Microstructure Refining of a Mo-Ni Brazing Filler by Nanoparticles Doping

Doping a binary eutectic Mo-Ni brazing filler metal with SiC nanoparticles leads to enhanced mechanical integrity of the joint

BY D. P. SEKULIC, H. FU, A. RABINKIN, D. BUSBAHER, E. LEONE, AND T. PREUSS

ABSTRACT

A hypothesis has been introduced that a doping by SiC nanoparticles of a binary eutectic Mo-Ni brazing filler metal may impact the mechanical properties of the formed brazed joint. It was conjectured that the microstructure of the solidified brazement would be refined via doping, thus leading to the enhancement in mechanical integrity of the joint vs. a nondoped material system. The paper provides evidence of a marked shear stress improvement with doping vs. a nondoped system. The changes in the joint’s mechanical properties are attributed to this newly discovered dramatic microstructure refinement of the solidified fillers doped with SiC.

KEYWORDS

- Brazing • Nanoparticles • SiC • Mo-Ni • Microstructure

Introduction

Motivation

The present work is a continuation of an initially imposed engineering task — altering an excessive wettability of Mo0.4Ni0.6 brazing filler metal (BFM) used for bonding refractory metals, e.g., molybdenum, rhenium, and/or porous tungsten (Ref. 1). New BFM were made by adding nanoscale SiC particles to the microsized Mo0.4Ni0.6 powder. The Mo0.4Ni0.6 wettability change was achieved by adding nanoparticles of the same material (Mo-Ni) or a distinct material, such as SiC (Ref. 2).

In the latter case, a marked difference in the joint microstructure was noticed after solidification of the BFM liquid phase (Ref. 3). However, these microstructural changes were not analyzed at the time of discovery. This led to the hypothesis that refinement of the microstructures of solidified Mo-Ni-SiC using nano-micro powder composite brazes may lead to a better mechanical integrity of the brazements (Refs. 4, 5). Hence, a more detailed study of this phenomenon would be warranted.

This paper offers a detailed account of these observations. More specifically, it addresses a shear stress improvement upon doping due to microstructural modifications, and offers a detailed discussion of the reasons for the microstructural changes induced by adding SiC nanoparticles to the eutectic Mo-Ni powder.

State of the Art

Brazing is used in many molybdenum applications (Refs. 6–8). Unfortunately, low-melting brazing filler metals, such as BAg-series alloys, cannot be used at high temperatures when Mo is predominantly utilized. As a response to Mo service conditions, high-temperature BFM such as V-35Nb, V-Mo (Ref. 9), Ni-14Cr-6Fe (wt-%) (Ref. 7), Ti-based alloys (Refs. 6, 8), Fe-15Mo-5Ge-4C-1B (Ref. 10), and Ni-Mo eutectic alloys (Ref. 7) were developed and have been used. The Ni-14Cr-6Fe (wt-%) filler metal yields joints with a rather low, 132-MPa shear strength (Ref. 8).

Transient liquid phase (TLP) processing, in which a thin layer of Ni is used for diffusion bonding, requires a long temperature dwell that could cause undesirable molybdenum embrittlement due to the recrystallization process (Ref. 9). The binary Mo-Ni BFM has been used for a long time in refractory metal bonding (Ref. 7).

Recently, Mo-Ni BFM with eutectic composition was exploited in joining molybdenum to porous tungsten for microwave technology applications (Ref. 11). The filler metal powder was produced using elemental powder milling. Brazing was carried out at 1400°C for 15 min. The resulting joint tensile strength was rather low, about 88 MPa. No detailed description of the joint microstructure was presented.

In our study, we decided to explore the behavior of Ni-Mo eutectic BFM doped by SiC. We aimed at examining the mechanical integrity of the doped

D. P. SEKULIC (sekulicd@engr.uky.edu) and H. FU are with the College of Engineering, University of Kentucky, Lexington, Ky. SEKULIC is also with the State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, China. A. RABINKIN is with Brazing and Joining Consultant, LLC, Watertown, Mass. D. BUSBAHER is with Ceradyne, Inc., Lexington, Ky. E. LEONE and T. PREUSS are with Excel Laboratory Services, Dover, N.J.
joints. To achieve that objective, we performed two distinct sets of experiments with the same set of filler metal systems (Mo-Ni + x% SiC). The first was a shear stress testing of the brazed Mo-Mo lap joint samples of a distinct geometry. The second was a detailed microstructural study of a semi-infinite brazed joint involving molybdenum as the base metal substrate.

