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Modification of Liquid Steel Viscosity and Surface Tension for Inert Gas Atomization of Metal Powder

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Abstract: Inert gas atomization is one of the main sources for production of metal powder for powder metallurgy and additive manufacturing. The obtained final powder size distribution is controlled by various technological parameters: gas flow rate and pressure, liquid metal flow rate, gas type, temperature of spraying, configuration of nozzles, etc. This work explores another dimension of the atomization process control: modifications of the liquid metal properties and their effect on the obtained powder size. Series of double-alloyed Cr-Mn-Ni steels with sulfur and phosphorus were atomized with argon at 1600 °C. The results indicate that surface tension and viscosity modifications lead to yielding finer powder fractions. The obtained correlation is compared with the individual modification of surface tension with S and Se and modification of viscosity with phosphorus. Discrepancy of the results is discussed. Additives of surfactants and viscosity modifiers can be a useful measure for powder fractions control.

Keywords: surface tension; viscosity; inert-gas atomization; sulfur; phosphorus; selenium; TRIP/TWIP steel

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1. Introduction

Powder production remains one of the bottlenecks for the widespread use of metal additive manufacturing. The best quality powder—especially in regard to the sphericity of particles—is currently achieved in two processes: rotary plasma spraying and inert gas atomization. The shape of the particles and low oxidation of powder are achieved by well-controlled gas atmosphere during their spraying and cooling in free fall. At the same time, both are small-volume technologies, i.e. batch-type processes, and, therefore, are associated with a high cost of powder produced. The cost is further magnified by the use of neutral gases and wide particle size distribution (PSD) of obtained powder, which brings considerable amounts of over- and undersized products.

The inert gas atomization process is based on the spraying of the liquid metal stream by the pressurized gas jets. Nitrogen and argon are typically used as atomizing media. The control of the process is usually achieved by the technological (e.g., equipment) parameters: temperature of atomization, metal flow rate and atomizing gas pressure [1]. Meanwhile, further shift of PSD towards target values is possible via thermophysical properties: surface tension (ST), viscosity and density of the liquid metal. Given the temperature dependence of these thermophysical properties, the required shift of PSD is feasible via the temperature adjustment. Nevertheless, the spraying temperature (i.e., the melt temperature during its release into the spraying area) can only be varied within a narrow range due to process and equipment limitations. For example, the presence of elements with high vapor pressure, such as manganese, limits the overheating time.

The Lubanska equation [2] (Equation (1)) shows the dependence of the median particle size of obtained powder on the various parameters:

$$\frac{d_m}{d_{Met\ Str}} = K\left[\frac{v_m}{v_g}\frac{1}{W}\left(1+\frac{M}{A}\right)\right]^{\frac{1}{2}} \quad (1)$$

where W is the Weber number, defined as:

$$W = \rho\frac{V^2 D}{\gamma} \quad (2)$$

d_m is the mass median particle diameter (d_{50}), $d_{Met\ Str}$ is the diameter of metal stream; v_m is the kinematic viscosity of liquid metal, v_g is the kinematic viscosity of atomizing gas, V is the velocity of atomizing gas, M is the mass flow rate of liquid metal, ρ is the density of the gas, γ is the surface tension of liquid metal, A is the mass flow rate of atomizing medium, D is the diameter of the metal nozzle and K is a constant [1].

As shown in the above equations, surface tension and viscosity decrease should reduce the median particle size of the powder.

The steel alloy with the TRIP/TWIP effect (TRansformation Induced Plasticity/TWinning Induced Plasticity) and internal name 16-7-6 (16 mass% Cr, 7 mass% Mn, 6 mass% Ni) was developed under the framework of Collaborative Research Centre 799 TRIP-Matrix-Composite [3,4]. One of the key targets of CRC799 was binding TRIP-matrix steels with fine zirconia ceramics, also having TRIP-effect, via different production routes. It was estimated that, for successful composite production, the size of the steel powder should be as close as possible to the one of ceramic powder (ca. 1 µm). The research unit for atomization provided median powder size in the range of 30–40 µm. To further reduce d_{50} and overcome the limitations of equipment, the properties of the liquid must be adjusted. For example, Putimtsev [5] reported that steels atomized with air demonstrated fewer fine particles compared to those atomized with nitrogen. The author explained this effect through an increase of the melt viscosity. The same effect was reported by Kunin [6]. The results indicate that the viscosity increase associated with the oxides formation on the dispersed droplets' surface was more effective than surface tension reduction due to enrichment of the metal with oxygen. However, surface tension and viscosity of the liquid metals can be changed not only due to oxidation. Many data on the surface-active elements and their effects on the liquid metals surface tension [7–10] are already accumulated in the scientific literature. Dubberstein et al. [11,12] showed that modifications of liquid steels' surface tension using sulfur and selenium or viscosity using phosphorus are possible for the already low-ST and low-viscosity steels, and these modifications bring measurable effects on the powder particle size distribution.

