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Electrical resistivity and Seebeck coefficient of $Pd_{81}Ge_{19}$

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We report on the simultaneous measurement of resistivity and Seebeck coefficients in samples of $Pd_{81}Ge_{19}$ ribbons prepared by the melt spinning technique method and having a typical dimension of 40.0 mm × 1.75 mm × 0.028 mm. The investigation was performed using a new completely automated device in a large temperature range (from room to 700°C). Structural changes, crystallization times and heat treatments on several samples of the same composition were followed as a function of temperature. Seebeck coefficients, reported for the first time in these samples, varied roughly between -2 and -21 µV/K in the temperature range of 25 to 700°C, while the electrical resistivity varied roughly between 35 and 120 µΩ.cm in agreement with the literature. Complementary differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) experiments were also carried out and confirm the phase transitions observed by the above mentioned techniques.

Key words: Seebeck coefficient, melt spinning technique, crystallization temperature, electrical resistivity, phase transitions.

INTRODUCTION

Crystallization kinetics of metallic glasses have been studied for many years (Calvo-Dahlborg et al., 1997) and they continue to be an attractive field because of their interesting properties for industrial applications. The physical properties depend on their chemical composition and production process (Calvo-Dahlborg et al., 2011). Among their cited properties are electrical resistivity and Seebeck coefficient, which are directly related to the atomic structure and the coupling between them can often be used to characterize the electrical conduction mechanisms in solids (Dordor et al., 1980; Mott and Davis, 1971). They are sensitive to structural, magnetic and alloying phase transformations. Measurements of the electrical resistivity and Seebeck coefficient allow a better

understanding of electrical properties of amorphous alloys. It is well-known that they can be used to study the kinetics of crystallization during thermal processes or other structural changes such as particle growth. The Pd-Ge amorphous alloy is among the most studied systems. It can be amorphous for a large Germanium content. Few studies concerning crystallization of $Pd_{81}Ge_{19}$ amorphous alloys were performed by other techniques. Budhani et al. (1983) studied the variation of the resistivity as a function of temperature for $Pd_{80}Ge_{20}$ and $Pd_{77.5}Ge_{22.5}$ continuously heated at 10°C/min through the temperature range 300 to 710 K. They observed that the crystallization process starts around 600 and 550 K respectively in a direct transformation. They also found that the electrical

resistivity for the $Pd_{80}Ge_{20}$ alloy is greater than 100 µΩcm. The diffraction pattern of the $Pd_{80}Ge_{20}$ ribbon at room temperature is characterized by two broad intensity peaks at $2\theta = 40°$ and $72°$ (Budhani et al., 1983).

The aim of this paper is to present thermoelectric properties for an amorphous palladium-based alloy ribbon, $Pd_{81}Ge_{19}$, using a new completely automated device which measures simultaneously the resistivity and the Seebeck coefficient for liquid and amorphous conductors. Structural changes were followed as a function of temperature (from room temperature to 700°C), crystallization time and heat treatments on several samples of the same composition $Pd_{81}Ge_{19}$.

EXPERIMENTAL METHODS

Electrical resistivities and Seebeck coefficients are very sensitive to any structural change, and amorphous samples are a good example to assess the capability of our apparatus to determine crystallization temperatures and identify structural changes. If the change is not especially manifest in one property, it is hoped that it will be in the second one. It is therefore important to measure simultaneously these two properties. Measurements were obtained using an automated device developed and continuously improved for several years in the LCP-A2MC laboratory (Metz, France), which measures jointly (that is, simultaneously) or separately the electrical resistivity and the Seebeck coefficient. The electrical resistivity is measured using a four probes DC standard technique and the Seebeck coefficient using a small variation of temperature (around the measurement temperature) as described by Abadlia et al (2014). We measure the voltage between the same wire (V_{13} and V_{24}) when the temperature of one of the junctions varies from T-ΔT to T+ΔT (ΔT can vary from 1 to 6°C). The Seebeck coefficient (Absolute Thermoelectric Power) is given by the formula (Gasser, 2000):

$$S = \frac{S_{AB}}{p-1} + S_A \tag{1}$$

Where S_{AB} and S_A are respectively the Seebeck coefficient of a thermocouple AB and the Seebeck coefficient of an element A and p is the slope of thermoelectric power as a function V_{24}/V_{13} which does not depend on spurious voltages or drift.

