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Dilatometric investigations of Fe – Cr – Mo – C system

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Abstract. Sintering behavior in both high purity N_2 and H_2-containing atmosphere of Fe-(Cr)-(Mo)-C compacts was investigated. Turbula mixer was used for preparing the mixtures of powders with different Cr, Mo and C content. Following mixing, using single-action pressing in a rigid die at pressing pressure 400 MPa, green compacts with density level 5.9±0.17 g/cm^3 were pressed. Sintering was carried out in a horizontal push rod dilatometer Netzsch 402E at 1120 and 1250°C for 60 min. Heating and cooling rates were 10 and 20°C/min., respectively. After heating, compacts were isothermal sintered at 1120 or 1250°C for 60 minutes and cooled up to 200°C, then isothermally hold for 60 minutes and definitely cooled to the room temperature. Pure nitrogen and mixture of 5% H_2-95% N_2 were employed as sintering atmospheres. During investigations the influence of isothermal sintering temperature, chemical composition of sintering atmosphere, chromium, molybdenum and carbon content was followed by dilatometry. The aim of investigations was to determine transformation temperatures. It was shown that both sintering parameters and chemical composition of powder mixture has a great influence on sintering behaviour of Fe-(Cr)-(Mo)-C compacts.

Keywords: Powder Metallurgy, sintered steels, dilatometric investigation, phase transformation

1 Introduction

Powder Metallurgy (PM) technology can be used for production of structural material parts of machines. These include cogwheels, piston rings, compressor wings, even space shuttle skin plating, and household objects. More than 90% of world PM materials are iron-based materials (Ciaś, 1992; Mazahery & Shabani, 2012; Missol, 1972). The powder metallurgy route consists mainly of four stages: powders' production, mixing, the compacts fabrication and sintering. Very often the post-sintering treatment is needed for increasing the properties of PM parts (Mazahery & Shabani, 2012). Sintered materials based on pure iron are characterised by low mechanical properties. To increase the mechanical properties, the additives have to be employed. Very often it is carbon, added in the form of graphite in the maximum amount of 0.3% (Ciaś et al., 2003). According to the carbon content, several microstructures can result: ferrite-pearlite, pearlite or pearlite with pro-eutectoid cementite (Ciaś, 1992; German, 1994). Tensile strength of carbon steels does not exceed 520 MPa, and to obtain higher properties, it is necessary to introduce alloying elements such as Cu and Ni (Ciaś, 2004; Klein et al., 1985b; Šalak & Selecká, 2012; Zapf et al., 1975). However, problems with recycling scrap metal containing copper and the high price of nickel result in the substitution of these elements in sintered steels by Mn, Mo and Cr (Ciaś, 2004; Ciaś et al., 2003; Cygan, 2013; Gac, 2012). Such sintered steels attain higher mechanical properties in comparison with Cu and Ni steels. What is more, they can be produced with lower costs (Gac, 2012; Hryha et al., 2007; Sułowski & Ciaś, 2011).

Chromium is a very important alloying element in PM steels. It increases strength, hardness and hardenability and forms hard carbides. Chromium, which has a somewhat stronger carbide-forming tendency than iron, partitions between the ferrite and carbide phases ($(Fe, Cr)_3C$, Cr_7C_3 and $Cr_{23}C_6$). Chromium also influenced the toughness and the wear resistance of steel.

Molybdenum is also very often used as an alloying element in sintered steels. Because of its high affinity for carbon Mo forms carbides (e.g. Mo_6C) which improves the hardenability of steel (Ciaś, 2013; Gac, 2012; Kulecki, 2013; Lichańska, 2014; Hryha et al., 2007; Sułowski & Ciaś, 2011; Höganäs, 2002; Bergman & Bengston, 2009).

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Manganese is potentially and important alloying element in sintered steels. To date it has not been exploited beyond 0.7 wt.% due to its extremely high affinity for oxygen (Klein, Oberacker, & Thummler, 1985a; Klein et al., 1985b; Šalak, 1980a, 1980b). Therefore, the use of Mn as an alloying element requires special precautions. The Mn oxides cannot be reduced during sintering at conventional temperatures and atmospheres without strict dew point control. To protect the material from oxidation, the combination of "high" sintering temperature and a "low" dew point is required, e.g. at 1120°C -55°C is required. However as was shown in (Sułowski & Ciaś, 2011), the mechanical properties of Mn and Mn-Cr-Mo steels after sintering in low-hydrogen atmospheres or in air are comparable to those obtained after sintering in rich-hydrogen atmospheres. Usually PM steels are sintered at 1120°C, but high temperature sintering (HTS) - at for example 1250°C - give the possibility of oxide reduction because the thermodynamic stability of an oxides decreasing with increasing the sintering temperature. HTS promotes also homogenization of the microstructure and leads to increasing the mechanical properties of sintered steels.

PM industry needs that during production of PM high precise parts, dimensional changes must be known and controlled very carefully to keep tolerances of sintered materials. Thus, in this paper a study of the temperature and atmosphere effect on dimensional changes of Fe-Cr-Mo-C compacts is presented.

2 Experimental procedure

The following commercial pre-alloyed Höganäs iron powders were used:

- Astaloy CrA grade powder (Fe-1.8% Cr),
- Astaloy CrL grade powder (Fe-1.5% Cr-0.2%Mo),
- Astaloy CrM grade powder (Fe-3% Cr-0.5% Mo),
- commercial C-UF Höganäs fine graphite powder.

The starting powders were mixed without lubricant in Turbula mixer for 30 minutes. The following mixtures were prepared:

- Astaloy CrA +0.4% wt.-%C, Astaloy CrA + 0.8 wt.-%C
- Astaloy CrL + 0.4 wt.-% C, Astaloy CrL + 0.8 wt.-% C,
- Astaloy CrM + 0.4 wt.-% C, Astaloy CrM + 0.8 wt.-% C.

