IWT

Leibniz-Institut für
Werkstofforientierte
Technologien

Cooling strategies for the atomization of glass-forming alloys

Nevaf Ciftci

BAND 82

Verfahrenstechnik

Cooling strategies for the atomization of glass-forming alloys

Vom Fachbereich Produktionstechnik

der

UNIVERSITÄT BREMEN

zur Erlangung des Grades

Doktor-Ingenieur

genehmigte

Dissertation

von

Nevaf Ciftci, M.Sc.

Gutachter:

Prof. Dr.-Ing. habil. Lutz Mädler (Universität Bremen)
Prof. Dr.-Ing. habil. Dr. h.c. Jürgen Eckert (Montanuniversität Leoben/Österreich)

Tag der mündlichen Prüfung: 26.05.2020

Forschungsberichte aus dem Leibniz-Institut für
Werkstofforientierte Technologien

Band 82

Nevaf Ciftci

Cooling strategies for the atomization of glass-forming alloys

D 46 (Diss. Universität Bremen)

Shaker Verlag
Düren 2020

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: Bremen, Univ., Diss., 2020

Printed in Germany.

ISBN 978-3-8440-7462-8
ISSN 2626-658X

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren
Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9
Internet: www.shaker.de • e-mail: info@shaker.de

Zusammenfassung

Metallische Gläser bzw. massive metallische Gläser (bulk metallic glasses, BMG) sind relativ neue Werkstoffe, die aufgrund ihrer regellosen atomaren (amorphen) Anordnung gegenüber kristallinen Werkstoffen hohe Festigkeiten, Härten, elastische Dehnungen sowie gute Korrosionseigenschaften und besondere weichmagnetische Eigenschaften aufweisen. Außerdem zeichnen sie sich durch eine einmalige Prozessierbarkeit aus, da sie sich in einem bestimmten Temperaturfenster — ähnlich wie Kunststoffe — plastisch verformen lassen. Trotz ihrer relativ geringen plastischen Bruchdehnung werden sie häufig als Strukturwerkstoffe in Erwägung gezogen und haben bereits erste kristalline Werkstoffe in industriellen Anwendungen (Transformatoren, Spulen, Induktoren, Federn, Gehäuse, Skalpelle, Sportartikel etc.) ersetzt.

Die Herstellbarkeit von amorphen Produkten ist abhängig von der Legierungszusammensetzung und den Abkühlbedingungen. Die Legierung muss schnell abgekühlt werden, damit sich die Atome nicht zu einer Kristallstruktur ordnen können. Die Schmelze erstarrt bei der Glasübergangstemperatur kristallin, wenn die Abkühlrate nicht ausreichend ist. Die erforderlichen Abkühlraten führen dazu, dass die erzielbaren Bauteilabmessungen auf kleine Dimensionen beschränkt sind. Diese geometrischen Restriktionen können durch einen zweistufigen Prozess aus Pulververdüsung und anschließender Pulververdichtung überwunden werden. Zerstäubungstechniken sind vielversprechende Techniken, da die Schmelzetropfen durch das große Oberflächen-Volumen-Verhältnis in den amorphen Zustand überführt werden können. Bei der Pulververdüsung werden typischerweise Abkühlraten von 10^2 bis 10^5 $\mathrm{K\,s^{-1}}$ erreicht.

Das Ziel der Dissertation war die Erweiterung der Abkühlstrategien bei der Zerstäubung glasbildender Schmelzen. Der Fokus lag auf der Verdüsung von Legierungen mit Einschmelzmaterialien, die zu moderaten Preisen erhältlich sind. Diese Glasbilder können aufgrund des geringeren Reinheitsgrades (commercial purity, CP) im Vergleich zu Materialien mit Laborreinheit (high purity, HP) nur durch höhere Abkühlraten amorph verdüst werden. Hierbei war es notwendig, den Wärmeübergangskoeffizienten zu erhöhen. Dies setzte eine gezielte Abstimmung hinsichtlich der Prozessgrößen voraus, sodass neben Legierungen mit geringen Reinheitsgraden auch größere Schmelzetropfen amorph verdüst werden konnten. Durch den Einsatz verschiedener Abkühlstrategien sollten neue Prozessfenster eröffnet werden, die bei der konventionellen Pulververdüsung nicht erreicht werden. Die entwickelten Abkühlstrategien wurden erstmalig auf glasbildende Legierungen übertragen: (i) Variation der Überhitzungstemperatur, (ii) Heißgaszerstäubung, (iii) Sprühkegelkühlung sowie (iv) Flüssigabschreckung. Diese Abkühlstrategien hatten zusätzlich das Ziel, heterogene Keimbildung zu minimieren und kleinere Partikel zu erzeugen, da die Abkühlrate der Schmelzetropfen während der Erstarrungsphase im Wesentlichen von der Partikelgrösse und dem GMR (Massenstromverhältnis aus Gas zu Metallschmelze) abhängig ist.