The experimental device and a LabVIEW software allow measurements in the temperature range -200 to 1330°C using any type of standard thermocouple. The sample is placed into a quartz tube connected to a vacuum pump and argon gas to avoid oxidation at high temperature. Two K-type thermocouples are used (whose calibration polynomials exist in the NIST tables) (Standard, 1995) to measure temperature (within 1% error) and different voltages for resistivity and Seebeck coefficient. Connections between sample and thermocouples are realised using stainless connectors. A temperature difference between the junctions is created using a heater controlled by the software. Two other K-type thermocouples are used to control temperature inside the furnace and give the operator an idea about how to position the furnace to insure temperature homogeneity. The general description of the experimental setup is described in the work of Abadlia et al (2014). For this work, the resistivity and the Seebeck coefficient have been measured between room temperature and 700°C (at this latter temperature, close to the fusion temperature, we might assert that crystallisation is complete and we do not need to heat the sample

any more), both by increasing then by decreasing temperature. The heating and cooling rate is 0.3°C per minute in order ascertain permanent thermal equilibrium between the system and the furnace (quasi-static regime).

Resistivity measurements are relatively simple even though our experimental setup requires the precise knowledge of sample geometry. For amorphous ribbons, the length and the width are easy to determine but thickness is too small to be determined with reasonable precision (20 µm) in addition to being not constant along the sample. For these reasons, we prefer to present measurements relative to the room temperature resistivity value. Measurements of Seebeck coefficients are more complicated than those of resistivity but one does not need the knowledge of geometry and the result is in absolute value.

Our samples are $Pd_{81}Ge_{19}$ ribbons which were prepared by the melt spinning technique method (Liebermann and Graham, 1976) with a typical dimension of 40.0 mm × 1.75 mm × 0.028 mm.

RESULTS AND DISCUSSION

In this work, we have measured the resistivity and the Seebeck coefficient for $Pd_{81}Ge_{19}$, as a function of temperature. Resistivity and Seebeck coefficient are measured simultaneously at exactly the same time, in the same sample under the same conditions. One of the measured quantities might change while the other remains constant. Therefore, it is important to measure the two properties for the same sample and the same time.
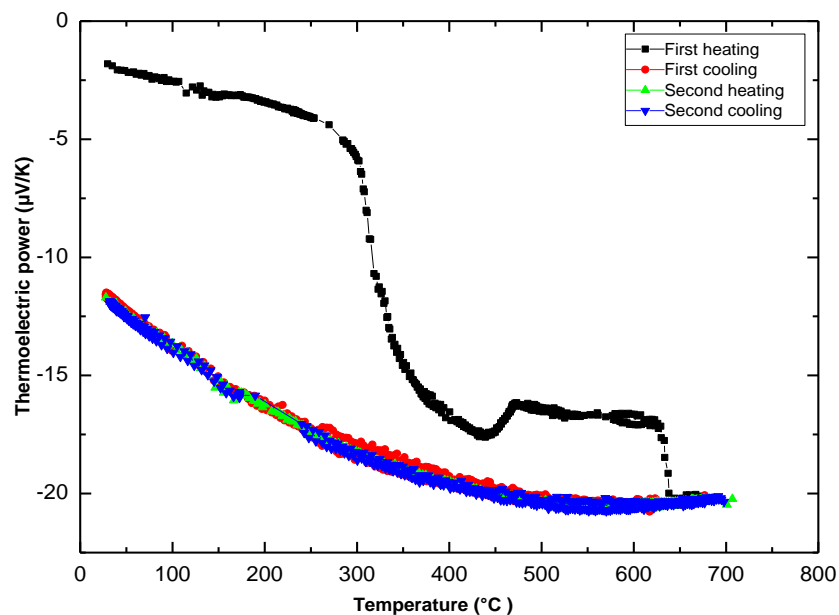
Resistivity and the Seebeck coefficient as a function of temperature

Continuous resistivity and Seebeck coefficient measurement curves show a drastic and important change before the melting temperature is reached characteristic of a behaviour which occurs in amorphous phases. When heated, the amorphous material crystallizes and a marked change is observed in resistivity and Seebeck coefficient curves corresponding to crystallization temperatures.