The mixtures were compacted, using uniaxial pressing at 400 MPa, into rectangular specimens of size 4x4x15 mm^3 and green densities of about 5.9±0.17 g/cm^3 (Table 1). The sintering experiments were carried out in a horizontal push rod dilatometer NETZSCH 402E both in pure N_2 (purity 5.0) and in mixture of 5%H_2-95%N_2 (purity 4.6). The dew point of atmosphere was at least -55°C. The flow rate of atmosphere was 10 ml/min.

Compacts were heated at 10°C/min to the isothermal sintering temperature of either 1120°C or 1250°C. Isothermal sintering time was 60 minutes. It should be noted that the dilatometer used could not maintain the constant cooling rate during the whole cooling period. Thus, the cooling rate from isothermal temperature down to about 380°C was 20°C/min (0.33°C/s). To obtain constant cooling rate up to room temperature, samples were isothermally hold at 200°C for 60 minutes and then cooled to the room temperature. The temperature control was accurate to ± 1°C. In Table 1 the scheme of dilatometric investigations is shown. As-sintered density of samples were in the range of about 5.91±0.12 g/cm^3 (Table 1). Dilatometric curves were afterwards analysed by Netzsch Thermal Analysis computer program.

3 Results

The results of dilatometric investigation of Fe-Cr-Mo-C are presented in Figs. 1-8 and divided into three parts: the effect of carbon concentration, the effect of chemical composition of sintering atmosphere and the effect of sintering temperature on dimensional changes of C containing compacts based on Astaloy CrA, Astaloy CrL and Astaloy CrM Höganäs grade powders.

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Table 1. The scheme of dilatometric investigations.

Carbon content, wt.-%	Type of base powder	Sintering temperature, °C, and atmosphere		Sample description	Green density, d_0, g/cm^3	As-sintered density, d_1, g/cm^3
0.4	CrA	1120	N_2	1A	5.70	5.72
		1250		3A	5.95	6.01
	CrL	1120		1L	5.86	5.82
		1250		3L	5.86	5.85
	CrM	1120		1M	5.85	5.73
		1250		3M	5.69	5.70
	CrA	1120	5%H_2-95%N_2	2A	5.81	5.88
		1250		4A	5.78	5.90
	CrL	1120		2L	5.97	6.04
		1250		4L	5.74	5.77
	CrM	1120		2M	5.79	5.70
		1250		4M	6.03	5.83
0.8	CrA	1120	N_2	5A	5.93	5.83
		1250		7A	6.09	5.98
	CrL	1120		5L	5.97	5.88
		1250		7L	6.03	6.11
	CrM	1120		5M	5.98	5.97
		1250		7M	5.97	5.97
	CrA	1120	5%H_2-95%N_2	6A	5.36	5.95
		1250		8A	6.11	6.01
	CrL	1120		6L	6.03	6.08
		1250		8L	6.17	6.12
	CrM	1120		6M	6.11	6.05
		1250		8M	5.82	5.85

3.1 The effect of carbon concentration

In Figs. 1-4 dilatometric curves for steels containing different carbon concentration are presented.

From Fig. 1 can, be observed that after sintering at 1120°C in nitrogen atmosphere, the highest dimensional stability was obtained for the steel sample based on Astaloy CrA powder with addition of 0.4 wt.-% C (1A). The highest dimensional changes were recorded for steel based on Astaloy CrL powder with addition of 0.4 wt.-% C (1L). The temperature of $\alpha \rightarrow \gamma$ phase transformation was in the range 774°C-911°C and 827°C-904°C for steels containing 0.4 and 0.8 wt.-% C, respectively.

After sintering at 1120°C in the mixture of 5%H_2-95%N_2 (Fig. 2), the highest dimensional stability was obtained for the steel sample based on Astaloy CrM powder with addition of 0.4 wt.-% C (2M). The lowest dimensional stability was observed for steel based on Astaloy CrA powder with addition of 0.4 wt.-% C (2A). The increasing the carbon content in steels caused the bigger dimensional changes during the whole sintering cycle (sample 6M and 6L in the contrary to the sample 2M and 2L). The carbon content in steels based on Astaloy CrA powder has an influence on their shrinkage during $\alpha \rightarrow \gamma$ phase transformation. The temperature range of this transformation was 750°C-912°C and 752°C-886°C for steels containing 0.4 and 0.8wt.-%C.

After sintering at 1250°C in nitrogen atmosphere (Fig. 3), the highest dimensional stability was obtained for the steel sample based on Astaloy CrA powder with addition of 0.4 wt.-% C (3A). The highest shrinkage was recorded for steel based on Astaloy CrM powder with addition of 0.8 wt.-% C (7M). The temperature of $\alpha \rightarrow \gamma$ phase transformation was in the range 767°C-892°C and 751°C-891°C for steels containing 0.4 and 0.8 wt.-% C, respectively.

After sintering at 1250°C in the mixture of 5%H_2-95%N_2 (Fig. 4), the highest dimensional stability was obtain for the steel sample based on Astaloy CrL powder with addition of 0.4 wt.-% C (4L). The lowest dimensional stability was observed for steel based on Astaloy CrA powder with addition of 0.8 wt.-% C (8A). After sintering at 1250°C for all samples shrinkage was observed. The temperature range of this transformation was 846°C-914°C and 747°C-815°C for steels containing 0.4 and 0.8 wt.-%C.