Experimental

Materials and Procedures

Brazing filler metal preparation. All BFMs used in this work were manufactured from a binary Mo-Ni micron-scale powder as their major base component. The powder had 34.71 at.-% Mo and 65.28 at.-% Ni (46.5/53.5 wt-%) composition and <350 mesh dimensions (40–150 μm particle size). The first specimen material designated as 4-2a (Table 1) consisted only of Mo-Ni powder and served as the baseline for comparison of metallurgical effects on joint properties via additions of SiC powder to the binary Mo-Ni powder. The SiC powder particle dimensions were in the nano range, i.e., <50 nm. Three doped powder mixtures were prepared via additions of 1, 3, and 5 wt.% (2.44, 6.96, and 10.88 at.-%) of SiC to Mo-Ni microscale size powder.

Differential thermal analysis and alloy melting characteristics. Differential thermal analysis (DTA) was carried out on a NETZSCH STA 449 C instrument. The alloys’ melting temperatures were determined from cooling segments of DTA of Mo-Ni + SiC alloys. The considered alloys were heated up to 1460°C. It was observed that the crystallization temperature (Tc) monotonously decreased with the SiC addition, from 1310°C for binary base Mo-Ni alloys containing no SiC addition to 1285°C for alloys containing 5 wt-% SiC. This was expected from the well-known impact of metalloids on transition metals, i.e., decreasing transition metals’ melting temperatures (observed in our DTA measurements) and decreasing surface tensions of these alloys in the liquid state (Ref. 12).

Joint Integrity Testing Procedures

Shear stress testing. Mechanical evaluation was made using the two-dimensional pure shear-mode testing method developed by Rabinkin and Pounds (Ref. 13). In our case, we prepared specimens consisting of two rectangular molybdenum blocks with 10 x 10 x 50 mm linear dimensions, which were machined from solid Mo rods. The blocks were placed in a fixture in which they were tack welded to the supporting plates in the lap-type configuration in which a 50 μm brazing gap between molybdenum blocks was secured — Fig. 1A.

After the brazing operation, the tack-welded plates (i.e., fixers) and an excessive amount of the solidified filler metal in the fillets were machined off the brazed samples to create a well-defined rectangular cross-section geometry of both the specimens and brazements. Figure 1B shows samples after brazing and machining operations together with the appearance of brazed samples after mechanical testing.

To compare the strength of the joint with virgin Mo base metal, the step-like specimens (Fig. 1C), so-called Z-specimens, were machined from the solid Mo block to make their geometry similar to that of the brazed ones. These Z-specimens were placed in the furnace together with specimens to be brazed during brazing operation to get
the same state of the virgin Mo as in the brazed samples.

**Semi-infinite Mo/BFM joint configuration for metallography.** Mo/BFM joints convenient for metallographic studies were manufactured from caps made of pure molybdenum, and each was loaded by BFM powders with different compositions. These loaded specimens were subjected to the same heat treating cycle as those made for shear testing. Namely, the loaded caps were placed together in a controlled atmosphere furnace (75% \( \text{H}_2 + 25\% \text{N}_2 \)) and heated until the powders within the caps melted. During heating, the specimens were at temperatures above 1319°C for about 1 min with the temperature peak achieving 1362°C. A fast cooling to room temperature followed.

All four specimen materials were then used to study metallurgical reactions between Mo and Mo-Ni + SiC at the joint interface and the microstructure of a brazing filler metal in the interface vicinity and beyond. They were cut in half, imbedded in the standard 31-mm-diameter resin cylinders, and subjected to the following multistage polishing procedure.

First, specimens were polished using different silica sandpapers followed by diamond suspension polishing. Lastly, Struers OPU paste was applied to finish diamond suspension polishing. Lastly, Struers OPU paste was applied to finish polishing procedure.