Similar effects are well-known for the spraying of liquid media. For example, Rizkala and Lefebvre [13] experimentally obtained a correlation for droplet size in airblast atomization, which suggests that droplet size grows with the increase of surface tension and density of the atomized liquid. Lefebvre [14], in a literature review, found that a decrease in surface tension and viscosity leads to finer particles in the airblast atomization.

The present work is targeted towards widening the horizons of the initial study [12] and specifying whether a simultaneous modification of surface tension and viscosity of liquid steel can give a cumulative effect on the median particle size of the powder and exceed the individual modifications of surface tension or viscosity. A series of five experiments was executed varying surface tension and viscosity of atomized steels. The surface tension and viscosity were estimated based on the experimental data for similar alloys reported earlier [11,12]. Surface tension dependence from sulfur was taken as that of the alloy 16-7-9 [12] (with 9 mass% Ni), which has the same initial surface tension as 16-7-6. The surface tension and viscosity plots and the regressions used for calculations in the present study are shown in Figure 1.

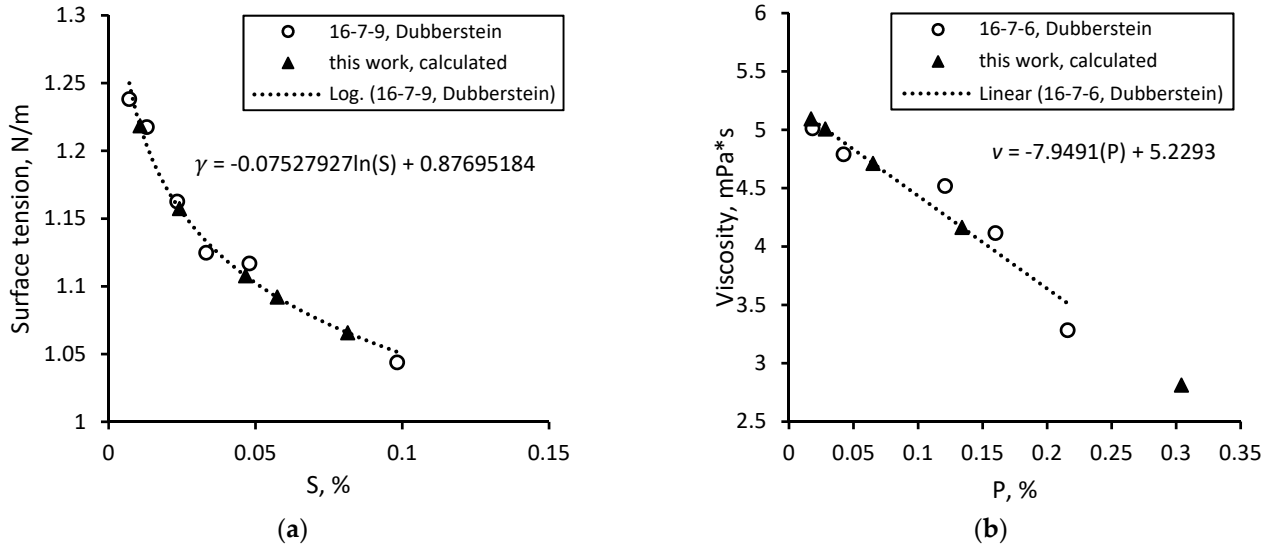


Figure 1. Effect of sulfur content on the surface tension γ of liquid 16-7-9 steel at 1600 °C and calculated values for the samples in present work (**a**), modified after [11]; and effect of phosphorus content in the steel 16-7-6 on the viscosity v of the melt at 1600 °C and calculated values for the samples atomized in present work, modified after [12] (**b**).