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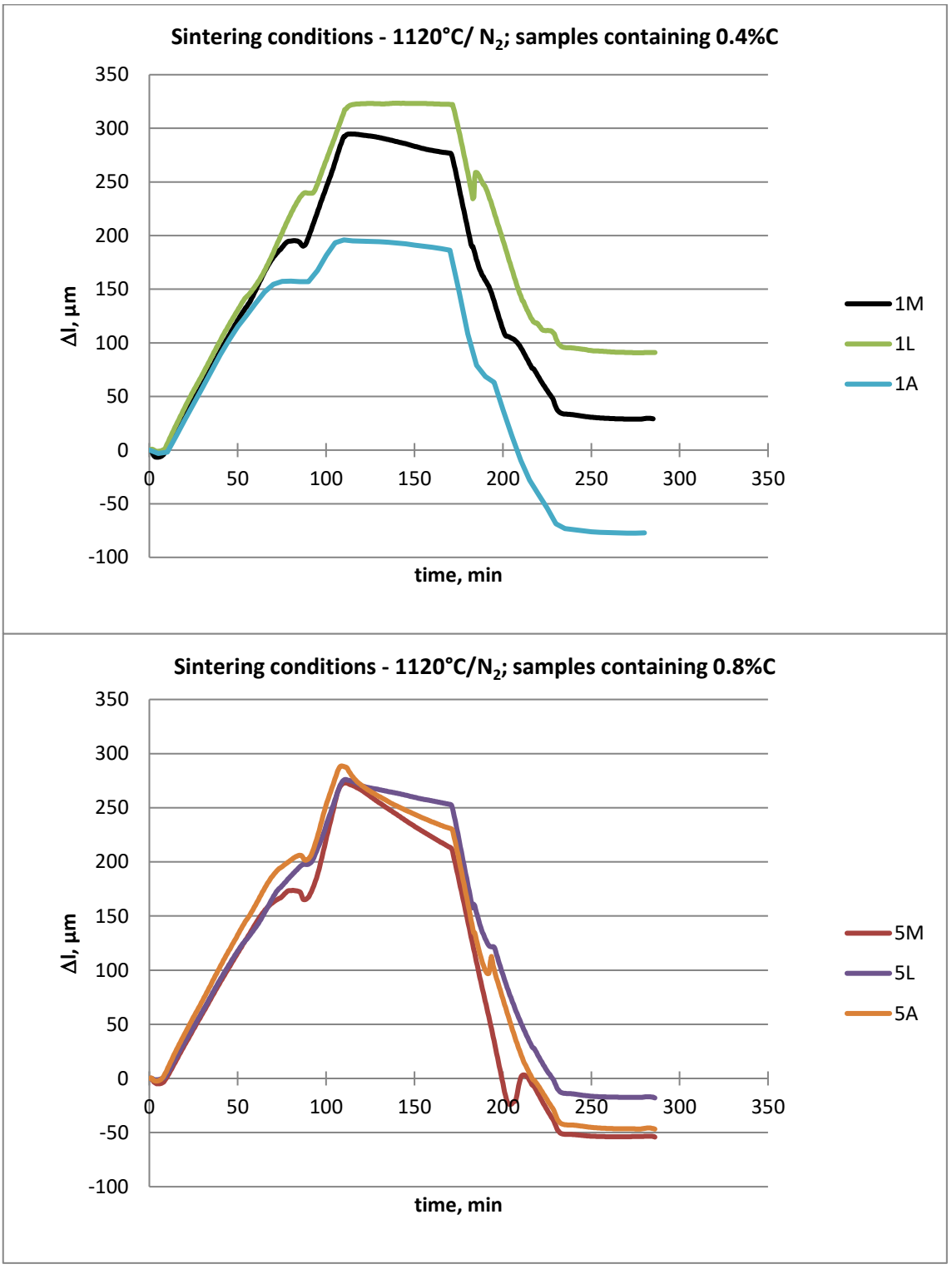

Fig. 1. Dilatometric curves for sintering cycles at 1120ºC in nitrogen (samples: CrA+0.4%C (1A), CrA+0.8%C (5A), CrL+0.4%C (1L), CrL+0.8%C (5L), CrM+0.4%C (1M), CrM+0.8%C (5M))

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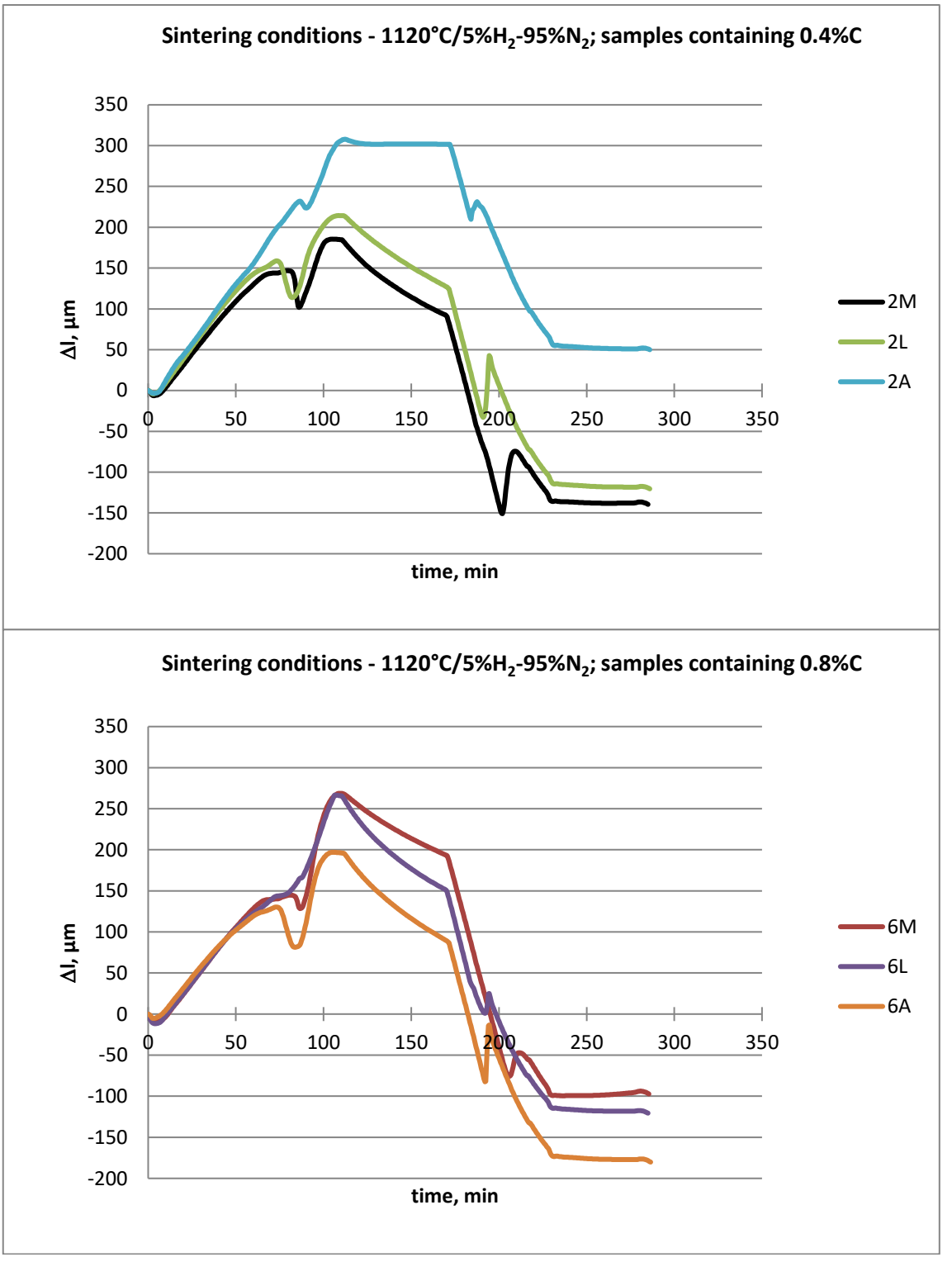