Die höchsten Abkühlraten wurden für flüssig-abgeschreckte Partikel erreicht. Die $\{(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}\}_{96}Nb_4$ bzw. $Fe_{76}B_{10}Si_9P_5$ Pulver konnten dabei vollständig amorph erzeugt werden (< 200 µm), wohingegen FeCoBSiNb Partikel bei der konventionellen Pulververdüsung nur bis zu 63 µm amorph waren. Selbst die kleinsten FeBSiP Partikel (< 25 µm) waren bei der konventionellen Pulververdüsung nur teilamorph. Ferner zeigte sich, dass induzierter Wasserstoff (10^2 - 10^4 ppm) beim Abschrecken mit Wasser die Glasbildungseigenschaften und die Sättigungsmagnetisierung der Pulver verbesserte. Eine weitere Fragestellung im Rahmen der Arbeit war, inwieweit die flüssig-abgeschreckten Partikel weiterverarbeitet werden können, da ein starker Oxidfilm um die Partikel vermutet wurde. Mittels Spark Plasma Sintering konnten unabhängig von den verwendeten Abkühlstrategien amorphe Ringe mit einer relativen Dichte > 98% erzeugt werden. Die Ringe zeigten dabei eine nahezu unveränderte Sättigungsmagnetisierung, wobei die Koerzitivfeldstärke leicht anstieg bzw. die Permeabilität stark abnahm. Durch den Einsatz der Flüssigabschreckung konnten diese Legierungen mit CP erstmalig in feste Probekörper gepresst werden und bieten dabei durch ihre guten magnetischen Eigenschaften (unabhängig von der Reinheit) ein hohes Potential für industrielle Anwendungen.

Die zweithöchsten Abkühlraten wurden für die Abkühlstrategie Sprühkegelkühlen beobachtet. Die FeCoBSiNb bzw. FeBSiP Partikel waren bis zu 125 µm bzw. 45 µm vollständig amorph. Eine erhöhte Überhitzungstemperatur führte trotz der Annahme, dass Nukleationskeime in der Schmelze aufgelöst bzw. verringert werden nicht zu einer signifikanten Erhöhung des amorphen Anteils. Es zeigte sich jedoch, dass höhere Überhitzungstemperaturen die Partikelformfaktoren vebesserten. Höhere Formfaktoren führen dabei zu einer höheren Pulverfließfähigkeit. Es wurden neben den beiden Fe-Legierungen zwei weitere Legierungen betrachtet: $Zr_{59.3}Cu_{28.8}Al_{10.4}Nb_{1.5}$ und $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$. Die ZrCuAlNb Legierung wies unabhängig von der Überhitzungstemperatur eine hohe Anzahl an nicht-sphärischen Partikeln auf. Dieses Verhalten war konträr zu den anderen Legierungen und kann auf unterschiedliche Viskositäten zurückgeführt werden. Eine hohe Schmelzeviskosität beeinflusst maßgeblich die Tropfenverformung.

Erhöhte Zerstäubergastemperaturen führten zu einer geringeren Gasdichte und damit zu einer höheren Gas- bzw. Relativgeschwindigkeit, wobei der Temperaturgradient zwischen Schmelzetropfen und Gas abnahm. Dieser gegenseitige Effekt führte zu einer Kompensation, sodass der amorphe Anteil unverändert blieb bzw. leicht abnahm. Neue semi-empirische Korrelationen zur Bestimmung der Abkühlraten bestätigten dabei die experimentellen Beobachtungen. Die Heißgaszerstäubung ist jedoch eine vielversprechende Methode zur industriellen Großproduktion von amorphen Metallpulvern. Am Beispiel der FeCoBSiNb Legierung wurde gezeigt, dass durch die verringerte Gasdichte des Zerstäubergases signifikant kleinere Partikel erzeugt wurden und der Gasverbrauch um bis zu 50% gesenkt werden konnte. Ferner konnte die amorphe Pulverausbringung um ca. 20% erhöht werden. Jedoch verschlechterten sich die Partikelformfaktoren zu geringeren Werten.