**Joint mechanical integrity testing.** Two types of mechanical integrity testing procedures followed. These included shear tests as well as nano-indentation tests. Due to space limitation, only the former will be discussed, with the latter addressed briefly and elaborated elsewhere.

The shear testing specimen guide fixture was placed on the Instron 5582 machine table to provide lateral support to specimens in the lap-type configuration, thus avoiding formation of the three-dimensional stress field during vertical loading (Ref. 13). The loading of all tested specimens was applied with 1.25 mm/min rate.

Nano-indentation experiments were performed using atomic force microscopy (AFM) to characterize the relative hardness of phases in the Mo/Mo-Ni brazed joints that were modified by the addition of SiC nanoparticles.

AFM has been used so far not only for the specimen’s surface characterization but also for assessment of the elastic modulus of some polymer fibers and creep evaluation (Ref. 14). Traditionally, AFM utilizes a fine tip probe mounted at the end of a cantilever to measure the surface morphology. In our case, for hardness assessment, we used Veeco (Digital Instruments) Dimension 3100 AFM instrumentation. For this instrument, a special diamond tip was mounted to a stainless steel cantilever. This diamond tip was pressed into the surface of a sample with a known force to create a nano indentation. The cantilever force used in this study was 1.73 \( \times 10^{-5} \) N.

For each indent, a plot of the cantilever deflection versus the Z displacement (called a force plot) was created. An image of the indent was recorded by SEM. Afterward, the depth of the indent was determined by performing a cross-section scanning analysis through the center of the indent with the diamond tip movement used to perform this scanning. It was proven by the same method of measurements on standard gold and molybdenum specimens that the phase hardness on the nano scale is inversely proportional to the depth of the imprint. Therefore, the comparative hardness of our alloy phases can be expressed well via corresponding indent depth.

Because silicon and carbon were found to be nonuniformly distributed among the Mo/Ni phases, the AFM nano-indentation measurements characterize the role of the silicon and carbon as active factors changing the joint microstructure morphology, and as potentially hardening components in the joints’ phases.

Metallographic studies were made using optical microscopy (OM) and SEM performed on a JEOL JXA 840 electron microprobe. Both secondary electron imaging (SEI) and backscattered electron imaging (BSE) techniques were used. Part of the SEM analysis was performed with both energy dispersive x-ray (EDX) spectroscopy and wavelength dispersive x-ray (WDX) spectroscopy analytical methods.

WDX analysis was used to provide additional information not obtainable from the EDX analysis, such as the valence band transitions of silicon in the alloy compared to that in pure reference Si standards (Ref. 15). Specifically, the chemical state of silicon in the Mo-Ni + SiC alloy was determined together with the carbon content in different phases identified in the alloy. The Si K\( \alpha \) and Si K\( \beta \) analysis was performed using a polyethylene terephthalate (PET) crystal at 10 kV and with a beam current of 200 nA.

The C K\( \alpha \) analysis was performed using a LDEC crystal. Pure standards of silicon, silicon carbide, and carbon were used for calibration purposes. The average of a two-point background was subtracted from the measured peak intensities, and the positions were counted for 10 s. Estimates of the C K-ratios were determined sim-

---

**Fig. 2 — Stress/strain curves of tested brazed samples and the solid Mo block.**
ply from the following ratio: \( \text{wt-% C} = \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \times 100 \), where \( I_{\text{unk}} \) is the intensity of the unknown, and \( I_{\text{std}} \) is the intensity of pure C. The values reported in this study are not absolute; they represent ratios of the unknown to the standard.

**Results**

**Joint Shear Strength**

The load/displacement curves of all brazed and virgin Mo specimens upon testing are shown in Fig. 2. As seen in Fig. 2, all doped specimens are stronger than the undoped one. The best result, shear strength increase of about 26%, was obtained in the brazement with 3% SiC. The nonlinear shear strength concentration dependence with maximum value at 3% SiC doping, we hypothesize, was because this alloy had the finest mixture of the joint eutectic phases and advantageous morphology in the joint interface zone (see later for the justification). The failure of all brazed specimens occurred in the brazement zone and proceeded in a brittle mode. No plastic deformation stage is present on the loading curves in Fig. 2.