Fig. 2. Dilatometric curves for sintering cycles at 1120ºC in mixture of 5%H_2-95%N_2 (samples: CrA+0.4%C (2A), CrA+0.8%C (6A), CrL+0.4%C (2L), CrL+0.8%C (6L), CrM+0.4%C (2M), CrM+0.8%C (6M))

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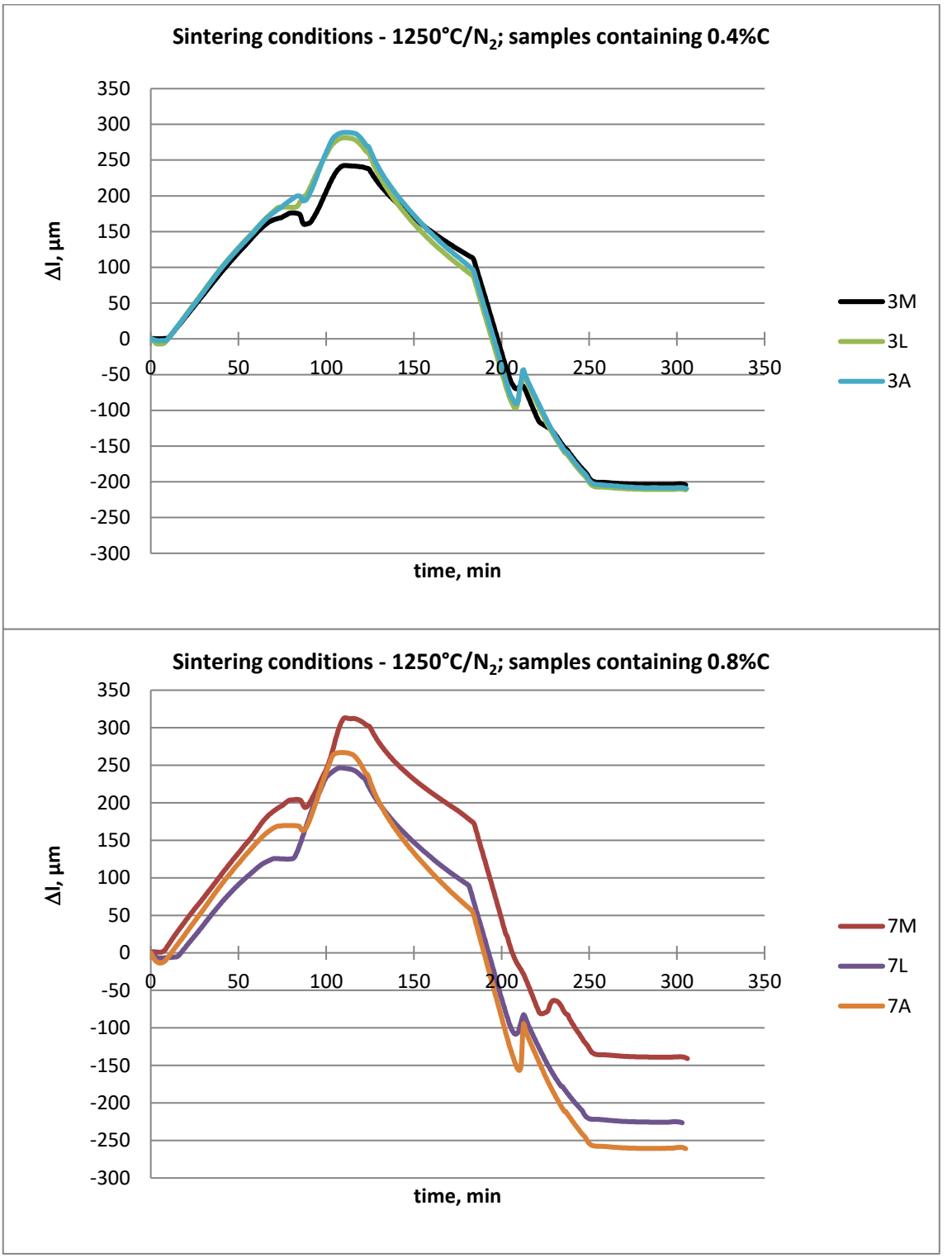