Summary

Metallic glasses or bulk metallic glasses are a new class of materials. These amorphous metals have a disordered structure, resulting in outstanding properties when compared to crystalline materials such as high hardness, strength, elasticity, good wear and corrosion resistance, and superior soft magnetic properties. Similar to thermoplastics, they are easily deformable due to a highly viscous state between the glass transition temperature and the crystallization temperature. Despite their low plasticity and tendency for catastrophic failure through instantaneous shear band propagation, they are often considered as structural materials and have already been implemented in industrial applications (transformers, coils, inductors, springs, micro gears, cases, scalpels, sporting goods etc.).

The properties of metallic glasses depend on alloy composition and cooling conditions during solidification. The liquid must be cooled rapidly to avoid crystallization, forcing the melt to retain its liquid atomic structure. The required cooling rates to obtain an amorphous solid are limited by time-dependent heat conduction, restricting product dimensions. Geometric limitations can be overcome by powder synthesis and consolidation to introduce metallic glasses to the commercial market. Gas atomization is a promising technique in the commercial production of metallic glasses, as amorphous particles can be produced due to the high surface-to-volume ratio through conduction and radiation. The cooling rate in molten gas atomization typically ranges from 10^2 to 10^5 $K\,s^{-1}$.

The aim of this PhD thesis was the development of novel cooling strategies for the atomization of glass-forming alloys to increase cooling rates during droplet solidification. The focus was on the atomization of soft ferromagnetic glass-forming alloys with commercial purity. These alloys are difficult to atomize into an amorphous state due to cooling rate limitations and their low glass-forming ability. For this purpose, it was necessary to increase the heat transfer coefficient. This resulted in higher cooling rates, allowing for the atomization of soft ferromagnetic glass-forming alloys with commercial purity and larger particle sizes that normally tend to crystallize during droplet solidification. With the development of novel cooling strategies, new process windows have been made available that are typically inaccessible in conventional gas atomization. Therefore, four cooling strategies were developed for the atomization of glass-forming alloys: (i) increasing the melt superheat temperature, (ii) hot gas atomization, (iii) spray cone cooling, and (iv) liquid quenching. The developed cooling strategies were used to decrease potent nucleation sites in the melt as well as to produce smaller particles, as the cooling rate strongly depends on droplet size and gas-to-melt mass flow ratio.

The highest cooling rates were achieved for liquid quenched particles, as the $\{(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}\}_{96}Nb_4$ and $Fe_{76}B_{10}Si_9P_5$ powders were fully amorphous for the entire particle size range (< 200 µm). Conventionally atomized FeCoB-

SiNb particles were only fully amorphous up to 63 μm and FeBSiP particles were partially-crystalline even for the smallest particle size class (< 25 μm). Hydrogen inducement during water quenching (10^2 - 10^4 ppm) had a positive effect on the glass-forming ability and saturation magnetization. Since it was expected that an oxide film would be formed during liquid water quenching, the powder consolidation ability was also investigated. Amorphous rings with a relative density > 98% were produced via Spark Plasma Sintering, regardless of the cooling strategies used. The saturation magnetization of the sintered rings remained nearly constant, while the coercivity slightly increased and the permeability distinctly decreased. Liquid quenching resulted in an increased amorphous fraction and improved powder properties as well as consolidation feasibility, making liquid quenching an influential opportunity for the commercialization of these alloys with commercial purity feedstock.

The second highest cooling rates were achieved for spray cone cooling. The FeCoBSiNb and FeBSiP particles were amorphous up to 125 μm and 45 μm, respectively. An increased melt superheat temperature resulted in a slightly higher amorphous fraction. It was assumed that a high melt superheat temperature reduced or destroyed any potential nucleation sites in the melt.

An increased melt superheat temperature ranging from 250 to 450 K significantly increased particle shape factors such as sphericity and aspect ratio. For the particle shape study, a $Zr_{59.3}Cu_{28.8}Al_{10.4}Nb_{1.5}$ and a $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$ (at%) alloy were also selected. The ZrCuAlNb glass-forming alloy showed a significantly higher amount of non-spherical particles and had a rougher surface, while the three other glass-forming alloys exhibited smooth surfaces and a nearly spherical particle morphology. This is due to the higher viscosity as the droplet break-up and formation process depends on viscosity.

