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Cryogenic thermal storage system for discontinuous industrial vacuum processes

M. Bruzzi[a], A. Chesi, A. Baldi, F. Tarani, R. Mori, M. Scaringella and E. Carnevale

Dipartimento di Energetica, Università di Firenze, Via S. Marta 3, 50139 Firenze, Italy

Abstract. Phase Change Materials are proposed for refrigerating systems in discontinuous industrial vacuum processes where temperatures as low as -140 ÷ -100°C are necessary within time-frames representing 10÷20% of total operating time. An application is proposed for cooling systems used in a Physical Vapour Deposition (PVD) apparatus. A prototype has been manufactured which couples a cryopump with a reservoir filled with MethylCycloPentane (MCP-C_6H_{12}) and a distribution line where nitrogen in the gaseous state is flowing. Preliminary tests show that temperatures of about -120°C are actually achieved within time windows compatible with PVD applications.

1 Introduction

Thermal energy storage is recognized as one of the key technologies in the near future to ensure energy efficiency in thermal management [1]. Attractive approaches are based on phase change materials (PCMs): latent heat storage, being a nearly isothermal process with a high storage density, is in fact in general preferable to sensible heat storage. The use of a PCM enables the temporary storage of high or low temperature energy that will be stored in or released from the PCM during the phase transition process, allowing to both bridge time gaps in discontinuous energy requirements and reduce the required installed power through peak energy shaving. For this peculiarity, PCM storage is undoubtedly attractive for any relevant application where thermal systems are routinely used in discontinuous processes. A wide range of practical applications of PCM storages has been investigated in the recent past for solar energy applications, passive storage in buildings (air conditioning and domestic heating), ice-banks, thermal protection of electronic devices, as well as in medical and food agro-industrial fields. Typical melting temperatures in this studies range from 0°C to 900°C depending on the application considered [1-4]. With the exception of spaceflight equipments, where a few examples of refrigerating systems based on two-phase loops at cryogenic

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[a] e-mail : mara.bruzzi@unifi.it

temperatures have been taken into consideration [5], a significant lack of literature concerns applications to discontinuous processes involving refrigeration in the temperature range below 0°C.

In this work we investigate the use of a PCM reservoir in industrial discontinuous processes where temperatures as low as -140 ÷ -100°C are needed. As a practical application example, our study focuses on refrigerating systems for thin film vacuum coating manufactured through a Physical Vapour Deposition (PVD) process. Here a high level of vacuum must be achieved quickly and for short time intervals. Usually, the process of decreasing pressure to obtain the required vacuum is fastened by decreasing the temperature of a cold surface (cryopanel) inside the vacuum chamber in order to promote the condensation of the residual gases. A cryopump is generally used to capture water vapour (which typically comprises 65% to 95% of the gas load in high vacuum systems), which is able to significantly lowering water vapour partial pressure within a few minutes [6]. Typically, a surface temperature of -130 ºC is required in order to condense water vapour at a pressure of 10^{-8} mbar in the PVD process and this low temperature is required within time-windows representing 10÷20% of the total operating time. Presently, the most common layout in PVD industrial set-ups involves a separate cryopump for each vacuum chamber. Each chiller is thus used at full power during a small fraction of the production time (about 1:5). As a matter of fact, a significant increase of efficiency would be achieved if a single cryopump, coupled to a PCM reservoir, drove a set of PVD systems in parallel. Moreover, this setup would permit both to produce part of the needed cold during off-peak hours, in order to save on energy costs and to avoid the pull-down phase of the cryopump.

In order to investigate the main features of this novel refrigerating scheme, in this work we present an experimental feasibility study on a system where a PCM thermal energy storage reservoir, able to store energy at low temperature, is coupled with a cryopump and a gas circuit. A refrigerating cycle typical of a PVD system in operative conditions is taken into consideration.