Fig. 3. Dilatometric curves for sintering cycles at 1250ºC in nitrogen (samples: CrA+0.4%C (3A), CrA+0.8%C (7A), CrL+0.4%C (3L), CrL+0.8%C (7L), CrM+ 0.4%C (3M), CrM+.8%C (7M))

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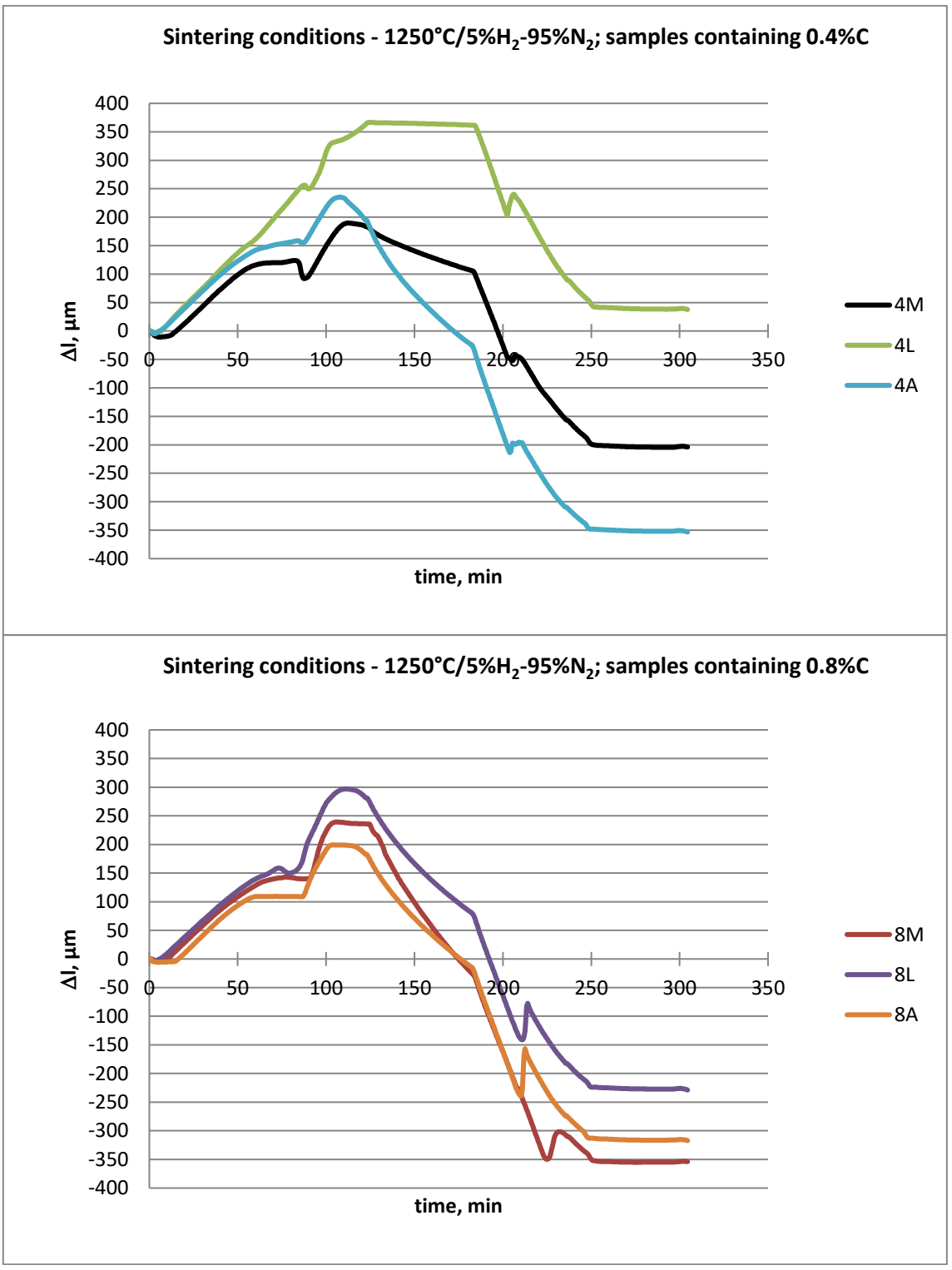

Fig. 4. Dilatometric curves for sintering cycles at 1250ºC in mixture of 5%H_2-95%N_2 (samples: CrA+0.4%C (4A), CrA+0.8%C (8A), CrL+ 0.4%C (4L), CrL+0.4%C (8L), CrM+0.4%C (4M), CrM+0.8%C (8M))

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3.2 The effect of chemical composition of sintering atmosphere

In Figs. 5-8 the dilatometric curves for sintering in atmosphere with different chemical composition are presented.