The FeCoBSiNb glass-forming alloy was used to demonstrate the effect of hot gas atomization on cooling rates. A higher gas velocity was introduced by a decreased gas density (through elevated gas temperatures), leading to a higher relative velocity, while the temperature gradient between the melt droplet and surrounding gas was reduced. The relative velocity and the temperature gradient compensated for each other and resulted in nearly unchanged cooling rates. Thus, the amorphous fraction remained the same or slightly decreased. Newly developed semi-empirical correlations to predict average cooling rates confirmed these results. Despite the fact that the cooling rate remained constant, hot gas atomization provided many advantages over conventional gas atomization. For instance, hot gas atomization is a promising design tool for the commercialization of bulk metallic glasses with the benefits of producing smaller amorphous powders, reducing gas consumption up to 50%, retaining the amorphous fraction, and increasing the amorphous yield by 20%. By contrast, particle shape factors decreased due to the attachment of smaller particles on larger semi-solidified droplets known as satellites. An increase in particle shape factors typically results in improved powder flowability.

List of publications and conference contributions

List of publications

[1] N. Ciftci, N. Ellendt, L. Mädler, V. Uhlenwinkel. Impact of Hot Gas Atomization on Glass Forming Alloys. Hamburg: World PM 2016, European Powder Metallurgy Association, ISBN: 978-1-899072-48-4, 2016.

[2] N. Ciftci, N. Ellendt, E. Soares Barreto, L. Mädler, V. Uhlenwinkel. Increasing the amorphous yield of $\{(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}\}_{96}Nb_4$ powders by hot gas atomization. Advanced Powder Technology, 29(2):380-385, 2018.

[3] N. Ciftci, N. Ellendt, G. Coulthard, E. Soares Barreto, L. Mädler, V. Uhlenwinkel. Novel Cooling Rate Correlations in Molten Metal Gas Atomization. Metallurgical and Materials Transactions B, 50(2):666-677, 2019.

[4] N. Ciftci, N. Yodoshi, S. Armstrong, L. Mädler, V. Uhlenwinkel. Processing soft ferromagnetic metallic glasses: on novel cooling strategies in gas atomization, hydrogen enhancement, and consolidation. Journal of Materials Science & Technology, 2020 (accepted for publication).

[5] V.C. Srivastava, G.K. Mandal, N. Ciftci, V. Uhlenwinkel, L. Mädler. Processing of High-Entropy $AlCoCr_{0.75}Cu_{0.5}FeNi$ Alloy by Spray Forming. Journal of Materials Engineering and Performance, 26(12):5906-5920, 2017.

[6] T. He, O. Ertuğrul, N. Ciftci, V. Uhlenwinkel, K. Nielsch, S. Scudino. Effect of particle size ratio on microstructure and mechanical properties of aluminum matrix composites reinforced with $Zr_{48}Cu_{36}Ag_8Al_8$ metallic glass particles. Materials Science and Engineering: A, 742:517-525, 2019.

[7] T. He, T. Lu, N. Ciftci, V. Uhlenwinkel, K. Nielsch, S. Scudino. Mechanical properties and tribological behavior of aluminum matrix reinforced with Fe-based metallic glass: Influence of particle size. Powder Technology, 361:12-19, 2019.

[8] J. Lehtoonen, Y. Ge, N. Ciftci, O. Heczko, V. Uhlenwinkel, S-P. Hannula. Phase structures of gas-atomized equiatomic CrFeNiMn high entropy alloy powder. Journal of Alloys and Compounds, 827(154142):1-6, 2020.

[9] N. Luo, C. Scheitler, N. Ciftci, F. Galgon, Z. Fu, V. Uhlenwinkel, M. Schmidt, C. Körner. Preparation of Fe-Co-B-Si-Nb bulk metallic glasses by selective laser melting: microstructure and properties. Materials Characterization, 162

(110206):1-9, 2020.

Conference contributions

[1] N. Ciftci, N. Ellendt, L. Mädler, V. Uhlenwinkel. Impact of Hot Gas Atomization on Glass Forming Alloys. World PM 2016 Congress & Exhibition, European Powder Metallurgy Association, Hamburg, Germany, 09-13 October 2016.

[2] N. Ciftci, N. Ellendt, L. Mädler, V. Uhlenwinkel. Cooling strategies for the droplet solidification of glass-forming alloys. 25^{th} International Conference on Metastable, Amorphous, and Nanostructured Materials (ISMANAM 2018), Rome, Italy, 02-06 July 2018.

Acknowledgements

Writing a good acknowledgement is not as easy as you might think. Obviously, you do not want to be too emotional, but you also want to find the right words to say thank-you to the people who have accompanied you through your academic journey. I hope this note communicates what it means to have gone the extra mile to finalize this work, including the countless hours during long weekends that went into it, and that it reflects the spirit of dedication and support behind this thesis.