The thermal storage system employs MethylCycloPentane (MCP- C_6H_{12}) as the solid-liquid phase change material. The cryopump is a Gifford Mac-Mahon apparatus, the melting latent-heat of the MCP is used to promote refrigeration of nitrogen flowing in the loop connecting the pipe coils placed into the vacuum chambers with the end-user.

2 Selection of phase-change material

The Montréal Protocol, signed some years ago, restricts the use of ozone-depleting substances, as e.g. chlorofluorocarbons (CFCs). Recently an extensive search has been undertaken for alternatives that would replace CFCs. Ozone depletion potential (ODP) is an index that indicates the ability of a gas to deplete the ozone layer: the refrigerant should obviously have a low or zero ODP. Among several groups of alternatives, hydrochlorofluorocarbons (HCFCs) were developed to serve as interim replacements for CFCs. They are used in existing equipment for the remainder of the equipment life and in new systems, until a permanent replacement becomes available. The HCFCs contain chlorine and therefore are still ozone-depleting substances. Aliphatic hydrocarbons could offer long-term alternatives to CFCs and HCFCs, as they have zero ODP, being also more environmental friendly than the greenhouse-gases HFC. To choose the right refrigerant material for the reservoir we looked, among them, for compounds with melting temperatures in the range of -140 ÷ -150°C. A selection of compounds with characteristics in the desired range are listed in Table 1.

Among them, best candidates are methylcyclopentane and isopentane. In making the right choice, boiling point is a key parameter, as it should preferably be well above ambient temperature in order to avoid vaporisation and overpressure, thus ensuring a safe industrial storage. In this respect methilcyclopentane (MCP), being characterised by a boiling point much higher than ambient temperature, represents the best choice in terms of industrial storage. Its chemico-physical properties are presented in Table 2.

Table 1. Properties of a set of aliphatic hydrocarbons selected as possible cryogenic reservoirs based on solid-liquid transition.

Compound	**Chemical Formula**	**Melting point [°C]**	**Boiling Point [°C]**
Propane	$CH_3CH_2CH_3$	-187.69	-42.07
Etane	CH_3CH_3	-183.27	-88.62
Isopentane (R601a)	$(CH_3)_2CHCH_2CH_3$	-159.9	27.85
Isobutane (R600a)	$(CH_3)_2CHCH_3$	-159.6	-11.73
Methylcyclopentane	$CH_3CH(CH_2)_4$	-142.4	71.8
Butane	$CH_3(CH_2)_2CH_3$	-138.35	-0.5
Pentane	$CH_3(CH_2)_3CH_3$	-129.72	36.07

Table 2. Chemico-physical properties of methylcyclopentane (MCP)

Boiling T[K]	345
Melting T [K]	130.7
Molecular Weigth [g/mol]	84.16
Melting H [kJ/ml]	6.93
Density (20°C, 1.1bar) [kg/m^3]	748.6
Density (frozen) [kg/m^3]	875.9
C_p liquid [J/mol/K]	158
Latent heat [kJ/kg]	172

3 Experimental Set-up

Plant layout investigated in this study is shown in figure 1. The refrigeration system used in this work is a 80 W two-stage Gifford-McMahon [7] produced by Galileo Vacuum Tec of Firenze (K1 model) [8]. Helium is used as the refrigerant which circulates in a closed cycle with the aid of the compressor, which is controlled by an on-off thermostat. Figure 2 (a) shows the schematic of the system equipped with the MCP steel reservoir, with an internal volume of 3.15 dm^3, directly mounted on the first and second stages of the cryogenerator and designed to maximise the thermal contact between the cold finger surface and the reservoir. The latter, in steel and manufactured taking into account of the criteria for hydrocarbons containment, is equipped with an internal coil pipe, 3 m long, 1 mm thick, 10 mm internal diameter, made with copper, which occupies approximately 10% of the internal volume of the reservoir. The vacuum chamber of the cryogenerator is connected with a rotative pump and typical working pressures within the chamber are 10^{-2} – 10^{-3} mbar. A photograph of the system during assembling is shown in figure 2 (b).