We report in Figures 1 and 2 relative resistivity and Seebeck coefficient measurements for amorphous and crystallised $Pd_{81}Ge_{19}$ with respect to temperature. The resistivity increases slightly from 117 µΩ.cm at room temperature up to 120 µΩ.cm at 270°C where we see clearly a sharp bend between 270 and 300°C. Then, we notice a first phenomenon consisting of a rapid decrease from the value 117 µΩ.cm down to 68 µΩ.cm between 300 and 360°C before stabilizing then increasing slightly between 370 and 440°C. Next, the resistivity continues its slight increase up to 74.5 µΩ.cm at 470°C, where it is found that the second phenomenon is completed. The augmentation of resistivity is enhanced between 470 and 625°C (from 74.5 to 87.5 µΩ.cm). A third downward transition begins at 625°C and persists up to 640°C (from 87.5 to 81 µΩ.cm). Once heated at 685°C, the curves of second heating and second cooling of the sample
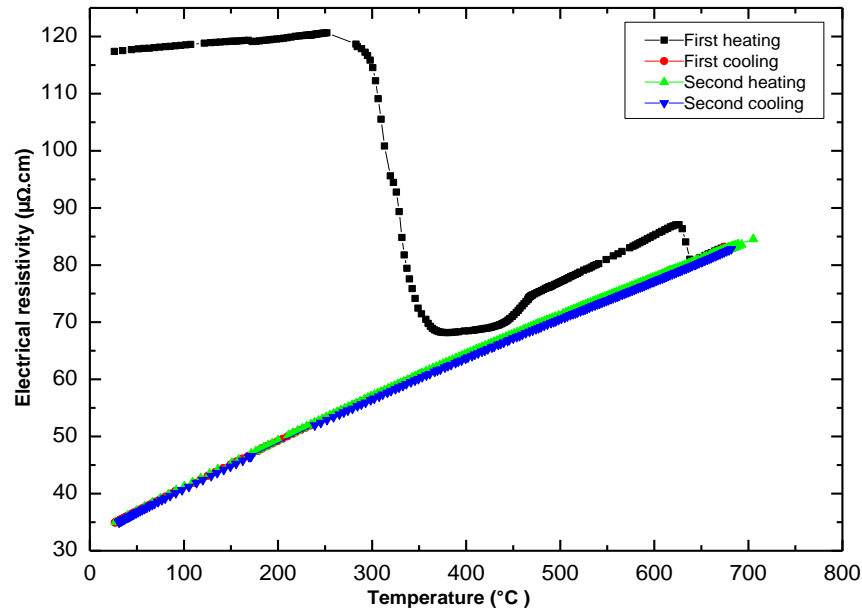
**Figure 1.** Electrical resistivity of $Pd_{81}Ge_{19}$ as a function of temperature.

Figure 2. Seebeck coefficient of $Pd_{81}Ge_{19}$ as a function of temperature.

become superposed with the first cooling one and there is no more change in the resistivity curve. The linear increase of resistivity with temperature (from ambient to 700°C) is indicative of a metallic nature for $Pd_{81}Ge_{19}$.

For the Seebeck coefficient, we can observe that the starting value -2 µV/K is negative when $Pd_{81}Ge_{19}$ is amorphous, where it decrease slightly with increasing temperature, then starts bending like the resistivity between 260 and 300°C, before decreasing abruptly from

