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(54) **METHOD FOR THE COMMENCEMENT DIAGNOSIS OF A HEAT STORAGE MATERIAL**

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(57) **ABSTRACT**

The invention relates to a method and an apparatus for detecting the point in time of commencement of crystallization of a heat storage material (**40**), in particular a latent heat storage material, which is supercooled by means of a Peltier element (**32**). The profile (**10**) of the current I of the Peltier element (**32**) is measured. The commencement of the crystallization process in the heat storage material (**40**) is deduced when a discontinuity (**20**, **22**) which follows a continuous decrease (**16**) in the current and after which the current (I) increases again (**18**) is detected in the current profile (**10**).

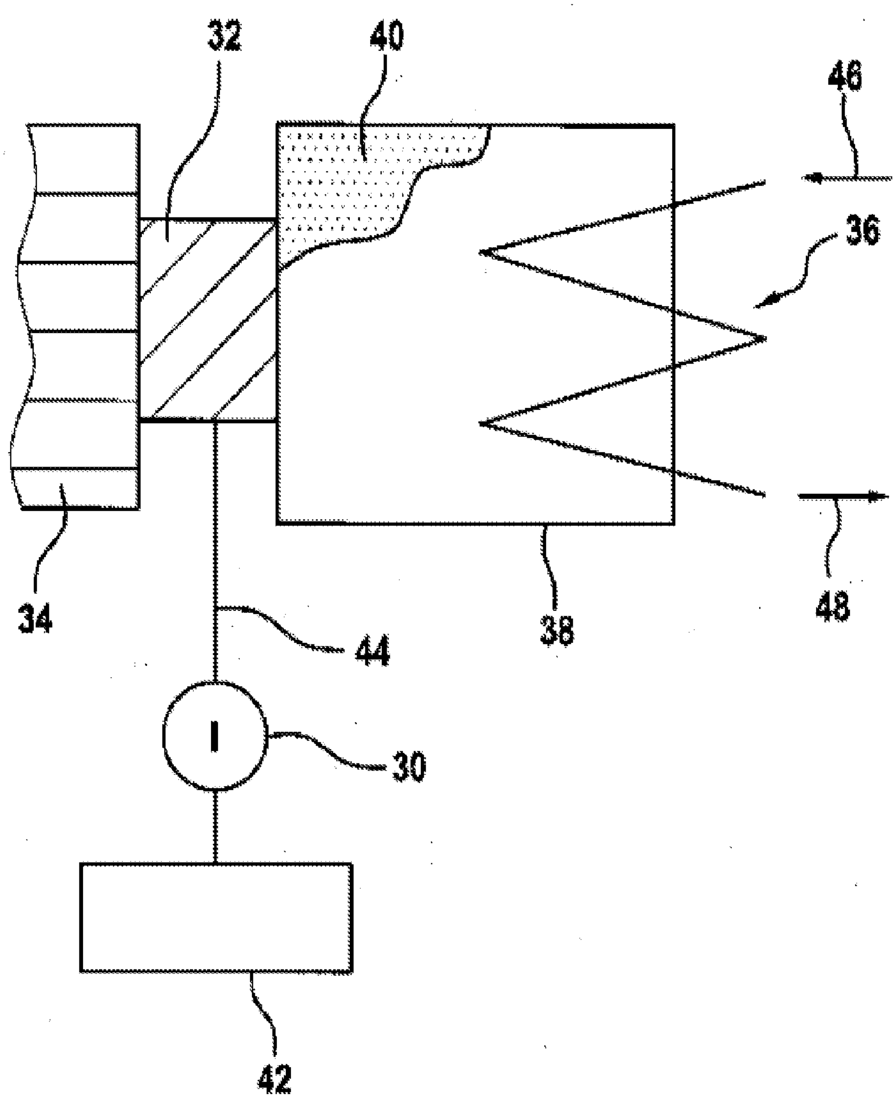


Fig. 1

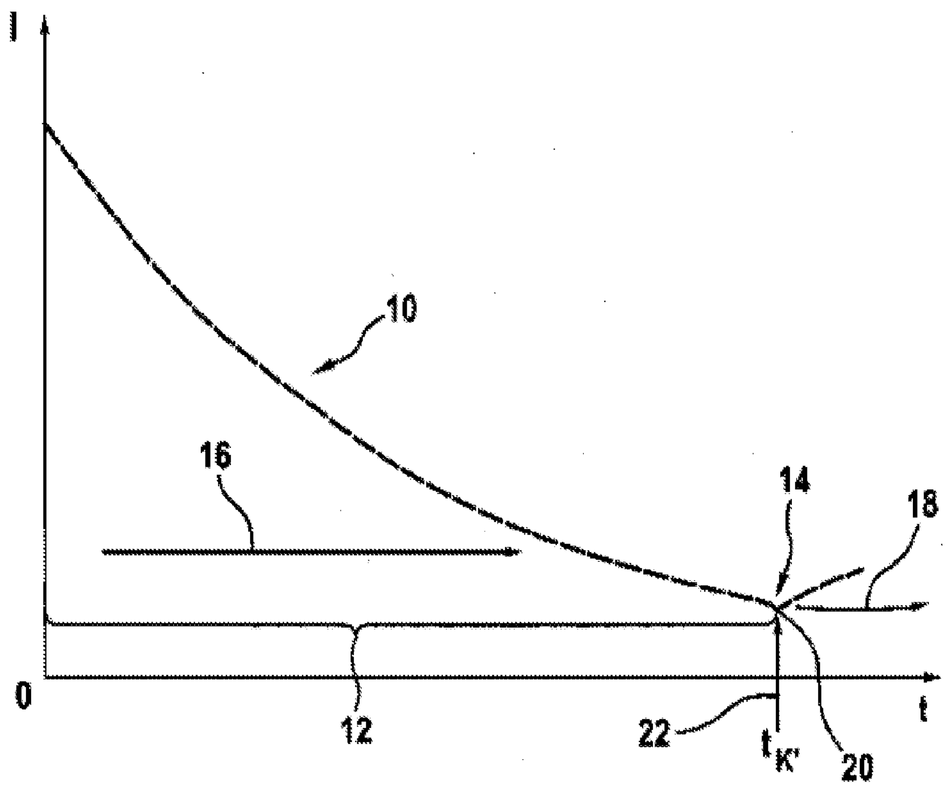
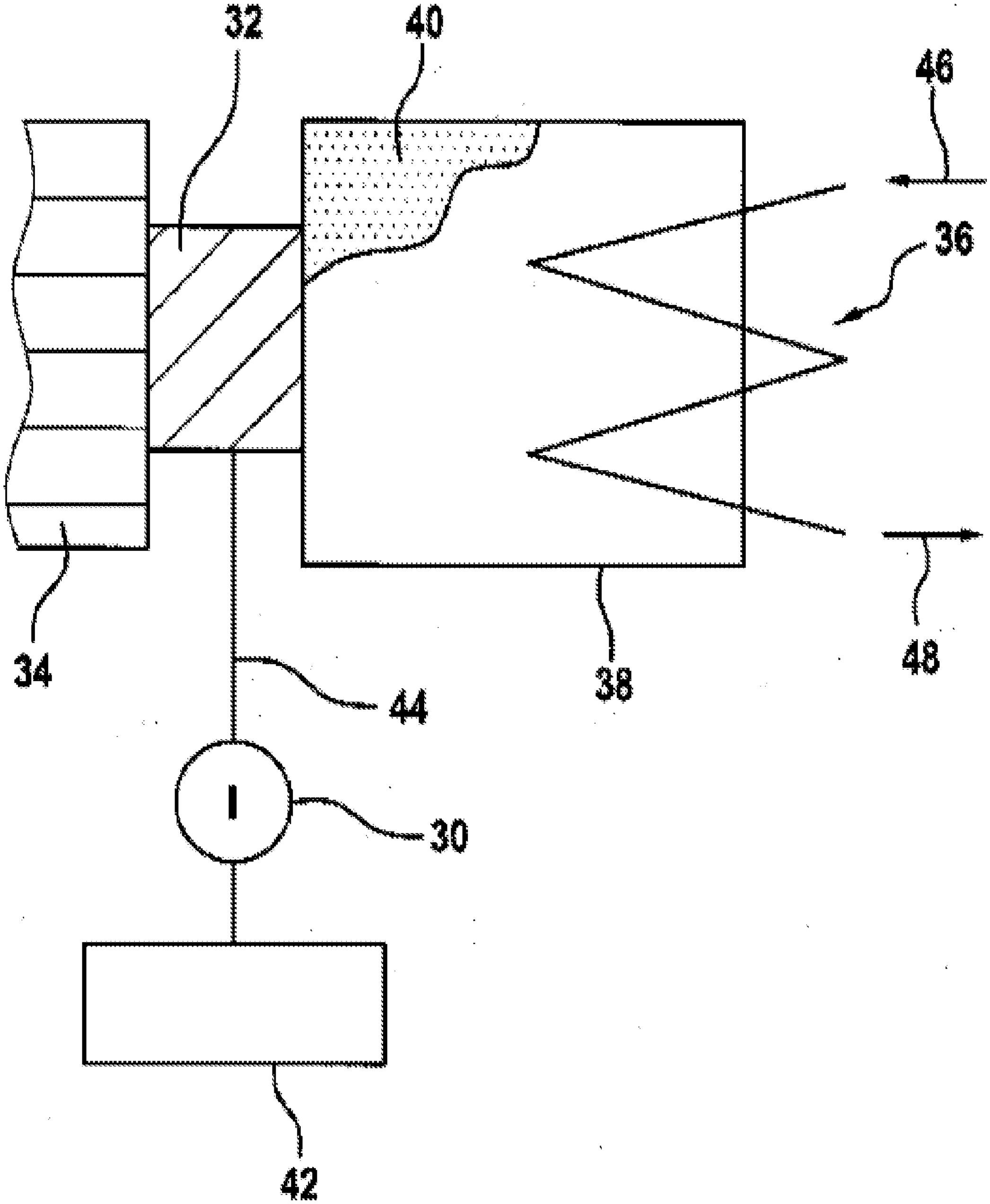