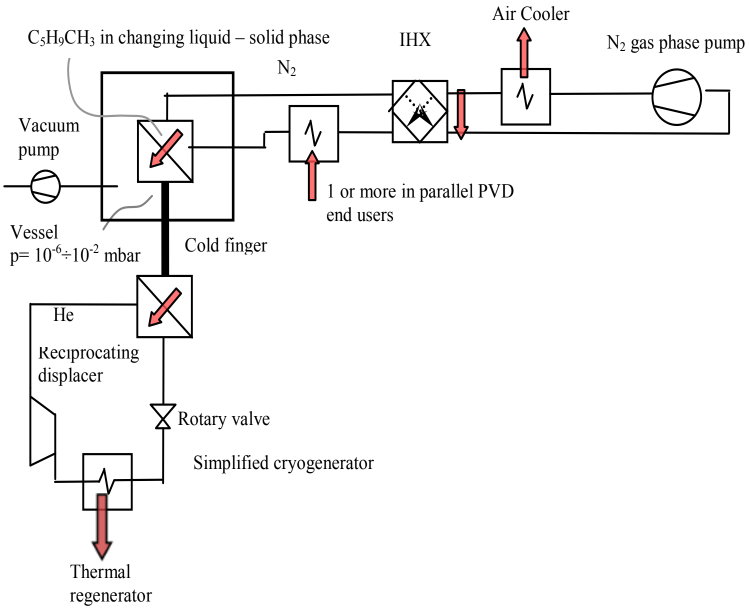

Fig. 1. Plant Schematic

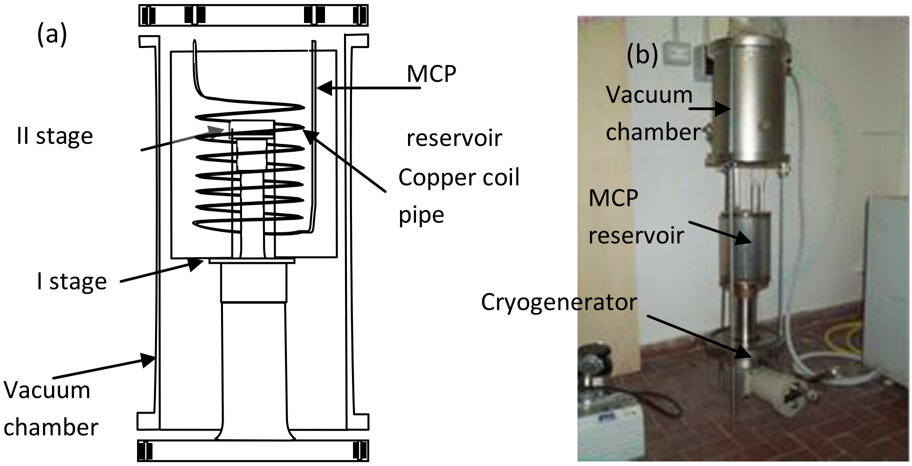

Fig. 2. Schematics of the cryogenerator Galileo model K1 used in this study equipped with the MCP reservoir and internal coil pipe for gas flow. (b) Photograph of the system during assembling.

After assembling, the vacuum vessel is covered with a mylar sheet in order to reduce the entering heat flow from the environment. Another compressor (KNF N 0150.1.2 ANE) is used to make N_2 flow in the circuit. A set of temperature sensors (Pt thermoresistances, thermocouples and silicon diodes) has been placed to monitor the temperature in various points of the system: on the external walls of reservoir; within the coil (when in the coil pipe no gas is flowing); outside the reservoir on the external walls of the pipe coil when gas is flowing. System is controlled by a PC, driving software is in Labview 8.0 (National Instruments).