In the case of the molybdenum Z-specimen, failure occurred at about 436 MPa, which is close to the data on upper shear strength under torsion testing (Ref. 16). An agreement of the results for pure Mo, strain rate 1.25 mm/min, with that of the ASM standard data proves that the implemented measurements method is reliable to apply in brazement testing for characterizing the joint strength. The pure Mo specimen failure was also initiated in the ends of the overlap neck area (i.e., simulating brazement), with failure cracks propagating in the specimen body at about 45 deg upon failure. The strength of brazements manufactured in the current work is equal to, or even exceeds, 50% of that of pure Mo (i.e., twice as high as that obtained in Ref. 11).

**Joint Phase Microhardness**

The relative nano hardness of brazement phases was assessed via indent depth. The smaller the imprint, the higher the nano hardness. It can be ranked in the following order (from soft to hard): [Mo crucible, 5.5 nm] < [control 4-2A (0% SiC – Ni-rich phase, 6.8 nm]) < [control 4-2A – Mo-rich phase, 5.1 nm] < [5% SiC 9-2A – Ni-rich phase, 4.0 nm] < [5% SiC 9-2A – Mo-rich phase, 2.0 nm].

The AFM nano hardness analysis correlates with the EDX and WDX microprobe analysis results on silicon and carbon concentration in joint phases (Ref. 4). Both of these analyses revealed that silicon and carbon are dissolved as solutes in basic Mo-Ni and Ni(Mo) joint phases without changes in their crystal structure. It was also found that silicon and carbon concentrations are higher in the Mo-rich phases in the samples with nano SiC additions.

The observed increase of hardness...
in both Ni- and Mo-rich phases was consistent with the increase of carbon and silicon concentrations. The strengthening effect relative to the nondoped sample was the most pronounced (about three times the increase) in the Mo-based phase of the alloy with 5% SiC. It can be assigned to the solid-solution strengthening effect in both phases (Ref. 17).

**Joint Microstructure**

Figure 3 represents joint microstructures of the interface domain for Mo/binary Mo-Ni, specimens with 0, 1, 3, and 5 wt-% of SiC additions (see Table 1 for the samples’ designations and compositions). In all cases, alloys reacted well with pure Mo, forming a good joint. For example, in the case of 0 wt-% (Sample material 4-2a, Table 1)(Fig. 3A), the interface between Mo and Mo-Ni, was well developed, showing a strong bonding of the crystallized Mo-

<table>
<thead>
<tr>
<th>Table 2 — Phase Composition at Location A (Fig. 4A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>MoL</td>
</tr>
<tr>
<td>NiK</td>
</tr>
</tbody>
</table>

Fig. 4 — A — Microstructure of Mo-Ni 4-2a (Table 1) control specimen without SiC (see Tables 2 and 3 for the phase composition at the locations A and B); B — microstructure of Mo-Ni specimen containing 1 wt-% SiC (7-2A). Note that there are two types of Mo-rich phases containing different concentrations of Mo and having different morphology; C — Microstructure of Mo-rich phase observed in Mo-Ni 7-2a specimen containing 1 wt.-% SiC; D — EDX spot composition analysis of Mo-rich phase observed in a specimen containing 1 wt.-% of SiC.
Ni with Mo. No apparent defects at the interface (e.g., pores, etc.) are seen (Fig. 3A, inset). Joint crystallizations started at the interface with formation of a thin layer of the high-melting phase, namely Mo0.34 Ni0.65 (Fig. 3A). This continuous, 5–10-μm thick layer consisted of rounded crystals of Mo-rich phase. The area in the vicinity of the Mo base metal surface, outlined by a dashed line in Fig. 4A, is enriched in Mo as a result of its dissolution in the liquid filler metal, and not sufficient compositional equilibration of the filler metal liquid phase during brazing (Tables 2 and 3). The excessive, relative to the pure eutectic composition, amount of Mo was present in Mo-Ni dendrites formed in the interface area.