Fig. 2



# METHOD FOR THE COMMENCEMENT DIAGNOSIS OF A HEAT STORAGE MATERIAL

## BACKGROUND

[0001] There are various salt hydrates which can form super-cooled melts and are therefore suitable for low-loss heat storage. To start the release of heat from a heat storage material, a crystallization nucleus is necessary. The provision of the crystallization nucleus can be carried out in various ways. For example, the crystallization nucleus can be provided in the form of a cold finger, with this finger being continuously kept so cold in a region in the heat storage material so that the heat storage material never melts completely and a crystallization nucleus thus remains continually.

[0002] DE 103 03 498 A1 relates to an apparatus and a method for cooling the heat material of a latent heat store. The apparatus comprises a Peltier element which is controlled by a temperature sensor. When a first predetermined temperature is exceeded, the Peltier element cools the heat material in its environment. If a second predetermined temperature is exceeded, the further supply of heat is interrupted. Parts of the latent heat storage material are locally maintained at a lower temperature level.

[0003] Further methods for inducing a regenerable, supersaturated aqueous solution to crystallize by means of local supercooling or thermal separation are known. Here too, Peltier elements are used in order to generate local supercooling in the latent heat storage material.

[0004] At present, only methods which allow commencement of the crystallization process to be concluded directly from a temperature measurement are known. The use of a temperature sensor is indispensible for measuring the temperature.

## SUMMARY

[0005] It is an object of the present invention to be able to determine the commencement of crystallization and thus the commencement of the release of heat from a latent heat storage material without use of a temperature sensor.

[0006] It is proposed according to the invention that the power supply of a single-stage or multistage Peltier element used for cooling be provided with at least one current sensor and the profile of the current be measured, analyzed and evaluated. When Peltier elements made of, for example, bismuth telluride $Bi_2Te_3$ are supplied with a constant operating voltage, heat flow and current decrease with increasing temperature difference between the hot side and the cold side of the Peltier element.

[0007] At the commencement of crystallization of a latent heat storage material, which is generally a phase change material (PCM), by means of local supercooling from a thermal equilibrium state, a high heat flow and a high current initially flow because of the small temperature difference between the hot side and the cold side. Subsequently, the temperature difference between the hot side and the cold side of the Peltier element increases. The heat flow and the current decrease. At the commencement of crystallization and the commencement of the release of heat in the heat storage material, the temperature in the heat storage material increases very quickly. The temperature difference between the hot side and the cold side of the Peltier element consequently drops again and a discontinuity occurs in the power uptake of the Peltier element. The discontinuity marks, with negligible delay, the commencement of crystallization and can be utilized for diagnosis of a successful start of the crystallization process.