Nitrogen gauge pressure when the system is off is 0.5 bar. An internal heat exchanger (IHX) is also present, in a tube-in-tube counter-flow configuration and insulated from the environment with a 10 cm thick layer of expanded polystyrene. The use of the internal heat exchanger allows one to save power, reducing the heat discharged to the cryogenic storage while only slightly increasing compression work. A 10 m-long custom-made counterflow IHX was manufactured as a best compromise for the built prototype. As for what concerns the end-user, it was simulated by exposing a part of the external circuit, made of copper tubes (8 mm and 10 mm internal and external diameter respectively), approximately 20 cm long, to atmospheric air.

4 Experimental Results

First experimental measurements have been carried out without N_2 flowing. The prototype has been operated during several hours in order to investigate the repeatability of the refrigerating cycles during a routinely use. Measurements reported in figure 3 are related to five consecutive cycles: data show that at each cycle temperature profiles flatten around the MCP melting point T_f, as the MCP undergoes the liquid-solid transition phase. In this test, thermostat was set to keep temperature in the coil within 5K from T_f; the corresponding O/I ratio of the cryopump is about 4.

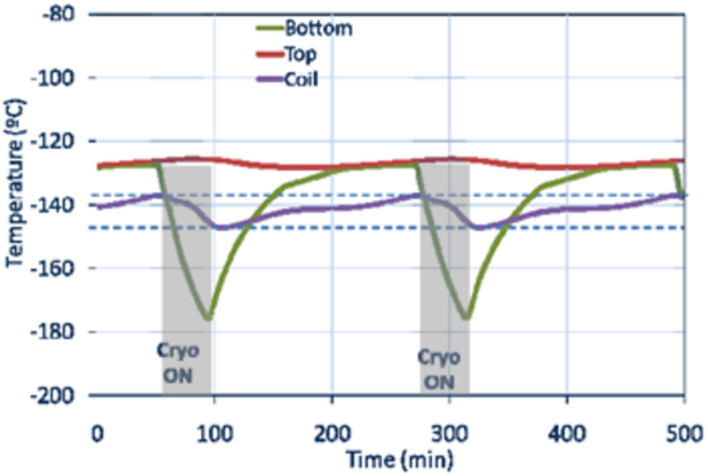

Fig. 3. Temperatures measured at the bottom and top f the MCP reservoir and into the coil within the MCP reservoir during five cycles of operation, without gas flowing in the circulating circuit.

A set of measurements has been then performed by making the N_2 gas flowing within the pipe coil. Figures 4 and 5 show two cycles performed with different modalities. In the first cycle (figure 4) gas starts flowing at t = 0 and stops after 18min. The cryopump is started immediately after the end-user has reached a minimum temperature (approximately at -129°C), it is then stopped when the temperature of the MCP has reached again its value at t = 0 (T_{MCP} = -175°C). We observe that, after switching off the circulator, the cryopump is able to bring the MCP back to its initial temperature conditions in about 57min, a time definitely shorter than the entire cycle period (~100min). In this example the O/I of the end-user is about 5.5.