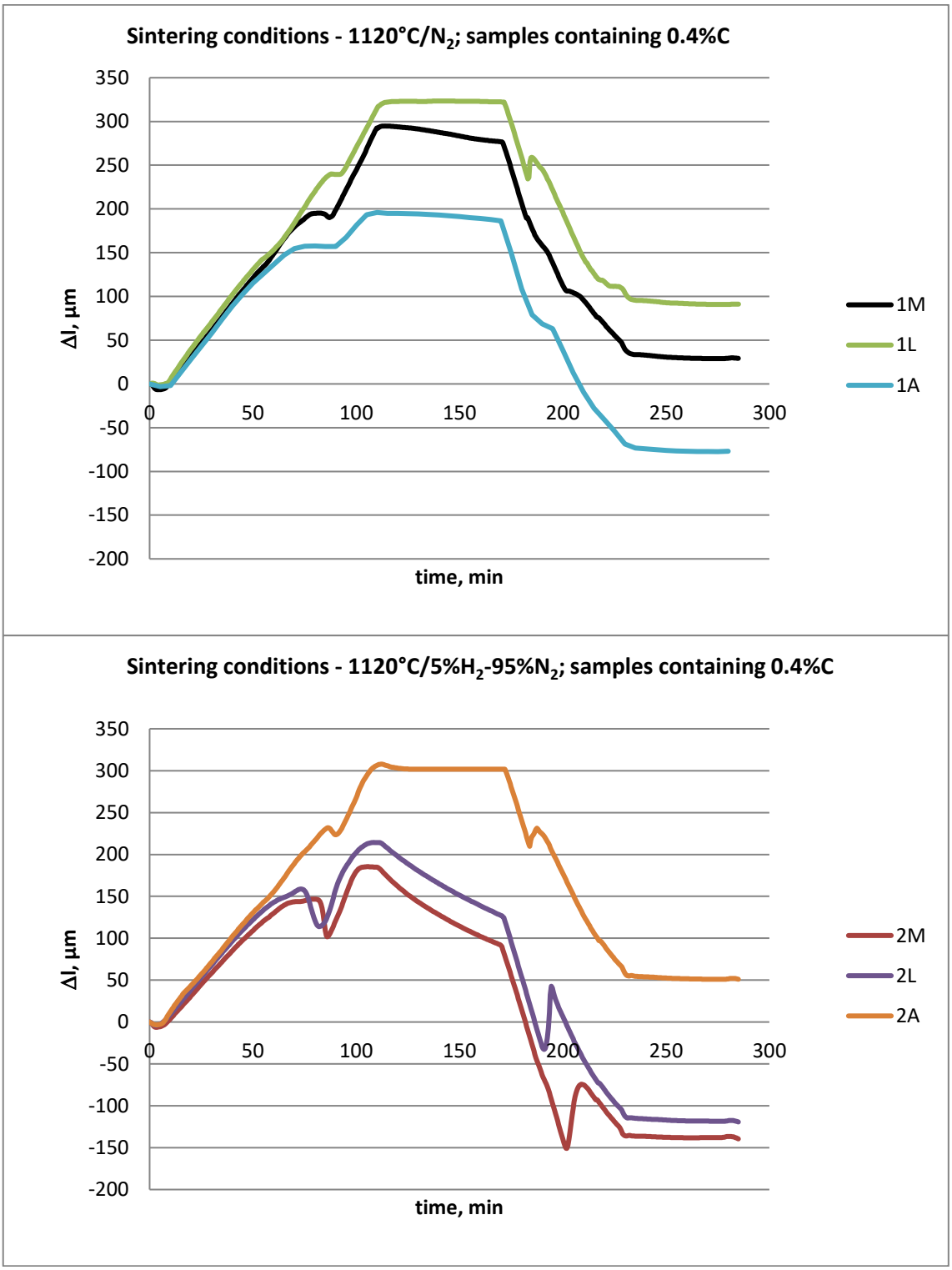

Fig. 5. Dilatometric curves for sintering cycles at 1120ºC of samples containing 0.4 wt.-% carbon after sintering in N_2 (samples: CrA+0.4%C (1A), CrL+0.4%C (1L), CrM+0.4%C (1M)) and in the mixture of 5%H_2-95%N_2 (samples: CrA+0.4%C (2A), CrL+0.4%C (2L), CrM+0.4%C (2M))

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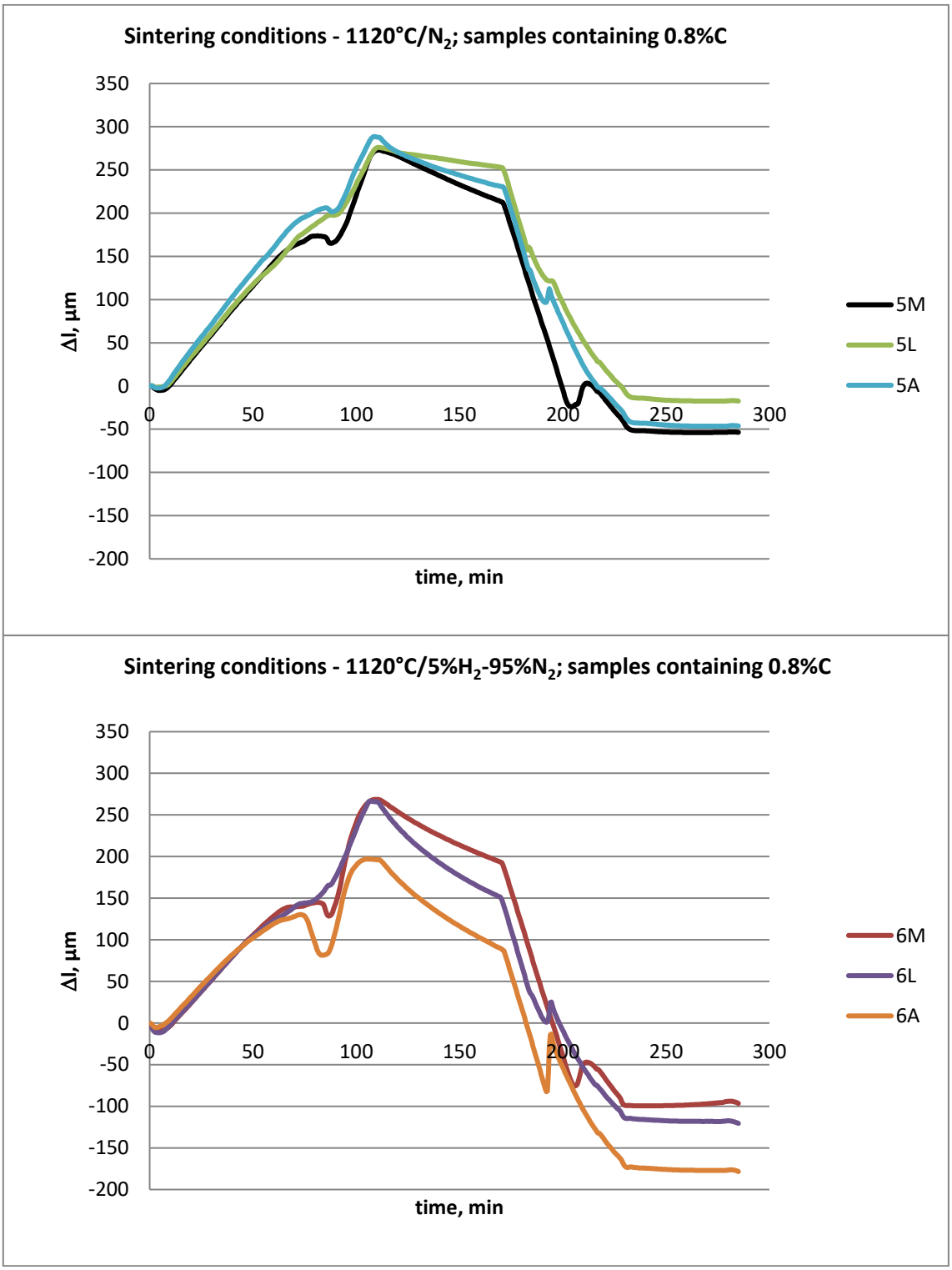