If someone asks me what I have personally learned the most, I would probably say learning from my mistakes, as it is the mistakes that lead to knowledge. I believe this outstanding characteristic can be attributed to my supervisor Prof. Dr.-Ing. habil. Lutz Mädler. My journey has always involved curiosity, which has sometimes turned into disappointment, as attempting great work can lead to failure. Prof. Lutz Mädler had the right intuition to turn frustration into lessons learned, but also for exploring alternatives and setting new research goals. I would also like to thank him for the fruitful scientific discussions and for his advice and feedback when preparing manuscripts for publications, which greatly improved their readability, structure, and scientific argumentation.

I would like to express my appreciation to Univ. Prof. Dr.-Ing. habil. Dr. h.c. Jürgen Eckert for being co-reviewer of my thesis. I also wish to thank him for the fruitful scientific and personal discussions during international conferences.

This work would never be a success without the substantial contribution of my direct supervisor Dr.-Ing. Volker Uhlenwinkel. I truly thank him for the opportunity to work in his research group including the use of modern atomization facilities and measurement instruments, as well as the financial and scientific freedom to try unconventional ideas that were not always successful. I am indebted to his patience, outstanding knowledge of atomization that he taught me, as well as for refining my thesis topic together. We have known each other for so many years, which has truly resulted in profound trust and constant scientific and personal support.

I am very grateful for the opportunity to work with Prof. Noriharu Yodoshi from Tohoku University in Sendai, Japan. During my stay, I had the chance to use his laboratories and discuss my research with him, resulting in substantial scientific progress. My stay was funded through two scholarships and I would like to thank the MAPEX Center for Materials and Processes at the University of Bremen and the Cooperative Research Center for Advanced Materials at Tohoku University for the financial support.

During this work, we had a joint collaboration with Prof. Dr. rer. nat. Ralf

Busch, Benedikt Bochtler, and Dr.-Ing. Simon Hechler from Lehrstuhl für Metallische Werkstoffe at Universität des Saarlandes. I am very thankful for the profound scientific discussions and the evenings we shared together before project meetings. A second collaboration was initiated with Prof. Livio Battezzati and Dario Gianoglio from the University of Turin. Dario joined our research group for three months and it was a pleasure working with him.

A thesis is always the product of many people setting the groundwork and for that I thank our technicians Stefan Evers, Rainer Lehmann, and Frank Peschel who helped me with experimental setups. Most of the experimental components were realized in the machine shop, and I am thankful to Dieter Brüns/Andreas Flunker and their teams. I thank Petra Witte for the SEM images, Dr. Michael Wendschuh for the help with the XRD measurements, and Ellen Matthaei-Schulz for the support with the hydrogen and oxygen measurements.

A big thank-you goes to the students who contributed to this thesis: Sarah Armstrong, Juliane Baumann, Malte Bloch, Evan Chow, Geoffrey Coulthard, Jasper Eitzen, Colm O'Fourthain, Zekiya Göktas, Sean Hickens, Philip Hopp, Luisa Ludwig, Waldemar Meinik, Viola Müller, Ronald Rosenberg, Patrik Sieverding, Nicole Temple, and Julian Wankelmann. I am grateful for your contribution as a student assistant, through a Bachelor/Master thesis, Master project, and UofA co-op program). All of you have found your way to my picture wall.

I am also very thankful for meeting and working with my colleagues in our Mechanische Verfahrenstechnik department, particularly to Prof. Dr.-Ing. habil. Udo Fritsching, Dr.-Ing. Nils Ellendt, and my closest peers: Erika Soares Barreto, Daniel Beckers, Eric Gärtner, Marcel Hesselmann, Shohag Hussain, Saeedeh Imani Moqadam, Farhad Mostaghimi, Dr.-Ing. Ilya Okulov, Lucas Barcelos Otani, Dustin Schröder and Anna Taruttis.

I would also like to thank the Friedrich-Ebert Foundation, which has supported me financially and personally through my entire studies. I am grateful for the beautiful personalities I have met during my time as a scholar and for the opportunity to learn what living in a free society means with the opportunities to participate on political, economic, social, and cultural levels regardless of one's origin, sex or religion.

Finally, this goes to my friends and family who were always supportive and have had unconditional trust and endless patience with me, especially when I canceled activities and family events at the last moment. I dedicate this work to all of you.

The last words are for a very special person in my life. I am really sorry for the late nights, early mornings, short weekends, and for all the things I missed that you personally enjoy. Thank you for being on my side, for your support and patience but also for reading drafts as well as accompanying and encouraging me through the toughest and most joyful moments. I owe you so much.

Contents