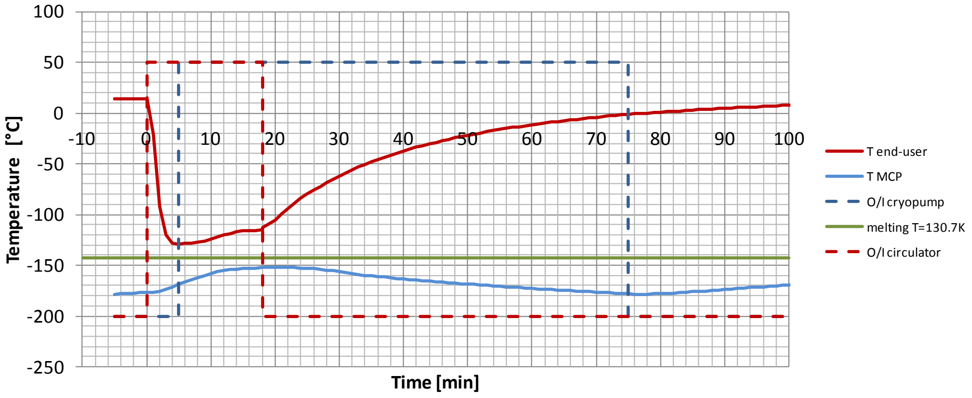

Fig. 4. Temperatures at reservoir and end-user as measured during a cycle when gas is flowing in the circuit in the time window [0,18min], short enough to leave the MCP frozen.

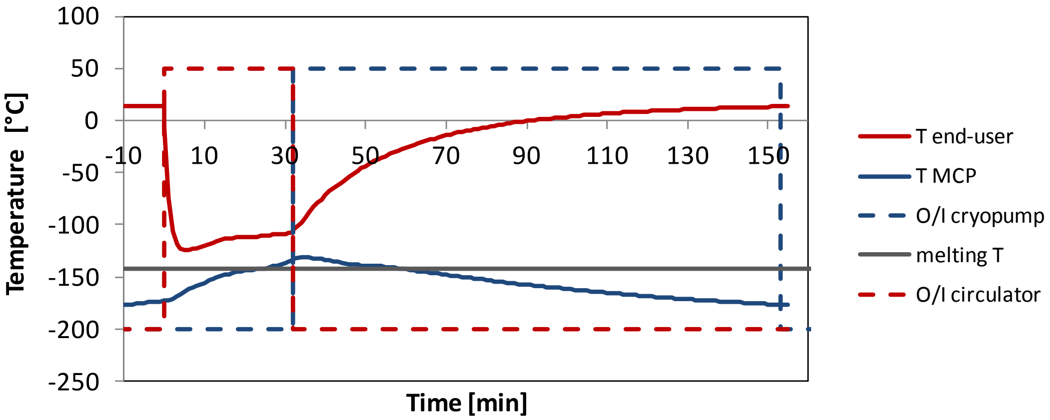

Fig. 5. Temperatures at reservoir and end-user as measured during a cycle when gas is flowing in the circuit in the time window [0,30min], long enough to bring the MCP through phase transition.

During cycle of figure 4 the MCP has been always kept under its melting temperature: measurements shown in figure 5 depict a different situation. Here gas starts flowing at t = 0, when MCP is at -175°C and stops after 30min; the cryopump is off for the entire circulating time, so MCP heats up enough to undergo the phase-transition. The cryopump is then started when the flow stops, and the time required by the cryopump to bring the MCP back to its initial value is obviously longer than before: approximately 80 min within a cycle period of approximately 150min. In this example the O/I of the end-user is about 4.8.

Both plots of figures 4 and 5 evidence that a temperature of about -120 ºC is achieved at the end-user with O/I of about 5: both parameters are quite compatible with PVD applications. A preliminary evaluation of the energies transferred has been carried out in particular for the second case, directly involving the MCP phase-transition. First results are given in figures 6 (a,b), respectively showing the power transferred to the user and that coming from the MCP storage.

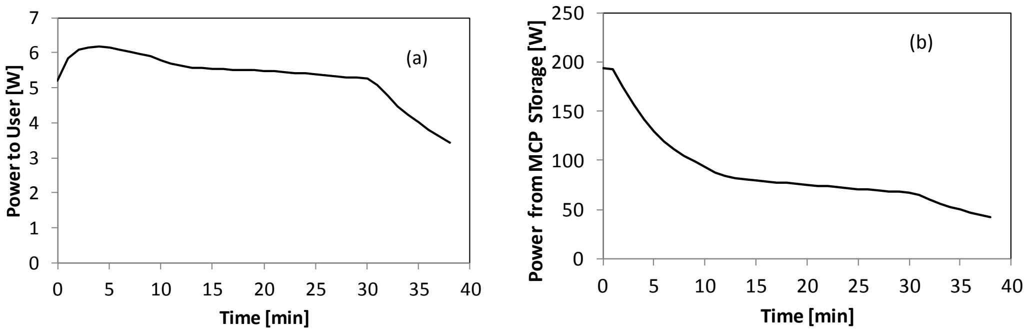

Fig. 6. (a) power transferred to the user and (b) power from MCP storage, both evaluated in the case that N_2 starts circulating at t = 0 and the N_2 gas pump is switched off after 30 min operation.