2. Materials and Methods

Steel samples were produced in the vacuum induction furnace VIM12 (ALD Vacuum Technologies) in the form of 20 kg cylindrical bars. The samples were analyzed with the use of the spark spectrometer Oxford Instruments Foundry-master for general analysis of chemical composition, combustion analyzer Bruker G8 Galileo for carbon and oxygen and combustion analyzer Bruker G4 Ikarus unit for sulfur and nitrogen content. The chemical composition is given in Table 1. The particle size distribution of the obtained powder was estimated using the laser diffractometer HORIBA LA-960.

Table 1. Chemical composition of the atomized samples, mass %.

Sample	C	Si	Cr	Mn	Ni	Al	Mo	V	N	O_{tot}	S	P
	%									ppm		
16-7-6SP1	0.0459	0.909	16.1	7.25	6.1	0.001	0.059	0.084	129	46	107	170
16-7-6SP2	0.0231	0.991	15.7	7.31	5.96	0.001	0.060	0.086	141	39	241	280
16-7-6SP3	0.0356	0.953	15.8	7.09	5.95	0.001	0.046	0.083	191	49	466	650
16-7-6SP4	0.0413	0.959	16	6.79	6.21	0.001	0.067	0.085	193	24	574	1340
16-7-6SP5	0.0334	1	15.5	7.08	5.97	0.001	0.046	0.084	184	60	814	3040

Atomizations of the metal samples were executed in the inert gas atomization unit VIGA-1B (supplied by ALD Vacuum Technologies) (Figure 2). A detailed description of the unit can be found in previous publications [15,16]. The atomizer consists of two vacuum-tight steel chambers. In the upper part, the sample is placed in the aluminum oxide crucible and inductively heated. The crucible has a bottom opening, which is closed by a boron nitride (BN) stopper rod. A zirconia ceramic nozzle with a 4-mm tapping orifice is attached to the bottom of the crucible. The temperature of the metal is controlled by two thermocouples inserted into the stopper rod.

The ceramic nozzle is placed inside the confined close-coupled stainless steel ring nozzle for spraying gas. In all experiments, the constant gas flow rate, maximum for the equipment, and pressure (ca. 26 Bar) were utilized. Argon gas was supplied from the liquid storage tank and had a maximum 5 ppm of O_2 as an impurity.