In addition, the excessive Mo amount yielded formation of large dendrites of hypoeutectic NiMo crystals grown in the eutectic mixture, which had the equilibrium eutectic composition (Fig. 4A, circle A). Because the average alloy composition is close to the eutectic one, no Mo-Ni dendrite should form. Thus, the presence of these hypoeutectic NiMo crystals confirmed nonequilibrium distribution of Mo and Ni in the joint interface vicinity.

A more or less uniformed typical eutectic mixture was formed in the rest of the specimen (Fig. 4A, circle B). All crystals formed in this specimen had rounded morphology. No faceted crystals typical for Mo-Ni intermetallic crystals and Mo-based carbides and silicides were observed. In the area 200–300 μm from the joint interface, the microstructure consisted of only a very fine mixture of Mo-Ni and Ni(Mo) eutectic phases. Their composition was close to an eutectic one, which can be found in the Mo-Ni phase paternal diagram.

A SEM image of the Mo-Ni filler metal + 1.22 at.-% SiC joint (Sample material 7-2a, 1 wt-% SiC) is given in Fig. 4B. A substantial number of well-faceted, Mo-enriched crystals were present in the eutectic crystal mixture (Fig. 4B, point 1, and Fig. 4C, D) beyond the interface area. Optical analysis revealed that these large, dozens-micron-sized Mo-rich crystals appeared to be much harder than the other phase structures based on variations in polishing edge retentions (see inset in Fig. 4C). Their composition (Table 4) was very close to that of the major Mo-Ni intermetallic phase existing in the Mo-Ni alloy system according to the Mo-Ni binary phase diagram (Ref. 18). They also contained 5.8 at.-% Si. This silicon concentration was higher than the average concentration of Si in the specimen. Therefore, it is obvious that Si preferred associating with the Mo-rich phase.

<table>
<thead>
<tr>
<th>Table 3 — Phase Composition at Location B (Fig. 4A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>MoL</td>
</tr>
<tr>
<td>NiK</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4 — SEM/EDX Composition of the Mo-Rich Phase (Fig. 4B, point 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
</tr>
<tr>
<td>SiK</td>
</tr>
<tr>
<td>MoL</td>
</tr>
<tr>
<td>NiK</td>
</tr>
</tbody>
</table>
A large fraction of Mo-Ni crystals was present in this sample. These crystals did not have strong faceting (Fig. 4B inset, points 2 and 3). These areas were similar to eutectic areas in nondoped alloys. They also contained less of both Mo and Si. Still, variations of Mo, Ni, and Si concentrations in various MoNi crystals observed in this alloy were insubstantial. Some Mo-NiSi crystals had well-distinguished small spherical particles located in their centers.

The 3 wt-% SiC sample (Mo-Ni filler metal + 3.48 at.-% SiC joint, Sample material 8-3a) had a substantially different microstructure compared to the 1 wt-% sample. Its SEM micrograph is given in Fig. 5A. As seen in Fig. 5A, a narrow, Mo-enriched layer is attached to Mo in a similar way as in a sample with 0 and 1 wt-% SiC (arrows). The interface region between the Mo crucible and the bulk of the brazing filler metal has a number of bands of Mo- and Ni-rich phases — Fig. 5A. These bands are alternating layers of large, fine, and intermediate sized Mo/Ni phases. The bulk of the joint material has a relatively fine Mo-Ni phase located in the Ni-rich matrix Fig. 5A. EDX analysis clearly indicates that the Si content is much higher in the bright Mo-rich phases.

An interesting result of the study is that the Ni is higher in the large Mo-rich phases in Band 1 adjacent to the Mo interface, compared to the finer Mo-rich structures in Band 2. Also, Si was lower in the large phase structures in Band 1, adjacent to the Mo crucible. Again, the concentration differences were not great enough to pay special attention to these variations.

The microstructure of the Mo-Ni filler metal + 5.44 at.-% SiC joint (Sample material 8-3a, 5 wt-% SiC) shown in Fig. 5B consists of two Mo-rich (point 3) and Ni-based (point 4) phases, which constitute the bulk of the eutectic. The phase dimensions in this area are smaller than 10 μm. Neither large Mo-Ni crystals, similar to those observed in the 1 wt-% SiC specimen, nor carbide or silicide crystals are found there.