We observe in figure 6 (a) a first peak in power due to a cooler fluid and T_{inlet} at the reservoir close to ambient temperature. Then, when phase-transition is occurring, power stabilizes to a value of about 5.5W for approximately 15min: after that, the circulating pump is switched off. Correspondingly, in figure 5 (b) power from MCP storage has an initial peak due to inlet T close to ambient temperature (max ΔT), then it decreases and stabilizes (until the circulating pump is switched off). Finally, the ratio of cooling energy from storage transferred to user is shown in figure 7. At first, for a transient time of about 10min, a linear increase in the transferred-energy ratio is observed, due to the pulldown effect. Then, in the range where the MCP phase transition is occurring, the energy transferred ratio stabilizes to a value of about 7-8%.

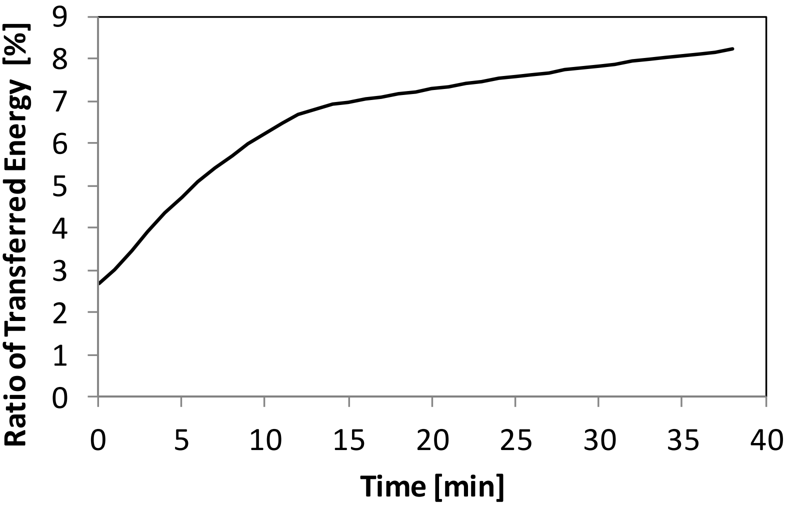

Fig. 7. Ratio of cooling energy from storage transferred to user.

5 Conclusions

The present work investigated the use of a cryogenic thermal storage in discontinuous industrial processes such as Physical Vapour Deposition (PVD). Refrigerant material chosen for the reservoir is methylcyclopentane (MCP), characterised by a melting T = 130.7K close to the typical working temperatures of cryopanels used in PVD systems. The boiling point of MCP, T_b=345K, well above ambient temperature, should avoid vaporisation and overpressure, thus ensuring a safe industrial storage.

A first prototype, composed by a reservoir with MCP coupled with a two-stage Gifford-McMahon refrigerating cryopump and connected to a distribution line where nitrogen gas was flowing, has been manufactured and an experimental investigation has been carried out.

First experimental results show that the circulating system is working properly, achieving temperatures around -120°C in time-windows compatible with PVD applications.

A preliminary evaluation of the energies transferred from the MCP storage to the end-user showed that , at regime, our system is characterized by an energy transferred ratio of about 7-8%. This first promising result can be improved by further engineering our system. In near future we plan to work in particular on the optimization of thermal insulation, N_2 pressurization and IHX geometry design: results will be reported in forthcoming works.

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