-7 µV/K at about 300°C to -15 µV/K at about 360°C. It continues to decrease but less steeply beginning at 360°C, passes through a minimum at -17.5 µV/K at 440°C and then increases slightly to -16.25 µV/K at 470°C. It stabilizes to approximately -16.5 µV/K in the interval 470 to 625°C. We can observe a third transition beginning from -17 µV/K at 625°C to -20 µV/K at 640°C and above. The first cooling and the second heating/ cooling of temperature give superimposed curves in the
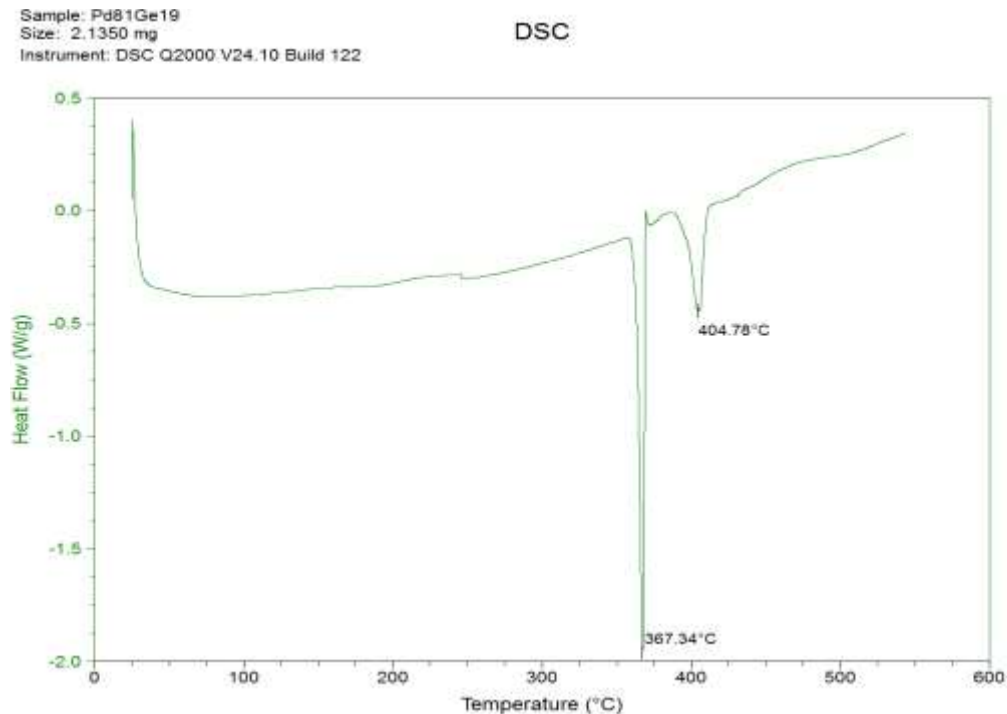
Figure 3. DSC trace of $Pd_{81}Ge_{19}$.

whole temperature range and no more changes are observed. It is interesting to remember that the two properties are measured simultaneously on the same sample. Between 300 and 450°C, resistivity and Seebeck coefficient changes are very important (The first from 120 to 70 $\mu\Omega.cm$ and the second from -6 to -17.5 $\mu V/K$). This shows that these two properties are complementary and resistivity measurements alone cannot give all information about crystallization kinetics.

Characterization techniques: DSC and SEM

DSC analysis

Phase transformations (or transitions) in matter can be followed by measuring some physical properties as a function of a given thermodynamic property such as temperature, pressure, etc. In this way, a simple technique called Differential Scanning Calorimetry (DSC) can be used to realise such kind of measurements. In general, it has the advantage of both simplicity and low cost but our apparatus had also the limitation of a minimal rate of 5°C/mn which is too high compared to the 0.3°C/mn rate used in the resistivity and ATP measurements. A lower rate would ordinarily produce larger measurement peaks. In addition, DSC cannot follow transformations as a function of time at constant temperature. The DSC experiment was performed on our $Pd_{81}Ge_{19}$ sample revealing a large transition at 367.34°C,

and a second at 404.78°C. A representative DSC curve of the $Pd_{81}Ge_{19}$ ribbon is shown in Figure 3. Comparing the DSC results to the electrical resistivity and thermoelectric power ones, the same phase transitions can be seen at about the same temperatures.

SEM observations

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) can also give topology of the surface and determine its structure. But these techniques have some inconveniences: (i) Their cost is very high (expensive); (ii) They must be supervised by a dedicated operator; (iii) they cannot follow the continuous evolution of the material as a function of temperature and the measurement must be done at a constant one.