As follows from the interface observations depicted in Fig. 5B, the interface zone is more or less similar in appearance, phase locations, and composition to that of the specimen containing only 1 wt-% SiC. Indeed, a narrow Mo-
enriched layer (arrows) is attached to Mo, followed by thin Ni-rich (point 1).

It is important to underline a drastic difference in morphology of the eutectic in the bulk of the joints having 0 vs. 3 and 5 wt-% Si. In the first case, the microstructure was a classical eutectic build of dendrite-like networks with rounded shapes. In joints containing 3 and 5 wt-% of SiC, it was an assembly of very fine cuboidal and trapezoidal particles of Mo-rich phase segregated in the Ni-rich matrix. All these particles had flat facets outlined by straight lines. The particle sizes were in order of a few micrometers. On the other hand, the morphology of the alloy with 1 wt-% SiC was transitional. It was a mixture of the classical, plate-like eutectic structure observed in the binary Mo-Ni alloy and newly observed combination of faceted crystals of the Mo-rich phase distributed evenly in the Ni-rich matrix. All these particles had flat facets outlined by straight lines. The particle sizes were in order of a few micrometers. On the other hand, the morphology of the alloy with 1 wt-% SiC was transitional. It was a mixture of the classical, plate-like eutectic structure observed in the binary Mo-Ni alloy and newly observed combination of faceted crystals of the Mo-rich phase distributed evenly in the Ni-rich matrix. All these particles had flat facets outlined by straight lines. The particle sizes were in order of a few micrometers.

State of Silicon and Carbon in Joint Phases

To prove that Si and C exist only as solid-solution components, the WDX analysis was used as an independent analytical method. Preliminary EDX analysis was performed on a lighter-contrasting Mo-rich phase, revealing that this phase contained the highest Si content (Fig. 5B, point 2). WDX Si analysis was performed on Sample 9-2a, which nominally had the highest level, 10.88 at.-% (5 wt-%) of SiC addition.

WDX analysis can probe valence band transitions of silicon in the alloy, and compare those to pure silicon, and SiC reference spectra. A comparison of the spectra in Fig. 6 clearly shows the disappearance of Si-C peak in this specimen. This proved that Si-C bonding was absent in the Mo-Ni alloy with 5 wt-% SiC. There is also a small, but systematic, shift in the wavelength position between elemental Si, SiC, and Si in the alloy.

The WDX results prove that the Si and C were not in the form of SiC. Dissolution reaction of the SiC in the liquid Mo-NiSiC phase appeared to be complete. Both of these metalloids continued to exist as solid-solution components in both solid Mo- and Ni-rich phases upon crystallization. Again, it is obvious from the EDX and WDX data that Si was dissolved mostly in the Mo-Ni phase as a solid-solution component. The WDX data presented in Fig. 6 also showed that a small part of Si is dissolved in Ni(Mo) solid-solution phase. Indeed, the amount of Si in the Ni(Mo) solid solution is for an order of magnitude smaller (0.32 vs. 2.31%) than that in the Mo-rich phase.

In addition, a separate silicon profiling was made across the complete interface area, including a few dozen microns deep in Mo to determine both the silicon distribution in each eutectic phase crystal and the depth of Si diffusion penetration in molybdenum. The average silicon concentration across the interface decreased until it became equal 0% at about a dozen micron within the molybdenum base metal — Fig. 7. At the same time, it varied strongly between the Mo-base phase crystals, where it was in the range of 4.4 to -2.3 wt-%, and Ni-based crystals, where Si concentration is about 0.2–0.3 wt-%. The Mo, Ni, and Si profiles showed that Si associated mostly with Mo, not with Ni — Fig. 8.

Such data showed that no noticeable Si penetration in Mo substrate (i.e., the base metal) was observed. The Si and C contents were relatively higher in the large Mo-rich phase, which is also consistent with the found hardness increase due to higher Si concentration in the solid-solution phase in accordance with the pertinent phase diagrams data for concentration ranges associated with the studied alloys given in Ref. 18.