Fig. 6. Dilatometric curves for sintering cycles at 1120ºC of samples containing 0.8 wt.-% carbon after sintering in N_2 (samples: CrA+0.8%C (5A), CrL+0.8%C (5L), CrM+0.8%C (5M)) and in the mixture of 5%H_2-95%N_2 (samples: CrA+0.8%C (6A), CrL+0.8%C (6L), CrM+0.8%C (6M))

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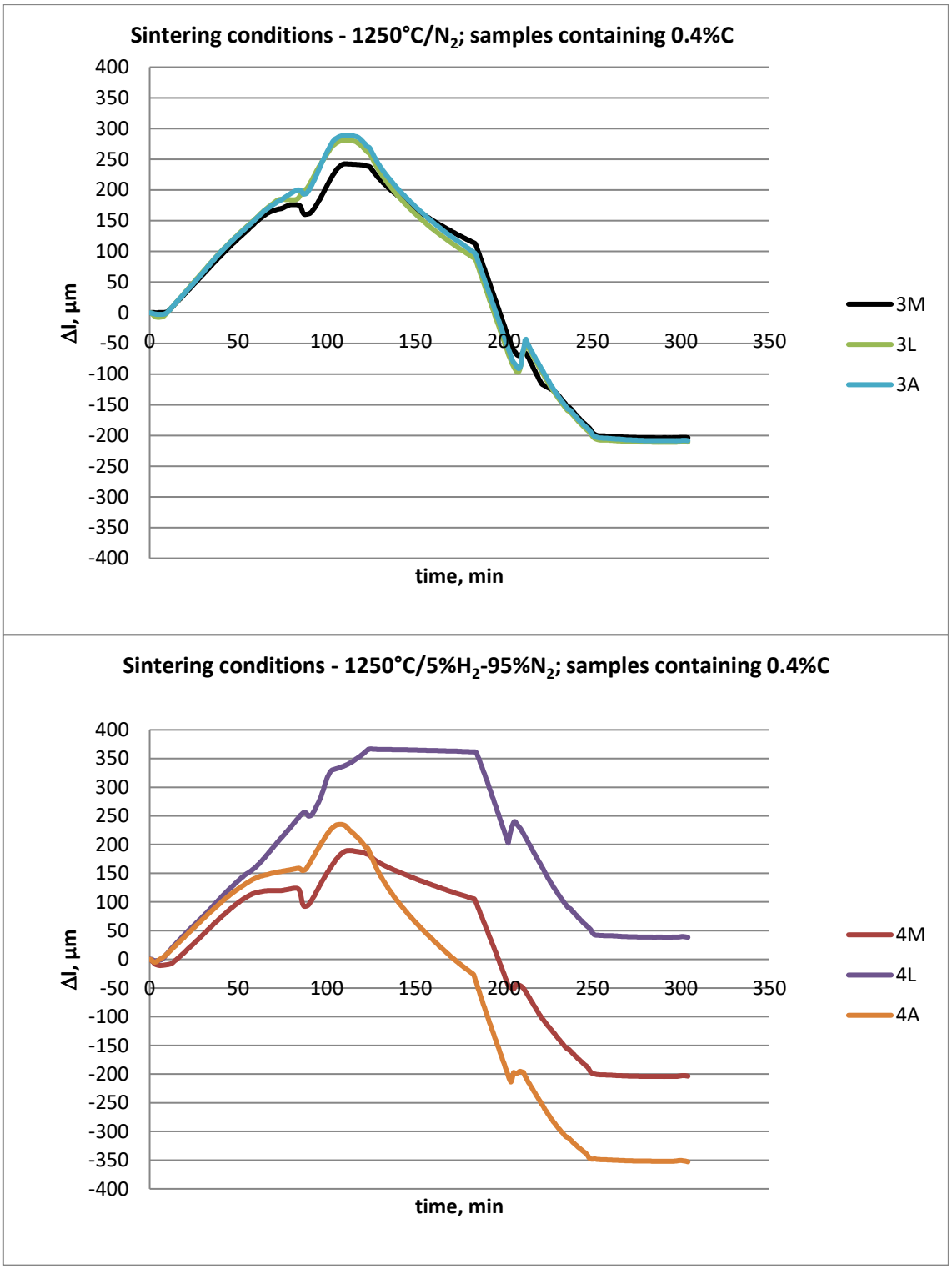

Fig. 7. Dilatometric curves for sintering cycles at 1250ºC of samples containing 0.4 wt.-% carbon after sintering in N_2 (samples: CrA+0.4%C (3A), CrL+0.4%C (3L), CrM+0.4%C (3M)) and in the mixture of 5%H_2-95%N_2 (samples: CrA+0.4%C (4A), CrL+0.4%C (4L), CrM+0.4%C (4M))

