthesizing methods. High-energy ball milling was utilized in this work to produce solar absorber material with a composition of $Al_{64}Cu_{25}Fe_{11}$ targeting a icosahedral quasicrystalline alloy. Thus, a detailed analysis is carried out in a small increments of time while milling and a sample is to be taken for SEM-EDS, XRD, thermal and optical analysis.

The system was produced by mechanically alloying 64 %wt of Al, 25 %wt of Cu and 11 %wt of Fe, for 56 hours of milling then annealed at temperature of 200 °C for 20 hours. SEM graphs showed the development of particles size with milling time, and the agglomeration of the powder. Where as the XRD graphs were utilized in identifying the new phases developed during the alloying process. It was seen that an iQC phase was produces after 52 h of milling and 20 hours of subsequent annealing. DSC analysis was used in correlation with the XRD graphs to prove the phases that were formed. It is clear that the absorption performance of Al-Cu-Fe is better than TiO_2 in the whole range of spectrum of the optical test graph (300 nm to 1000 nm).

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6. References

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