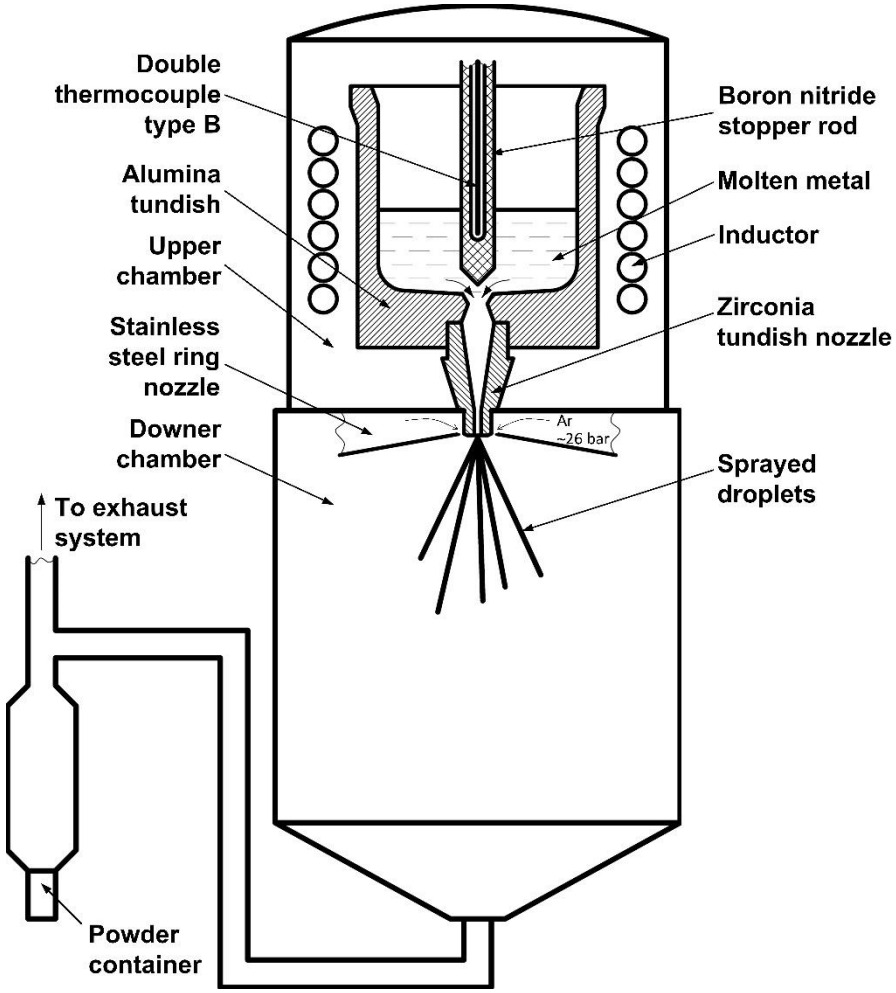


Figure 2. Scheme of inert gas atomization unit VIGA-1B [16] utilized in present study.

Atomizations were accomplished under the following conditions. The sample was heated under the argon gas atmosphere (99.999% Ar) to the liquidus temperature of steel. Then, the heating was slowed down to reduce liquid metal sparkling. After the full melting of the sample, it was rapidly heated to the target temperature of 1600 °C. As soon as the target temperature was achieved, the stopper rod of the tundish was released, and the gravity-induced fall of the liquid started. Simultaneously, the gas flow through the ring nozzle was launched. The duration of the atomization was controlled by the metal charge mass and flow rate. After the cooling of the powder, it was collected in the container. The powder was further sieved to <200 μm fraction and three randomly selected samples were analyzed on the laser diffractometer.

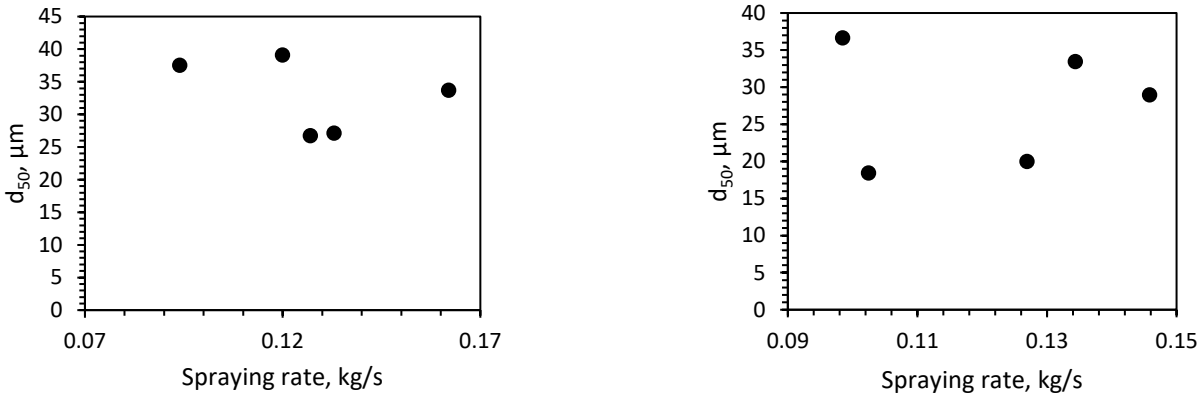
3. Results and Discussion

The results of atomizations are given in Table 2. The atomization time and, thus, the spraying rate varied considerably. In this work, the spraying rate is utilized as a substitute for the traditional gas-to-metal ratio parameter, which could not be defined precisely due to an absence of a gas flowmeter. Under the conditions of constant gas flow rate in atomizations, the spraying rate should give the same type of influence on the median particle size of the obtained powder as the gas-to-metal ratio. Nevertheless, in the present work, no correlation (Figure 3a) between spraying rate (i.e., gas-to-metal ratio) and median particle size d_{50} of the obtained powder was observed. The same applies to the comparative series with surface tension modification (Figures 3b and 4a) and for the series

with viscosity modification (Figure 4b) executed earlier. Consequently, the gas-to-metal ratio was not a decisive factor for the d_{50} of the obtained powder.