The surface morphology of our sample $Pd_{81}Ge_{19}$ was determined by SEM (Li et al., 1998; Maeda and Mater, 1994). According to the SEM picture in Figure 6, the $Pd_{81}Ge_{19}$ amorphous alloy is comprised of thousands of small particles distributed homogeneously on the surface. According to Figures 4 and 5, we cannot observe any anomalous features on the two types of ribbon surfaces which leads us to believe that our sample is in an amorphous phase at room temperature. From 400°C, just after the first phase transition, the crystal grains were observed on the thermal treatment generated matt and shiny sides of $Pd_{81}Ge_{19}$, indicating the onset of crystallization at this temperature (Figures 6 and 7). At
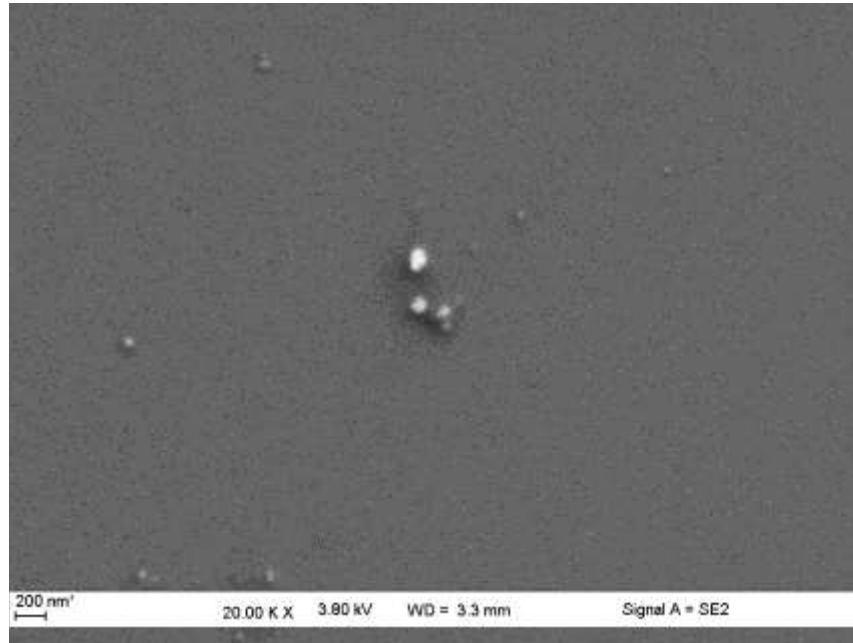
Figure 4. Scanning electron micrograph of $Pd_{81}Ge_{19}$, shiny side at room temperature.
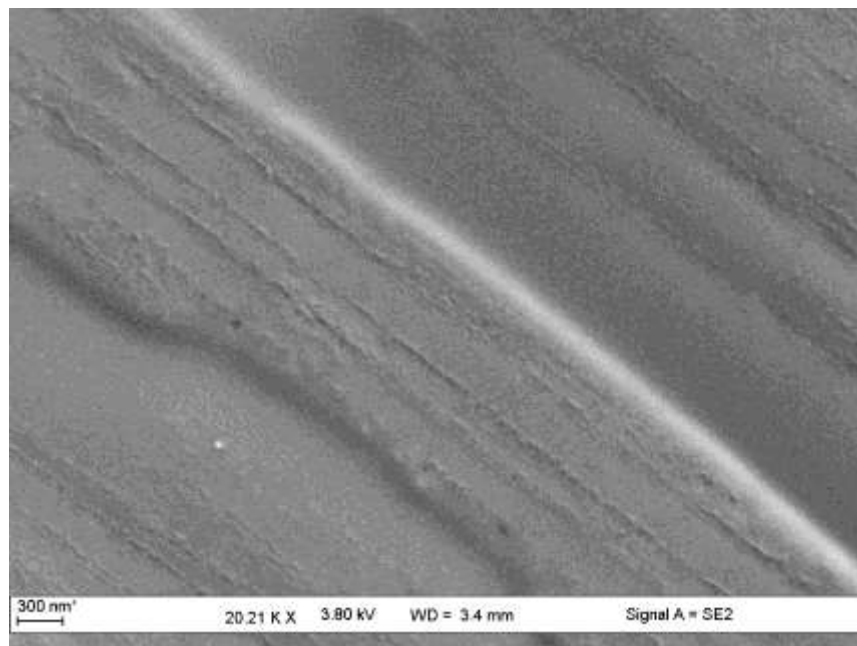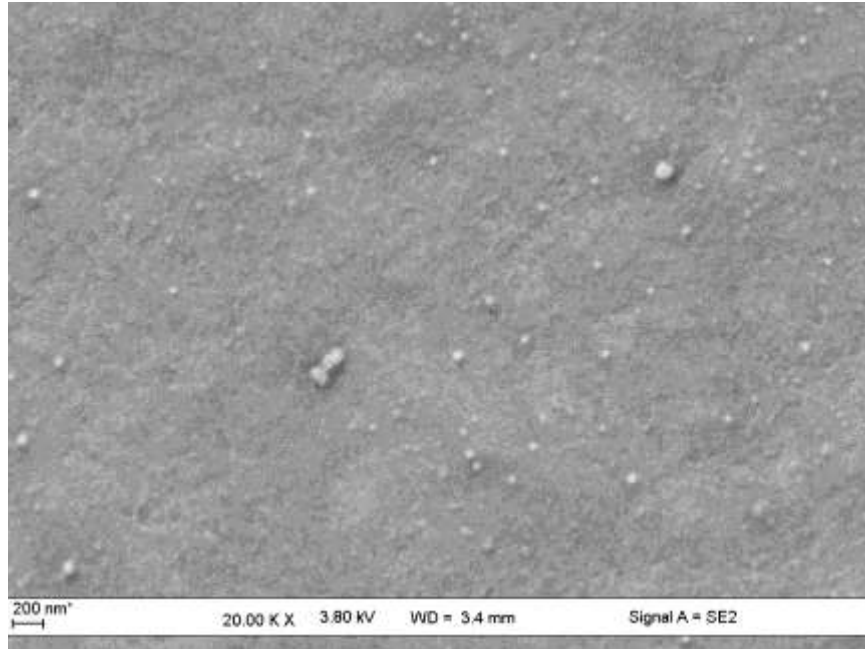