[0008] If other thermoelectrically active materials, for example BiSb, PbTE, SIGE, $CoSb_3$-based skutterudites and similar materials, are used for generating a temperature difference, the current can follow different profiles. In the extreme case, the current could initially increase and would drop again on commencement of the crystallization process.

[0009] A common feature when heat begins to be released by the heat storage material is the discontinuity in the current profile, which can be detected, taking into account a thermal delay, at the current sensor of the Peltier element.

[0010] The method proposed according to the invention or the Peltier element which has been modified according to the invention can be used as diagnosis unit for a latent heat store both in stationary operation, for example in the case of solar heat stores, and also in the mobile sector, for example in comfort heaters, stores for shortening the warming-up time in vehicles. Apart from the abovementioned salt hydrates as heat storage materials, it is in principle also possible to use all liquids which can be supercooled as heat storage materials, accordingly also high-purity water.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The invention is described in more detail below with the aid of the drawing. In the drawing:

[0012] FIG. **1** shows a profile of the current in a Peltier element at the commencement of the release of heat by a heat store by means of local supercooling, and

[0013] FIG. **2** schematically shows the components of an arrangement for measuring the profile of the current as per FIG. **1** in a Peltier element.

## DETAILED DESCRIPTION

[0014] FIG. **1** shows the profile of the current at the commencement of crystallization of a heat storage material, in particular a phase change material of a latent heat storage material, for example a salt hydrate.

[0015] The method proposed according to the invention is a commencement diagnosis for a phase change material (PCM) by evaluation of the current gradient.

[0016] It can be seen from the depiction in FIG. **1** that a high heat flow and a relatively high current flow at the commencement of crystallization of a heat storage material, in particular a phase change material (PCM), due to local supercooling by means of a Peltier element from a thermal equilibrium state because of the small temperature difference between hot side and cold side. The current profile **10** decreases continuously during a first period of time **12**. During this first period of time **12**, the temperature difference between the hot side and the cold side of the Peltier element employed for local supercooling increases. The heat flow established during the first period of time **12** and the current decrease continuously, cf. reference numeral **16**. It is a property of Peltier elements which are made, for example, of bismuth telluride $Bi_2Te_3$ and are operated at a constant operating voltage that heat flow and current I decrease with increasing temperature difference between hot side and cold side. This can clearly be seen in the current decrease **16** in the graph of FIG. **1**.

**[0017]** After the period of time **12** has elapsed, crystallization commences in the heat storage material, in particular the phase change material used therein, at a crystallization point in time $t_K$, cf. reference numeral **22** in FIG. **1**. With commencement of crystallization and thus the release of heat by the heat storage material, the temperature within the heat storage material, in particular the phase change material, increases rapidly. The temperature difference between the hot side and the cold side of the Peltier element therefore decreases again and the local minimum **20** shown in FIG. **1**, i.e. a discontinuity in the power uptake by the Peltier element, occurs. This discontinuity, which is encircled in FIG. **1**, represents a local minimum **20** which detects the commencement of crystallization in the heat storage material, i.e. in the phase change material of the latent heat storage material, and can be utilized for diagnosis of the successful commencement of crystallization. The use of a temperature sensor is therefore no longer necessary.

**[0018]** The commencement of crystallization **22** at the point in time $t_K$, and the associated commencement of release of heat by the heat storage material, in particular the phase change material, leads to a temperature increase **18** in the heat storage material which progresses rapidly and leads, cf. the graph in FIG. **1**, to the increase **18** in current which follows the achievement of the local minimum **20**, i.e. said discontinuity in the current curve **10**.

**[0019]** If other thermoelectrically active materials are used for generating a temperature difference, different profiles **10** of the current I can occur. In the extreme case, an increasing current would firstly be observed and this would decrease again on commencement of the crystallization process.

**[0020]** In the method proposed according to the invention, the characteristic of a heat storage material **40**, in particular a phase change material, that the commencement of the liberation of heat by this material is associated with a discontinuity in the current profile of a Peltier element **32** which locally supercools the heat storage material **40**, where this discontinuity can be detected, taking into account a thermal delay, at at least one current sensor **30** arranged in the power supply to the single-stage or multistage Peltier element **32**, is exploited.

**[0021]** As heat storage material **40** (phase change material), it is in principle possible to use paraffins, carbonates and also fluorides. The heat storage materials used all have to meet the requirement that they are a supercoolable heat storage material. The supercoolability of the heat storage material used is the key requirement for usability of the material.