It is important to outline that Mo-rich phases in alloy containing 1 wt-% of SiC had substantial elemental concentration variations of all three components. These variations are much smaller in alloys containing 3 and 5 wt-% of SiC. Within the middle of the joint with 5 wt-% of SiC, the distribution of silicon was more or less uniform among Mo- and Ni-based crystal.
The difference between Si concentrations in these phases is about 2% or only about two times. It may indicate that the crystallization of joints starts in the Mo base metal vicinity with sufficient time for elemental, particularly Si, redistribution followed by instant mass eutectic formation during the crystallization progress where this difference is not that substantial.

Consideration of the parental phase diagram of C-Mo, C-Ni, C-Si, Mo-Ni, Mo-Si, Ni-Si binary systems (Ref. 18) and C-Mo-Ni, C-Ni-Si, as well as Mo-Ni-Si ternary alloy systems (Ref. 19), shows what kinds of probable changes in composition of the liquid Mo-Ni-C-Si phase as well as eutectic Mo-Ni and Ni(Mo) phases can be expected as a result of SiC alloy doping. The large body of experimental data acquired in our work confirms the following trends:

- SiC should dissolve in liquid Mo-Ni on separate elemental components, which exist as such in forming solid phases upon crystallization. This dissolution was confirmed via application of both EDX and WDX spectroscopy analytical methods (Ref. 15). Melting and crystallization temperatures of Mo-Ni alloys should be lower with the addition of SiC. The DTA data during crystallization proved this hypothesis.

- Both Mo-Ni and Ni(Mo) eutectic phases may contain Si and C as solid-solution components without changes in the crystal structure of these phases in Si and C concentration ranges studied in the present work.

Addition of Si and C seemed to move the liquid composition closer to the quaternary eutectic point. This decreases the likelihood for segregation of prime hypo-eutectic dendrites in the middle of solidifying alloys. No dendrites were observed in the microstructures of doped compositions in contrast to what was observed in the nondoped alloy.

The change in Mo-Ni morphology from spherical to faceted is consistent with the decrease of the surface energy of liquid and solid phases when Si is added. This is the consequence of the well-known effect of Si additions on transition metal surface tensions (Ref. 12). The decrease in surface tension, in turn, leads to a lower driving force for crystal rounding in lamellae formation. The latter phenomenon is always an expression of high surface energy contribution to the total crystal-free energy and thus its substantial effect on phase morphology. The dramatic increase of the number of crystals formed in the bulk of Mo-Ni + SiC alloy upon crystallization yielded more and more finer eutectic mixture. This phenomenon is also the result of a very strong decrease in surface tension of Mo-Ni liquid and solid phases due to the addition of Si.

It is well established in theory and proven experimentally that the critical diameter of solid nuclei in a crystallizing liquid decreases with the decrease in surface tension $\gamma_{liq}$ at the solid/liquid interface. For the nucleation rate $N$, this dependence is much stronger — $N \propto \exp(-A/(\Delta T \gamma_{liq}^2))$, where $N$ is the number of critical-sized nuclei forming in the volume unit; $A$ is a complex constant that is weakly dependent on composition; and $\Delta T$ is temperature supercooling (Ref. 20).

For all our samples, undoped and doped, the supercooling was the same during crystallization. It is no wonder that Si, which has $\gamma_{liq}=865$ dyn/cm vs. $\gamma_{liq}=1778$ for Ni and $\gamma_{liq}=2250$ for Mo (Ref. 12), refines eutectic microstructure due to decreasing the nuclei size and increasing the nucleation rate. As our observations demonstrate, the more Si is added to Mo-Ni alloy, the larger the number of nucleating eutectic crystals and the smaller their size.