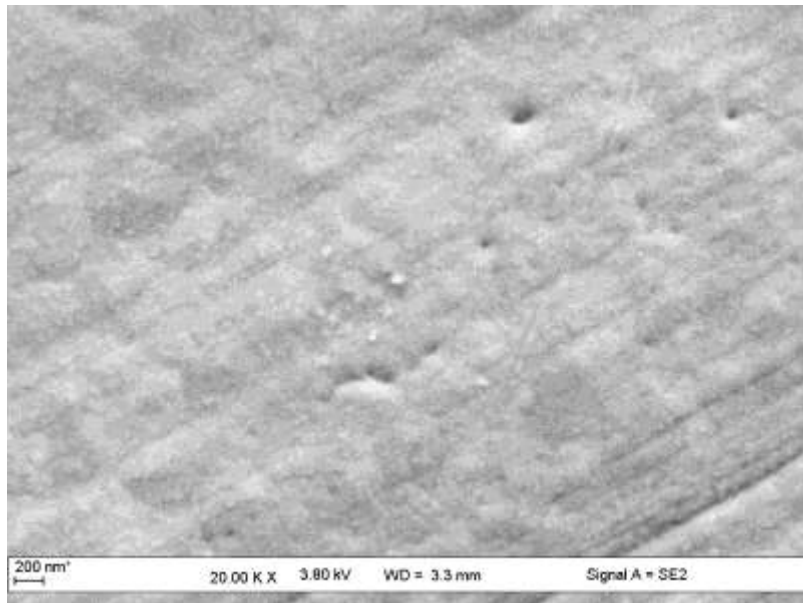**Figure 5.** Scanning electron micrograph of $Pd_{81}Ge_{19}$, Matt face at room temperature.

500°C, we observe clearly the formation of crystal grains on both bright and matt sides of our ribbon (Figures 8 and 9).

Finally, the crystal grains enlarge gradually up to 600°C, indicating that crystallization was essentially complete at 600°C (Figures 10 and 11). Preliminary X-ray diffraction results , not shown here, indicate the presence of a two-phase mixture of $Pd_{25}Ge_9$ and Pd_5Ge in these samples in partial agreement with published results by Nava et al. (1981) who observed only $Pd_{25}Ge_9$ (as well as