**[0022]** FIG. **2** shows a schematic arrangement of a latent heat store **38** having a heat storage material **40**, in particular a phase change material (PCM), a Peltier element **32** which generates local supercooling and in whose power supply at least one current sensor is installed.

**[0023]** FIG. **2** schematically shows the components of an arrangement for detecting a discontinuity in the current profile of a Peltier element.

**[0024]** It can be seen from the greatly simplified depiction in FIG. **2** that a Peltier element **32** is arranged between the latent heat store **38** and a heat dissipation device **34**—here indicated roughly by finning. At least one current sensor **30** is located in a control line **44** which extends from a control device **42** to the single-stage or multistage Peltier element **32**. The current profile established in the Peltier element **32**, in particular the discontinuity depicted in FIG. **1**, cf. position **14** in FIG. **1**, can be measured by means of this at least one current sensor **30**. The heat storage material **40**, which is a supercoolable heat storage material, is present in the latent heat store **38**, where the salt hydrate can in principle be any supercoolable liquid, i.e. including high-purity water, paraffins, carbonates, fluorides and the like. As shown in FIG. **2**, it is possible for heat to be both introduced into and removed from the heat storage material **40**, which is a phase change material, present in the latent heat store **38** by means of a heat exchanger **36**. An entry side of the heat exchanger **36** indicated schematically in FIG. **2** is denoted by position **46**, and an exit of the heat exchanger **36** is indicated by position **48**.

**[0025]** A discontinuity **14** established in the current profile **10** as per FIG. **1** can be detected by means of the arrangement depicted in FIG. **2** since at least one current sensor **30** is arranged in the control line **44** which extends from the control device **42** to the single-stage or multistage Peltier element **32**. This current sensor makes it possible to detect the current profile **10** in the Peltier element **32**, so that a discontinuity in the profile of the current can be measured, analyzed and evaluated.

**[0026]** The Peltier element **32** is, for example, a Peltier element which is made of bismuth telluride $Bi_2Te_3$ and is operated at constant operating voltage.

What is claimed is:

**1**. A method of detecting a point in time of commencement of crystallization of a supercoolable heat storage material (**40**), which is supercooled by a Peltier element (**32**), characterized in that a profile (**10**) of a current (I) of the Peltier element (**32**) is measured and a commencement of the crystallization process in the heat storage material (**40**) is deduced when a discontinuity (**20**, **22**) in the profile (**10**) is detected.

**2**. The method according to claim **1**, characterized in that the heat storage material (**40**) is a latent heat storage material.

**3**. The method according to claim **1**, characterized in that the discontinuity in the profile (**10**) is an increase in the current I (**18**) following a continuous decrease (**16**) in the current I.

**4**. The method according to claim **1**, characterized in that the commencement of crystallization of the heat storage material (**40**) occurs as a result of local supercooling from a metastable state in a thermal equilibrium.

**5**. The method according to claim **4**, characterized in that the heat storage material (**40**) is a salt hydrate,

**6**. The method according to claim **1**, characterized in that a temperature difference between a hot side and a cold side of the Peltier element (**32**) increases and the current I decreases (**16**) during a period of time (**12**).

**7**. The method according to claim **1**, characterized in that a temperature increase in the heat storage material (**40**) occurs at the commencement of crystallization (**22**).

**8**. The method according to claim **1**, characterized in that the discontinuity (**20**) in the current profile (**10**) is detected, with a thermally produced delay, at a current sensor (**30**).

**9**. An apparatus for carrying out the method according to claim **1**, having a Peltier element (**32**) which locally supercools a heat storage material (**40**), of a latent heat store (**38**), characterized in that a power supply (**44**) to the Peltier element (**32**) has at least one current sensor (**30**).

**10**. The method according to claim **9**, characterized in that the heat storage material (**40**) is a phase change material.

**11**. The method according to claim **9**, characterized in that the Peltier element (**32**) is a single-stage element.

**12**. The method according to claim **9**, characterized in that the Peltier element (**32**) is a multistage element.

**13**. An apparatus according to claim **9**, characterized in that the at least one current sensor (**30**) is located in the power supply (**44**) to the Peltier element (**32**)

**14**. An apparatus according to claim **9**, characterized in that the at least one current sensor (**30**) is integrated into a control device (**42**).

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