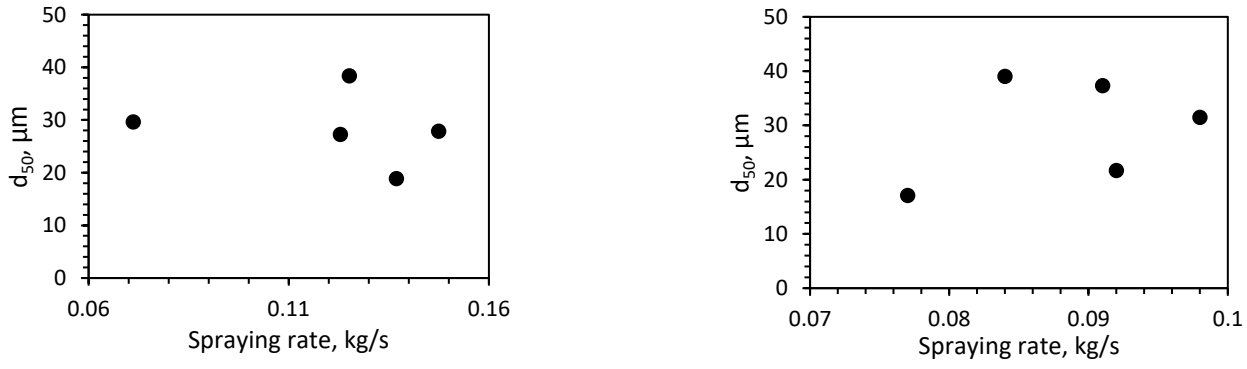
Table 2. Parameters of the atomizations and obtained powder.

	Experiment				
	SP1	**SP2**	**SP3**	**SP4**	**SP5**
Sample mass, g	5776	5850	6001	5868	5827
Spraying temperature, °C			1650		
Atomizing media			argon		
Atomization time, s	48	62	37	44	46
Spraying rate, kg/s	0.120	0.094	0.162	0.133	0.127
Median particle size d_{50}, μm	39.1 ± 0.73	37.5 ± 1.99	33.7 ± 1.29	27.1 ± 0.30	26.7 ± 0.2



(**a**) (**b**)

Figure 3. Effect of spraying rate on the median particle size of atomized powder d_{50}: in this work (**a**); and in the selenium alloyed series (ST-modified) reported in [17]–(**b**).



(**a**) (**b**)

Figure 4. Effect of spraying rate on the median particle size of atomized powder d_{50}: for viscosity modified 16-7-6 steel [12] (**a**); and for ST-modified 16-7-6 steel [11] (**b**).

At the same time, there are strong correlations between median particle size and surface tension (Figure 5a) and viscosity modification (Figure 5b). Specifically, R^2 is over 70% for viscosity and almost 90% for surface tension. It should be noted that, the present work, due to the limited number of experimental trials, is not targeted towards building a numerical model, but it rather seeks to clarify qualitative dependencies. For comparison, the obtained correlations were plotted in the three-dimensional diagram together with

the previous results for surface tension modification of the 16-7-6 alloy and viscosity modification of the same alloy (Figure 6). Surprisingly, simultaneous modification of ST and viscosity did not surpass the individual change of either ST or viscosity. From the previous work [15], it is known that formation of the frozen metal "crown" on the ceramic nozzle during the spraying may significantly affect the dynamic of metal flow rate from the tundish. In addition, during crown formation, the cone of gas jet should be distorted. This phenomenon might influence the spraying rate and d_{50}. However, the intensive crown formation was not observed in the present study.