Figure 6. Scanning electron micrograph of $Pd_{81}Ge_{19}$, Shiny side at 400°C.
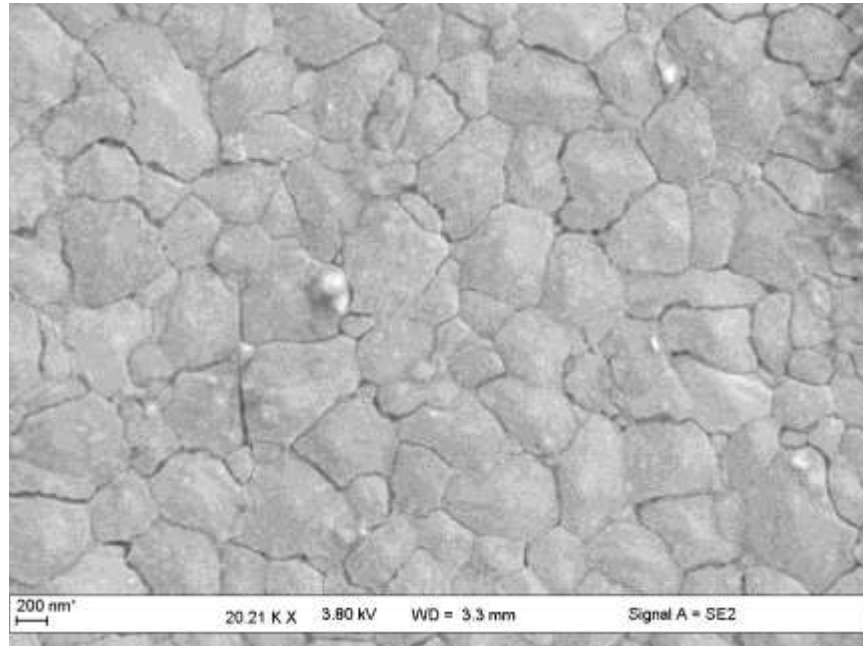

Figure 7. Scanning electron micrograph of $Pd_{81}Ge_{19}$, Matt face at 400°C.

α-Pd) and with Khalaff and Schubert (1974) who detected only the Pd_5Ge (as well as Pd_3Ge) phases.