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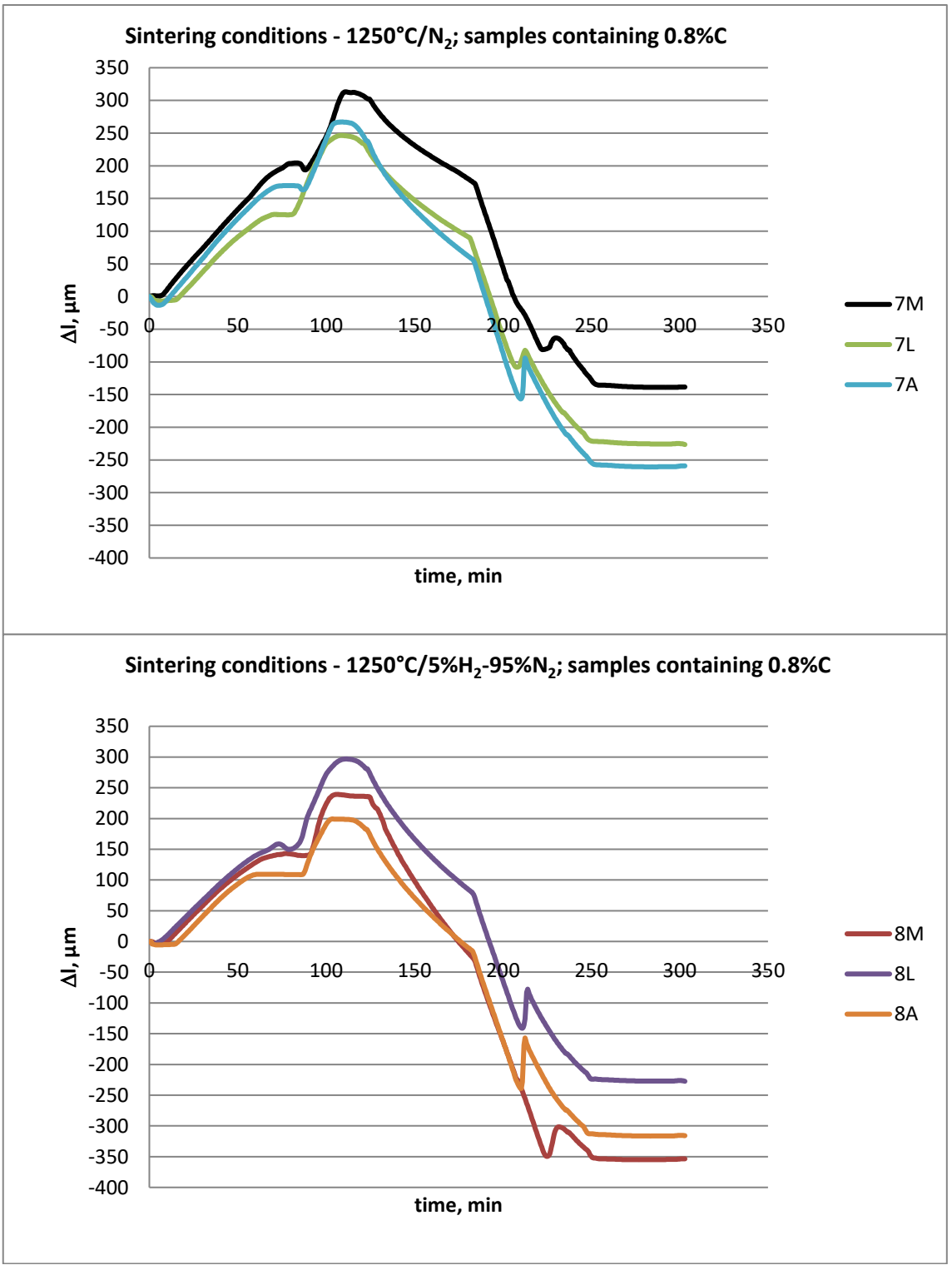

Fig. 8. Dilatometric curves for sintering cycles at 1250ºC of samples containing 0.8 wt.-% carbon after sintering in N_2 (samples: CrA+0.8%C (7A), CrL+0.8%C (7L), CrM+0.8%C (7M)) and in the mixture of 5%H_2-95%N_2 (samples: CrA+0.8%C (8A), CrL+0.8%C (8L), CrM+0.8%C (8M))

From Figs. 5-8 can be concluded that after sintering steels containing 0.4 wt.-%C at 1120°C the highest dimensional stability was recorded for sample 1A, based on Astaloy CrA powder, sintered in nitrogen; the worst dimension stability was observed in sample 2M, based on Astaloy CrM powder,

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sintered in 5%H_2-95%N_2 mixture. The fastest $\alpha \rightarrow \gamma$ transformation was recorded in sample 2L - 750°C-883°C. On the opposite was transformation in 2A sample – its phase transformation temperature range was 872°C-912°C. Both samples were sintered in the mixture of 5%H_2-95%N_2. In the group of steels containing 0.8 wt.-% C, the best dimensional stability was observed of Sample 5L, based on Astaloy CrL powder, sintered in nitrogen and the lowest dimensional stability was obtained in sample 6A (Astaloy CrA based powder) after sintering in the mixture of 5%H_2-95%N_2. The fastest $\alpha \rightarrow \gamma$ transformation was recorded in sample 6L - 752°C-817°C. On the opposite was transformation in 5L sample – its phase transformation temperature range was 889°C-904°C.

The increase the sintering temperature had negligible effect on the $\alpha \rightarrow \gamma$ phase transformation temperature. The temperature range was varied from 767°C-822°C to 861°C-886°C and from 747°C-812°C to 847°C-891°C, for steels sintered in nitrogen and mixture of 5%H_2-95%N_2.

4 Conclusions

Based on present work, the following concluding remarks can be drawn:

- The $\alpha \rightarrow \gamma$ phase transformation range for all investigated steels was similar.
- During isothermal sintering in all sample's shrinkage was observed.
- The higher carbon concentration influenced bigger shrinkage in investigated steels.
- Sintering in nitrogen caused good dimensional stability of investigated steels.

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