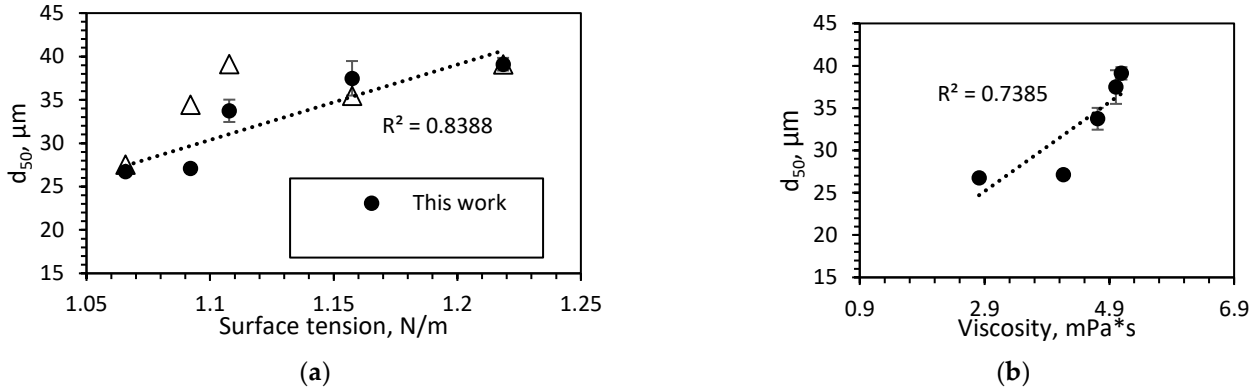


Figure 5. The effect of surface tension on d obtained in this work experimentally and calculated by Lubanska equation (Equation (1)) (**a**); and the effect of viscosity on the median particle size in present work (**b**).

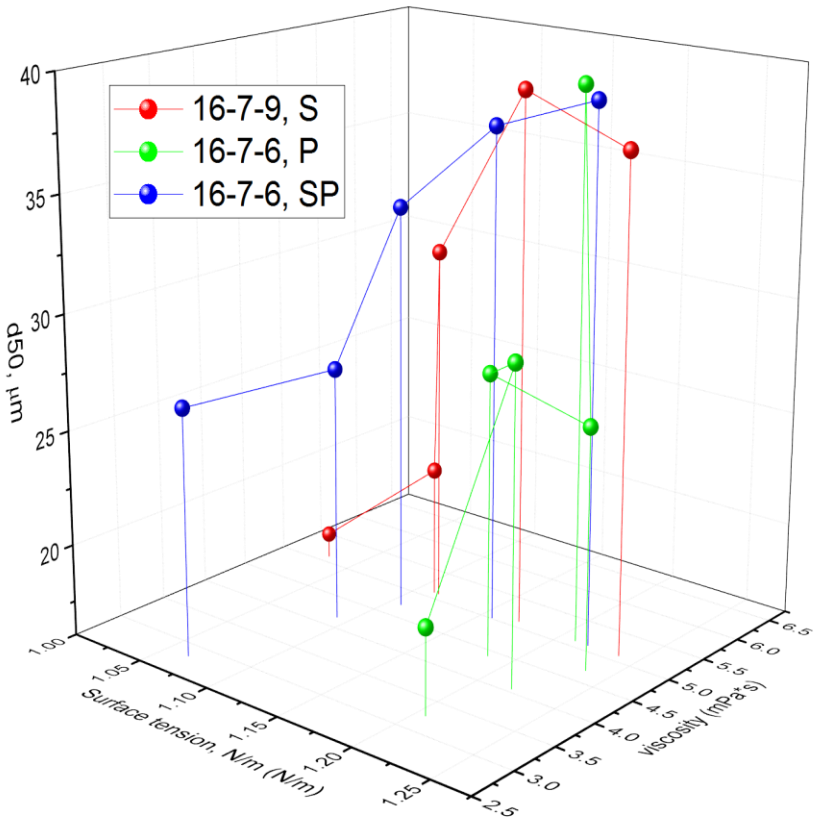


Figure 6. Surface tension modification [11], viscosity modification [12] and simultaneous viscosity and surface tension modification of liquid steel and their effect on the median particle size d_{50} of the inert-gas atomized powder.

It is also possible to compare the results of atomization with the prediction of Equation (1). In the calculations all factors except for ST, viscosity and spraying rate were fixed. The predicted value for SP1 was taken as 100%, and the values for SP2-5 were accordingly recalculated. As shown in Figure 6, Equation (1) predicts roughly the same magnitude of d_{50} reduction as was obtained in the experiments.