Conclusions

The shear strength of the brazed Mo-Mo joint with the Mo-Ni eutectic SiC doped filler was equal to, or even exceeded, 50% of that of pure Mo. It was twice as high as that reported for nondoped filler. The major beneficial changes of the brazed joint’s morphology due to alloying of Mo + Ni alloy with SiC moderate additions take place in the joint microstructure. These changes are expressed in a transformation, a replacement of typical eutectic morphology consisting of dendrites imbedded within a mixture of lamellae into a new type of refined microstructure consisting of a mixture of very small, evenly distributed eutectic crystals having cuboidal and trapezoidal forms. This transition expressed itself with changes in the forms and dimensions of crystallized eutectic phase components from rounded lamellae crystals to faceted ones.

Acknowledgments

The work of the lead authors has been supported in part through U.S. NSF Grant CBET 1234581. The authors acknowledge in-kind support from Ceradyne, Inc. (formerly Semicon Associates, a 3M Company). The first author acknowledges support by the 1000 Plan Foreign Expert Distinguished Professor program at the Harbin Institute of Technology, Harbin, China. Dr. Liu Wen, currently at Delphi Advanced Thermal Systems, Lockport, N.Y., contributed to the study in its early stage at the University of Kentucky Brazing Laboratory. Some parts of this work were reported at the AWS International Brazing and Soldering Conference, 2015, as an electronic preprint.

References


Appendix

An additional analysis was made to clarify, semiquantitatively, the difference in Si concentration between Mo- and Ni-rich phases obtained via both EDX and WDX methods. For this, we used the Si K-ratio values representing ratios of Si in the unknown sample to that of the pure Si standard (Table A-1). Similar observations were performed for carbon, results of which are presented in Table A-2.

### Table A-1 — Silicon K-Ratio in Mo-Ni-Based Nano Composite Fillers According to SEM/WDX Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area</th>
<th>Si K-ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-2a 1 wt-% SiC</td>
<td>Areas in Sample 7-2a, Wt=1% SiC</td>
<td>2.11</td>
</tr>
<tr>
<td>Large Mo phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Large Mo particle, point 1</td>
<td></td>
<td>1.56</td>
</tr>
<tr>
<td>Ni-based matrix, point 2</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>Mo phase near interface</td>
<td></td>
<td>1.47</td>
</tr>
</tbody>
</table>

#### Appendix Table A-1 — Silicon K-Ratio in Mo-Ni-Based Nano Composite Fillers According to SEM/WDX Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area</th>
<th>Si K-ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near interface with Mo container</td>
<td>Areas in Sample 9-2a, 5 wt-% SiC</td>
<td>0.01</td>
</tr>
<tr>
<td>Point 1</td>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td>Point 2</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>Point 4</td>
<td></td>
<td>3.50</td>
</tr>
<tr>
<td>Point 5</td>
<td></td>
<td>0.46</td>
</tr>
<tr>
<td>Point 6</td>
<td></td>
<td>4.42</td>
</tr>
</tbody>
</table>

### Table A-2 — Carbon K-Ratio in Various Phases of Mo-Ni-based Nano Composite Fillers According to SEM/WDX Carbon Analysis

<table>
<thead>
<tr>
<th>Areas in Sample 7-2a, 1 wt-% SiC</th>
<th>C Kα peak intensity (cps)</th>
<th>C Kα ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Mo-rich phase, Particle 1</td>
<td>625</td>
<td>1.10</td>
</tr>
<tr>
<td>Small Ni-rich phase, Particle 2</td>
<td>183</td>
<td>0.22</td>
</tr>
<tr>
<td>Small Ni-rich phase, Particle 3 in matrix</td>
<td>205</td>
<td>0.36</td>
</tr>
</tbody>
</table>

#### Appendix Table A-2 — Carbon K-Ratio in Various Phases of Mo-Ni-based Nano Composite Fillers According to SEM/WDX Carbon Analysis

<table>
<thead>
<tr>
<th>Areas in Sample 9-2a, 5 wt-% SiC</th>
<th>C Kα peak intensity (cps)</th>
<th>C Kα ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-2a 5 wt-% SiC in Mo-rich phase, point 1</td>
<td>706</td>
<td>2.41</td>
</tr>
<tr>
<td>9-2a 5 wt-% SiC in Ni-rich phase, point 2</td>
<td>122</td>
<td>0.21</td>
</tr>
</tbody>
</table>