Conclusion

We have performed precise and reproducible simultaneous measurements of electrical resistivity and Seebeck coefficient in a large temperature range by means of an automated device. Measurements were made as a function of temperature and time. Resistivity and Seebeck coefficient are very sensitive to structural changes and amorphous samples are illustrative of these amorphous-crystalline transformations and their
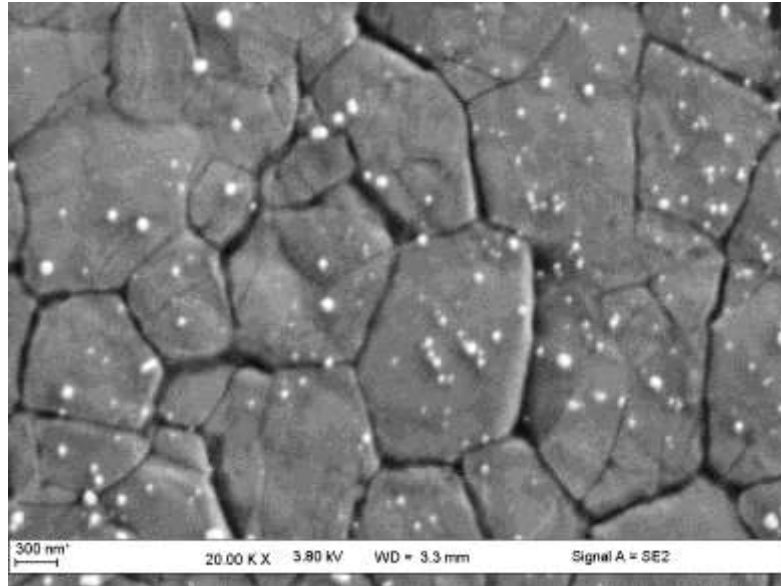
Figure 8. Scanning electron micrograph of Pd81Ge19, Shiny side at 500°C
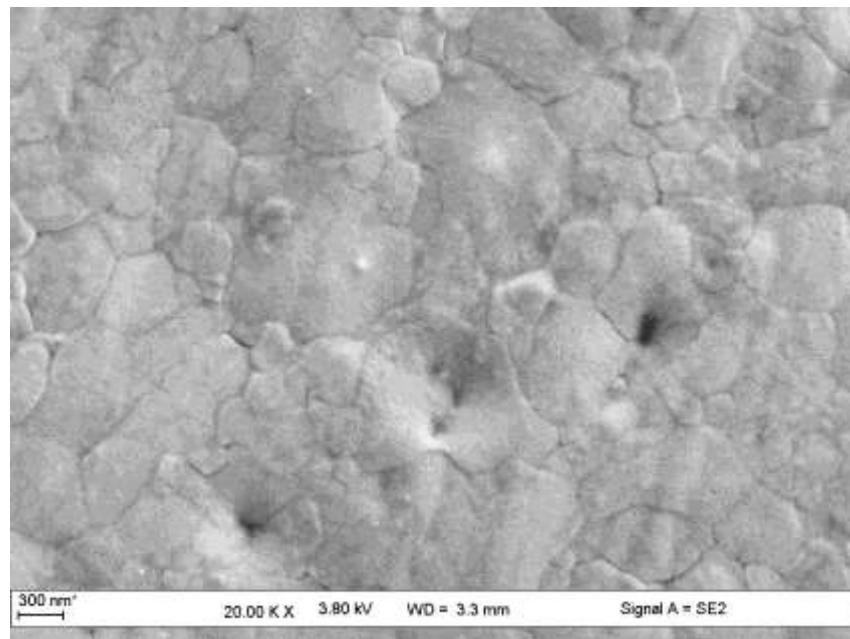
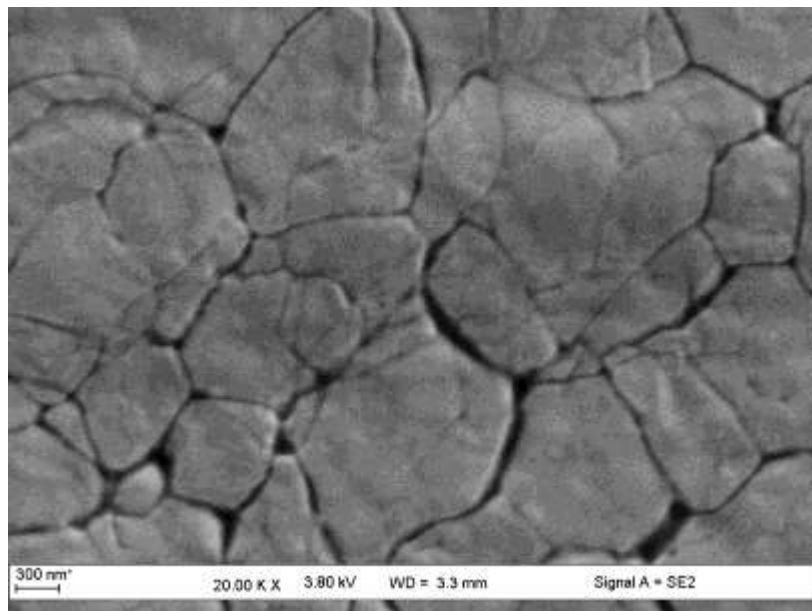**Figure 9.** Scanning electron micrograph of $Pd_{81}Ge_{19}$, Matt face at 500°C.

characteristic crystallization temperatures. It is reported in this paper that the Seebeck coefficients of the samples vary between approximately -2 µV/K when $Pd_{81}Ge_{19}$ is amorphous to -21 µV/K when crystallization is complete (in the temperature range from 25 to 700°C). Afterwards, a third transition begins starting from -17 µV/K at 625°C

down to -20 µV/K at 640°C and above. At the same time, the electrical resistivity diminishes approximately from 120 µΩ.cm (when $Pd_{81}Ge_{19}$ is amorphous) to 35 µΩ.cm (when crystallization has completed) in agreement with the literature. Measurement of resistivity and Seebeck coefficient as a function of temperature or time gives

Figure 10. Scanning electron micrograph of $Pd_{81}Ge_{19}$, Shiny side at 600°C

Figure 11. Scanning electron micrograph of $Pd_{81}Ge_{19}$, Matt face at 600°C.

complementary information about the kinetics of crystallization processes. As supplementary techniques, we completed the above results by using the DSC and SEM/TEM tools in the investigation of the kinetics and morphology of these crystalline-amorphous transitions.

Conflict of Interests

The authors have not declared any conflict of interests.

ACKNOWLEDGMENT

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