Furthermore, the results of the present study were compared with those of two other atomization series conducted on the same equipment [11,17] to estimate the effect of surface tension on the median particle size (see Figure 7). The highest d_{50} reduction effect was observed for the case of only sulfur alloying of the steel. Much deeper ST reduction in the case of selenium alloying—of 0.84 N/m compared to over 1.03 N/m for only S alloying—did not lead to further particle size reduction of the powder. To understand this phenomenon, it is useful to analyze other parameters of the process. Although it was shown previously that d_{50} has no correlation with the spraying rate, in the particular case of the three atomizations with very low surface tensions, the median particle size decreases with the spraying rate reduction. The smallest d_{50} size in the SP modification was achieved under 0.127 kg/s (26.7 μm), in the Se modification under 0.098 kg/s (18.5 μm) and in the S modification at 0.091 kg/s (17.1 μm).

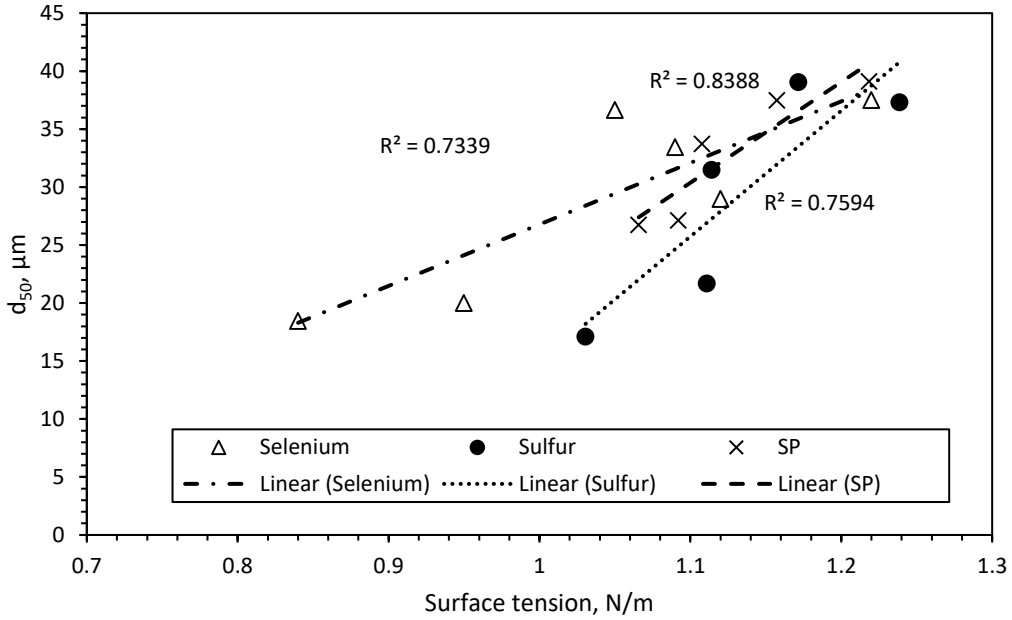


Figure 7. Effect of surface tension on the median powder size d_{50} for the steels modified with selenium [17], sulfur [11] and sulfur with phosphorus.

In general, modification of melt surface tension and viscosity led to fine powder fractions. For example, in laser-based additive manufacturing (known as Laser Powder Bed Fusion), the powder fraction of 10–60 μm is used [18]. Reduction of viscosity together with the surface tension led to increase of this powder size fraction from 66% in pure 16-7-6 alloy SP1 to 76% in alloy with maximum sulfur and phosphorus shares SP5 (Figure 8). In other words, modification of thermophysical properties increased the yield of the most useful powder fraction for additive manufacturing.

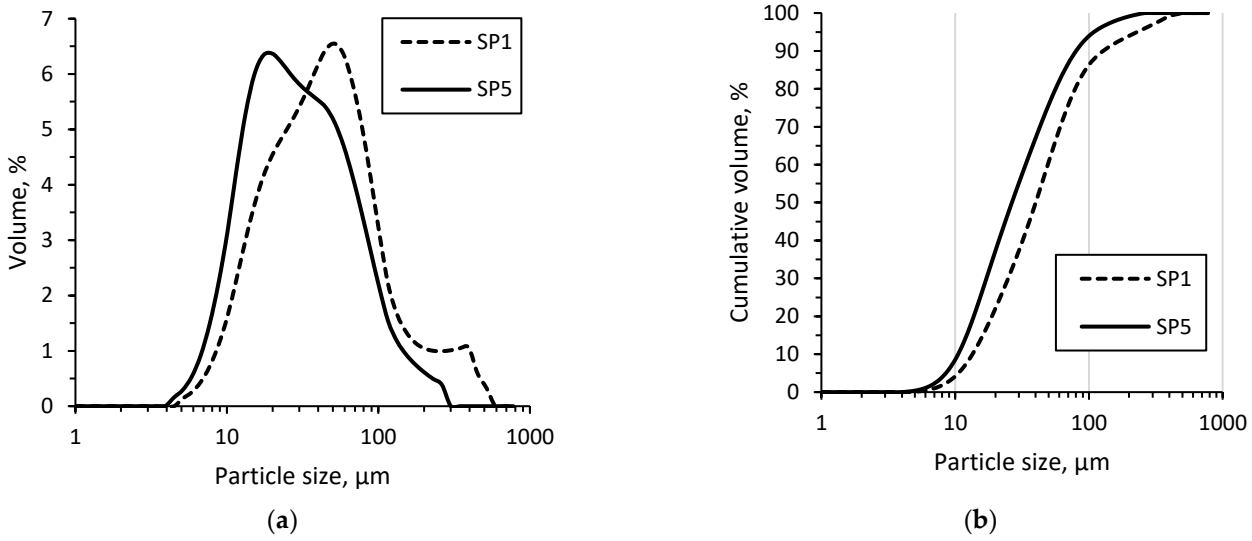


Figure 8. Particle size distribution of pure alloy 16-7-6 SP1 and 16-7-6 SP5 with maximum sulfur and phosphorus content (**a**); and cumulative volume of different size fractions (**b**) in this study.

The addition of sulfur to the steel as a surface-active element can raise concerns regarding the negative effect on the properties of final products made of such sulfur-containing powder. Sulfur is known for its brittleness effect on steel products. Thus, selenium appears to be a better alternative for surface tension modification of steel. To the authors' knowledge, there are no reported cases of a negative effect of Se on mechanical properties of steel products, and Se can bring significant surface tension reduction with smaller quantities of additive. For example, addition of only 200 ppm Se reduced surface tension of TRIP/TWIP steel to nearly the same level (1.05 N/m) as the addition of 1000 ppm S (1.03 N/m) [12]. However, S and Se are not the only options to reduce the surface tension. From the literature [7], it is known that tellurium is an even more surface-active element for liquid iron. In other words, if needed, surface tension can by modified in multiple ways and selection of optimum additives is a task for future research.

Phosphorus is also an undesirable component of the non-casting steel alloys. However, previous research of phosphorus-alloyed TRIP-steel properties [19] confirmed the absence of critical effects of phosphorus on the quality of as-casted samples. Moreover, the yield strength and ultimate tensile strength slightly increased upon P additions of up to 0.2%. This indicates that, in some cases of steel powder production, phosphorus and/or selenium micro-alloying can be a useful measure to control the obtained powder size. In addition, surface tension and viscosity modifications should affect the process of additive manufacturing of such powder. In particular, less viscous melt should affect the porosity and mechanical properties of 3D-printed parts.

4. Conclusions

A series of inert gas atomizations of liquid TRIP/TWIP steel was successfully executed. The powder analysis shows that, with the reduction of surface tension and viscosity of the liquid steel, the median particle size decreases. No correlation of gas-to-metal ratio was observed in the present experimental series. Comparison with the individual modification of either surface tension or viscosity characteristic of the same steel showed no cumulative effect of the simultaneous modification of surface tension and viscosity. The probable discrepancy of the results can stem from the variability of metal flow rate between atomizations series, as well as the multifactorial limitation of possible PSD reduction. However, for more reliable results, a higher number of atomizations is required.

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